

USE OF A CUSTOM QUARTZ CRYSTAL MICROBALANCE
VACUUM CHAMBER TO INVESTIGATE AREA-SELECTIVE
ATOMIC LAYER DEPOSITION

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Cornell University 2021

Atomic layer deposition (ALD) is a technique in which a substrate is exposed to precursor gases, which undergo self-limiting and irreversible chemical reactions, allowing for creation of conformal thin films with particular thickness and stoichiometric composition. ALD has shown tremendous potential for microelectronics fabrication and has been incorporated into various essential applications. In some cases, ALD is the only technique capable of controlling chemical reactions and thin film thickness with atomic precision. In area-selective ALD, one seeks to prevent irreversible growth in areas of the substrate where deposition is not desired. A novel idea to promote selective deposition is to introduce a co-adsorbate with the precursor, which should compete for binding sites and prevent precursor adsorption on one substrate, while allowing deposition on the other substrate to proceed unrestrained. The co-adsorbate molecule is chosen based on its expected binding interactions with dielectric vs. metallic surfaces.

We designed and constructed a vacuum chamber incorporating a quartz crystal microbalance (QCM) to explore methods to achieve area-selective ALD. Quartz wafers

are manufactured with a specific orientation relative to optical axes within the crystal, and these wafers have an intrinsic vibrational frequency, which can be exploited to measure deposition, adsorption behavior, and desorption behavior on the crystal. Because we could observe the crystal response and edit the process in real time, we were able to study the behavior of individual chemicals on various substrates and rapidly assess how experimental conditions such as chemical dose length, partial pressure, carrier gas flow rate, substrate temperature, and chamber pressure affect ALD experiments.

We utilized three different reactant delivery feedthrough configurations to investigate the influence of mixing the chemicals before delivery to the substrate. In the first, the metal precursor, the co-reactant, and the co-adsorbate were pre-mixed. In the second, the chemicals were all delivered independently. In the third, the metal precursor and the co-adsorbate were mixed, while the co-reactant was delivered separately. By comparing similar experiments performed using each of the feedthrough configurations, we discovered that pre-mixing the metal precursor and the co-adsorbate had important consequences on the ALD results.

BIOGRAPHICAL SKETCH

Colleen Lawlor grew up in Clinton, New York, with an enthusiasm for learning. In high school, her favorite subject was chemistry because it was challenging and visible in everyday life. During Colleen's junior year, she was awarded the Computing Medal and Scholarship from Rochester Institute of Technology (RIT). As she was still deciding on a college major, this award was instrumental in her consideration of a career in engineering. She contemplated other universities, but ultimately pursued a Bachelor of Science degree in chemical engineering at RIT. Throughout the five-year program, she completed over a year of full-time cooperative education experiences with three different employers. The co-op that had the largest impact was at NanoPower Research Labs with Professor Brian Landi, because she enjoyed learning new methods and analytical techniques, and participating in research in the collaborative laboratory atmosphere. In her last year at RIT, she was honored with the Outstanding Undergraduate Scholar Award, which recognizes the top 1 % of undergraduate students across the university and an influential teacher from their high school. After graduating summa cum laude from RIT in 2016, she entered the PhD program in the School of Chemical and Biomolecular Engineering at Cornell University. The same propensity for pursuing new experiences that drew her to the co-op program led her to join the research group of Professor James Engstrom, in an entirely different field of chemical engineering than her undergraduate work.

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TABLE OF CONTENTS

Biographical sketch	iii
Acknowledgements.....	iv
Table of contents	v
List of figures.....	viii
List of tables.....	xiii
List of equations.....	xiv
Introduction.....	1
Motivation	1
Background.....	2
Previous work	10
Internship at Lam Research Corporation.....	15
Introduction.....	15
Selective growth of silicon oxide on silicon oxide in the presence of copper.....	16
Novel claims for selective growth of silicon oxide on silicon oxide in the presence of copper.....	28
Summary.....	28
Methods	31
Conclusion	64
Use of amines to increase the deposition rate of an ALD process.....	68
Novel claims for the use of amines to increase the deposition rate of an ALD process.....	69
Summary.....	69
Methods	72
Conclusion	77
Cornell chamber design and assembly.....	82
Reactor design.....	82
Delivery design.....	92
Modifications to original design.....	105
Sizing equipment.....	109
Pneumatic valve setup.....	111
Powering equipment.....	113
Equipment details, serial communication, and equipment control.....	115
Installation in Olin Hall 310	120
Piping and instrumentation diagram	121
Characterizing the chamber	125
Reynolds number calculation	125
Residence time calculation	126
Diffusion length calculation.....	128
Knudsen number calculation.....	131
Plasma ion concentration calculation	132
Flow tests	135

Temperature calibration and PID tuning.....	136
Experimental setup.....	142
Sample preparation	142
Chamber setup	143
Investigating the behavior of individual reactants.....	147
Precursor: trimethylaluminum.....	147
Precursor: tetrakis(ethylmethyamido)zirconium(IV)	149
Precursor: di(sec-butylamino)silane	151
Oxidizing agent: water.....	152
Reducing agent: hydrogen plasma	155
Oxidizing agent: oxygen plasma	157
Co-adsorbate: 4-octyne	161
Pressure rise study	165
Pristine ALD	171
Trimethylaluminum water	171
DSBAS oxygen plasma	173
TEMAZ water	176
Impact of reactant delivery method.....	181
Reactant feedthrough version one	181
TEMAZ water	181
TEMAZ water with 4-octyne.....	184
Reactant feedthrough version two.....	194
TEMAZ water	195
TEMAZ water with 4-octyne.....	202
Reactant feedthrough version three.....	207
TEMAZ water with 4-octyne.....	207
Conclusion	212
Future directions.....	217
Appendix A: Run numbers associated with data in figures	221
Appendix B: Description of software used to perform QCM experiments	224
LabVIEW manual_control.....	225
LabVIEW automatic_process.....	232
STM-2	241
Excel Visual Basic for Applications (VBA)	249
Appendix C: Modified piping and instrumentation diagram for example experimental process.....	256
Appendix D: Spreadsheets used for chamber characterization calculations.....	275
Reynolds number.....	276
Residence time	280
Diffusion length	283
Knudsen number	287
Plasma ion concentration	290
Appendix E: Code written in Excel Visual Basic for Applications (VBA)	295
Density list for calculating Sauerbrey coefficient.....	296
Module 1	297
Module 2	304

Module 3	311
Module 4	318
Module 5	325
Module 6	328
Module 7	335
Module 8	341
Module 9	348
Module 10	354
Module 11	358
Module 12	362
Appendix F: Standard operating procedures for common lab tasks	367
Procedure: change mechanical pump oil	368
Procedure: standard clean for vacuum parts	382
Procedure: cleave wafer samples	388
Procedure: make chemical oxide on silicon wafer samples	391
Procedure: shut down chamber	401
Procedure: vent chamber	405
Procedure: restart chamber after vent	409
Procedure: after power outage	411
Procedure: helium leak check	424
Procedure: change gas cylinder	434
Procedure: change bubbler	438
Procedure: bake chamber	445
Procedure: change QCM crystal and wafer samples	452
Procedure: anneal QCM crystal and wafer samples	458
Procedure: experiment with delivery of reactants from panels 2–4	460
Procedure: experiment with delivery of reactants from panels 1–4	464
Procedure: measure pressure rise of reactant in bubbler, with flow from panels 2–4	469
Appendix G: Resume	475
References	479

LIST OF FIGURES

Figure 1: (a) Prediction by Gordon Moore in 1965 about the increase in the number of transistors per integrated circuit chip over time ¹ , (b) actual trend 1971–2019 ²	2
Figure 2: (a) 2015 International Technology Roadmap for Semiconductors forecast about device structures ³ , (b) 2020 International Roadmap for Devices and Systems forecast about the transition from equivalent scaling to power scaling ⁵	2
Figure 3: Depiction of an ALD cycle	3
Figure 4: (a) Demonstration of precise thickness control using ALD, (b) demonstration of conformal growth using ALD (300 nm aluminum oxide thin film on silicon wafer with trench structures).....	4
Figure 5: Depiction of area-selective ALD utilizing inherent selectivity.....	5
Figure 6: A QCM sensor manufactured by INFICON.....	6
Figure 7: Data collected using a QCM, demonstrating the high level of detail obtained with this technique ²⁶	6
Figure 8: Method for controlling QCM temperature by attaching an aluminum block to the sensor ²⁹	8
Figure 9: Method for controlling QCM temperature by using heaters with PID control ²⁶	9
Figure 10: Method for controlling QCM temperature by preheating reactants in a multi-stage oven ²⁸	9
Figure 11: Influence of reactant temperature on apparent mass gain when using a QCM ²⁸	10
Figure 12: Method of previous area-selective deposition work using self-assembled monolayers ³⁴	11
Figure 13: Method of previous area-selective deposition work using a chemoselective inhibitor in an ABC ALD process ⁴²	12
Figure 14: Method of previous area-selective deposition work using a co-adsorbate and a modified CVD process ⁴⁶	13
Figure 15: Results of previous area-selective deposition work using a co-adsorbate and a modified CVD process ⁴⁶	14
Figure 16: Lam Research Corporation vacuum chamber utilizing a quartz crystal microbalance for study of selective deposition processes ⁴⁸	16
Figure 17: Alternating hydrogen plasma and carbon dioxide plasma on copper.....	17
Figure 18: BDEAS carbon dioxide plasma ALD on silicon oxide, (a) twenty-five cycles, (b) cycles five and six	18
Figure 19: BDEAS carbon dioxide plasma ALD on copper, (a) sixty cycles, (b) cycles five and six, (c) cycles fifty and fifty-one.....	20
Figure 20: BDEAS carbon dioxide plasma hydrogen plasma ALD on copper, (a) thirty cycles, (b) cycles five and six	22
Figure 21: BDEAS carbon dioxide plasma hydrogen plasma ALD on silicon oxide, (a) thirty cycles, (b) cycles five and six	23
Figure 22: Butanethiol on copper.....	24
Figure 23: Butanethiol BDEAS carbon dioxide plasma hydrogen plasma ALD on silicon oxide, (a) first forty cycles, (b) cycles twenty-five and twenty-six.....	26
Figure 24: Butanethiol BDEAS carbon dioxide plasma hydrogen plasma ALD on copper, (a) 100 cycles, (b) cycles twenty-five and twenty-six.....	27
Figure 25: Schematic illustrations of a substrate undergoing a process to deposit metal in a via ⁴⁹	34

Figure 26: Schematic illustrations of a substrate undergoing a process for forming fully aligned vias using selective deposition of dielectric on dielectric ⁴⁹	35
Figure 27: Process flow diagram depicting operations for performing a method in accordance with certain disclosed embodiments ⁴⁹	40
Figure 28: Schematic diagrams of an example mechanism for selectively depositing dielectric material ⁴⁹	42
Figure 29: A timing sequence diagram showing an example of cycles in a method in accordance with certain disclosed embodiments ⁴⁹	47
Figure 30: A schematic diagram of an example process chamber for performing disclosed embodiments ⁴⁹	50
Figure 31: A schematic diagram of an example process tool for performing disclosed embodiments ⁴⁹	56
Figure 32: Triethylamine on copper	69
Figure 33: A flow chart of an ALD method with an increased deposition rate ⁵¹	75
Figure 34: A flow chart of an ALD method with an increased deposition rate ⁵¹	77
Figure 35: Initial design for Cornell vacuum chamber utilizing a quartz crystal microbalance for study of selective deposition processes	83
Figure 36: AutoCAD model of initial chamber design.....	83
Figure 37: AutoCAD model of reactor tube.....	84
Figure 38: Orthographic drawings of reactor tube	85
Figure 39: Orthographic drawings of support for translator	87
Figure 40: Orthographic drawings of side supports for reactor tube	88
Figure 41: Orthographic drawings of base support for reactor tube	89
Figure 42: AutoCAD model of initial chamber design including supports.....	90
Figure 43: (a) AutoCAD model of original sample holder, (b) AutoCAD model of modified sample holder.....	91
Figure 44: Orthographic drawings of sample holder	91
Figure 45: AutoCAD model of design of panel one.....	93
Figure 46: Custom tubing between MFCs and three-way valves.....	94
Figure 47: AutoCAD model of design of panels two through four, (a) path one of gas through bubbler traced in yellow, (b) path two of gas over bubbler traced in yellow	95
Figure 48: Orthographic drawings of panels.....	96
Figure 49: Orthographic drawings of mounting blocks for MFCs	97
Figure 50: Orthographic drawings of mounting blocks for two-way manual valves	98
Figure 51: Orthographic drawings of mounting blocks for two-way pneumatic valves.....	99
Figure 52: Orthographic drawings of mounting blocks for three-way pneumatic valves with bases parallel to panels	100
Figure 53: Orthographic drawings of mounting blocks for three-way pneumatic valves with bases perpendicular to panels.....	101
Figure 54: AutoCAD model of location of holes on panels for mounting blocks	103
Figure 55: AutoCAD model of panel designs with equipment fully assembled.....	103
Figure 56: (a) AutoCAD model of panel support system, (b) AutoCAD model of panels mounted on support system	104
Figure 57: Custom tubes, traced in orange, (a) connecting panels one through four for distribution of inert gas, (b) connecting panel one to plasma generator, (c) connecting panels two through four to original feedthrough on reactor	104
Figure 58: Gas cylinder including regulator and custom tubing with pigtail	105
Figure 59: AutoCAD model showing reactant triple feedthrough dimensions	106
Figure 60: (a) AutoCAD model of original reactant feedthrough, (b) AutoCAD model of modified reactant triple feedthrough	106

Figure 61: AutoCAD model of reactant line for trimethylaluminum (TMA) delivery	108
Figure 62: AutoCAD models of reactor after hardware modifications, (a) front with QCM in reactor tube, (b) back with QCM in load lock	109
Figure 63: Wiring diagram for solenoids controlling pneumatic valves on panels	112
Figure 64: Compressed air diagram for pneumatic valves	113
Figure 65: Electronics tower	116
Figure 66: Wiring diagram for pneumatic valve solenoids and plasma generator	118
Figure 67: (a) AutoCAD model of assembled reactor in laboratory, (b) photo of assembled reactor in laboratory	121
Figure 68: Piping and instrumentation diagram for reactor	122
Figure 69: Example modified piping and instrumentation diagram for reactor, for argon flow conditions during a temperature equilibration step	124
Figure 70: Pressure ² vs. flow rate	136
Figure 71: Thermocouple installed at location of QCM crystal	137
Figure 72: Temperature calibration, ΔT vs. pressure with fixed flow rate at relative position 0 in	138
Figure 73: Temperature calibration, ΔT vs. flow rate with fixed pressure at relative position 0 in	138
Figure 74: Temperature calibration, ΔT vs. flow rate with fixed pressure at relative position -2 in	139
Figure 75: Temperature calibration, ΔT vs. position with fixed flow rate and pressure	139
Figure 76: Temperature calibration curves	140
Figure 77: Temperature and frequency behavior, (a) before PID tuning, (b) after PID tuning	141
Figure 78: (a) Silicon oxide–gold-coated crystals, (b) copper-coated crystals ⁷³ , (c) silicon oxide–silicon wafer samples, (d) copper-silicon wafer samples	143
Figure 79: Crystal and wafer samples loaded in load lock	144
Figure 80: Crystal and wafer samples in reactor tube	145
Figure 81: Trimethylaluminum on silicon oxide, (a) ten cycles, (b) cycles two and three	149
Figure 82: TEMAZ on zirconium oxide, (a) ten cycles, (b) cycles two and three	150
Figure 83: DSBAS on gold, (a) twenty cycles, (b) cycles six and seven	152
Figure 84: Water on silicon oxide, (a) ten cycles, (b) cycles six and seven	153
Figure 85: Water on reduced copper, (a) twenty-five cycles, (b) cycles six and seven	154
Figure 86: Argon plasma followed by hydrogen plasma on silicon oxide, (a) five cycles, (b) cycles two and three	156
Figure 87: Argon plasma followed by hydrogen plasma on copper, (a) five cycles, (b) cycles two and three	157
Figure 88: Argon plasma followed by oxygen plasma on silicon oxide, (a) ten cycles, (b) cycles two and three	158
Figure 89: Argon plasma followed by oxygen plasma on reduced copper, (a) five cycles, (b) cycles two and three	159
Figure 90: Alternating argon plasma oxygen plasma and argon plasma hydrogen plasma on copper, (a) five cycles, (b) cycles two and three	161
Figure 91: 4-octyne on silicon oxide, (a) ten cycles, (b) cycles two and three	162
Figure 92: 4-octyne on reduced copper, (a) five cycles, (b) cycles two and three	164
Figure 93: Alternating 4-octyne and water on copper, (a) five cycles, (b) cycles two and three	165
Figure 94: Pressure and valve position behavior, (a) with pressure fixed, (b) with valve position fixed	166
Figure 95: Pressure profile of TEMAZ doses, (a) 2 sccm carrier gas flow rate, (b) 10 sccm carrier gas flow rate	168

Figure 96: (a) Pressure profile of TEMAZ doses with different carrier gas flow rates, (b) average pressure rise due to TEMAZ doses for different carrier gas flow rates	169
Figure 97: (a) Pressure profile of water doses with different carrier gas flow rates, (b) average pressure rise due to water doses for different carrier gas flow rates.....	169
Figure 98: (a) Pressure profile of 4-octyne doses with different carrier gas flow rates, (b) average pressure rise due to 4-octyne doses for different carrier gas flow rates.....	170
Figure 99: Trimethylaluminum water ALD on aluminum oxide, (a) fifteen cycles, (b) cycles ten and eleven.....	172
Figure 100: DSBAS oxygen plasma ALD on silicon oxide, (a) thirty cycles, (b) cycles fifteen and sixteen	174
Figure 101: DSBAS oxygen plasma ALD on copper, (a) thirty cycles, (b) cycles fifteen and sixteen	176
Figure 102: TEMAZ water ALD on silicon oxide during pressure study (0.5 Torr), (a) ten cycles, (b) cycles five and six	178
Figure 103: TEMAZ water ALD on silicon oxide during pressure study (1.5 Torr), (a) ten cycles, (b) cycles five and six	179
Figure 104: TEMAZ water ALD on silicon oxide during pressure study (1.0 Torr), (a) ten cycles, (b) cycles five and six	180
Figure 105: Reactant feedthrough version one	181
Figure 106: TEMAZ water ALD on silicon oxide, (a) thirty cycles, (b) cycles fifteen and sixteen	183
Figure 107: TEMAZ water ALD on copper, (a) thirty cycles, (b) cycles fifteen and sixteen	184
Figure 108: 4-octyne TEMAZ water ALD on copper, (a) thirty cycles, (b) cycles fifteen and sixteen	186
Figure 109: Depiction of a modified ALD cycle for use of a co-adsorbate	187
Figure 110: TEMAZ water with 4-octyne during TEMAZ ALD on copper, (a) thirty cycles, (b) cycles fifteen and sixteen.....	188
Figure 111: TEMAZ water with 4-octyne during TEMAZ ALD on copper at 180 °C, (a) thirty cycles, (b) cycles fifteen and sixteen	189
Figure 112: TEMAZ water with 4-octyne during TEMAZ ALD followed by TEMAZ water ALD on copper, (a) forty cycles (twenty cycles of each), (b) cycles fifteen and sixteen, (c) cycles thirty-five and thirty-six	191
Figure 113: TEMAZ water with 4-octyne during TEMAZ ALD followed by TEMAZ water ALD on copper at 180 °C, (a) forty cycles (twenty cycles of each), (b) cycles fifteen and sixteen, (c) cycles thirty-five and thirty-six	192
Figure 114: TEMAZ water with 4-octyne during TEMAZ ALD on silicon oxide, (a) thirty cycles, (b) cycles fifteen and sixteen.....	194
Figure 115: Reactant feedthrough version two.....	195
Figure 116: TEMAZ water ALD on aluminum oxide, (a) twenty cycles, (b) cycles three and four, (c) cycles seventeen and eighteen	197
Figure 117: TEMAZ water ALD on zirconium oxide, (a) twenty cycles, (b) cycles three and four, (c) cycles seventeen and eighteen	199
Figure 118: TEMAZ water ALD on zirconium oxide, (a) twenty cycles, (b) cycles three and four, (c) cycles seventeen and eighteen	201
Figure 119: TEMAZ water with 4-octyne during TEMAZ ALD on silicon oxide, (a) thirty cycles, (b) cycles five and six, (c) cycles twenty-five and twenty-six	204
Figure 120: TEMAZ water with 4-octyne during TEMAZ ALD on copper, (a) thirty cycles, (b) cycles five and six, (c) cycles twenty-five and twenty-six	206
Figure 121: Reactant feedthrough version three	207

Figure 122: TEMAZ water with 4-octyne during TEMAZ ALD followed by TEMAZ water ALD on copper, (a) thirty cycles (fifteen cycles of each), (b) cycles ten and eleven, (c) cycles twenty-five and twenty-six	210
Figure 123: TEMAZ water with 4-octyne during TEMAZ ALD on copper, (a) five cycles, (b) cycles two and three.....	215
Figure 124: (a) Clamp on QCM sensor ²⁷ , (b) load lock flange that could interfere with clamp on QCM sensor	219
Appendix B Figure 125: Screenshot of LabVIEW manual_control interface at startup	225
Appendix B Figure 126: Screenshot of LabVIEW manual_control interface when running	226
Appendix B Figure 127: Screenshot of LabVIEW automatic_process_1_4_1 interface at startup	233
Appendix B Figure 128: Screenshot of LabVIEW automatic_process_1_4_1 interface at startup	234
Appendix B Figure 129: Screenshot of LabVIEW automatic_process_3_6_2 interface at startup	235
Appendix B Figure 130: STM-2 screenshot 1, Setup tab (left: thickness display option, right: mass display option).....	243
Appendix B Figure 131: STM-2 screenshot 2, Operate tab (left: thickness display option, right: mass display option).....	245
Appendix B Figure 132: STM-2 screenshot 3, Films tab (left: thickness display option, right: mass display option).....	246
Appendix B Figure 133: STM-2 screenshot 4, Rate Graph tab (left: thickness display option, right: mass display option).....	246
Appendix B Figure 134: STM-2 screenshot 5, Mass/Thick Graph tab (left: thickness display option, right: mass display option).....	247
Appendix B Figure 135: STM-2 screenshot 6, Frequency Graph tab (left: thickness display option, right: mass display option)	247
Appendix B Figure 136: STM-2 screenshot 7, Help / About tab (left: thickness display option, right: mass display option).....	248

LIST OF TABLES

Table 1: Silicon oxide growth on silicon oxide and copper surfaces ⁴⁹	28
Table 2: Specifications for reactor tube fabrication	86
Table 3: Example calculation of conversion of mass flow controller specifications from nitrogen to argon	110
Table 4: Calculations of actual volumetric flow rate (V) for various conditions of temperature (T) and pressure (P).....	111
Table 5: Configuration of equipment to power	114
Table 6: Serial communication summary	117
Table 7: Reynolds number calculation as a function of temperature and pressure.....	126
Table 8: Residence time calculation as a function of temperature and pressure.....	127
Table 9: Residence time calculation as a function of temperature and flow rate	127
Table 10: Residence time calculation as a function of pressure and flow rate.....	128
Table 11: Diffusion length calculation as a function of temperature and pressure.....	129
Table 12: Diffusion length calculation as a function of temperature and residence time	130
Table 13: Diffusion length calculation as a function of pressure and residence time.....	131
Table 14: Knudsen number calculation as a function of temperature and pressure	132

LIST OF EQUATIONS

Equation 1: Sauerbrey equation.....	7
Equation 2: Sauerbrey equation for an AT-cut crystal	7
Equation 3: Sauerbrey equation rearranged to calculate thin film thickness for deposition on an AT-cut crystal.....	7
Equation 4: Hagen–Poiseuille equation.....	135
Equation 5: Hagen-Poiseuille equation rearranged to demonstrate the linear relationship between P_1^2 and Q	135
Equation 6: Equation of a line, for comparison to the rearranged Hagen-Poiseuille equation....	135

Introduction

Motivation

In the early 1960s, Gordon Moore, the future co-founder of Intel, observed that the number of transistors on integrated circuit chips was doubling every two years, and predicted that this rate of increase would continue “for at least ten years” (Figure 1a).¹ This trend became known as Moore’s Law, and it is still relevant today (Figure 1b).² For many years, this was achieved by decreasing the size of devices in both the horizontal and vertical dimensions.³ However, in 2015, the International Technology Roadmap for Semiconductors was published, which predicted that this approach would not continue past 2021 (Figure 2a).⁴ The report amplified interest in developing innovative three-dimensional device geometries to continue Moore’s Law.³ In 2020, the roadmap was updated to predict that devices would transition completely to vertical structures by 2025, at which time the focus would shift from scaling down the size of transistors to scaling down their power consumption (Figure 2b).⁵ Despite this, device fabrication processes that are inefficient or impractical for three-dimensional geometries continue to be used.⁶ Top-down methods such as lithography and etching require many steps, are expensive, and can result in edge placement errors.⁷ And bottom-up approaches such as line-of-sight deposition techniques are incompatible with complex three-dimensional features.⁸ Therefore, it is imperative that methods capable of self-aligned deposition on these device structures are identified.

Atomic layer deposition (ALD) is a technique in which a substrate is exposed to precursor gases, which undergo self-limiting and irreversible chemical reactions, allowing for creation of conformal thin films with particular thickness and stoichiometric composition (Figure 3 and Figure 4).⁹ A typical ALD cycle comprises an A-B sequence, where A is the metal precursor and B is the co-reactant. Half cycle reactions—exposure of A or B individually—are separated by inert gas purge steps, which leads to layer-by-layer thin film deposition. Plasma-enhanced ALD (PEALD) uses a plasma as the co-reactant so, for example, deposition can occur at a temperature lower than is necessary for traditional thermal ALD.¹⁰ Chemical vapor deposition (CVD) is a similar method but differs from ALD in that the precursor and the co-reactant are introduced simultaneously, and higher temperatures are generally required.^{11,12} Because there are no cycles, thickness control in CVD is achieved by limiting the time of exposure. ALD has shown tremendous potential for microelectronics fabrication and has been incorporated into various essential applications.^{6,13} In some cases, ALD is the only technique capable of controlling chemical reactions and thin film thickness with atomic precision.¹⁴

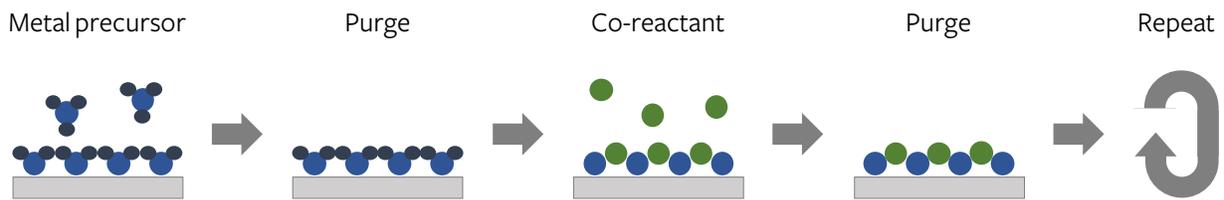


Figure 3: Depiction of an ALD cycle

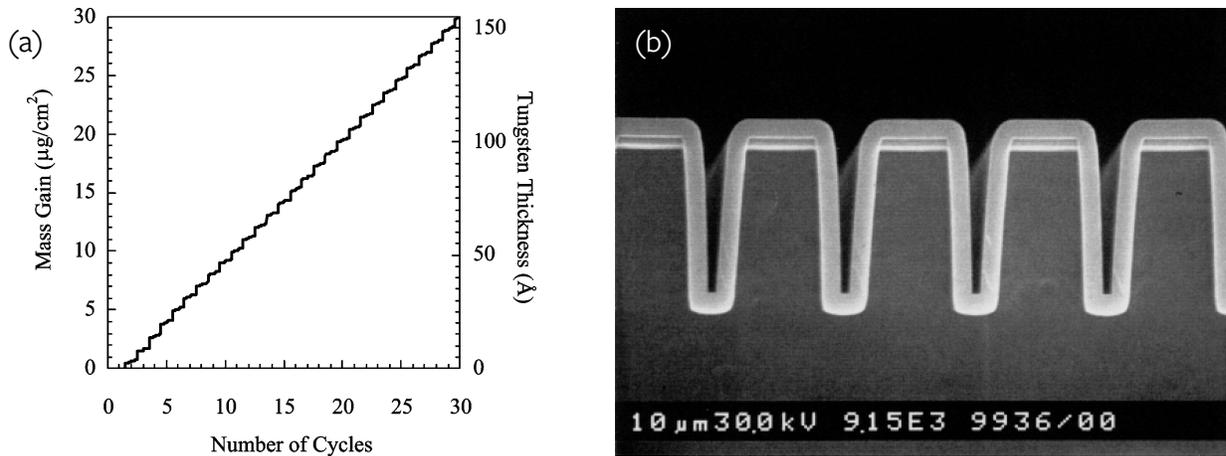


Figure 4: (a) Demonstration of precise thickness control using ALD¹⁵, (b) demonstration of conformal growth using ALD (300 nm aluminum oxide thin film on silicon wafer with trench structures)¹⁶

In area-selective ALD, one seeks to prevent irreversible growth in areas of the substrate where deposition is not desired. Successful self-aligned growth would reduce or eliminate the need for pre- or post-deposition lithography or patterning and diminish the severity of misalignment errors during fabrication.^{6, 17} One method for achieving area-selective ALD is to make use of inherent selectivity, where no blocking layer is needed on the non-growth surface (Figure 5).¹⁸ Much of the current research does not focus on inherent selectivity but uses a blocking layer to achieve area-selective deposition. Because this is a topic of great interest and industrial relevance, there are many researchers investigating solutions for a variety of substrate combinations, and I review only a subset of the methods here.⁶

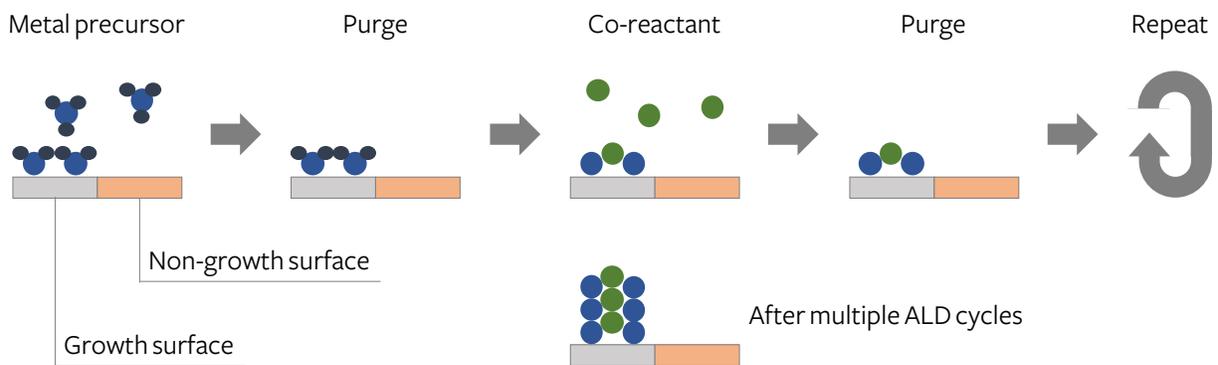


Figure 5: Depiction of area-selective ALD utilizing inherent selectivity

Researchers of area-selective deposition have recently increased interest in using quartz crystal microbalances (QCMs) to study substrate-dependent nucleation (Figure 6).^{19, 20, 21} Quartz wafers are manufactured with a specific orientation relative to optical axes within the crystal, and these wafers have an intrinsic vibrational frequency.^{22, 23} This frequency can be exploited to measure deposition, adsorption behavior, and desorption behavior on the crystal according to the Sauerbrey equation, from which the thin film thickness can be calculated by using the thin film density.^{24, 25} One benefit of in situ data analysis using a QCM is efficiency, because the user can observe the crystal response and edit the process in real time. Additionally, the dynamics and thickness changes of individual cycles can be analyzed, where ex situ analysis may provide the total film thickness only after a particular time or number of cycles (Figure 7).^{25, 26}



Figure 6: A QCM sensor manufactured by INFICON²⁷

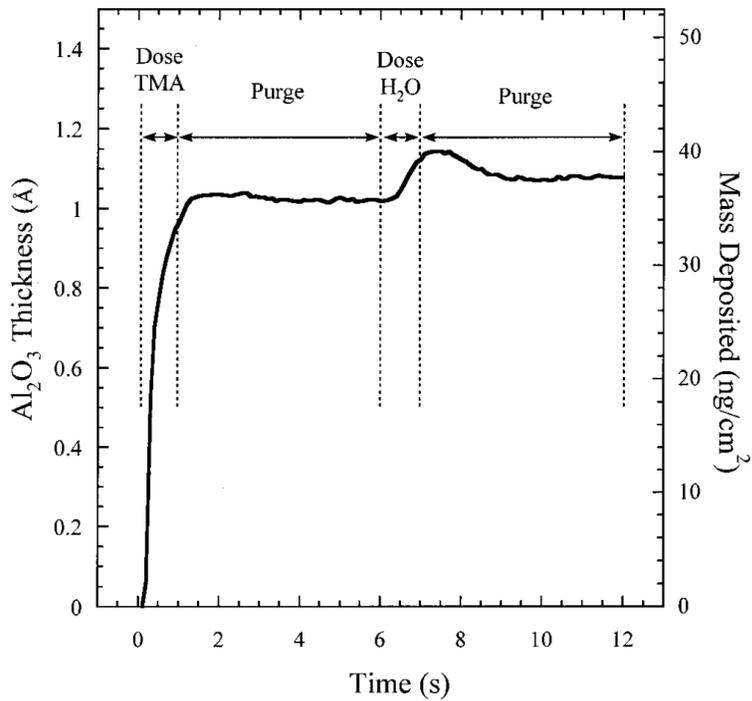


Figure 7: Data collected using a QCM, demonstrating the high level of detail obtained with this technique²⁶

In the Sauerbrey equation (Equation 1), Δm is the change in mass, A is the deposition area, ρ_q is the density of quartz, μ_q is the shear modulus of quartz, f is the crystal frequency after deposition, and f_q is the reference frequency of the quartz crystal, specific to a chosen “zero” for each experiment. A crystal-dependent constant can be defined for an AT-cut crystal, α_{AT} , demonstrating that the change in frequency should be a function only of change in mass, because the deposition area is constant (Equation 2). To calculate the thin film thickness from the Sauerbrey equation, thickness (t_f) multiplied by thin film density (ρ_f) is substituted for change in mass per area (Equation 3). Assumptions for using the Sauerbrey equation are that the deposited mass is small compared to the mass of the crystal, the deposited mass is rigid, and the deposited mass is evenly distributed over the exposed area of the crystal.²²

Equation 1: Sauerbrey equation

$$\Delta m = \frac{-A\sqrt{\rho_q\mu_q}}{2f_q^2}(f - f_q)$$

Equation 2: Sauerbrey equation for an AT-cut crystal

$$\Delta m = \frac{A\alpha_{AT}}{f_q^2}(f_q - f)$$

Equation 3: Sauerbrey equation rearranged to calculate thin film thickness for deposition on an AT-cut crystal

$$t_f = \frac{\alpha_{AT}}{f_q^2\rho_f}(f_q - f)$$

In practice, temperature also has a significant effect on the frequency of quartz crystals, and temperature variations in the chamber can appear in the data as changes in mass.²⁸ Additionally, some observed mass fluctuations in the QCM response can be attributed to changes in thermal conductivity of gas in the chamber as composition or flow rate is varied.²⁸ Previous chamber designs have addressed the challenge of separating thermal and mass effects in the crystal response in various ways. One scheme enhanced temperature stability by fixing a block of metal with a moderately high thermal conductivity (e.g., aluminum) to the QCM sensor (Figure 8).²⁹ Another successfully maintained a constant temperature throughout the chamber by employing a PID controller to regulate heaters along its length (Figure 9).²⁶ A third construction used a multi-stage oven to preheat reactants before they reached the QCM sensor (Figure 10).²⁸

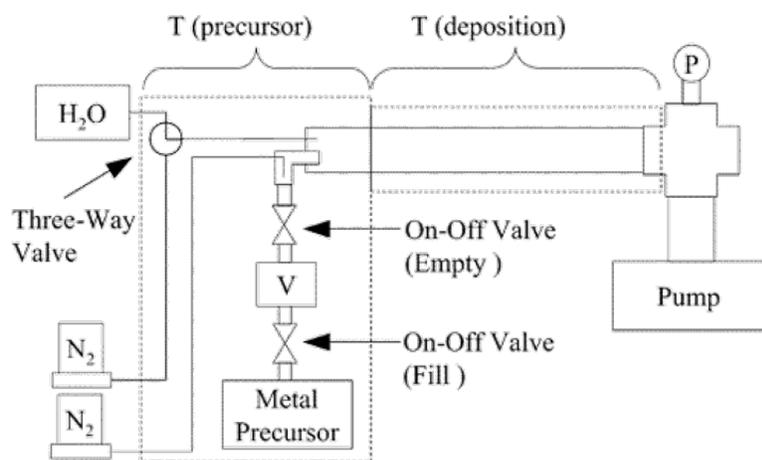


Figure 8: Method for controlling QCM temperature by attaching an aluminum block to the sensor²⁹

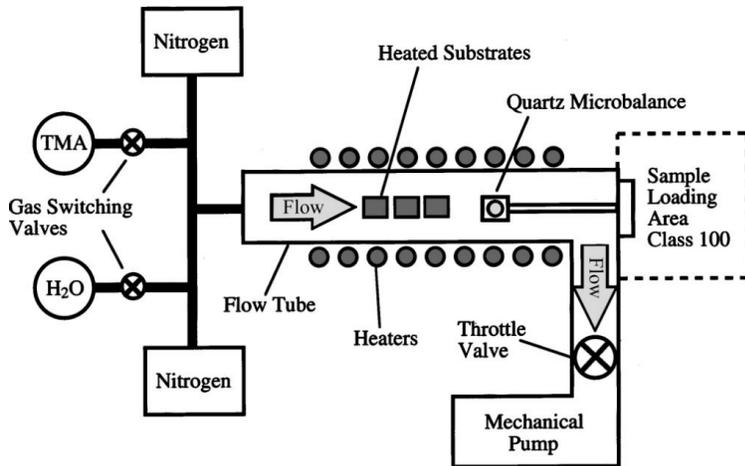


Figure 9: Method for controlling QCM temperature by using heaters with PID control²⁶

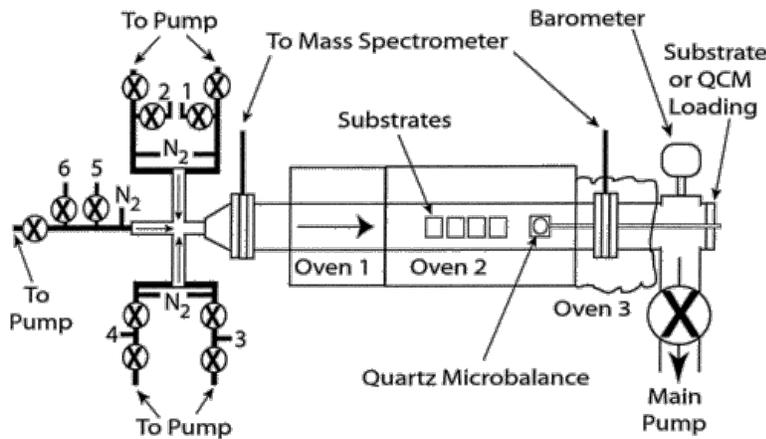


Figure 10: Method for controlling QCM temperature by preheating reactants in a multi-stage oven²⁸

The latter design was used to investigate the effects of different heating methods on the apparent mass gain during ALD.²⁸ The study found that when impinging reactants are hotter (colder) than the QCM, the apparent mass gain is less (more) than the apparent mass gain with a tuned temperature system (Figure 11). Therefore, the same gas can cause a positive or negative fluctuation in the QCM measurement depending on the

temperature profile of the reactor. Without utilizing a multi-stage oven, it is possible to determine whether the QCM results are accurate by comparing the calculated thickness with a thickness obtained using spectroscopic ellipsometry or another analytical technique.

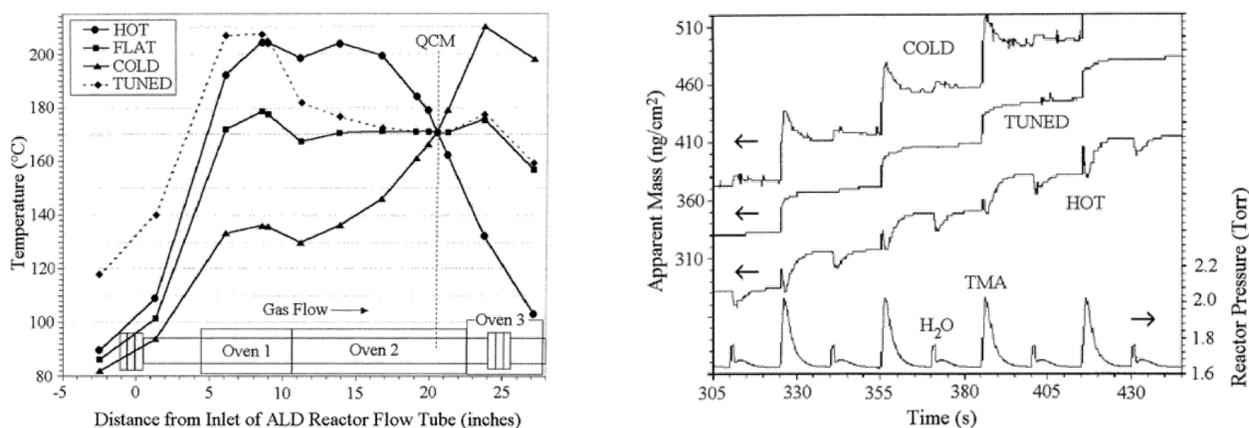


Figure 11: Influence of reactant temperature on apparent mass gain when using a QCM²⁸

Previous work

To achieve area-selective deposition, a self-assembled monolayer (SAM) deposited selectively can serve as a permanent blocking layer on the non-growth surface during subsequent ALD.^{20, 30, 31, 32, 33, 34} SAM molecules comprise a functionalized headgroup and an alkyl chain, with the option of adding a functionalized tail to the chain (Figure 12).^{35, 36} They are chosen to strongly interact with the non-growth surface and have little to no interaction with the growth surface. These optimized molecules spontaneously form monolayers and the densely packed alkyl chains can limit diffusion of the ALD precursor to the reactive surface sites on the substrate.^{37, 38} However, this technique typically

requires a solution-based procedure to deposit the SAM, which can have long processing times and is not compatible with current high-volume manufacturing semiconductor device tools.^{6,39} Further disadvantages of using SAMs are that the resolution is limited by the size of the molecule, the quality of the monolayer depends on substrate geometry, and they are incompatible with high temperatures and plasmas, which are often used as the co-reactant in ALD.^{35, 37, 40, 41}

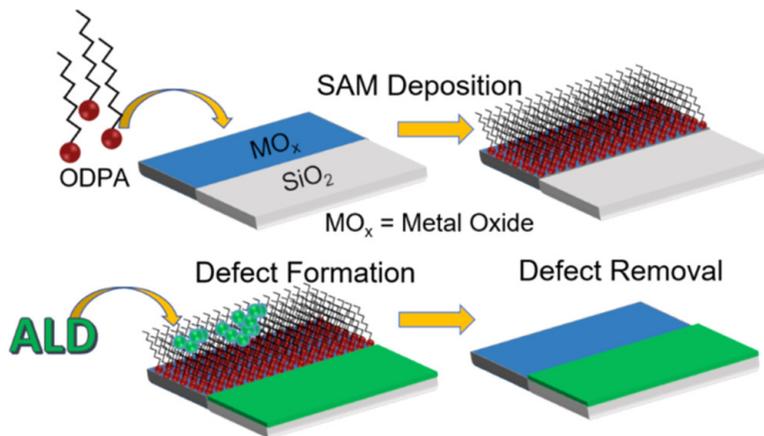


Figure 12: Method of previous area-selective deposition work using self-assembled monolayers³⁴

Another technique to achieve area-selective deposition is to introduce an inhibitor molecule before the ALD precursor, creating an ABC cycling sequence, where the inhibitor is chosen based on its chemoselective adsorption properties (Figure 13).^{42, 43, 44} Unlike SAMs, this approach has minimal impact on the total deposition time and the inhibitor is introduced in the gas phase, which would be compatible with industrial deposition tools.⁶ Because there is a purge between each component, the potential for undesirable gas-phase interactions between any of the inhibitor, precursor, and co-reactant is minimized.⁴⁵ However, the purge between introduction of the inhibitor and

the precursor requires potentially irreversible chemisorption of the inhibitor on the non-growth surface, so it is still present when the precursor flow is initiated. This method was shown to have selectivity only up to ~ 1 nm; loss of selectivity could be due to changes in the non-growth surface that affect adsorption of the inhibitor.^{8, 42, 43}

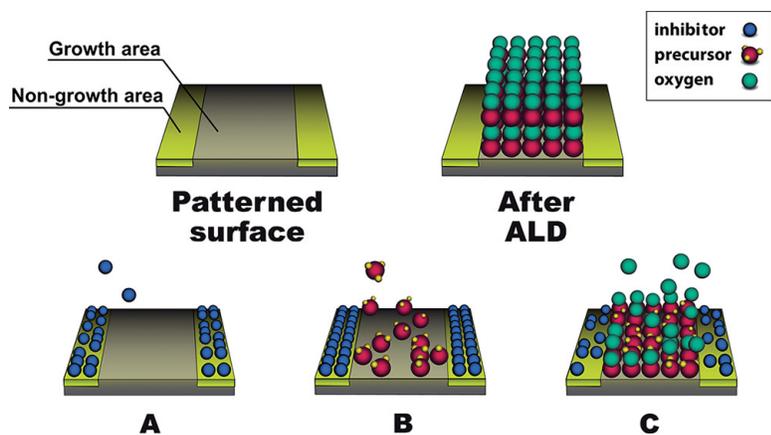


Figure 13: Method of previous area-selective deposition work using a chemoselective inhibitor in an ABC ALD process⁴²

By changing the flow pattern to introduce the inhibitor with the precursor, the molecule can be chosen to reversibly chemisorb, so the non-growth surface is preserved at the end of the deposition process.^{46, 47} The co-adsorbate molecule competes for binding sites and prevents precursor adsorption on the non-growth surface, while allowing deposition on the growth surface to proceed unrestrained. This method, applied to CVD rather than ALD, was published by the Engstrom Research Group in collaboration with the DiStasio Research Group in the Department of Chemistry and Chemical Biology at Cornell, and it demonstrated greater than 99 % selectivity up to ~ 30 nm for zirconium oxide on silicon oxide in the presence of copper (Figure 14 and Figure 15).⁴⁶ In CVD, the co-adsorbate, precursor, and co-reactant are all present simultaneously, so there are many interactions

to consider in choosing an appropriate molecule to prevent undesirable gas-phase reactions.⁴⁶ For ALD, the co-adsorbate would be introduced before, during, and after the precursor, with a purge before introduction of the co-reactant, but there would still be the potential for unwanted side reactions.⁴⁷ Similar to the ABC process, the increase in deposition time is minimal, and all components are introduced in the gas phase. This method is widely applicable, as the co-adsorbate can be chosen based on its binding interactions between any two surfaces, where deposition is desired on one and not the other.

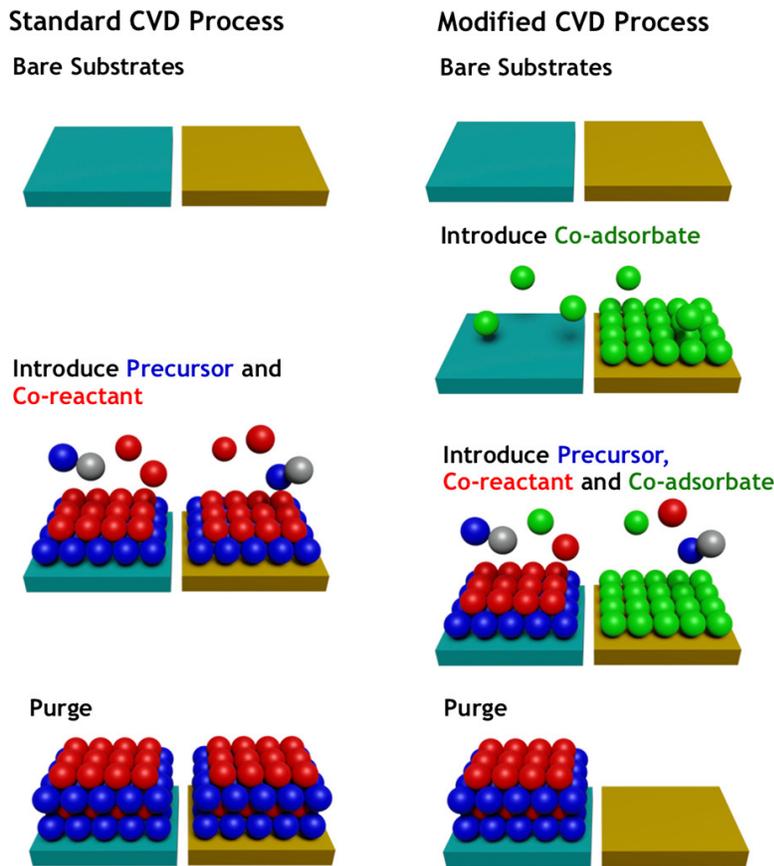


Figure 14: Method of previous area-selective deposition work using a co-adsorbate and a modified CVD process⁴⁶

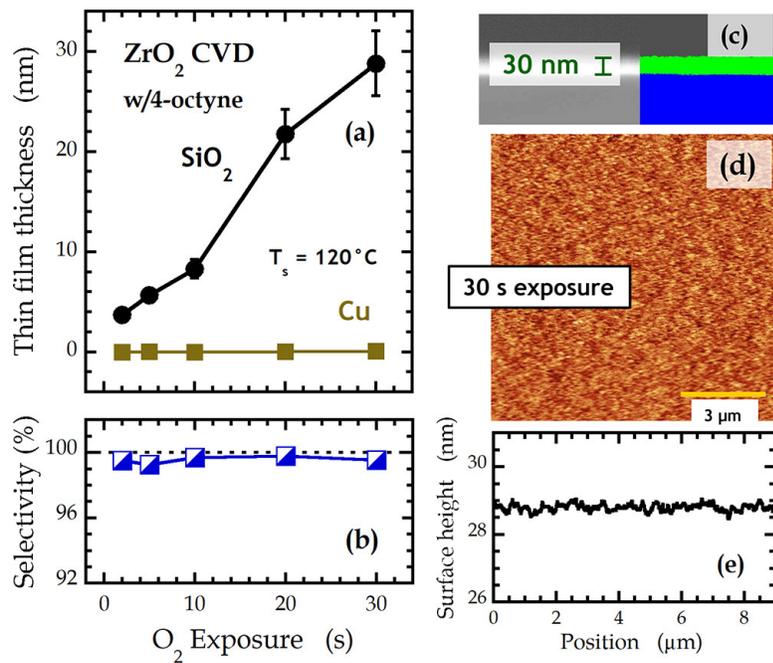


Figure 15: Results of previous area-selective deposition work using a co-adsorbate and a modified CVD process⁴⁶

A QCM is a particularly useful tool for study of area-selective ALD using a co-adsorbate, because it allows for assessment of the effectiveness of molecules as co-adsorbates under different conditions, including changes in temperature, pressure, and flow rates.

Internship at Lam Research Corporation

Introduction

During the summer of 2017, I completed an internship at Lam Research Corporation in Tualatin, Oregon, where I utilized the QCM reactor system in the Selective Deposition Group and became familiar with its construction and operation. One objective of my internship was to assess the experimental setup of the chamber and determine aspects to duplicate and to alter when assembling a similar system at Cornell. The chamber design at Lam used a tube furnace for heating the reactor and a glovebox for housing the precursors and changing crystals (Figure 16).⁴⁸ Throughout the internship, I managed and operated the reactor, participating in the development of novel deposition processes for the company. The main outcomes of that work were methods for selective growth of silicon oxide on silicon oxide in the presence of copper (resulted in one patent and one patent pending),^{49, 50} and for the use of amines to increase the deposition rate of an ALD process (resulted in one patent).⁵¹

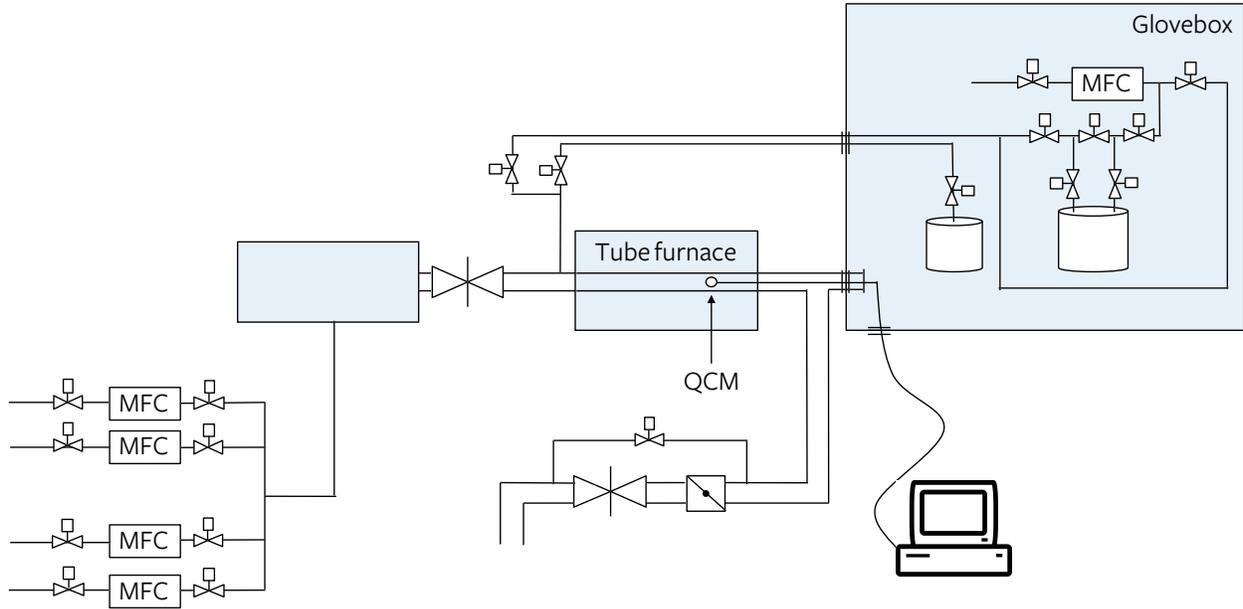


Figure 16: Lam Research Corporation vacuum chamber utilizing a quartz crystal microbalance for study of selective deposition processes⁴⁸

Selective growth of silicon oxide on silicon oxide in the presence of copper

Some of the fundamental questions we were investigating were: How do oxidizing and reducing plasmas affect oxide and metal surfaces? How do oxidizing and reducing plasmas affect ALD growth when dosed as part of the ALD sequence? How are ALD growth rates affected by introduction of additional species?

The system we were studying was selective growth of silicon oxide on silicon oxide in the presence of copper, using bis(diethylamino)silane, $\text{SiH}_2(\text{N}(\text{CH}_2\text{CH}_3)_2)_2$ (BDEAS) as the silicon-containing precursor and carbon dioxide plasma as the oxidizing co-reactant.

The reducing agent used was hydrogen plasma. Inert argon was used as the carrier gas for BDEAS, to dilute the carbon dioxide and hydrogen during plasma doses, and as the purge between reactants. By dosing each component individually, we could better understand how they behaved during the ALD experiments. Experiments were conducted to dose only argon plasma on copper and silicon oxide, and it was determined that the argon plasma did not significantly modify the surfaces. Repeated doses of hydrogen plasma and carbon dioxide plasma on the silicon oxide surface showed minimal impacts as well. On the copper surface, alternating doses of hydrogen plasma (10 seconds) and carbon dioxide plasma (1 s) showed that the surface could be repeatedly reduced and oxidized with only a small change in surface density (Figure 17). This result suggested that potential oxidation of the copper surface during the carbon dioxide plasma co-reactant dose of an ALD cycle could be managed by adding a hydrogen plasma step to the cycle.

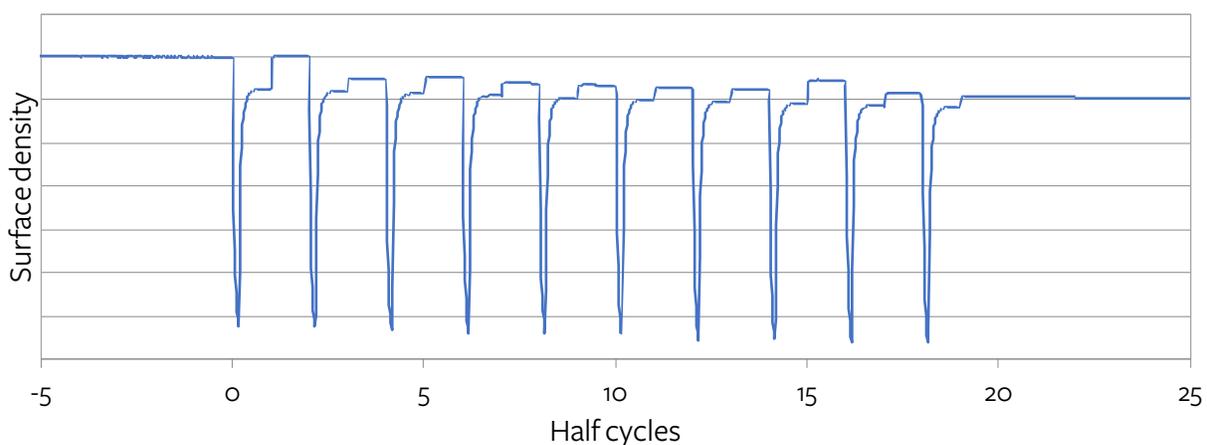


Figure 17: Alternating hydrogen plasma and carbon dioxide plasma on copper

A pristine ALD experiment includes only the precursor and the co-reactant. The pristine reference experiment for the system of interest was BDEAS (1 s) and carbon dioxide plasma (1 s) ALD, and it was first performed on a silicon oxide substrate (Figure 18a). During each cycle, the BDEAS dose resulted in an increase in thickness at the beginning, and, slightly after halfway through each cycle, the carbon dioxide plasma dose resulted in a slight change in thickness (Figure 18b).

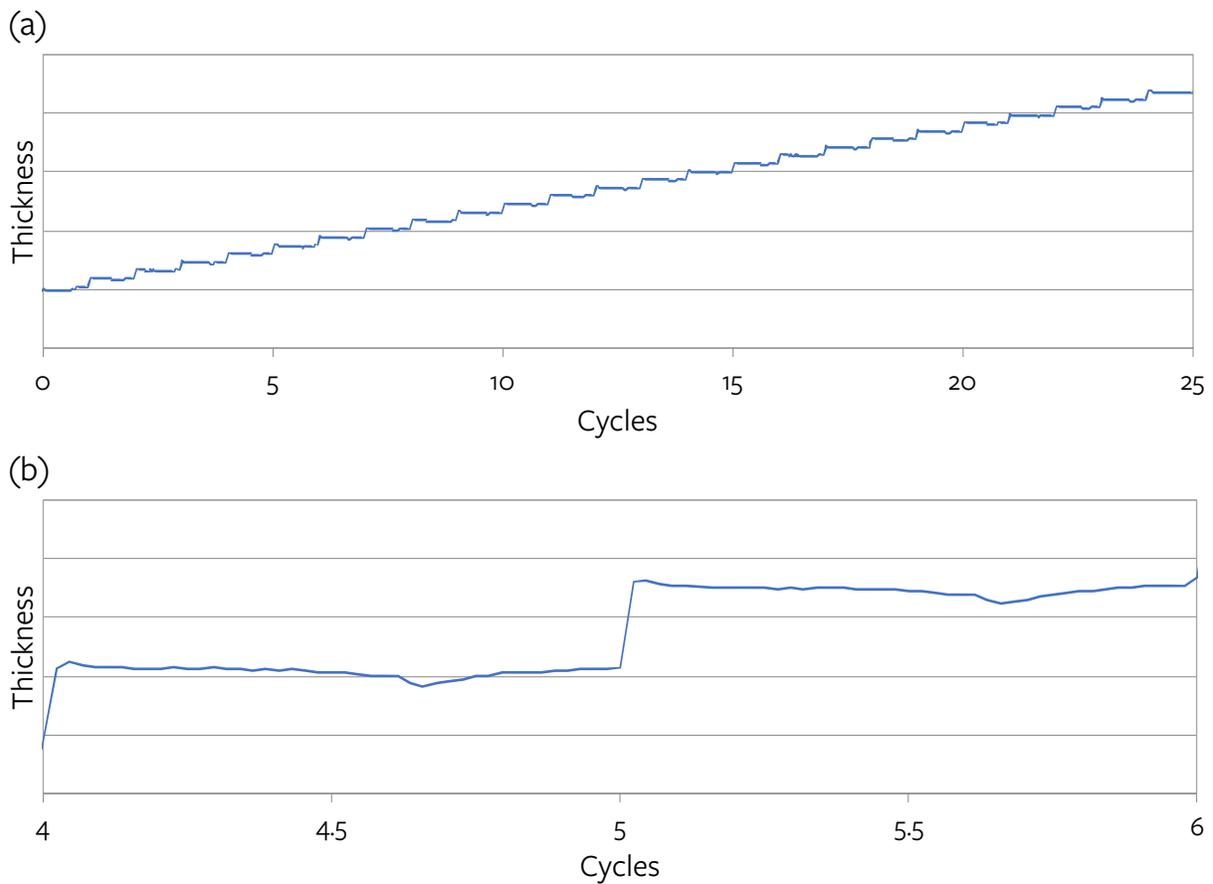


Figure 18: BDEAS | carbon dioxide plasma ALD on silicon oxide, (a) twenty-five cycles, (b) cycles five and six

The BDEAS and carbon dioxide plasma ALD experiment was repeated on copper (Figure 19). Before initiating the ALD experiment, the copper surface was exposed to five doses of hydrogen plasma (10 s), shown during the negative cycles (Figure 19a), and it was apparent that there was some mass loss during these cycles due to reduction of the copper surface. For the initial approximately twelve cycles of the experiment, there was a high apparent growth rate, and, subsequently, the growth rate slowed and reached a steady state. To understand this behavior, it was necessary to examine the change in thickness due to each reactant in individual cycles during each regime. In the cycles during the higher growth rate regime, the initial, smaller increase in thickness was due to the BDEAS dose and the second, greater increase in thickness was due to the carbon dioxide plasma dose (Figure 19b). As anticipated, the carbon dioxide plasma not only reacted with the adsorbed BDEAS to form silicon oxide, but also oxidized the copper surface. Once the copper surface was completely oxidized, the experiment transitioned to the lower growth rate regime. During these later cycles, an increase in thickness was observed due to the BDEAS dose, and the carbon dioxide plasma dose resulted in a smaller change in thickness (Figure 19c). This cycle shape resembled that of the pristine experiment on silicon oxide (Figure 18b).

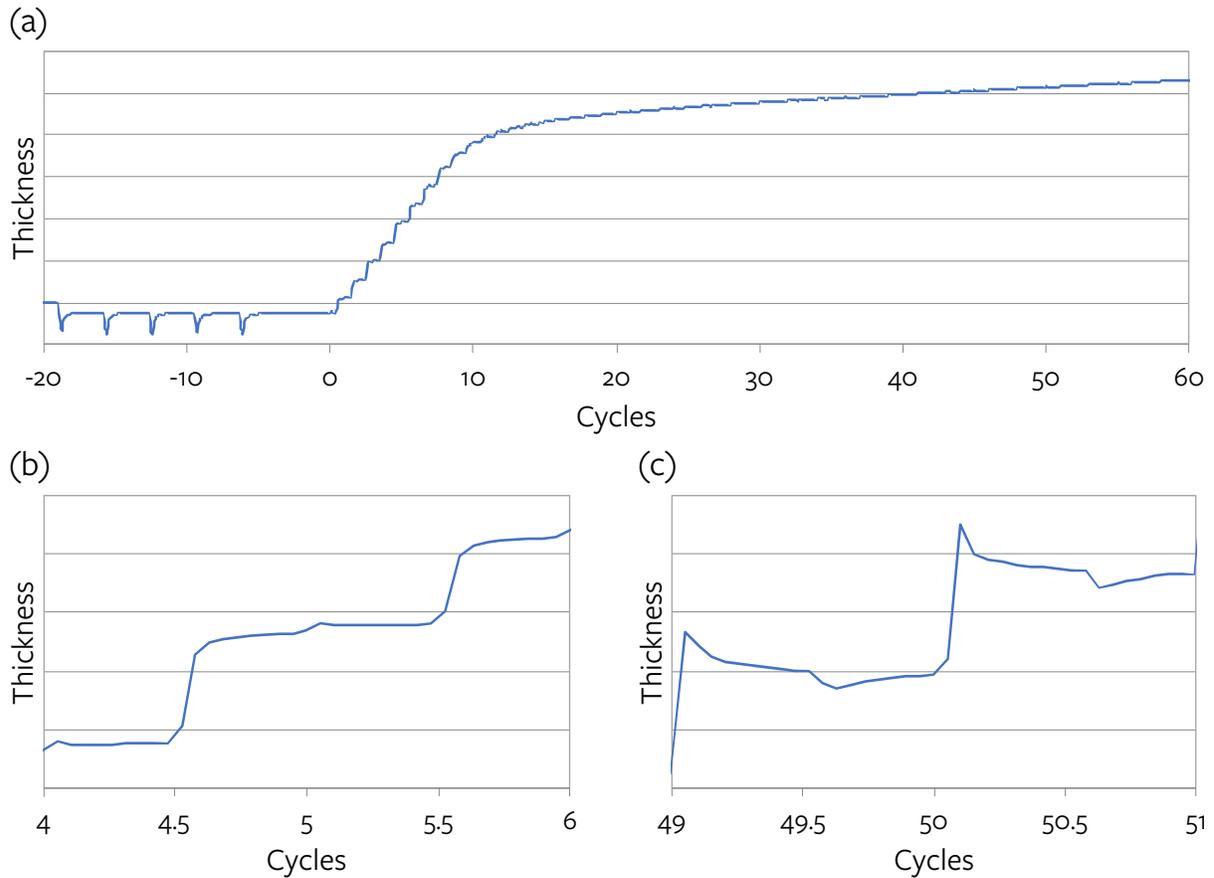


Figure 19: BDEAS | carbon dioxide plasma ALD on copper, (a) sixty cycles, (b) cycles five and six, (c) cycles fifty and fifty-one

After repeated hydrogen plasma doses on a copper surface, an ALD experiment was conducted with a hydrogen plasma step (30 s) after the carbon dioxide plasma step, to investigate whether this additional reducing dose could counteract the copper oxidation from the co-reactant dose (Figure 20). In this case, there was no high growth rate observed at the beginning of the experiment and the growth rate was steady over thirty cycles (Figure 20a), suggesting that the hydrogen plasma dose successfully reduced the copper surface after it was oxidized by the carbon dioxide plasma. Again, it was necessary to examine individual cycles to understand the impact of each reactant (Figure 20b). Similar

to the shape of the early cycles during the pristine experiment on copper (Figure 19b), the initial, smaller increase in thickness was due to the BDEAS dose and the second, greater increase in thickness was due to the carbon dioxide plasma dose. The hydrogen plasma dose resulted in the large decrease in thickness, and the subsequent increase in thickness occurred during the purge step. At the end of each cycle, the net thickness change was approximately the same magnitude as only the BDEAS dose, which was consistent with the steady state growth observed in the later cycles of the pristine experiment on copper (Figure 19c). This result demonstrated that adding a hydrogen plasma step to the end of the ALD cycle could manage oxidation of the copper surface during the carbon dioxide plasma co-reactant dose.

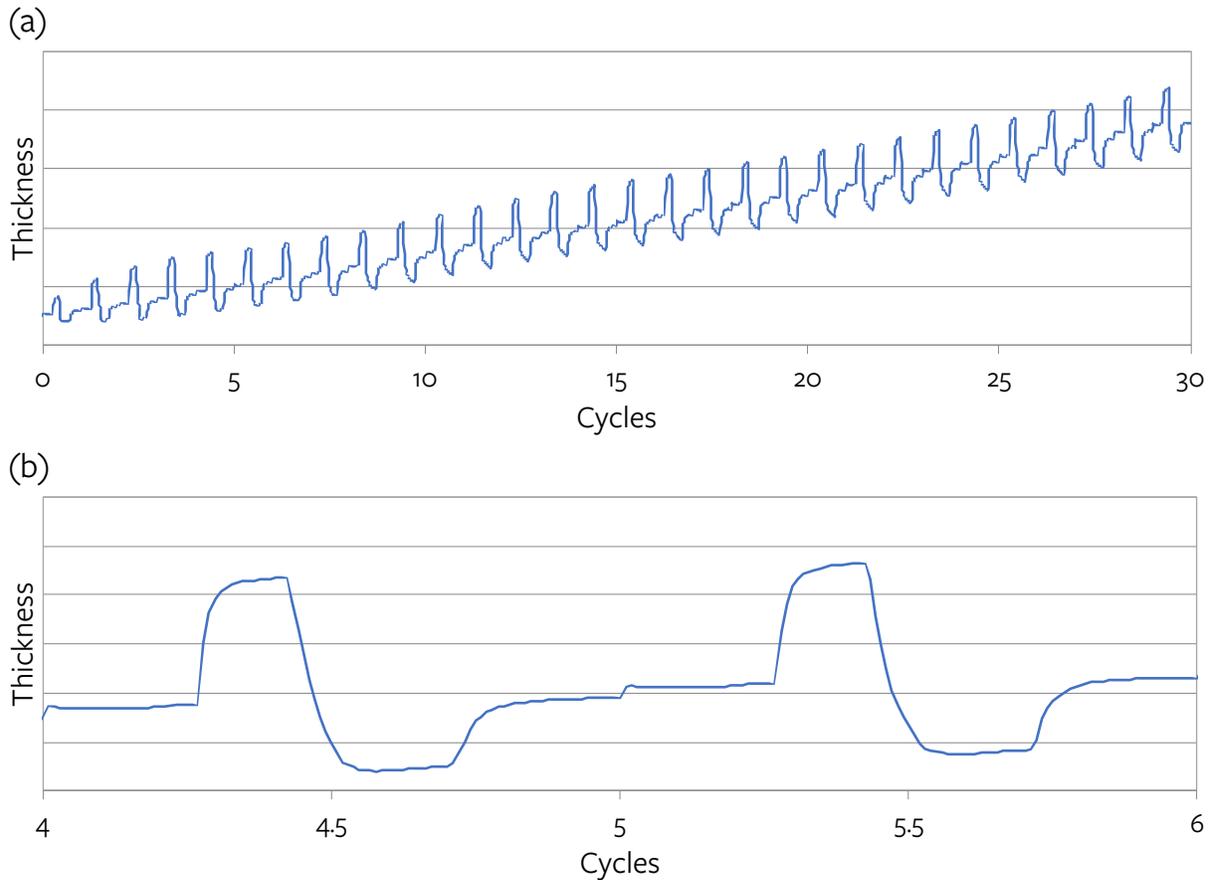


Figure 20: BDEAS | carbon dioxide plasma | hydrogen plasma ALD on copper, (a) thirty cycles, (b) cycles five and six

Incorporating the hydrogen plasma step into the ALD cycle on a silicon oxide substrate (Figure 21) was not expected to change the growth rate from the pristine experiment because it was previously observed that hydrogen plasma had a minimal effect on the silicon oxide surface. Similar to the pristine experiment (Figure 18b), the increase in thickness at the beginning of each cycle was due to the BDEAS dose and the carbon dioxide plasma dose resulted in a small change in thickness (Figure 21b). While the hydrogen plasma dose was on, the thickness appeared to decrease. However, once the

hydrogen plasma dose was turned off, the thickness returned to approximately the same value as before the hydrogen plasma dose was turned on. As a result, the growth rate of this modified ALD experiment was the same as that of the pristine ALD experiment.

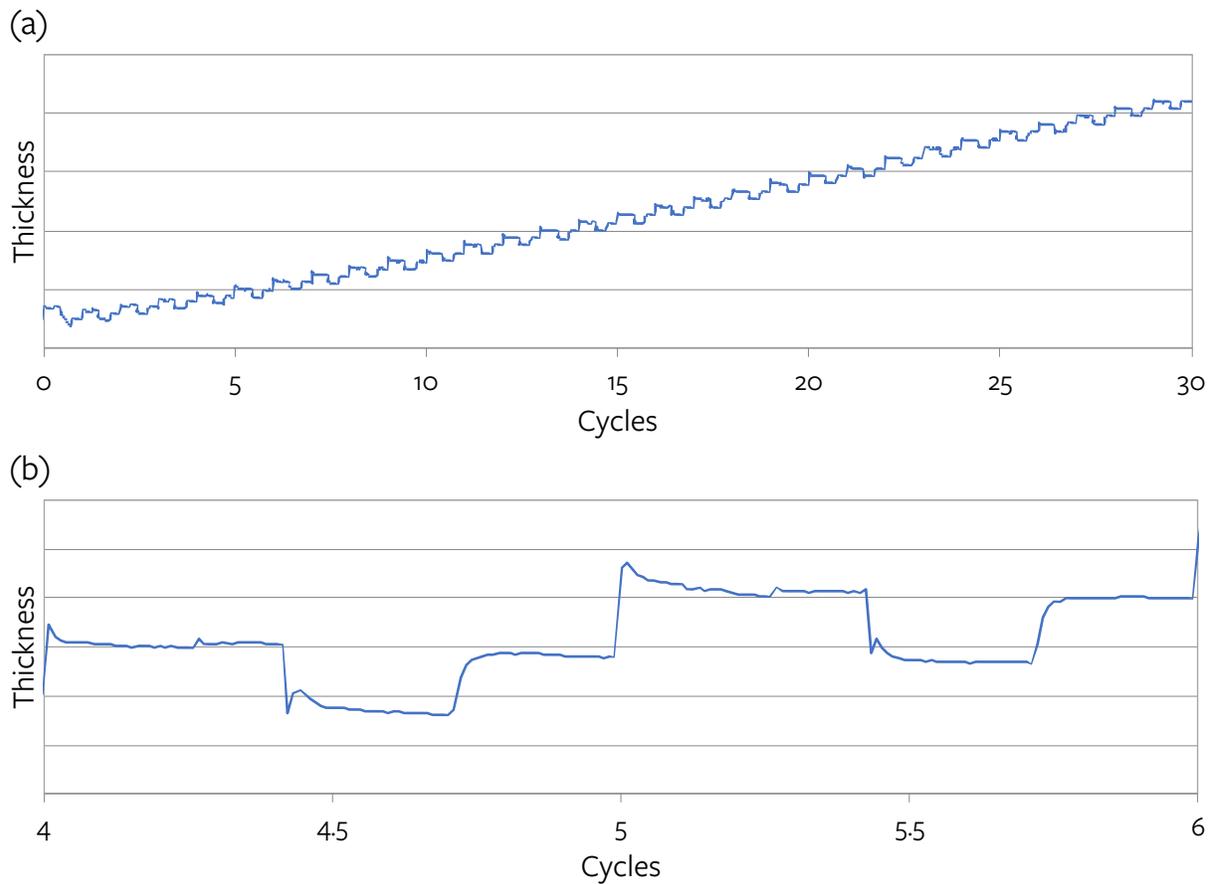


Figure 21: BDEAS | carbon dioxide plasma | hydrogen plasma ALD on silicon oxide, (a) thirty cycles, (b) cycles five and six

From these experiments, we understood how oxidizing and reducing plasmas affected silicon oxide and copper surfaces, and determined that a modified three-step ALD sequence could be employed to deposit silicon oxide on silicon oxide and copper in a

consistent and reproducible manner, which addressed the first two of our fundamental questions. To answer the third question, we added another step to the modified ALD sequence by introducing butanethiol before the BDEAS dose. The purpose of the butanethiol was to cover only the copper surface and prevent silicon oxide deposition on the copper, while allowing deposition to occur on the silicon oxide surface. Repeated doses of butanethiol on a reduced copper substrate showed strong adsorption and persistence of the butanethiol on the surface throughout the purge step (60 s), suggesting that the butanethiol could prevent adsorption of BDEAS on the copper surface (Figure 22).

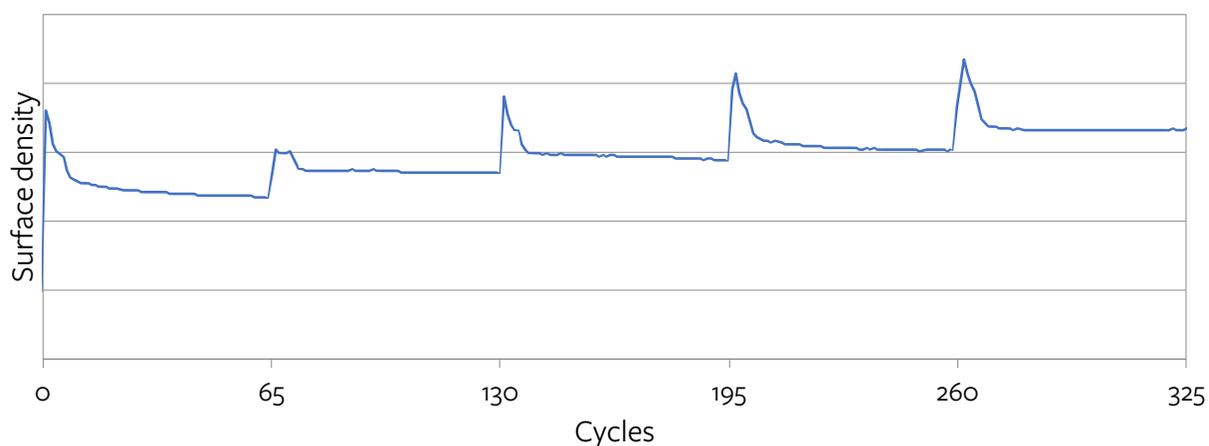


Figure 22: Butanethiol on copper

An experiment was conducted on a silicon oxide substrate and separately on a copper substrate to evaluate growth of silicon oxide on the two surfaces during cycling of butanethiol exposure, silicon oxide deposition, and reducing agent exposure. The silicon oxide and copper surfaces were each pretreated with repeated doses of hydrogen plasma,

then the following deposition sequence was cycled 100 times: butanethiol (step one, 2 s), purge using argon (step two, 10 s), BDEAS (step three, 1 s), purge using argon (step four, 16 s), carbon dioxide and argon (step five, 10 s), carbon dioxide and argon plasma (step six, 1 s), purge using argon (step seven, 16 s), hydrogen and argon plasma (step eight, 30 s), and purge using argon (step nine, 30 s).

Figure 23a and Figure 23b show the thickness on the silicon oxide surface for the first forty cycles and for only cycles twenty-five and twenty-six, respectively. Figure 24a and Figure 24b show the thickness on the copper surface for all 100 cycles and for only cycles twenty-five and twenty-six, respectively. The numeric labels in Figure 23b and Figure 24b correspond to the step number in the above deposition sequence.

The experiment on the silicon oxide substrate showed some deposition delay in the initial cycles, but then continued with a linear and steady growth rate of silicon oxide. While the butanethiol dose was on during step one, the thickness appeared to increase, but the thickness returned to its previous value once the butanethiol dose was turned off, demonstrating that the butanethiol did not persist on the silicon oxide surface. On the copper substrate, there was an initial large increase in thickness due to loading of butanethiol, which was followed by stagnant growth. The difference between the experiments on silicon oxide and copper can be understood by observing the difference in step three of the ALD sequence. Step three of Figure 23b shows the effect of BDEAS adsorbing onto the silicon oxide surface, while there is clear inhibition of BDEAS adsorption on the copper surface in step three of Figure 24b.

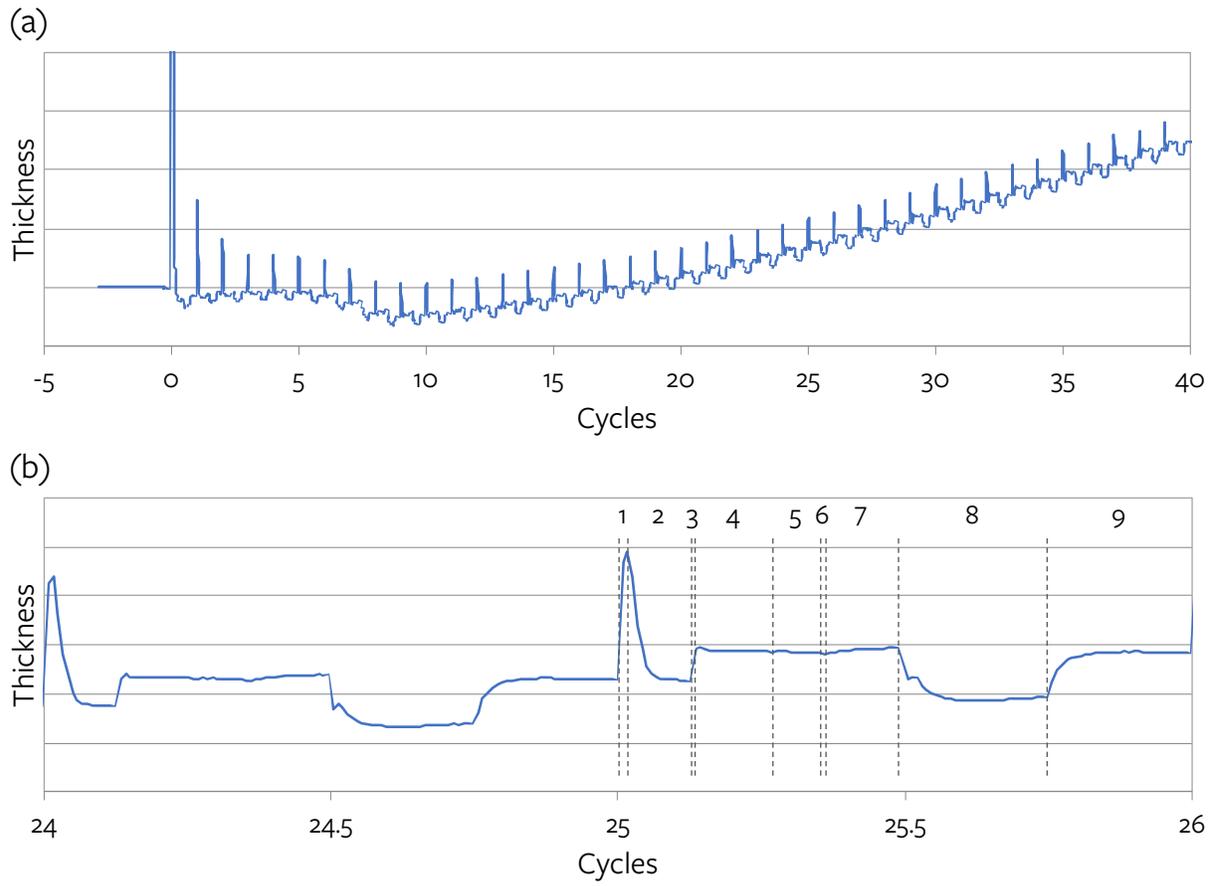


Figure 23: Butanethiol | BDEAS | carbon dioxide plasma | hydrogen plasma ALD on silicon oxide, (a) first forty cycles, (b) cycles twenty-five and twenty-six

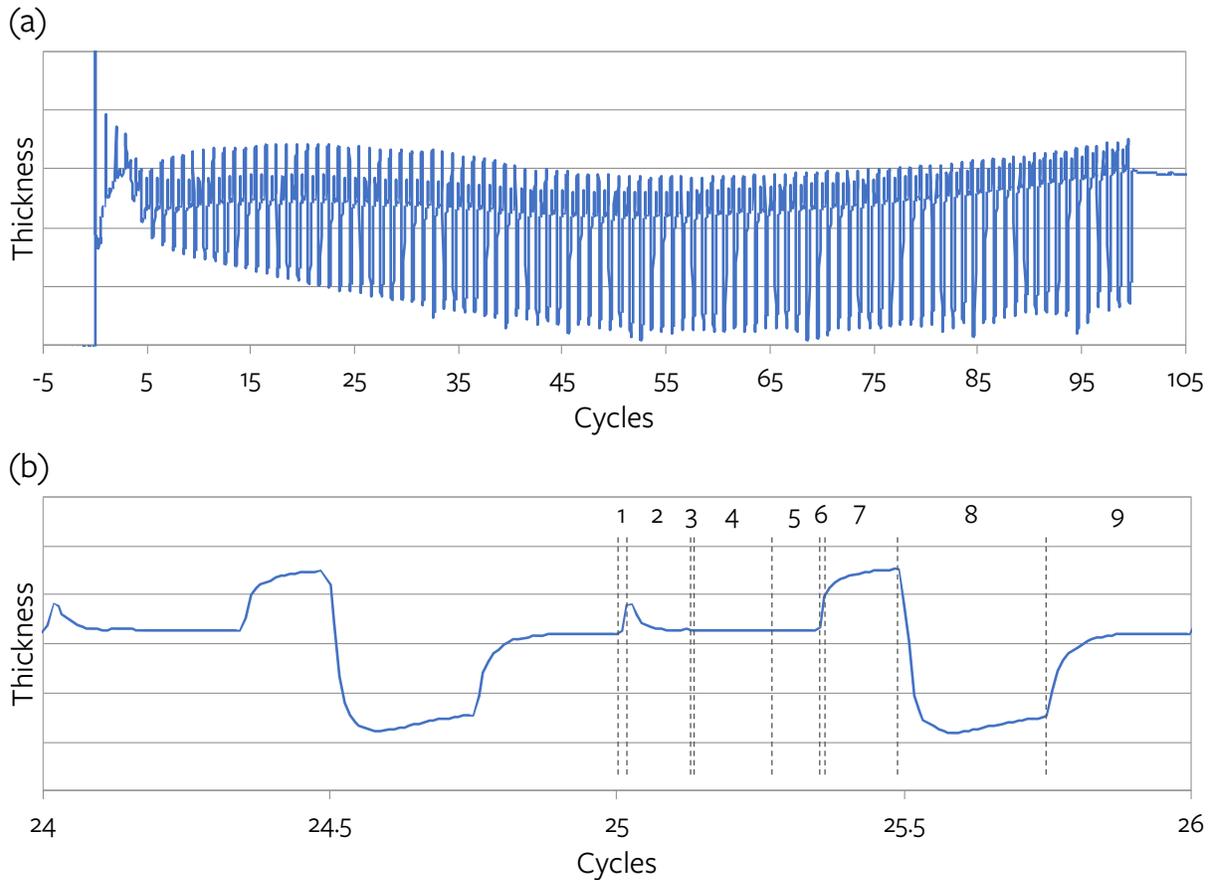


Figure 24: Butanethiol | BDEAS | carbon dioxide plasma | hydrogen plasma ALD on copper, (a) 100 cycles, (b) cycles twenty-five and twenty-six

While the data in Figure 23 and Figure 24 was collected using a QCM, wafer samples were also inserted into the chamber during the deposition process and were analyzed by X-ray photoelectron spectroscopy. Table 1 summarizes the thickness of silicon oxide deposited on the silicon oxide and copper wafer substrates and the relative selectivity.

Table 1: Silicon oxide growth on silicon oxide and copper surfaces⁴⁹

Substrate	Silicon oxide deposition (Å)	Relative selectivity
Silicon oxide	28	5.6
Copper	5	1

Novel claims for selective growth of silicon oxide on silicon oxide in the presence of copper

Summary

Provided herein are methods and apparatuses for processing semiconductor substrates, as disclosed in U.S. Patent Application Number 15/821,590 (now U.S. Patent Number 10,460,930), filed November 22, 2017, and U.S. Patent Application Number 16/575,214 (now U.S. Patent Number 10,825,679), filed September 18, 2019.^{49, 50}

One aspect involves a method of selectively depositing silicon oxide on a dielectric material relative to copper on a substrate. The method includes: (a) providing the substrate including the dielectric material and exposed copper metal surface; (b) exposing the substrate to a copper-blocking reagent to selectively adsorb onto the exposed copper metal surface to block subsequent deposition of the silicon oxide on the exposed copper metal surface; (c) exposing the substrate to a silicon-containing precursor to adsorb the silicon-containing precursor onto the dielectric material; (d) exposing the substrate to an oxidizing plasma generated in an environment comprising a weak oxidant to convert the

adsorbed silicon-containing precursors to silicon oxide; and (e) exposing the substrate to a reducing agent to reduce the exposed copper metal surface. The method may also include, prior to operation (b), introducing a reducing agent to reduce the exposed copper metal surface.

The copper-blocking reagent may include sulfur, and may be an alkyl thiol having a chemical formula $\text{SH}(\text{CH}_2)_n\text{CH}_3$, whereby n is an integer between and including two and twelve. The silicon-containing precursor may be an aminosilane. An aminosilane includes at least one nitrogen atom bonded to a silicon atom, but may also contain hydrogens, oxygens, halogens, and carbons. Examples of aminosilanes are mono-, di-, tri- and tetra-aminosilane ($\text{H}_3\text{Si}(\text{NH}_2)$, $\text{H}_2\text{Si}(\text{NH}_2)_2$, $\text{HSi}(\text{NH}_2)_3$ and $\text{Si}(\text{NH}_2)_4$, respectively). Further examples are substituted mono-, di-, tri- and tetra-aminosilanes: *t*-butylaminosilane, $\text{SiH}_3\text{NHC}(\text{CH}_3)_3$; bis(*t*-butylamino)silane, $\text{SiH}_2(\text{NHC}(\text{CH}_3)_3)_2$, (BTBAS); bis(diethylamino)silane, $\text{SiH}_2(\text{N}(\text{CH}_2\text{CH}_3)_2)_2$, (BDEAS); tris(dimethylamino)silane, $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$, (TDMAS); bis(dimethylamino)chlorosilane, $\text{SiHCl}(\text{N}(\text{CH}_3)_2)_2$; and bis(dimethylamino)dimethylsilane, $\text{Si}(\text{CH}_3)_2(\text{N}(\text{CH}_3)_2)_2$, (BDMADMS). Another example of an aminosilane is trisilylamine, $\text{N}(\text{SiH}_3)_3$. In some cases, the silicon-containing precursor is an alkylaminosilane having a central silicon atom bonded to four R groups, where at least one R group includes a primary or secondary amino group, and up to three of the R groups is a hydrogen atom. The weak oxidant may be any of carbon dioxide, CO_2 ; nitrous oxide, N_2O ; ozone, O_3 ; plasmas thereof; and water, H_2O . The reducing agent may be any of hydrogen gas, H_2 ; hydrogen plasma; hydrazine gas, N_2H_4 ; hydrazine plasma; ammonia gas, NH_3 ; ammonia plasma; alcohols (e.g., ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, and

isopropanol, $\text{CH}_3\text{CHOHCH}_3$); and aldehydes (e.g., formaldehyde, CH_2O). Utilizing a plasma instead of a gas can improve reduction efficiency. The dielectric material may be any of silicon oxide, aluminum oxide, silicon oxycarbides, silicon carbonitrides, and silicon oxycarbonitrides. The silicon oxide may be deposited at a temperature between about $70\text{ }^\circ\text{C}$ and about $200\text{ }^\circ\text{C}$. The method may also include repeating operations (b)–(e) in two or more cycles.

Another aspect involves a method of selectively depositing silicon oxide on a dielectric material relative to a metal-containing surface on a substrate, where the method is similar to that for depositing silicon oxide on a dielectric material relative to copper on a substrate, except in operation (b) the reagent is a metal-blocking reagent that selectively adsorbs onto the exposed metal-containing surface. The exposed metal-containing surface may include any of copper metal, copper oxide, ruthenium metal, and ruthenium oxide.

Another aspect involves an apparatus for processing semiconductor substrates, the apparatus including: at least one process chamber comprising a pedestal for holding a semiconductor substrate; at least one outlet for coupling to a vacuum; a plasma generator; one or more process gas inlets coupled to one or more gas sources; and a controller for controlling operations in the apparatus, including machine-readable instructions for: causing exposure of the semiconductor substrate to a copper-blocking reagent to selectively adsorb onto an exposed copper metal surface; causing exposure of the substrate to a silicon-containing precursor to adsorb the silicon-containing precursor onto

a dielectric material on the semiconductor substrate; causing exposure of the substrate to an oxidizing plasma generated in an environment comprising a weak oxidant to convert the adsorbed silicon-containing precursors to deposit silicon oxide; and causing exposure of the substrate to a reducing agent to reduce the exposed copper metal surface.

Another aspect involves an apparatus for processing semiconductor substrates, where the metal-containing surface of the substrate may include any of copper metal, copper oxide, ruthenium metal, and ruthenium oxide.

Methods

In the following description, numerous specific details are set forth to provide a thorough understanding of the presented concepts. The disclosed concepts may be practiced without some or all of these specific details. In other instances, well-known process operations have not been described in detail to not unnecessarily obscure the disclosed concepts.

Semiconductor manufacturing processes often involve deposition and etching of various materials in a patterning scheme to form specific types of semiconductor devices. For example, patterning schemes may be used to fabricate a static random-access memory (SRAM) cell. As devices shrink, however, the tolerance of a process for error becomes increasingly small, particularly for fabrication of metal interconnect between a metal trench above and below the metal interconnect. Further, while multiple patterning or

extreme ultraviolet lithography techniques may be used to fabricate small devices having a low critical dimension, such techniques are not yet capable of fabricating dense circuitry from the 10 nm technology node down to the 5–7 nm technology node. Thus, in conventional techniques, when one layer is misaligned with a preceding layer, the difference in alignment of a few nanometers becomes a challenge.

One example is provided in Figure 25. This figure depicts a conventional process for forming a via over an interconnect, which results in an “unlanded via,” whereby material deposited in the via does not align with the preceding interconnect layer due to misalignment in the formation of the mask before depositing the metal in the via. Figure 25a shows a substrate 101 with metal lines 103a and 103b and an etch stop layer 105a deposited over the entire surface. In Figure 25b, the etch stop layer is modified to form a patterned etch stop layer 105b. This etching process exposes the surface of metal line 103a but continues to mask metal line 103b. In Figure 25c, a dielectric material 107a is deposited over the entire surface. In Figure 25d, the dielectric material is etched to form a dielectric layer 107b including a via 109. A conventional technique for creating the via could involve forming a mask over the substrate, patterning the mask using etching techniques such as lithography, and etching the dielectric material to the pattern of the mask. However, since wafer transfer and alignment processes and etching processes may not always align the mask accurately over the metal line 103a, the via 109 may be misaligned to the metal line 103a, as shown in Figure 25d. In larger critical dimension features and for fabrication of larger devices, this misalignment may not be a concern, but where the distance between two metal lines 103a and 103b is on a nanometer scale,

misalignment of via 109 can cause it to be aligned too close to adjacent metal line 103b, which can cause a short or other device problems. Further, it is difficult to obtain a vertical profile in the via using conventional processes. In Figure 25e, the via 109 is filled with metal to connect to the metal line 103a. However, due to the misalignment of via 109, deposition of the metal into the via may penetrate into the substrate material 101, forming a “fang” or “tiger tooth” defect 111. This overlay deposition at fang 111 may cause device issues such as via-to-metal shorts, which results in high resistance and poor time-dependent dielectric breakdown (TDDB) lifetime.

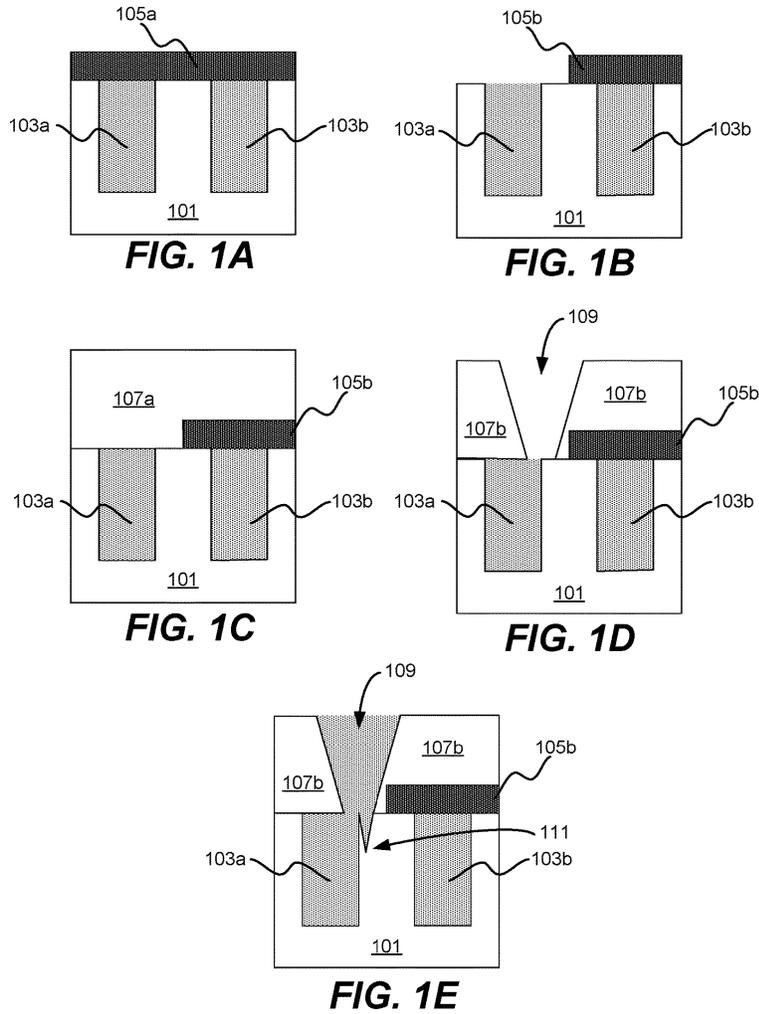


Figure 25: Schematic illustrations of a substrate undergoing a process to deposit metal in a via⁴⁹

It is desirable to form fully aligned vias, and one example of this process is provided in Figure 26. In Figure 26a, a dielectric substrate 201 includes copper vias 203a and 203b. In Figure 26b, a dielectric material 213 is deposited selectively on the dielectric 201 surfaces relative to the exposed copper surfaces. Such dielectric material 213 may have etch contrast to ultra-low-k (ULK) dielectric. In Figure 26c, blanket ULK dielectric material 211 is deposited over the entire substrate. The blanket ULK dielectric material 211 is etched

to form vias 215, shown in Figure 26d. In Figure 26e, the blanket ULK dielectric material is further etched to form etched ULK dielectric material 231. Since the selectively deposited dielectric material 213 has etch selectivity to the ULK dielectric material 231, the vias 235 are fully self-aligned. In Figure 26f, copper is filled into the vias to form the dual damascene structure.

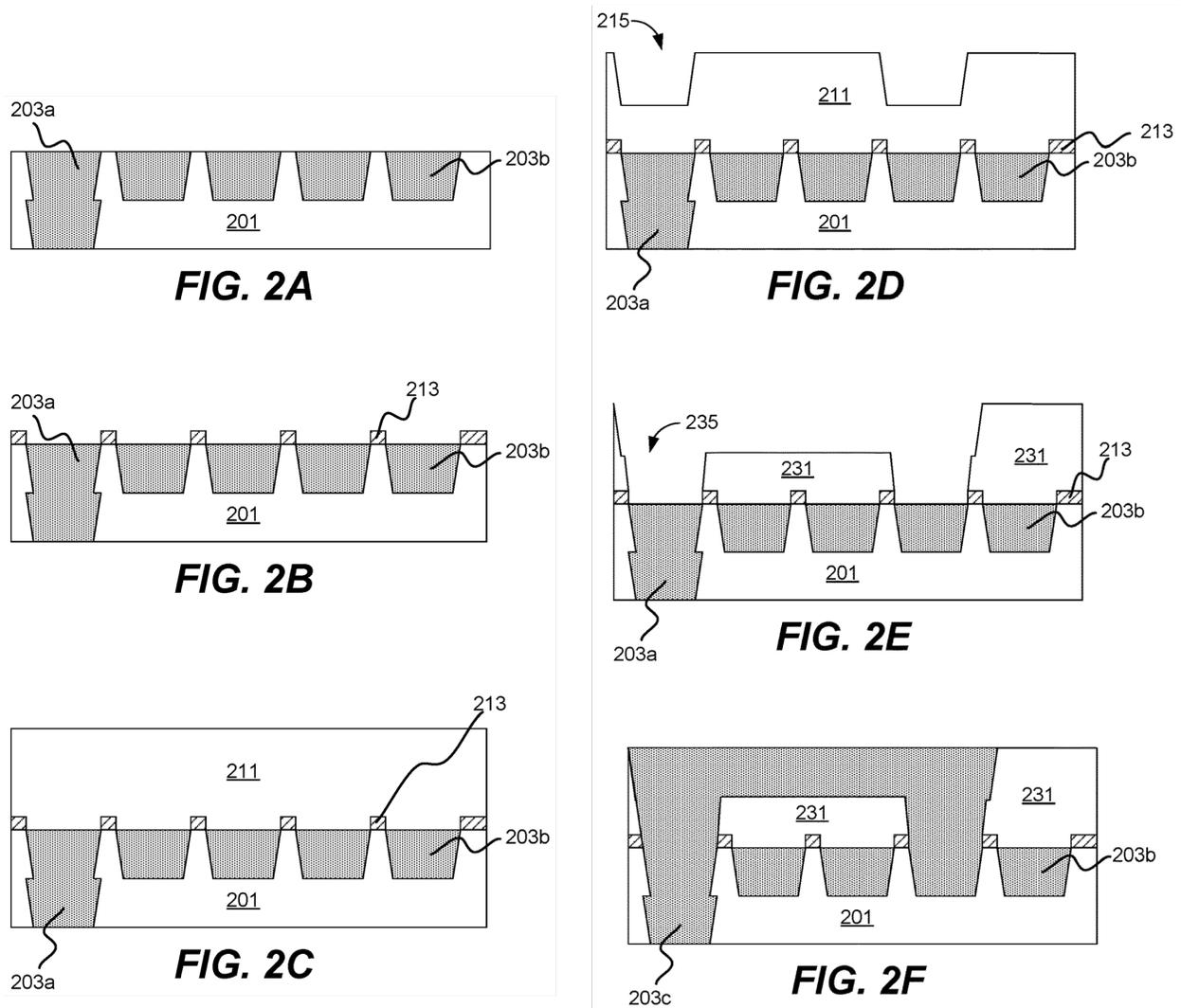


Figure 26: Schematic illustrations of a substrate undergoing a process for forming fully aligned vias using selective deposition of dielectric on dielectric⁴⁹

However, conventional techniques for depositing silicon oxide selectively on dielectric material relative to copper material are limited. For example, while silicon oxide could be deposited using a chlorine-containing precursor by a thermal reaction, chlorine will likely etch the copper surface. Additionally, if a plasma-based reaction is performed using plasma generated using oxygen gas, the strong oxidizing plasma of oxygen will oxidize the exposed copper surface. Thus, there is a need for selective deposition techniques of dielectric-on-dielectric material relative to copper to fabricate the fully aligned via. While techniques exist for depositing metal oxides (e.g., aluminum oxide, hafnium oxide, and zirconium oxide) using water as a reactant, these techniques may be selective to dielectrics having a high dielectric constant and are not suitable for selectively depositing silicon oxide.

Provided herein are methods of selectively depositing dielectric material on dielectric material relative to copper, copper oxides, ruthenium, or ruthenium oxides. For example, the process may involve depositing silicon oxide on silicon oxide, aluminum oxide, silicon oxycarbides, silicon carbonitrides, and silicon oxycarbonitrides. A non-limiting example of a silicon oxycarbide has the chemical formula SiO_xC_y where $2x+4y=4$ (x and y need not be integers). A non-limiting example of a silicon carbonitride has the chemical formula SiC_xN_y where $4x+3y=4$ (x and y need not be integers). A non-limiting example of a silicon oxycarbonitride has the chemical formula $\text{SiO}_x\text{C}_y\text{N}_z$ where $2x+4y+3z=4$ (x , y , and z need not be integers). This can be achieved by utilizing the reactivity difference between that of hydroxyl-terminated silicon oxide and of reduced copper to allow

selective deposition using exposure to a copper-blocking reagent, which preferentially adsorbs to the reduced copper surface and blocks subsequent deposition on the copper surface. Techniques described herein involve thermal atomic layer deposition (ALD) and plasma-enhanced atomic layer deposition (PEALD), which involve a reaction between a silicon-containing precursor and an oxidizing agent to form silicon oxide.

ALD is a technique that deposits thin layers of material using sequential self-limiting reactions. Typically, an ALD cycle includes operations to deliver and adsorb at least one reactant to the substrate surface, and then react the adsorbed reactant with one or more reactants to form the partial layer of film. As an example, a silicon oxide deposition cycle may include these operations: (i) delivery and adsorption of a silicon-containing precursor, (ii) purging of the silicon precursor from the chamber, (iii) delivery of an oxygen-containing reactant, and (iv) purging of the oxygen-containing reactant from the chamber.

Unlike a chemical vapor deposition (CVD) technique, ALD processes use surface-mediated deposition reactions to deposit films on a layer-by-layer basis. In one example of an ALD process, a substrate surface that includes a population of active sites is exposed to a gas phase distribution of a first precursor, such as a silicon-containing precursor, in a dose provided to a chamber that houses a substrate. Molecules of this first precursor are adsorbed onto the substrate surface, including chemisorbed or physisorbed species. When the compound is adsorbed onto the substrate surface, the adsorbed layer may include the compound and derivatives of the compound. For example, an adsorbed layer

of a silicon-containing precursor may include the silicon-containing precursor and derivatives of the silicon-containing precursor. After a first precursor dose, the chamber is then evacuated to remove most or all of first precursor remaining in gas phase so that mostly or only the adsorbed species remain. The chamber may not be fully evacuated; for example, the chamber may be evacuated such that the partial pressure of the first precursor in gas phase is sufficiently low to mitigate a reaction. A second reactant, such as an oxygen-containing reactant, is introduced to the chamber so that some of these molecules react with the first precursor adsorbed on the surface. In some processes, the second reactant reacts immediately with the adsorbed first precursor. The chamber may then be evacuated again to remove unbound second reactant molecules. As described above, the chamber may not be completely evacuated. Additional ALD cycles may be used to build film thickness.

In some processes, the ALD first precursor dose only partially saturates the substrate surface, and the dose phase of the ALD cycle may conclude before the precursor contacts the substrate to evenly saturate the surface. Typically, the precursor flow is then turned off or diverted and only purge gas flows. By operating in this sub-saturation regime, cycle time is reduced and throughput is increased. However, because precursor adsorption is not limited by saturation, the adsorbed precursor concentration may vary slightly across the substrate surface. Examples of ALD processes operating in the sub-saturation regime are provided in U.S. Patent Application Number 14/061,587 (now U.S. Patent Number 9,355,839), filed October 23, 2013, titled "Sub-saturated atomic layer deposition and conformal film deposition."

The ALD methods and apparatuses may be conformal film deposition (CFD) methods, which are described generally in U.S. Patent Application Number 13/084,399 (now U.S. Patent Number 8,728,956), filed April 11, 2011, titled "Plasma activated conformal film deposition," and in U.S. Patent Application Number 13/084,305, filed April 11, 2011, titled "Silicon nitride films and methods."

Figure 27 provides a process flow diagram depicting operations in a method performed under certain disclosed embodiments. In operation 301, a substrate having an exposed copper surface and an exposed dielectric surface is provided. The substrate may be a silicon wafer (e.g., a 200 mm wafer, a 300 mm wafer, or a 450 mm wafer), including wafers having one or more layers of material, such as dielectric, conducting, or semiconducting material deposited thereon. Non-limiting examples of under-layers include dielectric layers and conducting layers (e.g., silicon oxides, silicon nitrides, silicon carbides, metal oxides, metal nitrides, metal carbides, and metal layers). The substrate may include a dielectric material such as hydroxyl-terminated silicon oxide or a ULK dielectric, and vias filled with a metal such as copper, copper oxide, ruthenium, or ruthenium oxide. Sometimes, the substrate may include a semiconductor material instead of a dielectric material.

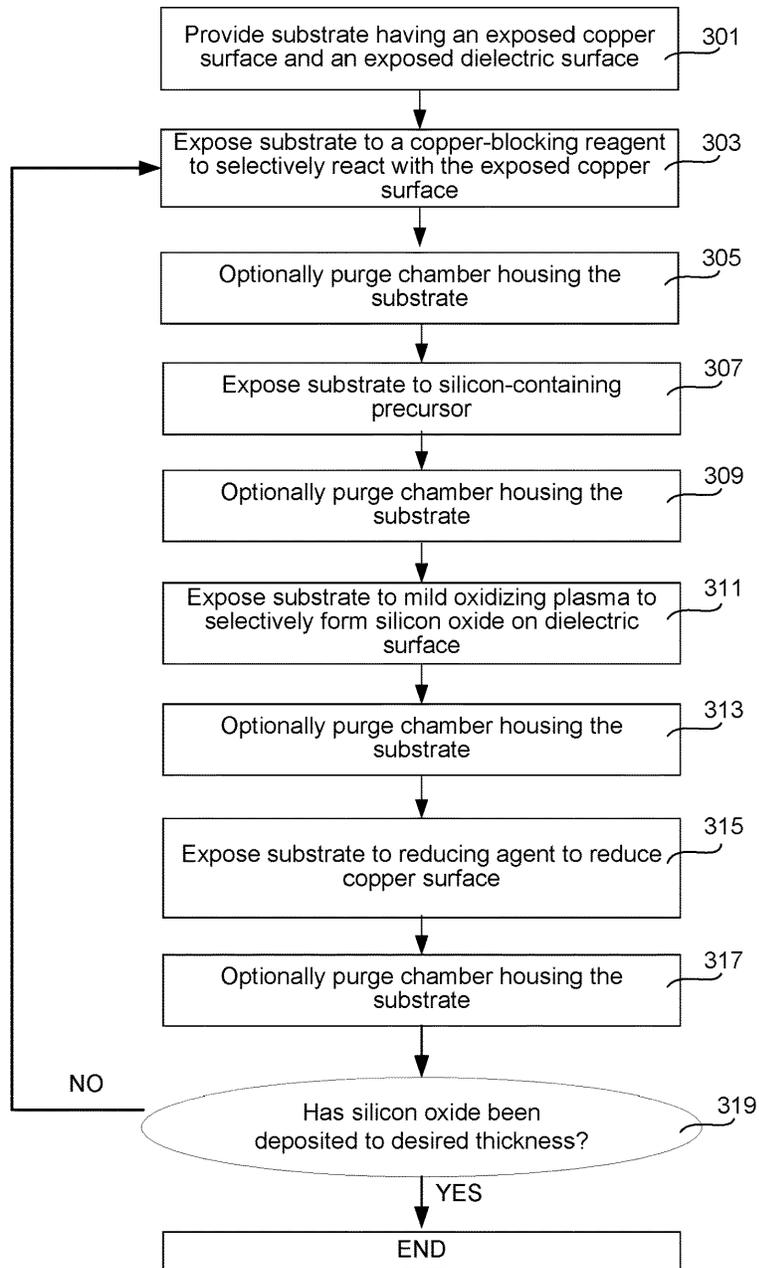


FIG. 3

Figure 27: Process flow diagram depicting operations for performing a method in accordance with certain disclosed embodiments⁴⁹

In operation 303, the substrate is exposed to a copper-blocking reagent to selectively react with the exposed copper surface. The copper-blocking reagent is selected to be reactive with copper and copper oxide surfaces but not reactive with dielectric surfaces such as hydroxyl-terminated silicon oxide surfaces. For example, thiols include a sulfur atom which may react with copper on the copper surface where the copper was reduced by a reducing agent. Since some copper surfaces have native oxides on the surface, forming copper oxide, thiols selected include sulfur atoms that react with copper oxide to form water and a thiolate. The blocked copper surface is both non-volatile and sterically crowded. Methanethiol is not used because it may not be sufficiently bulky to prevent oxidation of the copper surface. Octanethiol contains a long tail that is sufficiently bulky to prevent oxidation of the copper surface, but it may not be used because it cannot pack tightly enough to adsorb to most of the exposed copper surface. Generally, the alkyl chain is a carbon chain with only hydrogen atoms and no other non-hydrogen substituents.

Figure 28a is a schematic illustration of an example substrate having an exposed silicon oxide surface 401 and an exposed copper surface 403. Figure 28b shows the example substrate after introduction of the copper-blocking reagent butanethiol. The exposed silicon oxide surface 401 is unchanged, whereas the exposed copper surface 403 reacted with butanethiol to form blocked surface 405.

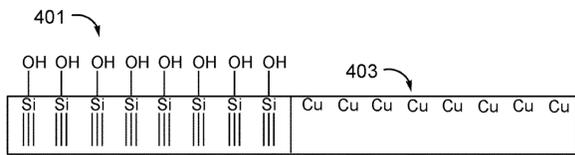


FIG. 4A

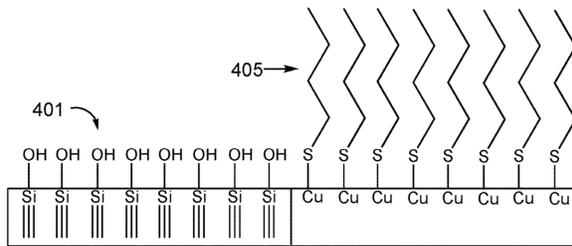


FIG. 4B

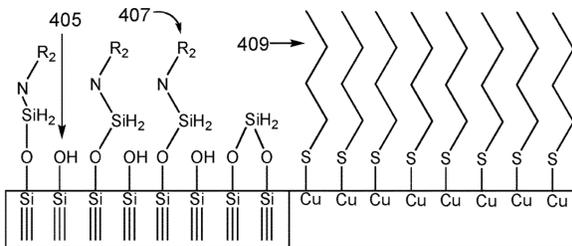


FIG. 4C

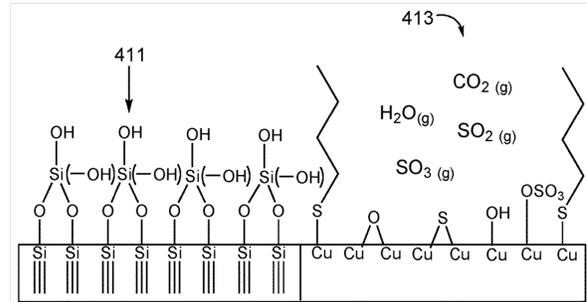


FIG. 4D

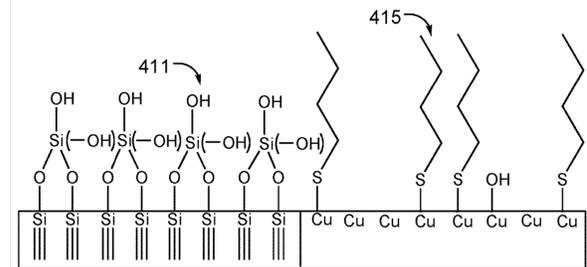


FIG. 4E

Figure 28: Schematic diagrams of an example mechanism for selectively depositing dielectric material⁴⁹

Returning to Figure 27, in operation 305, a chamber housing the substrate may be optionally purged for any suitable duration to remove excess copper-blocking reagent that does not react with the exposed copper surfaces. Purging the chamber may involve flowing a purge gas or a sweep gas, which could be a carrier gas used in other operations or could be a different gas. Example purge gases include argon, nitrogen, hydrogen, and helium. Purging may also involve evacuating the chamber, which could include one or more evacuation subphases. Increasing the flow rate of one or more purge gases may

decrease the duration of operation 305, which could improve substrate throughput. For example, a purge gas flow rate may be adjusted according to various reactant thermodynamic characteristics, geometric characteristics of the process chamber, or process chamber plumbing. After a purge, the copper-blocking reagent remains adsorbed onto the copper surface.

Operation 307 may be part of an ALD cycle, which generally contains one instance of a unique sequence of operations used to perform a surface deposition reaction. The result of one cycle is production of at least a partial film layer on the substrate surface. In operation 307, the substrate is exposed to a silicon-containing precursor such as an aminosilane. The silicon-containing precursor forms an adsorbed layer on the substrate surface, as depicted in Figure 28c. In some cases, the aminosilane precursor adsorbs onto the substrate surface in a self-limiting manner such that once active sites are occupied, little or no additional aminosilane precursor will be adsorbed on the substrate surface. For example, the aminosilane precursor may be adsorbed onto about 60 % of the substrate surface, and some hydroxyl-terminated groups 405 may remain on the surface. The adsorbed layer may be less than a monolayer and may have a thickness between about 0.2 Å and about 0.4 Å. Due to the blocking reagent on the copper surface 409, the silicon-containing precursor does not adsorb onto the copper surface.

In operation 309, the chamber housing the substrate may be optionally purged using any one or more techniques as described above regarding operation 305.

In operation 311, the substrate is exposed to a mild oxidizing plasma. A mild oxidizing plasma is generated using a weak oxidant, which is defined as an oxidant that limits oxidation of bulk copper to a depth of less than 10 Å from the surface. In some cases, water vapor is used instead of an oxidizing plasma. The oxidant may be selected such that it is not reactive with copper but is reactive with the adsorbed silicon-containing precursors on the dielectric surface. Figure 28d shows an example of a substrate after exposure to a carbon dioxide plasma such that hydroxyl-terminated silicon groups 411 are formed on the surface, building thickness of the silicon oxide. During oxidation, the blocking reagents may react with the oxide to form a variety of gases 413, such as water, carbon dioxide, sulfur dioxide, and sulfur trioxide. Such gases are mild oxidants and therefore may not necessarily oxidize the copper surface. However, as shown in Figure 28d, some copper may be oxidized or may form a hydroxyl-terminated copper surface. Some of the copper-blocking reagent may remain on the surface after the oxidation operation.

The chamber housing the substrate is optionally purged during operation 313 to remove excess byproducts, such as gases formed from reacting the mild oxidizing plasma with the blocking reagents and from reacting the mild oxidizing plasma with the silicon-containing precursor adsorbed onto the surface of the substrate. Purging may be performed using any one or more techniques as described above regarding operation 305.

In operation 315, the substrate is exposed to a reducing agent, which is selected such that it reduces the copper surface and does not affect the deposited silicon oxide material. The

reducing agent allows for subsequent selective deposition of dielectric material on the dielectric surface without depositing on the copper surface. In some cases, operation 315 is performed before performing operation 303, in addition to after performing operation 313. The reducing agent used before and after may be the same or different.

Figure 28e shows an example substrate whereby, after exposure to the reducing agent, silicon oxide 411 remains on the surface, some thiols 415 are replenished on the surface, and some oxidized copper is reduced to leave a copper surface.

Returning to Figure 27, in operation 317, the chamber housing the substrate is optionally purged to remove excess byproducts from exposing the substrate to the reducing agent in operation 315, such as water from the reaction between the reducing agent and oxidized copper.

In operation 319, it is determined whether the silicon oxide is deposited to a desired thickness. If so, the deposition process ends. If not, the deposition may resume by repeating operations 303–317 in cycles. Operations 303 and 315 may be performed in every cycle or less frequently, possibly every other cycle. However, it may be suitable to perform both operations 303 and 315 every cycle to continue blocking the copper surface from adsorption of the silicon-containing precursor, and to prevent oxidation of the copper surface and allow for selective deposition of silicon oxide. Each cycle may involve repeating the same operations using the same chemistries and process conditions, but each cycle may instead involve repeating the operations using different chemistries. For

example, a reducing agent used in one cycle may differ from a reducing agent used in another cycle.

Figure 29 provides a timing schematic diagram of various operations performed under certain disclosed embodiments. Although process 500 depicted in Figure 29 includes only two deposition cycles 599A and 599B, more than two deposition cycles (and possibly only one deposition cycle) may be performed. The lines indicate when the flow is turned on and off and when the plasma is turned on and off. Process parameters include, but are not limited to, flow rates for argon, thiol, silicon-containing precursor, and reducing agent gases, plasma conditions, substrate temperature, and process chamber pressure.

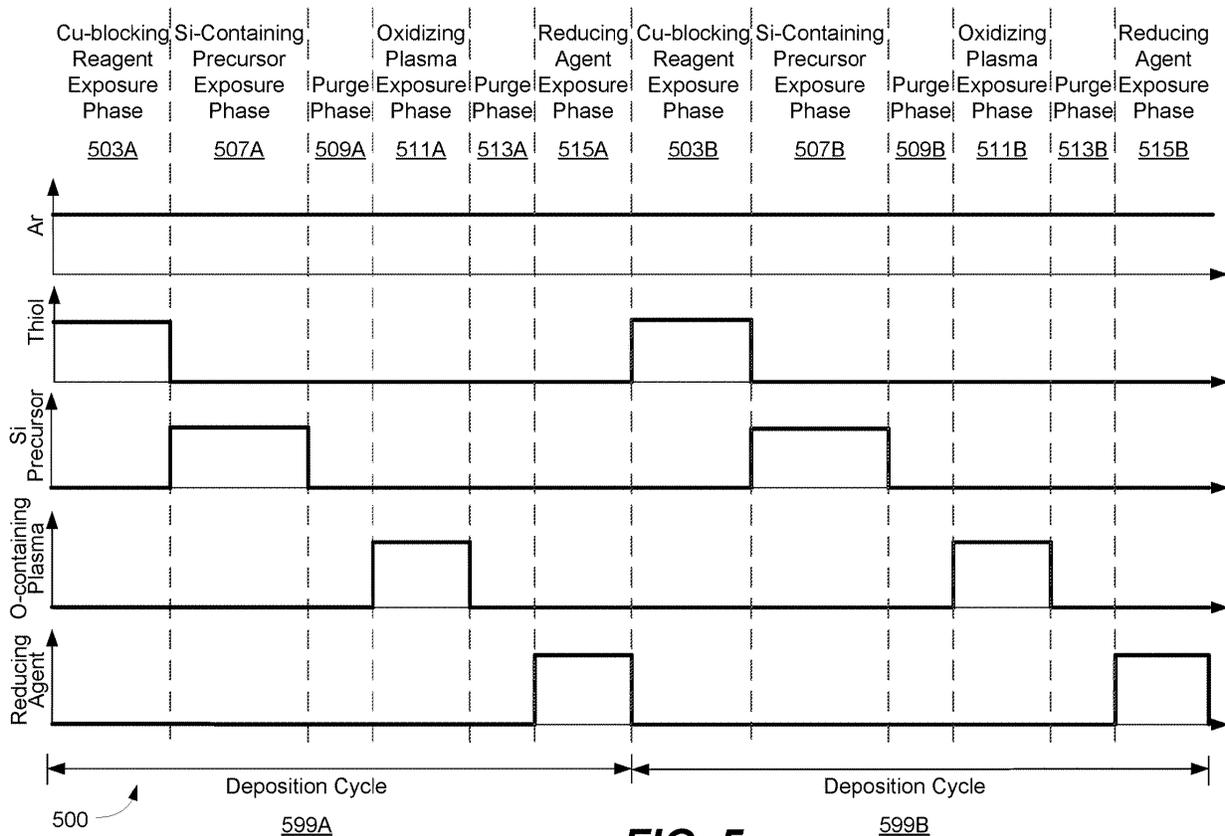


FIG. 5

Figure 29: A timing sequence diagram showing an example of cycles in a method in accordance with certain disclosed embodiments⁴⁹

Deposition cycle 599A includes copper-blocking reagent exposure phase 503A, silicon-containing precursor exposure phase 507A, purge phase 509A, oxidizing plasma exposure phase 511A, purge phase 513A, and reducing agent exposure phase 515A. Copper-blocking reagent exposure phase 503A may correspond to operation 303 of Figure 27. During copper-blocking reagent exposure phase 503A, argon flow may be on to bring the copper-blocking reagent to the chamber, thiol flow is on, silicon-containing precursor flow is off, oxygen-containing plasma is off, and reducing agent flow is off. Although not specified in this example, the thiol may be any suitable thiol such as those

described above regarding operation 303. Following copper-blocking reagent exposure phase 503A, silicon-containing precursor exposure phase 507A is performed. In this non-limiting example, purge operation 305 of Figure 27 is not performed. Silicon-containing precursor exposure phase 507A may correspond to operation 307. During silicon-containing precursor exposure phase 507A, argon flow may remain on to assist with delivery of the silicon-containing precursor, thiol flow is off, silicon-containing precursor flow is on, oxygen-containing plasma is off, and reducing agent flow is off. Purge phase 509A may correspond to operation 309. During purge phase 509A, argon flow is on to act as a purge gas, thiol flow is off, silicon-containing precursor flow is off, oxygen-containing plasma is off, and reducing agent flow is off. Oxidizing plasma exposure phase 511A may correspond to operation 311. During oxidizing plasma exposure phase 511A, argon flow may continue to be on, thiol flow is off, silicon-containing precursor flow is off, oxygen-containing plasma is on, and reducing agent flow is off. Purge phase 513A may correspond to operation 313. During purge phase 513A, argon flow is on to act as a purge gas, thiol flow is off, silicon-containing precursor flow is off, oxygen-containing plasma is off, and reducing agent flow is off. Reducing agent exposure phase 515A may correspond to operation 315. During reducing agent exposure phase 515A, argon flow may act as a carrier gas to assist with delivery of the reducing agent, thiol flow is off, silicon-containing precursor flow is off, oxygen-containing plasma is off, and reducing agent flow is on. Although the example depicted here involves a thermal reaction for the reducing agent exposure, a plasma may be ignited while the reducing agent flow is on during this exposure phase. In this non-limiting example, purge operation 317 is not performed after reducing agent exposure phase 515A.

In this example, it is determined that silicon oxide is not deposited to the desired thickness, so the operations are repeated in deposition cycle 599B. Deposition cycle 599B includes copper-blocking reagent exposure phase 503B, silicon-containing precursor exposure phase 507B, purge phase 509B, oxidizing plasma exposure phase 511B, purge phase 513B, and reducing agent exposure phase 515B, which are analogous to phases during deposition cycle 599A. After the silicon oxide is deposited to a sufficient thickness, the copper surface may be reduced by a reducing agent, and any remaining thiols on the copper surface may be removed by an acetic acid rinse.

Figure 30 depicts a schematic illustration of an ALD process station 600 having a process chamber body 602 for maintaining a low-pressure environment. A plurality of ALD process stations 600 may be included in a common low pressure process tool environment. For example, Figure 31 depicts a multi-station processing tool 700. One or more hardware parameters of ALD process station 600, including those discussed below, may be adjusted programmatically by one or more computer controllers 660.

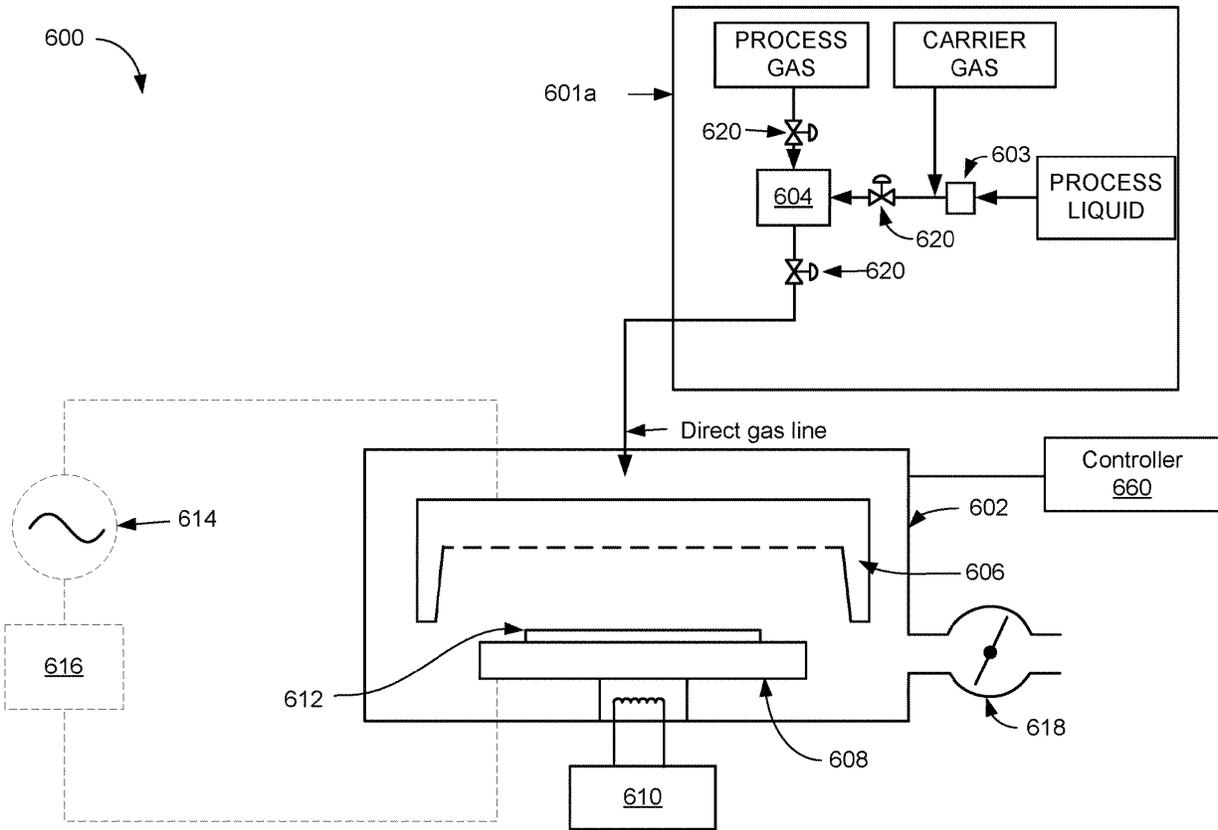


FIG. 6

Figure 30: A schematic diagram of an example process chamber for performing disclosed embodiments⁴⁹

Pressure control for ALD process station 600 may be provided by butterfly valve 618. As shown in Figure 30, butterfly valve 618 throttles a vacuum provided by a downstream vacuum pump (not shown). However, pressure control of process station 600 may also be adjusted by varying a flow rate of one or more gases introduced to the process station 600.

Process station 600 fluidly communicates with reactant delivery system 601a for delivering process gases to a distribution showerhead 606. Reactant delivery system 601a

includes a mixing vessel 604 for blending or conditioning process gases, such as an aminosilane precursor gas, or mild oxidant gas, or reducing agent gas, for delivery to showerhead 606. One or more mixing vessel inlet valves 620 may control introduction of process gases to mixing vessel 604. Mild oxidizing plasma or reducing agent plasma may also be delivered to the showerhead 606 or may be generated in the ALD process station 600.

Figure 30 includes a vaporization point 603, which may be a heated vaporizer, for vaporizing liquid reactant to be supplied to the mixing vessel 604. The saturated reactant vapor produced from such vaporizers may condense in downstream delivery piping. Exposure of incompatible gases to the condensed reactant may create small particles, which can clog piping, impede valve operation, contaminate substrates, and result in other undesirable scenarios. Some approaches to addressing these issues involve purging or evacuating the delivery piping to remove residual reactant. However, purging the delivery piping may increase process station cycle time, degrading process station throughput. Thus, delivery piping downstream of vaporization point 603 may be heat traced, and mixing vessel 604 may be heat traced as well. In one non-limiting example, piping downstream of vaporization point 603 has an increasing temperature profile extending from approximately 100 °C to approximately 150 °C at mixing vessel 604.

In some cases, liquid precursor or liquid reactant may be vaporized at a liquid injector. For example, a liquid injector may inject pulses of a liquid reactant into a carrier gas stream upstream of the mixing vessel. The liquid injector could vaporize the reactant by

flashing the liquid from a higher pressure to a lower pressure, or it could atomize the liquid into dispersed microdroplets that are vaporized in a heated delivery pipe. Smaller droplets may vaporize faster than larger droplets, reducing a delay between liquid injection and complete vaporization. Faster vaporization may reduce the length of piping downstream from vaporization point 603, which is desirable. A liquid injector may be mounted directly to mixing vessel 604, or directly to showerhead 606.

A liquid flow controller (LFC) upstream of vaporization point 603 can be provided for controlling a mass flow of liquid for vaporization and delivery to process station 600. For example, the LFC may include a thermal mass flow meter (MFM) located downstream of the LFC. A plunger valve of the LFC may then be adjusted responsive to feedback control signals provided by a proportional-integral-derivative (PID) controller in electrical communication with the MFM. However, it may take one second or more to stabilize liquid flow using feedback control, which could extend a time for dosing a liquid reactant. Thus, the LFC may be dynamically switched between a feedback control mode and a direct control mode, which can be performed by disabling a sense tube of the LFC and the PID controller.

Showerhead 606 distributes process gases toward substrate 612. In Figure 30, the substrate 612 is beneath showerhead 606 and is shown resting on a pedestal 608. Showerhead 606 may have any suitable shape and may have any suitable number and arrangement of ports for distributing process gases to substrate 612. Pedestal 608 may be raised or lowered to expose substrate 612 to a volume between the substrate 612 and the

showerhead 606. Adjusting the height of pedestal 608 may allow a plasma density to be varied during plasma activation cycles in a process where a plasma is ignited. Pedestal 608 may also include a rotational axis for rotating an orientation of substrate 612. At the conclusion of the process phase, pedestal 608 may be lowered during another substrate transfer phase to allow removal of substrate 612 from pedestal 608. One or more of these example adjustments may be performed programmatically by one or more suitable computer controllers 660. Heater 610 may be used to control the temperature of pedestal 608 between about 70 °C and about 200 °C.

In scenarios where plasma may be used, showerhead 606 and pedestal 608 electrically communicate with a radio frequency (RF) power supply 614 and matching network 616 for powering a plasma. The plasma energy may be controlled by controlling one or more of a process station pressure, a gas concentration, an RF source power, an RF source frequency, and a plasma power pulse timing. For example, RF power supply 614 and matching network 616 may be operated at any suitable power to form a plasma having a desired composition of radical species. Examples of suitable powers are about 150 W to about 6000 W. RF power supply 614 may provide RF power of any suitable frequency and may be configured to control high- and low-frequency RF power sources independently of one another. Example low-frequency RF frequencies may include, but are not limited to, frequencies between 0 kHz and 500 kHz. Example high-frequency RF frequencies may include, but are not limited to, frequencies between 1.8 MHz and 2.45 GHz. Any suitable parameters may be modulated discretely or continuously to provide plasma energy for the surface reactions.

The plasma may be monitored in situ by one or more plasma monitors. Plasma power can be monitored by one or more voltage, current sensors (e.g., VI probes), and plasma density and process gas concentration can be measured by one or more optical emission spectroscopy sensors (OES). Plasma parameters may be programmatically adjusted based on measurements from such in situ plasma monitors. For example, an OES sensor may be used in a feedback loop for providing programmatic control of plasma power. Other monitors may be used to monitor the plasma and other process characteristics. Such monitors may include, but are not limited to, infrared (IR) monitors, acoustic monitors, and pressure transducers.

Instructions for controller 660 may be provided via input/output control (IOC) sequencing instructions. In one example, the instructions for setting conditions for a process phase may be included in a corresponding recipe phase of a process recipe. Process recipe phases may be sequentially arranged, so all instructions for a process phase are executed concurrently with that process phase. Instructions for setting one or more reactor parameters may also be included in a recipe phase. For example, a first recipe phase may include instructions for setting a flow rate of a copper- or metal-blocking reagent gas, instructions for setting a flow rate of a carrier gas such as argon, and time delay instructions. A second recipe phase may include instructions for setting a flow rate of an aminosilane precursor gas, instructions for setting a flow rate of a carrier gas, and time delay instructions. A third, subsequent recipe phase may include instructions for modulating or stopping a flow rate of a reactant gas, instructions for

modulating a flow rate of a carrier or purge gas, and time delay instructions. A fourth recipe phase may include instructions for setting a flow rate of a weak oxidant gas, instructions for igniting a plasma, instructions for modulating a flow rate of a carrier gas, and time delay instructions. A fifth, subsequent recipe phase may include instructions for modulating or stopping a flow rate of a reactant gas, instructions for modulating a flow rate of a carrier or purge gas, and time delay instructions. A sixth recipe phase may include instructions for setting a flow rate of a reducing agent gas, instructions for igniting a plasma, instructions for modulating a flow rate of a carrier gas, and time delay instructions. These recipe phases may be further subdivided or iterated in any suitable way. The controller 660 may include any of the features described below regarding system controller 750 of Figure 31.

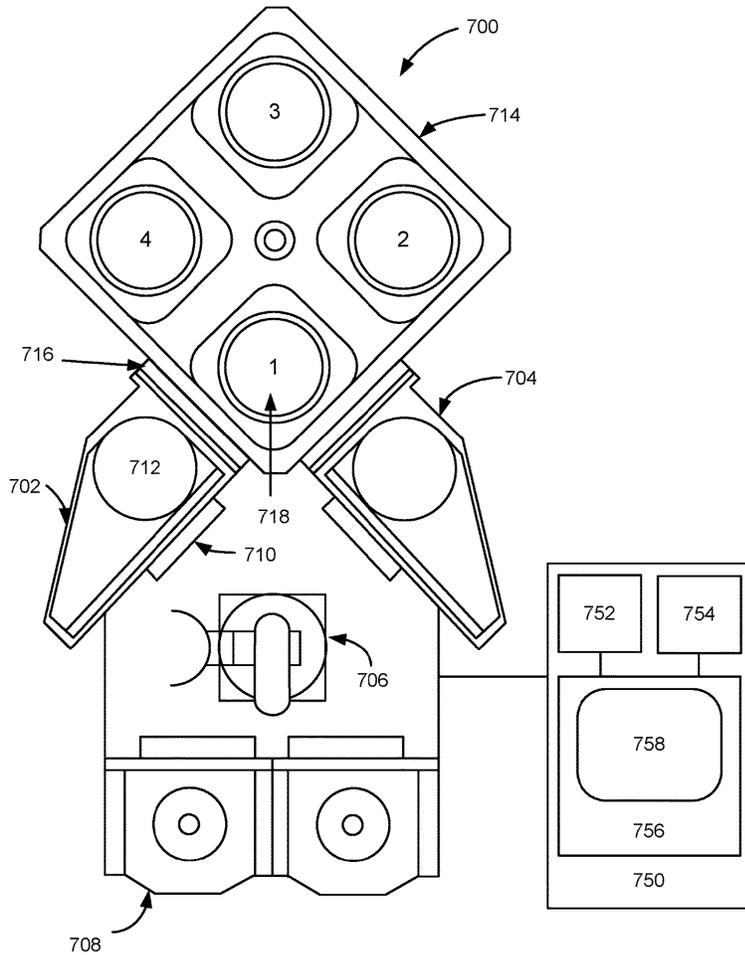


FIG. 7

Figure 31: A schematic diagram of an example process tool for performing disclosed embodiments⁴⁹

One or more process stations may be included in a multi-station processing tool. Figure 31 shows a schematic view of a multi-station processing tool 700 with an inbound load lock 702 and an outbound load lock 704, either or both of which may include a remote plasma source. A robot 706 at atmospheric pressure is configured to move wafers from a cassette loaded through a pod 708 into inbound load lock 702 via an atmospheric port 710. A wafer is placed by the robot 706 on a pedestal 712 in the inbound load lock 702, 710. A wafer is placed by the robot 706 on a pedestal 712 in the inbound load lock 702,

the atmospheric port 710 is closed, and the load lock is pumped down. The wafer may be heated in the inbound load lock 702, for example, to remove moisture and adsorbed gases. Next, a chamber transport port 716 to processing chamber 714 is opened, and another robot (not shown) places the wafer into the reactor on a pedestal of the first station in the reactor for processing. While the example process tool depicted in Figure 31 includes load locks, direct entry of a wafer into a process station may be provided.

The depicted processing chamber 714 includes four process stations, numbered from one to four. Each station has a heated pedestal (shown at 718 for station one), and gas line inlets. Each process station may have different or multiple purposes. For example, a process station may be switchable between an ALD and PEALD process mode. The processing chamber 714 may also include one or more matched pairs of ALD and PEALD process stations. While the depicted processing chamber 714 includes four stations, a processing chamber may have any suitable number of stations.

A wafer handling system is used to transfer wafers within processing chamber 714, which may include transferring wafers between various process stations or between a process station and a load lock. Any suitable wafer handling system may be employed. Non-limiting examples include wafer carousels and wafer handling robots. System controller 750 is employed to control process conditions and hardware states of process tool 700, and it may include one or more memory devices 756, one or more mass storage devices 754, and one or more processors 752. Processor 752 may include a CPU or computer,

analog or digital input/output connections, stepper motor controller boards, or other components.

System controller 750 may control the activities of process tool 700 by executing system control software 758 stored in mass storage device 754, loaded into memory device 756, and executed on processor 752. Alternatively, the control logic may be hard coded in the controller 750. Application-specific integrated circuits, programmable logic devices (e.g., field-programmable gate arrays, or FPGAs), or other components may be used for these purposes. In the following discussion, wherever “software” or “code” is used, functionally comparable hard coded logic may be used in its place. System control software 758 may include instructions for controlling the timing, mixture of gases, gas flow rates, chamber and station pressure, chamber and station temperature, wafer temperature, target power levels, RF power levels, substrate pedestal, chuck and susceptor position, and other parameters of a particular process performed by process tool 700. System control software 758 may be configured in any suitable way and may be coded in any suitable computer readable programming language. For example, various process tool component subroutines or control objects may be written to control operation of the process tool components used to carry out various process tool processes.

System control software 758 may include IOC sequencing instructions for controlling the parameters described above. Other computer software or programs stored on mass storage device 754 or memory device 756 associated with system controller 750 may be employed. Examples of programs or sections of programs for this purpose include a

substrate positioning program, a process gas control program, a pressure control program, a heater control program, and a plasma control program. A substrate positioning program may include program code for process tool components used to load the substrate onto pedestal 718 and to control the spacing between the substrate and other parts of process tool 700. A process gas control program may include code for controlling gas composition (e.g., copper or metal-blocking reagent gases, aminosilane gases, weak oxidant gases, reducing agent gases, and carrier gases) and flow rates, and optionally for flowing gas into one or more process stations before deposition to stabilize the pressure in the process station. A pressure control program may include code for controlling the pressure in the process station by regulating, for example, a throttle valve in the exhaust system of the process station or a gas flow into the process station. A heater control program may include code for controlling the current to a heating unit used to heat the substrate. Alternatively, the heater control program may control delivery of a heat transfer gas, such as helium, to the substrate. A plasma control program may include code for setting RF power levels applied to the process electrodes in one or more process stations.

There may be a user interface associated with system controller 750. The user interface may include a display screen, graphical software displays of the apparatus and process conditions, and user input devices such as pointing devices, keyboards, touch screens, and microphones. Parameters including, but not limited to, process gas composition, flow rates, pressure, temperature, and plasma conditions may be provided in the form of a recipe, which can be entered utilizing the user interface.

Signals for monitoring the process may be provided by analog or digital input connections of system controller 750 from various process tool sensors. The signals for controlling the process may be output on the analog and digital output connections of process tool 700. Non-limiting examples of process tool sensors that may be monitored include mass flow controllers, pressure sensors (e.g., manometers), and thermocouples. Appropriately programmed feedback and control algorithms may be used with data from these sensors to maintain process conditions.

The system controller 750 will typically include one or more memory devices and one or more processors configured to execute the instructions so the apparatus will perform a method. Machine-readable media containing instructions for controlling process operations may be coupled to the system controller 750.

In some implementations, the system controller 750 is part of a system. Such systems can include semiconductor processing equipment, including a processing tool or tools, chamber or chambers, platform or platforms for processing, or specific processing components (e.g., a wafer pedestal, a gas flow system). These systems may be integrated with electronics for controlling their operation before, during, and after processing of a semiconductor wafer or substrate. The electronics may be called the “controller,” and may control various components or subparts of the system or systems. The system controller 750, depending on the processing conditions and the system, may be programmed to control the processes discussed herein, including the delivery of

processing gases, temperature settings (e.g., heating and cooling), pressure settings, vacuum settings, power settings, radio frequency (RF) generator settings, RF matching circuit settings, frequency settings, flow rate settings, fluid delivery settings, positional and operation settings, wafer transfers into and out of a tool, and other transfer tools and load locks connected to or interfaced with a specific system.

Broadly speaking, the system controller 750 may be defined as electronics having various integrated circuits, logic, memory, and software that receive instructions, issue instructions, control operation, enable cleaning operations, enable endpoint measurements, and the like. The integrated circuits may include chips in the form of firmware that store program instructions, digital signal processors (DSPs), chips defined as application-specific integrated circuits (ASICs), and one or more microprocessors or microcontrollers that execute program instructions (e.g., software). Program instructions may be instructions communicated to the system controller 750 in the form of various individual settings (or program files), defining operational parameters for carrying out a particular process on or for a semiconductor wafer or to a system. The operational parameters may be part of a recipe defined by process engineers to accomplish one or more processing steps during the fabrication of one or more layers, materials, metals, oxides, silicon, silicon oxide, surfaces, circuits, or dies of a wafer.

The system controller 750, in some implementations, may be a part of or coupled to a computer that is integrated with, coupled to the system, otherwise networked to the system, or a combination thereof. For example, the system controller 750 may be in the

“cloud” or all or a part of a fab host computer system, which can allow for remote access of the wafer processing. The computer may enable remote access to the system to monitor current progress of fabrication operations, examine a history of past fabrication operations, examine trends or performance metrics from a plurality of fabrication operations, to change parameters of current processing, to set processing steps to follow a current processing, or to start a new process. In some examples, a remote computer (e.g., a server) can provide process recipes to a system over a network, which may include a local network or the internet. The remote computer may include a user interface that enables entry or programming of parameters or settings, which are then communicated to the system from the remote computer. In some examples, the system controller 750 receives instructions in the form of data, which specify parameters for each of the processing steps to be performed during one or more operations. The parameters may be specific to the process to be performed and the tool that the system controller 750 is configured to interface with or control.

Thus, the system controller 750 may be distributed, such as by including one or more discrete controllers networked together and working towards a common purpose, such as the processes and controls described herein. An example of a distributed controller for such purposes would be one or more integrated circuits on a chamber in communication with one or more integrated circuits located remotely (such as at the platform level or as part of a remote computer) that combine to control a process on the chamber.

Example systems may include a plasma etch chamber or module, a deposition chamber or module, a spin-rinse chamber or module, a metal plating chamber or module, a clean chamber or module, a bevel edge etch chamber or module, a physical vapor deposition (PVD) chamber or module, a CVD chamber or module, an ALD chamber or module, an atomic layer etch (ALE) chamber or module, an ion implantation chamber or module, a track chamber or module, and any other semiconductor processing systems that may be associated or used in the fabrication and manufacturing of semiconductor wafers. Depending on the process step or steps to be performed by the tool, the system controller 750 might communicate with one or more of other tool circuits or modules, other tool components, cluster tools, other tool interfaces, adjacent tools, neighboring tools, tools throughout a factory, a main computer, another controller, or tools used in material transport that bring containers of wafers to and from tool locations or load ports in a semiconductor manufacturing factory.

An appropriate apparatus for performing the methods discussed is further discussed and described in U.S. Patent Application Number 13/084,399 (now U.S. Patent Number 8,728,956), filed April 11, 2011, titled "Plasma activated conformal film deposition," and U.S. Patent Application Number 13/084,305, filed April 11, 2011, titled "Silicon nitride films and methods."

The apparatuses and process described may be used with lithographic patterning tools or processes, for example, for the fabrication or manufacture of semiconductor devices, displays, LEDs, and photovoltaic panels. Typically, though not necessarily, such tools

and processes will be used or conducted together in a common fabrication facility. Lithographic patterning of a film typically includes some or all of the following operations, each operation enabled with several possible tools: (i) application of photoresist on a workpiece, i.e., substrate, using a spin-on or spray-on tool; (ii) curing of photoresist using a hot plate or furnace or UV curing tool; (iii) exposing the photoresist to visible or UV or X-ray light with a tool such as a wafer stepper; (iv) developing the resist to selectively remove resist and pattern it using a tool such as a wet bench; (v) transferring the resist pattern into an underlying film or workpiece by using a dry or plasma-assisted etching tool; and (vi) removing the resist using a tool such as an RF or microwave plasma resist stripper.

Conclusion

Although the foregoing embodiments have been described in some detail for clarity of understanding, certain changes and modifications may be practiced within the scope of the appended claims. There are many alternative ways of implementing the processes, systems, and apparatuses of the present embodiments. Accordingly, the present embodiments are to be considered as illustrative and not restrictive, and the embodiments are not to be limited to the details given herein.

The following are claims disclosed in U.S. Patent Application Number 15/821,590 (now U.S. Patent Number 10,460,930), filed November 22, 2017, and U.S. Patent Application Number 16/575,214 (now U.S. Patent Number 10,825,679), filed September 18, 2019:^{49, 50}

1. A method of selectively depositing silicon oxide on a dielectric material relative to copper on a substrate, the method comprising:
 - a. providing the substrate comprising the dielectric material and exposed copper metal surface;
 - b. prior to depositing the silicon oxide, exposing the substrate to a copper-blocking reagent to selectively adsorb onto the exposed copper metal surface;
 - c. exposing the substrate to a silicon-containing precursor to adsorb the silicon-containing precursor onto the dielectric material;
 - d. exposing the substrate to an oxidizing plasma generated in an environment comprising a weak oxidant to convert the adsorbed silicon-containing precursor to silicon oxide; and
 - e. exposing the substrate to a reducing agent to reduce the exposed copper metal surface.
2. The method of claim one, wherein the copper-blocking reagent comprises sulfur.
3. The method of claim one, wherein the copper-blocking reagent is an alkyl thiol.
4. The method of claim three, wherein the copper-blocking reagent is selected from the group consisting of ethanethiol and butanethiol.
5. The method of claim one, wherein the copper-blocking reagent is an alkyl thiol having a chemical formula $\text{SH}(\text{CH}_2)_n\text{CH}_3$ whereby n is an integer between and including two and twelve.
6. The method of claim one, wherein the silicon-containing precursor is an aminosilane.

7. The method of claim one, wherein the silicon-containing precursor is selected from the group consisting of bis(diethylamino)silane, $\text{SiH}_2(\text{N}(\text{CH}_2\text{CH}_3)_2)_2$, (BDEAS); diisopropylaminosilane, $\text{SiH}_3\text{N}(\text{CH}(\text{CH}_3)_2)_2$, (DIPAS); diisobutylaminosilane, $\text{SiH}_3\text{N}(\text{CH}_2\text{CH}(\text{CH}_3)_2)_2$, (DIBAS); bis(t-butylamino)silane, $\text{SiH}_2(\text{NHC}(\text{CH}_3)_3)_2$, (BTBAS); and tris(dimethylamino)silane, $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$, (TDMAS).
8. The method of claim one, wherein the weak oxidant is selected from the group consisting of carbon dioxide, nitrous oxide, ozone, plasmas thereof, and water.
9. The method of claim one, wherein the reducing agent is selected from the group consisting of hydrogen gas, hydrogen plasma, hydrazine gas, hydrazine plasma, ammonia gas, ammonia plasma, alcohols, and aldehydes.
10. The method of claim one, wherein silicon oxide is deposited at a temperature between about 70 °C and about 200 °C.
11. The method of claim one, further comprising, prior to exposing the substrate to the copper-blocking reagent, introducing a second reducing agent to reduce the exposed copper metal surface.
12. The method of claim eleven, wherein the second reducing agent is selected from the group consisting of hydrogen gas, hydrogen plasma, hydrazine gas, hydrazine plasma, ammonia gas, ammonia plasma, alcohols, and aldehydes.
13. The method of claim one, wherein the dielectric material is selected from the group consisting of silicon oxide, aluminum oxide, silicon oxycarbides, silicon carbonitrides, and silicon oxycarbonitrides.
14. The method of claim one, further comprising repeating operations b–e in two or more cycles.

15. The method of claim one, wherein c is self-limiting.
16. The method of claim one, wherein the copper-blocking reagent preferentially adsorbs to the exposed copper metal surface to block subsequent deposition of the silicon oxide on the exposed copper metal surface.
17. A method of selectively depositing silicon oxide on a dielectric material relative to a metal-containing surface on a substrate, the method comprising:
 - a. providing the substrate comprising the dielectric material and exposed metal-containing surface;
 - b. prior to depositing the silicon oxide, exposing the substrate to a metal-blocking reagent to selectively adsorb onto the exposed metal-containing surface;
 - c. exposing the substrate to a silicon-containing precursor to adsorb the silicon-containing precursor onto the dielectric material;
 - d. exposing the substrate to an oxidizing plasma generated in an environment comprising a weak oxidant to convert the adsorbed silicon-containing precursor to silicon oxide; and
 - e. exposing the substrate to a reducing agent to reduce the exposed metal-containing surface.
18. The method of claim seventeen, wherein the exposed metal-containing surface comprises copper.
19. The method of claim seventeen, wherein the exposed metal-containing surface comprises ruthenium.

20. The method of claim seventeen, wherein the exposed metal-containing surface comprises a material selected from the group consisting of copper metal, copper oxide, ruthenium metal, and ruthenium oxide.

Use of amines to increase the deposition rate of an ALD process

ALD is a slow process because of the long cycle times required for proper purging of the chamber between introduction of reactants, and the layer-by-layer deposition nature of the technique.^{9, 45, 52} This slow deposition rate is considered its major limitation.⁵³ Deposition of silicon oxide using a conventional two precursor (e.g., aminosilane and oxidizing plasma) ALD process typically results in a deposition rate of about 1–2 Å per cycle, depending upon the experimental temperature.⁵⁴ Thus, it would be desirable for an ALD process to have a faster rate of deposition.

An approach to increasing the deposition rate is to change the environment of the substrate surface. It is believed that the ALD deposition rate can be increased by co-flowing a base with the first precursor, which could change surface pH and facilitate ligand removal as the precursor covers the substrate.^{55, 56, 57} Adding a base might enable more precursor to adsorb on the surface because more reactive sites are provided as the ligands are removed.⁵⁷ The base must not interfere with the deposition process in any undesirable way, such as by reacting with the first precursor or adsorbing onto the substrate.

Substrates of interest for this investigation were oxides and metals. Similar to the selective deposition study, silicon oxide and copper metal were used as representative substrates. Triethylamine is a common Lewis base that can hydrogen bond to a hydroxyl-terminated silicon oxide surface, but would not be expected to irreversibly react.⁵⁶ Repeated doses of triethylamine (2 s) on a reduced copper surface showed weak adsorption and complete removal of the triethylamine from the surface during the purge step (30 s), indicating that this base could be of interest for this application (Figure 32).

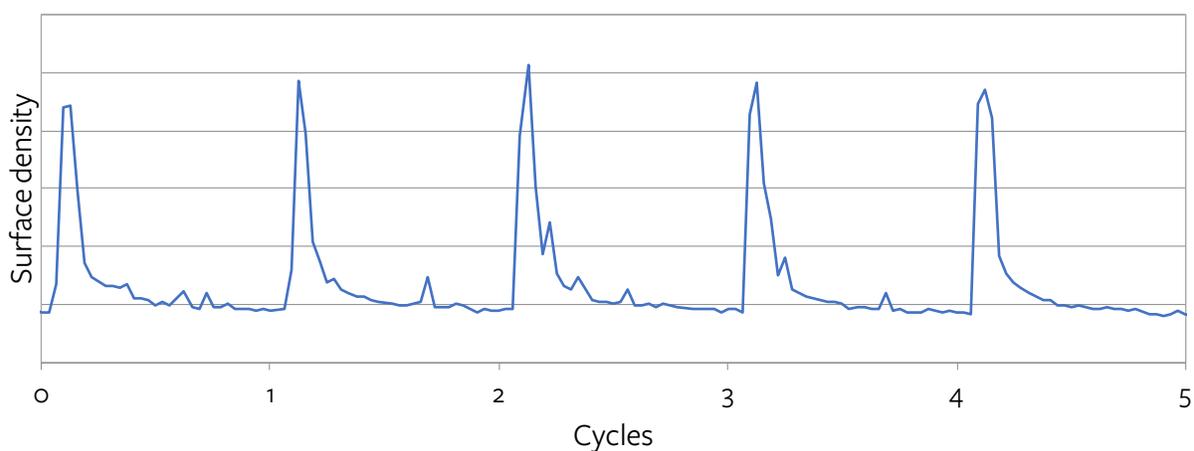


Figure 32: Triethylamine on copper

Novel claims for the use of amines to increase the deposition rate of an ALD process

Summary

Provided herein are methods for increasing the deposition rate of ALD processes, as disclosed in U.S. Patent Application Number 16/056,301, filed August 6, 2018.⁵¹

One method involves a thermal ALD process in which a base is introduced during one step of the ALD cycle. A processing chamber is provided with a substrate in the chamber. A first precursor (metal organic, metal halide, or metal hydride) is flowed into the chamber and adsorption on the substrate results in growth of a thin film. A volatile base is co-flowed with the first precursor into the chamber to expose the surface of the substrate to the first precursor and the base simultaneously. The base does not react with the first precursor, generate any measurable film on the surface of the substrate, or generate any measurable particles in the chamber. Adding the base catalyst increases the rate of adsorption of the precursor with which it is flowed. After a purge step, a second precursor is flowed into the chamber, and its adsorption on the substrate provides oxidation or nitridation of the film.

Another method involves a thermal ALD process in which a base is introduced during one step of the ALD cycle, and a base or acid is introduced during another step of the ALD cycle. A processing chamber is provided with a substrate in the chamber. A first precursor (metal organic, metal halide, or metal hydride) is flowed into the chamber and adsorption on the substrate results in growth of a thin film. A volatile base is co-flowed with the first precursor into the chamber to expose the surface of the substrate to the first precursor and the base simultaneously. The base does not react with the first precursor, generate any measurable film on the surface of the substrate, or generate any measurable

particles in the chamber. After a purge step, a volatile base or acid is co-flowed with a second precursor into the chamber, and adsorption of the second precursor on the substrate provides oxidation or nitridation of the film.

Another method involves a plasma-enhanced ALD (PEALD) process in which a base is introduced during one step of the ALD cycle. A processing chamber is provided with a substrate in the chamber. A first precursor (metal organic, metal halide, or metal hydride) is flowed into the chamber and adsorption on the substrate results in growth of a thin film. A volatile base is co-flowed with the first precursor into the chamber to expose the surface of the substrate to the first precursor and the base simultaneously. The base does not react with the first precursor, generate any measurable film on the surface of the substrate, or generate any measurable particles in the chamber. After a purge step, a second precursor, which is plasma-ignited, is flowed into the chamber, and its adsorption on the substrate provides oxidation or nitridation of the film.

The silicon-containing precursor (the first precursor) for depositing silicon oxide may be an aminosilane such as bis(diethylamino)silane, $\text{SiH}_2(\text{N}(\text{CH}_2\text{CH}_3)_2)_2$, (BDEAS); bis(*t*-butylamino)silane, $\text{SiH}_2(\text{NHC}(\text{CH}_3)_3)_2$, (BTBAS); and tris(dimethylamino)silane, $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$, (TDMAS). Suitable vaporizable bases for co-flowing with the first precursor include pyridines (e.g., pyridine, $\text{C}_5\text{H}_5\text{N}$); amines (e.g., triethylamine, $\text{N}(\text{CH}_2\text{CH}_3)_3$); and ammonia, NH_3 . The second precursor for depositing silicon oxide may be any of carbon dioxide, CO_2 ; oxygen, O_2 ; nitrous oxide, N_2O ; ozone, O_3 ; plasmas thereof; and water, H_2O .

The silicon-containing precursor (the first precursor) for depositing silicon nitride may be a halide-based precursor such as hexachlorodisilane, Si_2Cl_6 , and dichlorosilane, SiH_2Cl_2 . Suitable vaporizable bases for co-flowing with the first precursor include pyridines (e.g., pyridine, $\text{C}_5\text{H}_5\text{N}$) and amines (e.g., triethylamine, $\text{N}(\text{CH}_2\text{CH}_3)_3$). Ammonia cannot be used for co-flow combined with halide-based precursors because it will cause a CVD reaction. The second precursor for depositing silicon nitride may be any of hydrazine, N_2H_4 ; ammonia, NH_3 ; ammonia plasma; and nitrogen plasma, N_2 .

Methods

In the following description, numerous specific details are set forth to provide a thorough understanding of the presented concepts. The disclosed concepts may be practiced without some or all of these specific details. In other instances, well-known process operations have not been described in detail to not unnecessarily obscure the disclosed concepts.

An ALD cycle includes pulsing of a first precursor into a reaction chamber, time for the first precursor to adsorb on the surface of the substrate, purging of the chamber after all reactive sites on the substrate surface are consumed, pulsing of a second precursor into the reaction chamber, time for the second precursor to adsorb on the surface of the substrate, and purging of the chamber after all reactive sites on the substrate surface are

consumed. These cycles continue until the film on the substrate reaches the desired thickness.

Generally, conventional ALD processes “saturate” before a monolayer of film can be achieved on the substrate. That is, once the reactive sites on the surface of the substrate are consumed, the reaction between the precursor and the substrate surface stops. As noted above, after all the reactive sites on the substrate are consumed, the chamber is typically purged of the remaining precursor and any byproducts using inert carrier gas.

ALD is often used to deposit a metal oxide or silicon oxide layer. Thus, the first precursor is usually a metal oxide or silicon-based silane derivative. For silicon oxide ALD, deposition rates of about 1–2 Å/cycle correspond to about 25–50 % of a full monolayer (about 4 Å/cycle). Thus, it can take up to about four cycles to achieve a full monolayer.

By co-flowing a volatile base in a gaseous phase with the precursor, the ALD deposition rate can be increased by about 40 % (i.e., from about 1 Å/cycle to about 1.4 Å/cycle) compared with conventional ALD without co-flowing a base with the precursor. The base may be pulsed with the precursor, or the precursor and the base may be pulsed in an alternating fashion. The precursor and base may be flowed from the same nozzle or from separate nozzles.

In Figure 33, method 100 begins with operation 110 in which a substrate is provided in a semiconductor processing chamber. In operation 120, a first precursor and a suitable

volatile base are pulsed into the chamber. During operation 130, the first precursor is allowed to chemically react with and adsorb onto the surface of the substrate. Once all the reactive surface sites are consumed and the reaction stops, the chamber is purged using an inert purge gas (e.g., argon, nitrogen) to remove any unwanted precursor or byproducts in operation 140. In operation 150, the second precursor is pulsed into the chamber. During operation 160, the second precursor is allowed to chemically react with and adsorb onto the surface of the substrate. Once all the reactive surface sites are consumed and the reaction stops, the chamber is purged using an inert purge gas to remove any unwanted precursor or byproducts in operation 170. In operation 180, it is determined whether the film formed on the substrate has reached the desired thickness. If the desired thickness has not been reached, operations 110–170 are repeated until the film formed on the substrate is at the desired thickness. When it is determined that the film on the substrate has reached the desired thickness, the ALD process is ended.

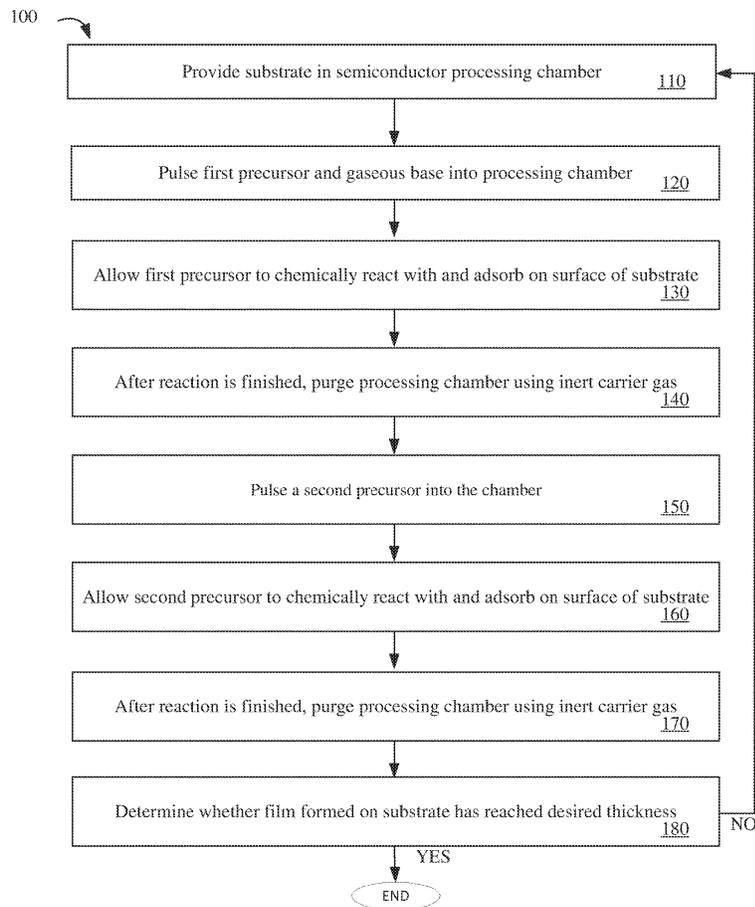


FIG. 1

Figure 33: A flow chart of an ALD method with an increased deposition rate⁵¹

Typically, the ALD processes described are carried out at a temperature of about 50 °C to about 600 °C, and at a pressure of about 100 mTorr to about 10 Torr. The ALD processes described are isobaric, meaning there are no pressure fluctuations. The dosing time of the first precursor with the base, the dosing time of the second precursor with or without the base or acid, and the purge time are each about one to five seconds. The precursor flow rate is in a range of about 100 sccm to about 1000 sccm. However, the parameters depend on the reactor used for the ALD process. The parameters given above are based on ALD

processes in a reactor such as the Striker[®] and Vector[®] Deposition Reactors, which are made by Lam Research Corporation of Fremont, California.

In Figure 34, method 200 begins with operation 210 in which a substrate is provided in a semiconductor processing chamber. In operation 220, a first precursor and a suitable volatile base are pulsed into the chamber. During operation 230, the first precursor is allowed to chemically react with and adsorb onto the surface of the substrate. Once all the reactive surface sites are consumed and the reaction stops, the chamber is purged using an inert purge gas (e.g., argon, nitrogen) to remove any unwanted precursor or byproducts in operation 240. In operation 250, the second precursor is pulsed into the chamber with a volatile base or acid. During operation 260, the second precursor is allowed to chemically react with and adsorb onto the surface of the substrate. Once all the reactive surface sites are consumed and the reaction stops, the chamber is purged using an inert purge gas to remove any unwanted precursor or byproducts in operation 270. In operation 280, it is determined whether the film formed on the substrate has reached the desired thickness. If the desired thickness has not been reached, operations 210–270 are repeated until the film formed on the substrate is at the desired thickness. When it is determined that the film on the substrate has reached the desired thickness, the ALD process is ended.

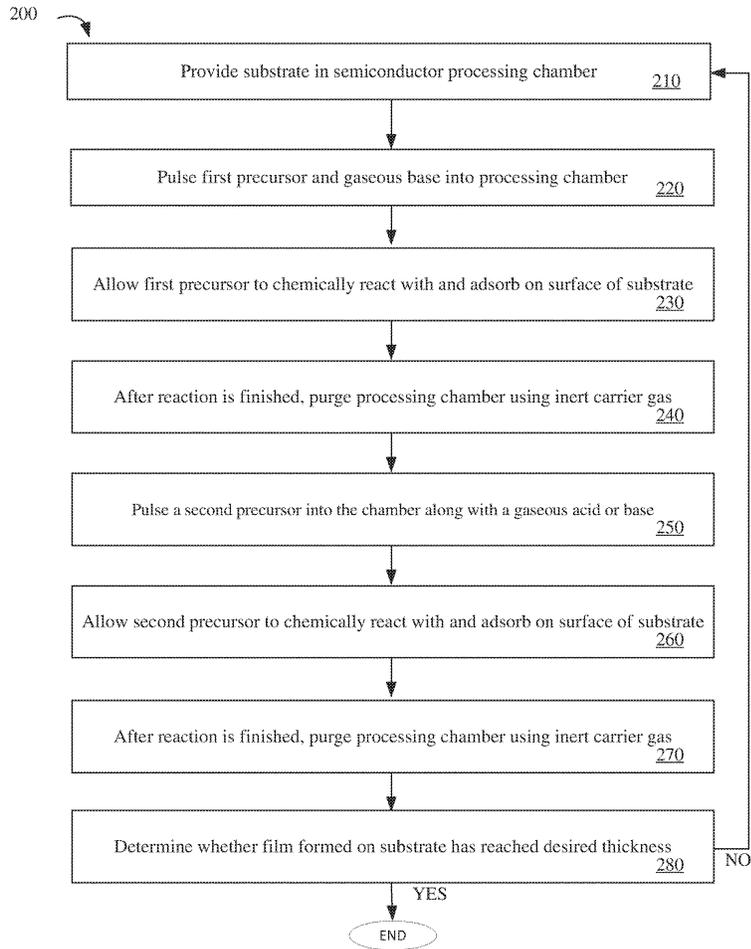


FIG. 2

Figure 34: A flow chart of an ALD method with an increased deposition rate⁵¹

Conclusion

Although the foregoing embodiments have been described in some detail for clarity of understanding, certain changes and modifications may be practiced within the scope of the appended claims. There are many alternative ways of implementing the methods and processes of the present embodiments. Accordingly, the present embodiments are to be

considered as illustrative and not restrictive, and the embodiments are not to be limited to the details given herein.

The following are claims disclosed in U.S. Patent Application Number 16/056,301, filed August 6, 2018:⁵¹

1. A method for increasing a deposition rate of an atomic layer deposition process, the method comprising:
 - a. providing a processing chamber, wherein a substrate is located;
 - b. flowing a first precursor into the chamber, the first precursor comprising a metal organic, metal halide, or metal hydride, which results in adsorption of the first precursor and growth of a thin film on the substrate;
 - c. co-flowing a base (that does not react with the first precursor, generate any measurable film on the surface of the substrate, or generate any measurable particles in the chamber) in a gaseous phase into the chamber with the first precursor to expose the surface of the substrate to the first precursor and the base simultaneously; and
 - d. flowing a second precursor into the chamber, which results in adsorption of the second precursor and provides oxidation or nitridation of the film.
2. The method of claim one, further comprising purging the processing chamber after co-flowing the base and before flowing the second precursor.
3. The method of claim one, wherein the base is selected from the group consisting of pyridines, amines, and ammonia.

4. The method of claim one, wherein co-flowing the base comprises pulsing the base and the first precursor together.
5. The method of claim one, wherein co-flowing the base comprises alternating pulses of the first precursor and pulses of the base.
6. The method of claim one, further comprising co-flowing a base with the second precursor.
7. The method of claim one, further comprising co-flowing an acid with the second precursor.
8. The method of claim seven, wherein the ALD process is not a plasma-enhanced process.
9. The method of claim two, further comprising purging the processing chamber after flowing the second precursor.
10. A method for increasing a deposition rate of an atomic layer deposition process, the method comprising:
 - a. providing a processing chamber, wherein a substrate is located;
 - b. flowing a first precursor into the chamber, the first precursor comprising a metal organic, metal halide, or metal hydride, which results in adsorption of the first precursor and growth of a thin film on the substrate;
 - c. co-flowing a base (that does not react with the first precursor, generate any measurable film on the surface of the substrate, or generate any measurable particles in the chamber) in a gaseous phase into the chamber with the first precursor to expose the surface of the substrate to the first precursor and the base simultaneously; and

- d. co-flowing a volatile base or acid with a second precursor into the chamber, which results in adsorption of the second precursor and provides oxidation or nitridation of the film.
11. The method of claim ten, wherein the base is selected from the group consisting of pyridines, amines, and ammonia.
 12. The method of claim ten, wherein co-flowing the base comprises pulsing the base and the first precursor together.
 13. The method of claim ten, wherein co-flowing the base comprises alternating pulses of the first precursor and pulses of the base.
 14. A method for increasing a deposition rate of a plasma-enhanced atomic layer deposition process, the method comprising:
 - a. providing a processing chamber, wherein a substrate is located;
 - b. flowing a first precursor into the chamber, the first precursor comprising a metal organic, metal halide, or metal hydride, which results in adsorption of the first precursor and growth of a thin film on the substrate;
 - c. co-flowing a base (that does not react with the first precursor, generate any measurable film on the surface of the substrate, or generate any measurable particles in the chamber) in a gaseous phase into the chamber with the first precursor to expose the surface of the substrate to the first precursor and the base simultaneously; and
 - d. flowing a second plasma-ignited precursor into the chamber, which results in adsorption of the second precursor and provides oxidation or nitridation of the film.

15. The method of claim fourteen, wherein the first precursor is selected from the group consisting of bis(diethylamino)silane, $\text{SiH}_2(\text{N}(\text{CH}_2\text{CH}_3)_2)_2$, (BDEAS); bis(*t*-butylamino)silane, $\text{SiH}_2(\text{NHC}(\text{CH}_3)_3)_2$, (BTBAS); and tris(dimethylamino)silane, $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$, (TDMAS).
16. The method of claim fourteen, wherein the base is selected from the group consisting of pyridines, amines, and ammonia.
17. The method of claim fourteen, wherein the second precursor is selected from the group consisting of carbon dioxide, oxygen, nitrous oxide, ozone, ammonia, and nitrogen.
18. The method of claim fourteen, wherein co-flowing the base comprises pulsing the base and the first precursor together.
19. The method of claim fourteen, wherein co-flowing the base comprises alternating pulses of the first precursor and pulses of the base.
20. The method of claim fourteen, wherein the base comprises triethylamine.

Cornell chamber design and assembly

Reactor design

Upon returning to Cornell in the fall of 2017, I began designing a vacuum chamber incorporating a QCM based on the chamber I operated at Lam (Figure 16). At Cornell, we did not want to use a glovebox, so the starting point for our design was simply a QCM, a tubular reactor, and a furnace. From that nascent concept, we added a load lock for changing samples, a manual gate valve to isolate the chamber under vacuum while opening the load lock to atmospheric pressure to change samples, and a translator for moving the QCM from the load lock into the furnace while under vacuum (Figure 35). A manual gate valve was chosen to prevent accidental closing of the gate valve while the QCM sensor was in the reactor. The QCM backside purge was included to prevent unwanted deposition on the electrodes on the underside of the crystal, and the load lock purge was used to vent the load lock to atmospheric pressure with inert gas.⁵⁸ To visualize and expand the design, I created a model of the chamber in AutoCAD using vendor drawings of catalog parts and custom drawings of parts to be fabricated (Figure 36). The main reactor section also included a plasma generator, a pneumatic gate valve to isolate it, and a custom tube (7 in length, 1.5 in outer diameter (OD)) to optimize entry of gas into the generator and ignition of the plasma.⁵⁹ A turbomolecular pump was attached below the load lock with a manual gate valve to isolate it.

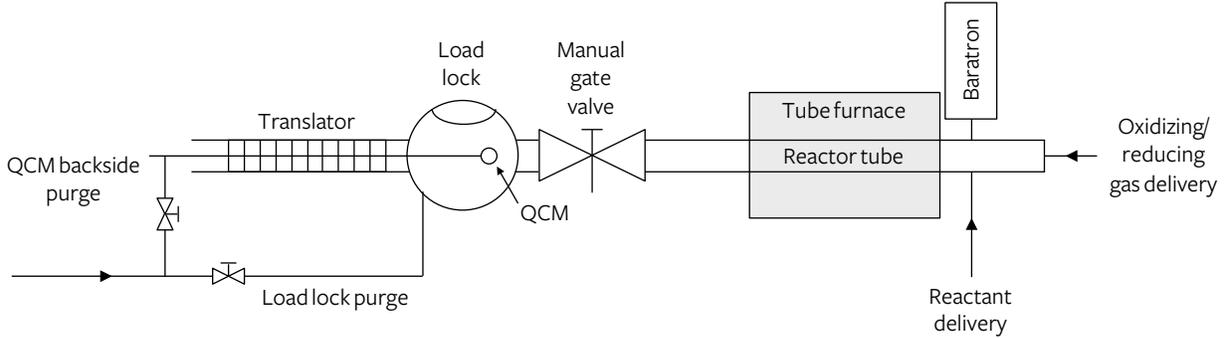


Figure 35: Initial design for Cornell vacuum chamber utilizing a quartz crystal microbalance for study of selective deposition processes

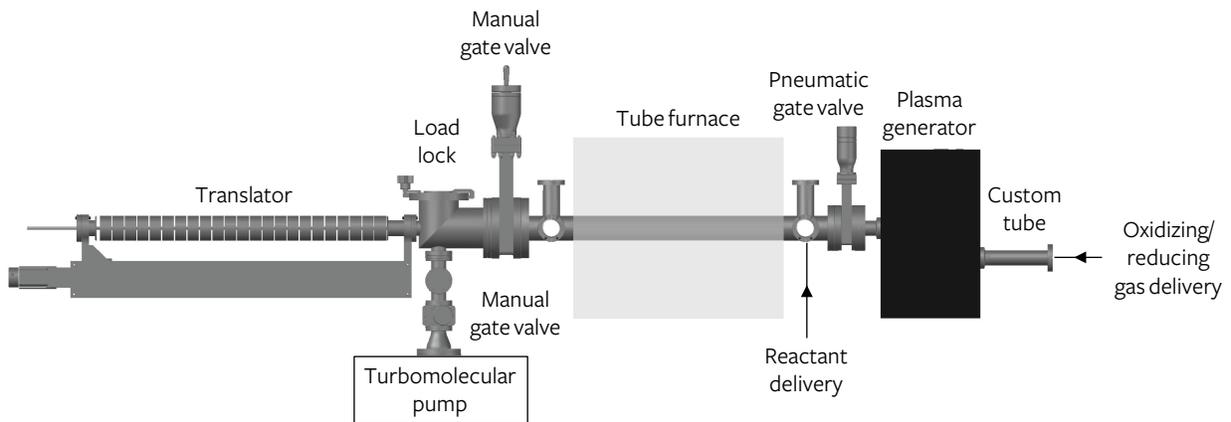


Figure 36: AutoCAD model of initial chamber design

The first item I designed was the reactor tube, which had a central tube of 2.5 in OD, three arms on either side of the furnace with 1.75 in OD, a 6 in flange at one end for compatibility with the load lock, and a 4.5 in flange at the other end, which is standard for a 2.5 in OD tube (Figure 37). The arm tubes were included for reactant delivery, attachment of the Baratron capacitance manometer, and connection to the pump, and although not all arm tubes were utilized, we wanted flexibility in where we could place

each connection. To have the reactor tube fabricated, I made orthographic drawings (Figure 38) and a table of specifications (Table 2), which were sent to various companies with a request for quote. The reactor tube was machined out of stainless steel 316 by Nor-Cal Products of Yreka, California.

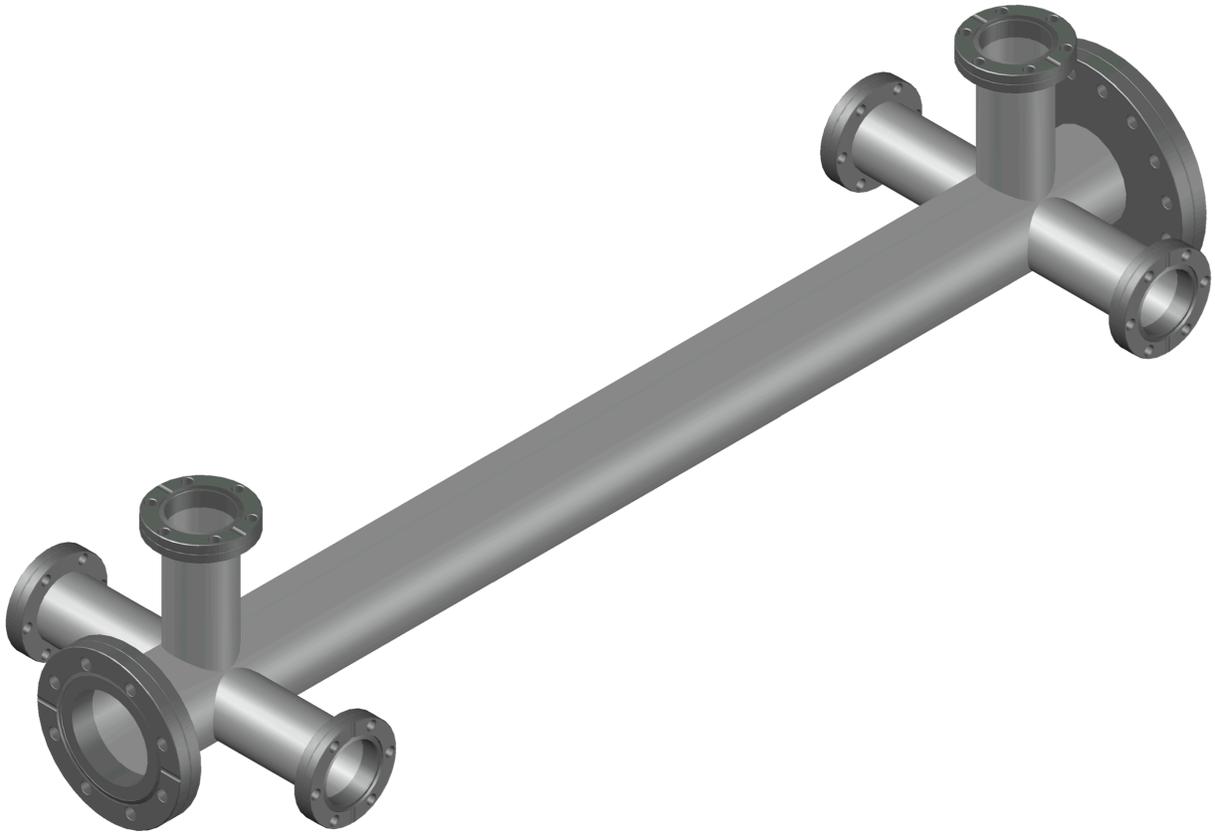


Figure 37: AutoCAD model of reactor tube

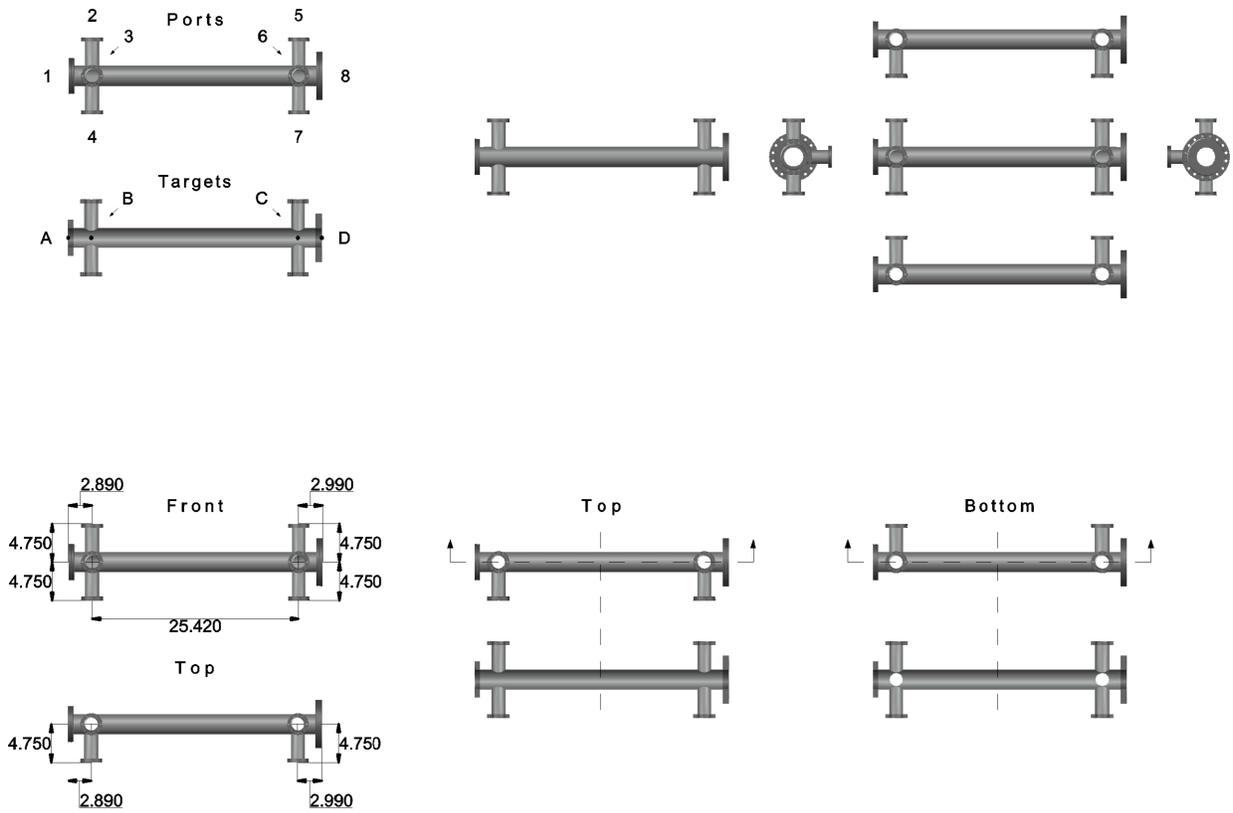


Figure 38: Orthographic drawings of reactor tube

Table 2: Specifications for reactor tube fabrication

Port number	Flange type	Flange size (in)	Flange width (in)	Tube OD (in)	Tube wall thickness (in)
1	CF, fixed, clearance holes	4.5	0.68	2.5	0.065
2	CF, fixed, clearance holes	2.75	0.5	1.75	0.065
3	CF, rotatable, clearance holes	2.75	0.5	1.75	0.065
4	CF, fixed, clearance holes	2.75	0.5	1.75	0.065
5	CF, fixed, clearance holes	2.75	0.5	1.75	0.065
6	CF, rotatable, clearance holes	2.75	0.5	1.75	0.065
7	CF, fixed, clearance holes	2.75	0.5	1.75	0.065
8	CF, fixed, clearance holes	6.0	0.78	2.5	0.065

Port number	Target point	Focal length (in to flange face)	Azimuthal angle (reference 2)	Polar angle (reference 1)	Function
1	A(0,0,0)	0	n/a	0	upstream
2	B(2.89,0,0)	4.75	0	90	reactant delivery
3	B(2.89,0,0)	4.75	90	90	Baratron
4	B(2.89,0,0)	4.75	180	90	unassigned
5	C(28.31,0,0)	4.75	0	90	unassigned
6	C(28.31,0,0)	4.75	90	90	unassigned
7	C(28.31,0,0)	4.75	180	90	pump
8	D(31.3,0,0)	0	n/a	180	load lock

We determined that supports were needed for the translator, because it was several inches shorter than the tube furnace, and for the reactor tube, to prevent damage to the furnace due to the heavy weight of the load lock and gate valve. The translator supports (Figure 39) were simple blocks with recesses in which the translator could sit, but the

reactor tube support (Figure 40 and Figure 41) was more complicated to contrive. The reactor tube support comprised three parts: one side matched the curvature of the reactor tube, the other side matched the curvature of the load lock, and the base had recessed holes to screw into the vertical sides. All supports were machined out of aluminum 6061 by Custom Machining Technology (CMT) of Cortland, New York.⁶⁰ By using the supports to bring all equipment to the same height as the tube furnace, stress on the CF flanges connecting the chamber components was minimized (Figure 42).

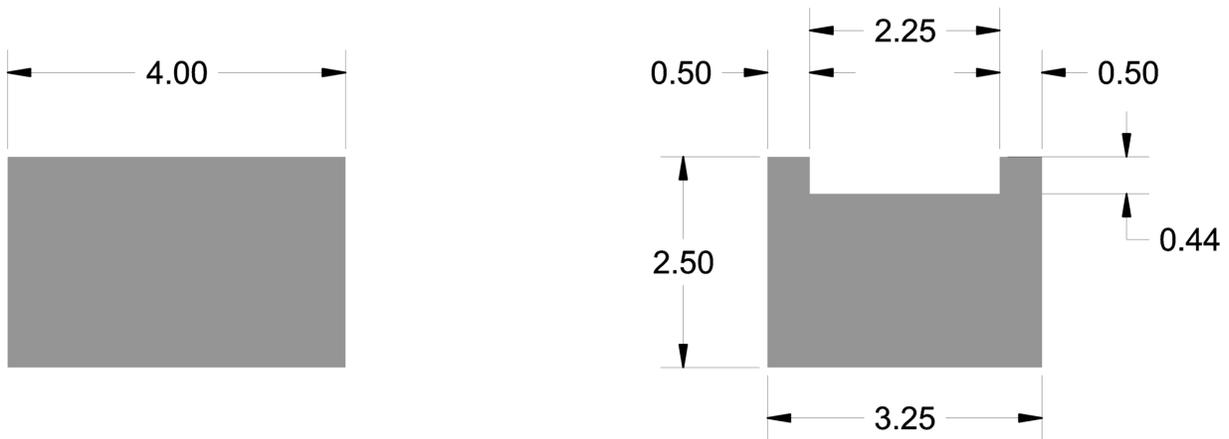


Figure 39: Orthographic drawings of support for translator

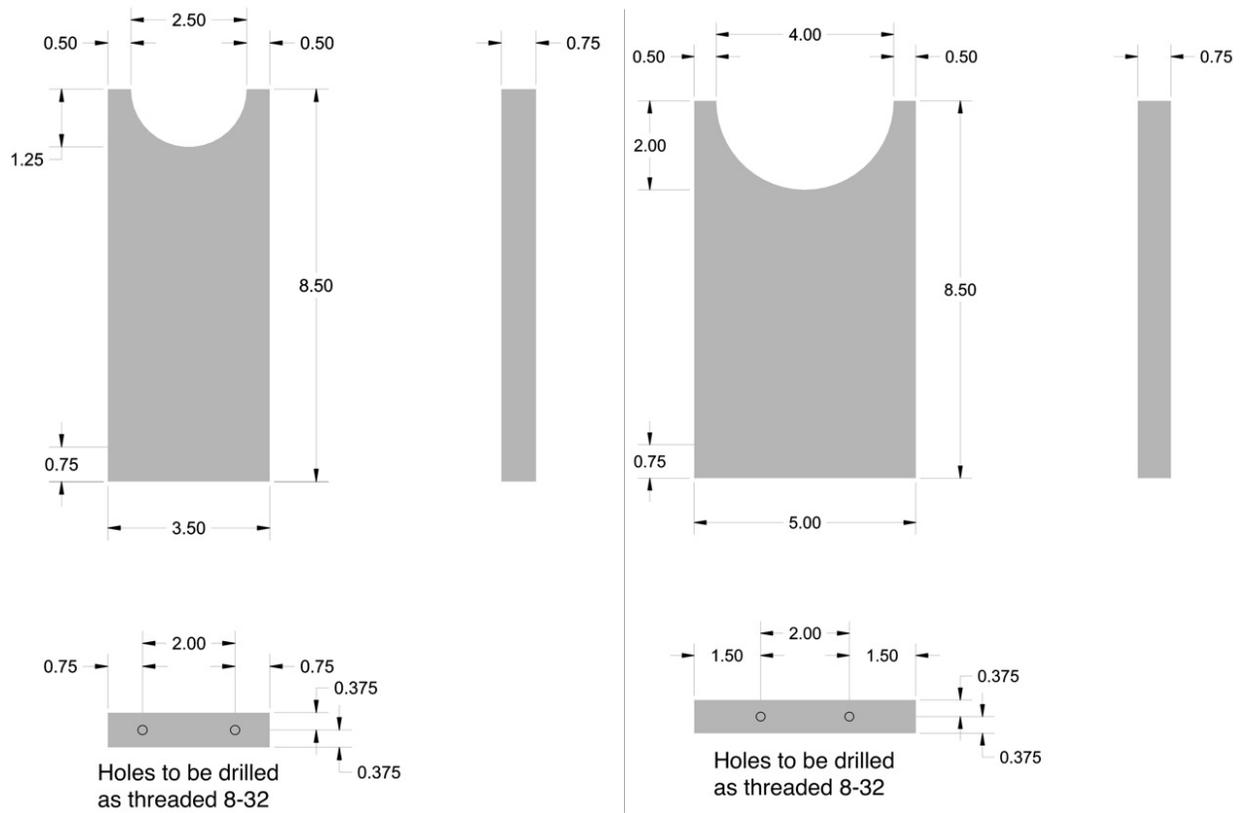


Figure 40: Orthographic drawings of side supports for reactor tube

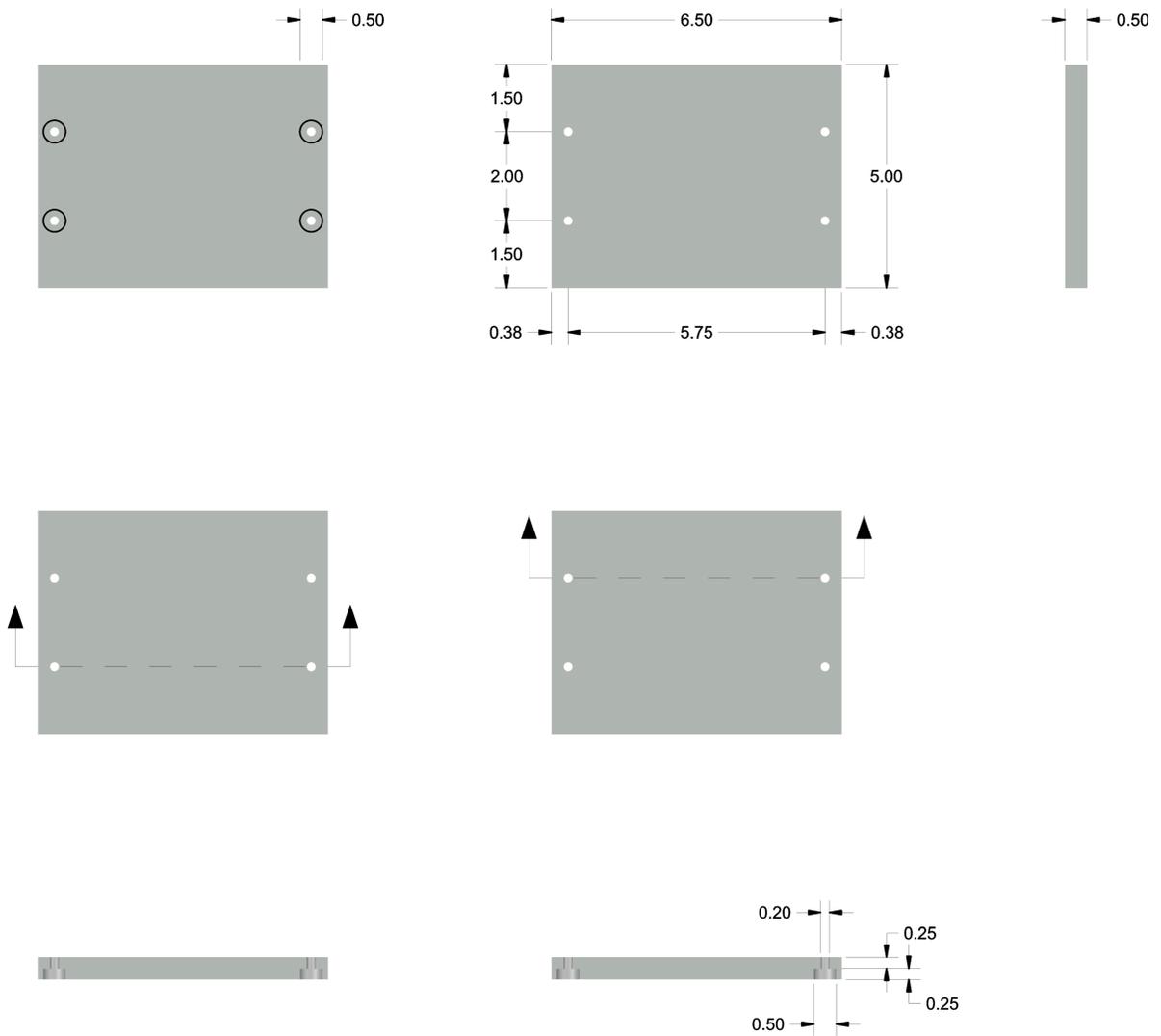


Figure 41: Orthographic drawings of base support for reactor tube

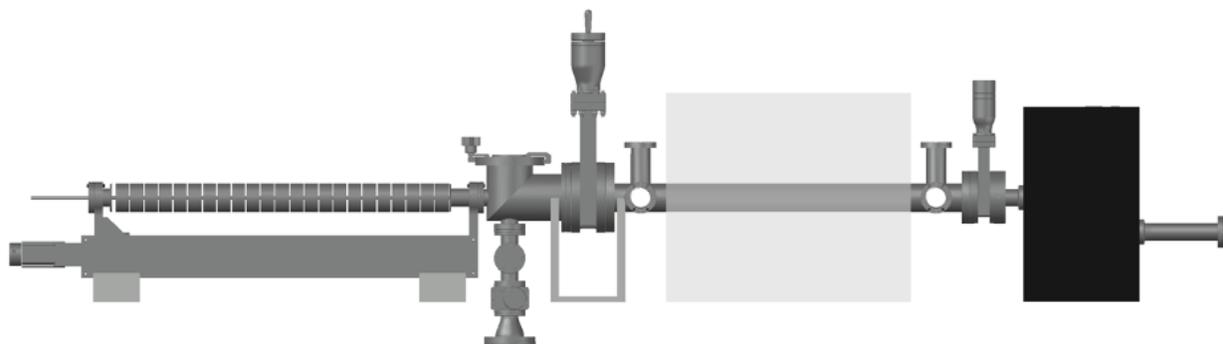


Figure 42: AutoCAD model of initial chamber design including supports

While this new chamber utilized a QCM, we also wanted the ability to study deposition on samples cut from wafers, which could be analyzed *ex situ* using X-ray photoelectron spectroscopy and spectroscopic ellipsometry, for example. I designed a sample holder that attached directly to the bottom of the QCM sensor and had a recess to hold up to two wafer samples (Figure 43a and Figure 44). The front of the sample holder was rounded to guide the QCM sensor into the reactor. The second piece, on the bottom, placed the QCM in the center of the reactor tube, to ensure consistent temperature and flow conditions between experiments. Initially, the back of the sample holder was not tapered, but, after using it, we discovered this was necessary, and the sample holder was modified (Figure 43b). The sample holder was also machined out of aluminum 6061 by CMT.

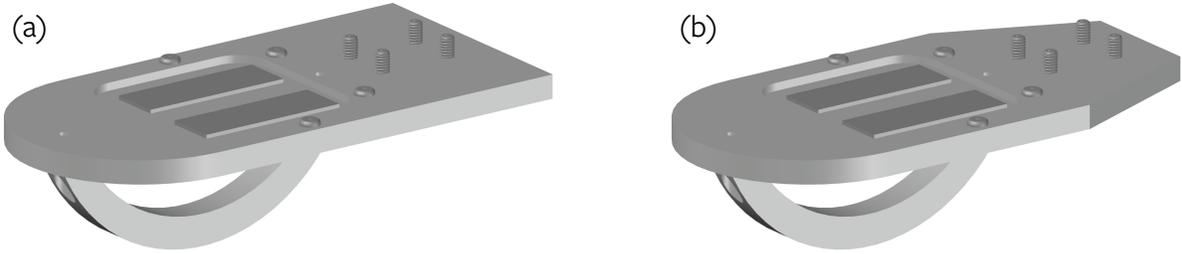


Figure 43: (a) AutoCAD model of original sample holder, (b) AutoCAD model of modified sample holder

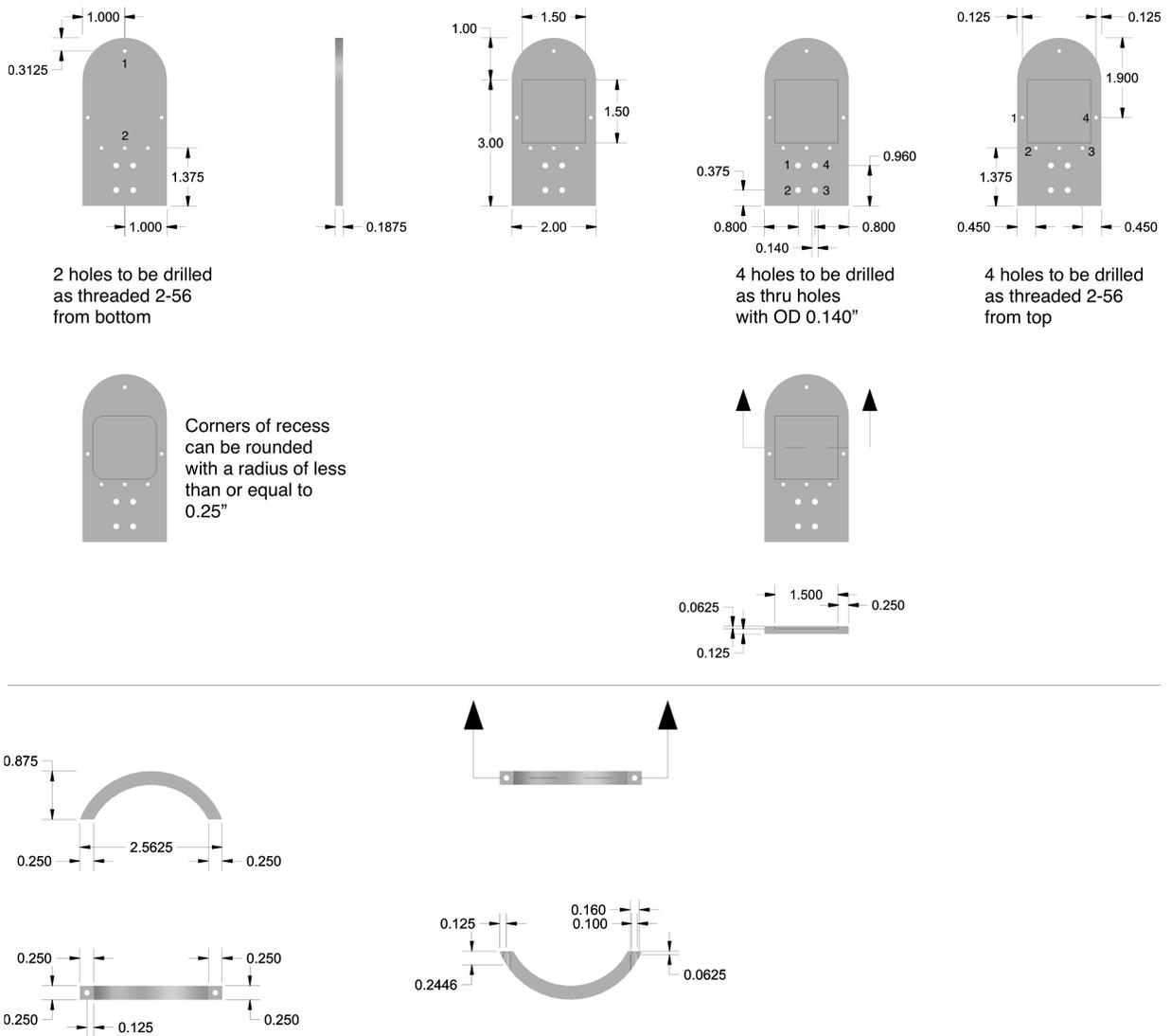


Figure 44: Orthographic drawings of sample holder

Delivery design

The reactant delivery system was designed to deliver three chemicals during a single experiment; to deliver oxidizing and reducing plasma; to purge the backside of the QCM to prevent undesired deposition on the electrical components; to minimize dead zones, or areas that were not being pumped and also did not have flow; and to direct flow from each of the chemical lines to the reactor or to the pump. The final design comprised four panels: one to deliver flow through the plasma generator and to the backside of the QCM, and three identical panels to deliver different chemicals.

Inert gas flow entered panel one (Figure 45) and travelled from right to left to the highest mass flow controller (MFC), which directed it to the QCM backside purge. Downstream of panel one, the QCM backside purge line included a flexible hose, which was chosen to withstand repeated bending as the QCM sensor was moved in and out of the chamber. The flexible hose also had to be sufficiently long that its dynamic radius of curvature limit was not exceeded when the QCM was in the reactor. The other three MFCs on panel one delivered inert, oxidizing, and reducing gases through the plasma generator to the reactor. These MFCs were connected to the three-way valves by custom tubing (Figure 46) that is not shown in the AutoCAD drawing, but is indicated by the grey, dashed lines. The flow was then directed to the reactor through each elbow on the right of the three-way valves, or to the pump through the elbows on the left of the three-way valves.

Panel 1

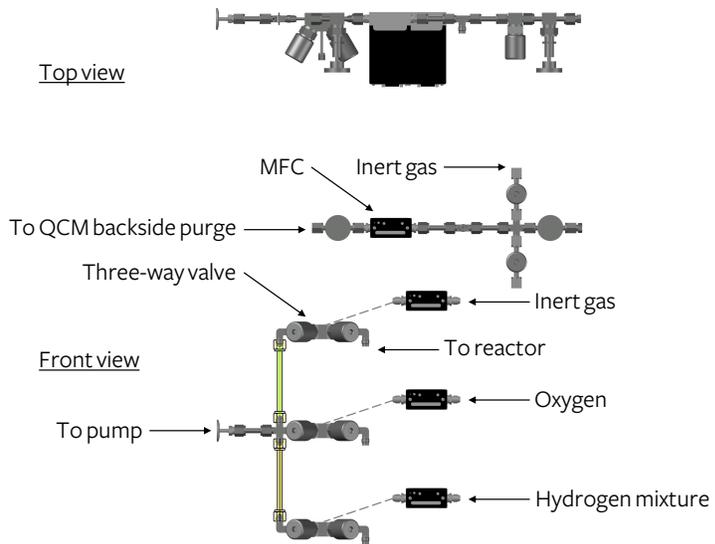


Figure 45: AutoCAD model of design of panel one



Figure 46: Custom tubing between MFCs and three-way valves

The inert gas for the QCM backside purge on panel one was also sent to panels two, three, and four to serve as the carrier gas for the chemicals. During dosing of a chemical through panel two, three, or four, the gas flow followed path one from right to left (Figure 47a). The gas entered the bubbler, which contained the liquid reactant. As the gas passed through the liquid, it picked up reactant molecules based on the vapor pressure. The gas mixed with the reactant then left the bubbler and was directed to the reactor or to the pump by the three-way valve. During a purge step, the gas flow followed path two from right to left over the bubbler to the three-way valve (Figure 47b). Based on these designs,

panel sizes were determined (Figure 48) and their fabrication was commissioned. The panels were machined out of aluminum Mic-6 by CMT.

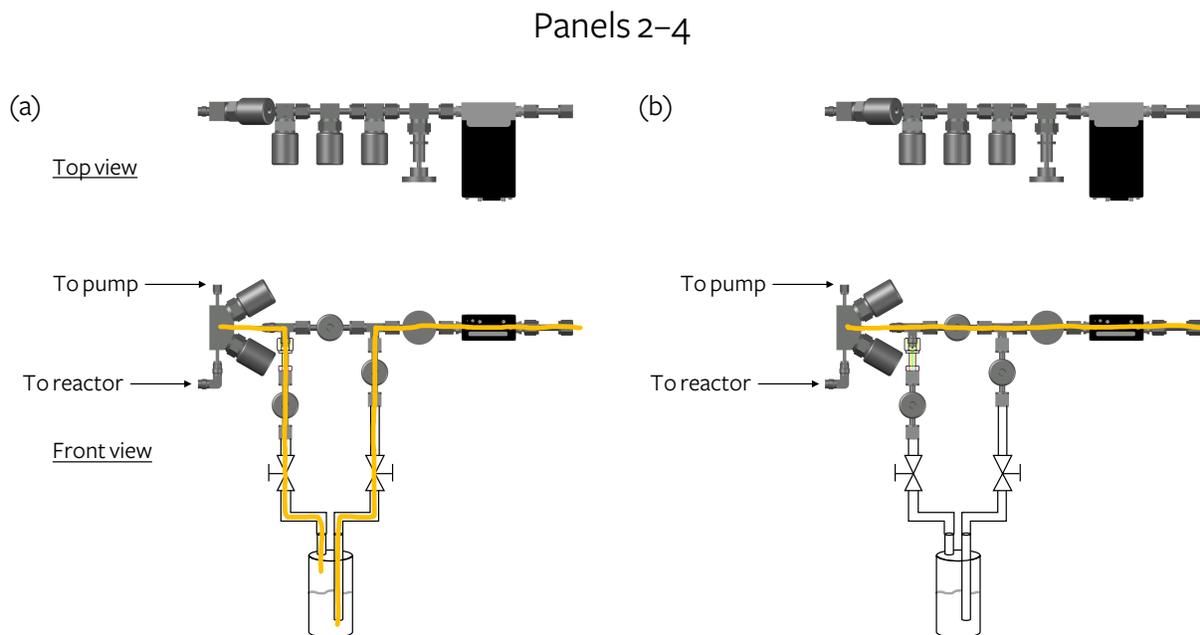


Figure 47: AutoCAD model of design of panels two through four, (a) path one of gas through bubbler traced in yellow, (b) path two of gas over bubbler traced in yellow

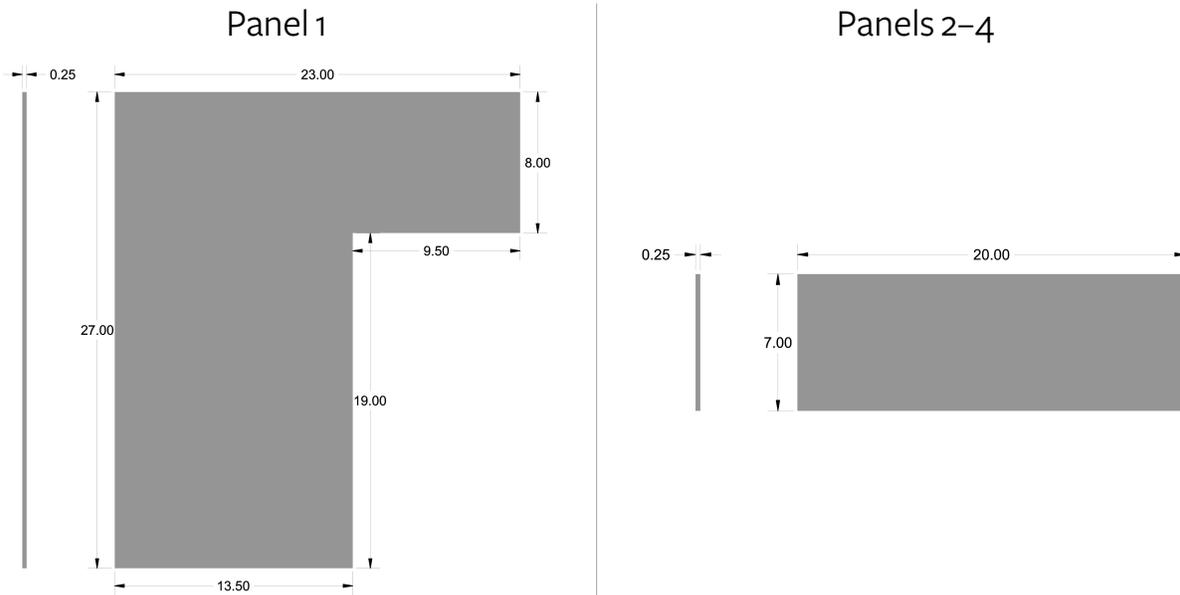


Figure 48: Orthographic drawings of panels

Equipment such as valves and MFCs are manufactured with threaded holes on their bases to allow for mounting on panels, but each piece of equipment had a different distance from its base plane to the center of the VCR fitting, so mounting blocks were needed to bring all equipment to the same plane. Separate mounting blocks were designed for MFCs (Figure 49), two-way manual valves (Figure 50), two-way pneumatic valves (Figure 51), and three-way pneumatic valves (Figure 52 and Figure 53), with recessed holes for the screws into the equipment and oblong holes for mounting to the panels. There were two different mounting blocks for the three-way pneumatic valves because those on panel one were mounted with their bases parallel to the panel, and those on panels two, three, and four were mounted with their bases perpendicular to the panel. All mounting blocks were machined out of aluminum 6061 by CMT.

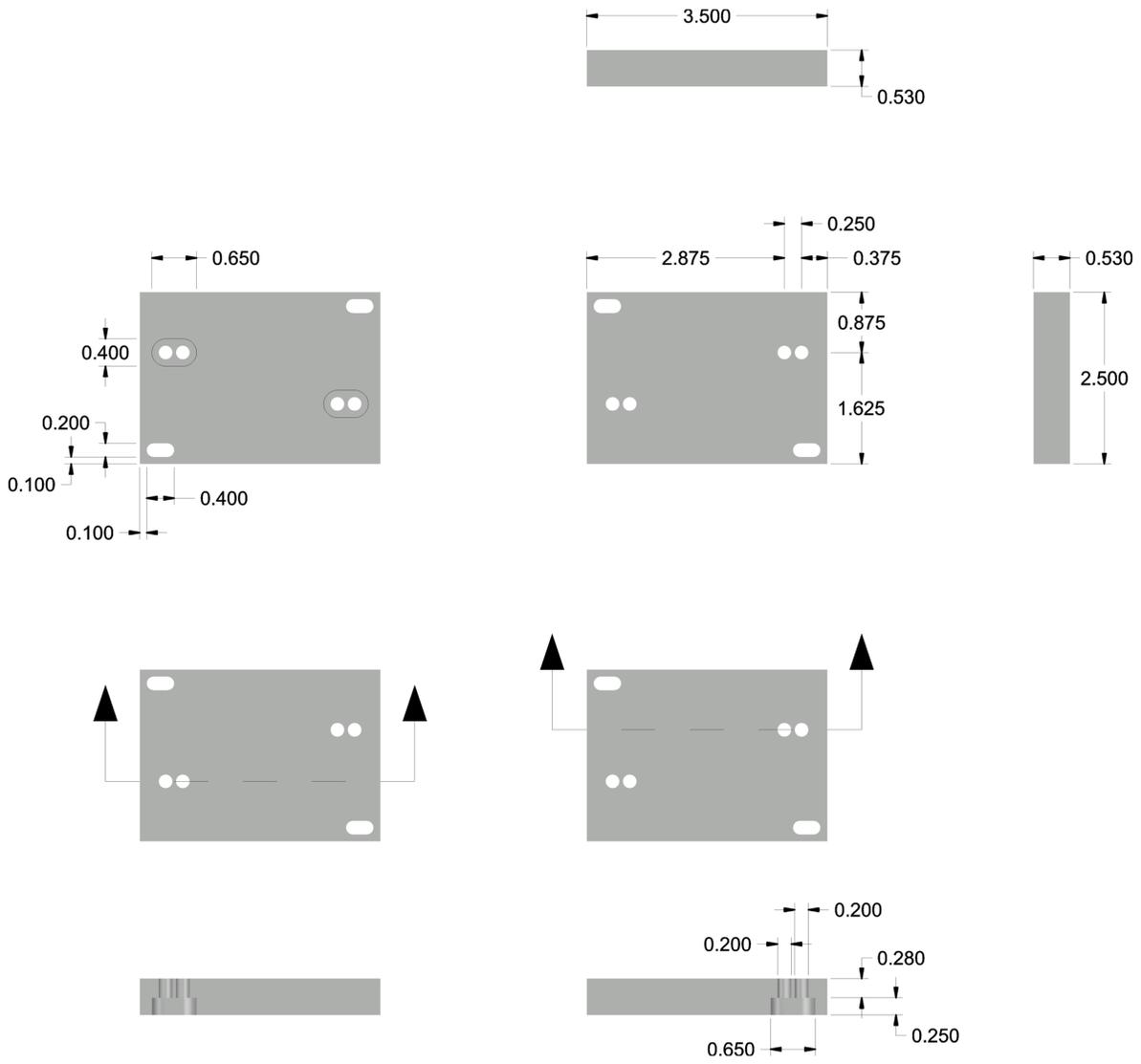


Figure 49: Orthographic drawings of mounting blocks for MFCs

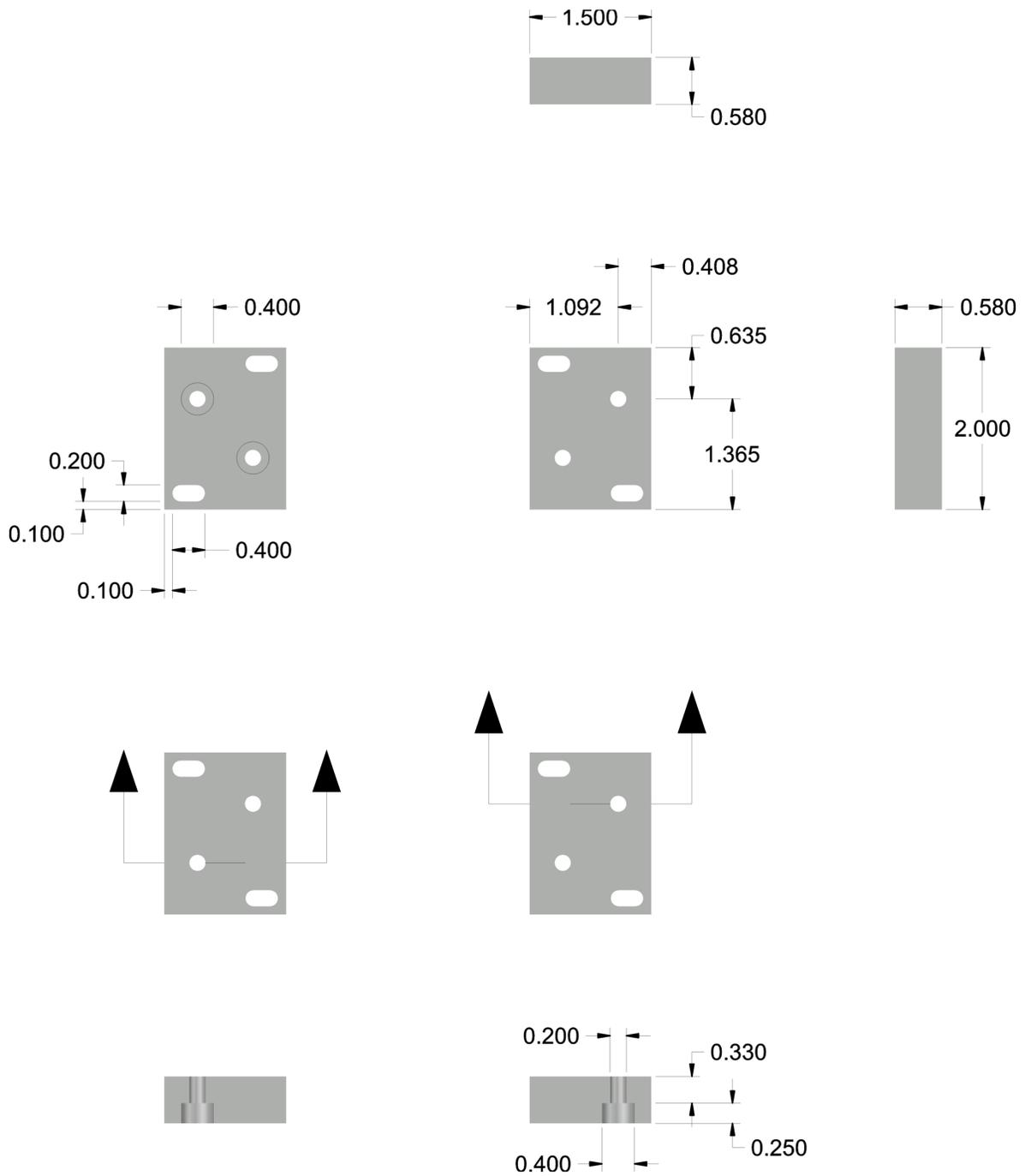


Figure 50: Orthographic drawings of mounting blocks for two-way manual valves

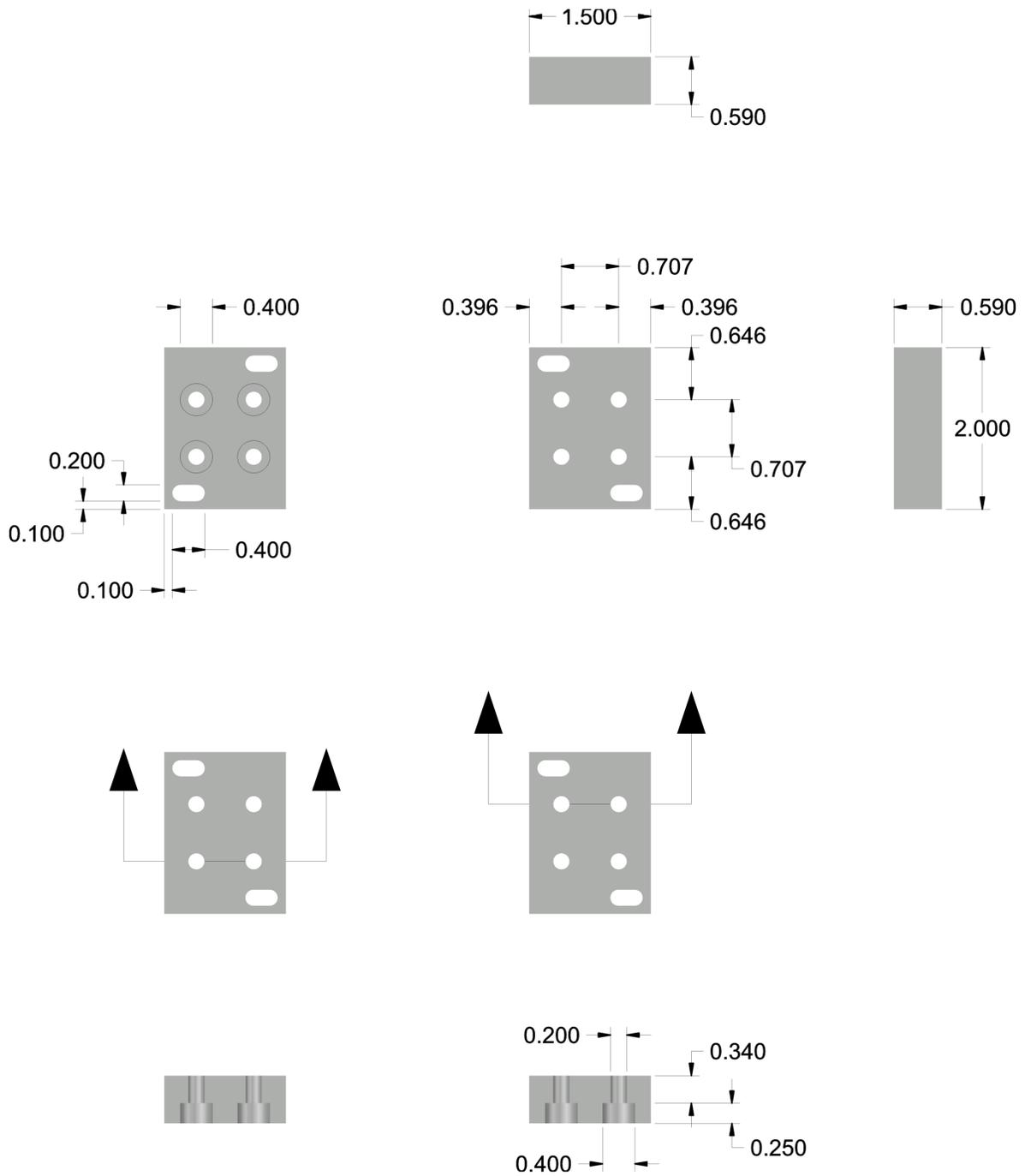


Figure 51: Orthographic drawings of mounting blocks for two-way pneumatic valves

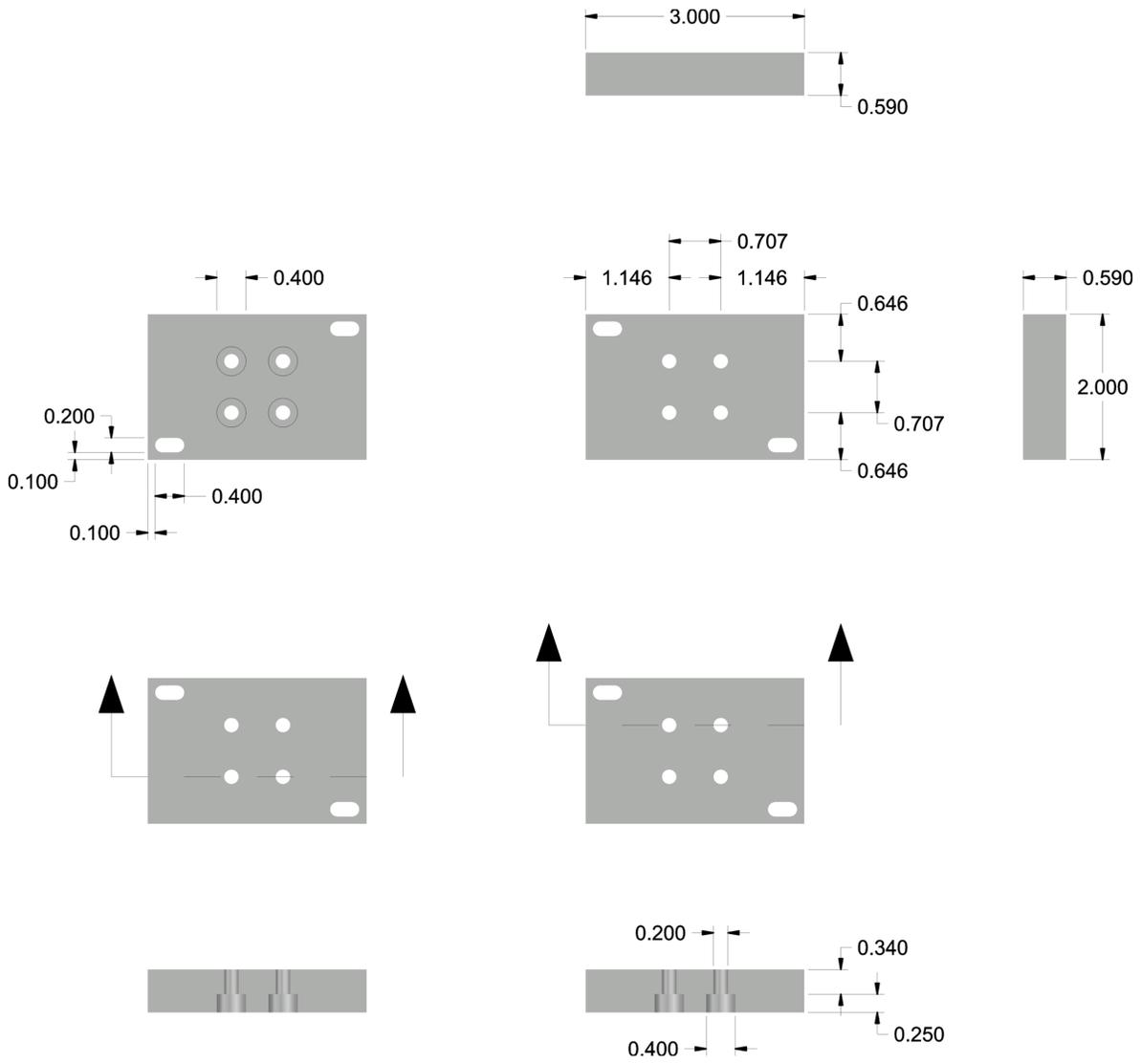


Figure 52: Orthographic drawings of mounting blocks for three-way pneumatic valves with bases parallel to panels

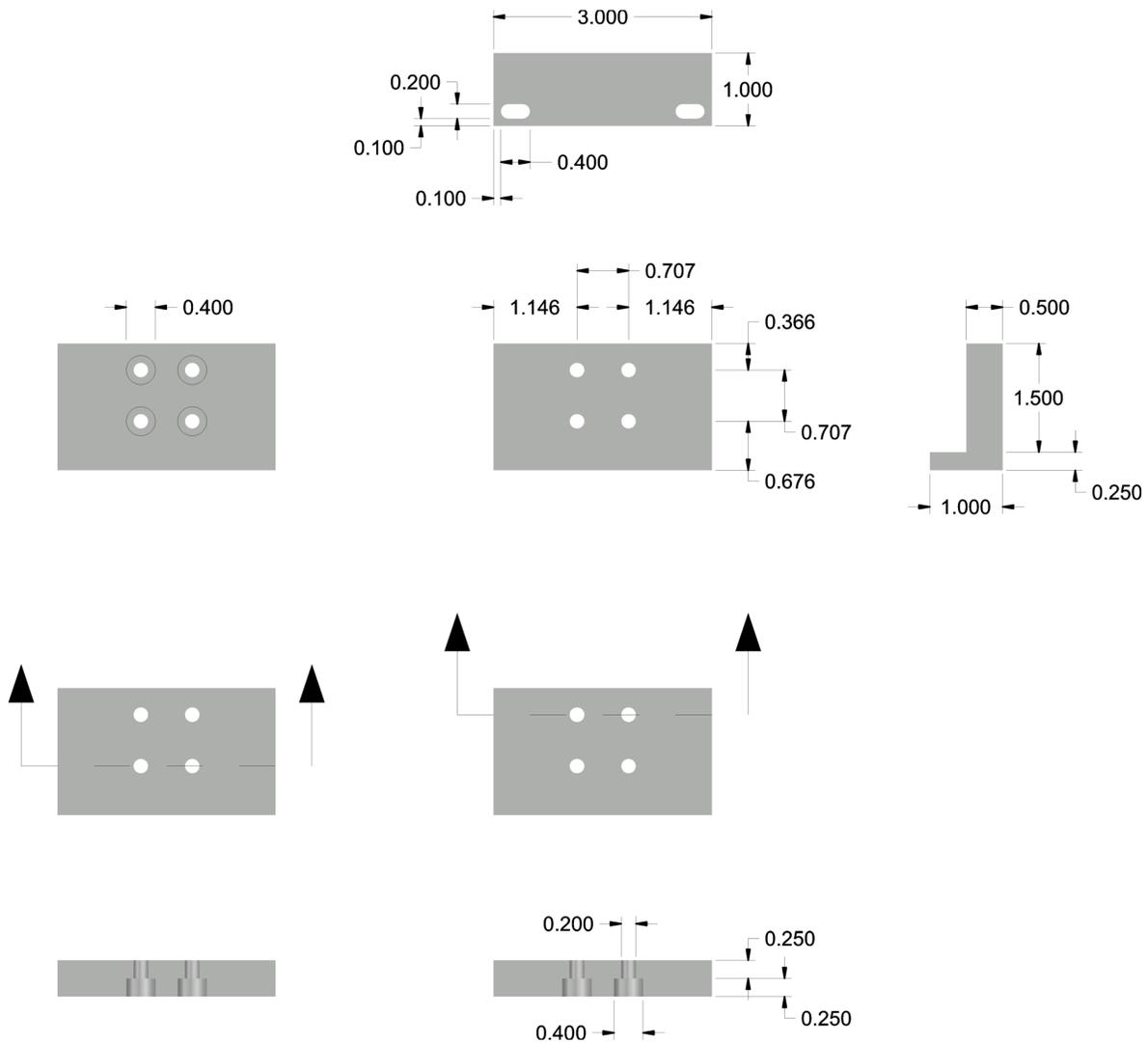


Figure 53: Orthographic drawings of mounting blocks for three-way pneumatic valves with bases perpendicular to panels

Once the panels were received and the final equipment locations were marked (Figure 54), holes were drilled into the panels and they were assembled (Figure 55). Each panel was labeled with its number in the top left corner. A support was designed for the panels using Unistrut metal framing because of its strength and the flexibility to alter the design,

with the panels sufficiently high for submersion of the reactant ampoules in temperature-controlled baths (Figure 56). To connect the gas cylinders to the panels, the panels to each other, and the panels to the reactor, 1/4 in stainless steel tubing was bent using a handheld tube bender, cut to a custom length using a handheld tube cutter, and VCR glands were welded to the tube ends in the Cornell NanoScale Science and Technology Facility (CNF) cleanroom. This process required precise measurement, as misaligned VCR fittings could lead to leaks, which would have contaminated the vacuum chamber. The panels were connected to each other by custom straight tubing for distribution of inert gas (Figure 57a). From panel one to the plasma generator, three custom tubes were made and met at a cross on the reactor (Figure 57b). From panels two, three, and four to the reactor, another three custom tubes were made, and met at a different cross (Figure 57c). The effluent of each of the chemical lines met at the reactor tube instead of near the panels to minimize reactions in the delivery tubing. A custom wall support was built to accommodate four gas cylinders (two inert, one oxidizing, and one reducing), with sufficient distance between the cylinders to attach a regulator and connect to the custom 1/4 in tubing. The distance between the cylinders and the panels was several meters, so the tubing downstream of each cylinder was bent into a pigtail to reduce tension at the fittings and allow for more flexibility (Figure 58).

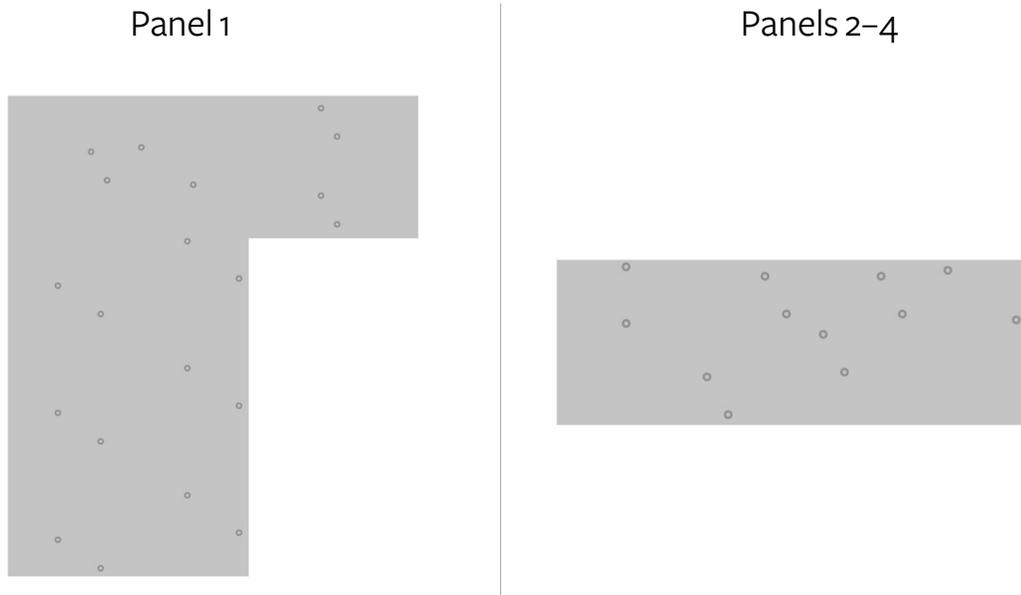


Figure 54: AutoCAD model of location of holes on panels for mounting blocks

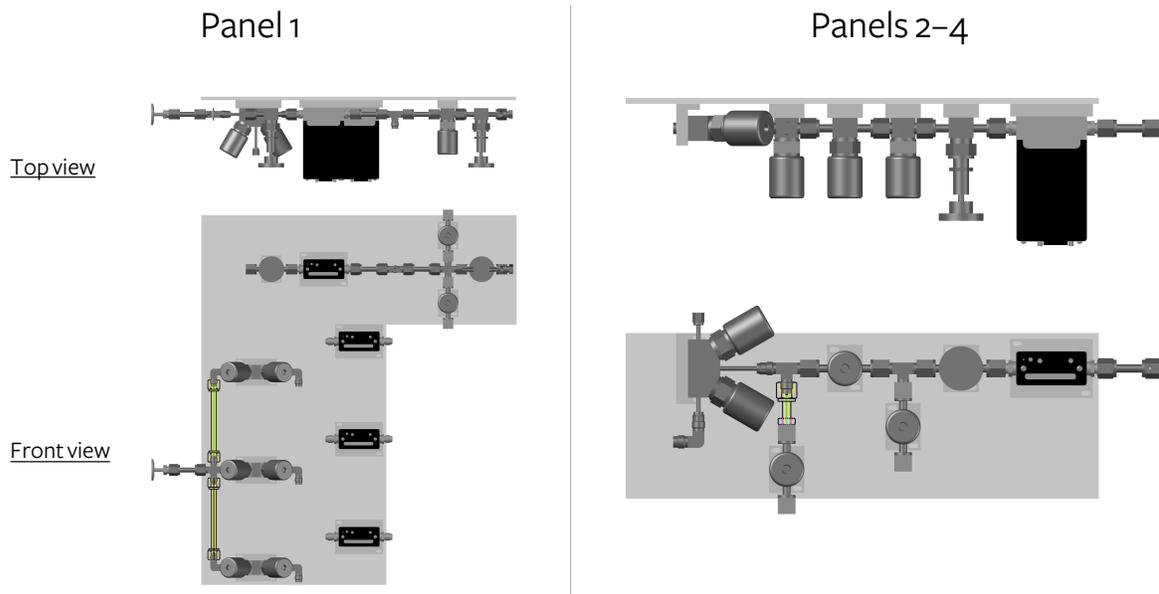


Figure 55: AutoCAD model of panel designs with equipment fully assembled

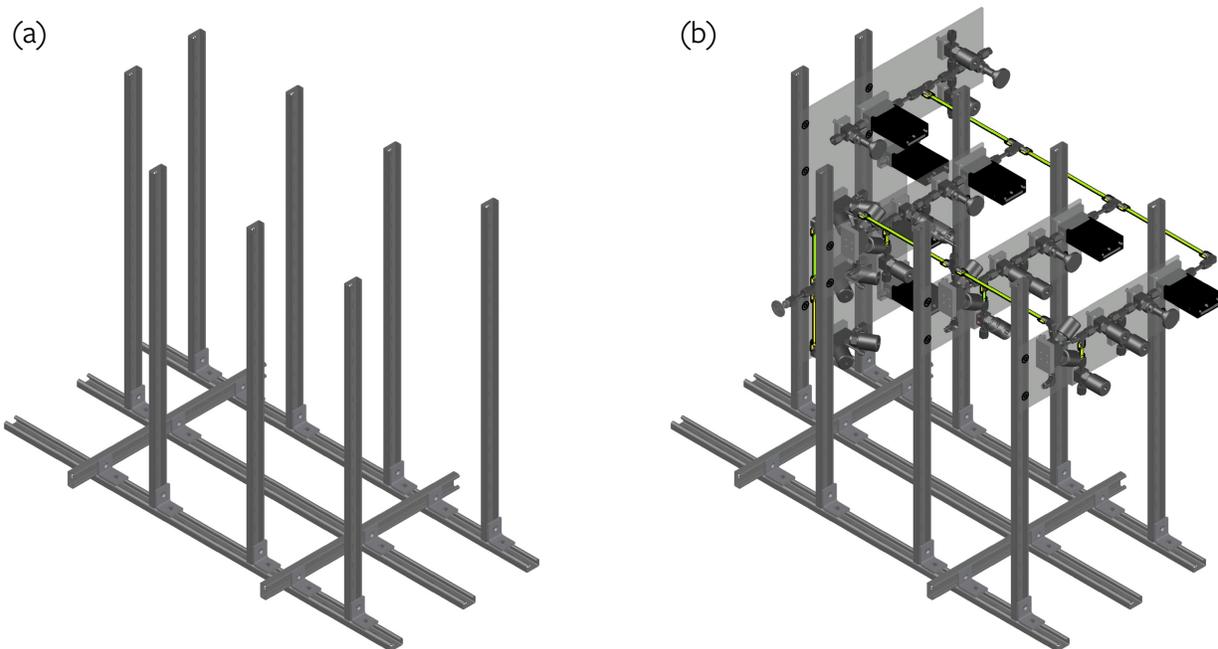


Figure 56: (a) AutoCAD model of panel support system, (b) AutoCAD model of panels mounted on support system

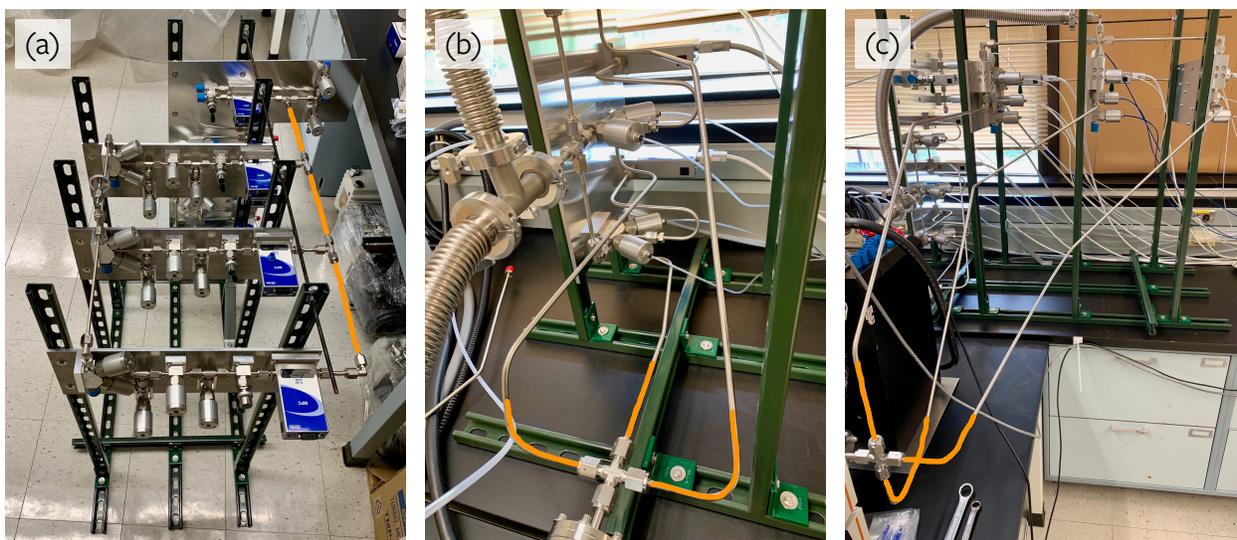


Figure 57: Custom tubes, traced in orange, (a) connecting panels one through four for distribution of inert gas, (b) connecting panel one to plasma generator, (c) connecting panels two through four to original feedthrough on reactor



Figure 58: Gas cylinder including regulator and custom tubing with pigtail

Modifications to original design

After we began experiments using the new chamber, we decided to make some hardware modifications. While the mixing of reactants in the delivery tubing was minimized, there was still a short section of 1/4 in tubing through which all the reactants passed. To eliminate any mixing of the reactants in the delivery tubing, a feedthrough was designed

with three independent 1/4 in tubes, which delivered the reactants directly to the center of the 2.5 in OD reactor tube (Figure 59). A comparison of the original and modified delivery feedthrough systems is shown in Figure 60.

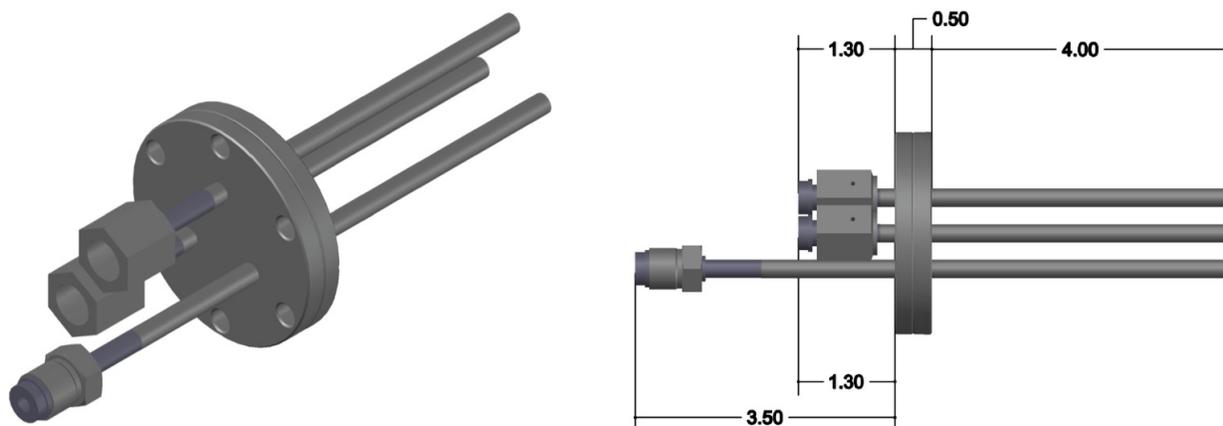


Figure 59: AutoCAD model showing reactant triple feedthrough dimensions

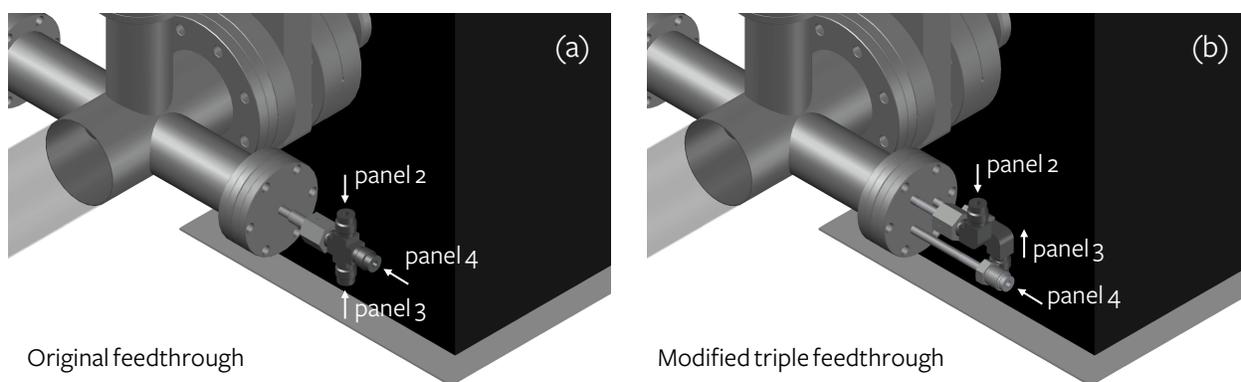


Figure 60: (a) AutoCAD model of original reactant feedthrough, (b) AutoCAD model of modified reactant triple feedthrough

On the opposite side of the reactor tube, a reactant delivery line was installed solely for addition of a trimethylaluminum ampoule (Figure 61). Unlike reactant delivery from the panels by bubbling through the liquid chemicals, this line delivered trimethylaluminum

by vapor draw; when the pneumatic valve above the ampoule opened, the pressure difference between the trimethylaluminum vapor pressure and the reactor drew the trimethylaluminum vapor into the reactor to the substrates.

The deposition of aluminum oxide by trimethylaluminum and water is well understood, so the dedicated line was added to assist with determining the state of the reactor.⁶¹ For example, if the base pressure of the chamber were high, we could determine whether the high pressure resulted from lingering water by repeatedly dosing trimethylaluminum onto a QCM crystal.⁶² If the crystal showed an increase in mass with each dose, it would be likely that residual water in the chamber was causing a CVD reaction with the trimethylaluminum to deposit aluminum oxide on the crystal. Permanently adding trimethylaluminum also provided the capability to deposit thick aluminum oxide to use as a starting substrate for further studies of deposition processes.

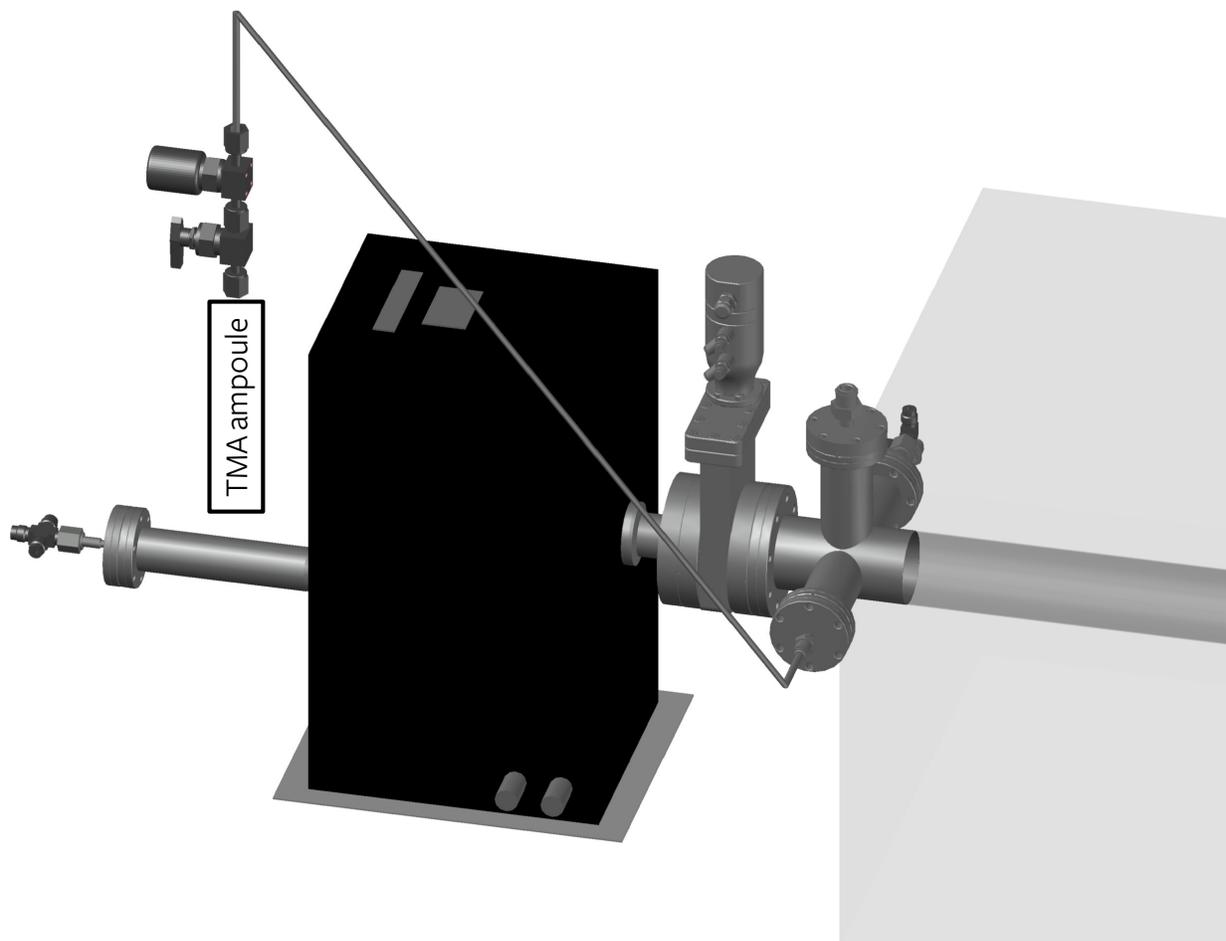


Figure 61: AutoCAD model of reactant line for trimethylaluminum (TMA) delivery

A model of the reactor section of the vacuum chamber, including the hardware modifications, is shown in Figure 62. The view in Figure 62a is from the front of the reactor with the QCM in its extended position halfway into the tube furnace. In Figure 62b, the reactor is shown from the back, and the QCM is positioned in the load lock.

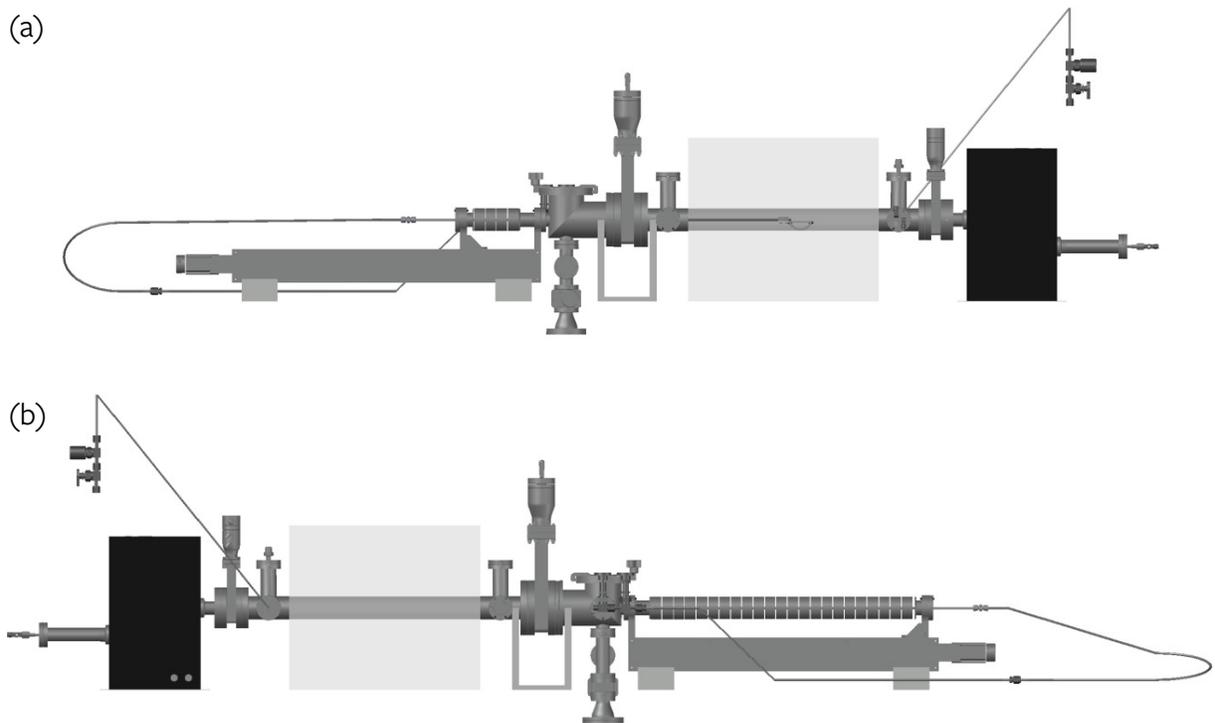


Figure 62: AutoCAD models of reactor after hardware modifications, (a) front with QCM in reactor tube, (b) back with QCM in load lock

Sizing equipment

The tube furnace was sized to have a single heating zone of 12 in length. With these specifications, a uniform temperature of ± 1 °C from the setpoint was achieved over 3 in about the center of the furnace, and ± 5 °C was achieved over 8 in.⁶³ The QCM sensor had a length of approximately 1.2 in along the axis of the reactor tube, and the wafer samples were located within approximately 1.8 in from the front of the sensor.⁵⁸ Based on these dimensions, the temperature difference between the locations of the crystal and the wafer samples was negligible.

The tables on which the chamber was built were sized such that the reactor section was split between two tables and the turbomolecular pump fit in the gap between them.

All MFCs were calibrated for nitrogen, but the full scale was chosen using the gas conversion factors for argon, oxygen, and a hydrogen mixture, considering the expected flow rate for each of the delivery lines (Table 3).

Table 3: Example calculation of conversion of mass flow controller specifications from nitrogen to argon

	Gas conversion factor	Full scale (FS) (sccm)	Control range 2–100 % of FS (sccm)	Accuracy 1% of FS (sccm)	Resolution 0.1% of FS (sccm)
Nitrogen	1	50	1–50	0.5	0.05
Argon	1.39	69.5	1.39–69.5	0.695	0.0695

Using deposition temperature, system pressure, and total volumetric flow rate through the reactor, a pump with sufficient speed was chosen. An example standard flow rate of 250 sccm was converted to an actual flow rate in ft^3/min . The data table function in Excel was used to calculate the flow rate for combinations of several temperatures and pressures (Table 4). These were then compared to the pumping speed of various pumps, and we chose one capable of operating at the conditions we expected to use. The red highlight indicates conditions that resulted in a volumetric flow rate greater than the pumping speed of the Edwards E2M28 pump, which is the pump we purchased.⁶⁴

Table 4: Calculations of actual volumetric flow rate (V) for various conditions of temperature (T) and pressure (P)

			T (K)								
			V (ft ³ /min)	6.4	323	373	393	453	473	523	573
standard T	273	K	P (Torr)	0.1	79.4	91.7	96.6	111.3	116.3	128.5	140.8
standard P	760	Torr		0.5	15.9	18.3	19.3	22.3	23.3	25.7	28.2
standard V	250	cm ³ /min		1	7.9	9.2	9.7	11.1	11.6	12.9	14.1
standard V	0.00883	ft ³ /min		1.5	5.3	6.1	6.4	7.4	7.8	8.6	9.4
T	393	K		2	4.0	4.6	4.8	5.6	5.8	6.4	7.0
P	1.5	Torr		5	1.6	1.8	1.9	2.2	2.3	2.6	2.8
				10	0.8	0.9	1.0	1.1	1.2	1.3	1.4

V > 19.5 ft³/min (E2M28 pumping speed)

The plasma generator and turbomolecular pump required cooling water during operation, so a chiller was chosen with an appropriate volume and cooling capacity.⁶⁵ Cooling water lines were set up to connect the plasma generator, turbomolecular pump, and chiller in a loop.

Pneumatic valve setup

There were twenty-seven pneumatic valves in the chamber design: twenty-three were normally-closed (NC) two-way or three-way valves on the panels, two were dual-acting gate valves, and two were NC isolation valves (one for each pump). To operate the pneumatic valves, they had to each be connected to a solenoid by compressed air, and the solenoid had to be connected to power and compressed air. The valves on the panels

were chosen to be NC, meaning they are closed when not supplied with compressed air, which would occur if the solenoid experienced a loss of power or compressed air, to prevent the chamber being exposed to air if a power outage occurred. The dual-acting gate valves can behave as NC or normally-open but were configured to behave as NC, and the isolation valves had to be NC to prevent back-streaming of pump oil into the chamber if loss of power to the mechanical pumps occurred. The gate valve and isolation valve solenoids plugged directly into outlets, but the valves on the panels were operated by data acquisition units (DAQs) so they could be controlled by LabVIEW software for running experiments, which required individually wiring their solenoids to the DAQs and to ground (Figure 63). Each DAQ was wired to a power supply and to ground.

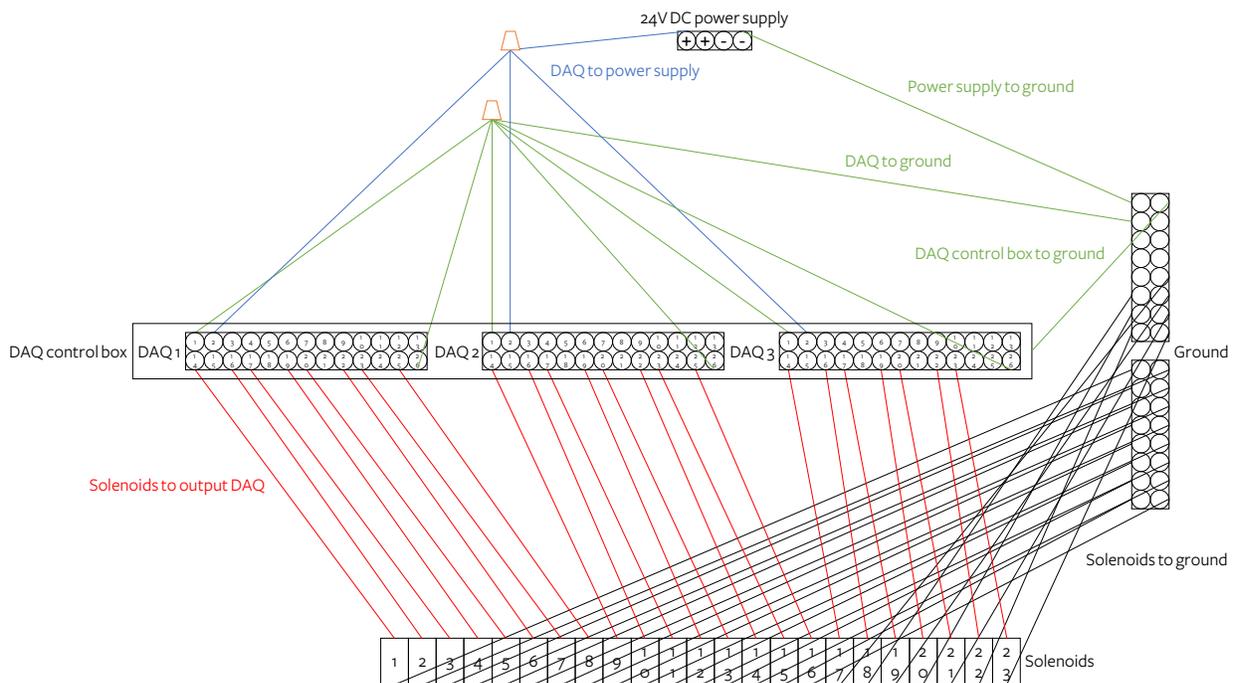


Figure 63: Wiring diagram for solenoids controlling pneumatic valves on panels

For the compressed air (Figure 64), a single tube of building air was split using a cross and then three tees. The first tee was connected to two solenoid bars, and the twenty-three solenoids on the bars were connected to the valves on the panels. Each of the compressed air lines between the solenoids and the valves was labeled to prevent any incorrect attachments. A manual valve was placed in the line upstream of the tee so the solenoid bars could be isolated for maintenance without needing to turn off the compressed air at the regulator. The second tee was connected to the two gate valve solenoids, which were connected to the gate valves. The third tee was connected to the two isolation valve solenoids, which were connected to the isolation valves.

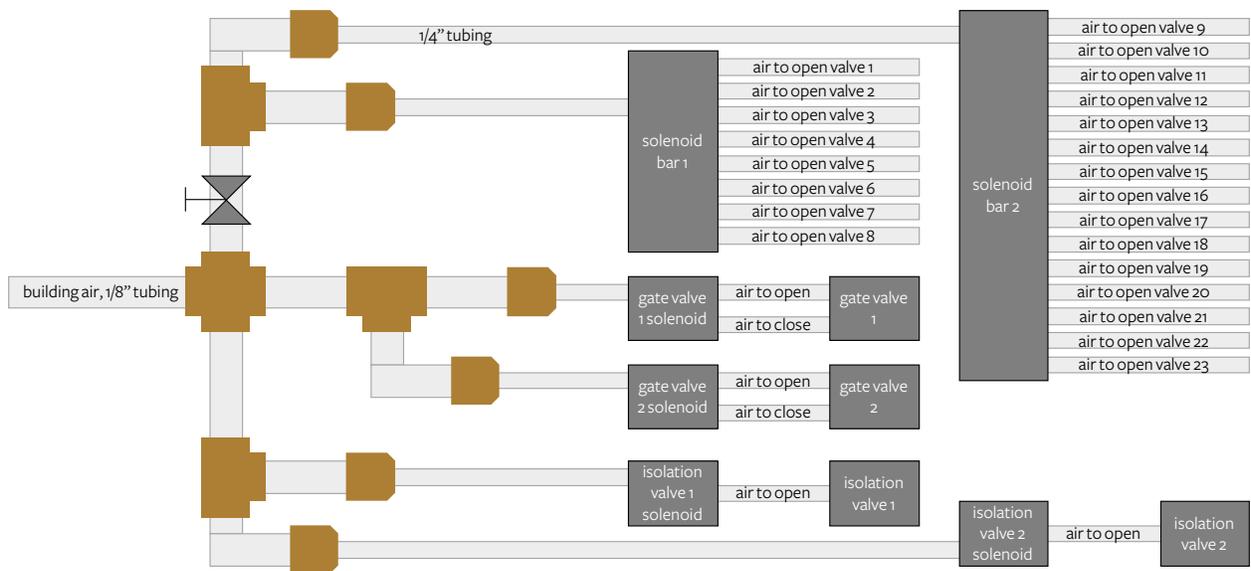


Figure 64: Compressed air diagram for pneumatic valves

Powering equipment

Twenty-one pieces of equipment required power for operation and control of the chamber, and the maximum distance to an outlet was often constrained by the length of specialty cables. The tube furnace and plasma generator both had non-standard power requirements, so they were plugged directly into specialty outlets on the wall.^{59, 63} The chiller had standard power requirements and was plugged directly into the wall.⁶⁵ The remaining equipment was plugged into power strips, considering the amperage of each piece of equipment and the maximum amperage of each power strip. Some equipment needed to be on the same power strip, such as a pump and its corresponding isolation valve, to ensure they would operate in coordination if a partial power outage occurred. The final configuration used five power strips (Table 5).

Table 5: Configuration of equipment to power

Direct to wall	Power strip 1	Power strip 2
Tube furnace	Translator	Computer
Plasma generator	Pump 1	Monitor
Chiller	Isolation valve 1 solenoid	Pump 2 Isolation valve 2 solenoid
Power strip 3	Power strip 4	Power strip 5
Gate valve 1 solenoid	MFC controller 1	Pressure controller
Gate valve 2 solenoid	MFC controller 2	Turbomolecular pump controller
	DAQ control box	Thermocouple gauge display
	DAQ power supply	Heating cord controller 1 Heating cord controller 2

Equipment details, serial communication, and equipment control

An electronics tower was used to house the DAQ components and mount the electronics for MFC control, pressure control, turbomolecular pump control, and thermocouple gauge display (Figure 65). Each piece of equipment was connected to its corresponding controller, and the necessary controllers were connected to the computer (Table 6).



Figure 65: Electronics tower

Table 6: Serial communication summary

Equipment to controllers	Controllers to computer
Solenoids and plasma generator to DAQs	DAQs
Four MFCs on panel 1 to MFC controller 1	MFC controller 1
Three MFCs on panels 2–4 to MFC controller 2	MFC controller 2
Throttle valve and Baratron to pressure controller	Pressure controller

No communication with computer
Tube furnace
Chiller
Translator
Turbomolecular pump controller
Thermocouple gauge display

Solenoids for pneumatic valves on the panels (two-way valves: Swagelok 6LVV-DPFR4-P-C-12935, three-way valves: Swagelok 6LVV-P2V222P-AA) and DAQs were located on the top shelf of the electronics tower. The solenoids (Mac 34B-L00-GDFE-1KT) were mounted on two twenty-port solenoid bars (Mac EBP34B-001B-20), with solenoid blanks (Mac EBP34B-001B-20) filling the empty ports. The twenty-three solenoids were connected to three eight-channel sourcing output DAQs (NI-9472 779137-01), which were housed in a four-unit relay control box (NI cDAQ-9174 781157-01) and powered by an external 24 VDC power supply (NI PS-14 783167-01). The twenty-fourth channel was used to operate the plasma generator (MKS ASTRON AX7670-21-C). One eight-channel sinking input DAQ (NI-9421 779002-01) filled the fourth spot in the relay control box and was used to monitor the status of the plasma generator. A wiring diagram for these

connections is shown in Figure 66. All solenoids and leads from the solenoids to the DAQs were labeled with the pneumatic valve number they connected to. The connection between solenoid and DAQ channel could also be verified by closing the manual valve on the compressed air line, releasing the air at the solenoid bars, using the NI MAX program to activate a channel, and comparing the LED lights on the solenoids and the DAQ. The status of the DAQ channels, and therefore of the pneumatic valves and the plasma generator, was controlled using LabVIEW.

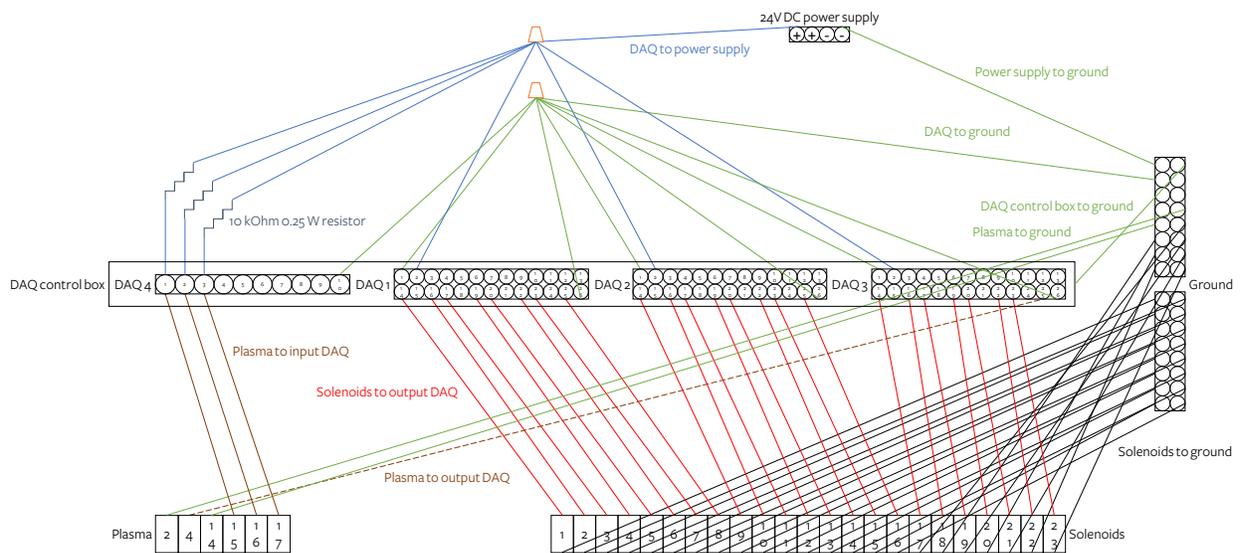


Figure 66: Wiring diagram for pneumatic valve solenoids and plasma generator

The throttle valve (MKS 253B-1-40-1) and Baratron (MKS 627F11TBC1B) connected to the same controller (MKS 651CD2S1N) for controlling the pressure in the chamber, which was located on the left of the second shelf from the top of the electronics tower. Operation of the controller could be done locally or remotely using LabVIEW, and was determined by the position of the key on the front of the controller.

The seven MFCs (MKS GM50A013xxxRBM020, where xxx represents the code for the full scale of the MFC) were connected to two six-channel controllers (MKS 946-US-FCFCFC-NA), which were labeled on the front as MFC 1 (located on the right of the second shelf of the electronics tower) and MFC 2 (located on the right of the third shelf of the electronics tower). Cables from the MFCs to the controllers were labeled QCM/LL purge, panel two, panel three, panel four, plasma inert, plasma O₂, and plasma H₂, which corresponded to MFCs A–G, respectively. The six channels on each controller were designated A1, A2, B1, B2, C1, C2. On MFC 1, A1 corresponded to MFC A, B2 to MFC E, C1 to MFC F, and C2 to MFC G. On MFC 2, A1 corresponded to MFC B, B1 to MFC C, and C1 to MFC D. The MFC status could be set locally or remotely using LabVIEW.

The turbomolecular pump (Pfeiffer Balzers TPU 060) was connected to a controller (Pfeiffer Balzers TCP 121), which was located on the left of the third shelf of the electronics tower. The status of the turbomolecular pump was controlled locally, and could be set to on, off, or in standby mode (two thirds of the rated rotation speed). The rotation speed of the turbomolecular pump was indicated by the LED lights on the controller.

The lowest controller (MKS 307502-A30-T1) in the electronics tower displayed the pressures measured by the two thermocouple gauges (Kurt J. Lesker KJL-6000SS). The cables into the controller were labeled A and B, where thermocouple A was above pump one and thermocouple B was above pump two.

The bottom shelf of the electronics tower contained power strips four and five (Table 5) for powering the controllers, and a USB hub for connection of the controllers to the computer. Plugs for the DAQ control box, DAQ power supply, pressure controller, both MFC controllers, turbomolecular pump controller, and thermocouple gauge display were labeled at the power strips. Cables from the DAQ control box, pressure controller, and both MFC controllers were labeled at their plug into the USB hub. The cables for the pressure controller and both MFC controllers were also labeled at the 9-pin D-sub connectors on the back of the controllers.

The thin film monitor (INFICON STM-2) attached directly to the feedthrough of the ALD QCM sensor (INFICON 750-713-G4) via a BNC cable and to the computer via a USB cable. Data collection from the monitor was done through STM-2 software.

The tube furnace (XST-3-0-12-1V2-F01-H-P) and chiller (Thermo-Fisher Scientific Cole-Parmer Polystat CR250WU) were controlled locally.

Installation in Olin Hall 310

To build this chamber, over 200 individual components were researched, ordered, and installed. The location of the system in the room was chosen to maximize access to the chamber on either side. A complete AutoCAD model of the lab was created to properly visualize the completed chamber and to expedite assembly (Figure 67).

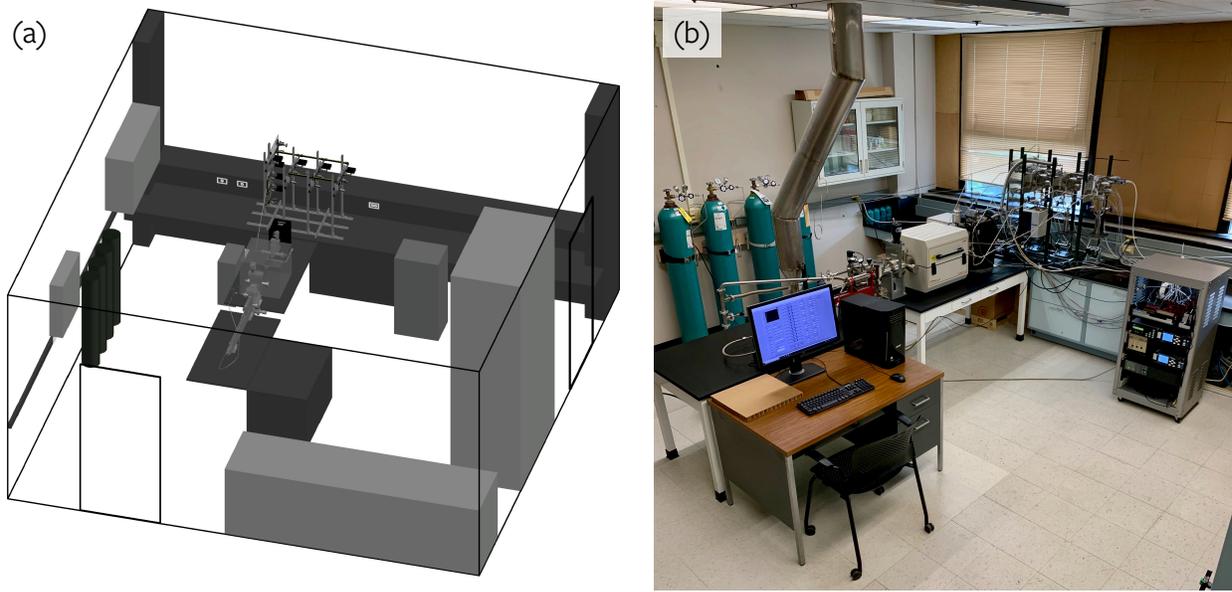


Figure 67: (a) AutoCAD model of assembled reactor in laboratory, (b) photo of assembled reactor in laboratory

We performed a helium leak check on all flanges and fittings in the system to ensure that all elements were leak tight. This required replacing the designed pumping configuration with a leak detector (which contained a turbomolecular pump, a mechanical backing pump, and a mass spectrometer) to monitor the quantity of helium in the system. Starting with all valves closed, the chamber was incrementally opened to the leak detector and each fitting was sprayed with helium. During the process, the smallest volume possible was open to the leak detector, to ensure accurate identification of any leaks.

Piping and instrumentation diagram

AutoCAD was used to visualize the design in three dimensions in the physical lab space, but a piping and instrumentation diagram (P&ID) was also drawn to determine flow and

pumping patterns during the initial pump down and subsequent experiments (Figure 68).

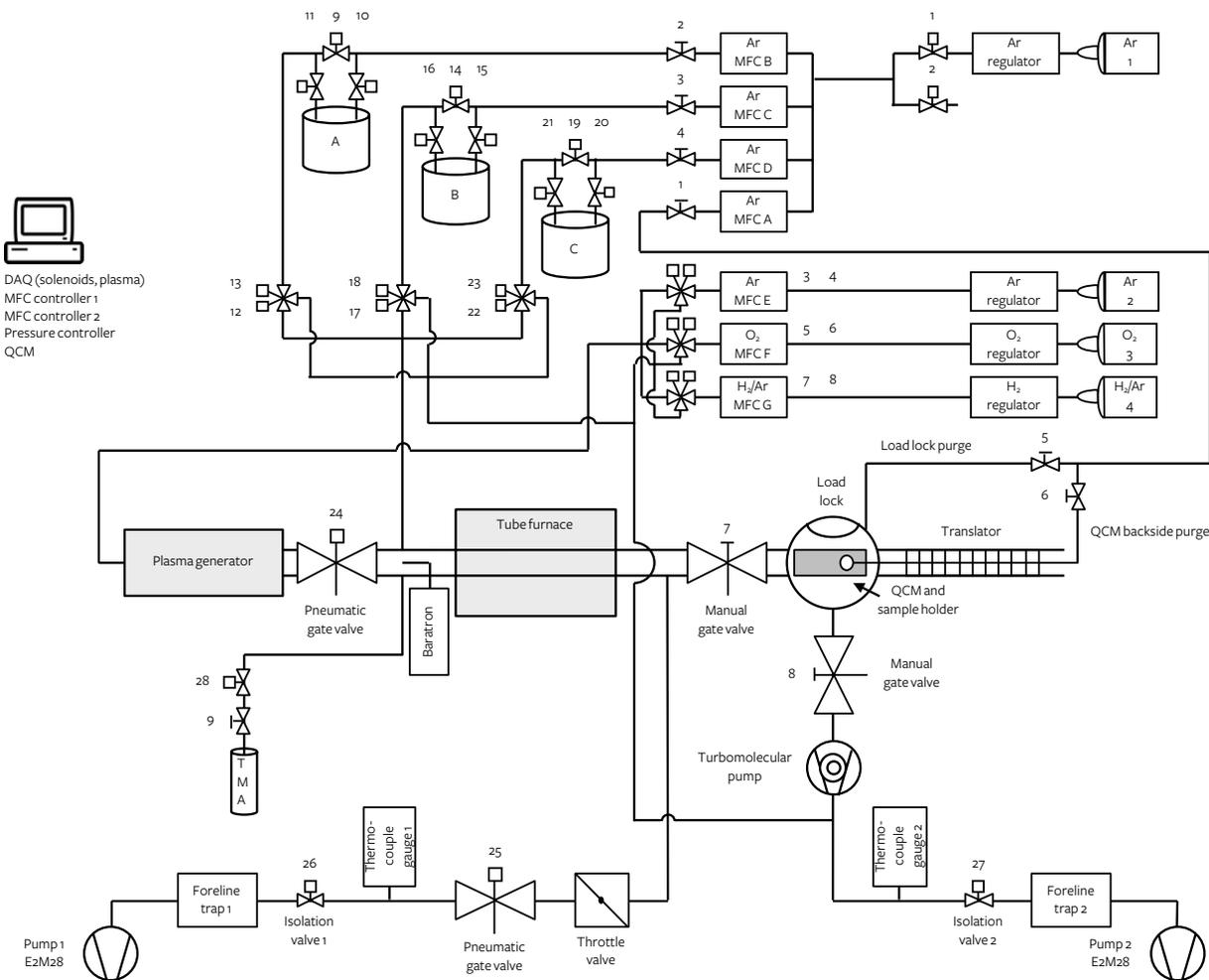


Figure 68: Piping and instrumentation diagram for reactor

On the P&ID, pneumatic valves were numbered one through twenty-eight and were indicated by a square handle, and manual valves were numbered one through nine and were indicated by a flat handle. For example, the fifth pneumatic and sixth manual valves were referenced as P5 and M6, respectively. There were additional manual or pneumatic

valves on the inlet and outlet tubes of bubblers, but they were not included in this diagram because they were not permanent aspects of the system. Pneumatic valves twenty-four through twenty-seven and manual valves one through nine were physically labeled for reference because they were controlled manually by individual solenoids and handles, respectively. There was one manual valve on the system that was not numbered or shown on the P&ID, located on panel one near P1 and P2. This was included in case a specific type of leak detector was used, but it need not be opened or closed for any routine procedures. The six three-way valves directed flow from the panels to the reactor or to the pump. The lower number always indicated to the reactor and the higher number always indicated to the pump (e.g., P5 to reactor, P6 to pump).

Opening P1 provided inert argon gas to MFCs A, B, C, and D. If another carrier gas were of interest (e.g., nitrogen), a cylinder could be installed upstream of P2 without having to disassemble the connections to P1. When the trimethylaluminum reactant delivery line was added, all twenty-four channels on the sourcing output DAQs were already occupied by P1–P23 and the plasma generator. Because P2 was not connected to anything on the upstream side, and therefore not in use, the compressed air line to P2 was repurposed and attached to P28 downstream of the trimethylaluminum ampoule. Consequently, when incorporating trimethylaluminum into an experiment, the control for P2 is used to open P28. However, if it were later of interest to utilize P2, the compressed air line could easily be switched back from P28 to P2.

We used a modified version of the P&ID to represent an experimental sequence, so we would know what was flowing to which pump during each step, and to ensure there were no areas where reactant chemicals could build up (Figure 69). This also elucidated which valves to keep closed while changing the crystal, to minimize lines exposed to atmospheric contaminants. The full series of the modified P&ID for an example experimental process is in Appendix C.

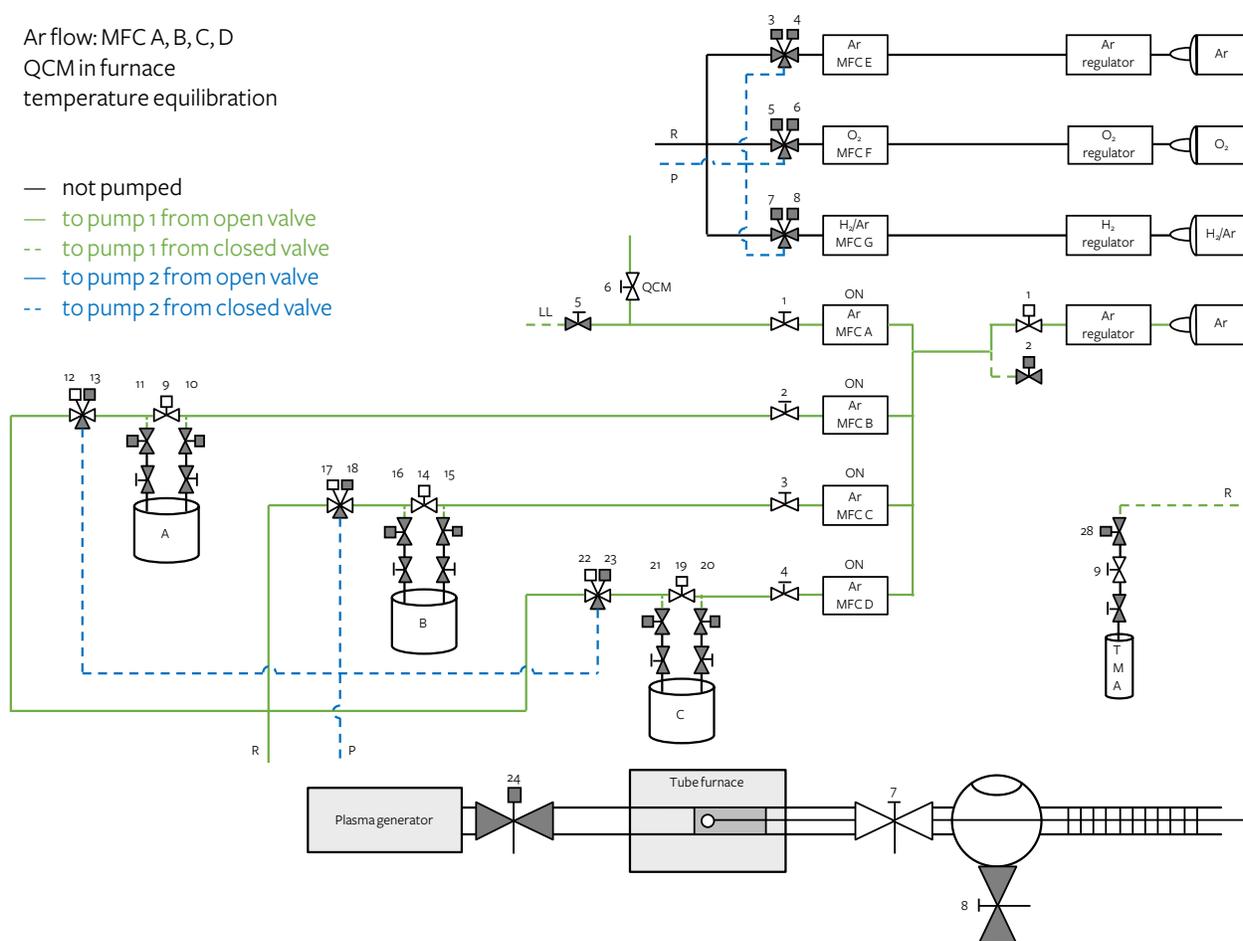


Figure 69: Example modified piping and instrumentation diagram for reactor, for argon flow conditions during a temperature equilibration step

Characterizing the chamber

The Excel spreadsheets used for the Reynolds number, residence time, diffusion length, Knudsen number, and plasma ion concentration calculations, including embedded formulas, are in Appendix D.

Reynolds number calculation

Calculating the Reynolds number was critical to understanding the behavior of flow in the reactor. For deposition reactions, laminar flow was necessary to ensure proper delivery of the reactants to the substrates. Laminar flow is also called viscous flow because the viscous forces dominate over the inertial forces. The Reynolds number is influenced by the reactor geometry and variables including gas species, reactor temperature, and gas flow rate. Assuming a gas flow containing only argon, the Reynolds number was calculated for various experimentally relevant temperatures and flow rates, and it was determined that the flow was laminar for all scenarios (Table 7). The dynamic viscosity of argon was plotted as a function of temperature, and the relevant value was used in the calculations.⁶⁶

Table 7: Reynolds number calculation as a function of temperature and pressure

		T (K)						
Re	1.15	323	373	393	453	473	523	573
V (sccm)	20	0.53	0.48	0.46	0.41	0.40	0.37	0.35
	30	0.80	0.72	0.69	0.62	0.60	0.56	0.52
	40	1.07	0.95	0.92	0.82	0.80	0.74	0.70
	50	1.33	1.19	1.15	1.03	1.00	0.93	0.87
	60	1.60	1.43	1.38	1.24	1.20	1.12	1.05
	70	1.87	1.67	1.60	1.44	1.40	1.30	1.22
	80	2.13	1.91	1.83	1.65	1.60	1.49	1.40
	90	2.40	2.15	2.06	1.86	1.80	1.68	1.57
	100	2.67	2.38	2.29	2.06	2.00	1.86	1.75

laminar flow: $Re < 2300$
intermittent flow: $2300 < Re < 2900$
turbulent flow: $Re > 2900$

Residence time calculation

It was necessary to calculate the residence time to inform ALD sequence times. For example, if the residence time of the precursor was ten seconds, the precursor purge should have been longer than ten seconds to allow sufficient time for all the chemical to exit the chamber. Variables upon which the residence time is based include reactor temperature, reactor pressure, and gas flow rate. Reactor geometry is also an important factor in determining the residence time. The residence time increases with decreasing temperature, increasing pressure, and decreasing flow rate (Table 8, Table 9, Table 10).

For representative experimental conditions of 393 K, 1.5 Torr, and 50 sccm, the residence time was 3.4 s.

Table 8: Residence time calculation as a function of temperature and pressure

		T (K)							
		323	373	393	453	473	523	573	
P (Torr)	τ (s)	3.4	0.3	0.2	0.2	0.2	0.2	0.2	0.2
	0.1	0.3	0.2	0.2	0.2	0.2	0.2	0.2	
	0.5	1.4	1.2	1.1	1.0	0.9	0.9	0.8	
	1	2.8	2.4	2.3	2.0	1.9	1.7	1.6	
	1.5	4.2	3.6	3.4	3.0	2.8	2.6	2.3	
	2	5.5	4.8	4.6	4.0	3.8	3.4	3.1	
	5	13.9	12.0	11.4	9.9	9.5	8.6	7.8	
	10	27.7	24.0	22.8	19.8	18.9	17.1	15.6	

Table 9: Residence time calculation as a function of temperature and flow rate

		T (K)							
		323	373	393	453	473	523	573	
V (sccm)	τ (s)	3.4	10.4	9.0	8.5	7.4	7.1	6.4	5.9
	20	10.4	9.0	8.5	7.4	7.1	6.4	5.9	
	30	6.9	6.0	5.7	4.9	4.7	4.3	3.9	
	40	5.2	4.5	4.3	3.7	3.6	3.2	2.9	
	50	4.2	3.6	3.4	3.0	2.8	2.6	2.3	
	60	3.5	3.0	2.8	2.5	2.4	2.1	2.0	
	70	3.0	2.6	2.4	2.1	2.0	1.8	1.7	
	80	2.6	2.3	2.1	1.9	1.8	1.6	1.5	
	90	2.3	2.0	1.9	1.6	1.6	1.4	1.3	
	100	2.1	1.8	1.7	1.5	1.4	1.3	1.2	

Table 10: Residence time calculation as a function of pressure and flow rate

		P (Torr)						
		0.1	0.5	1	1.5	2	5	10
V (sccm)	τ (s)	3.4						
	20	0.6	2.8	5.7	8.5	11.4	28.5	57.0
	30	0.4	1.9	3.8	5.7	7.6	19.0	38.0
	40	0.3	1.4	2.8	4.3	5.7	14.2	28.5
	50	0.2	1.1	2.3	3.4	4.6	11.4	22.8
	60	0.2	0.9	1.9	2.8	3.8	9.5	19.0
	70	0.2	0.8	1.6	2.4	3.3	8.1	16.3
	80	0.1	0.7	1.4	2.1	2.8	7.1	14.2
	90	0.1	0.6	1.3	1.9	2.5	6.3	12.7
	100	0.1	0.6	1.1	1.7	2.3	5.7	11.4

Diffusion length calculation

Comparing the diffusion length to the reactor dimensions could help ascertain whether the reactants diffused sufficiently in the radial direction, to ensure they were present at the location of the substrates. If the diffusion length was shorter than the reactor tube diameter, then the reactants would not be sufficiently distributed throughout the cross-sectional area of the tube. The diffusion length is a function of gas species, reactor temperature, reactor pressure, and residence time. Assuming argon was the only species present, it was determined there was sufficient diffusion for all experimentally relevant conditions (Table 11, Table 12, Table 13). Chapman–Enskog theory was used to calculate

the diffusion coefficient of argon, and the argon parameters used in the calculations were obtained from literature.⁶⁷

Table 11: Diffusion length calculation as a function of temperature and pressure

L (m)		T (K)						
		323	373	393	453	473	523	573
P (Torr)	0.1	0.742	0.838	0.877	0.992	1.031	1.128	1.227
	0.5	0.332	0.375	0.392	0.444	0.461	0.505	0.549
	1	0.235	0.265	0.277	0.314	0.326	0.357	0.388
	1.5	0.192	0.216	0.226	0.256	0.266	0.291	0.317
	2	0.166	0.187	0.196	0.222	0.231	0.252	0.274
	5	0.105	0.119	0.124	0.140	0.146	0.160	0.174
	10	0.074	0.084	0.088	0.099	0.103	0.113	0.123

sufficient diffusion: $L >$ tube diameter, 0.0602 m

insufficient diffusion: $L <$ tube diameter, 0.0602 m

Table 12: Diffusion length calculation as a function of temperature and residence time

		T (K)						
L (m)	0.226	323	373	393	453	473	523	573
τ (s)	0.1	0.033	0.037	0.039	0.044	0.046	0.050	0.054
	1	0.104	0.117	0.122	0.139	0.144	0.158	0.171
	2	0.147	0.166	0.173	0.196	0.204	0.223	0.242
	3	0.180	0.203	0.212	0.240	0.249	0.273	0.297
	4	0.207	0.234	0.245	0.277	0.288	0.315	0.343
	5	0.232	0.262	0.274	0.310	0.322	0.352	0.383
	10	0.328	0.370	0.387	0.438	0.455	0.498	0.542
	25	0.518	0.585	0.612	0.693	0.720	0.788	0.857
	50	0.733	0.828	0.866	0.980	1.018	1.114	1.212

sufficient diffusion: $L >$ tube diameter, 0.0602 m

insufficient diffusion: $L <$ tube diameter, 0.0602 m

Table 13: Diffusion length calculation as a function of pressure and residence time

		P (Torr)						
		0.1	0.5	1	1.5	2	5	10
L (m)	0.226	0.150	0.067	0.047	0.039	0.034	0.021	0.015
	0.1	0.335	0.150	0.106	0.087	0.075	0.047	0.034
	1	0.474	0.212	0.150	0.122	0.106	0.067	0.047
	2	0.670	0.300	0.212	0.173	0.150	0.095	0.067
	3	0.821	0.367	0.260	0.212	0.184	0.116	0.082
	4	0.948	0.424	0.300	0.245	0.212	0.134	0.095
	5	1.060	0.474	0.335	0.274	0.237	0.150	0.106
	10	1.499	0.670	0.474	0.387	0.335	0.212	0.150
	25	2.120	0.948	0.670	0.547	0.474	0.300	0.212

sufficient diffusion: $L >$ tube diameter, 0.0602 m

insufficient diffusion: $L <$ tube diameter, 0.0602 m

Knudsen number calculation

The Knudsen number was used to determine whether the flow in the reactor was in a continuum or molecular regime, indicating whether the gas species interacted more with themselves or with the walls of the chamber, respectively. Variables that influence the Knudsen number include gas species, reactor temperature, and reactor pressure. During an experiment, gas was sent to the reactor and the pressure was controlled at a relatively high value, so the flow was expected to be in the continuum flow regime. When there was no gas sent to the reactor, the flow should have been in the molecular flow regime, indicating a high level of vacuum, which was desirable for removing species between

experiments. Values of Knudsen number were calculated assuming the gas flow consisted only of argon (Table 14).⁶⁷

Table 14: Knudsen number calculation as a function of temperature and pressure

Kn		T (K)						
		323	373	393	453	473	523	573
P (Torr)	0.0008	0.9969	1.1512	1.2129	1.3981	1.4598	1.6141	1.7684
	0.001	0.0997	0.1151	0.1213	0.1398	0.1460	0.1614	0.1768
	0.01	0.0100	0.0115	0.0121	0.0140	0.0146	0.0161	0.0177
	0.1	0.0020	0.0023	0.0024	0.0028	0.0029	0.0032	0.0035
	0.5	0.0010	0.0012	0.0012	0.0014	0.0015	0.0016	0.0018
	1	0.0007	0.0008	0.0008	0.0009	0.0010	0.0011	0.0012
	1.5	0.0005	0.0006	0.0006	0.0007	0.0007	0.0008	0.0009
	2	0.0002	0.0002	0.0002	0.0003	0.0003	0.0003	0.0004
	5	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0002
10								

- continuum flow: $Kn < 0.01$
- slip flow: $0.01 < Kn < 0.1$
- transition flow: $0.1 < Kn < 10$
- molecular flow: $Kn > 10$

Plasma ion concentration calculation

When utilizing a plasma, it was important to understand the concentration of reactive species leaving the plasma generator and potentially arriving at the substrate. For our experiments, the gases flowing through the plasma generator were argon, oxygen as a process gas, and a 3 % hydrogen balance argon mixture as a process gas. Typically,

during an experiment that incorporated plasma ignition, argon would flow from MFC E, through P3, through the plasma generator, to the reactor for all steps in the ALD sequence not involving a process gas plasma. To ensure a consistent dose of process gas plasma throughout the cycles of an experiment, the plasma was ignited during flow of argon, and maintained through the switch to a process gas. At the initiation of a process gas plasma step, the argon was diverted from the reactor to the pump (i.e., close P3 and open P4). At the same time, the process gas was diverted from the pump to the reactor (i.e., close P6 and open P5 to dose oxygen, or close P8 and open P7 to dose the hydrogen mixture).

Species present after ionization of argon gas may include free electrons, Ar, Ar⁺, and Ar₂⁺.⁶⁸ Species present after ionization of oxygen gas may include free electrons, O⁻, O₂⁻, O₃⁻, O, O₂, O₃, O⁺, and O₂⁺.⁶⁹ Species present after ionization of hydrogen gas may include free electrons, H⁻, H, H₂, H⁺, H₂⁺, and H₃⁺.⁷⁰ Therefore, one mole of Ar gas undergoing complete dissociation in the plasma could result in at most two moles of products (one mole of free electrons and one mole of Ar⁺), one mole of O₂ gas could result in at most four moles of products (two moles of free electrons and two moles of O⁺), and one mole of H₂ gas could result in at most four moles of products (two moles of free electrons and two moles of H⁺).

For the following calculations, common experimental conditions of 1.5 Torr for pressure and 393 K for temperature were used, and it was assumed that the ideal gas law applied.

Due to dissociation, the pressure exiting the plasma generator was greater than the pressure entering the plasma generator.⁷¹ During an oxygen plasma step, oxygen was the only gas flowing through the plasma generator. Assuming complete dissociation of O_2 to O^+ and e^- , and no recombination, the maximum pressure was 6 Torr. The plasma generator had a maximum operating pressure of 10 Torr at the exit, which limited the experimental reactor pressure that could be used. To avoid exceeding the limit, a reactor pressure of no more than 2.5 Torr could be used during experiments involving oxygen plasma ignition. During a hydrogen plasma step, hydrogen and argon were flowing through the plasma generator. Assuming complete dissociation of H_2 to H^+ and e^- , and Ar to Ar^+ and e^- , and no recombination, the maximum pressure was 3.09 Torr. Therefore, a reactor pressure of no more than 4.85 Torr could be used during experiments involving hydrogen plasma ignition.

Of the species present after ionization of hydrogen gas, H^- was of interest because of its properties as a strong reducing agent. Assuming complete dissociation of H_2 to H^+ and H^- , and Ar to Ar^+ and e^- , and no recombination, the minimum mole fraction of H^- was 0.0076, compared to 0.03 of H_2 in the original gas, which corresponded to a partial pressure of 0.0225 Torr. Inevitably, some recombination would occur in the reactor tube between the exit of the plasma generator and the location of the QCM. To increase the amount of reducing species that contact the substrates, the length of the hydrogen plasma dose could be increased.

Flow tests

Before attempting any experiments, it was imperative to understand the system dynamics regarding pressure changes, time delays, and residence times when opening or closing valves and changing flow rates. We performed various flow tests and observed the expected linear relationship between the square of pressure and the flow rate, based on the Hagen–Poiseuille equation for long, straight tubes and viscous flow (Equation 4). Assumptions for using the Hagen–Poiseuille equation were fully developed flow (i.e., the velocity profile was not position-dependent along the tube), laminar flow, zero wall velocity, incompressible gas, and that the pressure at the pump was smaller than the inlet pressure (i.e., $P_2 < P_1$).⁷²

Equation 4: Hagen–Poiseuille equation

$$Q = \frac{\pi R^4}{16\eta L P_2} (P_1^2 - P_2^2)$$

Equation 5: Hagen–Poiseuille equation rearranged to demonstrate the linear relationship between P_1^2 and Q

$$P_1^2 = \frac{16\eta L P_2}{\pi R^4} Q + P_2^2$$

Equation 6: Equation of a line, for comparison to the rearranged Hagen–Poiseuille equation

$$y = mx + b$$

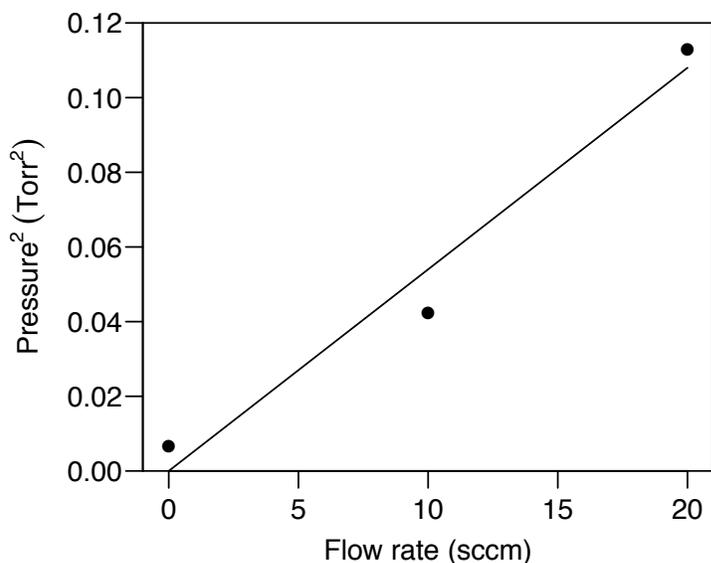


Figure 70: Pressure² vs. flow rate

Temperature calibration and PID tuning

Understanding the temperature profile in the reactor was extremely important for utilizing a QCM, so we performed a temperature calibration. We recorded the temperature as measured by a thermocouple at the location of the QCM crystal (Figure 71) for 130 conditions of various temperature, pressure, and flow rate at the experimental position. We also retracted the QCM sensor by two and four inches and recorded the temperature for eight conditions of various temperature and flow rate, narrowed down from the results of the previous measurements, at each location. By varying the axial position, we better understood how the temperature differed along the length of the reactor tube and confirmed that the wafer samples were under the same temperature conditions as the crystal. To analyze the data, we defined ΔT as the difference between

measurements from the QCM sensor thermocouple and the furnace thermocouple (not the furnace setpoint). Our conclusions were that the ΔT variation was small for changes in pressure at fixed flow rate and position (Figure 72); the ΔT variation was small for changes in flow rate at fixed pressure and position (Figure 73), except for the no flow condition, for which $|\Delta T|$ was greater (Figure 74); and $|\Delta T|$ increased with distance from the experimental position (Figure 75). From this data, we plotted linear calibration curves, which allowed us to determine the necessary setpoint temperature for a desired crystal temperature (Figure 76).



Figure 71: Thermocouple installed at location of QCM crystal

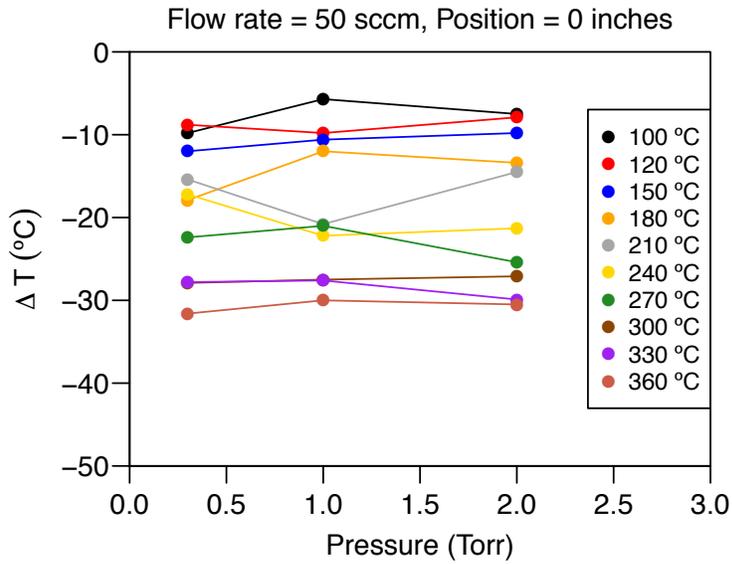


Figure 72: Temperature calibration, ΔT vs. pressure with fixed flow rate at relative position 0 in

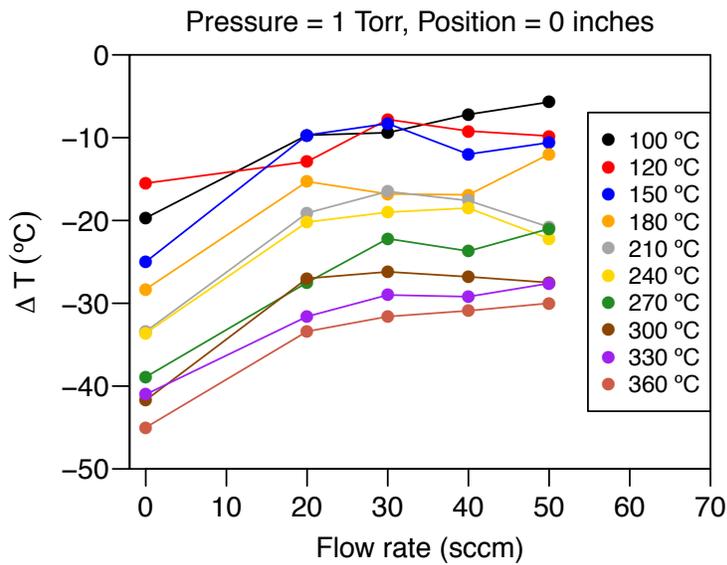


Figure 73: Temperature calibration, ΔT vs. flow rate with fixed pressure at relative position 0 in

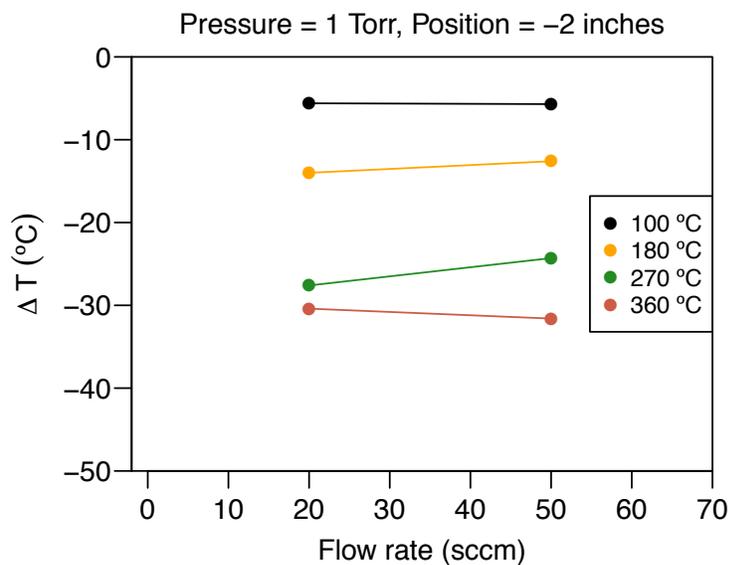


Figure 74: Temperature calibration, ΔT vs. flow rate with fixed pressure at relative position -2 in

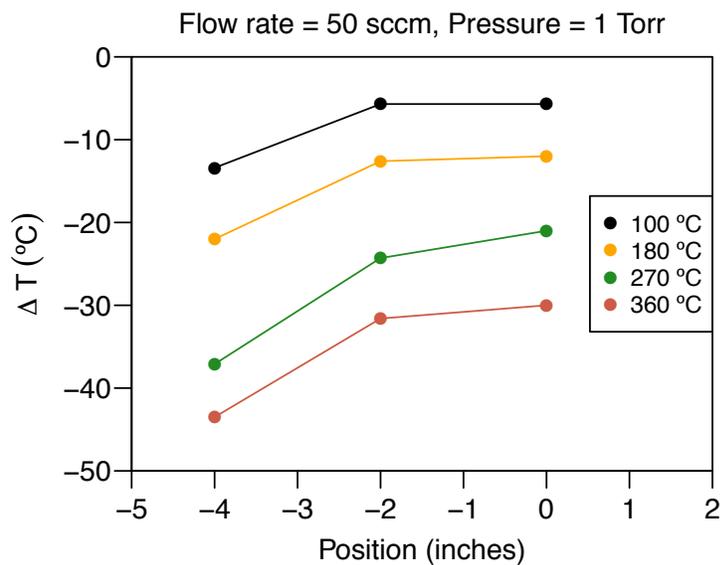


Figure 75: Temperature calibration, ΔT vs. position with fixed flow rate and pressure

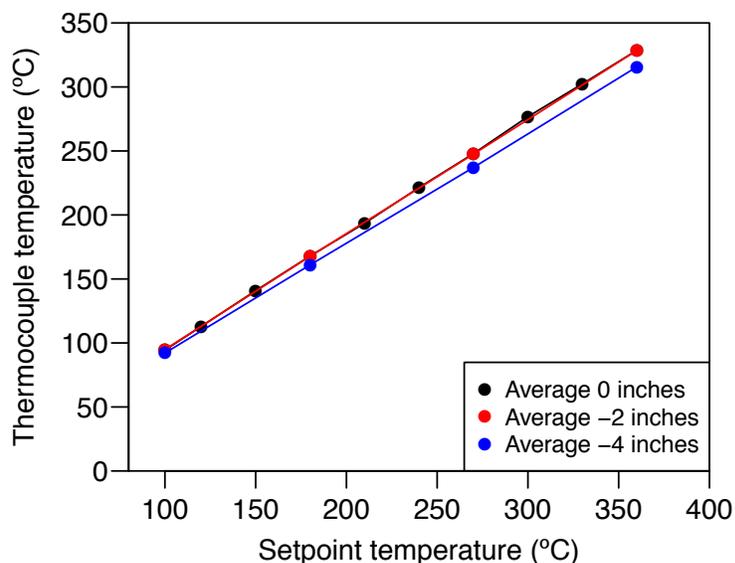


Figure 76: Temperature calibration curves

While the temperature profile allowed us to choose the correct furnace setpoint temperature for the desired substrate temperature, the furnace PID control needed to be optimized so the crystal frequency was not affected by the controller response behavior. With poor PID control, the temperature could deviate by several degrees from the setpoint and oscillate about the setpoint as the controller adjusted to reduce the error. Because of the temperature sensitivity of QCM crystals, the frequency would also oscillate and negatively affect experimental results. Figure 77a and Figure 77b show the temperature and frequency behavior before and after PID tuning, respectively, and it is clear that the temperature control was significantly improved by tuning the PID parameters.⁶³ However, the PID terms were also functions of temperature, so calibration curves were made for a range of common experimental temperatures, so the terms could be updated for the best control.

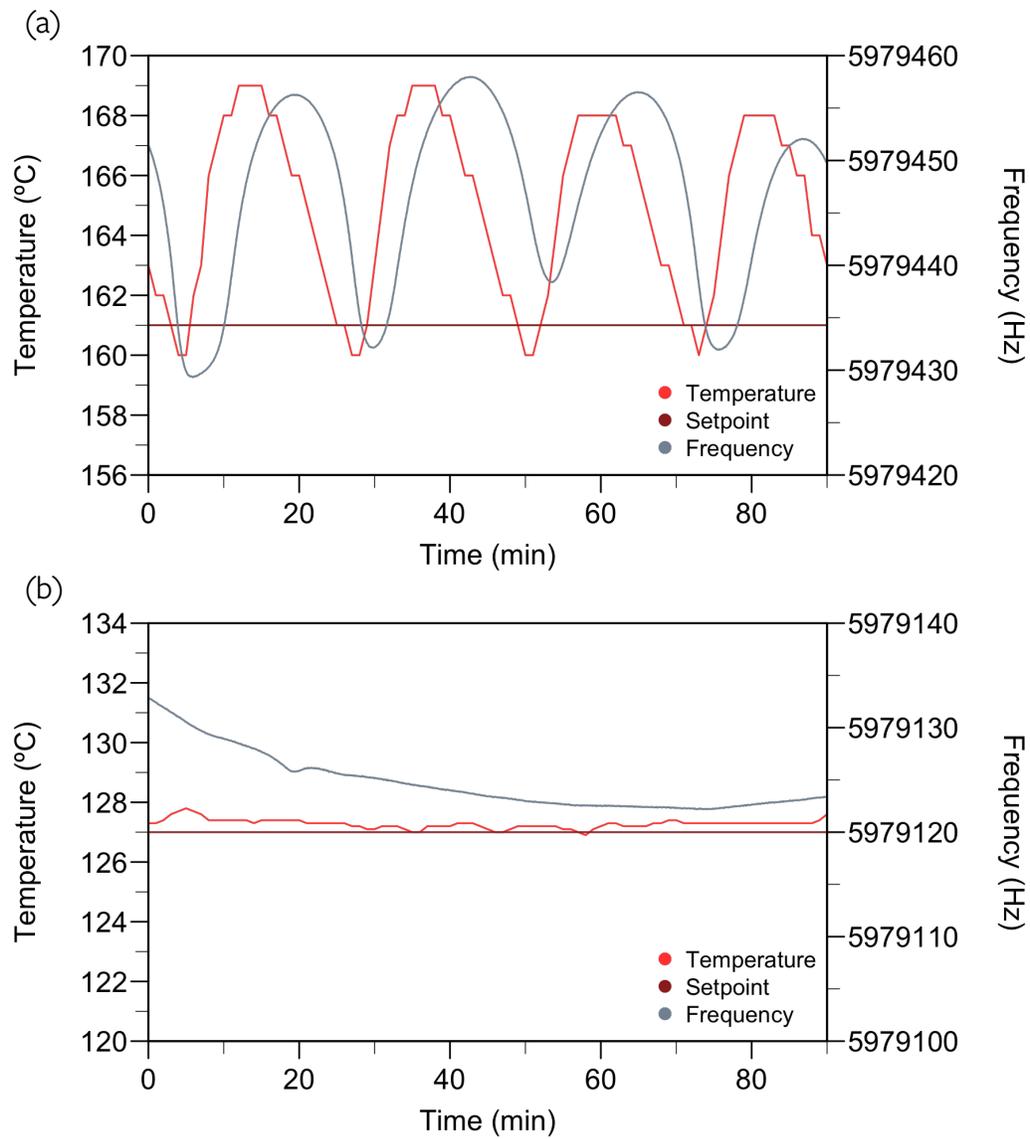


Figure 77: Temperature and frequency behavior, (a) before PID tuning, (b) after PID tuning

Experimental setup

Sample preparation

The preferred QCM crystals, purchased from INFICON, were coated completely with a metal substrate on the top and had patterned metal that served as electrodes on the bottom. The metal surface coating on catalog crystals was gold. All crystals were optimized for an operating temperature of 120 °C and had a starting frequency of 6 MHz.

The first focus of our area-selective ALD research was to deposit dielectric on dielectric in the presence of metal. Our dielectric starting substrate was amorphous silicon oxide, deposited on the top of gold-coated QCM crystals to a thickness of approximately 20 nm by PEALD in an Oxford FlexAL ALD system located in the CNF (Figure 78a). Our metal starting substrate was custom copper-coated QCM crystals, which were first annealed at 180 °C for one hour with argon purge gas flow or repeatedly dosed with hydrogen plasma to reduce surface oxide (Figure 78b). Both the gold-coated and copper-coated crystals were manufactured with an adhesion layer between the quartz and the metal surface layer. Although these were our primary starting substrates for comparison of the impact of a co-adsorbate on dielectric versus metal surfaces, other dielectric substrates such as aluminum oxide and zirconium oxide were used for some experiments.

When of interest, wafer samples of size of 1.15 in by 0.35 in were inserted into the chamber with the QCM. For the dielectric substrate, wafer samples were cleaved from double-side polished Si(100) wafers and chemically modified in the CNF using a buffered oxide etch/Nanostrip treatment to produce a hydroxyl-terminated silicon oxide surface with a density of $\sim 5 \times 10^{14}$ hydroxyl groups/cm² and a thickness of 15–20 Å (Figure 78c).⁴⁶ For the metal substrate, silicon wafers with a 100 nm thick film of physical vapor deposition (PVD) copper were cleaved and annealed at 180 °C for one hour with argon purge gas flow or repeatedly dosed with hydrogen plasma to reduce surface oxide (Figure 78d).⁴⁶

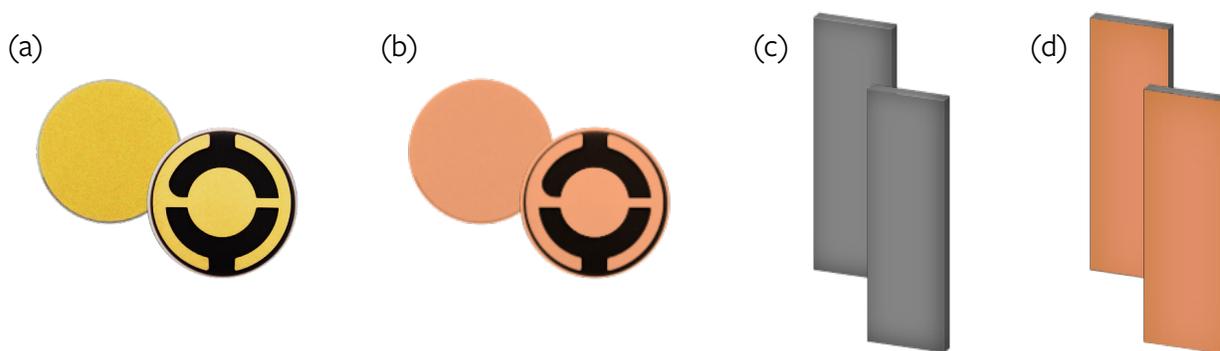


Figure 78: (a) Silicon oxide–gold-coated crystals⁷³, (b) copper-coated crystals⁷³, (c) silicon oxide–silicon wafer samples, (d) copper-silicon wafer samples

Chamber setup

The following basic description is for chamber setup for a standard experiment using flow from panels one through four. A step-by-step experimental procedure is in Appendix F.

To load the crystal and wafer samples, the load lock was isolated and vented to atmospheric pressure, while the rest of the chamber stayed under vacuum. The crystal was secured in the QCM housing, and the wafers were placed on the sample holder with their long sides parallel to the long axis of the reactor tube (Figure 79). After confirming that the crystal had proper electrical connections to the controller, the load lock was closed and pumped down using the turbomolecular pump. While the load lock was being pumped, the furnace was set to the anneal or experimental setpoint temperature. Once the load lock was at a pressure similar to the rest of the chamber, the gate valve used to isolate the load lock was opened and the QCM was moved into the furnace using the translator (Figure 80).

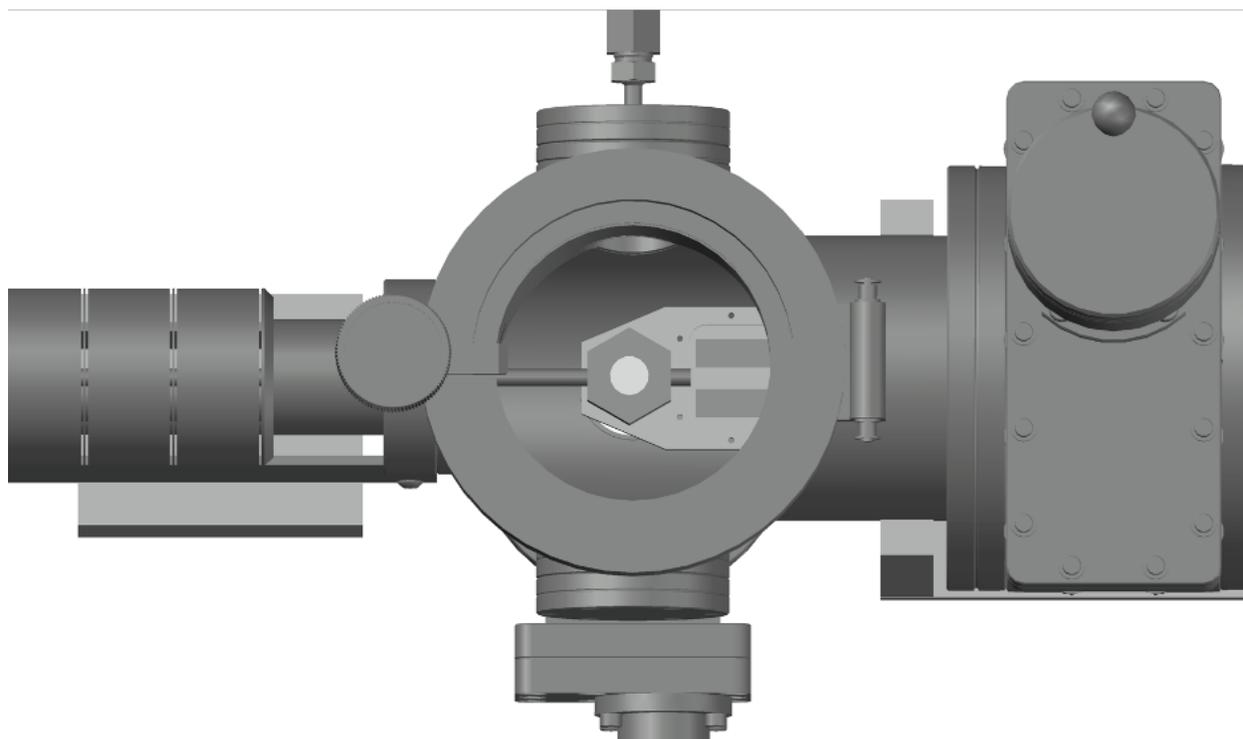


Figure 79: Crystal and wafer samples loaded in load lock

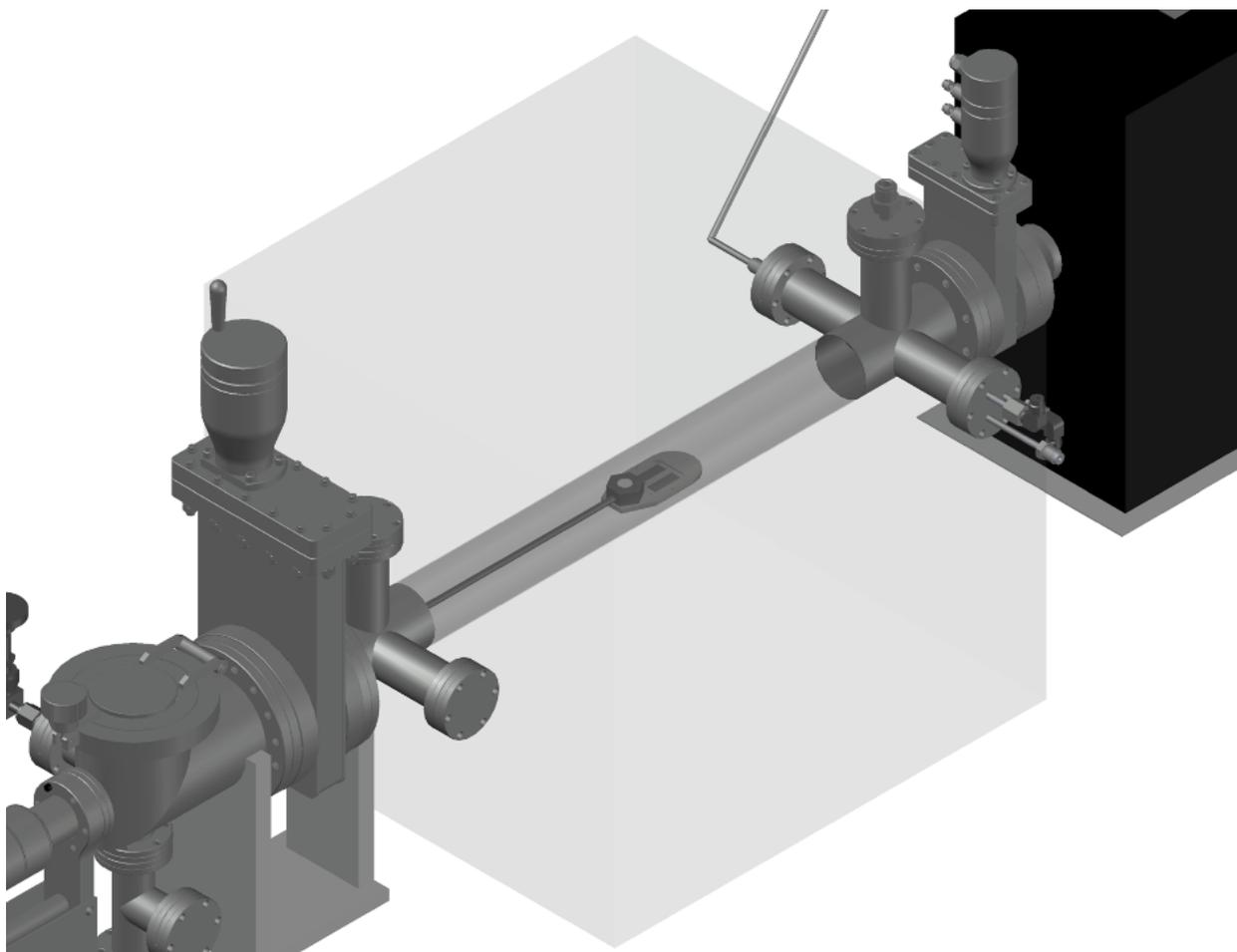


Figure 80: Crystal and wafer samples in reactor tube

The next steps were to initiate gas flow and prepare the substrates for an experiment. The gas cylinders and necessary valves were opened, and the MFCs were set to the desired setpoints. If annealing, the furnace program was launched, which held the temperature at 180 °C for one hour, then automatically changed the setpoint to 120 °C. At this point, the pressure controller was set to the desired setpoint, and the crystal needed to equilibrate to the reactor temperature and flow conditions before an experiment could be initiated. If not annealing, the pressure control was started with the MFC control. While

waiting for the crystal equilibration, the reactant ampoules were prepared by turning on heating baths or filling baths with ice. The heating cords downstream of panels two, three, and four were also turned on. Typically, the temperature along the path that the reactants travelled incrementally increased to prevent cold spots where the reactants could condense. For example, if the furnace temperature was 120 °C and an ampoule temperature was 50 °C, the heating cord setpoint was around 80 °C.

Once the frequency fluctuations were small, the ampoules were opened, and the experiment was started by turning on data collection in the STM-2 software and turning on a LabVIEW program to control opening and closing of the pneumatic valves. At the end of the experiment, the bubblers were closed, the data collection was stopped, the heating cords were turned off, the ampoule baths were turned off or emptied, and the gas flow was halted. If desired, the QCM was moved into the load lock using the translator to remove the crystal and wafer samples immediately.

Investigating the behavior of individual reactants

Before studying cycles of ALD, it was necessary to understand how each reactant affected the different substrates individually. For many combinations of reactant and substrate, the reactant was repeatedly dosed and the mass increase on the QCM crystal was measured. For all experiments, the substrate temperature was 120 °C. In some cases, we expected adsorption of the reactant, such as when dosing a metal-containing precursor on an oxide substrate. In others, we expected no adsorption, such as when dosing water on an oxide substrate. The results of these single reactant experiments also guided our decisions for dose times during ALD experiments. Due to different experimental conditions and reactor geometry, the results in the new chamber at Cornell could not be directly compared to those obtained in the chamber at Lam.

The light grey vertical lines in the following plots indicate when the doses were turned on and off, and the horizontal bars indicate the duration of the dose. The color of the horizontal bar corresponds to the type of reactant in the experiment, where dark blue represents a metal precursor, dark green represents an oxidizing co-reactant, dark grey represents an inert gas plasma, dark yellow represents a reducing plasma, and dark orange represents a co-adsorbate.

Precursor: trimethylaluminum

One of the most studied ALD experiments is the reaction between trimethylaluminum, $\text{Al}(\text{CH}_3)_3$, and water to form an aluminum oxide thin film.⁶¹ As such, it was the first ALD system we attempted in the new chamber. A silicon oxide–gold-coated crystal was exposed to repeated doses (5 seconds) of trimethylaluminum (ampoule temperature 0 °C, vapor pressure ~2.6 Torr). The resulting QCM data demonstrated the self-limiting nature of these repeated half-cycles (Figure 81). The first dose resulted in a surface density increase and subsequent doses had a diminished or negligible change in surface density, because the reactive surface sites became occupied.

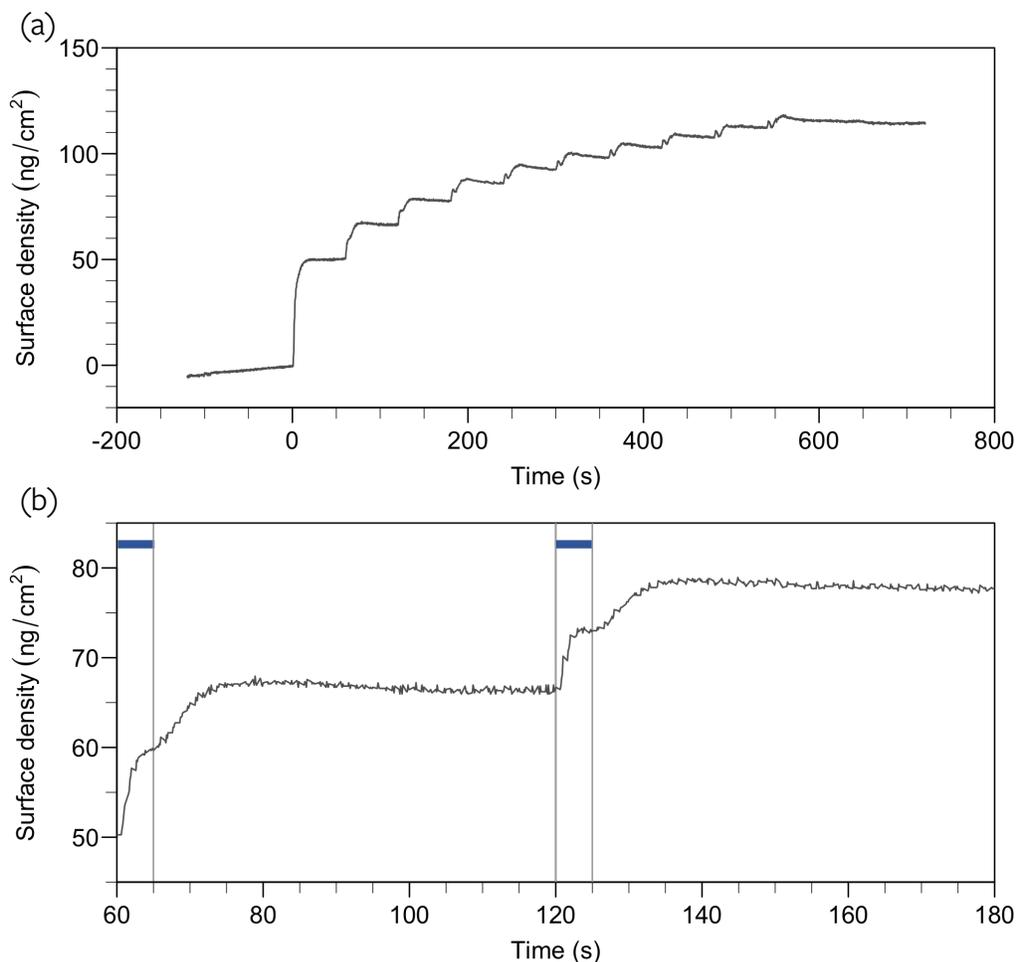


Figure 81: Trimethylaluminum on silicon oxide, (a) ten cycles, (b) cycles two and three

Precursor: tetrakis(ethylmethyamido)zirconium(IV)

Another common ALD system is the reaction between tetrakis(ethylmethyamido)zirconium(IV), $Zr(NCH_3CH_2CH_3)_4$, (TEMAZ) and water to form a zirconium oxide thin film.^{29, 74} A gold-coated crystal with prior zirconium oxide deposition was exposed to repeated doses (20 s) of TEMAZ (ampoule temperature 40 °C, vapor pressure ~0.02 Torr). The self-limiting behavior observed in the

trimethylaluminum experiment was also observed with TEMAZ, as there was a sharp increase in surface density during the first dose and the remaining doses resulted in smaller increases in surface density (Figure 82). By zooming in, we could see clearly that the increase in surface density during cycle three was smaller than the increase in surface density during cycle two.

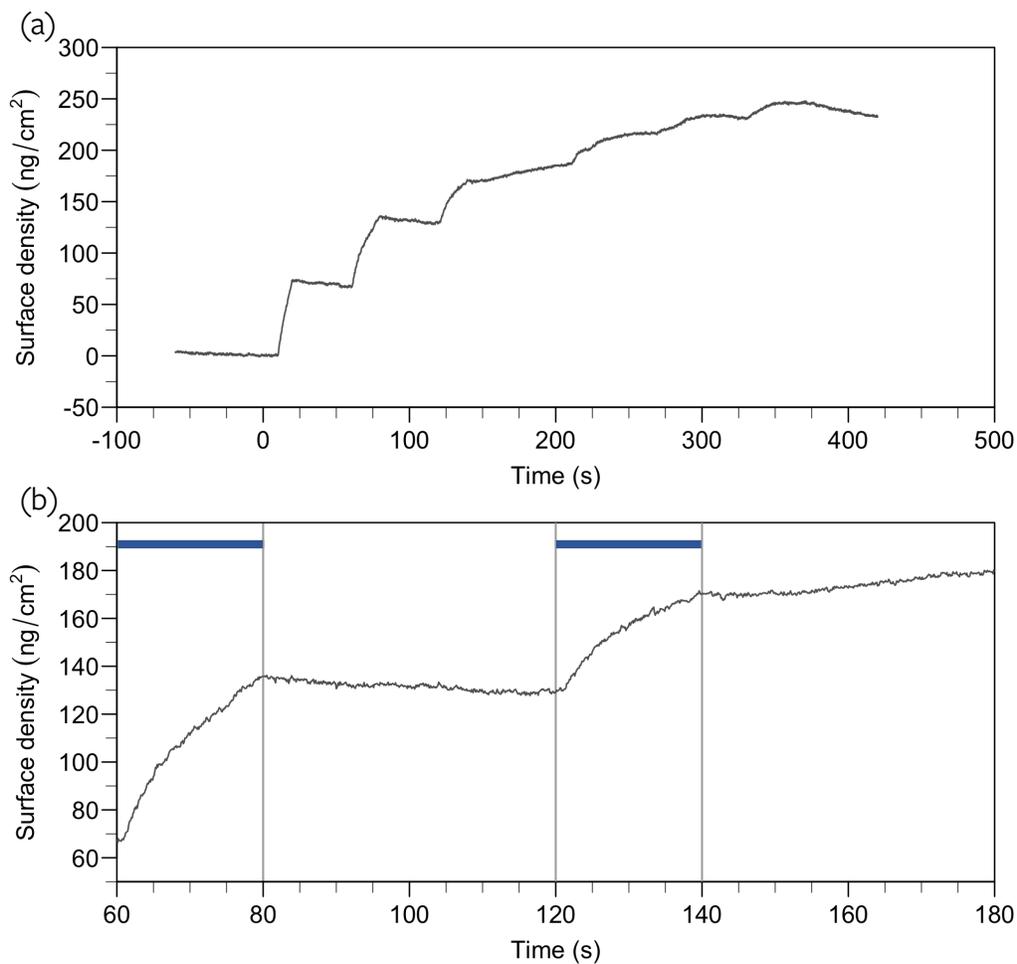


Figure 82: TEMAZ on zirconium oxide, (a) ten cycles, (b) cycles two and three

Precursor: di(sec-butylamino)silane

To deposit silicon oxide, we used the silicon-containing precursor di(sec-butylamino)silane, $\text{SiH}_3\text{N}(\text{CHCH}_3\text{CH}_2\text{CH}_3)_2$, (DSBAS) and oxygen plasma as the co-reactant. A gold-coated crystal was dosed with hydrogen plasma then exposed to repeated doses (10 s) of DSBAS (ampoule temperature 50 °C, vapor pressure ~12.6 Torr). Similar to the trimethylaluminum and TEMAZ experiments, the first dose resulted in the largest surface density increase, and the changes in surface density for the subsequent doses were smaller, demonstrating self-limiting behavior (Figure 83).⁷⁵ Unlike the other precursor exposure experiments, each dose after the first resulted in an apparent increase in mass that was reversed during the purge. It is possible that this was due to a delayed substitution of some of the amino groups as DSBAS adsorbed on the surface, but the phenomenon was not investigated further.

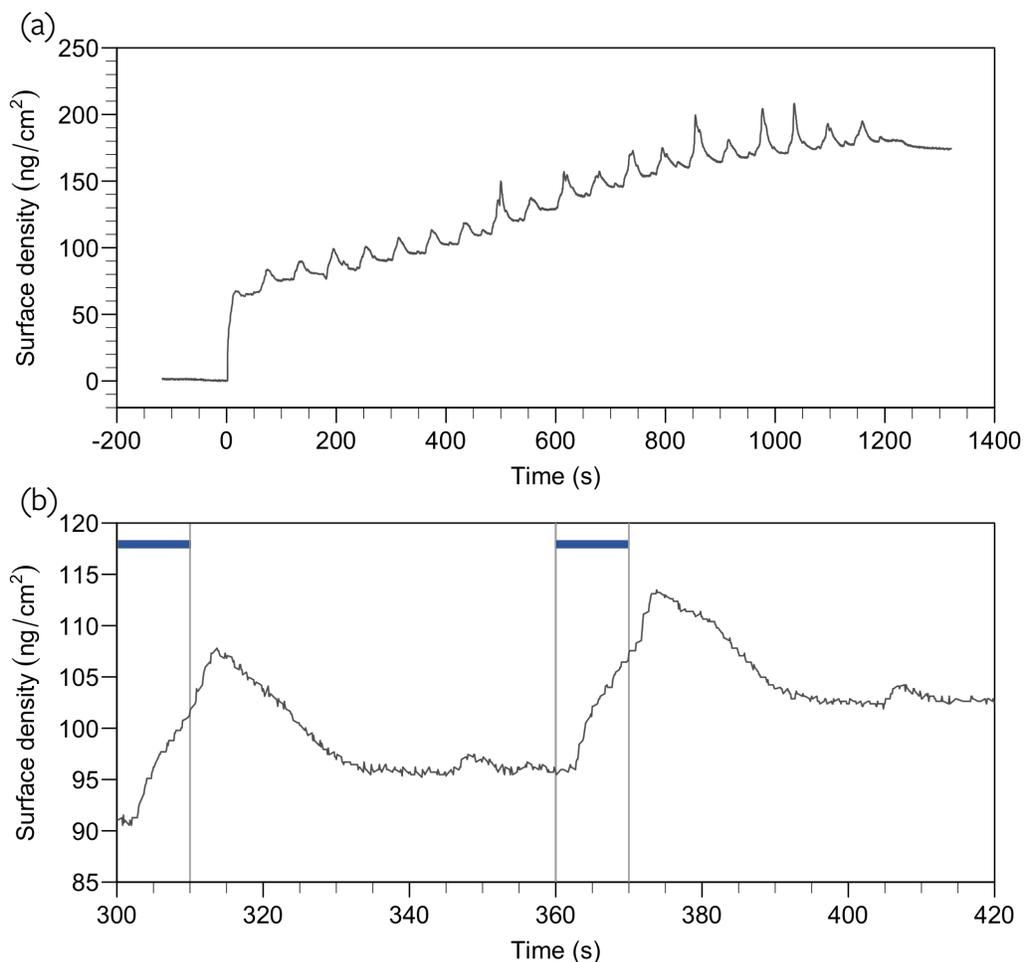


Figure 83: DSBAS on gold, (a) twenty cycles, (b) cycles six and seven

Oxidizing agent: water

As mentioned previously, an increase in surface density was not expected when dosing a weakly oxidizing co-reactant on an oxide surface. Indeed, for repeated doses (1 s) of water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) on a silicon oxide–gold-coated crystal, no change in surface density was observed (Figure 84). When the water dose was turned on, there was an apparent decrease in surface density, but the surface

density returned to its previous value during the purge, suggesting that the deviation was a thermal effect, not an actual decrease in mass on the surface. The thermal effect could have been caused by the temperature difference between the incoming water and the substrate, because the water bubbler was held at 0 °C and the substrate temperature was 120 °C.

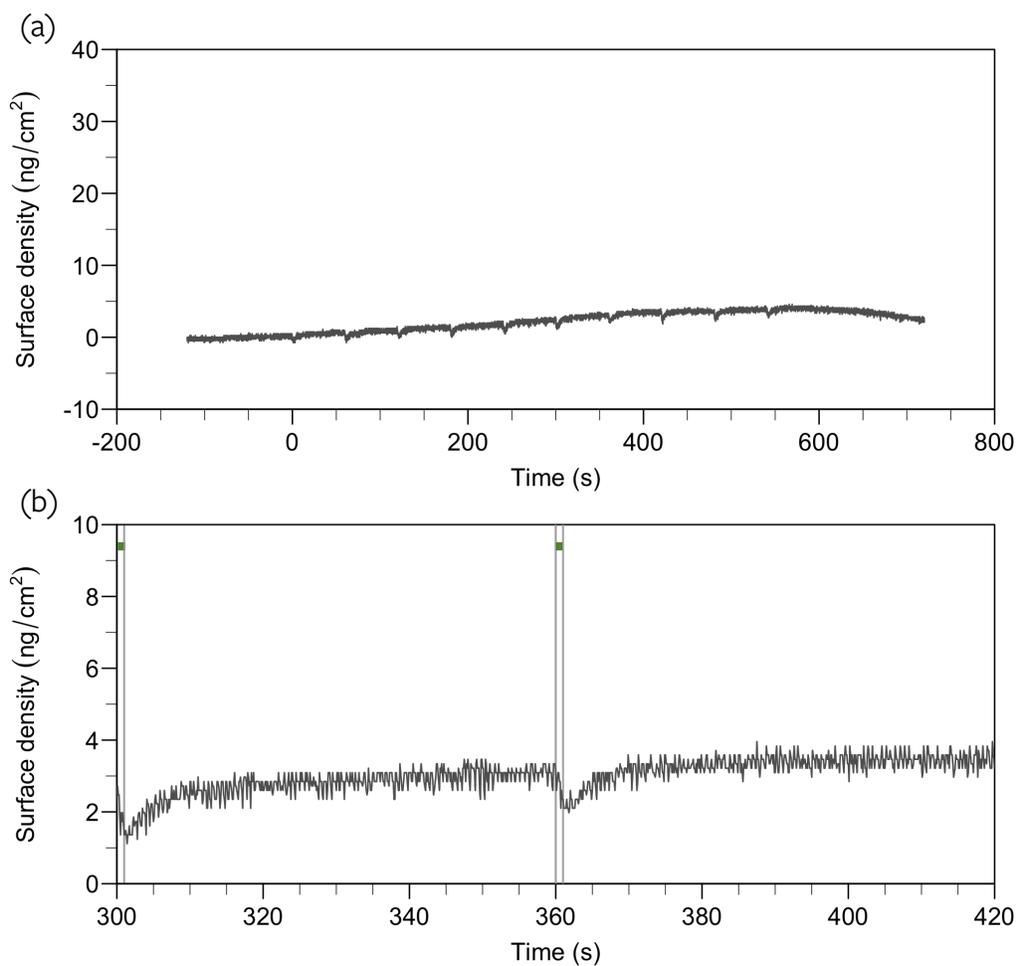


Figure 84: Water on silicon oxide, (a) ten cycles, (b) cycles six and seven

To achieve area-selective deposition, the composition of the reduced copper, the non-growth surface, cannot be altered by the co-reactant during the experiment. A copper-coated crystal was first annealed, then was exposed to repeated doses (1 s) of water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) and limited oxide formation was observed (Figure 85). This result was consistent over a range of substrate temperatures and water dose times. By zooming in on cycles six and seven, we could see the same behavior on the copper substrate as we observed on the oxide substrate.

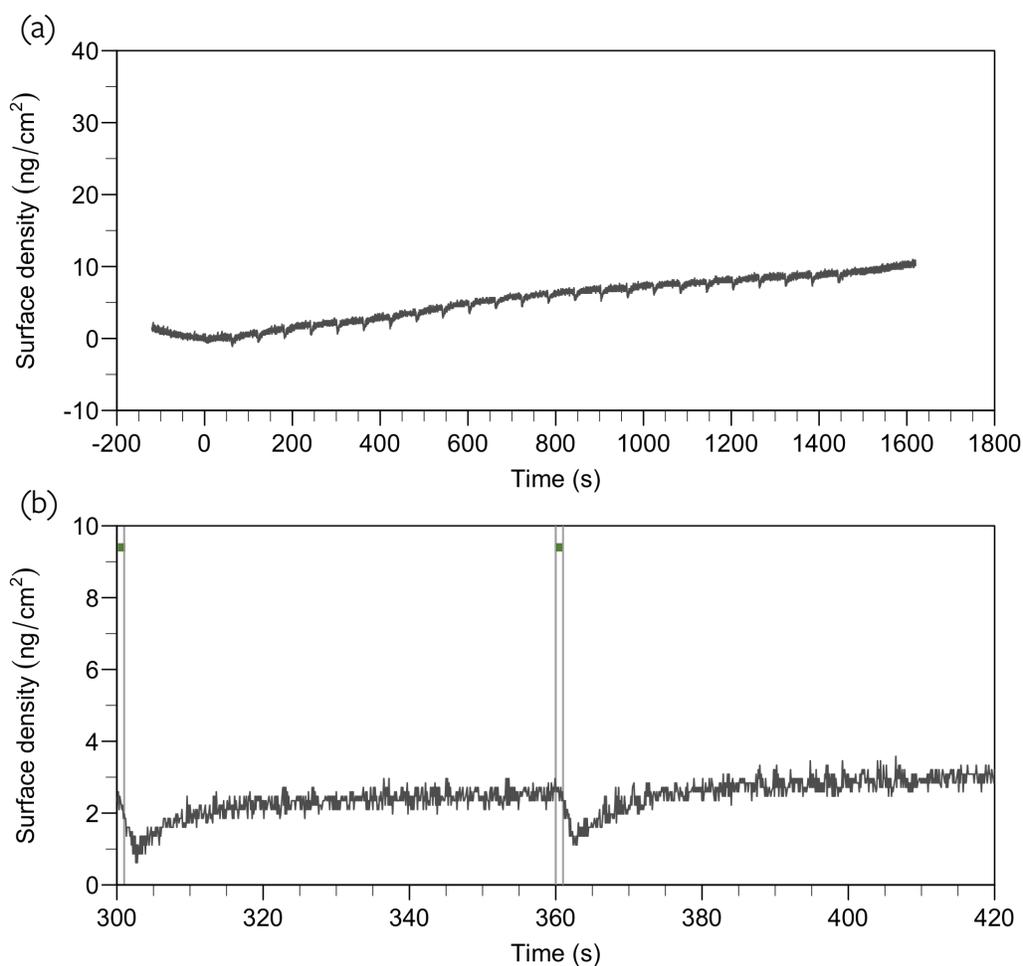


Figure 85: Water on reduced copper, (a) twenty-five cycles, (b) cycles six and seven

Reducing agent: hydrogen plasma

Reduction of silicon oxide by replacing surface hydroxyl groups with hydrogen is an unfavorable reaction.⁷⁶ A sequence comprising a dose (5 s) of argon plasma followed immediately by a dose (30 s) of hydrogen plasma followed by a purge (25 s) of argon gas was repeated five times on a silicon oxide–gold-coated crystal, and the experiment resulted in no overall change in surface density, as expected (Figure 86). The plasma was ignited during the argon dose, then the argon was diverted to the pump for the hydrogen dose. Because there was no change in frequency during the argon plasma step, we concluded that no surface modification occurred.

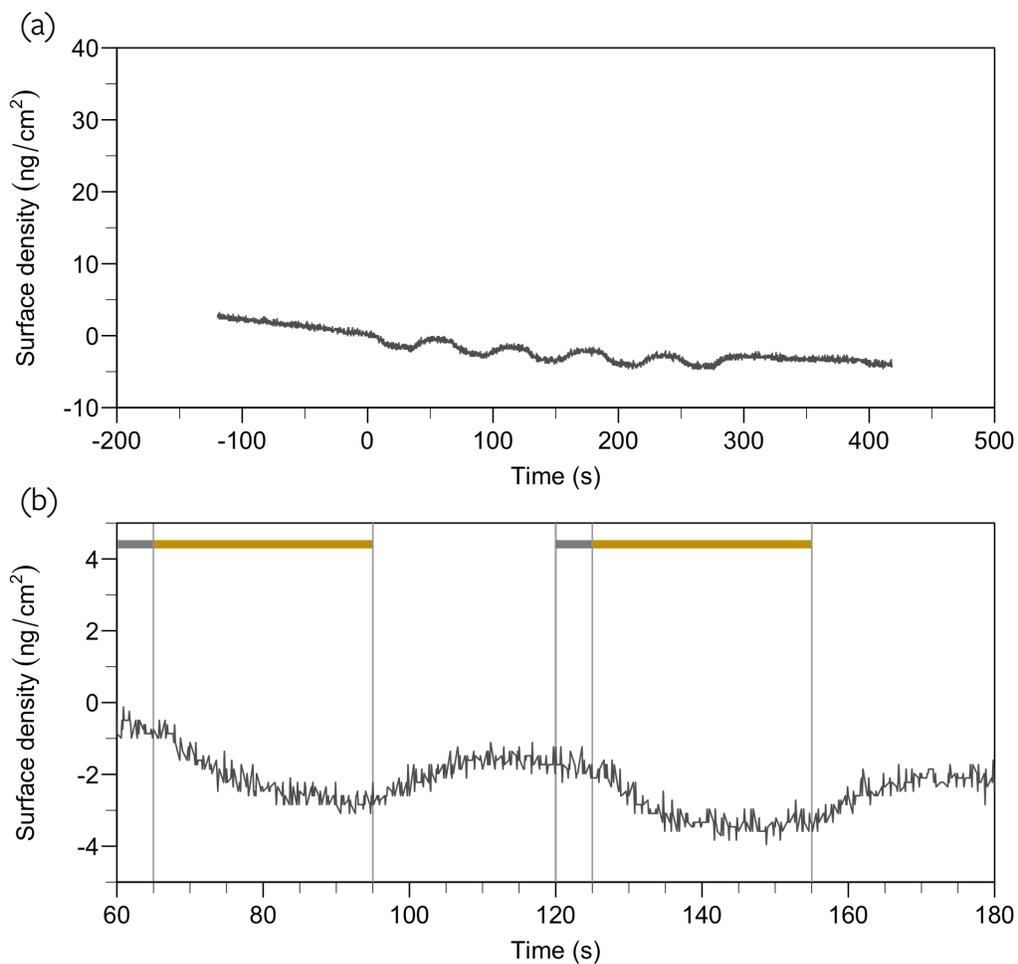


Figure 86: Argon plasma followed by hydrogen plasma on silicon oxide, (a) five cycles, (b) cycles two and three

A copper-coated crystal was also exposed to repeated doses (5 s) of argon plasma and doses (30 s) of hydrogen plasma, and no change in surface density was observed (Figure 87). This indicated that the copper surface was not significantly oxidized before the hydrogen plasma treatment.

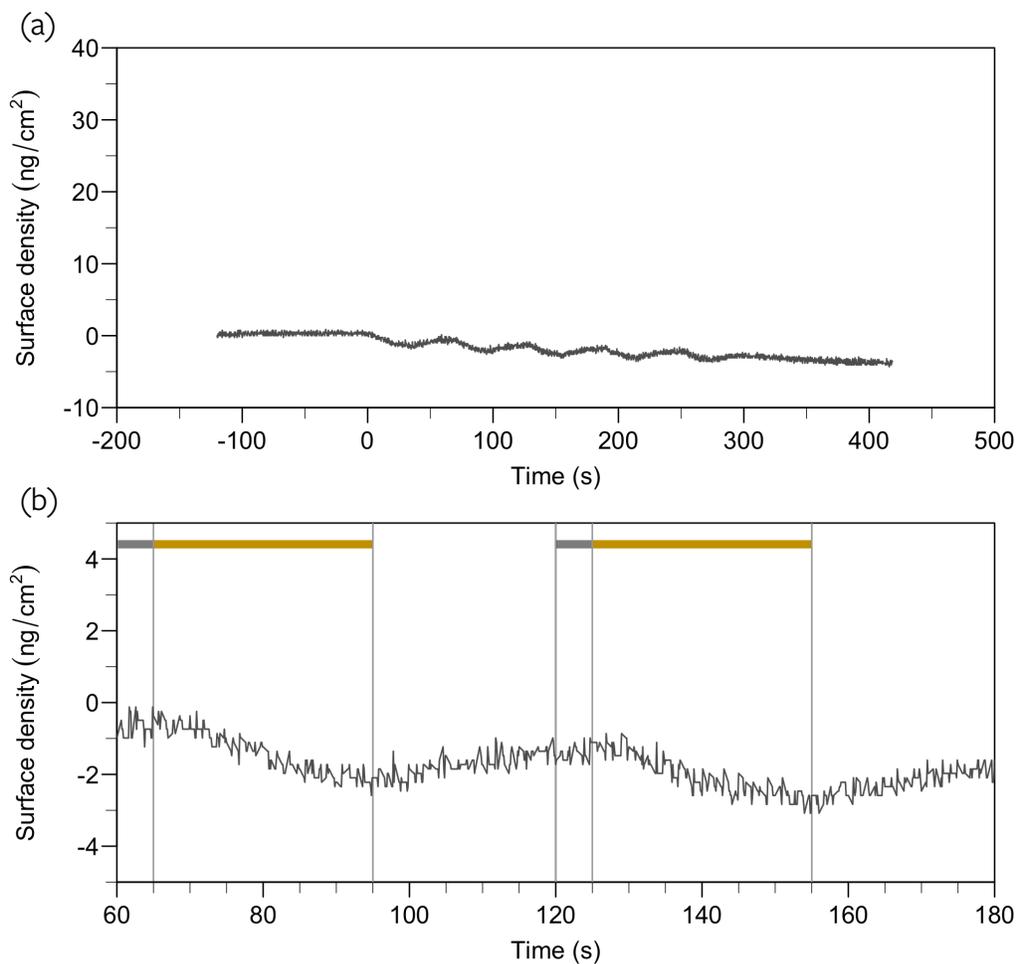


Figure 87: Argon plasma followed by hydrogen plasma on copper, (a) five cycles, (b) cycles two and three

Oxidizing agent: oxygen plasma

Similar to the hydrogen plasma exposures, the oxygen plasma exposures were immediately preceded by argon plasma. After repeated doses (5 s) of argon plasma and doses (10 s) of oxygen plasma on a silicon oxide–gold-coated crystal, there was a slight increase in surface density, suggesting that some oxidation of the surface occurred

(Figure 88). During deposition of the silicon oxide, it is possible that some silicon atoms in the surface layer may have remained hydrogen terminated. Once exposed to an oxidizing agent, the silicon-hydrogen bonds were readily oxidized to increase the surface concentration of hydroxyl group terminations.

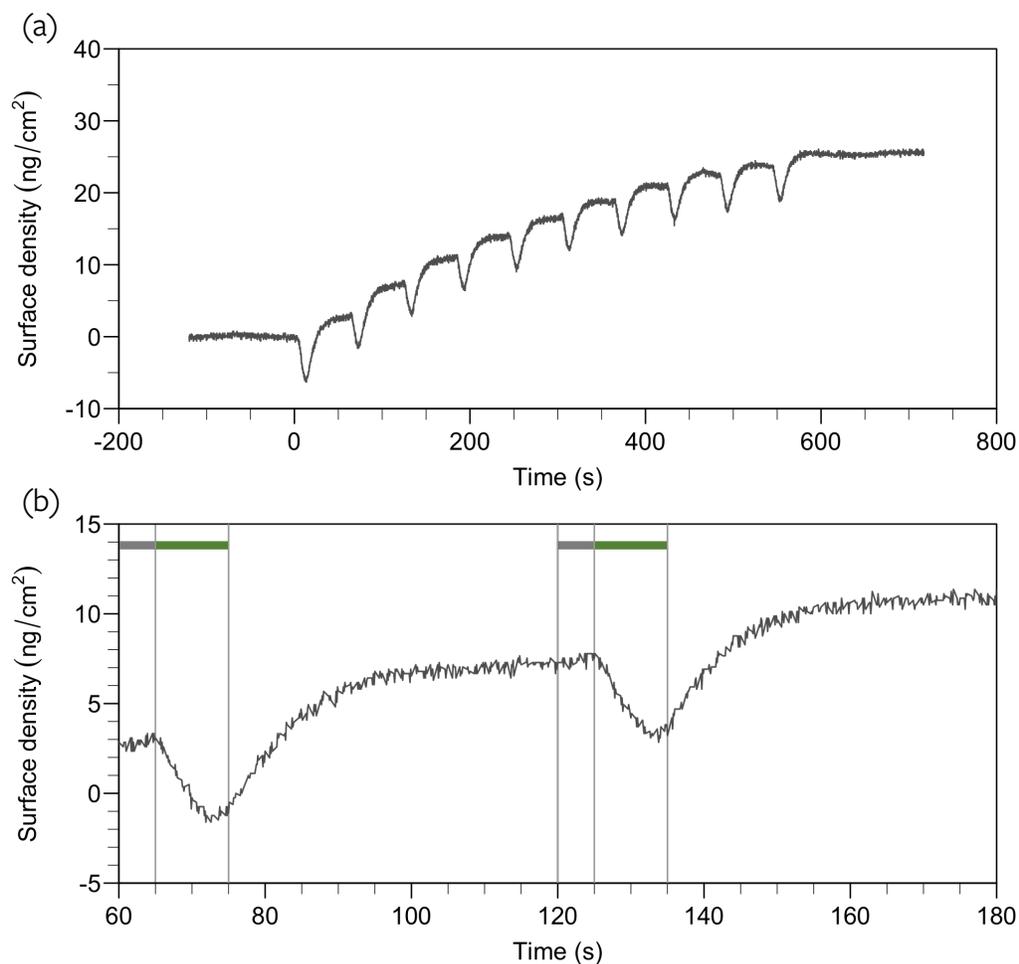


Figure 88: Argon plasma followed by oxygen plasma on silicon oxide, (a) ten cycles, (b) cycles two and three

As mentioned with respect to water as an oxidizing agent, the composition of the non-growth surface should not be modified by the co-reactant during an area-selective ALD

experiment. A copper-coated crystal was exposed to hydrogen plasma to reduce the surface, then exposed to repeated doses (5 s) of argon plasma and doses (5 s) of oxygen plasma. Despite the presence of the oxidizing agent, the surface density did not increase (Figure 89).

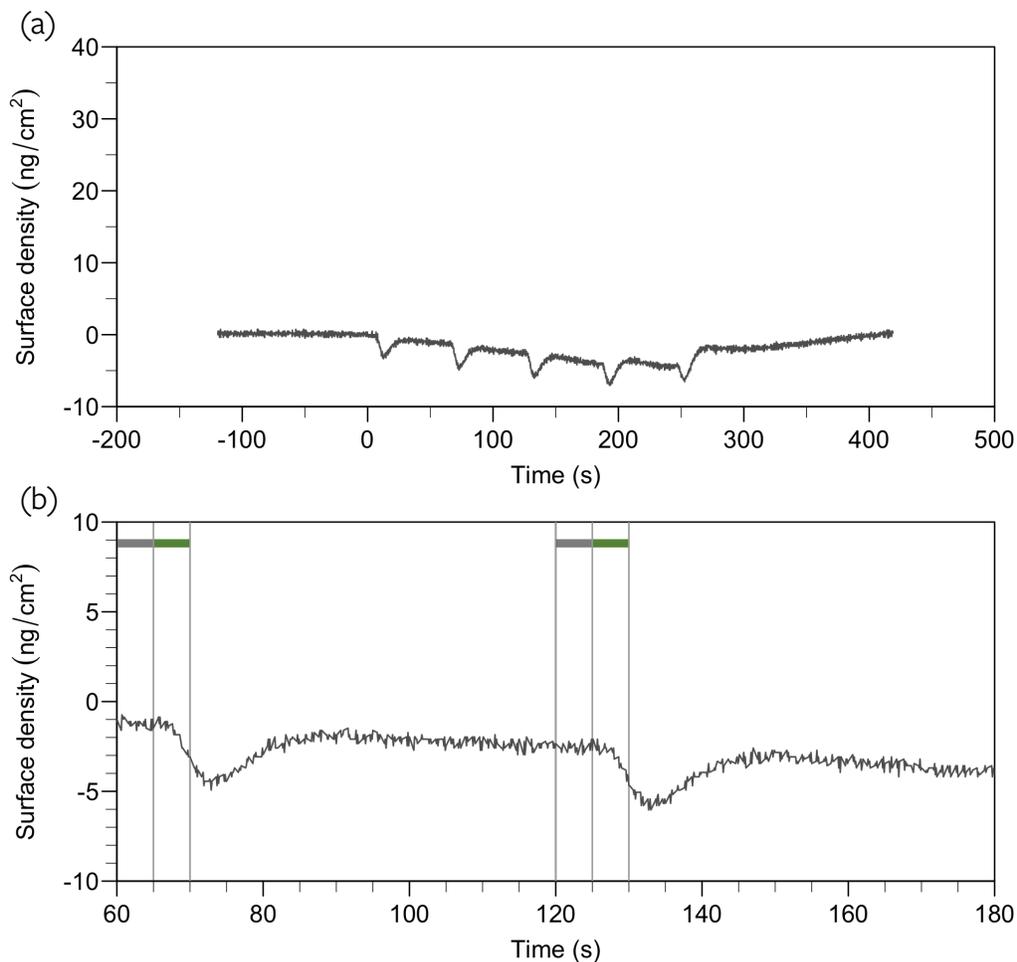


Figure 89: Argon plasma followed by oxygen plasma on reduced copper, (a) five cycles, (b) cycles two and three

To investigate this behavior, the oxygen plasma dose was increased (30 s) and alternately cycled with hydrogen plasma (30 s), with a purge (25 s) of argon gas between each plasma

dose, on the same copper-coated crystal (Figure 90). Several conclusions could be formed from this experiment. First, the increased dose of oxygen plasma caused a significant increase in surface density, indicating formation of surface oxide that did not occur during the shorter exposure experiment. Second, thirty seconds of hydrogen plasma is insufficient for countering the oxidation due to thirty seconds of oxygen plasma. This result could have been anticipated, due to the different concentrations of process gas flowing through the plasma generator (100 % oxygen compared to 3 % hydrogen balance argon). Third, it was later determined that five seconds of oxygen plasma was sufficient for deposition of silicon oxide when alternately cycled with DSBAS in an ALD experiment. Therefore, the experimental dose did not affect the copper surface and did not need to be offset by adding a hydrogen plasma step to the ALD cycle.

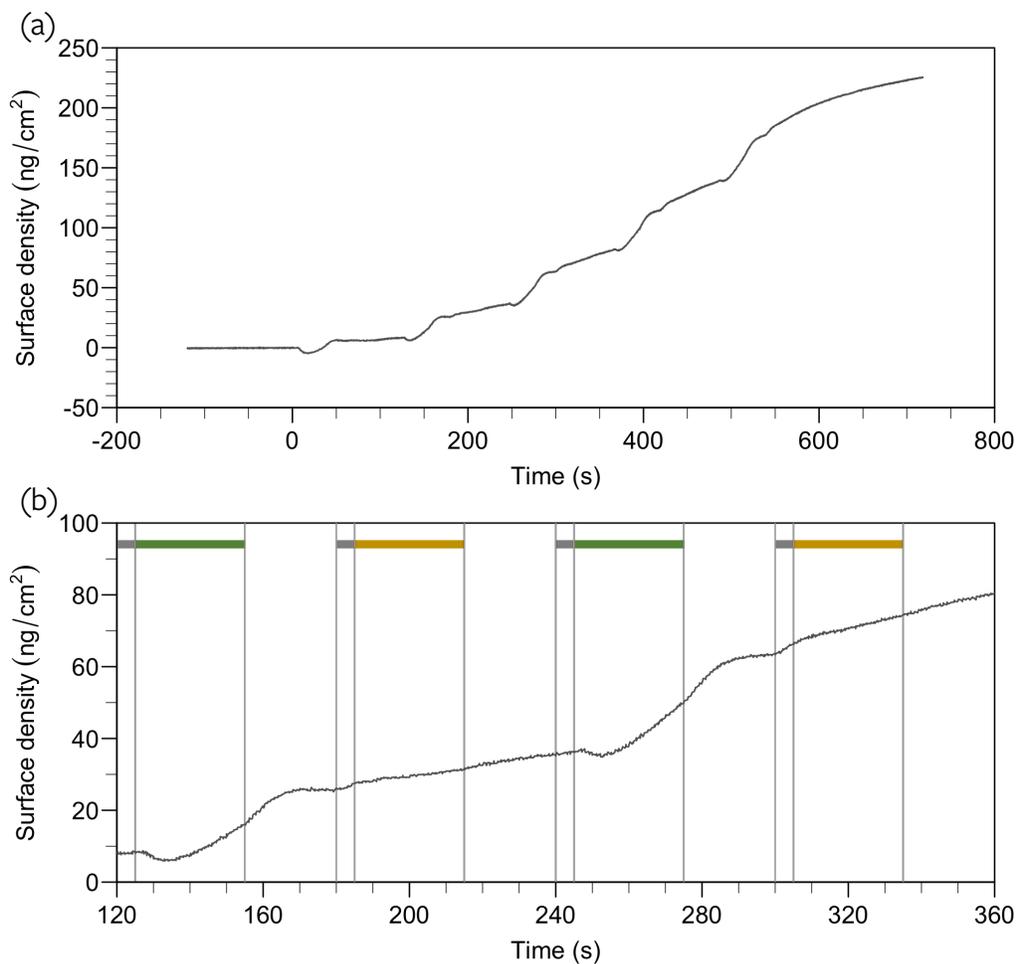


Figure 90: Alternating argon plasma | oxygen plasma and argon plasma | hydrogen plasma on copper, (a) five cycles, (b) cycles two and three

Co-adsorbate: 4-octyne

Previous work demonstrated successful blocking of growth of zirconium oxide on copper using 4-octyne as a co-adsorbate.⁴⁶ However, the results were obtained by CVD in a different vacuum chamber that was used to analyze the film thickness and composition at particular times during the experiment, but not continuously throughout, as is a

feature of using a QCM.⁷⁷ Therefore, it was of interest to study 4-octyne further using the QCM.

While the oxidizing co-reactant must not affect the non-growth surface, the co-adsorbate must not affect the growth surface. Repeated doses (50 s) of 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr) on an annealed silicon oxide–gold-coated crystal resulted in limited adsorption (Figure 91).

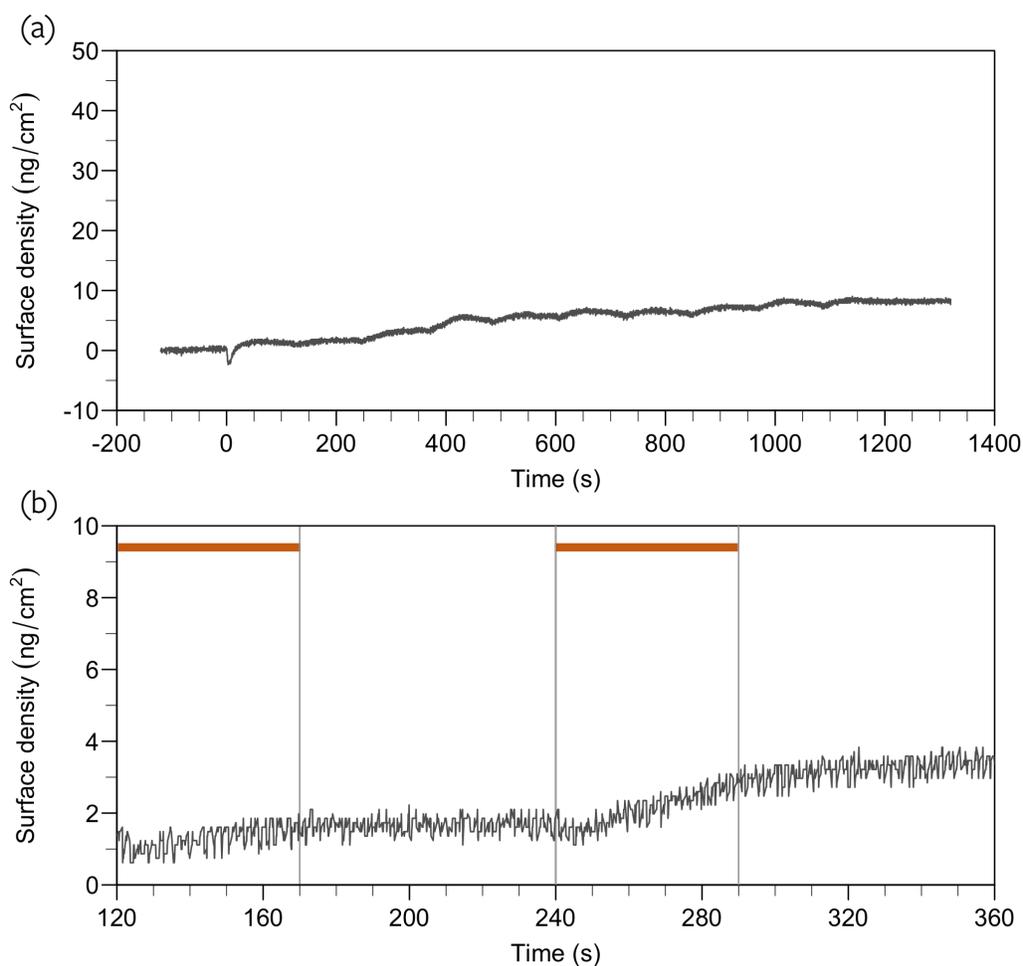


Figure 91: 4-octyne on silicon oxide, (a) ten cycles, (b) cycles two and three

A copper-coated crystal was annealed, then was exposed to repeated doses (50 s) of 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr). The 4-octyne appeared to saturate the surface after approximately fifteen seconds, but, when the dose was terminated, it appeared to immediately desorb from the substrate (Figure 92). There was some mass remaining after the doses, which supported one conclusion from the recent paper published by our group about use of 4-octyne as a co-adsorbate, which was that 4-octyne chemisorption on copper was reversible, but a carbon-containing contamination layer might remain on the surface.⁴⁶

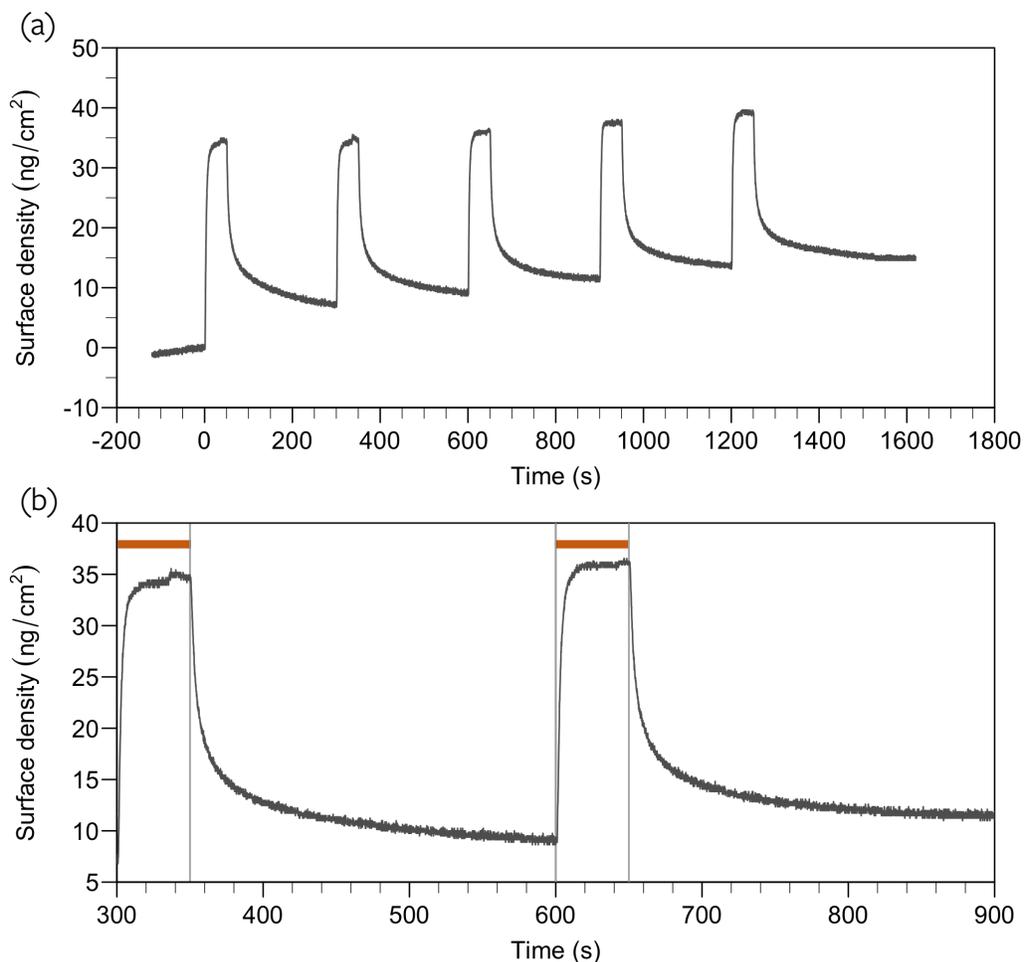


Figure 92: 4-octyne on reduced copper, (a) five cycles, (b) cycles two and three

It was important that no reaction occurred between the co-adsorbate and the co-reactant, to prevent any undesired deposition in the event of incomplete purge of either reactant or unreacted molecules on the substrate surface. After the 4-octyne exposure shown in Figure 92, the same crystal was exposed to alternating doses (50 s) of 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr) and doses (3 s) of water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) for five cycles (Figure 93). The behavior of this experiment closely resembled that of the experiment with only 4-octyne, and the

frequency change due to the water dose was negligible, which suggested there was no reaction between 4-octyne and water.

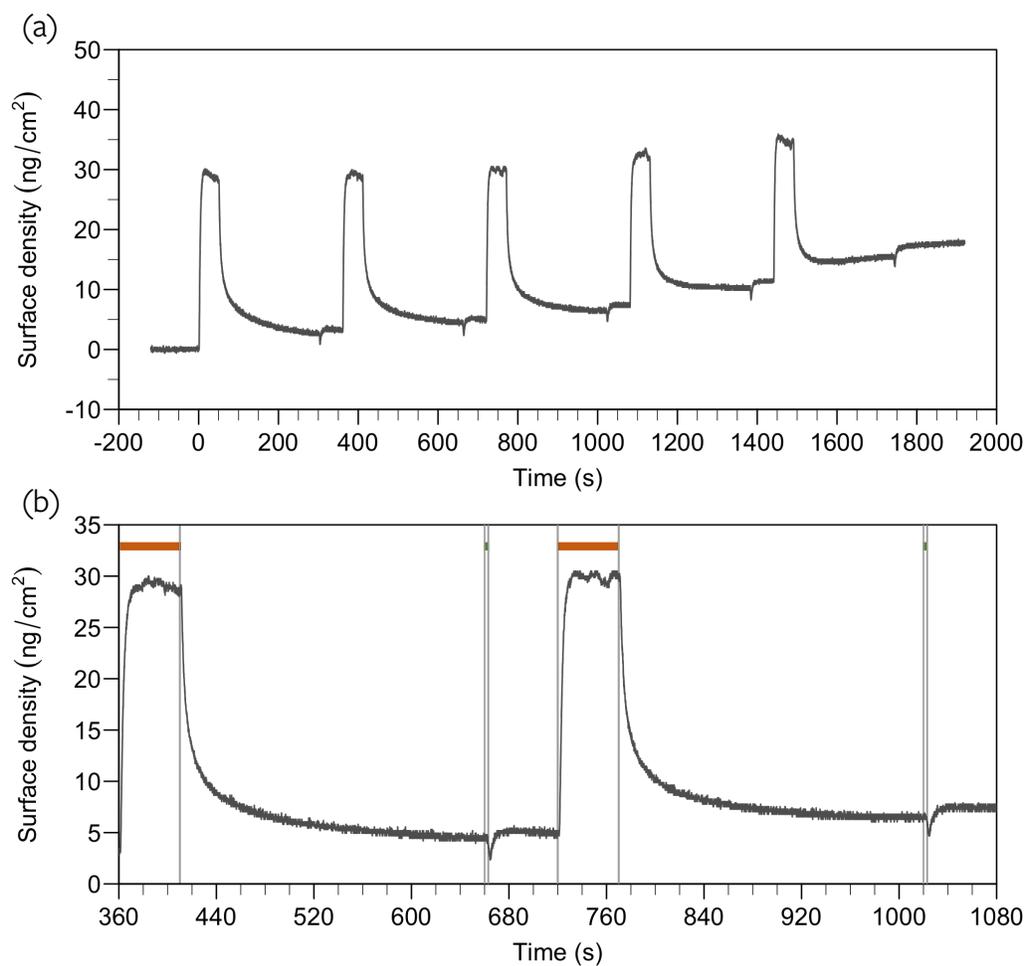


Figure 93: Alternating 4-octyne and water on copper, (a) five cycles, (b) cycles two and three

Pressure rise study

The partial pressure of a reactant is an important variable in a deposition experiment. In a pressure-controlled experiment, the pressure was fixed and the throttle valve position was variable. When reactants were introduced, the pressure would have increased, but the throttle valve opened to maintain the pressure at the setpoint. By fixing the throttle valve position and allowing the pressure to be variable, the pressure rise due to introduction of a reactant could be measured. Pressure control was used to stabilize the valve position at the desired pressure setpoint. The valve position was then recorded over time (Figure 94a) and the average value was used for a valve control setpoint (Figure 94b).

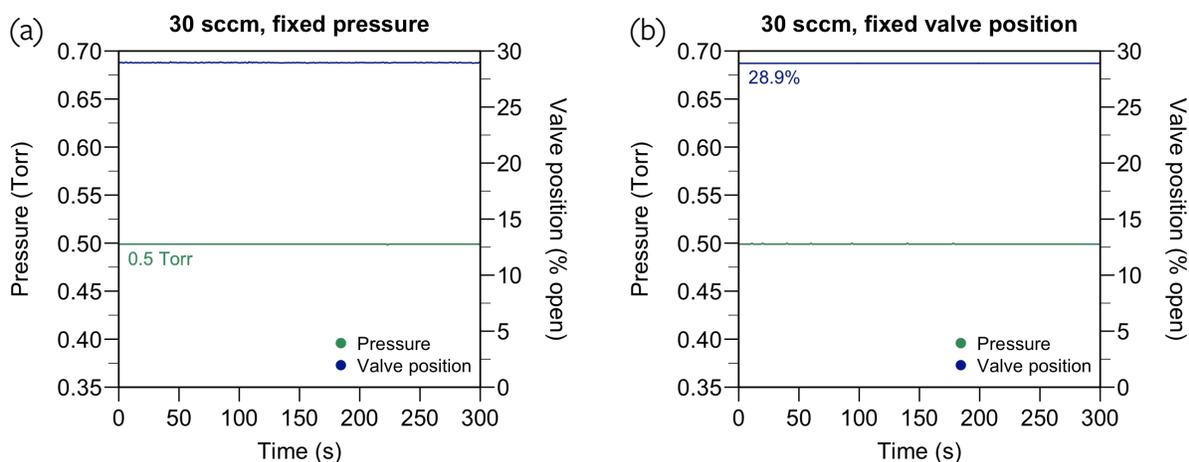


Figure 94: Pressure and valve position behavior, (a) with pressure fixed, (b) with valve position fixed

It was also of interest to determine whether the partial pressure of the reactant could be varied by manipulating the carrier gas flow rate through the bubbler. For consistency, a total gas flow rate of 30 sccm through panels two, three, and four was used for all experiments. Flow rates of 2, 4, 8, and 10 sccm were used to repeatedly dose TEMAZ,

water, and 4-octyne to the reactor while recording the pressure. For example, while 2 sccm was flowing through the panel housing TEMAZ, 14 sccm was flowing through each of the other two panels. The order in which the flow conditions were studied was randomized and there was a sufficient purge between experiments to prevent hysteretic effects.

With the throttle valve controlled at 28.9 % open, TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) was dosed five times (30 s). Figure 95a shows the pressure profile for a carrier gas flow rate of 2 sccm, and Figure 95b shows the pressure profile for a carrier gas flow rate of 10 sccm. The decrease in pressure between sixty and 150 seconds was due to diversion of flow through the panel housing TEMAZ, from the reactor to the pump. For chemicals with high vapor pressure, the diversion was necessary to clear the headspace of the bubbler to the pump before sending it to the reactor, to ensure a consistent dose of chemical throughout the experiment. While TEMAZ does not have a high vapor pressure, and the headspace of the bubbler was not cleared to the pump, the diversion was still performed for comparison of flow dynamics between the three panels.

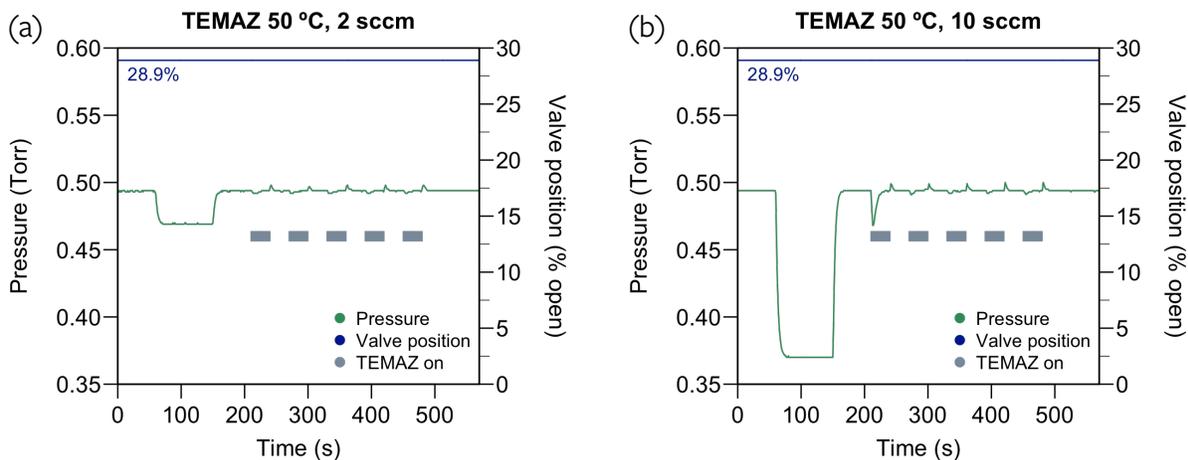


Figure 95: Pressure profile of TEMAZ doses, (a) 2 sccm carrier gas flow rate, (b) 10 sccm carrier gas flow rate

The pressure profile for each of the four carrier gas flow rate conditions was normalized to a pressure of 0.50 Torr at time 0 s and they were plotted together for comparison (Figure 96a). The pressure throughout each TEMAZ dose was averaged, the five average pressures were averaged, and the pressure difference between this value and 0.50 Torr was plotted (Figure 96b). This experiment was repeated for five doses (15 s) of water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (Figure 97), and five doses (50 s) of 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr) (Figure 98). For all experiments, the pressure profile was similar throughout the five successive doses, indicating that the system could deliver consistent amounts of each reactant. There was no clear trend between carrier gas flow rate and pressure increase, which suggested that varying the carrier gas flow rate was not a useful method for controlling the partial pressure. Additionally, it was concluded that this type of pressure test was not practical for reactants with low vapor pressure, such as TEMAZ, because the pressure rise was very small.

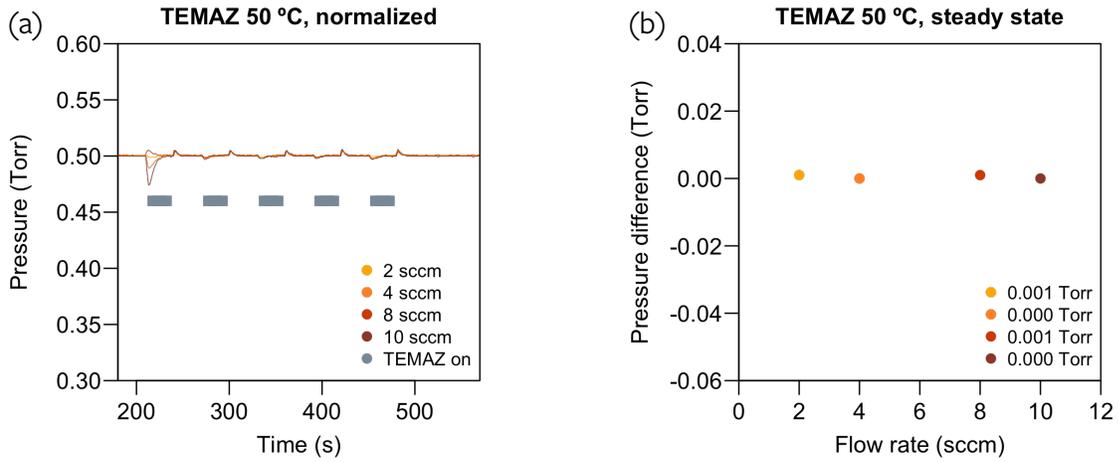


Figure 96: (a) Pressure profile of TEMAZ doses with different carrier gas flow rates, (b) average pressure rise due to TEMAZ doses for different carrier gas flow rates

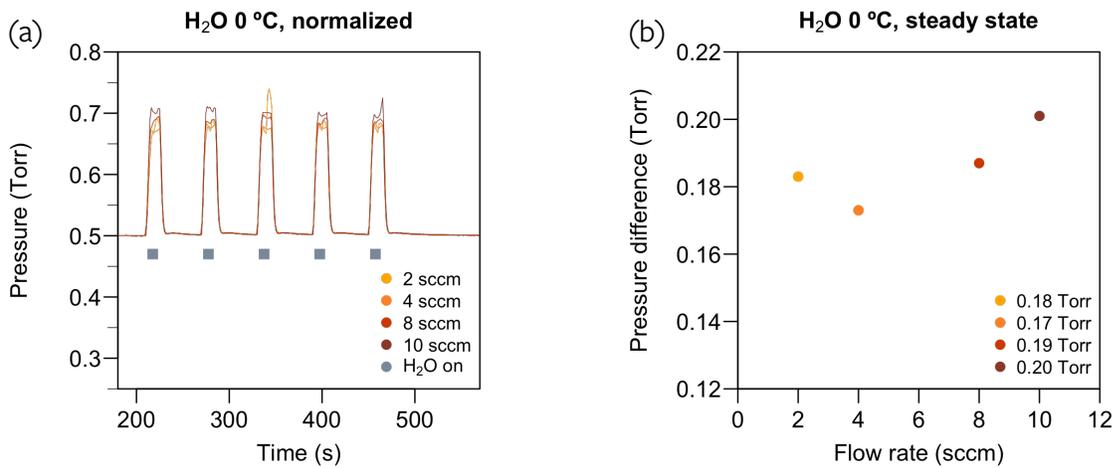


Figure 97: (a) Pressure profile of water doses with different carrier gas flow rates, (b) average pressure rise due to water doses for different carrier gas flow rates

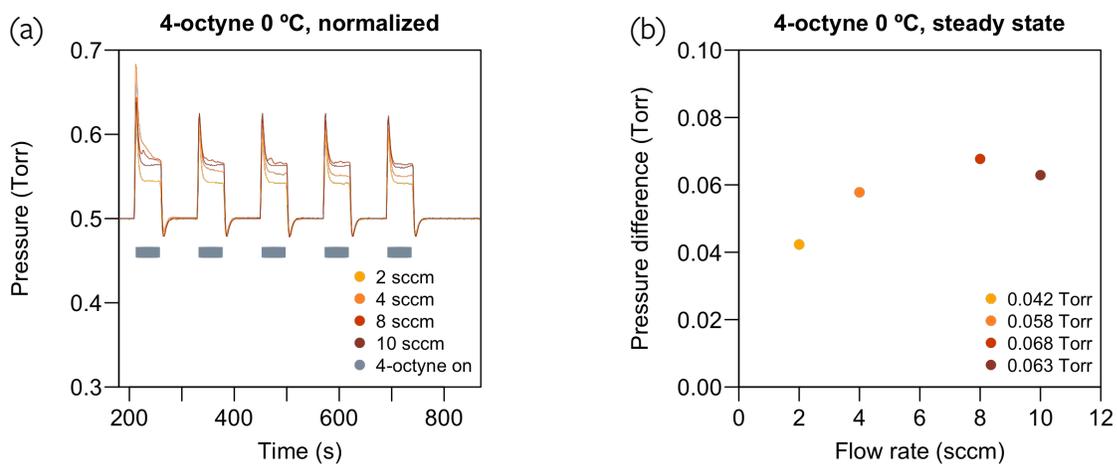


Figure 98: (a) Pressure profile of 4-octyne doses with different carrier gas flow rates, (b) average pressure rise due to 4-octyne doses for different carrier gas flow rates

Pristine ALD

Trimethylaluminum | water

As mentioned previously, the first ALD system studied in the new chamber was the reaction between trimethylaluminum and water to form an aluminum oxide thin film. QCM data from fifteen cycles of trimethylaluminum (ampoule temperature 0 °C, vapor pressure ~2.6 Torr) (1 s) | argon purge (59 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (1 s) | argon purge (89 s) ALD on an aluminum oxide substrate (~50 Å aluminum oxide on a silicon oxide–gold-coated crystal) at a temperature of 120 °C and a pressure of 1.5 Torr followed the expected linear increase in thickness with respect to time, or number of cycles (Figure 99). By zooming in on cycles ten and eleven, we could see thickness changes due to each reactant individually, and the characteristic step growth of ALD. The increase in thickness at the beginning of the cycle was due to adsorption of trimethylaluminum, and the second, smaller increase was due to replacement of methyl groups with hydroxyl groups on the adsorbed trimethylaluminum when water was introduced. However, the final thickness was greater than expected. This ALD cycling had a growth rate of ~3.2 Å/cycle, compared to the saturation growth rate of ~1.1 Å/cycle. It is possible that the high growth rate was due to underdosing of trimethylaluminum, which was found to lead to increased adsorption of water molecules in reactive surface sites not occupied by trimethylaluminum, causing parasitic reactions.⁷⁸

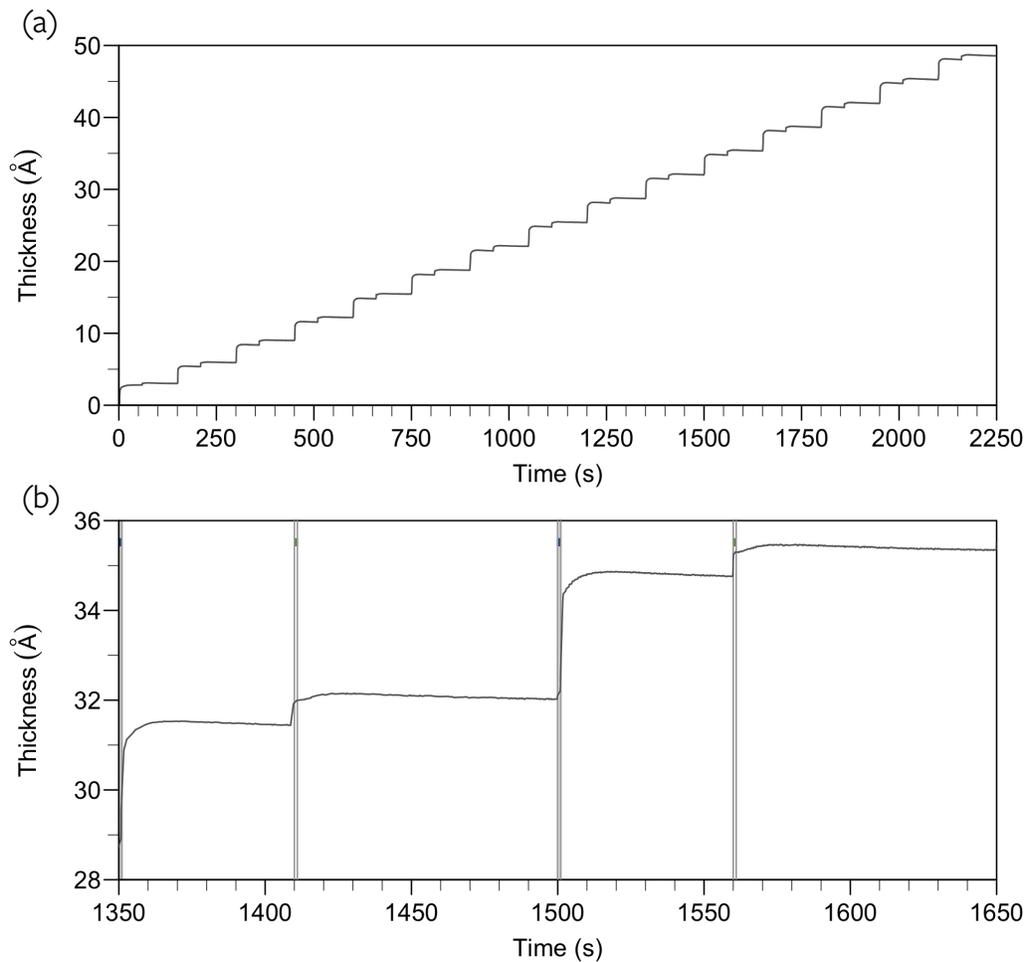


Figure 99: Trimethylaluminum | water ALD on aluminum oxide, (a) fifteen cycles, (b) cycles ten and eleven

Despite the high growth rate, the preliminary experiments with trimethylaluminum demonstrated that we could perform controlled deposition with the new chamber, and we began to investigate other ALD systems of interest.

DSBAS | oxygen plasma

An experiment was performed for thirty cycles of DSBAS (ampoule temperature 50 °C, vapor pressure ~12.6 Torr) (10 s) | argon purge (50 s) | argon plasma (5 s) | oxygen plasma (5 s) | argon purge (20 s) ALD on a silicon oxide substrate (~30 Å silicon oxide on a copper-coated crystal) at a temperature of 120 °C and a pressure of 5 Torr (Figure 100). The deposition increased linearly with a growth rate of ~0.75 Å/cycle. By zooming in on cycles fifteen and sixteen, it was apparent that the combination of these reactants behaved much differently than trimethylaluminum and water. The increase in thickness due to the precursor, DSBAS, at the beginning of the cycle was small, and the thickness increase due to the co-reactant, oxygen plasma, was larger. This behavior could be understood by reviewing the chemical reactions that occurred during the ALD experiment. DSBAS is a substituted mono-aminosilane, so it is reasonable that the amine ligand was exchanged during adsorption on the substrate due to steric effects, creating a hydrogen-terminated silicon surface layer. When the oxygen plasma was introduced, the silicon-hydrogen bonds were oxidized, causing an increase in surface mass density that was more than twice the increase due to DSBAS.

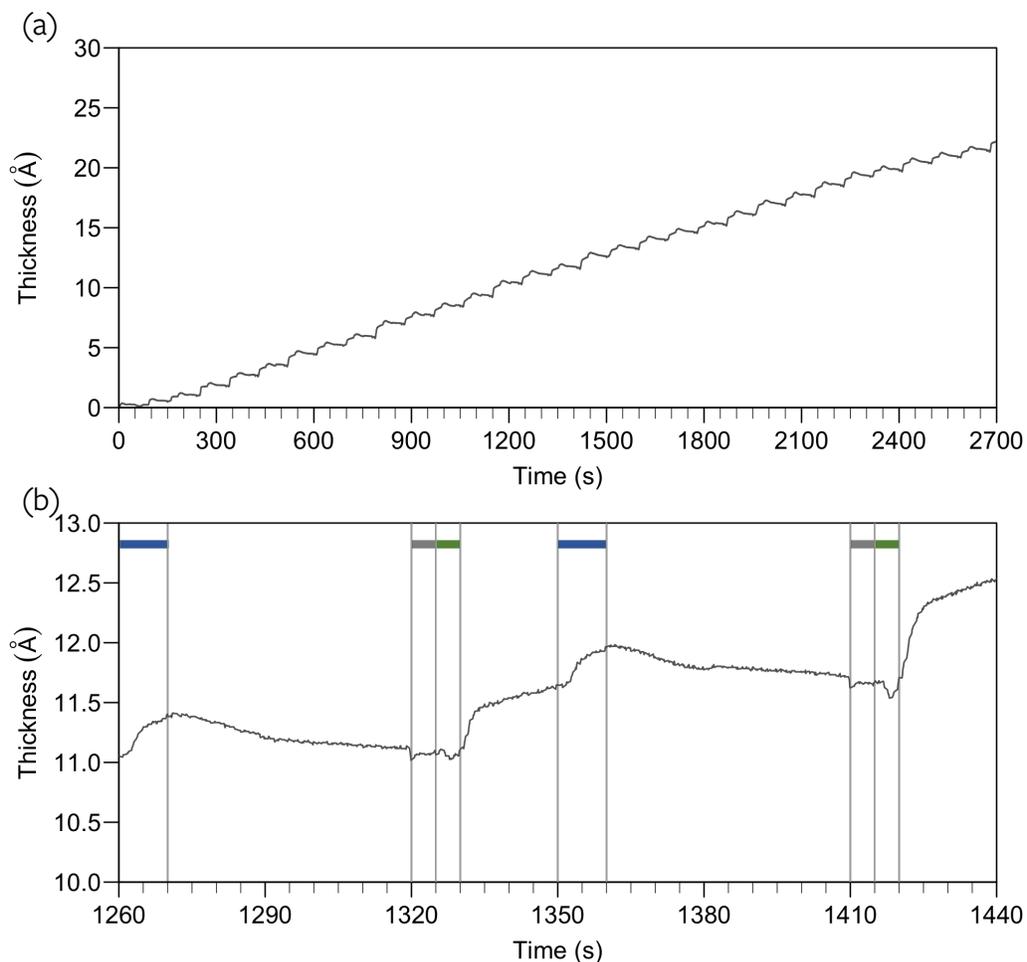


Figure 100: DSBAS | oxygen plasma ALD on silicon oxide, (a) thirty cycles, (b) cycles fifteen and sixteen

The experiment was repeated at a temperature of 120 °C and a pressure of 1.5 Torr on a copper-coated crystal after the crystal was reduced with hydrogen plasma, and the growth rate was ~ 0.95 Å/cycle (Figure 101). The large increase in thickness near the beginning of the experiment was due to the first oxygen plasma dose, presumably oxidizing the copper surface, which contradicted the results of the individual reactant study for oxygen plasma. One explanation for this discrepancy is a difference in surface preparation.⁵² While each copper-coated crystal was treated with hydrogen plasma

before the experiment containing oxygen plasma was performed, the crystals had been manufactured at different times, and, in this case, the copper surface was exposed to DSBAS before introduction of the oxygen plasma occurred. Examining individual cycles showed that there was an apparent decrease in thickness after the DSBAS dose, and that the oxygen plasma continued to have a greater impact on the copper substrate throughout the experiment than was observed during the equivalent experiment on silicon oxide. Despite the apparent decrease in thickness after the DSBAS dose, the growth per cycle was consistent, indicating that silicon oxide was being deposited.

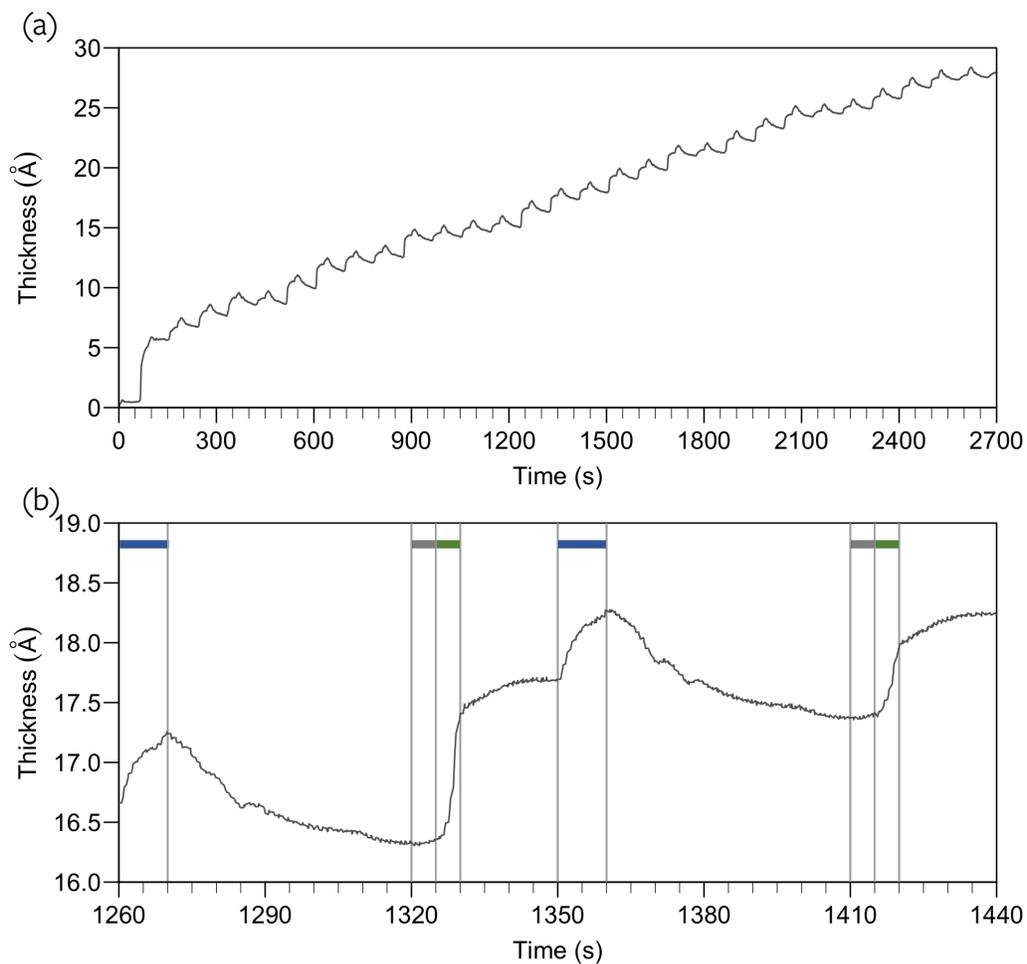


Figure 101: DSBAS | oxygen plasma ALD on copper, (a) thirty cycles, (b) cycles fifteen and sixteen

From these experiments, we concluded that we had a reproducible process for depositing silicon oxide by plasma-enhanced ALD, which allowed us to produce our own dielectric starting substrates for study of area-selective deposition.

TEMAZ | water

My area-selective ALD studies were based on the TEMAZ and water ALD system. Before studying deposition with a co-adsorbate, we needed to understand the pristine process. We started with ten cycles of TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | argon purge (15 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (72 s) at a temperature of 120 °C and a pressure of 0.5 Torr on an annealed silicon oxide–gold-coated crystal. The result was a very small growth rate of ~0.08 Å/cycle, but there was clearly some impact of the reactants during each dose (Figure 102). Looking at individual cycles, the initial, sloping increase in thickness was due to adsorption of TEMAZ, and the subsequent deviation in thickness was due to the reaction of adsorbed TEMAZ with water. We speculated that the residence time of the TEMAZ was too small, and that was preventing saturation of TEMAZ on the surface. To test this idea, we increased the pressure to 1.5 Torr and repeated the experiment on the same crystal (Figure 103). The growth rate increased to ~1.1 Å/cycle and the adsorption of TEMAZ was significantly larger. To further understand the relationship between growth rate and pressure, and to exclude any hysteretic effects, we then decreased the pressure to 1.0 Torr and repeated the experiment (Figure 104). The growth rate decreased to ~0.78 Å/cycle and the adsorption of TEMAZ was noticeably smaller. To complete the study, we repeated the experiment at 0.5 Torr, which resulted in a growth rate of ~0.08 Å/cycle that was consistent with the first experiment.

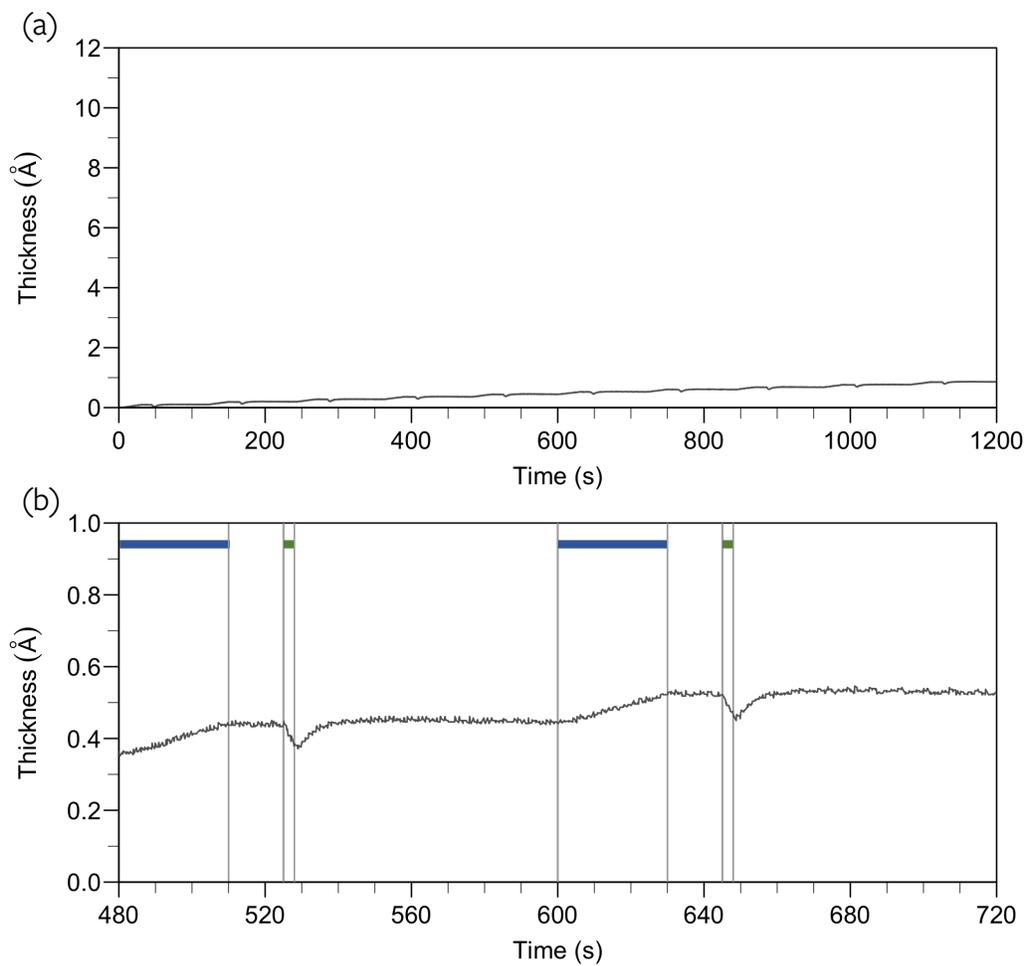


Figure 102: TEMAZ | water ALD on silicon oxide during pressure study (0.5 Torr), (a) ten cycles, (b) cycles five and six

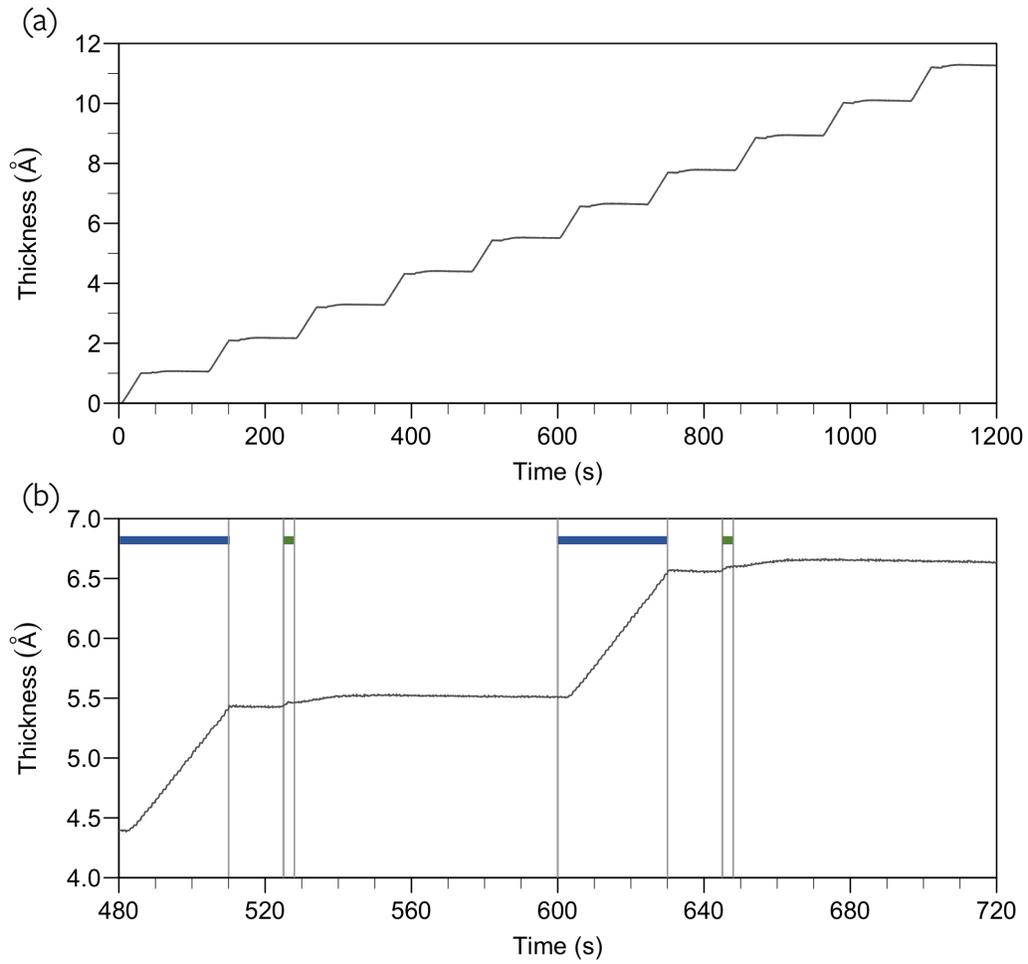


Figure 103: TEMAZ | water ALD on silicon oxide during pressure study (1.5 Torr), (a) ten cycles, (b) cycles five and six

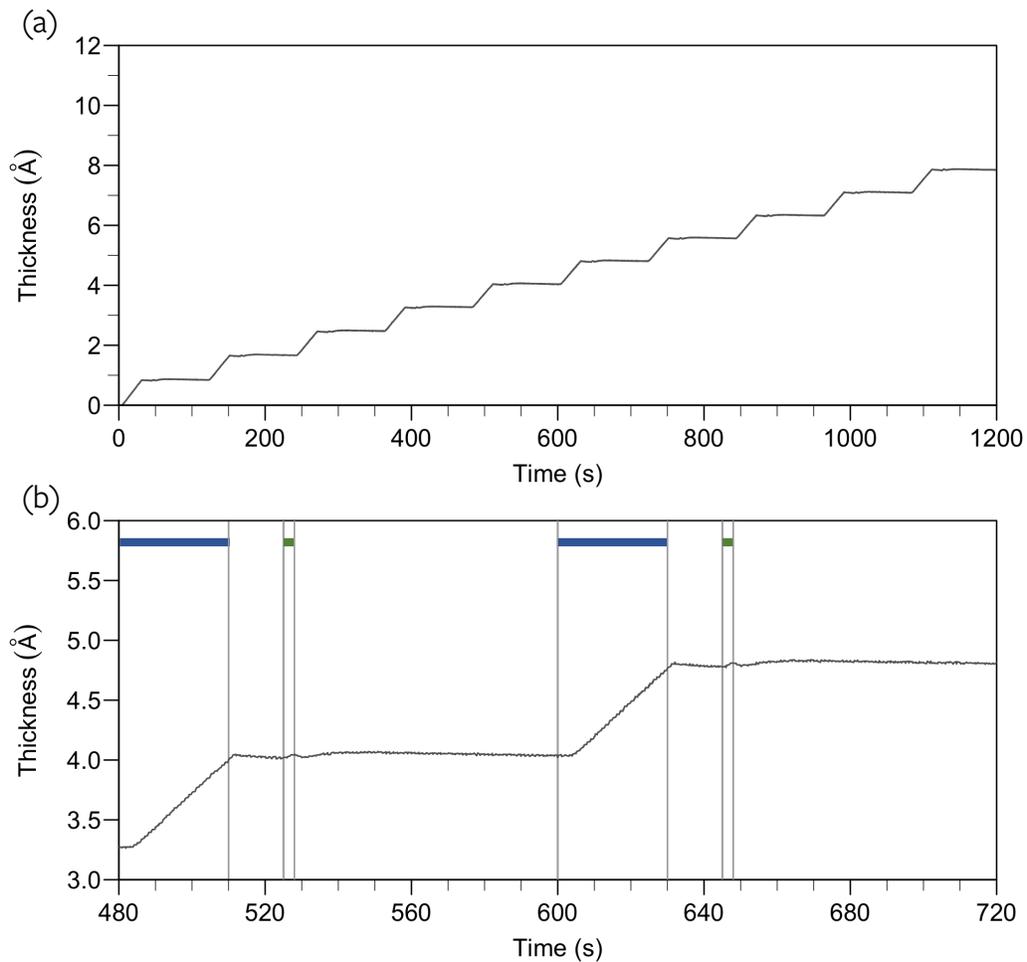


Figure 104: TEMAZ | water ALD on silicon oxide during pressure study (1.0 Torr), (a) ten cycles, (b) cycles five and six

From this study, we concluded that pressure was an important variable in the ALD process, but that there was not a linear relationship between pressure and growth rate, despite the linear relationship between pressure and residence time. The reference pristine experiment became TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | argon purge (15 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (72 s) at a temperature of 120 °C and a pressure of 1.5 Torr.

Impact of reactant delivery method

Reactant feedthrough version one

The initial TEMAZ | water ALD experiments were completed using the first version of the reactant feedthrough (Figure 105). In that configuration, all three panels containing ampoules met at one 1/4 in VCR cross and were mixed in 1/4 in tubing for a length of 2.83 in before entering the 1.75 in OD arm of the reactor tube. Refer to Figure 36 and Figure 60 for additional perspectives of the feedthrough position.

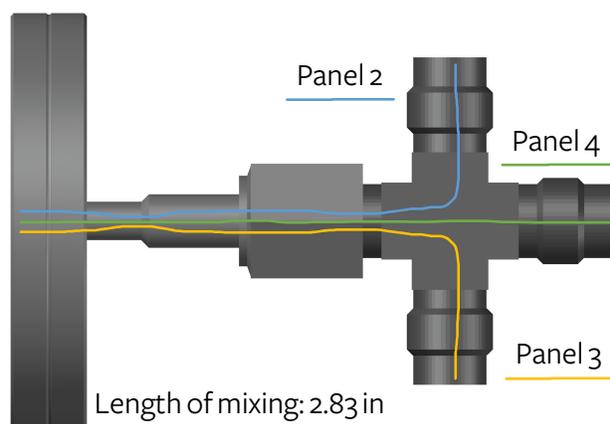


Figure 105: Reactant feedthrough version one

TEMAZ | water

The reference pristine experiment, TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | argon purge (15 s) | water (ampoule temperature 0 °C, vapor pressure

~4.5 Torr) (3 s) | argon purge (72 s) at a temperature of 120 °C and a pressure of 1.5 Torr, was performed on an annealed silicon oxide–gold-coated crystal, and the growth rate was ~0.85 Å/cycle over thirty cycles (Figure 106). This growth rate was smaller than that for the experiment at 1.5 Torr during the pressure study, which again suggested that surface preparation or another unexamined factor could affect the growth dynamics. The same experiment on an annealed copper-coated crystal yielded an almost identical result, with a growth rate of ~0.83 Å/cycle over thirty cycles (Figure 107).

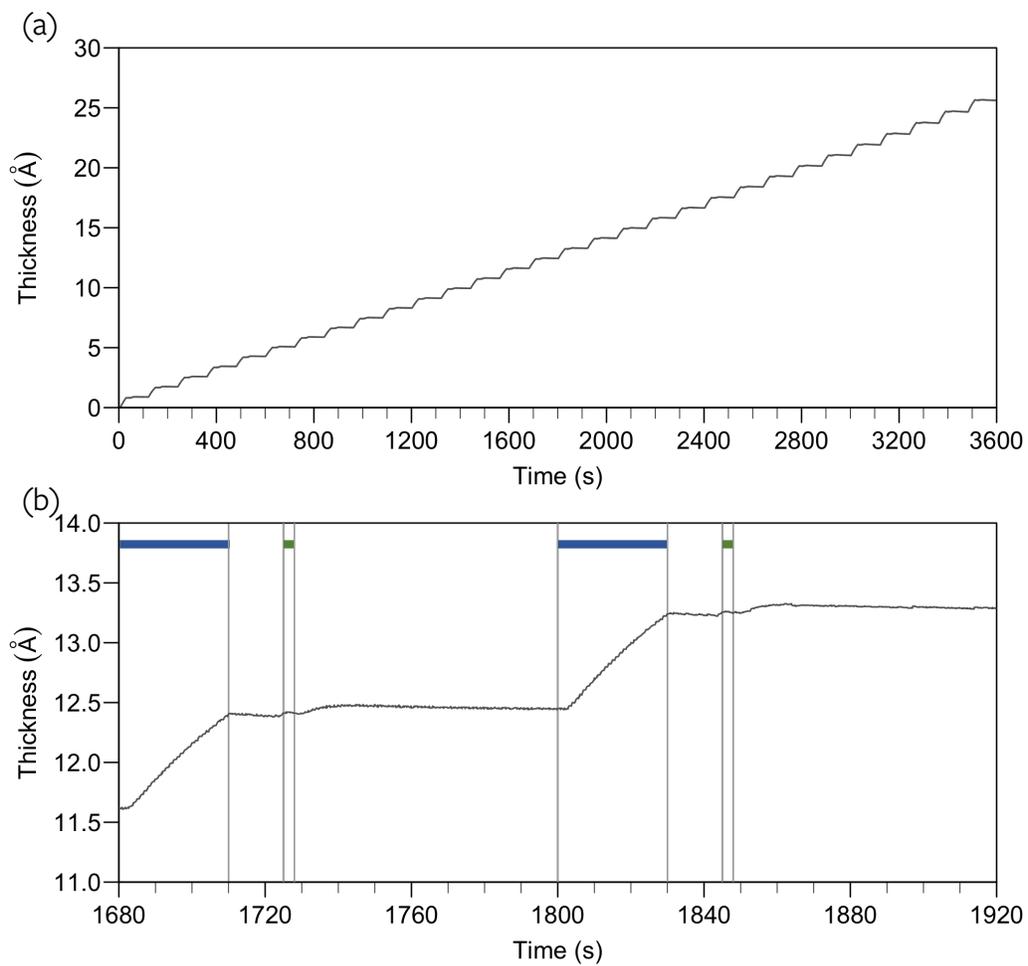


Figure 106: TEMAZ | water ALD on silicon oxide, (a) thirty cycles, (b) cycles fifteen and sixteen

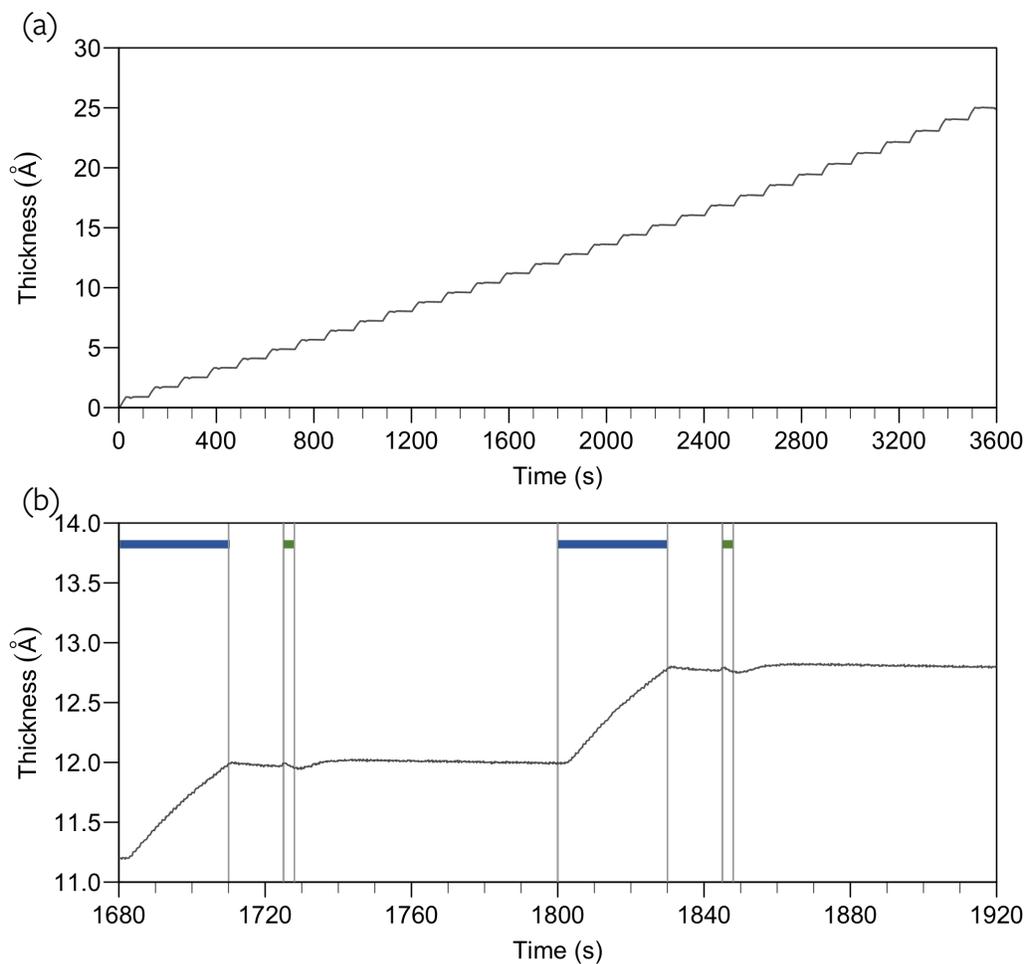


Figure 107: TEMAZ | water ALD on copper, (a) thirty cycles, (b) cycles fifteen and sixteen

TEMAZ | water with 4-octyne

The previous work determined that 4-octyne chemisorption on copper was reversible, and that it was necessary to dose the 4-octyne with the TEMAZ to obtain a blocking effect during a CVD experiment.⁴⁶ The individual reactant experiments with 4-octyne using the QCM also showed reversible adsorption on copper, which suggested that co-dosing 4-octyne and TEMAZ was necessary during an ALD experiment in the new chamber as

well. To investigate this, we performed an experiment with a pre-dose of 4-octyne and an inert gas purge before the TEMAZ dose. Thirty cycles of 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr) (15 s) | argon purge (15s) | TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | argon purge (15 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (42 s) were completed at a temperature of 120 °C and a pressure of 1.5 Torr on an annealed copper-coated crystal. As anticipated, growth was observed, and the growth rate was ~1.1 Å/cycle (Figure 108).

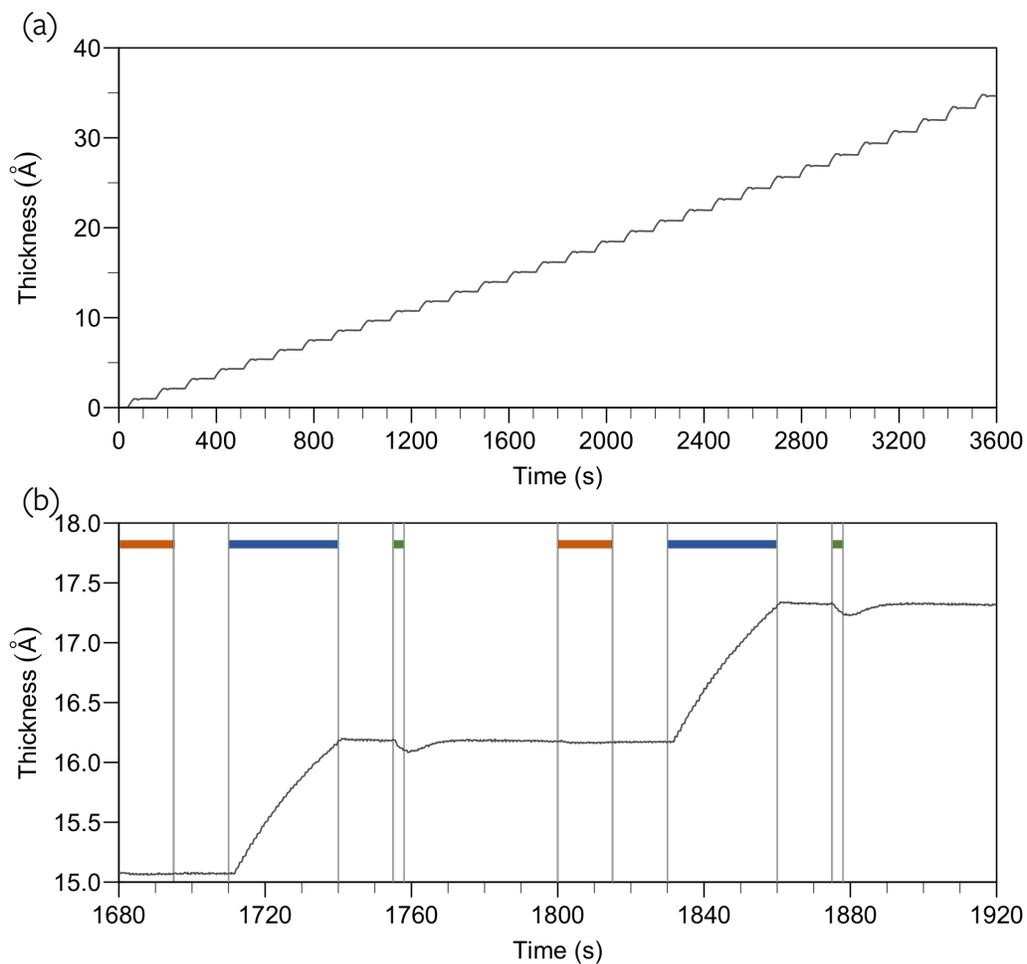


Figure 108: 4-octyne | TEMAZ | water ALD on copper, (a) thirty cycles, (b) cycles fifteen and sixteen

The reference pristine ALD sequence was modified so 4-octyne was dosed before, during, and after TEMAZ, with an inert gas purge before introduction of the co-reactant, which increased the sequence from four to six steps (Figure 109).

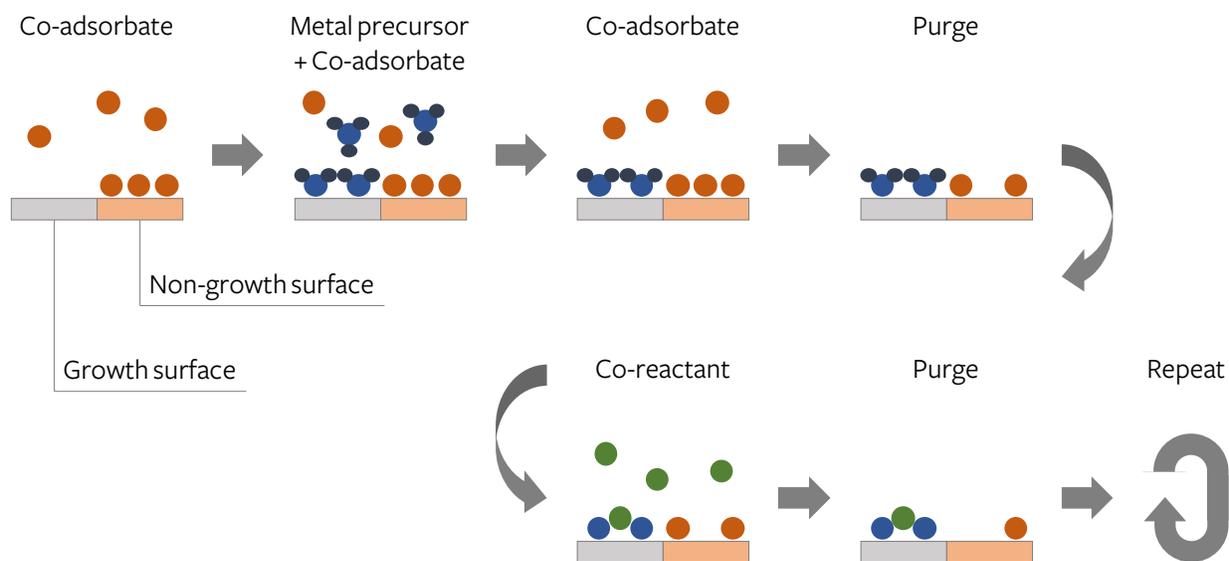


Figure 109: Depiction of a modified ALD cycle for use of a co-adsorbate

Thirty cycles of the sequence 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr) (15 s) | 4-octyne / TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | 4-octyne (5 s) | argon purge (10 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (57 s) were performed on an annealed copper-coated crystal at a temperature of 120 °C and a pressure of 1.5 Torr, and almost no increase in thickness was observed (Figure 110). This result was consistent with the CVD results using the microreactor, which was encouraging for the use of 4-octyne as a co-adsorbate during ALD.⁴⁶

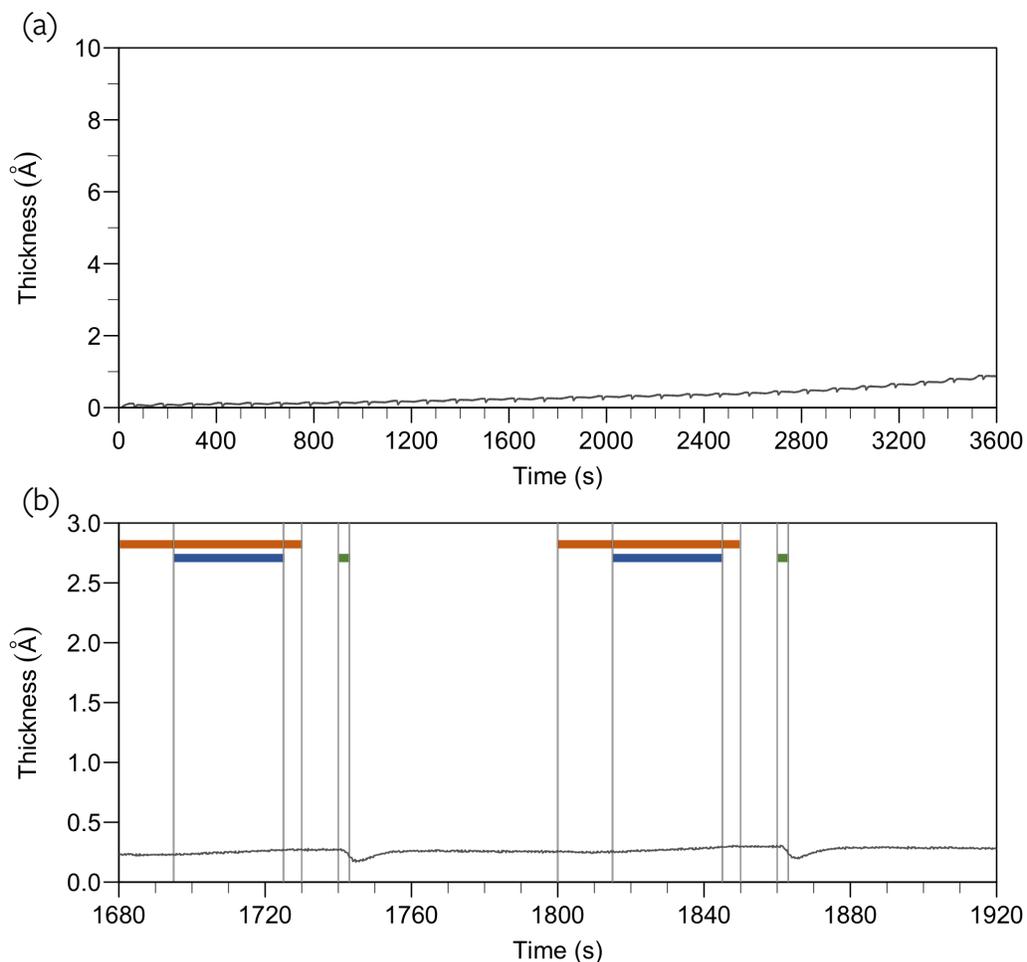


Figure 110: TEMAZ | water with 4-octyne during TEMAZ ALD on copper, (a) thirty cycles, (b) cycles fifteen and sixteen

Assuming that a Langmuir isotherm applied to the copper substrate, the surface coverage of 4-octyne was expected to decrease as the substrate temperature increased, so the experiment was repeated at 180 °C (Figure 111).^{46,79} While the thickness appeared to have decreased throughout the experiment, we did not believe that this was a physical change, but rather an artifact of using a crystal optimized for 120 °C at an increased temperature.⁵⁸ At the higher temperature, the introduction of water caused a more pronounced deviation in the QCM frequency, but there was no increase in thickness during the

TEMAZ dose. Because no growth occurred, we concluded that the 4-octyne coverage was not sufficiently diminished at 180 °C to allow TEMAZ to adsorb on the substrate. We increased the temperature further to 210 °C and 240 °C, but the frequency drift due to the increased departure from the optimization temperature was too significant to allow for proper analysis of the results.

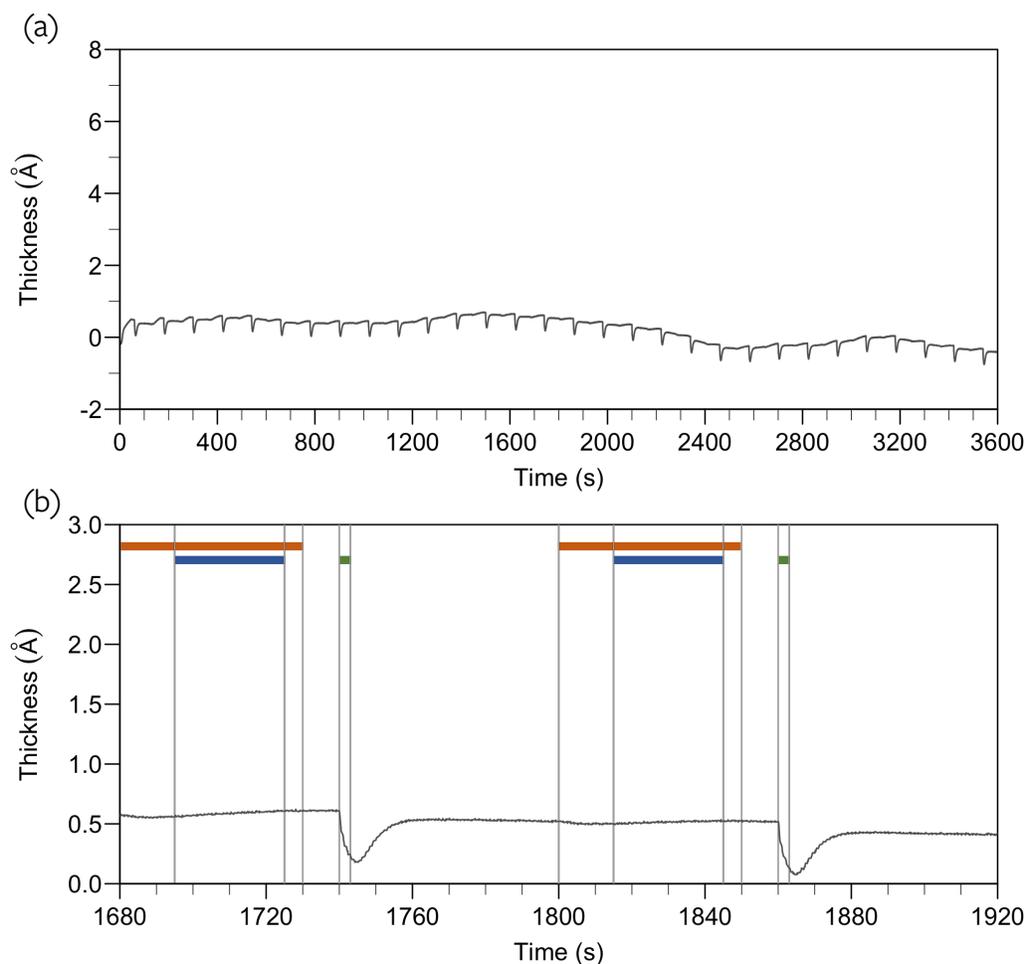


Figure 111: TEMAZ | water with 4-octyne during TEMAZ ALD on copper at 180 °C, (a) thirty cycles, (b) cycles fifteen and sixteen

A combination experiment was conducted on an annealed copper-coated crystal at a temperature of 120 °C and a pressure of 1.5 Torr, wherein pristine ALD immediately followed ALD with 4-octyne (Figure 112). After twenty cycles of ALD with 4-octyne, the thickness had increased slightly and seemed to approach an asymptote. During the first cycle without 4-octyne, there was immediate growth, and the growth rate remained steady at $\sim 0.79 \text{ \AA/cycle}$ throughout twenty cycles. This result reinforced the understanding that 4-octyne adsorption on copper was reversible and demonstrated that we could grow zirconium oxide on the copper surface after many repeated 4-octyne exposures. The experiment was repeated at 180 °C and a similar result was observed (Figure 113). Deposition occurred during the first cycle without 4-octyne and the growth rate over twenty cycles was $\sim 1.2 \text{ \AA/cycle}$.

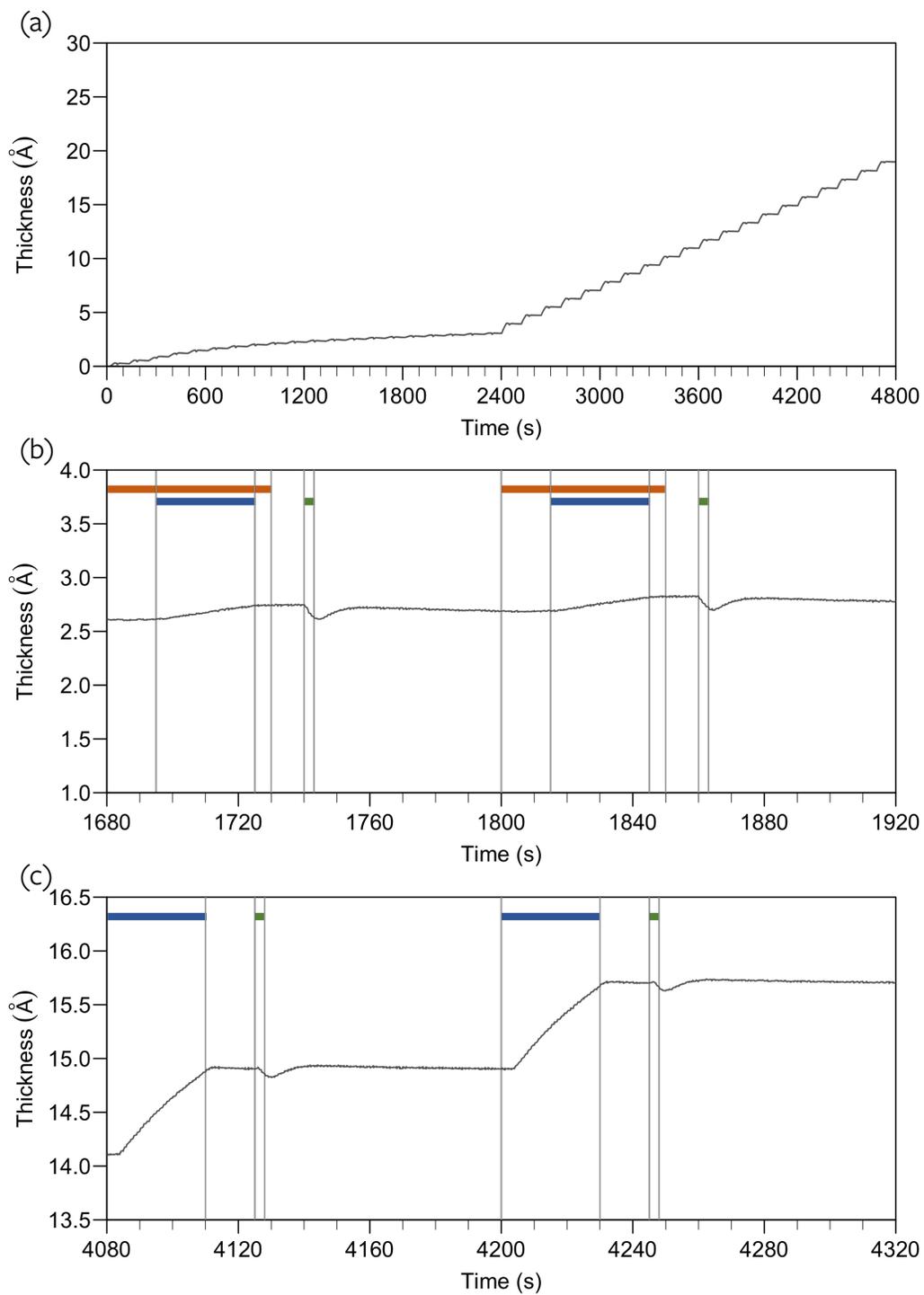


Figure 112: TEMAZ | water with 4-octyne during TEMAZ ALD followed by TEMAZ | water ALD on copper, (a) forty cycles (twenty cycles of each), (b) cycles fifteen and sixteen, (c) cycles thirty-five and thirty-six

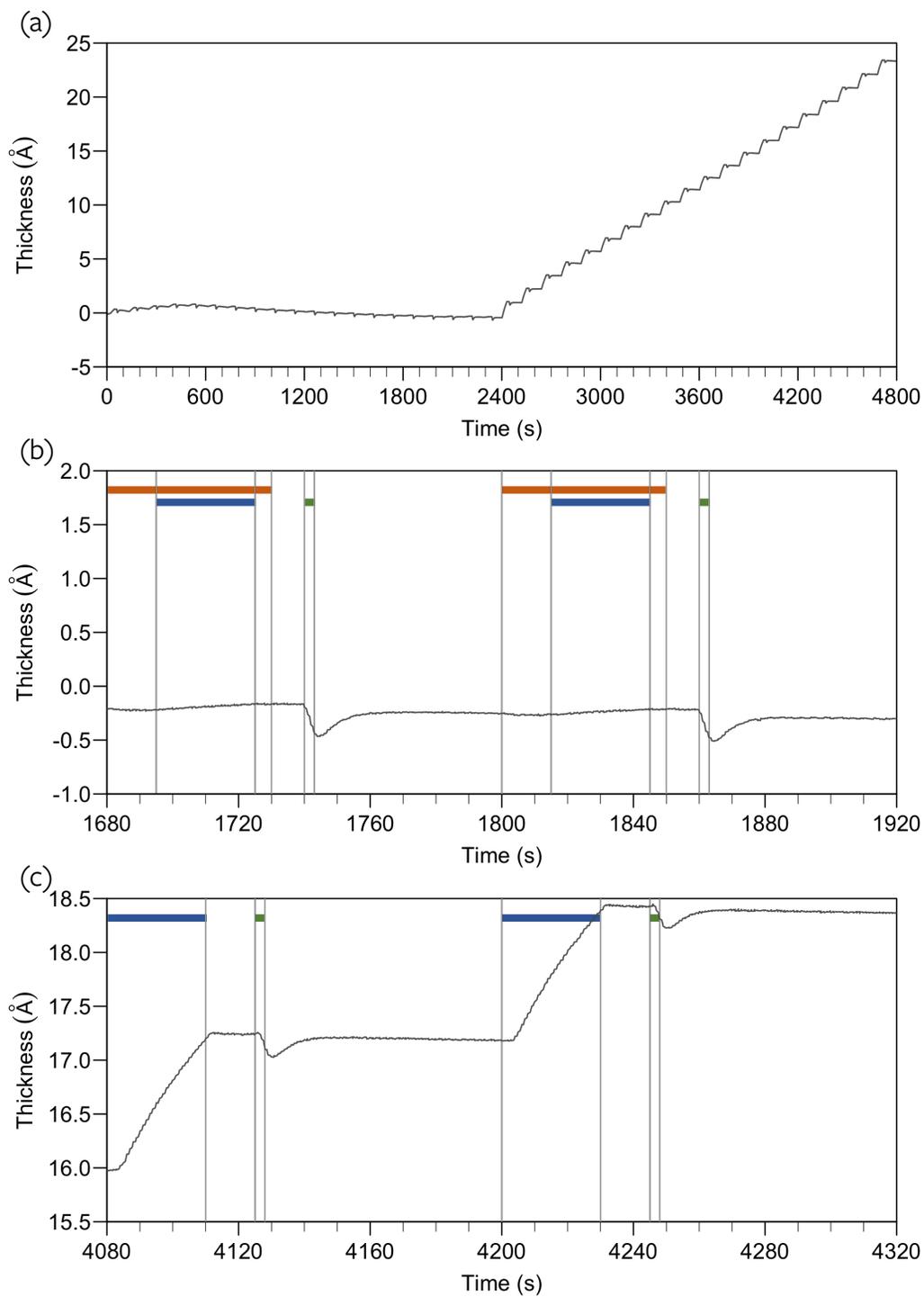


Figure 113: TEMAZ | water with 4-octyne during TEMAZ ALD followed by TEMAZ | water ALD on copper at 180 °C, (a) forty cycles (twenty cycles of each), (b) cycles fifteen and sixteen, (c) cycles thirty-five and thirty-six

The ALD with 4-octyne sequence, 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr) (15 s) | 4-octyne / TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | 4-octyne (5 s) | argon purge (10 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (57 s), was performed on an annealed silicon oxide–gold-coated crystal at a temperature of 120 °C and a pressure of 1.5 Torr, and almost no growth was observed after thirty cycles (Figure 114). This was an unexpected outcome, as it contradicted the CVD results obtained using the microreactor and the theoretical results that found minimal interaction of the 4-octyne with the silicon oxide surface. We hypothesized that the method of delivery could have been influencing the behavior of 4-octyne, specifically the mixing of reactants before delivery to the reactor tube.

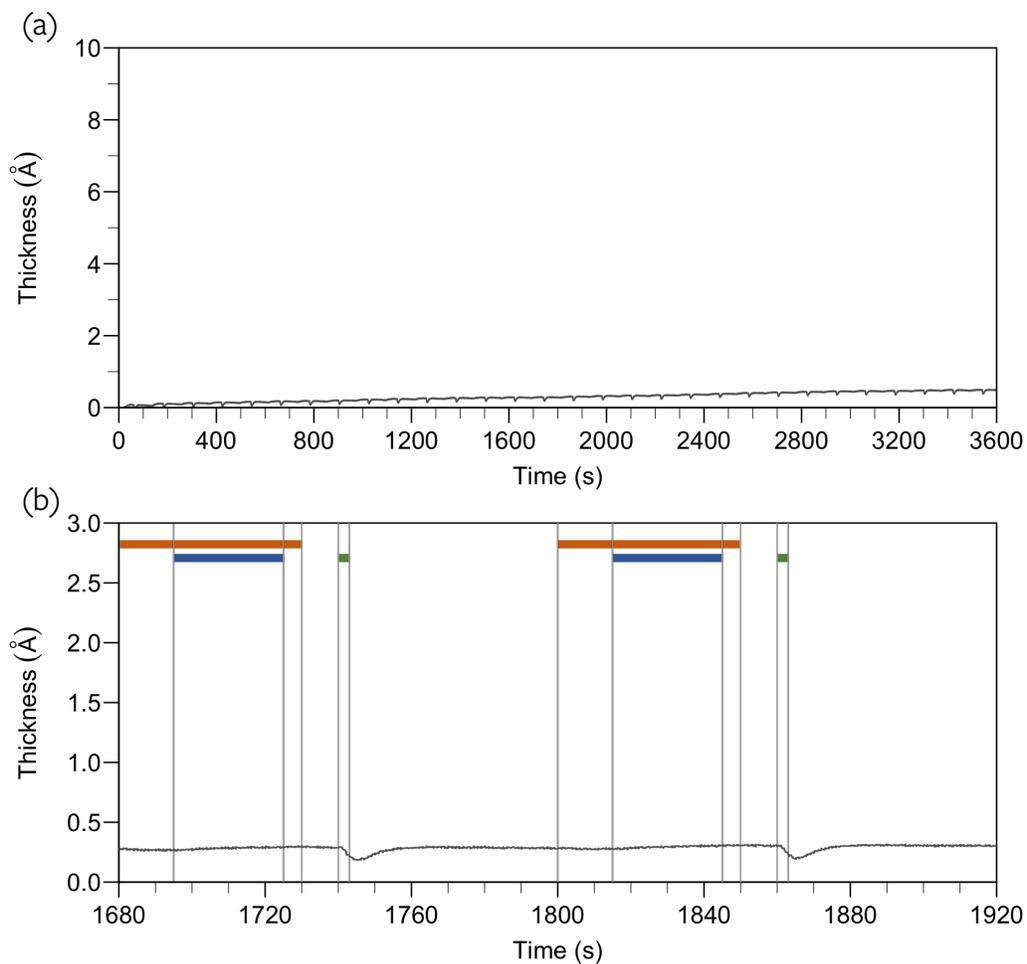


Figure 114: TEMAZ + water with 4-octyne during TEMAZ ALD on silicon oxide, (a) thirty cycles, (b) cycles fifteen and sixteen

Reactant feedthrough version two

The reactant feedthrough was then replaced with version two, where the three panels containing ampoules did not mix in 1/4 in tubing, but were delivered separately to the center of the 2.5 in OD reactor tube (Figure 115).

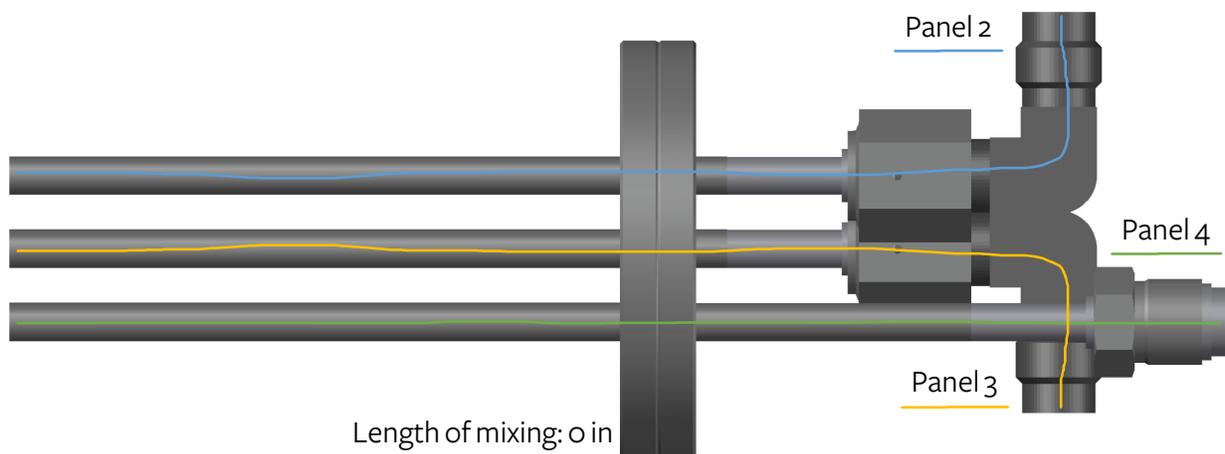


Figure 115: Reactant feedthrough version two

TEMAZ | water

The reference pristine experiment was modified slightly to decrease the purge after water: TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | argon purge (15 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (42 s). Twenty cycles were performed on an aluminum oxide substrate (~300 Å aluminum oxide on a silicon oxide–gold-coated crystal) at a temperature of 120 °C and a pressure of 1.5 Torr (Figure 116), and there were noticeable differences between the pristine process using feedthrough version two and the previous experiments using feedthrough version one. The growth rate in this experiment was ~3.9 Å/cycle, compared to ~0.85 Å/cycle, and the shape of the cycle changed significantly from the first to the twentieth cycle, although the growth rate was steady throughout the experiment. The early cycles resembled previous experiments, but, in the later cycles, there was a large apparent increase in thickness during the TEMAZ dose that appeared to be reversed

during the purge steps. Additionally, the deviation due to introduction of water was much larger.

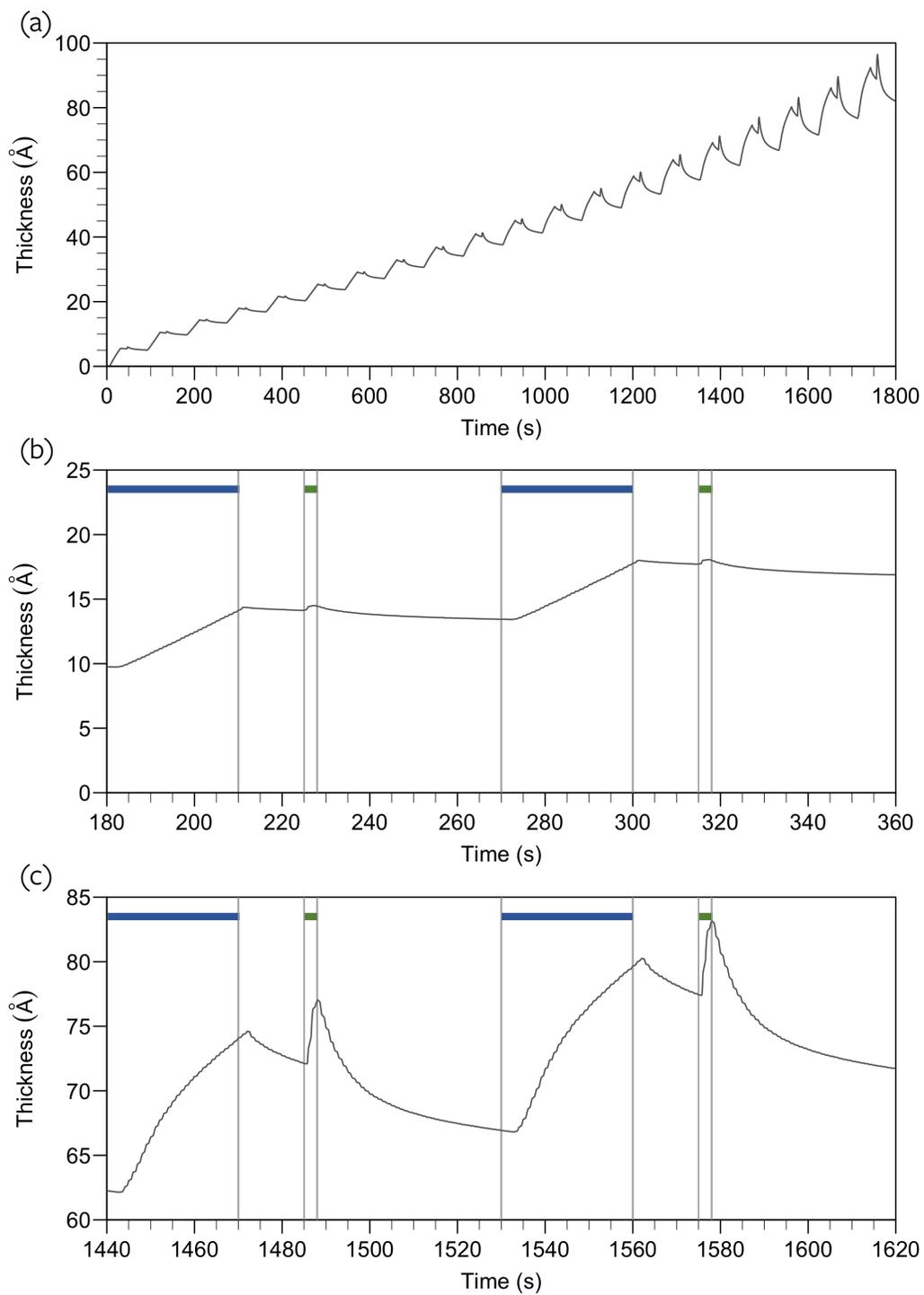


Figure 116: TEMAZ | water ALD on aluminum oxide, (a) twenty cycles, (b) cycles three and four, (c) cycles seventeen and eighteen

To ensure no CVD reactions were occurring and leading to the high growth rate, we decreased the pressure and increased the purge times for each reactant: TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | argon purge (30 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (87 s). The sequence was cycled twenty times on a zirconium oxide substrate (~25 Å zirconium oxide on a silicon oxide–gold-coated crystal) at a temperature of 120 °C and a pressure of 0.5 Torr (Figure 117). The TEMAZ and water ALD pressure study was completed using feedthrough version one, so it was also of interest to observe how changing the pressure affected deposition processes using feedthrough version two. The cycle shape did not change during the experiment, but the growth rate did decrease slightly. Despite the small decrease in growth rate, the average was still large at ~3.2 Å/cycle. This suggested that the pressure and purge lengths were influencing the cycle shape but not the deposition rate.

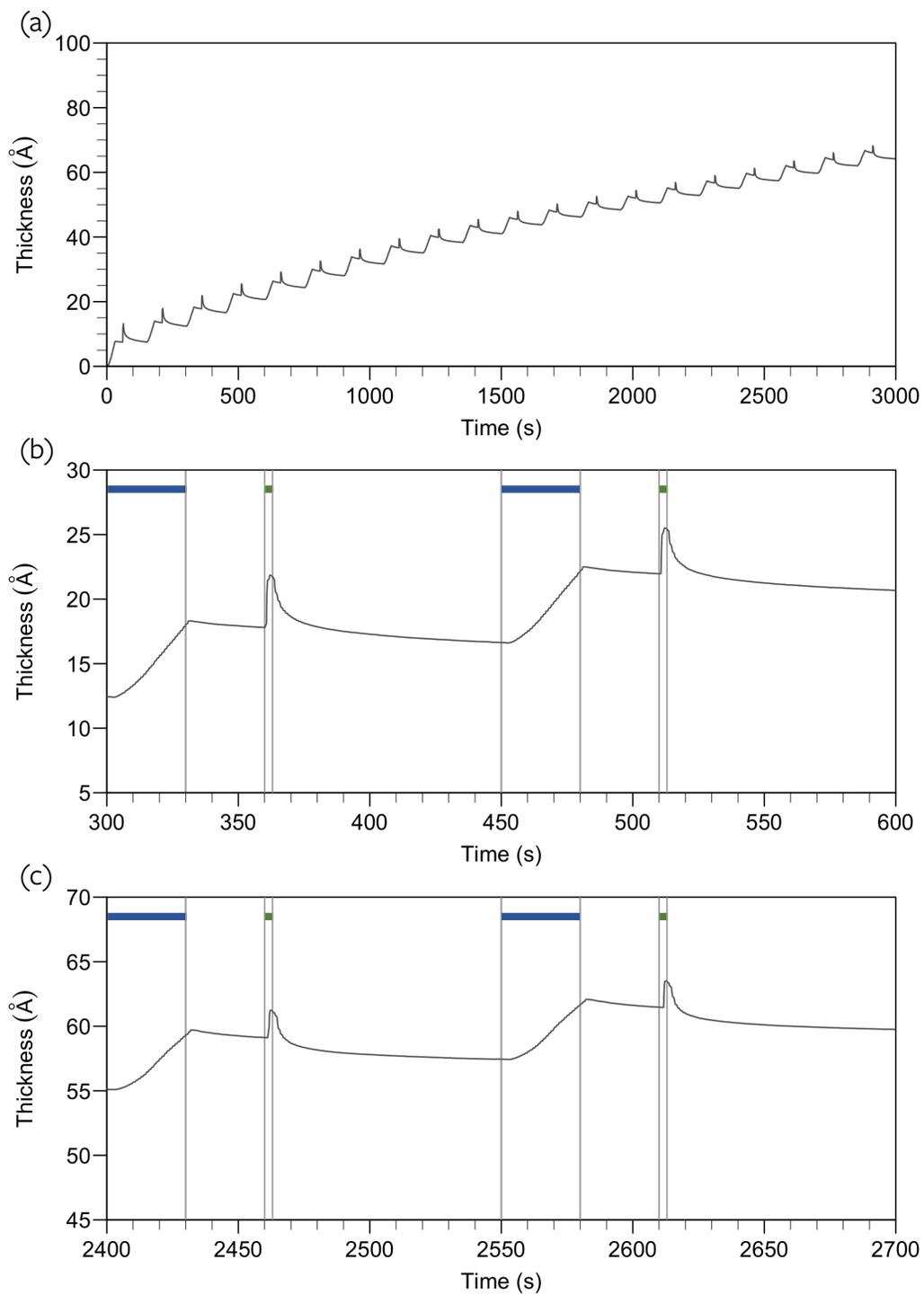


Figure 117: TEMAZ | water ALD on zirconium oxide, (a) twenty cycles, (b) cycles three and four, (c) cycles seventeen and eighteen

From the previous experiment, we concluded that the high growth rate was not due to the products of gas-phase CVD reactions condensing on the substrate. However, it was possible that the reactant doses were too large, resulting in an oversaturation of molecules on the surface that were not removed during the purge step.^{80, 81} The sequence TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (10 s) | argon purge (80 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (1 s) | argon purge (149 s) was cycled twenty times on a zirconium oxide substrate (~18 Å zirconium oxide on a silicon oxide–gold-coated crystal) at a temperature of 120 °C and a pressure of 1.5 Torr (Figure 118). With the decreased reactant doses, the growth rate decreased to ~1.2 Å/cycle, which was comparable to results using feedthrough version one. However, the change in cycle shape was observed again, although not as significantly, indicating that the pressure was a more important factor than purge length in understanding the phenomenon.

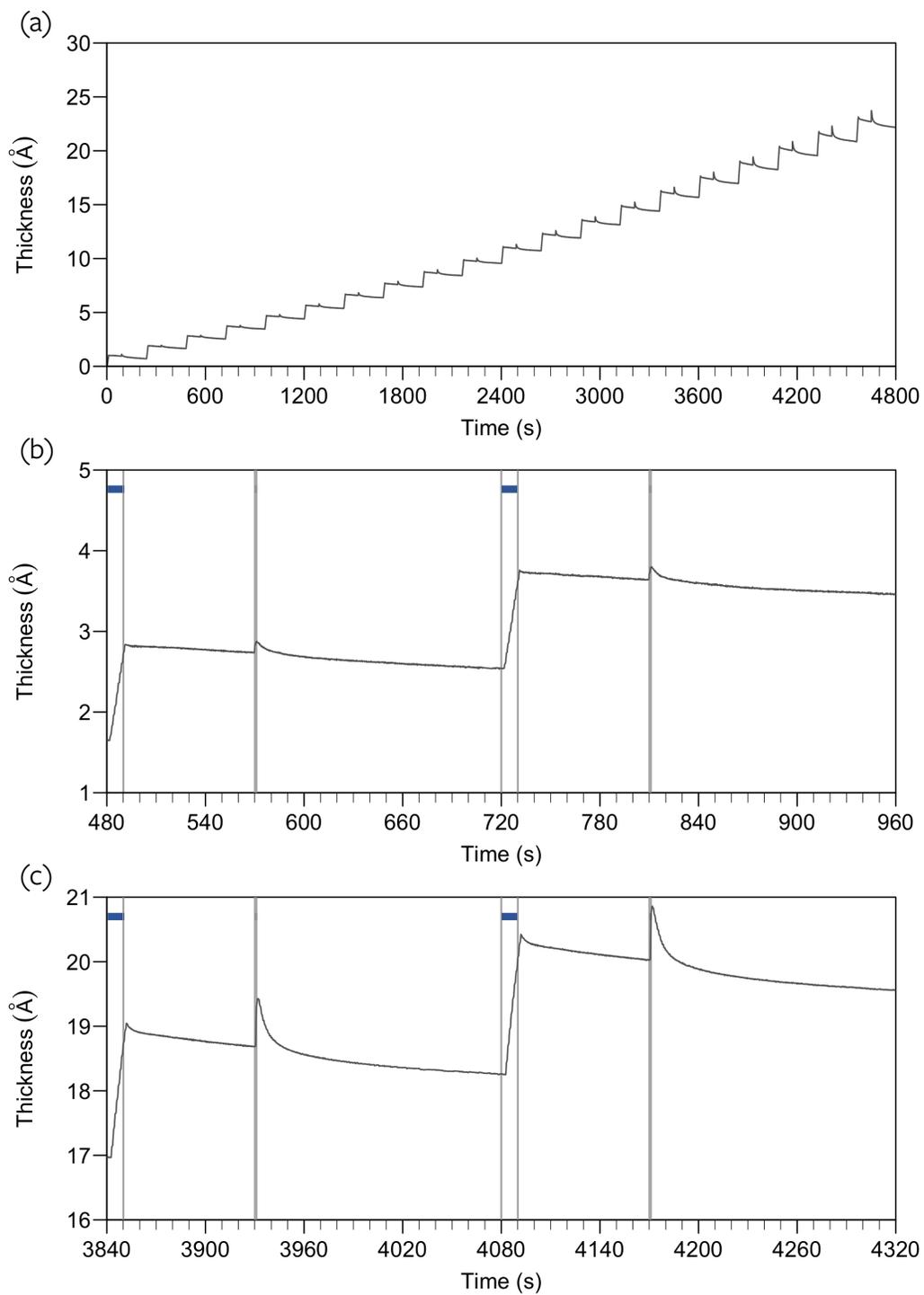


Figure 118: TEMAZ | water ALD on zirconium oxide, (a) twenty cycles, (b) cycles three and four, (c) cycles seventeen and eighteen

TEMAZ | water with 4-octyne

To have a direct comparison between feedthrough versions, we returned to the reference sequence including 4-octyne: 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr) (15 s) | 4-octyne / TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | 4-octyne (5 s) | argon purge (10 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (57 s). The sequence was cycled thirty times on an annealed silicon oxide–gold-coated crystal at a temperature of 180 °C and a pressure of 1.5 Torr (Figure 119). Theoretically, growth was expected because there should have been no interaction between 4-octyne and the silicon oxide surface. However, no growth was observed for the same experiment on silicon oxide using feedthrough version one (Figure 114).

With feedthrough version two, the growth rate increased from ~2 Å/cycle at the beginning to ~3.5 Å/cycle at the end, resulting in an average of ~2.8 Å/cycle, and the cycle shape changed throughout the experiment, although it differed from what was observed during the pristine experiments. Similar to the pristine experiments, in the later cycles there was a large apparent increase in thickness during the TEMAZ dose and an apparent decrease in thickness during the purge steps. However, the deviation due to introduction of water was negative thickness rather than positive, and the reason for the QCM behavior in response to the water dose was not understood. While the growth rate was larger than expected for this ALD process, it was not as large as for the reference pristine experiment on aluminum oxide using feedthrough version two. We

hypothesized that surface preparation was a factor in this difference, because the pristine experiment was performed on a thick and possibly porous oxide layer deposited by thermal ALD, and the oxide substrate in this experiment was thinner and denser due to the use of PEALD. Importantly, by changing the method of reactant delivery to eliminate mixing in the 1/4 in tubing, we achieved growth of zirconium oxide on silicon oxide while incorporating 4-octyne into the ALD process.

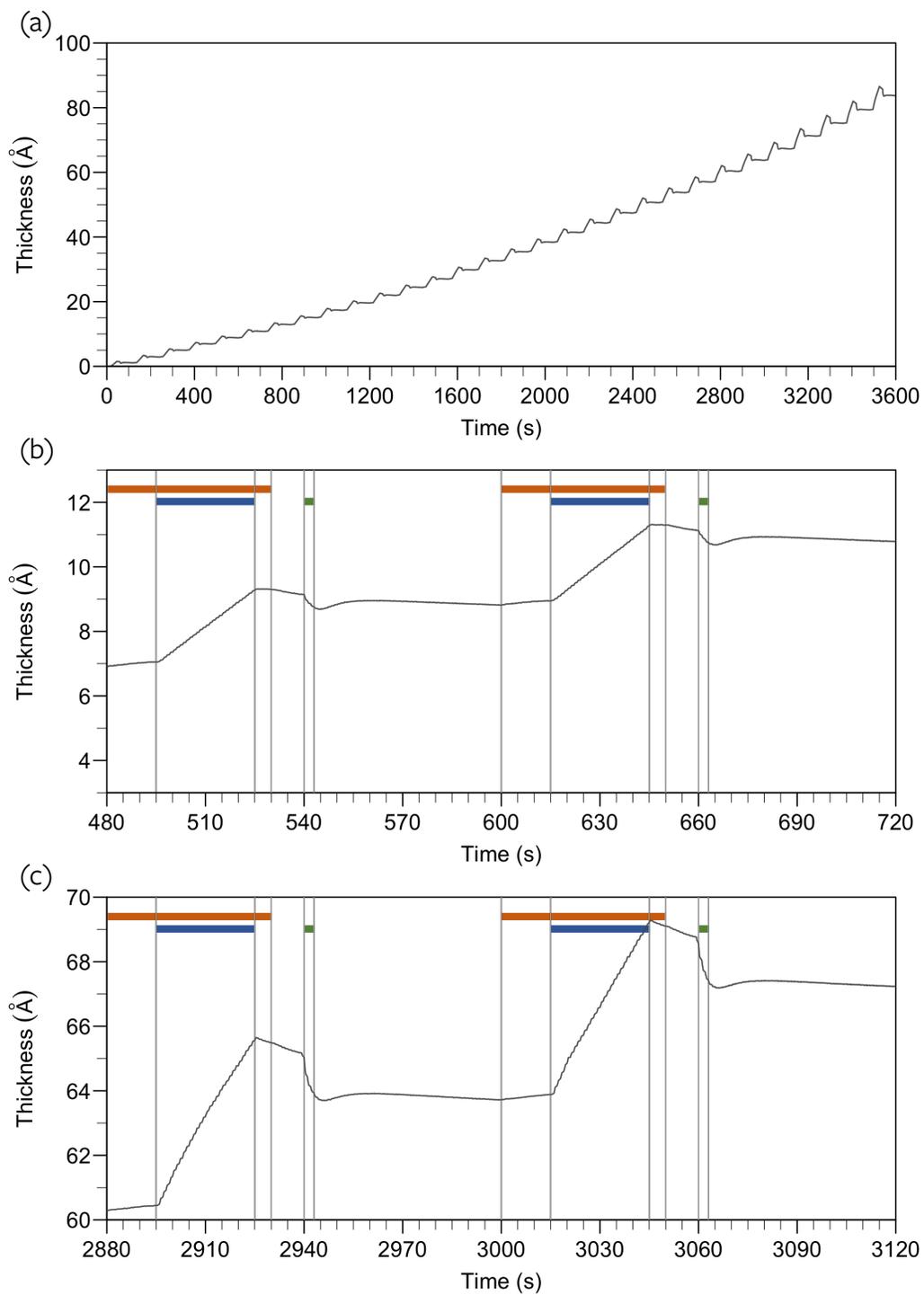


Figure 119: TEMAZ + water with 4-octyne during TEMAZ ALD on silicon oxide, (a) thirty cycles, (b) cycles five and six, (c) cycles twenty-five and twenty-six

The reference experiment including 4-octyne was then repeated for thirty cycles on an annealed copper-coated crystal at a temperature of 120 °C and a pressure of 1.5 Torr (Figure 120). Theoretically, no growth was expected because the surface should have been blocked by the 4-octyne, and that would have been consistent with results using feedthrough version one (Figure 110). However, significant growth was observed, with an initial growth rate of $\sim 1 \text{ \AA}/\text{cycle}$, a final growth rate of $\sim 3 \text{ \AA}/\text{cycle}$, and an average growth rate of $\sim 2.3 \text{ \AA}/\text{cycle}$. This growth rate was comparable to the experiment on silicon oxide, leading to the assumption that 4-octyne was not interacting with the copper surface at all. By zooming in on individual cycles, it was clear that the 4-octyne was not preventing adsorption of TEMAZ on the substrate, even during the early cycles, and the cycle shape was very similar to the experiment on silicon oxide.

We theorized that the mixing of reactants in 1/4 in tubing during ALD experiments with 4-octyne was leading to a complexation or reaction between the TEMAZ and 4-octyne that prevented TEMAZ adsorption on both copper and silicon oxide. Without the pre-mixing, the 4-octyne did not prevent growth on copper as expected.

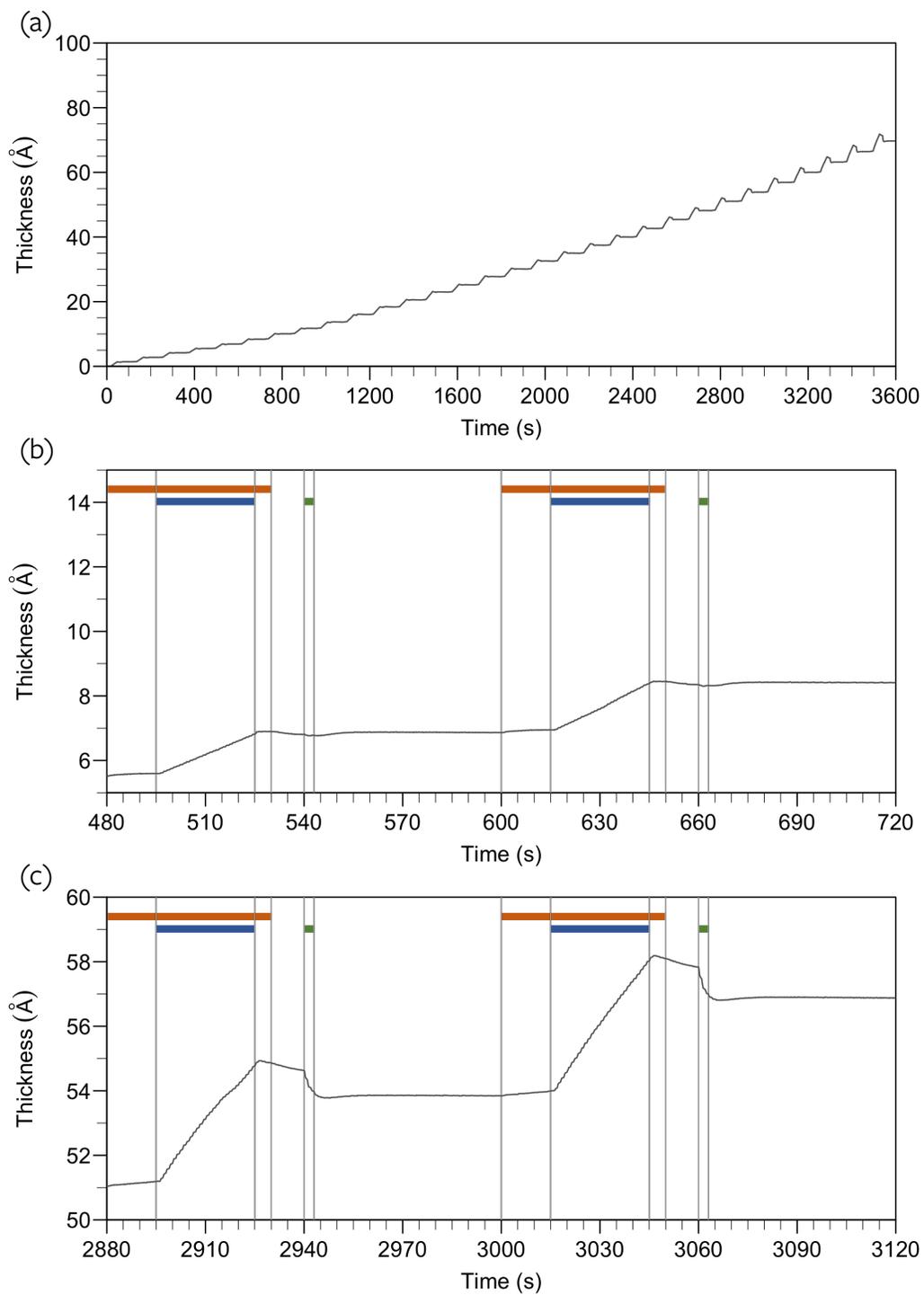


Figure 120: TEMAZ + water with 4-octyne during TEMAZ ALD on copper, (a) thirty cycles, (b) cycles five and six, (c) cycles twenty-five and twenty-six

Reactant feedthrough version three

To understand further the role of reactant mixing on the deposition process, the reactant feedthrough was modified to version three (Figure 121). In that configuration, panels two and four (TEMAZ and 4-octyne, respectively) entered the same inlet of the triple feedthrough and mixed for 6.87 in before being delivered to the center of the 2.5 in OD reactor tube. The delivery of the reactant from panel three (water) was kept in its individual feedthrough separate from the other reactants. The feedthrough through which the reactant on panel four was previously delivered was capped and not used in this configuration.

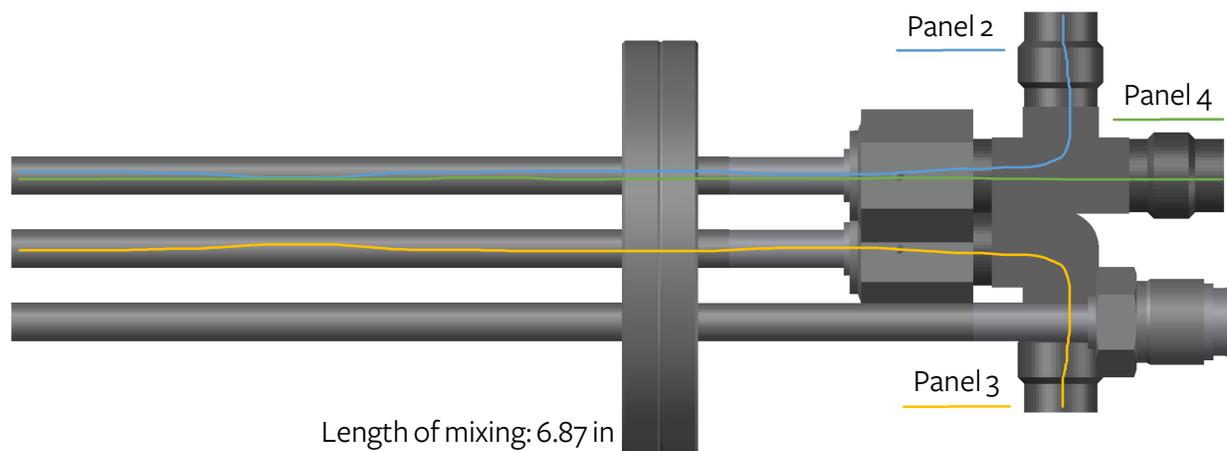


Figure 121: Reactant feedthrough version three

TEMAZ | water with 4-octyne

The sequence 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr) (25 s) | 4-octyne / TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (10 s) | 4-octyne (5 s) | argon purge (50 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (57 s) was cycled fifteen times on a copper-coated crystal at a temperature of 180 °C and a pressure of 1.5 Torr, followed by fifteen cycles of TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (10 s) | argon purge (50 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (87 s) (Figure 122). Although the sequence was different, this experiment was based on one performed using feedthrough version one (Figure 113). The thickness increased slightly due to introduction of 4-octyne during the first few cycles, but, subsequently, growth was prevented and the thickness did not increase. Growth of zirconium oxide began during the first cycle without 4-octyne, and the growth rate was steady at ~0.65 Å/cycle for fifteen cycles.

Looking at only cycles ten and eleven, there was a sloping increase in thickness during the 4-octyne dose, with no apparent change when the TEMAZ was turned on or off. Although there was a fluctuation in thickness due to the water dose, we did not believe the water was reacting with the 4-octyne because there was no significant thickness difference between the beginning and end of the cycles and this cycle shape was also observed in experiments using feedthrough version one. The sloping decrease after the 4-octyne was turned off indicated that the 4-octyne was reversibly adsorbing to the substrate. Focusing next on cycles twenty-five and twenty-six, there was an increase in thickness due to the TEMAZ dose, and the thickness remained constant during the

subsequent purge. This cycle shape was consistent with the experiments performed using feedthrough version one.

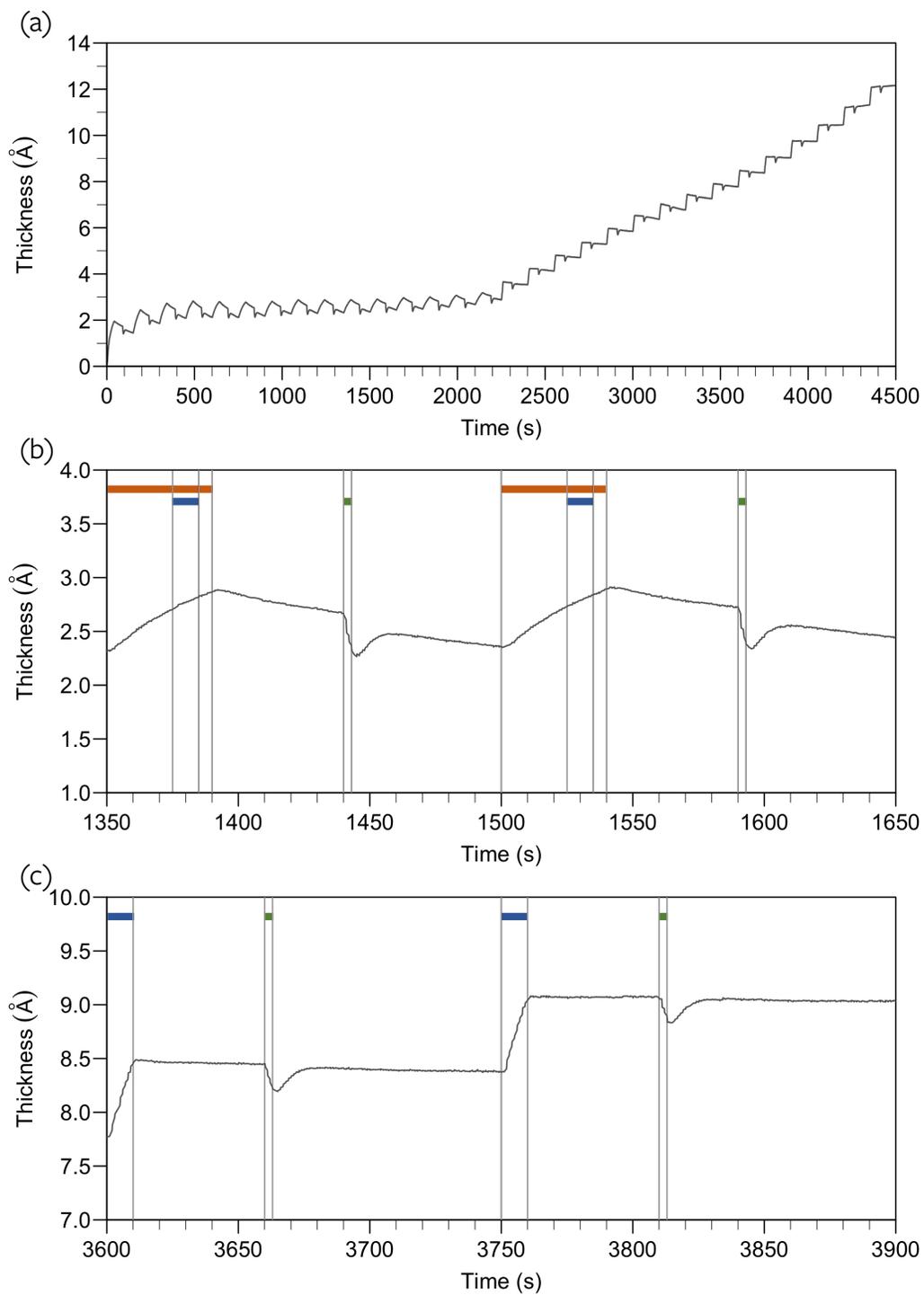


Figure 122: TEMAZ | water with 4-octyne during TEMAZ ALD followed by TEMAZ | water ALD on copper, (a) thirty cycles (fifteen cycles of each), (b) cycles ten and eleven, (c) cycles twenty-five and twenty-six

The results of this investigation into feedthrough configurations were that growth of zirconium oxide was prevented on silicon oxide and copper when the 4-octyne and TEMAZ were pre-mixed in 1/4 in tubing, and that growth of zirconium oxide proceeded on silicon oxide and copper when the reactants were delivered individually. I mentioned previously that one of the potential disadvantages of using the co-adsorbate method to investigate area-selective deposition is unwanted side reactions. Based on these results, it appeared that a reaction or complexation of 4-octyne and TEMAZ occurred when they were pre-mixed. Also, these results suggested that the interaction between 4-octyne and copper was not as strong as previously believed.

Conclusion

I designed and built a highly useful custom QCM chamber that addressed our objectives for studying area-selective ALD. Design of the QCM chamber began in late 2017, the first major components arrived in mid-2018, hardware assembly began in late 2018 and was completed in mid-2019, serial communication cable installation and software setup was completed in late 2019, and the first ALD experiment was performed in January of 2020. After I completed construction of the chamber, it was properly characterized, including calculations of important parameters, validation of flow dynamics, and optimization of temperature control. I demonstrated that the chamber can be used to effectively study the behavior of individual chemicals on various substrates. I also developed a working understanding of how experimental conditions such as dose length, partial pressure, carrier gas flow rate, substrate temperature, and chamber pressure affect ALD experiments.

Although the TEMAZ and water ALD experiments incorporating 4-octyne as the co-adsorbate did not validate the results obtained from CVD experiments using the microreactor vacuum chamber, much was learned about the impact of pre-mixing the TEMAZ and 4-octyne on the adsorption behavior of TEMAZ on both silicon oxide and copper substrates. Based on the CVD results, we expected to observe growth of zirconium oxide on silicon oxide and no growth of zirconium oxide on copper when 4-octyne was co-dosed with TEMAZ. Instead, we observed no growth on either substrate when the reactants were pre-mixed, and growth on both substrates when the reactants were

delivered independently. We concluded that a complexation or reaction was occurring between the TEMAZ and 4-octyne when they were pre-mixed, which altered the behavior of the TEMAZ and prevented it from adsorbing on either substrate. When the reactants were delivered in separate feedthroughs, the coverage of 4-octyne on copper was insufficient to prevent adsorption of TEMAZ on the surface. The mechanism of the interaction between TEMAZ and 4-octyne is not well understood from the completed experiments, and, therefore, continued investigation is necessary to elucidate what occurs as a result of the pre-mix. Additional experiments are also necessary to understand why the behavior of 4-octyne on copper appears to be inconsistent with the theoretical calculations.

From this work, we believe that proper surface preparation is essential to ensuing experiments on the substrate. For example, the copper crystal that was exposed to repeated doses of 4-octyne (Figure 92) followed by alternating doses of 4-octyne and water (Figure 93) was subsequently used as the substrate for a TEMAZ and water ALD experiment with 4-octyne as the co-adsorbate (Figure 123). This experiment was performed when feedthrough version one was installed, and the ALD sequence comprised 4-octyne (ampoule temperature 0 °C, vapor pressure ~5.6 Torr) (15 s) | 4-octyne / TEMAZ (ampoule temperature 50 °C, vapor pressure ~0.04 Torr) (30 s) | 4-octyne (5 s) | argon purge (10 s) | water (ampoule temperature 0 °C, vapor pressure ~4.5 Torr) (3 s) | argon purge (57 s). At the beginning of the 4-octyne dose, there was clear adsorption and the QCM response began to plateau, suggesting that saturation was achieved. However, once the TEMAZ dose was initiated, the thickness increased linearly,

indicating that the surface was not sufficiently covered with 4-octyne to prevent adsorption of TEMAZ. After the TEMAZ dose was concluded, but while the 4-octyne dose continued, the thickness was flat and no additional 4-octyne adsorbed on the substrate. Once the 4-octyne dose was turned off, the thickness decreased by approximately the same magnitude as the initial increase, which was attributed to desorption of the 4-octyne from the surface. This cycle shape was consistent for all five cycles, and we concluded that the 4-octyne was reversibly adsorbing to, and preventing growth on, a limited area of the copper surface. Throughout the experiment, the growth rate was $\sim 0.5 \text{ \AA}/\text{cycle}$, which was consistent with partial coverage of 4-octyne and partial coverage of the newly deposited zirconium oxide thin film.

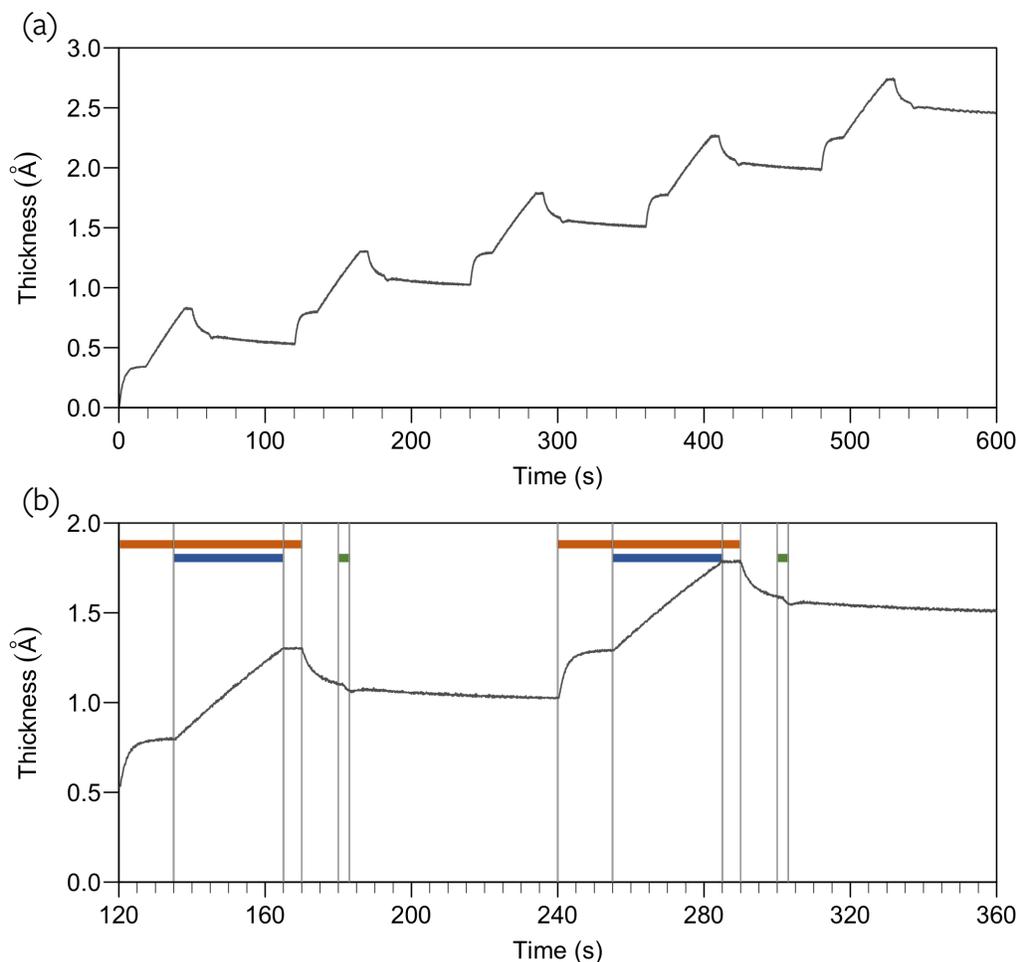


Figure 123: TEMAZ | water with 4-octyne during TEMAZ ALD on copper, (a) five cycles, (b) cycles two and three

Because the crystal was not annealed or reduced by hydrogen plasma immediately before the experiment, it was possible that the surface was partly oxidized or contained a noncontinuous contamination layer. In that case, the 4-octyne would only have adsorbed on the reduced copper and would not have adsorbed on the oxidized copper, and the observed cycle shape could have been expected. This result suggested that growth should have been observed on silicon oxide when 4-octyne was used as a co-adsorbate in the TEMAZ and water ALD system, which emphasizes further the need for additional

experiments to understand the effect of surface treatment on reactant adsorption behavior.

My work in constructing and operating the QCM reactor helped me understand the complexity of vacuum chamber design; expanded the analytical capabilities of the Engstrom Research Group; provided valuable insight into the area-selective ALD system of TEMAZ, water, and 4-octyne; and built a foundation for future area-selective ALD studies using a QCM.

Future directions

The QCM chamber remains new, having been in use for less than two years—and for only sixteen months by me due to the 2020 shutdown—so there is still much to learn about its operation. Besides the chamber itself, the field of area-selective deposition is active and manufacturing companies remain interested in new discoveries and techniques.

Continued collaboration with the DiStasio Research Group can be leveraged for enhanced understanding of surface interactions between co-adsorbates and substrates of industrial relevance. The theoretical insight from their calculations can help guide experiments by advising what molecules could be effective co-adsorbates, and what molecules are not worth investigating. Through the collaboration, substrate combinations for area-selective ALD experiments can be expanded beyond the initial focus of differentiating between silicon oxide and copper. Members of the DiStasio Research Group already started to model potential co-adsorbate interactions with cobalt surfaces, so experiments in the QCM chamber with this substrate as the non-growth surface, rather than copper, would be useful for comparison with the theoretical results. They have also started modelling potential co-adsorbate interactions with silicon nitride surfaces, which would be of interest for investigating selective growth of silicon oxide on silicon oxide in the presence of silicon nitride. Other substrates of interest are the metals ruthenium and tungsten, and the dielectrics aluminum oxide and hafnium oxide.

As mentioned previously, complete reduction of the copper substrate was necessary before dosing 4-octyne to ensure maximum surface coverage. However, no investigation into the evolution of the reduced copper surface was performed. Before the plasma generator was functional, the method used to reduce the surface was a high temperature anneal. Typically, an anneal was started in the afternoon, the tube furnace was left to cool to the experimental temperature overnight, and an experiment was performed the following morning. It would be of interest to examine whether the surface changed during the hours it took for the tube furnace to cool, or during the hours the sample was held at the experimental temperature. This analysis could utilize the X-ray photoelectron spectroscopy system to quantify oxygen on the surface immediately after the anneal and at the two times of interest, or water contact angle to measure the wettability as a function of time.⁷⁷ Once the plasma generator was installed, hydrogen plasma was used to reduce the copper surface, so this condition should also be included in the study. If the copper surface became even partially oxidized, it is possible that this prevented adsorption of 4-octyne. This would be especially important in the case of feedthrough version two, which resulted in growth on silicon oxide in the presence of 4-octyne.

There are several further hardware modifications that could be considered for the QCM chamber. For example, there is a clamp along the length of the QCM sensor that secures the backside purge and electrical components tubes together (Figure 124a).⁵⁸ When retracting the QCM from the tube furnace to the load lock, the translator can be moved only from a position of 24 in to a position of 0.75 in, rather than 0 in, or the clamp will catch on one of the load lock flanges and cause damage to the sensor (Figure 124b). The

shape of the sample holder positions the QCM and its tubes along the central axis of the reactor tube, but when the sensor is in the load lock it is not supported by the reactor tube, so the QCM and its tubes sink slightly and are instead supported by the load lock flange. Replacing the clamp with an alternative that is flush with the tubes on the underside, or perhaps one that is tapered so it slides past the edge of the flange, would lessen the risk of damage to the QCM sensor and reduce the number of steps in the standard operating procedures for experiments.

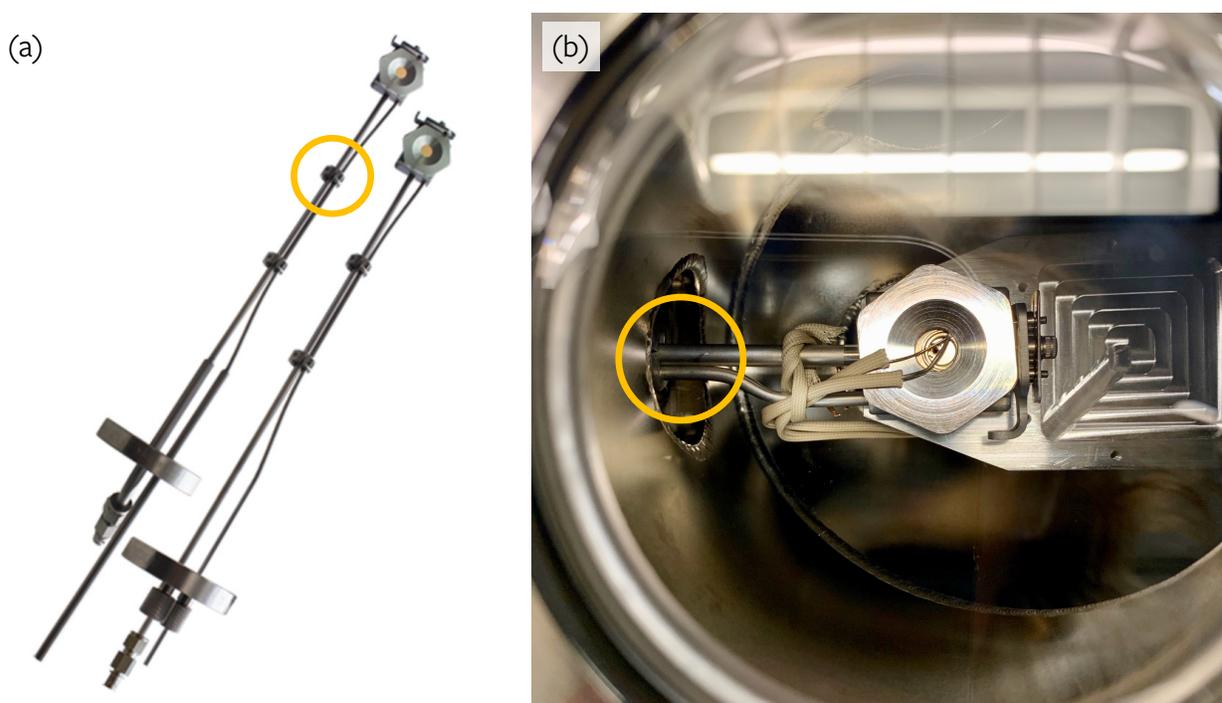


Figure 124: (a) Clamp on QCM sensor²⁷, (b) load lock flange that could interfere with clamp on QCM sensor

There is only one pressure monitor and one turbomolecular pump connected to the reactor. The existing pressure monitor has a minimum detection limit of 5 mTorr, which is sufficient for measuring the pressure during experiments, but the ability to measure

lower pressure might be desirable. Adding a second, larger turbomolecular pump would also be of interest to decrease the base pressure of the chamber, and therefore the risk of contamination from reactants lingering in the reactor tube between experiments. Further, these enhancements would be necessary if additional capabilities that require ultra-high vacuum were added to the chamber, such as a mass spectrometer. The benefit of utilizing a mass spectrometer would be to know the exact composition of gas in the chamber, which would aid in detection of any potential leaks and provide better understanding of any fluctuations in the base pressure of the chamber.

The future of this work could proceed in many directions, and I covered only a small selection here.

Appendix A: Run numbers associated with data in figures

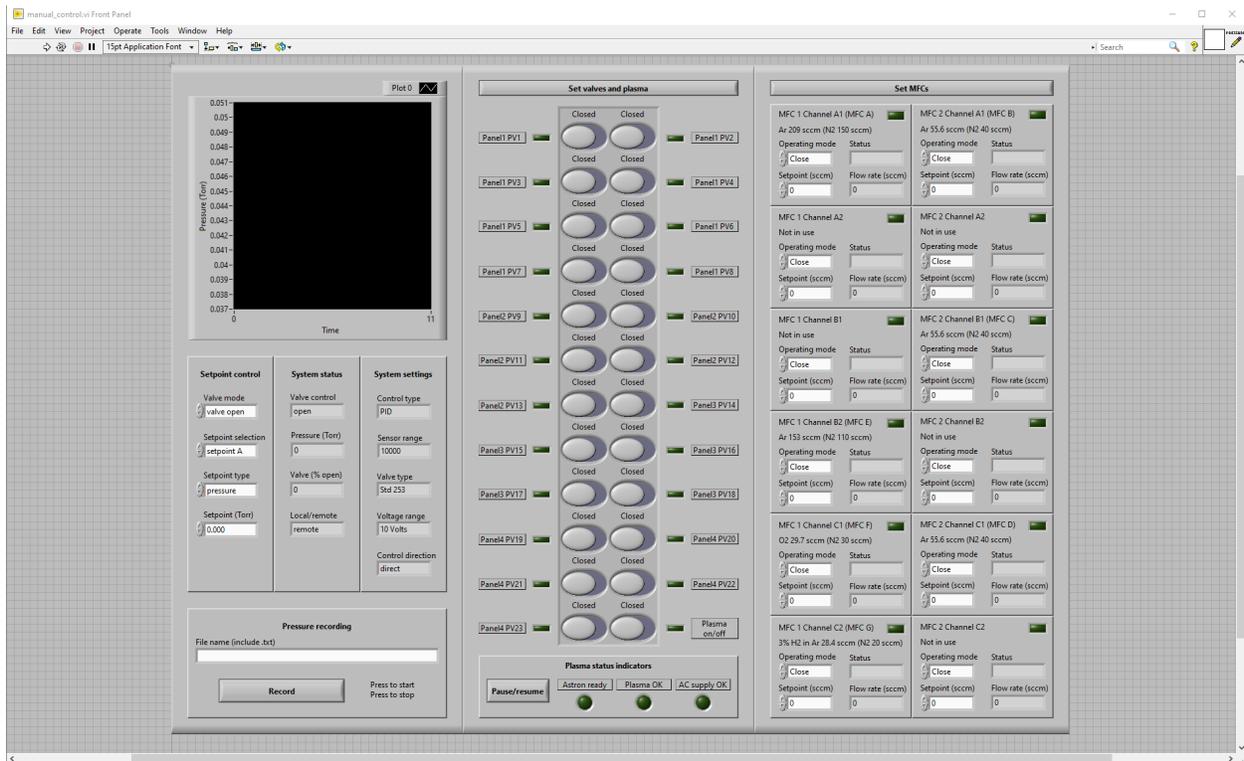
Figure number	Run number
Figure 77	20200723 run 5, 20200729 run 1
Figure 81	20210812 run 1
Figure 82	20200130 run1
Figure 83	20210803 run 2
Figure 84	20200910 run 1
Figure 85	20201014 run 1
Figure 86	20210811 run 1
Figure 87	20210819 run 1
Figure 88	20210811 run 2
Figure 89	20210712 run 6
Figure 90	20210712 run 8
Figure 91	20210416 run 1
Figure 92	20201028 run 1
Figure 93	20201028 run 2
Figure 94	20201217 run 1, 20201217 run 2
Figure 95	20210111 run 5, 20210111 run 7
Figure 96	20210111 runs 5–8
Figure 97	20201219 runs 5–8
Figure 98	20201209 runs 7–10
Figure 99	20210630 run 5

Figure 100	20210809 run 4
Figure 101	20210810 run 2
Figure 102	20210122 run 2
Figure 103	20210122 run 3
Figure 104	20210122 run 4
Figure 106	20210412 run 1
Figure 107	20210409 run 1
Figure 108	20210428 run 1
Figure 110	20210318 run 4
Figure 111	20210324 run 2
Figure 112	20210414 run 1
Figure 113	20210415 run 1
Figure 114	20210416 run 2
Figure 116	20210623 run 3
Figure 117	20210625 run 7
Figure 118	20210708 run 3
Figure 119	20210602 run 1
Figure 120	20210601 run 2
Figure 122	20210728 run 6
Figure 123	20201029 run 3

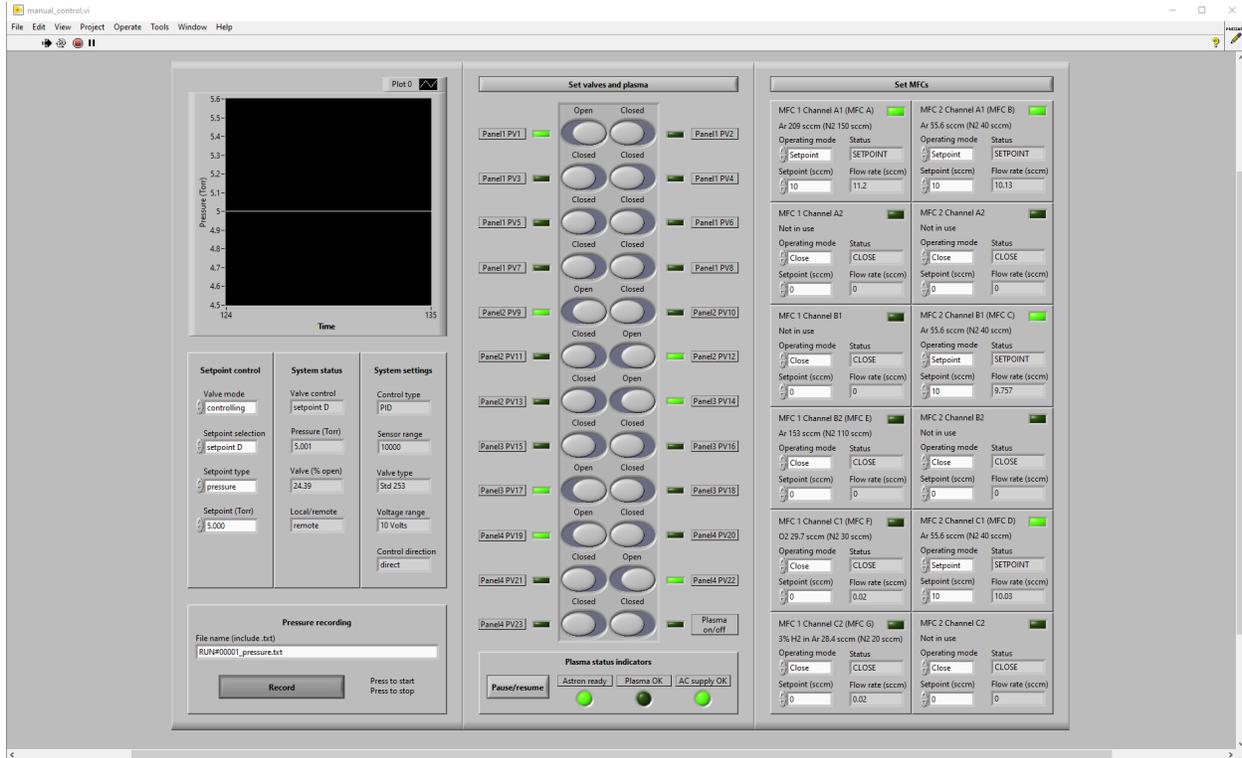
Appendix B: Description of software used to perform QCM experiments

LabVIEW manual_control

The manual control program (Appendix B Figure 125 and Appendix B Figure 126) is used to monitor the status of the plasma generator and manipulate pressure, solenoid channels (valve positions, plasma generator on/off), and MFC settings manually. The program interface comprises three panels: the left is for pressure control, the middle is for solenoid channel control and plasma generator status monitoring, and the right is for MFC control. When the program starts running, the pressure plot, the status of the throttle valve and Baratron settings, and the status of the MFCs update. The status of the pneumatic valves does not update. All changes to the startup conditions are made manually.



Appendix B Figure 125: Screenshot of LabVIEW manual_control interface at startup



Appendix B Figure 126: Screenshot of LabVIEW manual_control interface when running

1. Pressure control

a. Plot 0

i. Shows the pressure measured by the Baratron as a function of time

b. Setpoint control

i. Valve mode

1. Update the throttle valve control mode by selecting an option from the dropdown (valve open, valve close)

ii. Setpoint selection

1. Update the setpoint by selecting an option from the dropdown (A, B, C, D, E)
- iii. Setpoint type
 1. After selecting a setpoint to edit, update whether the setpoint controls the throttle valve position or the Baratron pressure by selecting an option from the dropdown (position, pressure)
 - iv. Setpoint (Torr)
 1. After selecting a setpoint to edit, update the setpoint by entering a value in the box
 2. If entering a pressure setpoint, enter a value in torr
 3. If entering a valve position setpoint, divide the percent open by 10 (e.g., for a valve position setpoint of 43.21% open, enter 4.321) and note that the units of Torr in the label are incorrect
- c. System status
 - i. Valve control
 1. Displays the throttle valve control mode (open, close, setpoint)
 - ii. Pressure (Torr)
 1. Displays the pressure in torr
 - iii. Valve (% open)
 1. Displays the throttle valve position in percent
 - iv. Local / remote

1. Displays whether the controller is being operated locally or remotely
2. Remote operation must be used in combination with the LabVIEW program

d. System settings

i. Control type

1. Displays the type of control
2. PID control is selected and this should not be changed

ii. Sensor range

1. Displays the pressure range of the Baratron in millitorr
2. The Baratron in use has a range of 10 Torr, so 10000 is selected and this should not be changed

iii. Valve type

1. Displays the type of throttle valve, as defined by the manufacturer
2. The throttle valve in use is a standard 253 valve, so Std 253 is selected and this should not be changed

iv. Voltage range

1. Displays the voltage range of the Baratron
2. The Baratron in use has a range of 10 V, so 10 Volts is selected and this should not be changed

v. Control direction

1. Displays the type of control direction

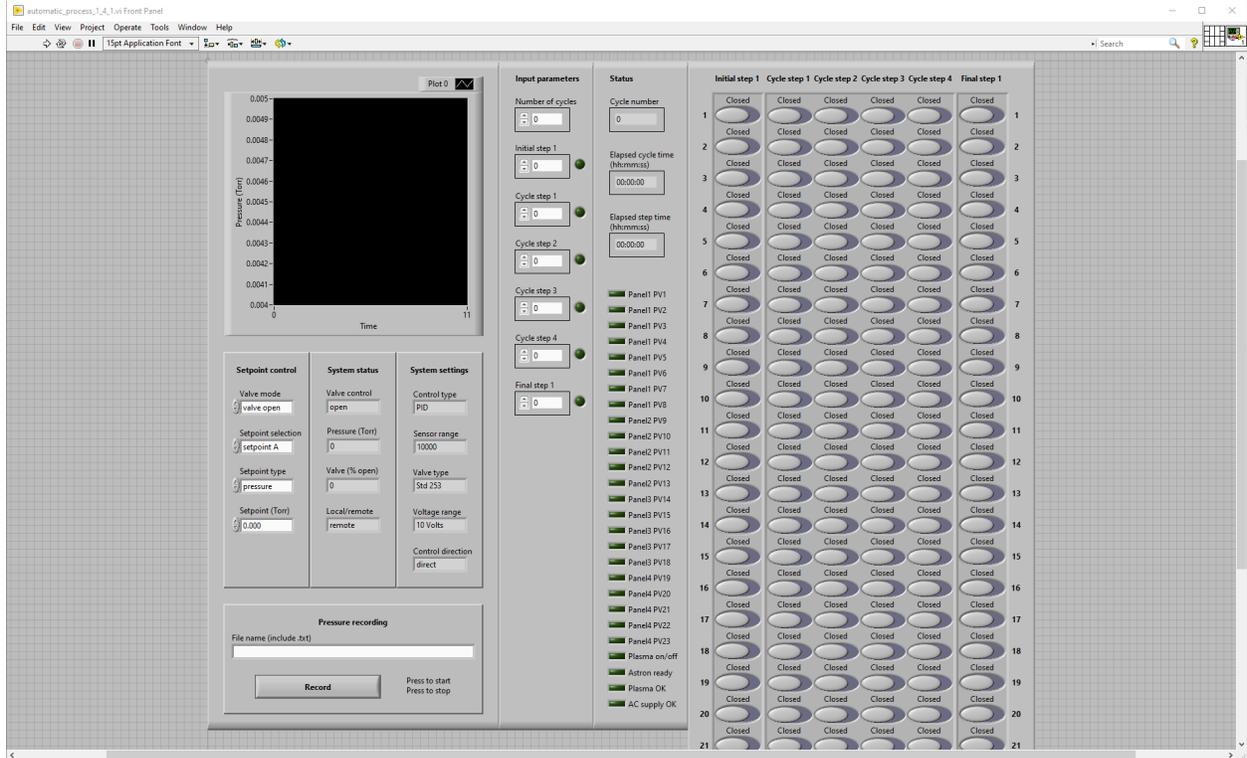
2. Direct is selected and this should not be changed
- e. Pressure recording
 - i. Use this section to create a text file recording of date, time, pressure, and throttle valve position
 - ii. File name (include .txt)
 1. Enter a name for the text file to be saved as
 2. The file is saved to Desktop/310 Data/Pressure Output
 - iii. Record
 1. Press the button to start and stop recording
 2. The button turns dark grey when the recording is on
2. Solenoid channel control and plasma generator status monitoring
 - a. Set valves and plasma
 - i. After moving slide switches, press the button to update status of solenoid channels
 - b. Slide switch array
 - i. Click the slide switches to choose a status for each valve, P1–P23 (left indicates closed, right indicates open), and for plasma on/off (left indicates off, right indicates on)
 - ii. The text above the slide switch updates when the slide switch is moved (closed, open)
 - iii. The valve position does not change until the “Set valves and plasma” button is pressed

- iv. When a channel is on, the indicator light next to the slide switch turns on
- c. Plasma status indicators
 - i. Astron ready, Plasma OK, AC supply OK indicator lights are on or off in accordance with the status of the plasma generator
 - ii. Pause/resume
 - 1. Press the button to pause and resume updating of the plasma generator status
 - 2. Multiple LabVIEW programs cannot simultaneously read continuously from the DAQ, so updating must be paused in the manual program before an automatic program is turned on
- 3. MFC control
 - a. This panel has twelve replicate sections (one for each MFC channel), split into two columns of six sections each (MFC controller 1 on the left, MFC controller 2 on the right)
 - b. Set MFCs
 - i. After changing MFC settings, press the button to update status of MFCs
 - c. MFC 1 Channel A1 (MFC A)
 - i. When an MFC is set to open or setpoint, the indicator light next to the channel name turns on
 - ii. Ar 209 sccm

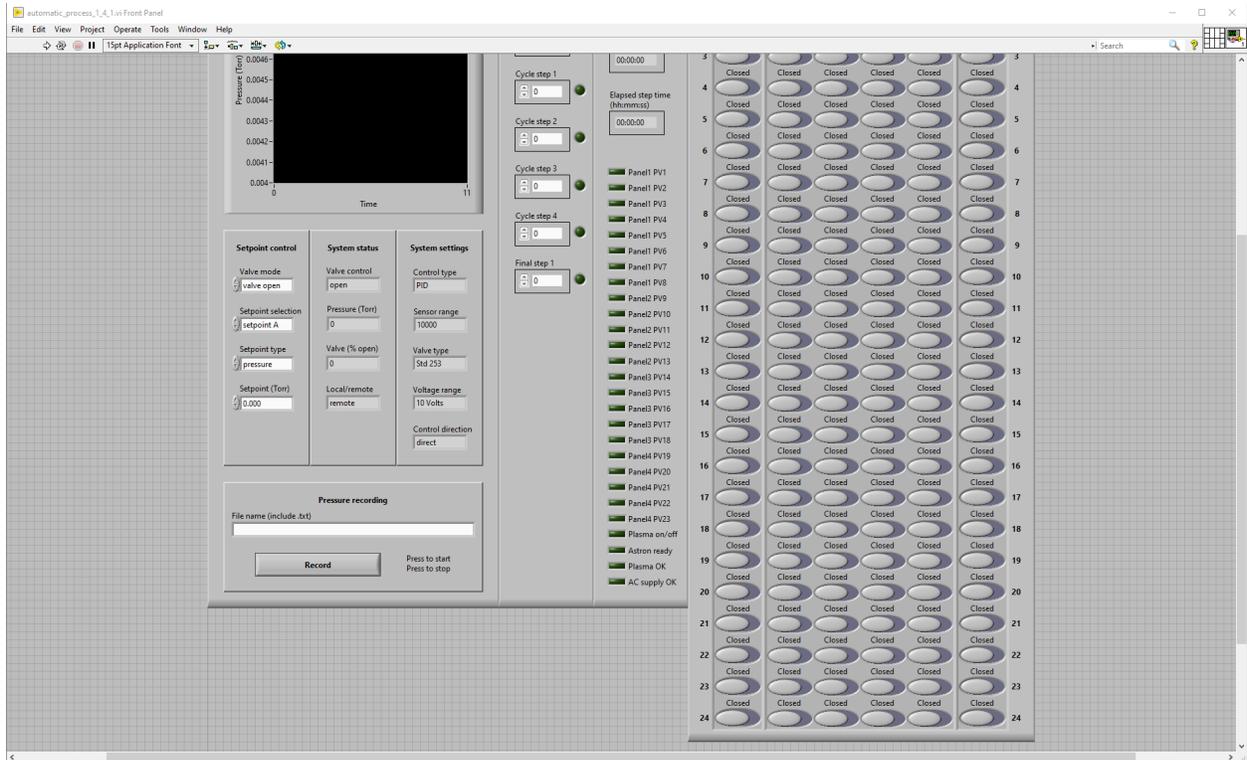
1. Full scale for flow of gas used, calculated using the gas conversion factor
- iii. (N2 150 sccm)
 1. Reference full scale for flow of nitrogen
- iv. Operating mode
 1. Update the operating mode by selecting an option from the dropdown (close, open, setpoint)
- v. Setpoint (sccm)
 1. Update the setpoint by entering a value in sccm in the box
- vi. Status
 1. Displays the status (close, open, setpoint)
- vii. Flow rate (sccm)
 1. Displays the actual flow rate in sccm

LabVIEW automatic_process

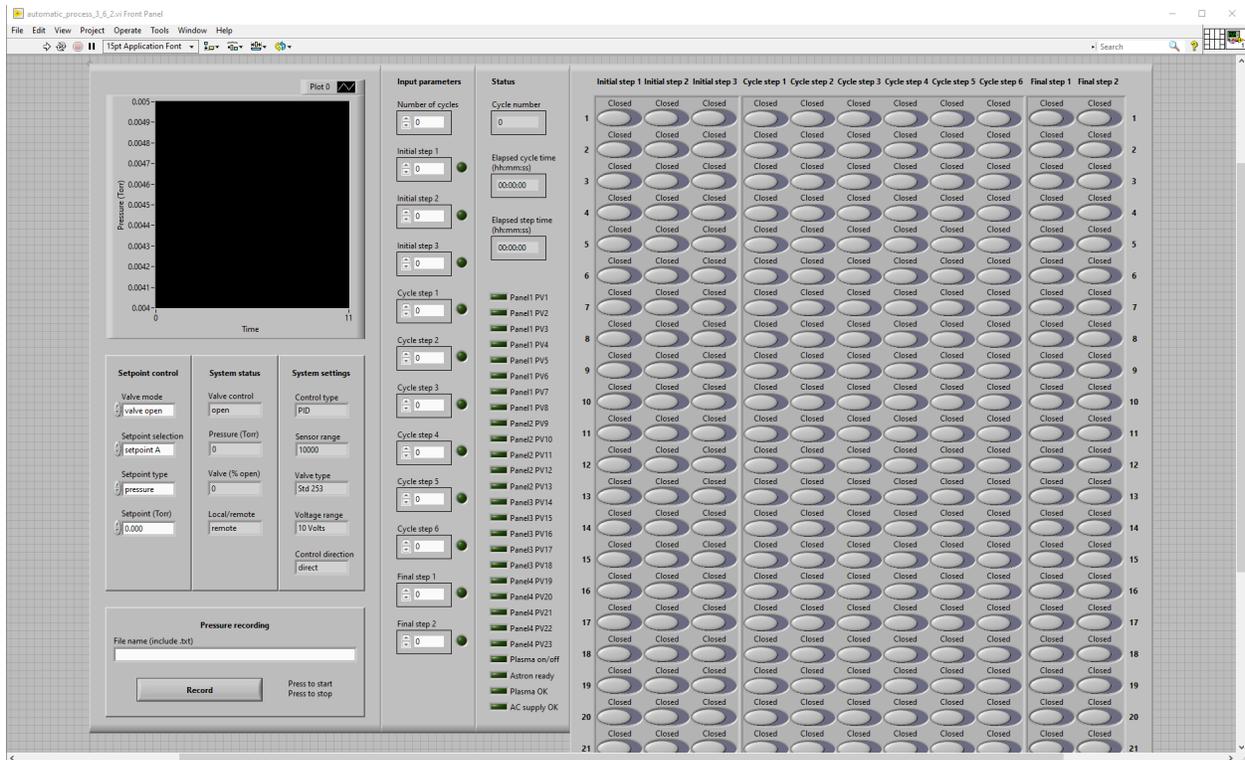
The automatic process programs (Appendix B Figure 127, Appendix B Figure 128, and Appendix B Figure 129) are used to display pressure and manipulate solenoid channels (valve positions, plasma generator on/off) automatically according to a timed process. The timed process comprises three phases: initial, cycle, and final. The initial phase is completed one time, the cycle phase is repeated a number of times determined by a user input, and the final phase is completed one time. The number of steps in each phase is indicated in the filename (e.g., automatic_process_3_6_2 has three initial steps, six cycle steps, and two final steps). The program interface comprises four panels: the left is for pressure display, the middle left is for inputting process parameters, the middle right is for status display, and the right is for solenoid channel control. When the program starts running, the pressure plot, the status of the throttle valve and Baratron settings, and the status of the DAQ channels update. Initial step 1 starts immediately and the elapsed step time starts counting.



Appendix B Figure 127: Screenshot of LabVIEW automatic_process_1_4_1 interface at startup



Appendix B Figure 128: Screenshot of LabVIEW automatic_process_1_4_1 interface at startup



Appendix B Figure 129: Screenshot of LabVIEW automatic_process_3_6_2 interface at startup

1. Pressure display

- a. The pressure can be controlled using this panel by following the descriptions below, but the pressure should already be at the desired setpoint when the automatic process is started (initial setup should be completed in the manual control program), so this panel is generally used only for display
- b. Either the manual control program or the automatic process program can be used to record pressure during an experiment, but using the manual control program is preferred in case the automatic program must be stopped and restarted during the experiment

- c. Plot 0
 - i. Shows the pressure measured by the Baratron as a function of time
- d. Setpoint control
 - i. Valve mode
 - 1. Update the throttle valve control mode by selecting an option from the dropdown (valve open, valve close)
 - ii. Setpoint selection
 - 1. Update the setpoint by selecting an option from the dropdown (A, B, C, D, E)
 - iii. Setpoint type
 - 1. After selecting a setpoint to edit, update whether the setpoint controls the throttle valve position or the Baratron pressure by selecting an option from the dropdown (position, pressure)
 - iv. Setpoint (Torr)
 - 1. After selecting a setpoint to edit, update the setpoint by entering a value in the box
 - 2. If entering a pressure setpoint, enter a value in torr
 - 3. If entering a valve position setpoint, divide the percent open by 10 (e.g., for a valve position setpoint of 43.21% open, enter 4.321) and note that the units of Torr in the label are incorrect
- e. System status
 - i. Valve control

1. Displays the throttle valve control mode (open, close, setpoint)
 - ii. Pressure (Torr)
 1. Displays the pressure in torr
 - iii. Valve (% open)
 1. Displays the throttle valve position in percent
 - iv. Local / remote
 1. Displays whether the controller is being operated locally or remotely
 2. Remote operation must be used in combination with the LabVIEW program
- f. System settings
 - i. Control type
 1. Displays the type of control
 2. PID control is selected and this should not be changed
 - ii. Sensor range
 1. Displays the pressure range of the Baratron in millitorr
 2. The Baratron in use has a range of 10 Torr, so 10000 is selected and this should not be changed
 - iii. Valve type
 1. Displays the type of throttle valve, as defined by the manufacturer

- c. Cycle steps
 - i. Enter the time in seconds for each of the cycle steps
 - d. Final step(s)
 - i. Enter the time in seconds for each of the final steps
 - e. When a step is active, the indicator light next to the input box turns on
3. Status display
- a. Cycle number
 - i. Displays the current cycle number
 - ii. This value is zero during initial step(s)
 - b. Elapsed cycle time
 - i. Displays the time elapsed since the beginning of the cycle steps
 - ii. This value is zero during initial step(s) and does not increase during final step(s)
 - c. Elapsed step time
 - i. Displays the time elapsed since the beginning of the current step
 - d. DAQ channel indicators
 - i. When a channel is on, the indicator light next to the label turns on
4. Solenoid channel control
- a. Each step in the timed process is a column in the slide switch array
 - i. Valves P1–P23 correspond to numbers 1–23 on each side of the array
 - ii. Plasma on/off is channel 24

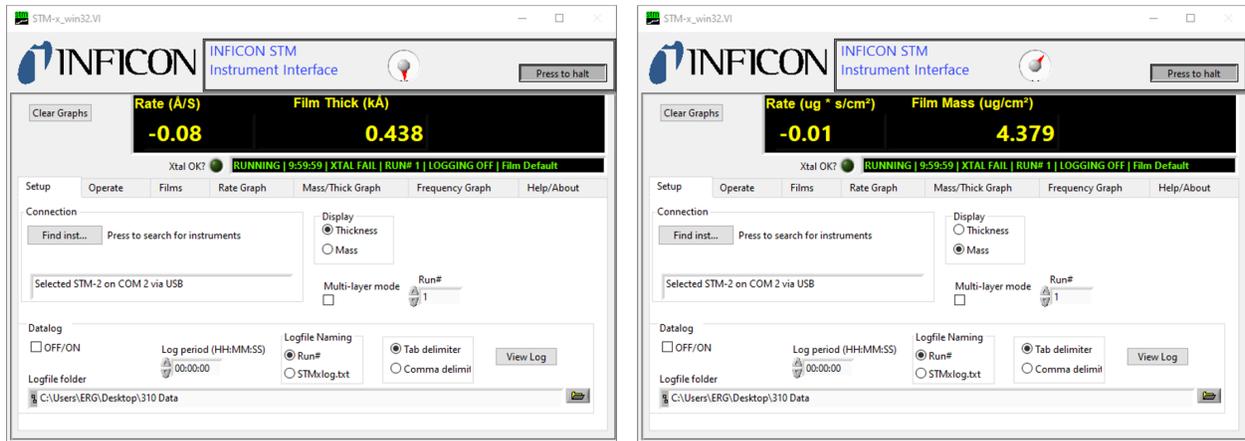
- b. Click the slide switches to choose a status for each valve, P1–P23 (left indicates closed, right indicates open), and for plasma on/off (left indicates off, right indicates on)
- c. The text above the slide switch updates when the slide switch is moved (closed, open)
- d. The background of each slide switch is grey when in the closed position and black when in the open position

STM-2

The STM-2 program is used to record data from the QCM. The following description focuses only on changes made to the software startup settings for routine data recording, and the STM-2 operating manual should be reviewed for a detailed description of the functionality of each tab.

1. Interface header (Appendix B Figure 130)
 - a. Clear Graphs
 - i. Click to clear Rate, Mass/Thick, and Frequency graphs
 - b. Film Thick (kÅ) [Film Mass (ug/cm²)]
 - i. Displays the calculated film thickness [mass] since the film thickness [mass] was last reset, based on the change in frequency and properties of the active film
 - ii. Reset the film thickness [mass] in the Operate tab
 - c. Xtal OK?
 - i. The indicator light is off when there is no crystal in use or when a crystal fail occurs
 - ii. The indicator light turns on when a good crystal is in use
 - d. Timer
 - i. Displays the elapsed time since the timer was reset
 - ii. The maximum time allowed is 9:59:59 (hh:mm:ss)
 - iii. Reset the timer in the Operate tab

- e. XTAL FAIL or Life %
 - i. Displays XTAL FAIL when a crystal fail occurs
 - ii. Displays the percentage of crystal life remaining when a good crystal is in use
- f. RUN#
 - i. Displays the active run number
 - ii. The run number is changed in the Setup tab
- g. LOGGING OFF or LOGGING ON
 - i. Displays whether the program is recording data or not
 - ii. Data logging is turned on and off in the Setup tab
- h. Film
 - i. Displays the active film name
 - ii. The active film is changed in the Operate tab
- i. Press to halt
 - i. Click to exit the program



Appendix B Figure 130: STM-2 screenshot 1, Setup tab (left: thickness display option, right: mass display option)

2. Setup (Appendix B Figure 130)

a. Display

- i. Select whether film thickness or mass data is displayed in the interface header and on the Mass/Thick graph

b. Run#

- i. Change the run number by clicking the up and down arrows or by entering a number in the box
- ii. The updated run number is displayed in the interface header

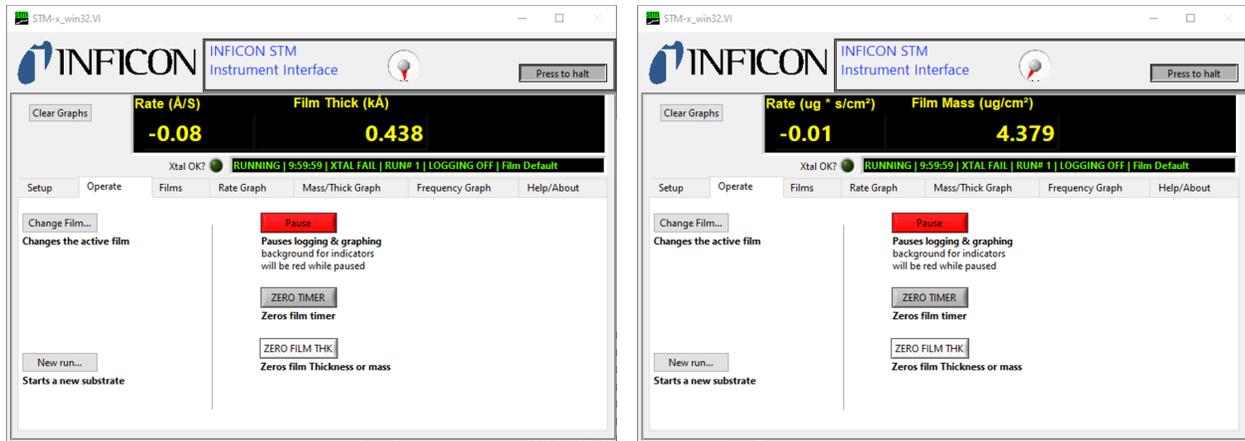
c. Datalog OFF/ON

- i. Turn data logging on or off by clicking in the box
- ii. The data logging status is displayed in the interface header

d. Log period

- i. Change the log period by clicking the up and down arrows or by entering a number in the box

- e. Logfile folder
 - i. Change the logfile folder by clicking the folder icon on the right and selecting a folder from the directory
3. Operate (Appendix B Figure 131)
- a. Change Film
 - i. Click to change the active film
 - ii. Choose the film that is deposited based on the precursor and co-reactant used
 - iii. The active film is displayed in the interface header
 - b. ZERO TIMER
 - i. Click to reset the timer to zero
 - ii. The timer is displayed in the interface header
 - c. ZERO FILM THK
 - i. Click to reset the film thickness (or mass) to zero
 - ii. The film thickness (or mass) is displayed in the interface header



Appendix B Figure 131: STM-2 screenshot 2, Operate tab (left: thickness display option, right: mass display option)

4. Films (Appendix B Figure 132)

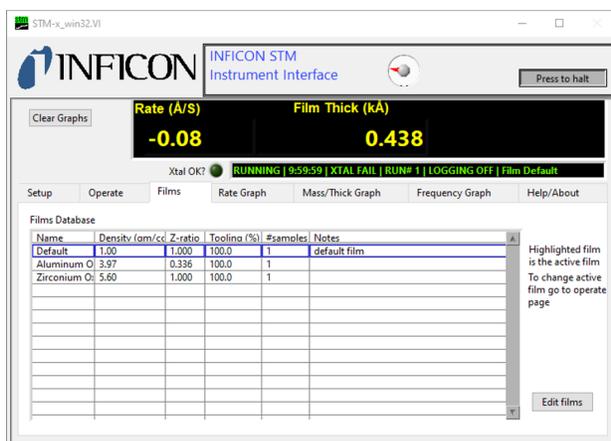
a. Films Database

- i. Displays a list of film options

b. Edit films

- i. Click to add a new film or edit properties for existing films

- c. The properties of the active film are used to calculate the thickness and mass data displayed in the interface header and on the Mass/Thick Graph from the change in frequency



Appendix B Figure 132: STM-2 screenshot 3, Films tab (left: thickness display option, right: mass display option)

5. Rate Graph (Appendix B Figure 133)

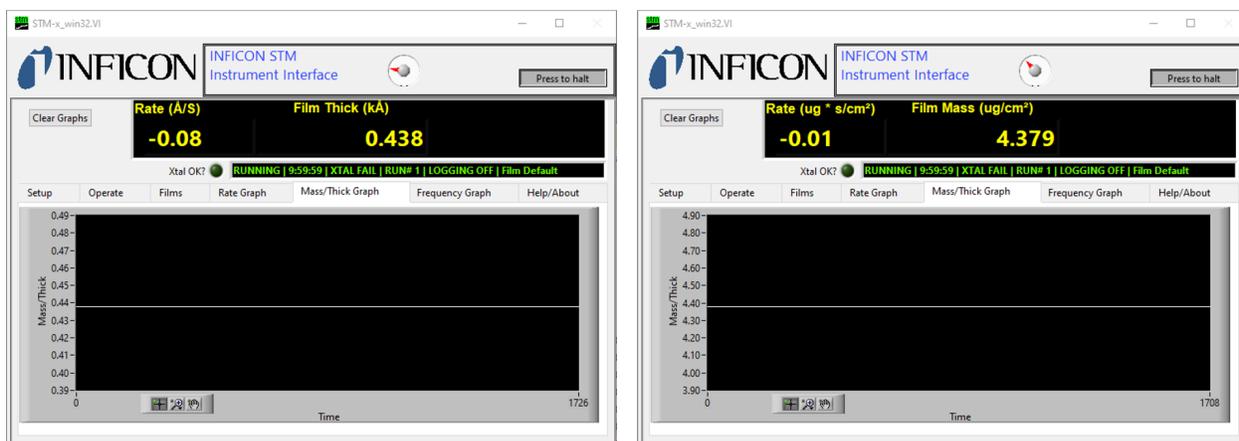
- a. Not needed for routine data collection



Appendix B Figure 133: STM-2 screenshot 4, Rate Graph tab (left: thickness display option, right: mass display option)

6. Mass/Thick Graph (Appendix B Figure 134)

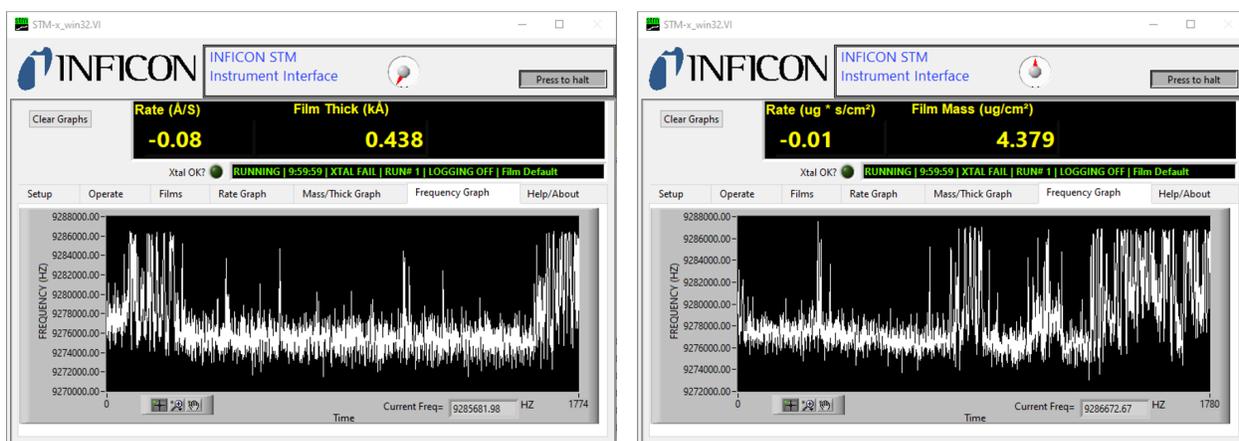
- a. Not needed for routine data collection



Appendix B Figure 134: STM-2 screenshot 5, Mass/Thick Graph tab (left: thickness display option, right: mass display option)

7. Frequency Graph (Appendix B Figure 135)

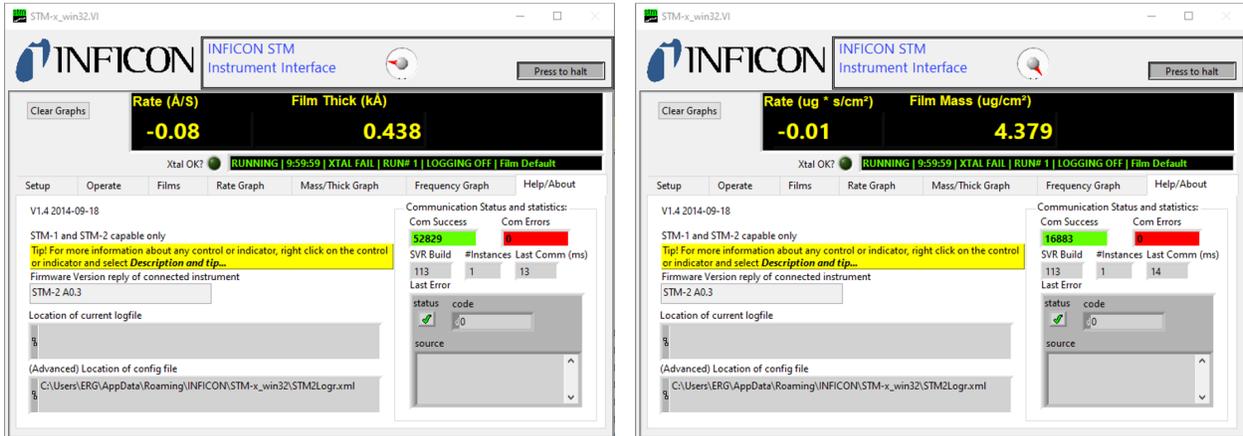
- a. Monitor the experiment in real time by observing the change in frequency as each reactant is introduced
- b. By the Sauerbrey equation, frequency has an inverse relationship with thickness, so a decrease in frequency corresponds to an increase in thickness



Appendix B Figure 135: STM-2 screenshot 6, Frequency Graph tab (left: thickness display option, right: mass display option)

8. Help/About (Appendix B Figure 136)

a. Not needed for routine data collection



Appendix B Figure 136: STM-2 screenshot 7, Help/About tab (left: thickness display option, right: mass display option)

Excel Visual Basic for Applications (VBA)

VBA is the programming language used in Excel and other Microsoft Office programs to automate tasks in the form of macros. In the Visual Basic window, which is accessed through the Developer tab in Excel, modules can be added and populated with subs, which run as macros. The modules must be located in the PERSONAL VBAProject for the computer so they can be accessed through all open Excel workbooks.

There are twelve macros used to analyze frequency data collected by the STM-2 software and pressure data collected through LabVIEW, and each should be contained in its own module. The naming convention of the modules explains the function of each macro and when it should be used, based on the way the data was collected in the STM-2 software or LabVIEW.

Modules 1–4 reference a text file containing a list of common thin film types and their densities. The information in the text file is imported into Excel, the user chooses a film type, and the density is used to calculate the thickness using the Sauerbrey equation. The text file must be named “density_list_Sauerbrey_coefficient.txt” and must have a local path on the computer so it can be read by the macros during their operation. After the file is placed in a permanent location, the file pathname must be updated in modules 1–4 (see the “Update path for density list” note below where the variables are declared in each module). The text file can be updated with new thin film types on additional lines

as necessary, using a tab as the delimiter between columns. The text file also contains the value of α_{AT} , which is the Sauerbrey constant for AT-cut quartz.

The contents of the modules and the text file are in Appendix E. The modules were written for use on a Mac, so some modifications to the code would be necessary to run them on a Windows computer.

1. Module 1: QCM_T_thickness_milliseconds
 - a. QCM: analyzes data from the QCM
 - b. T: thickness display option was chosen in the STM-2 Setup tab
 - c. thickness: plots surface density vs. time and thickness vs. time
 - d. milliseconds: log period 00:00:00 was chosen in the STM-2 Setup tab
2. Module 2: QCM_T_thickness_seconds
 - a. QCM: analyzes data from the QCM
 - b. T: thickness display option was chosen in the STM-2 Setup tab
 - c. thickness: plots surface density vs. time and thickness vs. time
 - d. seconds: log period 00:00:01 or greater was chosen in the STM-2 Setup tab
3. Module 3: QCM_M_thickness_milliseconds
 - a. QCM: analyzes data from the QCM
 - b. M: mass display option was chosen in the STM-2 Setup tab
 - c. thickness: plots surface density vs. time and thickness vs. time
 - d. milliseconds: log period 00:00:00 was chosen in the STM-2 Setup tab
4. Module 4: QCM_M_thickness_seconds

- a. QCM: analyzes data from the QCM
 - b. M: mass display option was chosen in the STM-2 Setup tab
 - c. thickness: plots surface density vs. time and thickness vs. time
 - d. seconds: log period 00:00:01 or greater was chosen in the STM-2 Setup tab
5. Module 5: QCM_thickness_continue
- a. QCM: analyzes data from the QCM
 - b. thickness_continue: this macro is incorporated into all macros that plot thickness vs. time
6. Module 6: QCM_T_density_milliseconds
- a. QCM: analyzes data from the QCM
 - b. T: thickness display option was chosen in the STM-2 Setup tab
 - c. density: plots frequency vs. time and surface density vs. time
 - d. milliseconds: log period 00:00:00 was chosen in the STM-2 Setup tab
7. Module 7: QCM_T_density_seconds
- a. QCM: analyzes data from the QCM
 - b. T: thickness display option was chosen in the STM-2 Setup tab
 - c. density: plots frequency vs. time and surface density vs. time
 - d. seconds: log period 00:00:01 or greater was chosen in the STM-2 Setup tab
8. Module 8: QCM_M_density_milliseconds
- a. QCM: analyzes data from the QCM
 - b. M: mass display option was chosen in the STM-2 Setup tab
 - c. density: plots frequency vs. time and surface density vs. time
 - d. milliseconds: log period 00:00:00 was chosen in the STM-2 Setup tab

9. Module 9: QCM_M_density_seconds
 - a. QCM: analyzes data from the QCM
 - b. M: mass display option was chosen in the STM-2 Setup tab
 - c. density: plots frequency vs. time and surface density vs. time
 - d. seconds: log period 00:00:01 or greater was chosen in the STM-2 Setup tab
10. Module 10: QCM_thickness_cycles_density
 - a. QCM: analyzes data from the QCM
 - b. thickness_cycles_density: after running a macro that plots surface density vs. time and thickness vs. time, plots individual cycles of surface density vs. time
11. Module 11: QCM_thickness_cycles_thickness
 - a. QCM: analyzes data from the QCM
 - b. thickness_cycles_thickness: after running a macro that plots surface density vs. time and thickness vs. time, plots individual cycles of thickness vs. time
12. Module 12: QCM_pressure
 - a. QCM: analyzes data from the QCM
 - b. pressure: plots pressure and valve position vs. time

The code for all of the macros is annotated (text preceded by an apostrophe) to explain all of the processes in detail, but a general description is below.

1. Modules 1–4
 - a. Copies text file with data from STM-2 software

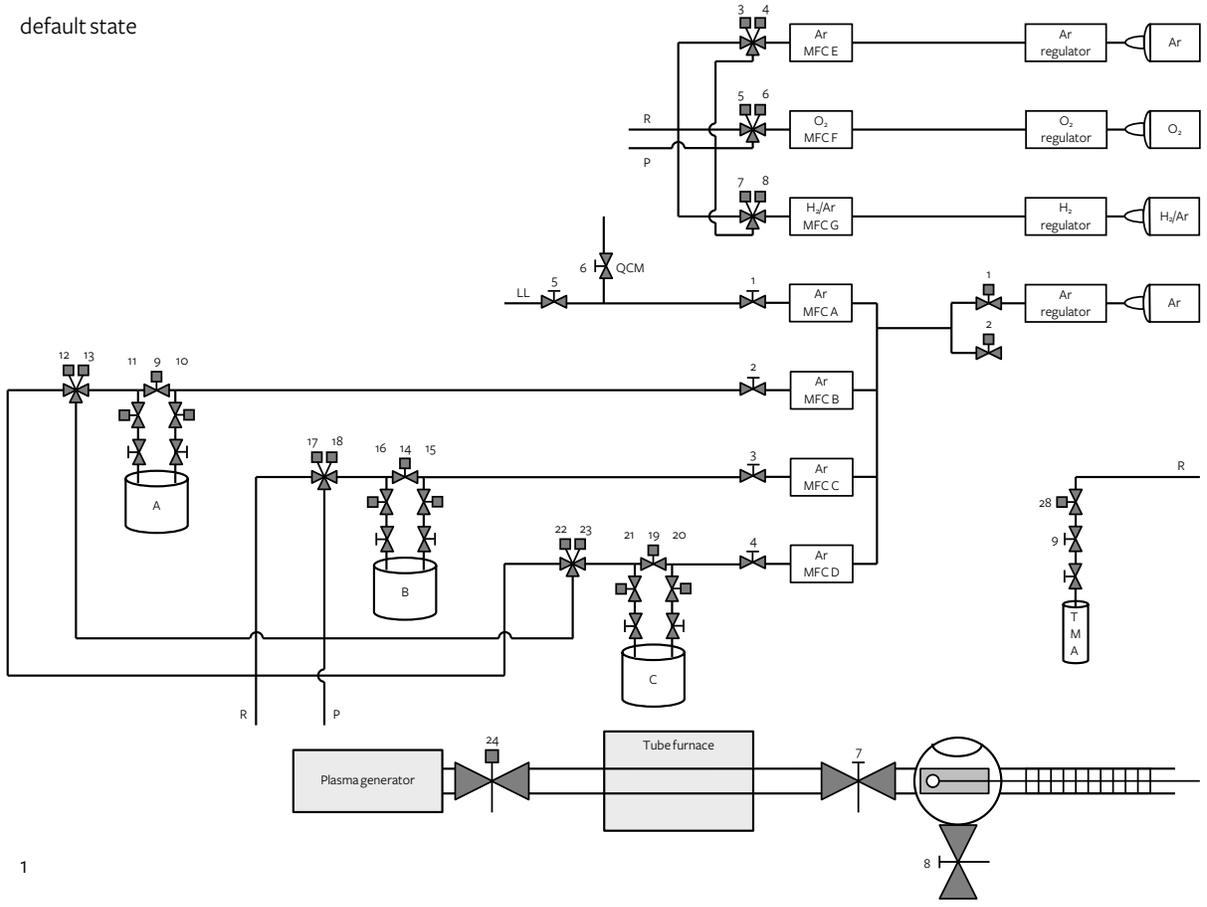
- i. Contains: Timestamp, StatusLine, Rate, Film Thickness/Mass, Substrate Thickness/Mass, Frequency
 - b. Uses timestamp data to calculate seconds elapsed relative to a time zero (determined by user input in cell N11 after completion of macro)
 - c. Calculates surface density at all times from frequency change relative to time zero
 - d. Imports text file with list of possible thin film types (can be updated) and asks for user input to specify thin film type
 - i. Contains: Film, Density
 - ii. Also contains value of α_{AT} (for use in Sauerbrey equation) for reference, but it is not imported into Excel
 - e. Displays a “Continue” button, to be pressed after choosing a thin film type, that runs the macro in Module 5
2. Module 5
- a. Calculates thickness at all times from thin film type and frequency change relative to time zero
 - b. Plots surface density vs. time and thickness vs. time
3. Modules 6–9
- a. Copies text file with data from STM-2 software
 - i. Contains: Timestamp, StatusLine, Rate, Film Thickness/Mass, Substrate Thickness/Mass, Frequency
 - b. Uses timestamp data to calculate seconds elapsed relative to a time zero (determined by user input in cell M5 after completion of macro)

- c. Calculates surface density at all times from frequency change relative to time zero
 - d. Plots frequency vs. time and surface density vs. time
4. Modules 10–11
- a. Asks for numerical input for number of steps in the sequence
 - i. Example 1: an ALD experiment where each cycle comprises 5 seconds precursor|10 seconds purge|5 seconds co-reactant|10 seconds purge has four steps
 - ii. Example 2: an ALD experiment where each cycle comprises 5 seconds co-adsorbate|5 seconds co-adsorbate and precursor|5 seconds co-adsorbate|10 seconds purge|5 seconds co-reactant|10 seconds purge has six steps
 - b. Asks for numerical inputs for time of each step in the sequence
 - i. Example 1: based on first response, the macro will ask for four inputs, and the responses would be 5, 10, 5, 10
 - ii. Example 2: based on first response, the macro will ask for six inputs, and the responses would be 5, 5, 5, 10, 5, 10
 - c. Asks for numerical input for number of cycles to analyze
 - i. Example 1: the experiment was ten cycles, and individual plots are desired for all cycles, so the response would be 10
 - ii. Example 2: the experiment was twenty cycles, but individual plots are desired only for the first five cycles, so the response would be 5

- iii. Note: the size of the Excel file increases greatly with the addition of many plots
 - d. Plots surface density vs. time or thickness vs. time for individual cycles, including indicator lines for each step
- 5. Module 12
 - a. Copies text file with data from LabVIEW (recorded through the manual_control or automatic_process LabVIEW program)
 - b. Uses timestamp data to calculate seconds elapsed relative to a time zero (assumed to be the first row of data)
 - c. Plots pressure and valve position vs. time (one plot with pressure on y1 and valve position on y2)

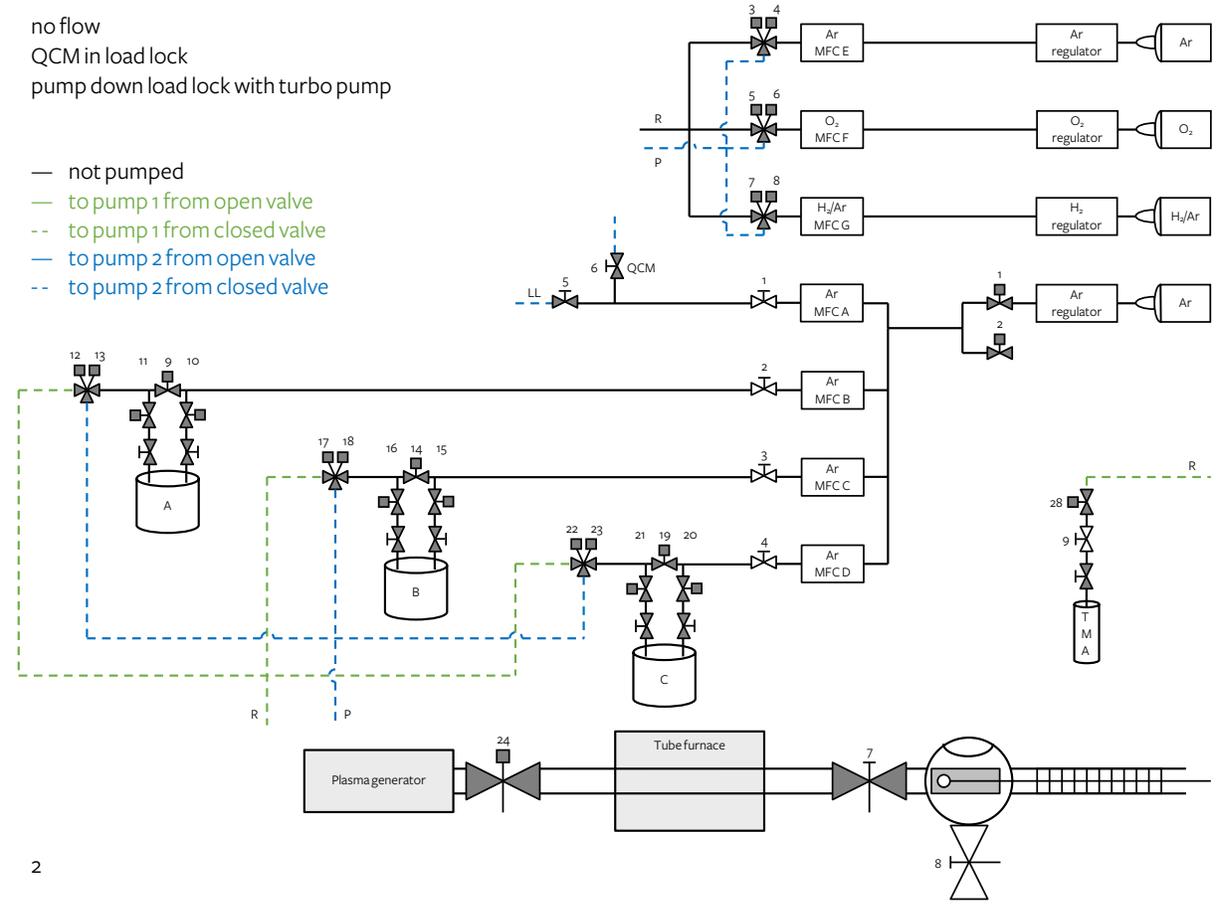
Appendix C: Modified piping and instrumentation diagram for example experimental process

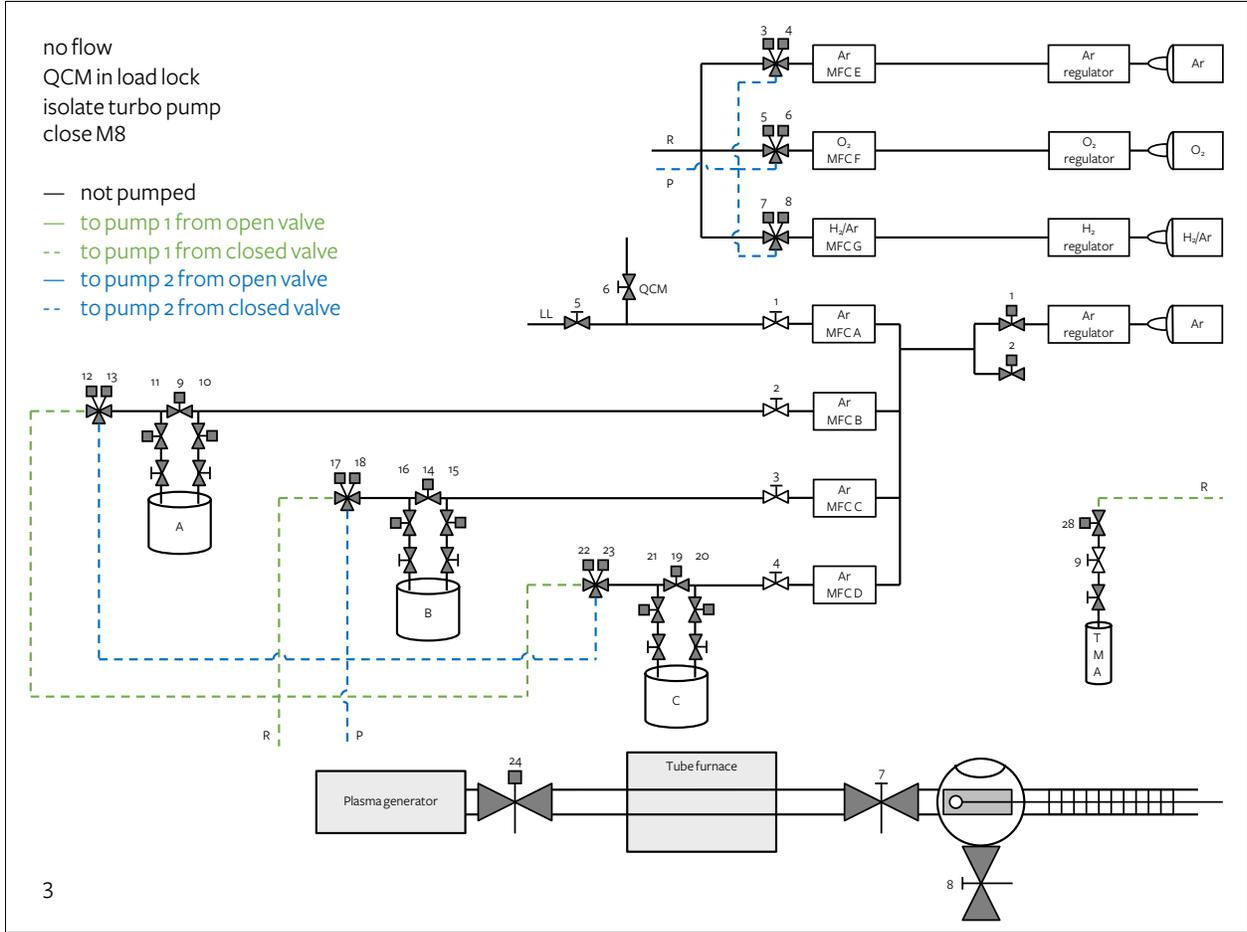
default state



no flow
 QCM in load lock
 pump down load lock with turbo pump

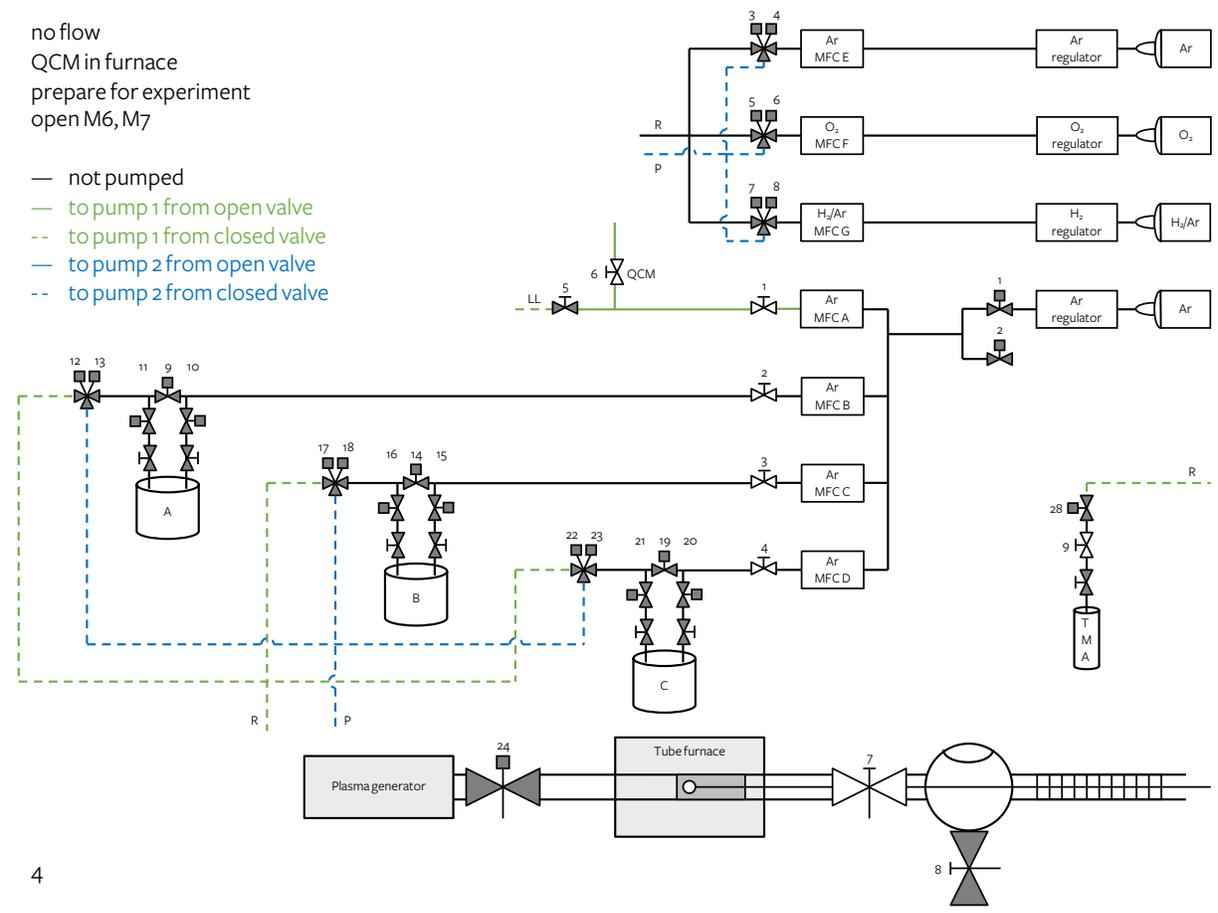
- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve





no flow
 QCM in furnace
 prepare for experiment
 open M6, M7

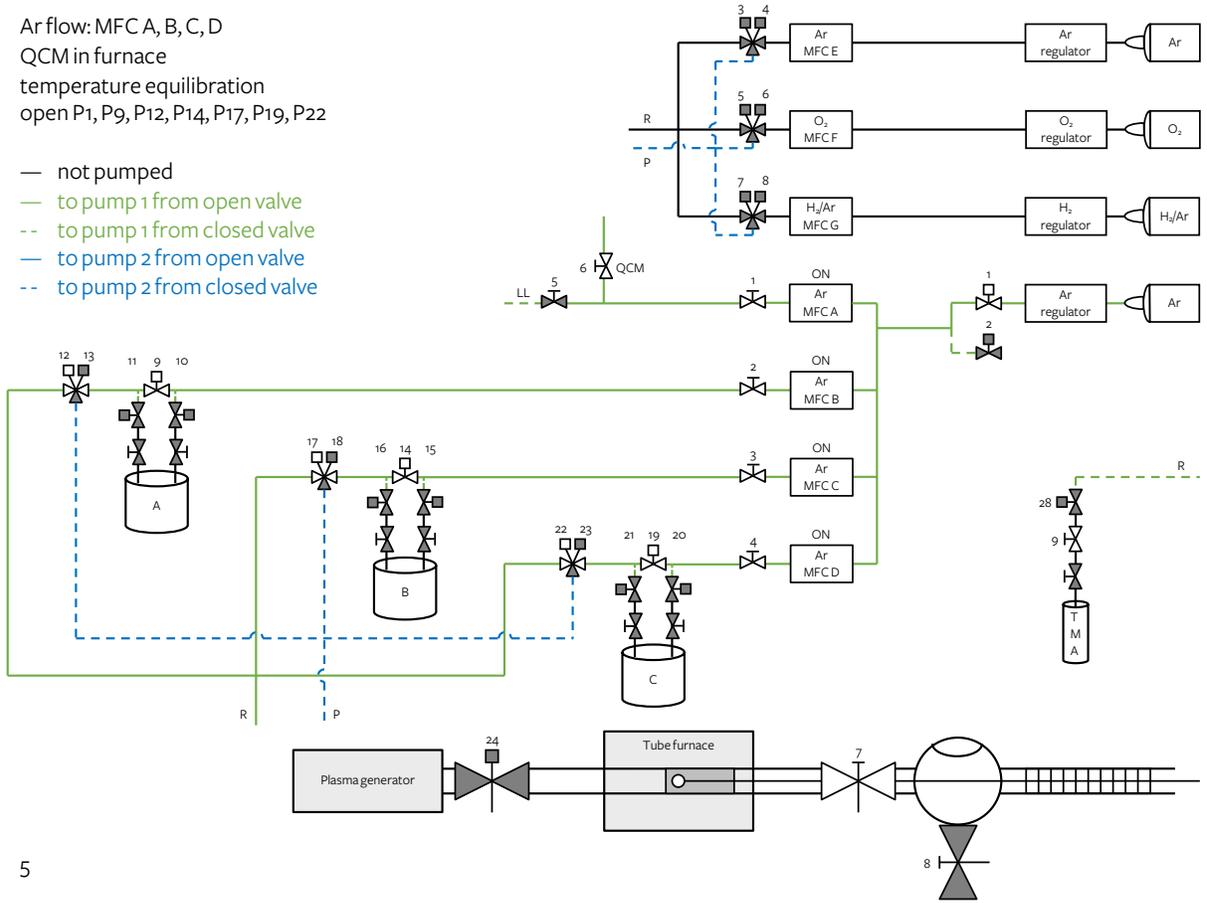
- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



4

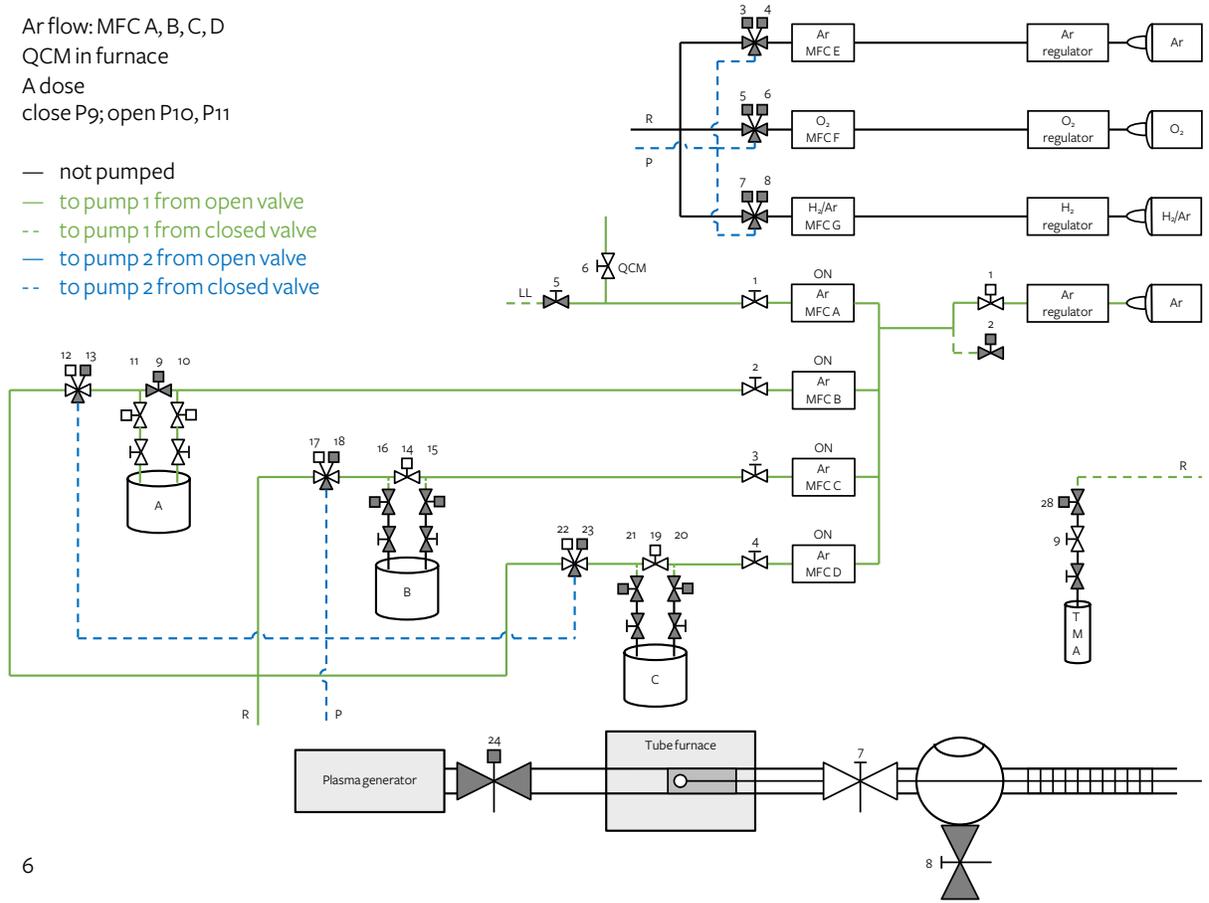
Ar flow: MFC A, B, C, D
 QCM in furnace
 temperature equilibration
 open P1, P9, P12, P14, P17, P19, P22

- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



Ar flow: MFC A, B, C, D
 QCM in furnace
 A dose
 close P9; open P10, P11

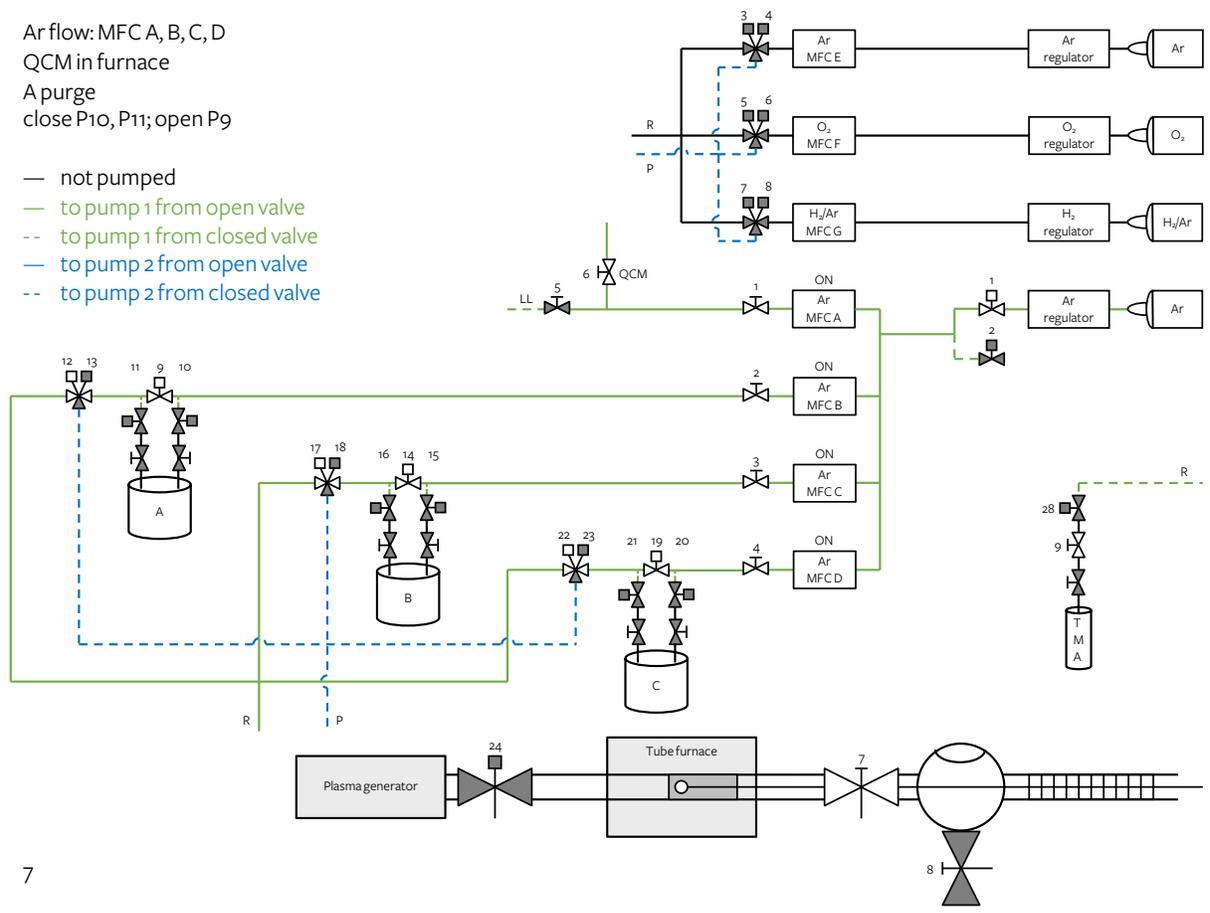
- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



6

Ar flow: MFC A, B, C, D
 QCM in furnace
 A purge
 close P10, P11; open P9

- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



7

Ar flow: MFC A, B, C, D

QCM in furnace

B dose

close P14; open P15, P16

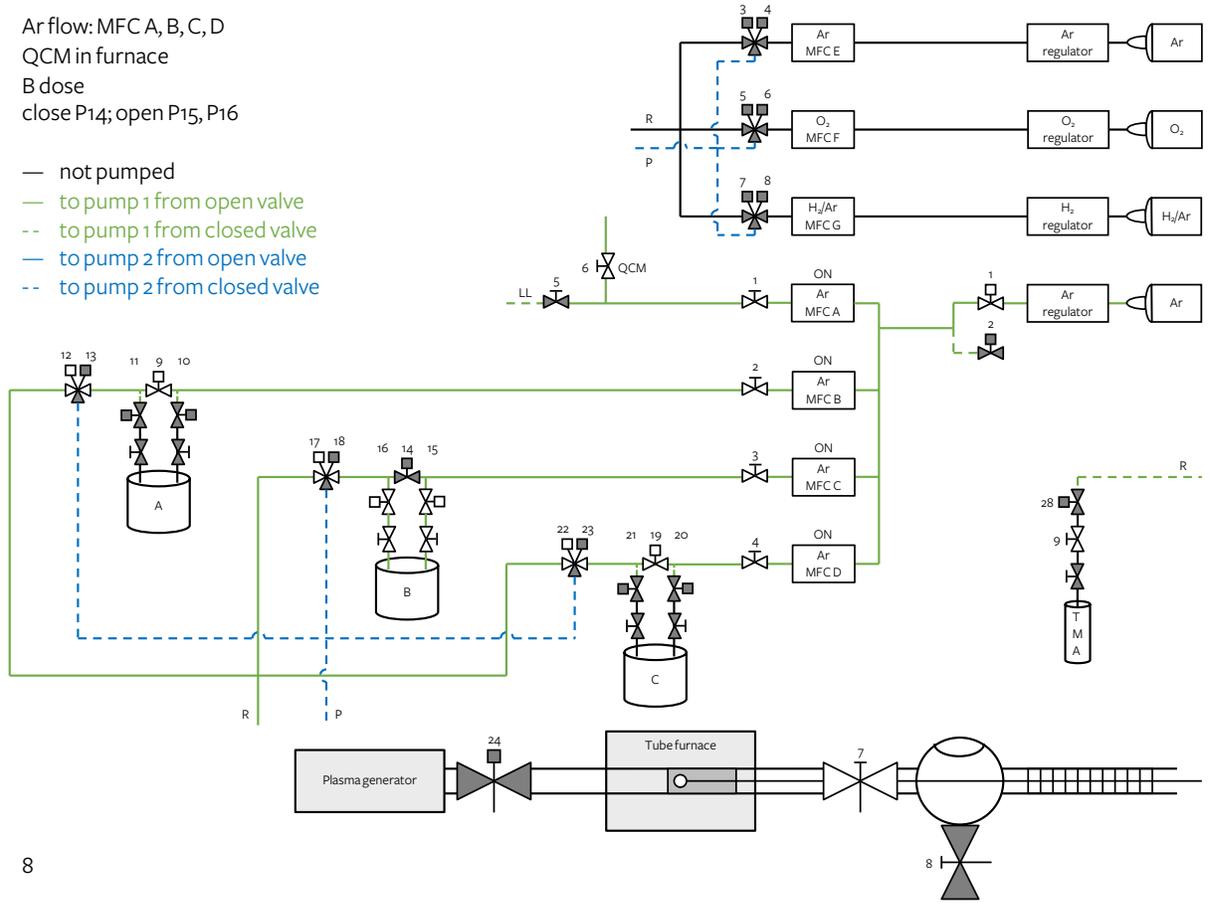
— not pumped

— to pump 1 from open valve

-- to pump 1 from closed valve

— to pump 2 from open valve

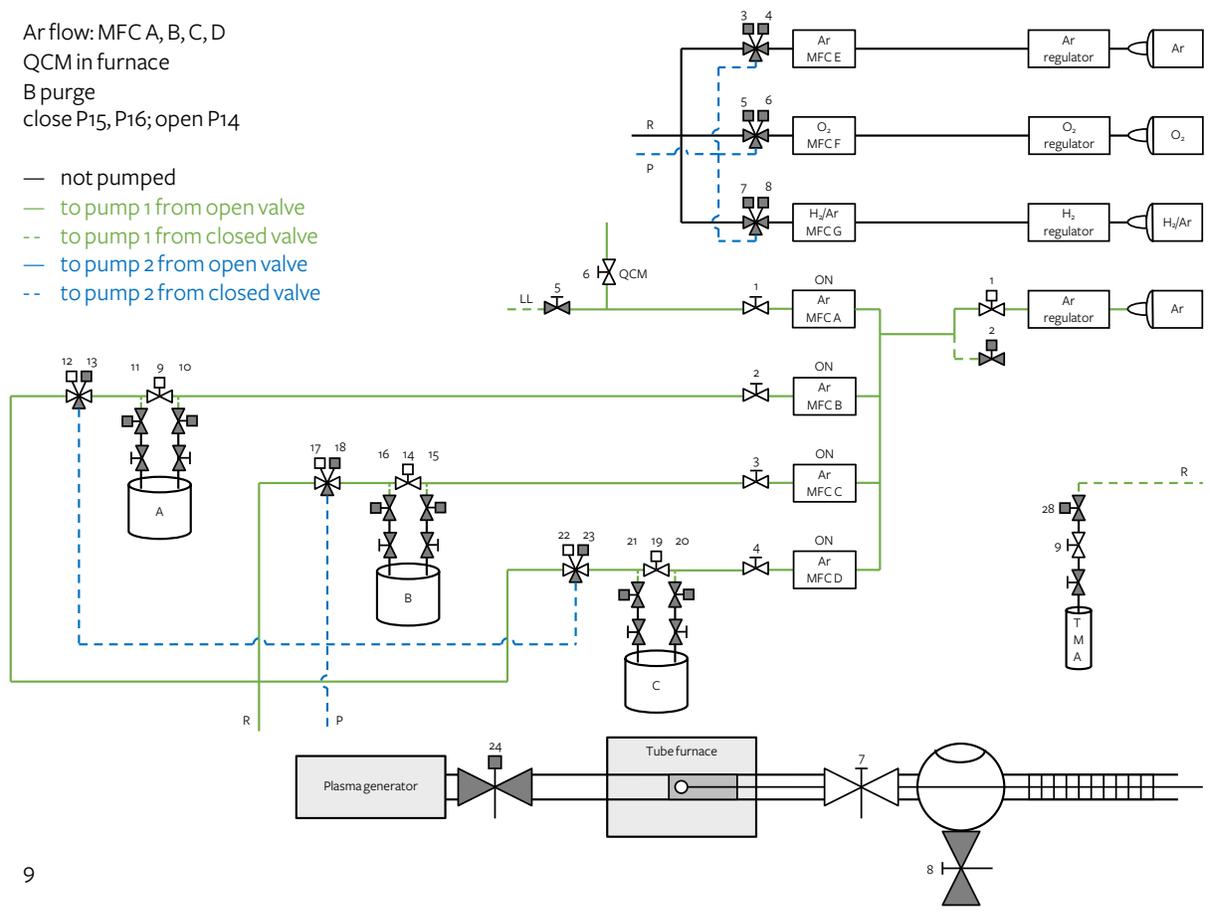
-- to pump 2 from closed valve



8

Ar flow: MFC A, B, C, D
 QCM in furnace
 B purge
 close P15, P16; open P14

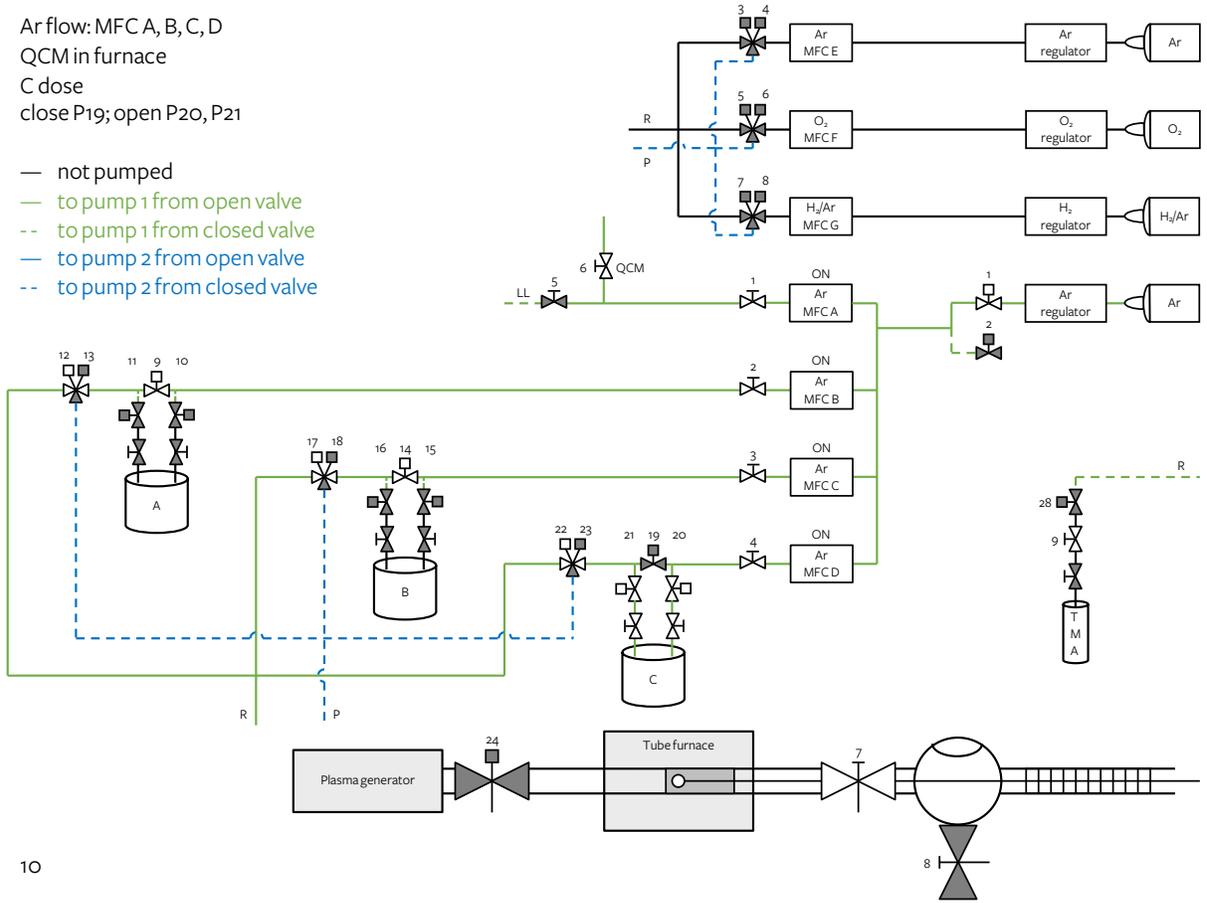
- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



9

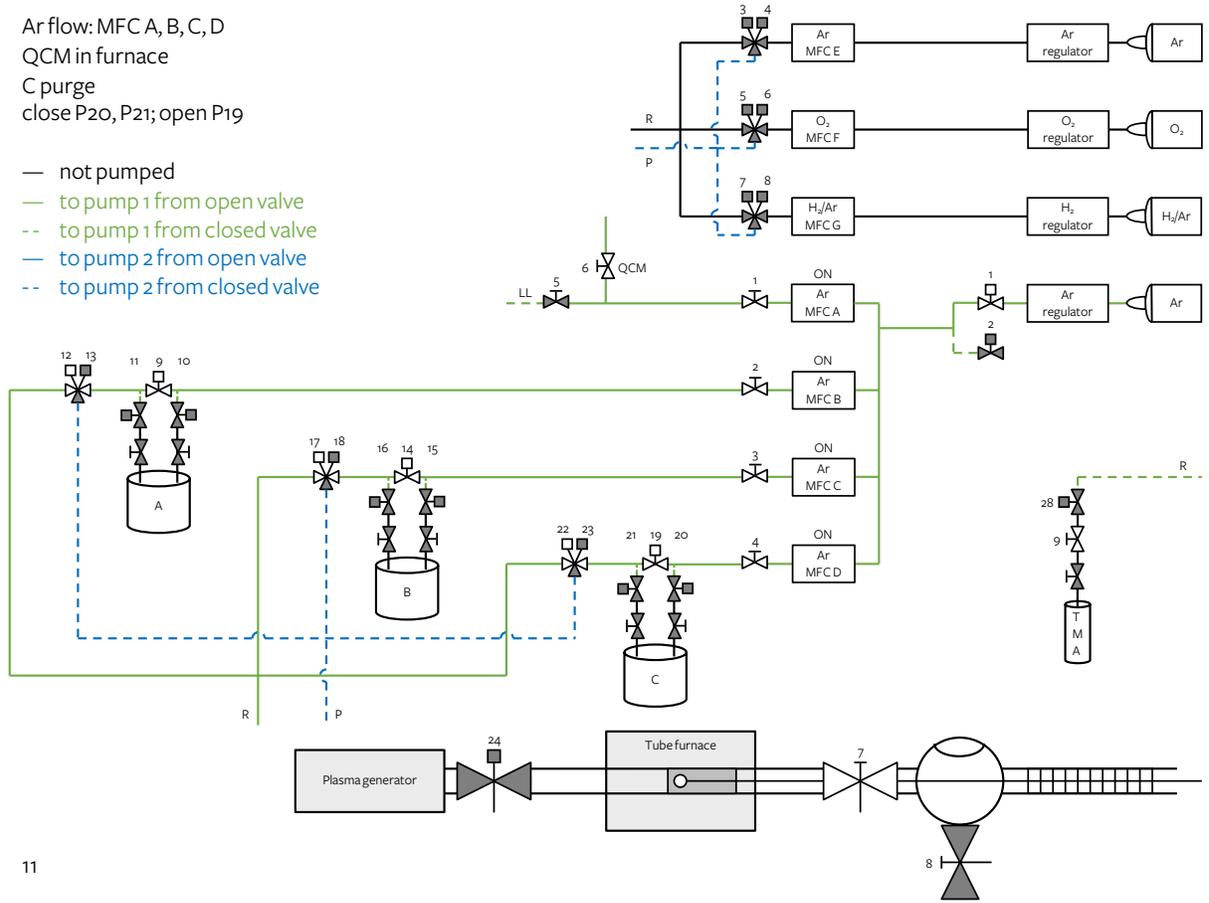
Ar flow: MFC A, B, C, D
 QCM in furnace
 C dose
 close P19; open P20, P21

- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



Ar flow: MFC A, B, C, D
 QCM in furnace
 C purge
 close P20, P21; open P19

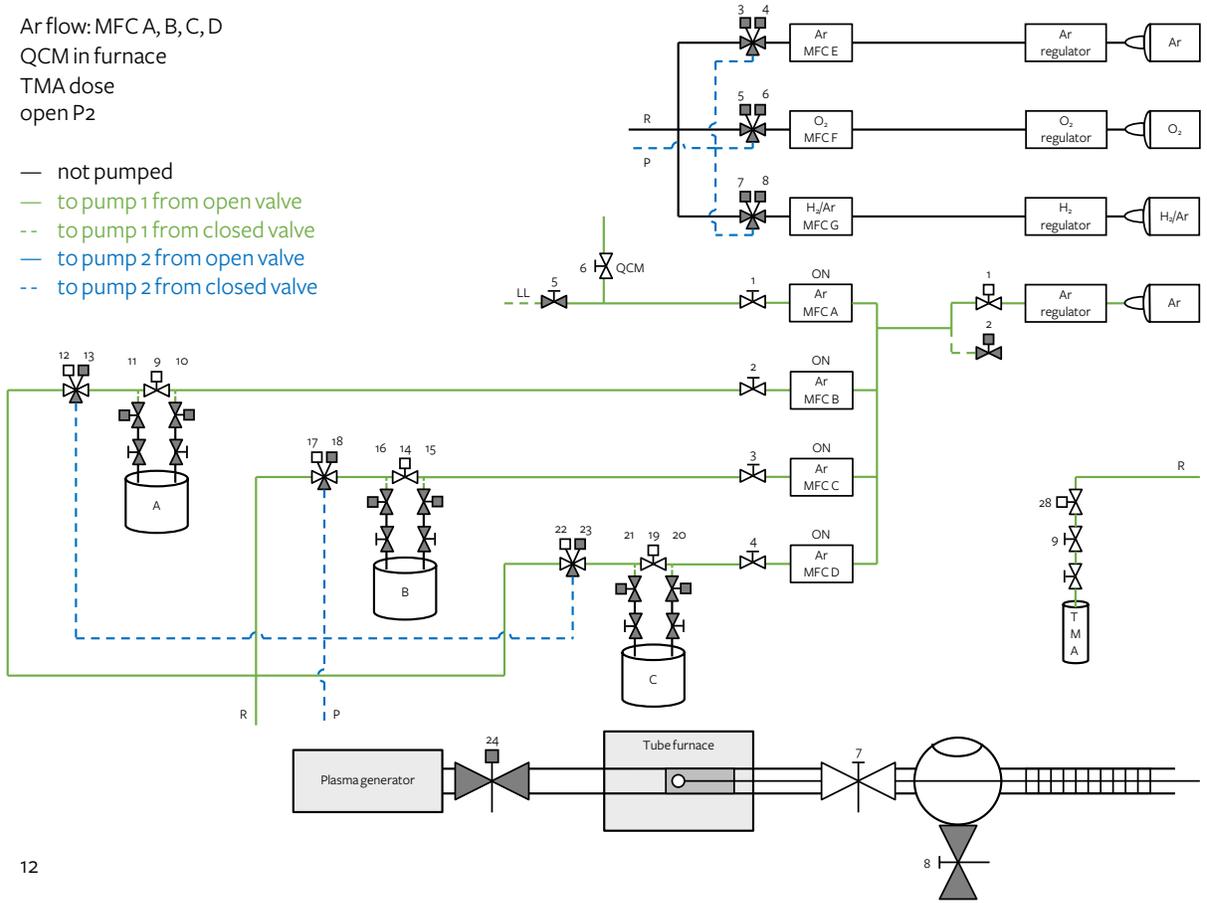
- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- - to pump 2 from open valve
- - to pump 2 from closed valve



11

Ar flow: MFC A, B, C, D
 QCM in furnace
 TMA dose
 open P2

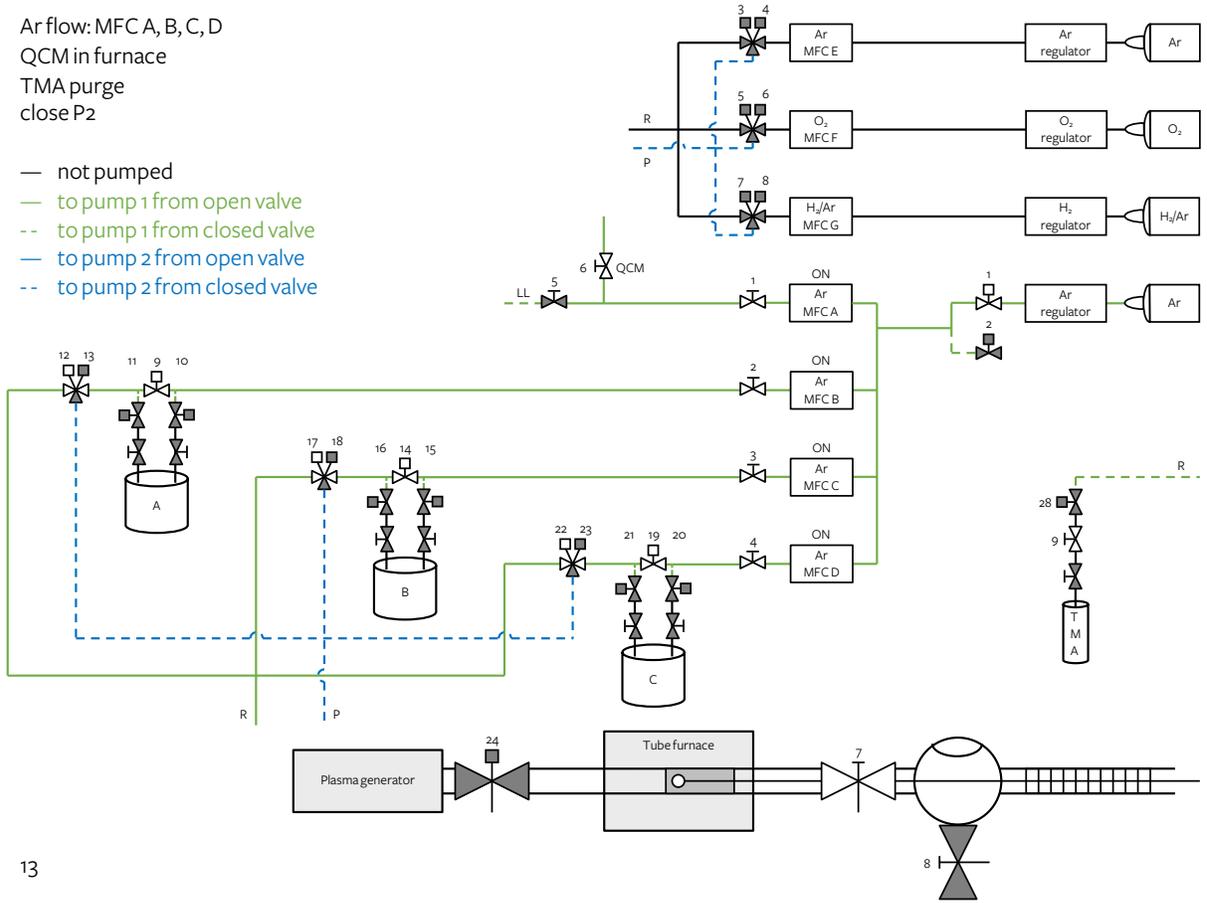
- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



12

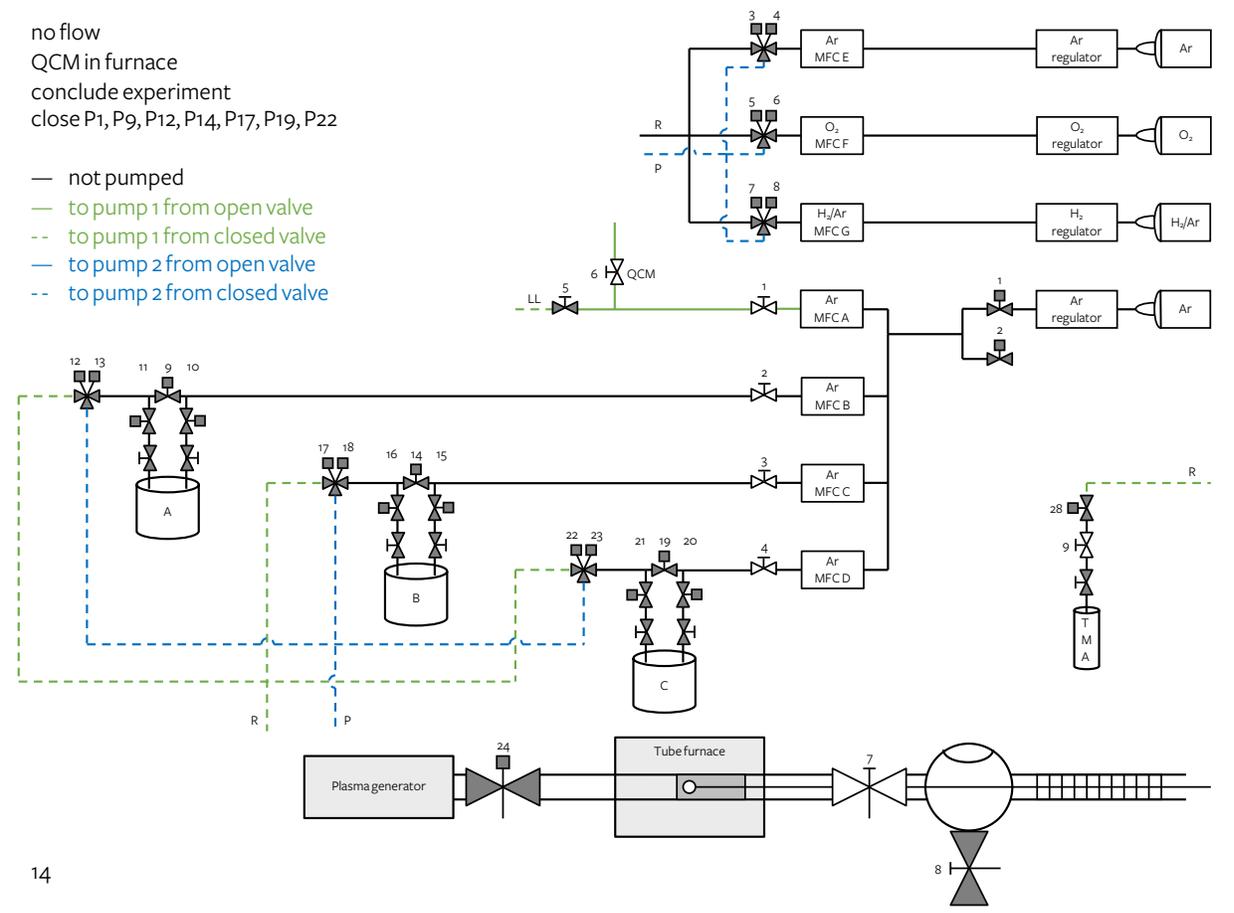
Ar flow: MFC A, B, C, D
 QCM in furnace
 TMA purge
 close P2

- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



no flow
 QCM in furnace
 conclude experiment
 close P1, P9, P12, P14, P17, P19, P22

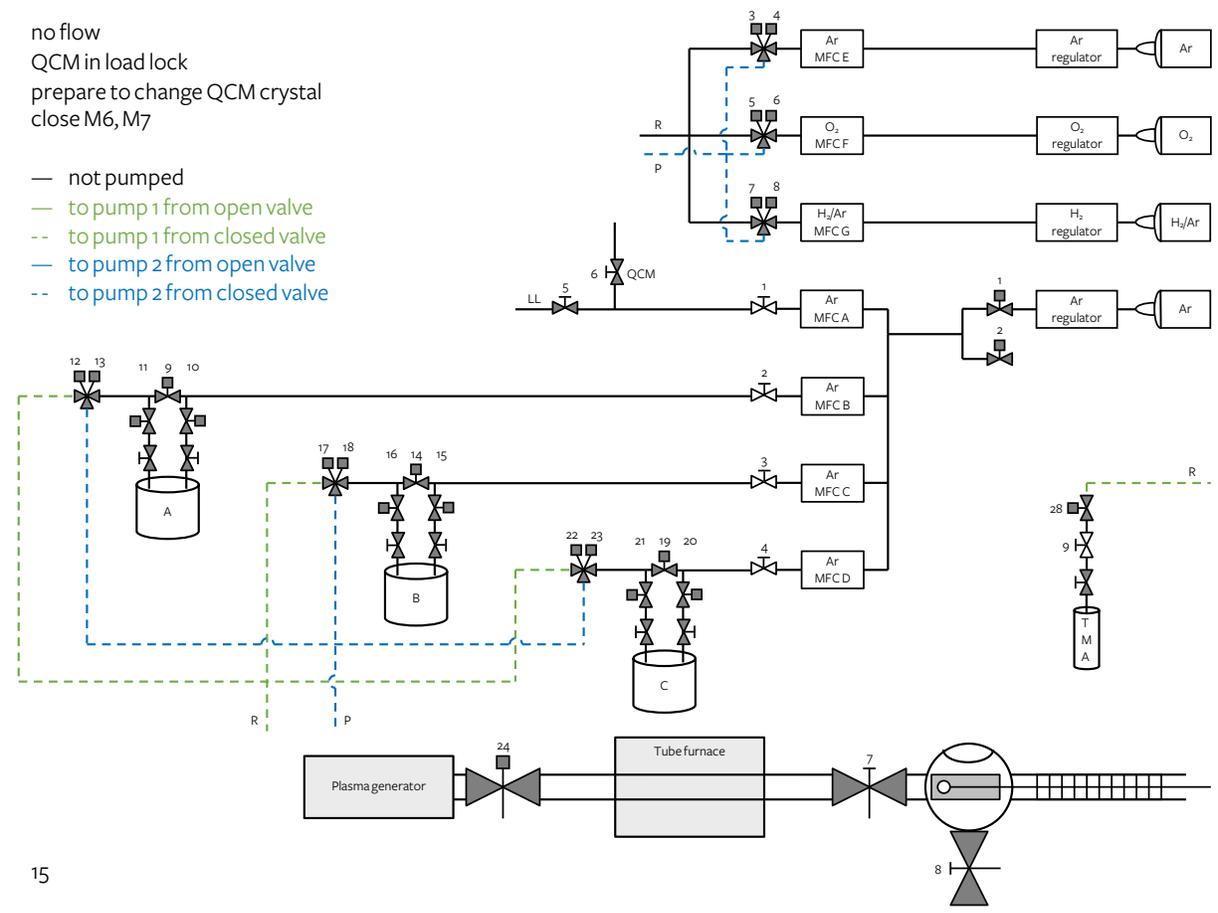
- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



14

no flow
 QCM in load lock
 prepare to change QCM crystal
 close M6, M7

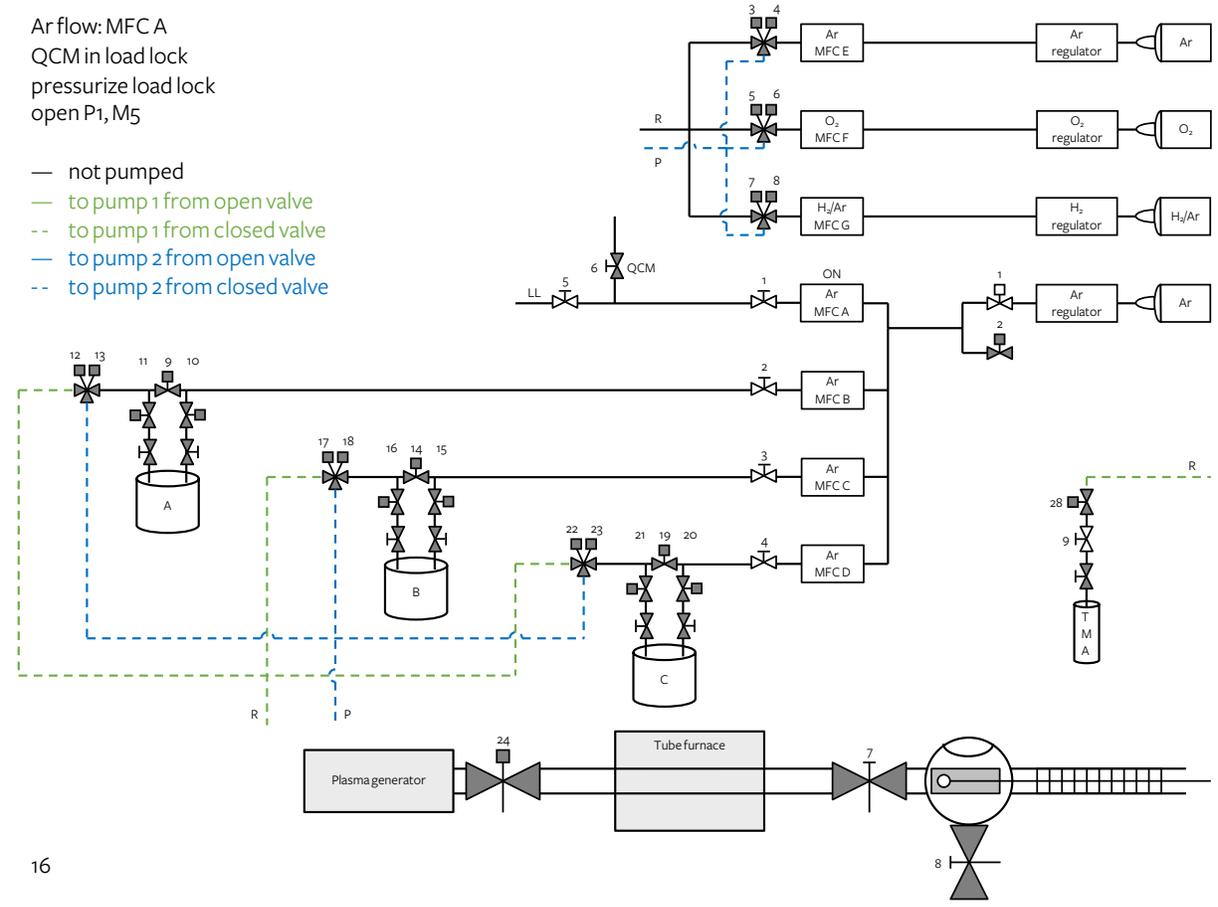
- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



15

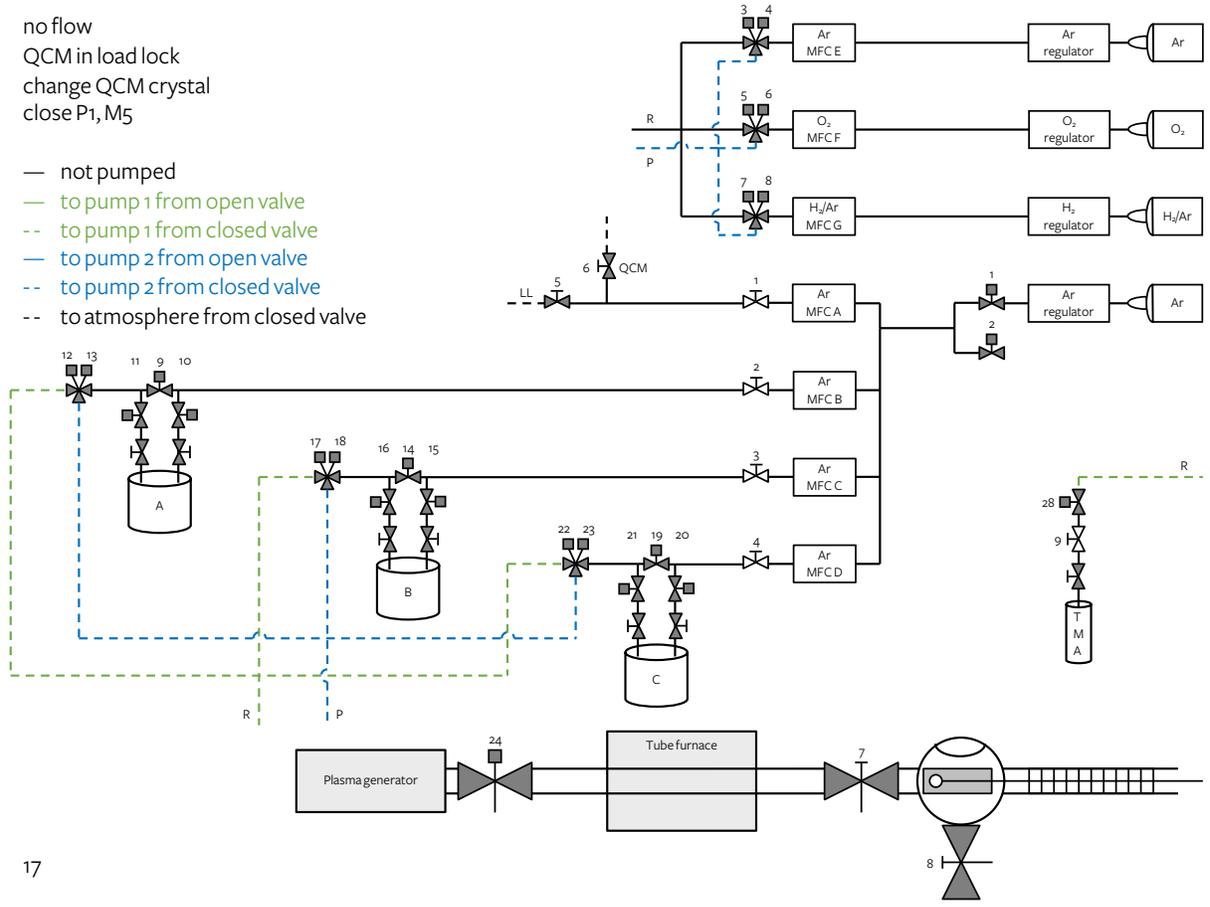
Ar flow: MFC A
 QCM in load lock
 pressurize load lock
 open P1, M5

- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



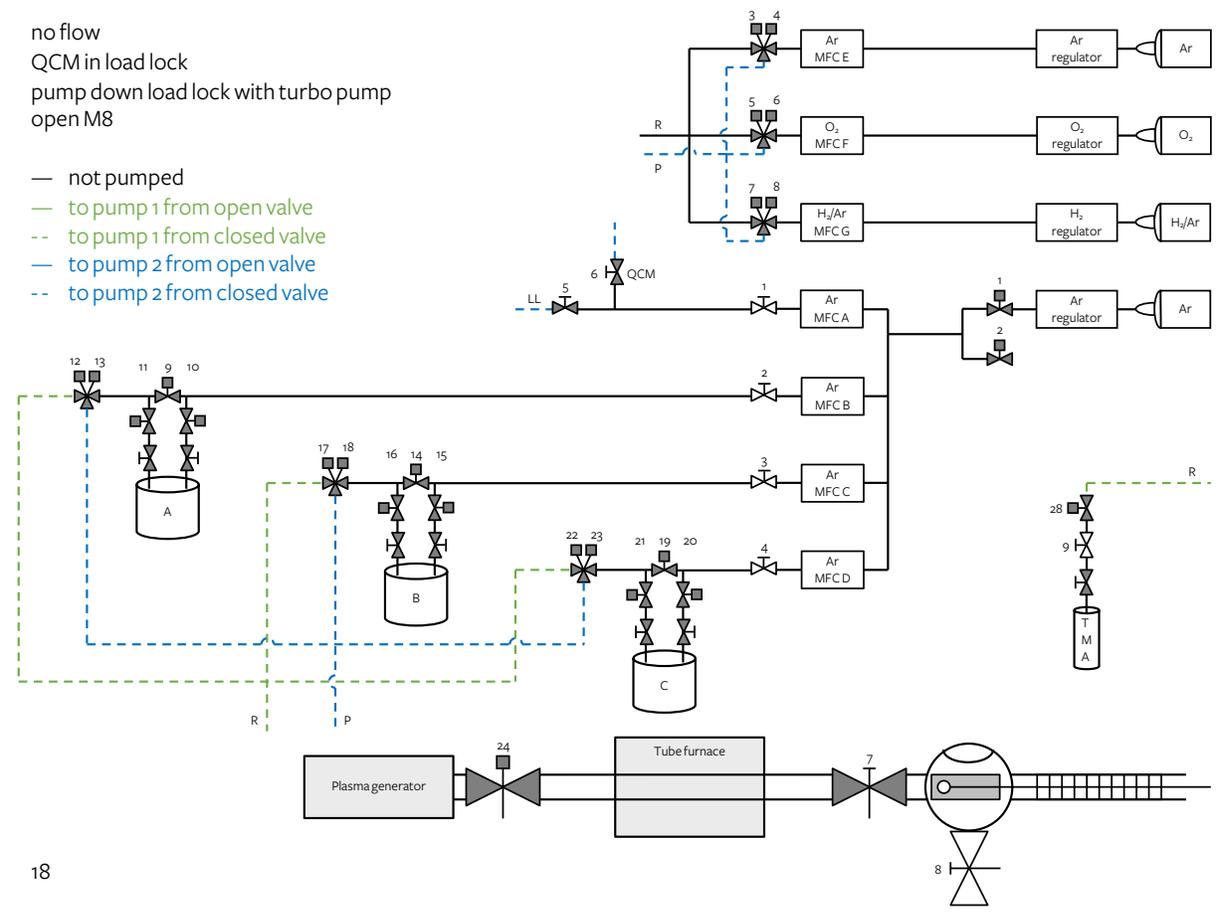
no flow
 QCM in load lock
 change QCM crystal
 close P1, M5

- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve
- - to atmosphere from closed valve



no flow
 QCM in load lock
 pump down load lock with turbo pump
 open M8

- not pumped
- to pump 1 from open valve
- - to pump 1 from closed valve
- to pump 2 from open valve
- - to pump 2 from closed valve



18

Appendix D: Spreadsheets used for chamber characterization calculations

Reynolds number

- Sheet 1
 - Calculation of Reynolds number, displaying numbers
 - Boxed numbers indicate inputs based on experimental conditions
- Sheet 2
 - Literature data and plot for dynamic viscosity of argon as a function of temperature
- Sheet 3
 - Calculation of Reynolds number, displaying formulas

Re	$V \cdot \rho d / A \eta$	dimensionless	Reynolds number
$V \bullet$	$T P_{std} V \bullet_{std} / T_{std} P$	m ³ /s	volumetric flow rate
T_std		273 K	standard temperature
P_std		760 Torr	standard pressure
$V \bullet_{std}$		50 cm ³ /min	standard volumetric flow rate
T		393 K	temperature
P		1.5 Torr	pressure
P		199.984 Pa (kg/m.s ²)	pressure
$V \bullet$		36468.864 cm ³ /min	volumetric flow rate
$V \bullet$		0.000608 m ³ /s	volumetric flow rate
ρ	$P M / R T$	kg/m ³	gas mass density
M_Ar		0.039948 kg/mol	Ar molecular weight
R		8.3145 kg.m ² /K.mol.s ²	gas constant
ρ		0.002445 kg/m ³	gas mass density
A	$\pi d^2 / 4$	m ²	pipe cross-sectional area
d		0.060198 m	pipe diameter
A		0.002846 m ²	pipe cross-sectional area
$\eta_{Ar} (T = 393 K)$		2.74E-05 Pa.s (kg/m.s)	Ar dynamic viscosity (Vogel)
Re_Ar (T = 393 K)		1.146057 dimensionless	Reynolds number

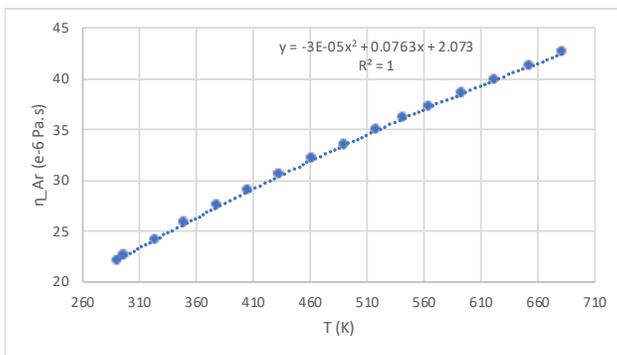
T (K)	η_{Ar} (e-6 Pa.s)
291.09	22.116
296.8	22.49
323.48	24.151
350.45	25.777
378.1	27.389
405.85	28.954
433.85	30.49
462.03	31.992
490.39	33.456
518.75	34.886
542.58	36.068
565.36	37.177
594.12	38.525
623.22	39.869
652.3	41.179
681.82	42.496

linear, $y = A x + B$, $R^2 = 0.9973$

$$y = 0.0523 x + 7.4456$$

quadratic, $y = C x^2 + D x + E$, $R^2 = 1$

$$y = -3.00E-05 x^2 + 0.0763 x + 2.073$$



Vogel, E. (2010). Reference Viscosity of Argon at Low Density in the Temperature Range from 290 K to 680 K.

Re	$V \cdot \rho d / A \eta$	dimensionless	Reynolds number
V•	$T P_{std} V_{std} / T_{std} P$	m ³ /s	volumetric flow rate
T_std	273	K	standard temperature
P_std	760	Torr	standard pressure
V•_std	50	cm ³ /min	standard volumetric flow rate
T	=120+273	K	temperature
P	1.5	Torr	pressure
P	=B7/760*101325	Pa (kg/m.s ²)	pressure
V•	=B6/B3*B4/B7*B5	cm ³ /min	volumetric flow rate
V•	=B9/60000000	m ³ /s	volumetric flow rate
ρ	$P M / R T$	kg/m ³	gas mass density
M_Ar	=39.948/1000	kg/mol	Ar molecular weight
R	8.3145	kg.m ² /K.mol.s ²	gas constant
ρ	=B8*B12/B13/B6	kg/m ³	gas mass density
A	$\pi d^2 / 4$	m ²	pipe cross-sectional area
d	=(2.5-0.065*2)*0.0254	m	pipe diameter
A	=PI()*B16^2/4	m ²	pipe cross-sectional area
η_{Ar} (T = 393 K)	=(G23*B6^2+I23*B6+K23)*0.000001	Pa.s (kg/m.s)	Ar dynamic viscosity (Vogel)
Re_Ar (T = 393 K)	=B10*B14*B16/B17/B18	dimensionless	Reynolds number

Residence time

- Sheet 1
 - Calculation of residence time, displaying numbers
 - Boxed numbers indicate inputs based on experimental conditions
- Sheet 2
 - Calculation of residence time, displaying formulas

τ	V / V_{\bullet}	s	residence time
D1		2.37 in	tube diameter
L1		25.42 in	tube length
D2		1.62 in	arm diameter
L2		3.565 in	arm length
V1		0.001837652 m ³	volume without arms
V2		0.002078482 m ³	volume with 2 arms
V_{\bullet}	$T P_{\text{std}} V_{\text{std}} / T_{\text{std}} P$	m ³ /s	volumetric flow rate
T_std		273 K	standard temperature
P_std		760 Torr	standard pressure
V_{\bullet_std}		50 cm ³ /min	standard volumetric flow rate
T		393 K	temperature
P		1.5 Torr	pressure
P		199.984 Pa (kg/m.s ²)	pressure
V_{\bullet}		36468.864 cm ³ /min	volumetric flow rate
V_{\bullet}		0.000608 m ³ /s	volumetric flow rate
τ		3.419599744 s	residence time

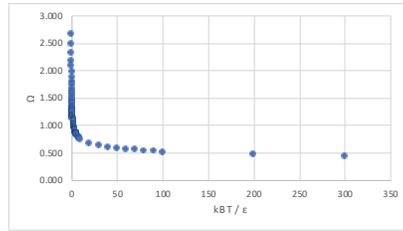
τ	$V / V\bullet$	s	residence time
D1	$=2.5-0.065*2$	in	tube diameter
L1	25.42	in	tube length
D2	$=1.75-0.065*2$	in	arm diameter
L2	$=4.75-B2/2$	in	arm length
V1	$=(PI()*(B2/2)^2*B3)*0.0254^3$	m3	volume without arms
V2	$=(PI()*(B2/2)^2*B3+2*PI()*(B4/2)^2*B5)*0.0254^3$	m3	volume with 2 arms
V•	$T P_std V_std / T_std P$	m3/s	volumetric flow rate
T_std	273	K	standard temperature
P_std	760	Torr	standard pressure
V•_std	50	cm3/min	standard volumetric flow rate
T	$=120+273$	K	temperature
P	1.5	Torr	pressure
P	$=B13/760*101325$	Pa (kg/m.s2)	pressure
V•	$=B12/B9*B10/B13*B11$	cm3/min	volumetric flow rate
V•	$=B15/60000000$	m3/s	volumetric flow rate
τ	$=B7/B16$	s	residence time

Diffusion length

- Sheet 1
 - Calculation of diffusion length, displaying numbers
 - Boxed numbers indicate inputs based on experimental conditions
- Sheet 2
 - Literature data and plot for collision integral as a function of temperature
- Sheet 3
 - Calculation of diffusion length, displaying formulas

L	$v(D, t)$	m	diffusion length
D	$[A T^{1.5} v(1/M_1 + 1/M_2)] / [0.25 (\sigma_1 + \sigma_2)^2 P \Omega]$	m ² / s	diffusion coefficient (two species), Chapman-Enskog theory
D	$[A T^{1.5} v(2 / M)] / [\sigma^2 P \Omega]$	m ² / s	diffusion coefficient (one species)
A		0.001859 atm Å ² cm ² v(g) / K ^{3/2} s v(mol)	empirical coefficient (Chapman-Enskog theory)
A		4.46779E-26 Torr m ⁴ v(kg) / K ^{3/2} s v(mol)	empirical coefficient
T		393 K	temperature
M_Ar		0.039948 kg / mol	Ar molecular weight
σ_{Ar}		3.542E-10 m	Ar collision diameter (Molecular Theory of Gases and Liquids)
P		1.5 Torr	pressure
ϵ_{Ar} / k_B		93.3 K	Ar molecular temperature (Molecular Theory of Gases and Liquids)
k _B		1.38065E-23 kg m ² / s ² K	Boltzmann constant
ϵ_{Ar}		1.28815E-21 kg m ² / s ² (J)	Ar molecular energy
k _B T / ϵ_{Ar}		4.21221865 dimensionless	thermal energy / Ar molecular energy
Ω (linear interpolation)		0.873437942 dimensionless	temperature-dependent collision integral (Molecular Theory of Gases and Liquids)
D_Ar		0.014984038 m ² / s	Ar diffusion coefficient (one species)
τ (50 sccm, 1.5 Torr)		3.419599744 s	residence time (calculated in separate workbook)
L		0.226361241 m	diffusion length

$k_B T / \epsilon$	Q
0.3	2.662
0.35	2.476
0.4	2.318
0.45	2.184
0.5	2.066
0.55	1.966
0.6	1.877
0.65	1.798
0.7	1.729
0.75	1.667
0.8	1.612
0.85	1.562
0.9	1.517
0.95	1.476
1	1.439
1.05	1.406
1.1	1.375
1.15	1.346
1.2	1.320
1.25	1.296
1.3	1.273
1.35	1.253
1.4	1.233
1.45	1.215
1.5	1.198
1.55	1.182
1.6	1.167
1.65	1.153
1.7	1.140
1.75	1.128
1.8	1.116
1.85	1.105
1.9	1.094
1.95	1.084
2	1.075
2.1	1.057
2.2	1.041
2.3	1.026
2.4	1.012
2.5	0.9996
2.6	0.9878
2.7	0.9770
2.8	0.9672
2.9	0.9576
3	0.9490
3.1	0.9406
3.2	0.9328
3.3	0.9256
3.4	0.9186
3.5	0.9120
3.6	0.9058
3.7	0.8998
3.8	0.8942
3.9	0.8888
4	0.8836
4.1	0.8788
4.2	0.8740
4.3	0.8694
4.4	0.8652
4.5	0.8610
4.6	0.8568
4.7	0.8530
4.8	0.8492
4.9	0.8456
5	0.8422
6	0.8124
7	0.7896
8	0.7712
9	0.7556
10	0.7424
20	0.6640
30	0.6232
40	0.5960
50	0.5756
60	0.5596
70	0.5464
80	0.5352
90	0.5256
100	0.5130
200	0.4644
300	0.4360



Hirschfelder, J.; Curtiss, C. F.; Bird, R. B. (1954). Molecular Theory of Gases and Liquids.

L	$\sqrt{D \tau}$	m	diffusion length
D	$[A T^{1.5} v(1/M_1 + 1/M_2)] / [0.25 (\alpha_1 + \alpha_2)^2 P \Omega]$	m ² / s	diffusion coefficient (two species), Chapman-Enskog theory
D	$[A T^{1.5} v(2 / M)] / [\alpha^2 P \Omega]$	m ² / s	diffusion coefficient (one species)
A	0.001859	atm Å ² cm ² v(g) / K ^{3/2} s v(mol)	empirical coefficient (Chapman-Enskog theory)
A	$=B4^*760/1000000000^2/100^2/SQRT(1000)$	Torr m ⁴ v(kg) / K ^{3/2} s v(mol)	empirical coefficient
T	393	K	temperature
M_Ar	$=39.948/1000$	kg / mol	Ar molecular weight
σ_{Ar}	0.000000003542	m	Ar collision diameter (Molecular Theory of Gases and Liquids)
P	1.5	Torr	pressure
ϵ_{Ar} / k_B	93.3	K	Ar molecular temperature (Molecular Theory of Gases and Liquids)
k _B	1.38064852E-23	kg m ² / s ² K	Boltzmann constant
ϵ_{Ar}	$=B10*B11$	kg m ² / s ² (J)	Ar molecular energy
k _B T / ϵ_{Ar}	$=B6/B10$	dimensionless	thermal energy / Ar molecular energy
Ω (linear interpolation)	$=Q58+(B13-P58)*(Q59-Q58)/(P59-P58)$	dimensionless	temperature-dependent collision integral (Molecular Theory of Gases and Liquids)
D_Ar	$=B5*B6^*1.5^*SQRT(2/B7)/B8^2/B9/B14$	m ² / s	Ar diffusion coefficient (one species)
τ (50 sccm, 1.5 Torr)	3.41959974427193	s	residence time (calculated in separate workbook)
L	$=SQRT(B15*B16)$	m	diffusion length

Knudsen number

- Sheet 1
 - Calculation of Knudsen number, displaying numbers
 - Boxed numbers indicate inputs based on experimental conditions
- Sheet 2
 - Calculation of Knudsen number, displaying formulas

Kn	λ/d	dimensionless	Knudsen number
λ	$k_B T / \sqrt{2} \pi \sigma^2 P$	m	mean free path
kB	1.38065E-23	kg m ² / s ² K	Boltzmann constant
T	393	K	temperature
σ_{Ar}	3.542E-10	m	Ar collision diameter (Molecular Theory of Gases and Liquids)
P	1.5	Torr	pressure
P	199.9835526	Pa (kg/m.s ²)	pressure
λ_{Ar}	4.86765E-05	m	Ar mean free path
d	0.060198	m	characteristic dimension of system, reactor tube diameter
Kn	0.000808607	dimensionless	Knudsen number

Kn	λ/d	dimensionless	Knudsen number
λ	$k_B T / \sqrt{2} \pi \sigma^2 P$	m	mean free path
k_B	1.38064852E-23	kg m ² / s ² K	Boltzmann constant
T	=120+273	K	temperature
σ_{Ar}	0.000000003542	m	Ar collision diameter (Molecular Theory of Gases and Liquids)
P	1.5	Torr	pressure
P	=B6/760*101325	Pa (kg/m.s ²)	pressure
λ_{Ar}	=B3*B4/SQRT(2)/PI()/B5^2/B7	m	Ar mean free path
d	=(2.5-0.065*2)*0.0254	m	characteristic dimension of system, reactor tube diameter
Kn	=B8/B9	dimensionless	Knudsen number

Plasma ion concentration

- Sheet 1
 - Calculation of maximum plasma pressure for dissociation of 3 % hydrogen balance argon, displaying numbers
 - Boxed numbers indicate inputs based on experimental conditions
- Sheet 2
 - Calculation of maximum plasma pressure for dissociation of oxygen, displaying numbers
 - Boxed numbers indicate inputs based on experimental conditions
- Sheet 3
 - Calculation of maximum plasma pressure for dissociation of 3 % hydrogen balance argon, displaying formulas
- Sheet 4
 - Calculation of maximum plasma pressure for dissociation of oxygen, displaying formulas

H₂: e⁻, H, H, H₂, H⁺, H₂⁺, H₃⁺

Ar: e⁻, Ar, Ar⁺, Ar₂⁺

P	1.5	Torr	outlet pressure
P	199.983553	Pa (kg/m.s ²)	outlet pressure
D1	2.37	in	tube diameter
L1	25.42	in	tube length
D2	1.62	in	arm diameter
L2	3.565	in	arm length
V2	0.00183765	m ³	volume without arms
V2	0.00207848	m ³	volume with 2 arms
R	8.3145	m ³ .Pa/K.mol	gas constant
T	393	K	temperature
n	0.00012721	mol	total moles of gas
y_H2	0.03	mol/mol total	H2 mole fraction
y_Ar	0.97	mol/mol total	Ar mole fraction
n_H2	3.8162E-06	mol	moles of H2
n_Ar	0.00012339	mol	moles of Ar
n_H-	1.9081E-06	mol	min moles of reducing H2 ionization products (H ₂ > H ⁺ + H ⁻)
y_H-	0.00761421	mol/mol total	min mole fraction of reducing H2 ionization products
p_H-	2.99975329	Pa	min partial pressure of reducing H2 ionization products
p_H-	0.0225	Torr	min partial pressure of reducing H2 ionization products
n_H2_i	1.5265E-05	mol	max moles of H2 ionization products (H ₂ > 2 H ⁺ + 2 e ⁻)
n_Ar_i	0.00024678	mol	max moles of Ar ionization products (Ar > Ar ⁺ + e ⁻)
p_H2_i	23.9980263	Pa	max partial pressure of H2 ionization products
p_H2_i	0.18	Torr	max partial pressure of H2 ionization products
p_Ar_i	387.968092	Pa	max partial pressure of Ar ionization products
p_Ar_i	2.91	Torr	max partial pressure of Ar ionization products
P_plasma	3.09	Torr	max plasma pressure

O₂: e⁻, O⁻, O₂⁻, O₃⁻, O, O₂, O₃, O⁺, O₂⁺

P	<input type="text" value="1.5"/>	Torr	outlet pressure
P	199.9835526	Pa (kg/m.s ²)	outlet pressure
D1	2.37	in	tube diameter
L1	25.42	in	tube length
D2	1.62	in	arm diameter
L2	3.565	in	arm length
V2	0.001837652	m ³	volume without arms
V2	0.002078482	m ³	volume with 2 arms
R	8.3145	m ³ .Pa/K.mol	gas constant
T	<input type="text" value="393"/>	K	temperature
n	0.000127207	mol	total moles of O ₂ gas
n_O2_i	0.000508829	mol	max moles of O ₂ ionization products (O ₂ > 2 O ⁺ + 2 e ⁻)
p_O2_i	799.9342105	Pa	max partial pressure of O ₂ ionization products
p_O2_i	6	Torr	max partial pressure of O ₂ ionization products
P_plasma	6	Torr	max plasma pressure

P	1.5	Torr	outlet pressure
P	$=B5/760*101325$	Pa (kg/m.s2)	outlet pressure
D1	$=2.5-0.065*2$	in	tube diameter
L1	25.42	in	tube length
D2	$=1.75-0.065*2$	in	arm diameter
L2	$=4.75-B7/2$	in	arm length
V2	$=(Pi()*(B7/2)^2*B8)*0.0254^3$	m3	volume without arms
V2	$=(Pi()*(B7/2)^2*B8+2*Pi()*(B9/2)^2*B10)*0.0254^3$	m3	volume with 2 arms
R	8.3145	m3.Pa/K.mol	gas constant
T	$=120+273$	K	temperature
n	$=B6*B12/B13/B14$	mol	total moles of gas
y_H2	0.03	mol/mol total	H2 mole fraction
y_Ar	0.97	mol/mol total	Ar mole fraction
n_H2	$=B16*B15$	mol	moles of H2
n_Ar	$=B17*B15$	mol	moles of Ar
n_H-	$=B18/2$	mol	min moles of reducing H2 ionization products ($H_2 > H^+ + H$)
y_H-	$=B20/(B18+B25)$	mol/mol total	min mole fraction of reducing H2 ionization products
p_H-	$=B20*B13*B14/B12$	Pa	min partial pressure of reducing H2 ionization products
p_H	$=B22*760/101325$	Torr	min partial pressure of reducing H2 ionization products
n_H2_i	$=B18*4$	mol	max moles of H2 ionization products ($H_2 > 2 H^+ + 2 e^-$)
n_Ar_i	$=B19*2$	mol	max moles of Ar ionization products ($Ar > Ar^+ + e^-$)
p_H2_i	$=B24*B13*B14/B12$	Pa	max partial pressure of H2 ionization products
p_H2_i	$=B26*760/101325$	Torr	max partial pressure of H2 ionization products
p_Ar_i	$=B25*B13*B14/B12$	Pa	max partial pressure of Ar ionization products
p_Ar_i	$=B28*760/101325$	Torr	max partial pressure of Ar ionization products
P_plasma	$=B27+B29$	Torr	max plasma pressure

P	1.5	Torr	outlet pressure
P	=G5/760*101325	Pa (kg/m.s2)	outlet pressure
D1	=2.5-0.065*2	in	tube diameter
L1	25.42	in	tube length
D2	=1.75-0.065*2	in	arm diameter
L2	=4.75-G7/2	in	arm length
V2	=(Pi()*(G7/2)^2*G8)*0.0254^3	m3	volume without arms
V2	=(Pi()*(G7/2)^2*G8+2*Pi()*(G9/2)^2*G10)*0.0254^3	m3	volume with 2 arms
R	8.3145	m3.Pa/K.mol	gas constant
T	=120+273	K	temperature
n	=G6*G12/G13/G14	mol	total moles of O2 gas
n_O2_i	=G15*4	mol	max moles of O2 ionization products ($O_2 > 2 O^+ + 2 e^-$)
p_O2_i	=G16*G13*G14/G12	Pa	max partial pressure of O2 ionization products
p_O2_i	=G17*760/101325	Torr	max partial pressure of O2 ionization products
P_plasma	=G18+G20	Torr	max plasma pressure

Appendix E: Code written in Excel Visual Basic for Applications (VBA)

Density list for calculating Sauerbrey coefficient

Text file must be titled: density_list_Sauerbrey_coefficient.txt

Film	Density (kg/m ³)	alpha_AT (kg·Å/m ³ ·s)
Al	2700	4.416915e16
Al ₂ O ₃	3970	
Co	8710	
CoO	6440	
Cu	8930	
CuO	6310	
Cu ₂ O	6000	
C in Cu ₂ C ₂	922.5	
Hf	13090	
HfO ₂	9680	
O in CuO	1310.7	
Si	2320	
Si ₃ N ₄	3170	
SiO ₂	2650	
Zr	6510	
ZrO ₂	5680	

Module 1

```
Sub QCM_T_thickness_milliseconds()  
  
Application.ScreenUpdating = False  
  
Dim inFilePath As Variant, outFilePath As Variant  
Dim inFile As Integer, outFile As Integer, listFile As Integer  
Dim lineCount As Long  
Dim listFilePath As String, fileLine As String, frequencyStr As String,  
dropdownStr As String  
Dim i As Long 'Loop to remove carriage return  
Dim t As Long 'Count row number of last filled row in columnA data  
Dim m As Long 'Count row number of last filled row for loop  
Dim n As Long 'Count number equivalent data points  
Dim j As Long 'Loop to count equivalent data points  
Dim k As Long 'Loop to fill equivalent data points  
Dim r As Long 'Count row number of last filled row in columnA list  
  
'Update path for coefficient list  
listFilePath = "/Users/.../density_list_Sauerbrey_coefficient.txt"  
  
'Rename sheet for reference to be true later  
ActiveSheet.Name = "Sheet1"  
  
'Format sheet  
Cells.Select 'Select all cells  
Selection.Delete Shift:=xlUp 'Clear cells  
With Selection.Font  
    .Name = "Calibri"  
    .Size = 12  
    .Strikethrough = False  
    .Superscript = False  
    .Subscript = False  
    .OutlineFont = False  
    .Shadow = False  
    .Underline = xlUnderlineStyleNone  
    .ThemeColor = xlThemeColorLight1  
    .TintAndShade = 0  
    .ThemeFont = xlThemeFontMinor  
End With  
Selection.ColumnWidth = 10  
Selection.RowHeight = 16
```

Range("A1").Select

```
'Create temporary txt file without carriage return in first line
inFilePath = Application.GetOpenFilename(".txt") 'Choose data file
outFilePath = Replace(inFilePath, ".txt", "_temp.txt") 'Create temporary file
If Dir$(inFilePath) = "" Then Exit Sub 'Confirm that path exists
inFile = FreeFile 'Assign file number
Open inFilePath For Input As #inFile 'Open file
outFile = FreeFile 'Assign file number
Open outFilePath For Output As #outFile 'Open file
lineCount = 0
Do Until EOF(inFile) 'Repeat loop command until end of file
    Line Input #inFile, fileLine
    lineCount = lineCount + 1 'Increase lineCount with each loop
    If lineCount > 1 Then
        Print #outFile, fileLine 'Print line2 to end into temporary file
    End If
Loop
Close #inFile 'Close file
Close #outFile 'Close file
```

```
'Copy txt file into Excel
Range("A4").Activate
Open outFilePath For Input As #outFile 'Open temporary file
lineCount = 0 'Reset lineCount
Do Until EOF(outFile) 'Repeat loop command until end of file
    Line Input #outFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
    column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
    column2
    ActiveCell.Offset(lineCount, 2).Value = LineItems(2) 'Fill xlsx column3 with txt
    column3
    ActiveCell.Offset(lineCount, 3).Value = LineItems(3) 'Fill xlsx column4 with txt
    column4
    ActiveCell.Offset(lineCount, 4).Value = LineItems(4) 'Fill xlsx column5 with txt
    column5
    ActiveCell.Offset(lineCount, 5).Value = LineItems(5) 'Fill xlsx column6 with txt
    column6
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #outFile 'Close file
Kill outFilePath 'Delete temporary file
```

'Remove carriage return from frequency column

```

i = 4 'First row of data
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
While i < t 'Repeat loop until end of data
    Cells(i, "F").Activate
    frequencyStr = ActiveCell.Value
    ActiveCell.Value = Left(frequencyStr, Len(frequencyStr) - 1) 'Remove
rightmost character from cell
    i = i + 1
Wend

'Save file As
Application.Dialogs(xlDialogSaveAs).Show

'Fill header information
Range("A1").Value = "Date"
Range("B1").Value = "Run #"
Range("C1").Value = "Precursor"
Range("D1").Value = "Co-reactant"
Range("E1").Value = "Co-adsorbate"
Range("F1").Value = "Carrier gas"
Range("G1").Value = "Process"
Range("H1").Value = "Sequence"
Range("I1").Value = "Crystal substrate"
Range("J1").Value = "Wafer substrate"
Range("K1").Value = "Furnace T (°C)"
Range("L1").Value = "Pressure (Torr)"
Range("M1").Value = "Total flow (sccm)"
Range("N1").Value = "z position (in)"
Range("O1").Value = "Panel 2 chemical"
Range("P1").Value = "Panel 2 flow (sccm)"
Range("Q1").Value = "Panel 2 line T (°C)"
Range("R1").Value = "Panel 2 ampoule T (°C)"
Range("S1").Value = "Panel 3 chemical"
Range("T1").Value = "Panel 3 flow (sccm)"
Range("U1").Value = "Panel 3 line T (°C)"
Range("V1").Value = "Panel 3 ampoule T (°C)"
Range("W1").Value = "Panel 4 chemical"
Range("X1").Value = "Panel 4 flow (sccm)"
Range("Y1").Value = "Panel 4 line T (°C)"
Range("Z1").Value = "Panel 4 ampoule T (°C)"
Range("AA1").Value = "Panel 1-1 flow (sccm)"
Range("AB1").Value = "Panel 1-2 flow (sccm)"
Range("AC1").Value = "Panel 1-3 flow (sccm)"
Range("AD1").Value = "Panel 1-4 flow (sccm)"
Range("C4").Value = "Rate (Å/s)"

```

```

Range("D4").Value = "Film thickness (kÅ)"
Range("E4").Value = "Substrate thickness (kÅ)"
Range("H4").Value = "Time"
Range("I4").Value = "Time"
Range("J4").Value = "Time (min)"
Range("K4").Value = "Time (s)"
Range("L4").Value = "Surface density (ng/cm2)"
Range("M4").Value = "Thickness (Å)"
Range("N4").Value = "Film density (kg/m3)"
Range("N10").Value = "Zero row number"

```

'Fill columnH with date

```

Range("A5").Select
Range(Selection, Selection.End(xlDown)).Copy 'Copy data from columnA
Range("H5").Select
ActiveSheet.Paste 'Paste data from columnA into columnH
Application.CutCopyMode = False
Selection.Replace What:="T", Replacement:=" ", LookAt:=xlPart, _
    SearchOrder:=xlByRows, MatchCase:=False, FormulaVersion:= _
    xlReplaceFormula2 'Replace T in pasted data with a space
Range("H5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnH and columnI
as date
Range("H:H").Columns.AutoFit

```

'Fill columnI with time

```

'Add milliseconds to first second of data
m = 4 'Row number of last filled row in columnI
n = 1 'Start with 1 point to check for equivalency of others
Cells((m + 1), "H").Select 'Select cell in columnH below the last filled row in
columnI
For j = 1 To 12 'Count number of equivalent points
    If ActiveCell.Offset(j, 0).Value = ActiveCell Then n = n + 1
Next
'Fill time with milliseconds for first second of data
For k = 1 To n 'For the number of equivalent points
    Cells((m + 1), "I").Select 'Select cell below the last filled row in columnI
    ActiveCell.FormulaR1C1 = "= RC[-1]+1/864000*" & 9 + k - n
    m = Cells(Rows.Count, "I").End(xlUp).Row 'Row number of last filled row in
columnI
Next
'Add milliseconds for remaining data
While m < t 'Repeat loop until end of data
    n = 1 'Reset used loop variable
    j = 1 'Reset used loop variable
    k = 1 'Reset used loop variable

```

```

Cells((m + 1), "H").Select 'Select cell in columnH below the last filled row in
columnI
For j = 1 To 12 'Count number of equivalent points
    If ActiveCell.Offset(j, 0).Value = ActiveCell Then n = n + 1
Next
'Fill time with milliseconds for remaining data
For k = 1 To n 'For the number of equivalent points
    Cells((m + 1), "I").Select 'Select cell below the last filled row in columnI
    ActiveCell.FormulaR1C1 = "= RC[-1]+1/864000*" & k - 1
    m = Cells(Rows.Count, "I").End(xlUp).Row 'Row number of last filled row in
columnI
Next
Wend
Range("I:I").Columns.AutoFit

```

```

'Fill columnJ with time (min) elapsed
Cells(11, "N").Value = 5
Range("J5:M" & t).Select
Selection.NumberFormat = "0.000" 'Format columnJ, columnK, and columnL as
number
Cells(5, "J").FormulaR1C1 = "= (RC[-1]-INDEX(R1C[-1]:R" & t & "C[-
1],R11C14))*1440" 'Calculate time elapsed
Range("J5:J" & t).FillDown 'Fill calculation for remaining rows
Range("A1").Select

```

```

'Fill columnK with time (s) elapsed
Cells(5, "K").FormulaR1C1 = "=RC[-1]*60" 'Calculate time elapsed
Range("K5:K" & t).FillDown 'Fill calculation for remaining rows

```

```

'Fill columnL with surface density
Cells(5, "L").FormulaR1C1 = "=4.416915e14*(INDEX(R1C[-6]:R" & t & "C[-
6],R11C14)-RC[-6])/(INDEX(R1C[-6]:R" & t & "C[-6],R11C14)^2)" 'Calculate
surface density
Range("L5:L" & t).FillDown 'Fill calculation for remaining rows
ActiveWorkbook.Save 'Save xlsx file

```

```

'Fill columnM with thickness
'Copy txt file into Excel
Sheets.Add(After:=Sheets(Sheets.Count)).Name = "Films"
listFile = FreeFile 'Assign file number
Open listFilePath For Input As #listFile 'Open file with coefficient list
lineCount = 0 'Reset lineCount
Do Until EOF(listFile) 'Repeat loop command until end of file
    Line Input #listFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab

```

```

    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #listFile 'Close file

'Create dropdown list of film types
r = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
For Each Value In Range("A2:A" & r) 'Repeat loop until end of data
    dropdownStr = dropdownStr & "," & Value
Next Value
dropdownStr = Right(dropdownStr, Len(dropdownStr) - 1) 'Create string for
dropdown list
With ActiveSheet.Range("D2").Validation 'Create dropdown list
    .Delete
    .Add Type:=xlValidateList, AlertStyle:=xlValidAlertStop, Operator:= _
xlBetween, Formula1:=dropdownStr 'Add string to dropdown list
    .IgnoreBlank = True
    .InCellDropdown = True
    .InputTitle = ""
    .ErrorTitle = ""
    .InputMessage = ""
    .ErrorMessage = ""
    .ShowInput = True
    .ShowError = True
End With

'Add border around dropbox
Range("D2").Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
With Selection.Borders(xlEdgeLeft)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
With Selection.Borders(xlEdgeTop)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With

```

```

With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
With Selection.Borders(xlEdgeRight)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone

'Create continue button
ActiveSheet.Buttons.Add(195, 48, 65, 16).OnAction = "QCM_thickness_continue"
ActiveSheet.Shapes.Range(Array("Button 2")).Select
Selection.Characters.Text = "Continue"
With Selection.Characters(Start:=1, Length:=6).Font
    .Name = "Calibri"
    .FontStyle = "Regular"
    .Size = 12
    .Strikethrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ColorIndex = xlAutomatic
End With

Range("A1").Select
ActiveWorkbook.Save 'Save xlsx file

MsgBox "Choose film type from the dropdown list in Cell D2, then click the
button to continue."

End Sub

```

Module 2

```
Sub QCM_T_thickness_seconds()

Application.ScreenUpdating = False

Dim inFilePath As Variant, outFilePath As Variant
Dim inFile As Integer, outFile As Integer, listFile As Integer
Dim lineCount As Long
Dim listFilePath As String, fileLine As String, frequencyStr As String,
dropdownStr As String
Dim i As Long 'Loop to remove carriage return
Dim t As Long 'Count row number of last filled row in columnA data

'Update path for coefficient list
listFilePath = "/Users/.../density_list_Sauerbrey_coefficient.txt"

'Rename sheet for reference to be true later
ActiveSheet.Name = "Sheet1"

'Format sheet
Cells.Select 'Select all cells
Selection.Delete Shift:=xlUp 'Clear cells
With Selection.Font
    .Name = "Calibri"
    .Size = 12
    .Strikethrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ThemeColor = xlThemeColorLight1
    .TintAndShade = 0
    .ThemeFont = xlThemeFontMinor
End With
Selection.ColumnWidth = 10
Selection.RowHeight = 16
Range("A1").Select

'Create temporary txt file without carriage return in first line
inFilePath = Application.GetOpenFilename(".txt") 'Choose data file
outFilePath = Replace(inFilePath, ".txt", "_temp.txt") 'Create temporary file
```

```

If Dir$(inFilePath) = "" Then Exit Sub 'Confirm that path exists
inFile = FreeFile 'Assign file number
Open inFilePath For Input As #inFile 'Open file
outFile = FreeFile 'Assign file number
Open outFilePath For Output As #outFile 'Open file
lineCount = 0
Do Until EOF(inFile) 'Repeat loop command until end of file
    Line Input #inFile, fileLine
    lineCount = lineCount + 1 'Increase lineCount with each loop
    If lineCount > 1 Then
        Print #outFile, fileLine 'Print line2 to end into temporary file
    End If
Loop
Close #inFile 'Close file
Close #outFile 'Close file

'Copy txt file into Excel
Range("A4").Activate
Open outFilePath For Input As #outFile 'Open temporary file
lineCount = 0 'Reset lineCount
Do Until EOF(outFile) 'Repeat loop command until end of file
    Line Input #outFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
    ActiveCell.Offset(lineCount, 2).Value = LineItems(2) 'Fill xlsx column3 with txt
column3
    ActiveCell.Offset(lineCount, 3).Value = LineItems(3) 'Fill xlsx column4 with txt
column4
    ActiveCell.Offset(lineCount, 4).Value = LineItems(4) 'Fill xlsx column5 with txt
column5
    ActiveCell.Offset(lineCount, 5).Value = LineItems(5) 'Fill xlsx column6 with txt
column6
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #outFile 'Close file
Kill outFilePath 'Delete temporary file

'Remove carriage return from frequency column
i = 4 'First row of data
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
While i < t 'Repeat loop until end of data
    Cells(i, "F").Activate

```

```

    frequencyStr = ActiveCell.Value
    ActiveCell.Value = Left(frequencyStr, Len(frequencyStr) - 1) 'Remove
rightmost character from cell
    i = i + 1
Wend

```

```

'Save file As
Application.Dialogs(xlDialogSaveAs).Show

```

'Fill header information

```

Range("A1").Value = "Date"
Range("B1").Value = "Run #"
Range("C1").Value = "Precursor"
Range("D1").Value = "Co-reactant"
Range("E1").Value = "Co-adsorbate"
Range("F1").Value = "Carrier gas"
Range("G1").Value = "Process"
Range("H1").Value = "Sequence"
Range("I1").Value = "Crystal substrate"
Range("J1").Value = "Wafer substrate"
Range("K1").Value = "Furnace T (°C)"
Range("L1").Value = "Pressure (Torr)"
Range("M1").Value = "Total flow (sccm)"
Range("N1").Value = "z position (in)"
Range("O1").Value = "Panel 2 chemical"
Range("P1").Value = "Panel 2 flow (sccm)"
Range("Q1").Value = "Panel 2 line T (°C)"
Range("R1").Value = "Panel 2 ampoule T (°C)"
Range("S1").Value = "Panel 3 chemical"
Range("T1").Value = "Panel 3 flow (sccm)"
Range("U1").Value = "Panel 3 line T (°C)"
Range("V1").Value = "Panel 3 ampoule T (°C)"
Range("W1").Value = "Panel 4 chemical"
Range("X1").Value = "Panel 4 flow (sccm)"
Range("Y1").Value = "Panel 4 line T (°C)"
Range("Z1").Value = "Panel 4 ampoule T (°C)"
Range("AA1").Value = "Panel 1-1 flow (sccm)"
Range("AB1").Value = "Panel 1-2 flow (sccm)"
Range("AC1").Value = "Panel 1-3 flow (sccm)"
Range("AD1").Value = "Panel 1-4 flow (sccm)"
Range("C4").Value = "Rate (Å/s)"
Range("D4").Value = "Film thickness (kÅ)"
Range("E4").Value = "Substrate thickness (kÅ)"
Range("I4").Value = "Time"
Range("J4").Value = "Time (min)"
Range("K4").Value = "Time (s)"

```

```
Range("L4").Value = "Surface density (ng/cm2)"
Range("M4").Value = "Thickness (Å)"
Range("N4").Value = "Film density (kg/m3)"
Range("N10").Value = "Zero row number"
```

```
'Fill columnH with date
Range("H5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnH and columnI
as date
Range("H:H").Columns.AutoFit
```

```
'Fill columnI with date
Range("A5").Select
Range(Selection, Selection.End(xlDown)).Copy 'Copy data from columnA
Range("I5").Select
ActiveSheet.Paste 'Paste data from columnA into columnI
Application.CutCopyMode = False
Selection.Replace What:="T", Replacement:=" ", LookAt:=xlPart, _
    SearchOrder:=xlByRows, MatchCase:=False, FormulaVersion:= _
    xlReplaceFormula2 'Replace T in pasted data with a space
Range("I5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnI as date
Range("I:I").Columns.AutoFit
```

```
'Fill columnJ with time (min) elapsed
Cells(11, "N").Value = 5
Range("J5:M" & t).Select
Selection.NumberFormat = "0.000" 'Format columnJ, columnK, and columnL as
number
Cells(5, "J").FormulaR1C1 = "=(RC[-1]-INDEX(R1C[-1]:R" & t & "C[-
1],R11C14))*1440" 'Calculate time elapsed
Range("J5:J" & t).FillDown 'Fill calculation for remaining rows
Range("A1").Select
```

```
'Fill columnK with time (s) elapsed
Cells(5, "K").FormulaR1C1 = "=RC[-1]*60" 'Calculate time elapsed
Range("K5:K" & t).FillDown 'Fill calculation for remaining rows
```

```
'Fill columnL with surface density
Cells(5, "L").FormulaR1C1 = "=4.416915e14*(INDEX(R1C[-6]:R" & t & "C[-
6],R11C14)-RC[-6])/(INDEX(R1C[-6]:R" & t & "C[-6],R11C14)^2)" 'Calculate
surface density
Range("L5:L" & t).FillDown 'Fill calculation for remaining rows
ActiveWorkbook.Save 'Save xlsx file
```

```
'Fill columnM with thickness
```

```

'Copy txt file into Excel
Sheets.Add(After:=Sheets(Sheets.Count)).Name = "Films"
listFile = FreeFile 'Assign file number
Open listFilePath For Input As #listFile 'Open file with coefficient list
lineCount = 0 'Reset lineCount
Do Until EOF(listFile) 'Repeat loop command until end of file
    Line Input #listFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
    column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
    column2
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #listFile 'Close file

'Create dropdown list of film types
r = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
For Each Value In Range("A2:A" & r) 'Repeat loop until end of data
    dropdownStr = dropdownStr & "," & Value
Next Value
dropdownStr = Right(dropdownStr, Len(dropdownStr) - 1) 'Create string for
dropdown list
With ActiveSheet.Range("D2").Validation 'Create dropdown list
    .Delete
    .Add Type:=xlValidateList, AlertStyle:=xlValidAlertStop, Operator:= _
xlBetween, Formula1:=dropdownStr 'Add string to dropdown list
    .IgnoreBlank = True
    .InCellDropdown = True
    .InputTitle = ""
    .ErrorTitle = ""
    .InputMessage = ""
    .ErrorMessage = ""
    .ShowInput = True
    .ShowError = True
End With

'Add border around dropbox
Range("D2").Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
With Selection.Borders(xlEdgeLeft)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0

```

```

    .Weight = xlThin
End With
With Selection.Borders(xlEdgeTop)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
With Selection.Borders(xlEdgeRight)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone

```

```

'Create continue button
ActiveSheet.Buttons.Add(195, 48, 65, 16).OnAction = "QCM_thickness_continue"
ActiveSheet.Shapes.Range(Array("Button 2")).Select
Selection.Characters.Text = "Continue"
With Selection.Characters(Start:=1, Length:=6).Font
    .Name = "Calibri"
    .FontStyle = "Regular"
    .Size = 12
    .Strikethrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ColorIndex = xlAutomatic
End With

```

```

Range("A1").Select
ActiveWorkbook.Save 'Save xlsx file

```

MsgBox "Choose film type from the dropdown list in Cell D2, then click the button to continue."

End Sub

Module 3

```
Sub QCM_M_thickness_milliseconds()  
  
Application.ScreenUpdating = False  
  
Dim inFilePath As Variant, outFilePath As Variant  
Dim inFile As Integer, outFile As Integer, listFile As Integer  
Dim lineCount As Long  
Dim listFilePath As String, fileLine As String, frequencyStr As String,  
dropdownStr As String  
Dim i As Long 'Loop to remove carriage return  
Dim t As Long 'Count row number of last filled row in columnA data  
Dim m As Long 'Count row number of last filled row for loop  
Dim n As Long 'Count number equivalent data points  
Dim j As Long 'Loop to count equivalent data points  
Dim k As Long 'Loop to fill equivalent data points  
Dim r As Long 'Count row number of last filled row in columnA list  
  
'Update path for coefficient list  
listFilePath = "/Users/.../density_list_Sauerbrey_coefficient.txt"  
  
'Rename sheet for reference to be true later  
ActiveSheet.Name = "Sheet1"  
  
'Format sheet  
Cells.Select 'Select all cells  
Selection.Delete Shift:=xlUp 'Clear cells  
With Selection.Font  
    .Name = "Calibri"  
    .Size = 12  
    .Strikethrough = False  
    .Superscript = False  
    .Subscript = False  
    .OutlineFont = False  
    .Shadow = False  
    .Underline = xlUnderlineStyleNone  
    .ThemeColor = xlThemeColorLight1  
    .TintAndShade = 0  
    .ThemeFont = xlThemeFontMinor  
End With  
Selection.ColumnWidth = 10  
Selection.RowHeight = 16
```

Range("A1").Select

```
'Create temporary txt file without carriage return in first line
inFilePath = Application.GetOpenFilename(".txt") 'Choose data file
outFilePath = Replace(inFilePath, ".txt", "_temp.txt") 'Create temporary file
If Dir$(inFilePath) = "" Then Exit Sub 'Confirm that path exists
inFile = FreeFile 'Assign file number
Open inFilePath For Input As #inFile 'Open file
outFile = FreeFile 'Assign file number
Open outFilePath For Output As #outFile 'Open file
lineCount = 0
Do Until EOF(inFile) 'Repeat loop command until end of file
    Line Input #inFile, fileLine
    lineCount = lineCount + 1 'Increase lineCount with each loop
    If lineCount > 1 Then
        Print #outFile, fileLine 'Print line2 to end into temporary file
    End If
Loop
Close #inFile 'Close file
Close #outFile 'Close file
```

```
'Copy txt file into Excel
Range("A4").Activate
Open outFilePath For Input As #outFile 'Open temporary file
lineCount = 0 'Reset lineCount
Do Until EOF(outFile) 'Repeat loop command until end of file
    Line Input #outFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
    column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
    column2
    ActiveCell.Offset(lineCount, 2).Value = LineItems(2) 'Fill xlsx column3 with txt
    column3
    ActiveCell.Offset(lineCount, 3).Value = LineItems(3) 'Fill xlsx column4 with txt
    column4
    ActiveCell.Offset(lineCount, 4).Value = LineItems(4) 'Fill xlsx column5 with txt
    column5
    ActiveCell.Offset(lineCount, 5).Value = LineItems(5) 'Fill xlsx column6 with txt
    column6
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #outFile 'Close file
Kill outFilePath 'Delete temporary file
```

'Remove carriage return from frequency column

```

i = 4 'First row of data
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
While i < t 'Repeat loop until end of data
    Cells(i, "F").Activate
    frequencyStr = ActiveCell.Value
    ActiveCell.Value = Left(frequencyStr, Len(frequencyStr) - 1) 'Remove
rightmost character from cell
    i = i + 1
Wend

'Save file As
Application.Dialogs(xlDialogSaveAs).Show

'Fill header information
Range("A1").Value = "Date"
Range("B1").Value = "Run #"
Range("C1").Value = "Precursor"
Range("D1").Value = "Co-reactant"
Range("E1").Value = "Co-adsorbate"
Range("F1").Value = "Carrier gas"
Range("G1").Value = "Process"
Range("H1").Value = "Sequence"
Range("I1").Value = "Crystal substrate"
Range("J1").Value = "Wafer substrate"
Range("K1").Value = "Furnace T (°C)"
Range("L1").Value = "Pressure (Torr)"
Range("M1").Value = "Total flow (sccm)"
Range("N1").Value = "z position (in)"
Range("O1").Value = "Panel 2 chemical"
Range("P1").Value = "Panel 2 flow (sccm)"
Range("Q1").Value = "Panel 2 line T (°C)"
Range("R1").Value = "Panel 2 ampoule T (°C)"
Range("S1").Value = "Panel 3 chemical"
Range("T1").Value = "Panel 3 flow (sccm)"
Range("U1").Value = "Panel 3 line T (°C)"
Range("V1").Value = "Panel 3 ampoule T (°C)"
Range("W1").Value = "Panel 4 chemical"
Range("X1").Value = "Panel 4 flow (sccm)"
Range("Y1").Value = "Panel 4 line T (°C)"
Range("Z1").Value = "Panel 4 ampoule T (°C)"
Range("AA1").Value = "Panel 1-1 flow (sccm)"
Range("AB1").Value = "Panel 1-2 flow (sccm)"
Range("AC1").Value = "Panel 1-3 flow (sccm)"
Range("AD1").Value = "Panel 1-4 flow (sccm)"
Range("C4").Value = "Rate (µg.s/cm2)"

```

```

Range("D4").Value = "Film mass ( $\mu\text{g}/\text{cm}^2$ )"
Range("E4").Value = "Substrate mass ( $\mu\text{g}/\text{cm}^2$ )"
Range("H4").Value = "Time"
Range("I4").Value = "Time"
Range("J4").Value = "Time (min)"
Range("K4").Value = "Time (s)"
Range("L4").Value = "Surface density ( $\text{ng}/\text{cm}^2$ )"
Range("M4").Value = "Thickness ( $\text{\AA}$ )"
Range("N4").Value = "Film density ( $\text{kg}/\text{m}^3$ )"
Range("N10").Value = "Zero row number"

```

'Fill columnH with date

```

Range("A5").Select
Range(Selection, Selection.End(xlDown)).Copy 'Copy data from columnA
Range("H5").Select
ActiveSheet.Paste 'Paste data from columnA into columnH
Application.CutCopyMode = False
Selection.Replace What:="T", Replacement:=" ", LookAt:=xlPart, _
    SearchOrder:=xlByRows, MatchCase:=False, FormulaVersion:= _
    xlReplaceFormula2 'Replace T in pasted data with a space
Range("H5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnH and columnI
as date
Range("H:H").Columns.AutoFit

```

'Fill columnI with time

```

'Add milliseconds to first second of data
m = 4 'Row number of last filled row in columnI
n = 1 'Start with 1 point to check for equivalency of others
Cells((m + 1), "H").Select 'Select cell in columnH below the last filled row in
columnI
For j = 1 To 12 'Count number of equivalent points
    If ActiveCell.Offset(j, 0).Value = ActiveCell Then n = n + 1
Next
'Fill time with milliseconds for first second of data
For k = 1 To n 'For the number of equivalent points
    Cells((m + 1), "I").Select 'Select cell below the last filled row in columnI
    ActiveCell.FormulaR1C1 = "= RC[-1]+1/864000*" & 9 + k - n
    m = Cells(Rows.Count, "I").End(xlUp).Row 'Row number of last filled row in
columnI
Next
'Add milliseconds for remaining data
While m < t 'Repeat loop until end of data
    n = 1 'Reset used loop variable
    j = 1 'Reset used loop variable
    k = 1 'Reset used loop variable

```

```

Cells((m + 1), "H").Select 'Select cell in columnH below the last filled row in
columnI
For j = 1 To 12 'Count number of equivalent points
    If ActiveCell.Offset(j, 0).Value = ActiveCell Then n = n + 1
Next
'Fill time with milliseconds for remaining data
For k = 1 To n 'For the number of equivalent points
    Cells((m + 1), "I").Select 'Select cell below the last filled row in columnI
    ActiveCell.FormulaR1C1 = "= RC[-1]+1/864000*" & k - 1
    m = Cells(Rows.Count, "I").End(xlUp).Row 'Row number of last filled row in
columnI
Next
Wend
Range("I:I").Columns.AutoFit

```

```

'Fill columnJ with time (min) elapsed
Cells(11, "N").Value = 5
Range("J5:M" & t).Select
Selection.NumberFormat = "0.000" 'Format columnJ, columnK, and columnL as
number
Cells(5, "J").FormulaR1C1 = "= (RC[-1]-INDEX(R1C[-1]:R" & t & "C[-
1],R11C14))*1440" 'Calculate time elapsed
Range("J5:J" & t).FillDown 'Fill calculation for remaining rows
Range("A1").Select

```

```

'Fill columnK with time (s) elapsed
Cells(5, "K").FormulaR1C1 = "=RC[-1]*60" 'Calculate time elapsed
Range("K5:K" & t).FillDown 'Fill calculation for remaining rows

```

```

'Fill columnL with surface density
Cells(5, "L").FormulaR1C1 = "=4.416915e14*(INDEX(R1C[-6]:R" & t & "C[-
6],R11C14)-RC[-6])/(INDEX(R1C[-6]:R" & t & "C[-6],R11C14)^2)" 'Calculate
surface density
Range("L5:L" & t).FillDown 'Fill calculation for remaining rows
ActiveWorkbook.Save 'Save xlsx file

```

```

'Fill columnM with thickness
'Copy txt file into Excel
Sheets.Add(After:=Sheets(Sheets.Count)).Name = "Films"
listFile = FreeFile 'Assign file number
Open listFilePath For Input As #listFile 'Open file with coefficient list
lineCount = 0 'Reset lineCount
Do Until EOF(listFile) 'Repeat loop command until end of file
    Line Input #listFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab

```

```

ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #listFile 'Close file

'Create dropdown list of film types
r = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
For Each Value In Range("A2:A" & r) 'Repeat loop until end of data
    dropdownStr = dropdownStr & "," & Value
Next Value
dropdownStr = Right(dropdownStr, Len(dropdownStr) - 1) 'Create string for
dropdown list
With ActiveSheet.Range("D2").Validation 'Create dropdown list
    .Delete
    .Add Type:=xlValidateList, AlertStyle:=xlValidAlertStop, Operator:= _
xlBetween, Formula1:=dropdownStr 'Add string to dropdown list
    .IgnoreBlank = True
    .InCellDropdown = True
    .InputTitle = ""
    .ErrorTitle = ""
    .InputMessage = ""
    .ErrorMessage = ""
    .ShowInput = True
    .ShowError = True
End With

'Add border around dropbox
Range("D2").Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
With Selection.Borders(xlEdgeLeft)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
With Selection.Borders(xlEdgeTop)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With

```

```

With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
With Selection.Borders(xlEdgeRight)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone

'Create continue button
ActiveSheet.Buttons.Add(195, 48, 65, 16).OnAction = "QCM_thickness_continue"
ActiveSheet.Shapes.Range(Array("Button 2")).Select
Selection.Characters.Text = "Continue"
With Selection.Characters(Start:=1, Length:=6).Font
    .Name = "Calibri"
    .FontStyle = "Regular"
    .Size = 12
    .Strikethrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ColorIndex = xlAutomatic
End With

Range("A1").Select
ActiveWorkbook.Save 'Save xlsx file

MsgBox "Choose film type from the dropdown list in Cell D2, then click the
button to continue."

End Sub

```

Module 4

```
Sub QCM_M_thickness_seconds()

Application.ScreenUpdating = False

Dim inFile As Variant, outFile As Variant
Dim inFile As Integer, outFile As Integer, listFile As Integer
Dim lineCount As Long
Dim listFilePath As String, fileLine As String, frequencyStr As String,
dropdownStr As String
Dim i As Long 'Loop to remove carriage return
Dim t As Long 'Count row number of last filled row in columnA data

'Update path for coefficient list
listFilePath = "/Users/.../density_list_Sauerbrey_coefficient.txt"

'Rename sheet for reference to be true later
ActiveSheet.Name = "Sheet1"

'Format sheet
Cells.Select 'Select all cells
Selection.Delete Shift:=xlUp 'Clear cells
With Selection.Font
    .Name = "Calibri"
    .Size = 12
    .Strikethrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ThemeColor = xlThemeColorLight1
    .TintAndShade = 0
    .ThemeFont = xlThemeFontMinor
End With
Selection.ColumnWidth = 10
Selection.RowHeight = 16
Range("A1").Select

'Create temporary txt file without carriage return in first line
inFilePath = Application.GetOpenFilename(".txt") 'Choose data file
outFilePath = Replace(inFilePath, ".txt", "_temp.txt") 'Create temporary file
```

```

If Dir$(inFilePath) = "" Then Exit Sub 'Confirm that path exists
inFile = FreeFile 'Assign file number
Open inFilePath For Input As #inFile 'Open file
outFile = FreeFile 'Assign file number
Open outFilePath For Output As #outFile 'Open file
lineCount = 0
Do Until EOF(inFile) 'Repeat loop command until end of file
    Line Input #inFile, fileLine
    lineCount = lineCount + 1 'Increase lineCount with each loop
    If lineCount > 1 Then
        Print #outFile, fileLine 'Print line2 to end into temporary file
    End If
Loop
Close #inFile 'Close file
Close #outFile 'Close file

'Copy txt file into Excel
Range("A4").Activate
Open outFilePath For Input As #outFile 'Open temporary file
lineCount = 0 'Reset lineCount
Do Until EOF(outFile) 'Repeat loop command until end of file
    Line Input #outFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
    ActiveCell.Offset(lineCount, 2).Value = LineItems(2) 'Fill xlsx column3 with txt
column3
    ActiveCell.Offset(lineCount, 3).Value = LineItems(3) 'Fill xlsx column4 with txt
column4
    ActiveCell.Offset(lineCount, 4).Value = LineItems(4) 'Fill xlsx column5 with txt
column5
    ActiveCell.Offset(lineCount, 5).Value = LineItems(5) 'Fill xlsx column6 with txt
column6
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #outFile 'Close file
Kill outFilePath 'Delete temporary file

'Remove carriage return from frequency column
i = 4 'First row of data
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
While i < t 'Repeat loop until end of data
    Cells(i, "F").Activate

```

```

    frequencyStr = ActiveCell.Value
    ActiveCell.Value = Left(frequencyStr, Len(frequencyStr) - 1) 'Remove
rightmost character from cell
    i = i + 1
Wend

```

```

'Save file As
Application.Dialogs(xlDialogSaveAs).Show

```

'Fill header information

```

Range("A1").Value = "Date"
Range("B1").Value = "Run #"
Range("C1").Value = "Precursor"
Range("D1").Value = "Co-reactant"
Range("E1").Value = "Co-adsorbate"
Range("F1").Value = "Carrier gas"
Range("G1").Value = "Process"
Range("H1").Value = "Sequence"
Range("I1").Value = "Crystal substrate"
Range("J1").Value = "Wafer substrate"
Range("K1").Value = "Furnace T (°C)"
Range("L1").Value = "Pressure (Torr)"
Range("M1").Value = "Total flow (sccm)"
Range("N1").Value = "z position (in)"
Range("O1").Value = "Panel 2 chemical"
Range("P1").Value = "Panel 2 flow (sccm)"
Range("Q1").Value = "Panel 2 line T (°C)"
Range("R1").Value = "Panel 2 ampoule T (°C)"
Range("S1").Value = "Panel 3 chemical"
Range("T1").Value = "Panel 3 flow (sccm)"
Range("U1").Value = "Panel 3 line T (°C)"
Range("V1").Value = "Panel 3 ampoule T (°C)"
Range("W1").Value = "Panel 4 chemical"
Range("X1").Value = "Panel 4 flow (sccm)"
Range("Y1").Value = "Panel 4 line T (°C)"
Range("Z1").Value = "Panel 4 ampoule T (°C)"
Range("AA1").Value = "Panel 1-1 flow (sccm)"
Range("AB1").Value = "Panel 1-2 flow (sccm)"
Range("AC1").Value = "Panel 1-3 flow (sccm)"
Range("AD1").Value = "Panel 1-4 flow (sccm)"
Range("C4").Value = "Rate (µg.s/cm2)"
Range("D4").Value = "Film mass (µg/cm2)"
Range("E4").Value = "Substrate mass (µg/cm2)"
Range("I4").Value = "Time"
Range("J4").Value = "Time (min)"
Range("K4").Value = "Time (s)"

```

```
Range("L4").Value = "Surface density (ng/cm2)"
Range("M4").Value = "Thickness (Å)"
Range("N4").Value = "Film density (kg/m3)"
Range("N10").Value = "Zero row number"
```

```
'Fill columnH with date
Range("H5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnH and columnI
as date
Range("H:H").Columns.AutoFit
```

```
'Fill columnI with date
Range("A5").Select
Range(Selection, Selection.End(xlDown)).Copy 'Copy data from columnA
Range("I5").Select
ActiveSheet.Paste 'Paste data from columnA into columnI
Application.CutCopyMode = False
Selection.Replace What:="T", Replacement:=" ", LookAt:=xlPart, _
    SearchOrder:=xlByRows, MatchCase:=False, FormulaVersion:= _
    xlReplaceFormula2 'Replace T in pasted data with a space
Range("I5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnI as date
Range("I:I").Columns.AutoFit
```

```
'Fill columnJ with time (min) elapsed
Cells(11, "N").Value = 5
Range("J5:M" & t).Select
Selection.NumberFormat = "0.000" 'Format columnJ, columnK, and columnL as
number
Cells(5, "J").FormulaR1C1 = "=(RC[-1]-INDEX(R1C[-1]:R" & t & "C[-
1],R11C14))*1440" 'Calculate time elapsed
Range("J5:J" & t).FillDown 'Fill calculation for remaining rows
Range("A1").Select
```

```
'Fill columnK with time (s) elapsed
Cells(5, "K").FormulaR1C1 = "=RC[-1]*60" 'Calculate time elapsed
Range("K5:K" & t).FillDown 'Fill calculation for remaining rows
```

```
'Fill columnL with surface density
Cells(5, "L").FormulaR1C1 = "=4.416915e14*(INDEX(R1C[-6]:R" & t & "C[-
6],R11C14)-RC[-6])/(INDEX(R1C[-6]:R" & t & "C[-6],R11C14)^2)" 'Calculate
surface density
Range("L5:L" & t).FillDown 'Fill calculation for remaining rows
ActiveWorkbook.Save 'Save xlsx file
```

```
'Fill columnM with thickness
```

```

'Copy txt file into Excel
Sheets.Add(After:=Sheets(Sheets.Count)).Name = "Films"
listFile = FreeFile 'Assign file number
Open listFilePath For Input As #listFile 'Open file with coefficient list
lineCount = 0 'Reset lineCount
Do Until EOF(listFile) 'Repeat loop command until end of file
    Line Input #listFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #listFile 'Close file

'Create dropdown list of film types
r = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
For Each Value In Range("A2:A" & r) 'Repeat loop until end of data
    dropdownStr = dropdownStr & "," & Value
Next Value
dropdownStr = Right(dropdownStr, Len(dropdownStr) - 1) 'Create string for
dropdown list
With ActiveSheet.Range("D2").Validation 'Create dropdown list
    .Delete
    .Add Type:=xlValidateList, AlertStyle:=xlValidAlertStop, Operator:= _
xlBetween, Formula1:=dropdownStr 'Add string to dropdown list
    .IgnoreBlank = True
    .InCellDropdown = True
    .InputTitle = ""
    .ErrorTitle = ""
    .InputMessage = ""
    .ErrorMessage = ""
    .ShowInput = True
    .ShowError = True
End With

'Add border around dropbox
Range("D2").Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
With Selection.Borders(xlEdgeLeft)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0

```

```

    .Weight = xlThin
End With
With Selection.Borders(xlEdgeTop)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
With Selection.Borders(xlEdgeRight)
    .LineStyle = xlContinuous
    .ColorIndex = 0
    .TintAndShade = 0
    .Weight = xlThin
End With
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone

```

```

'Create continue button
ActiveSheet.Buttons.Add(195, 48, 65, 16).OnAction = "QCM_thickness_continue"
ActiveSheet.Shapes.Range(Array("Button 2")).Select
Selection.Characters.Text = "Continue"
With Selection.Characters(Start:=1, Length:=6).Font
    .Name = "Calibri"
    .FontStyle = "Regular"
    .Size = 12
    .Strikethrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ColorIndex = xlAutomatic
End With

```

```

Range("A1").Select
ActiveWorkbook.Save 'Save xlsx file

```

MsgBox "Choose film type from the dropdown list in Cell D2, then click the button to continue."

End Sub

Module 5

```
Sub QCM_thickness_continue()

Application.ScreenUpdating = False

Dim r As Long 'Count row number of last filled row in columnA list
Dim t As Long 'Count row number of last filled row for loop

'Define c based on user input
r = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
Range("A1:A" & r).Select 'Select film list to search
Selection.Find(What:=Cells(2, "D").Value, After:=ActiveCell,
LookIn:=xlFormulas2, _
    LookAt:=xlPart, SearchOrder:=xlByColumns, SearchDirection:=xlNext, _
    MatchCase:=False).Activate 'Search film list for film selected from dropdown
list
Sheets("Sheet1").Cells(5, "N").Value = ActiveCell.Value 'Fill N5 with film type
ActiveCell.Offset(0, 1).Select 'Activate cell with corresponding density
Sheets("Sheet1").Cells(6, "N").Value = ActiveCell.Value 'Fill N6 with density

'Fill columnM with thickness
Sheets("Sheet1").Select
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
Cells(5, "M").FormulaR1C1 = "=RC[-1]/R6C14*100"
Range("M5:M" & t).FillDown 'Fill calculation for remaining rows
Application.DisplayAlerts = False 'Prevent popup confirming delete sheet
Sheets("Films").Delete 'Delete sheet with film coefficients
Application.DisplayAlerts = True
ActiveWorkbook.Save 'Save xlsx file

'Plot surface density vs. time
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart
ActiveChart.SetSourceData Source:=Range("$K$5:$L$" & t) 'Select data
ActiveChart.Parent.Cut
Range("P4").Select
ActiveSheet.Paste 'Paste chart in P4
ActiveSheet.ChartObjects(1).Name = "Chart 1" 'Rename chart
ActiveSheet.ChartObjects(1).Height = 216 'Size chart
ActiveSheet.ChartObjects(1).Width = 360 'Size chart
```

```

ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"L").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Name = "Series1" 'Rename Series1 as Series1
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

```

'Plot thickness vs. time

```

ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart
ActiveChart.SetSourceData Source:=Range("$K$5:$M$" & t) 'Select data
ActiveChart.Parent.Cut
Range("V4").Select
ActiveSheet.Paste 'Paste chart in V4
ActiveSheet.ChartObjects(2).Name = "Chart 2" 'Rename chart
ActiveSheet.ChartObjects(2).Height = 216 'Size chart
ActiveSheet.ChartObjects(2).Width = 360 'Size chart
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title

```

```

ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"M").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Delete 'Delete Series1
ActiveChart.FullSeriesCollection(1).Name = "Series1" 'Rename Series2 as Series1
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

Range("A1").Select
ActiveWorkbook.Save 'Save xlsx file

End Sub

```

Module 6

```
Sub QCM_T_density_milliseconds()

Application.ScreenUpdating = False

Dim inFile As Variant, outFile As Variant
Dim inFile As Integer, outFile As Integer
Dim lineCount As Long
Dim fileLine As String, frequencyStr As String
Dim i As Long 'Loop to remove carriage return
Dim t As Long 'Count row number of last filled row in columnA data
Dim m As Long 'Count row number of last filled row for loop
Dim n As Long 'Count number equivalent data points
Dim j As Long 'Loop to count equivalent data points
Dim k As Long 'Loop to fill equivalent data points

'Rename sheet
ActiveSheet.Name = "Sheet1"

'Format sheet
Cells.Select 'Select all cells
Selection.Delete Shift:=xlUp 'Clear cells
With Selection.Font
    .Name = "Calibri"
    .Size = 12
    .Strikethrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ThemeColor = xlThemeColorLight1
    .TintAndShade = 0
    .ThemeFont = xlThemeFontMinor
End With
Selection.ColumnWidth = 10
Selection.RowHeight = 16
Range("A1").Select

'Create temporary txt file without carriage return in first line
inFilePath = Application.GetOpenFilename(".txt") 'Choose data file
outFilePath = Replace(inFilePath, ".txt", "_temp.txt") 'Create temporary file
```

```

If Dir$(inFilePath) = "" Then Exit Sub 'Confirm that path exists
inFile = FreeFile 'Assign file number
Open inFilePath For Input As #inFile 'Open file
outFile = FreeFile 'Assign file number
Open outFilePath For Output As #outFile 'Open file
lineCount = 0
Do Until EOF(inFile) 'Repeat loop command until end of file
    Line Input #inFile, fileLine
    lineCount = lineCount + 1 'Increase lineCount with each loop
    If lineCount > 1 Then
        Print #outFile, fileLine 'Print line2 to end into temporary file
    End If
Loop
Close #inFile 'Close file
Close #outFile 'Close file

'Copy txt file into Excel
Range("A4").Activate
Open outFilePath For Input As #outFile 'Open temporary file
lineCount = 0 'Reset lineCount
Do Until EOF(outFile) 'Repeat loop command until end of file
    Line Input #outFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
    ActiveCell.Offset(lineCount, 2).Value = LineItems(2) 'Fill xlsx column3 with txt
column3
    ActiveCell.Offset(lineCount, 3).Value = LineItems(3) 'Fill xlsx column4 with txt
column4
    ActiveCell.Offset(lineCount, 4).Value = LineItems(4) 'Fill xlsx column5 with txt
column5
    ActiveCell.Offset(lineCount, 5).Value = LineItems(5) 'Fill xlsx column6 with txt
column6
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #outFile 'Close file
Kill outFilePath 'Delete temporary file

'Remove carriage return from frequency column
i = 4 'First row of data
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
While i < t 'Repeat loop until end of data
    Cells(i, "F").Activate

```

```

    frequencyStr = ActiveCell.Value
    ActiveCell.Value = Left(frequencyStr, Len(frequencyStr) - 1) 'Remove
rightmost character from cell
    i = i + 1
Wend

```

```

'Save file As
Application.Dialogs(xlDialogSaveAs).Show

```

'Fill header information

```

Range("A1").Value = "Date"
Range("B1").Value = "Run #"
Range("C1").Value = "Precursor"
Range("D1").Value = "Co-reactant"
Range("E1").Value = "Co-adsorbate"
Range("F1").Value = "Carrier gas"
Range("G1").Value = "Process"
Range("H1").Value = "Sequence"
Range("I1").Value = "Crystal substrate"
Range("J1").Value = "Wafer substrate"
Range("K1").Value = "Furnace T (°C)"
Range("L1").Value = "Pressure (Torr)"
Range("M1").Value = "Total flow (sccm)"
Range("N1").Value = "z position (in)"
Range("O1").Value = "Panel 2 chemical"
Range("P1").Value = "Panel 2 flow (sccm)"
Range("Q1").Value = "Panel 2 line T (°C)"
Range("R1").Value = "Panel 2 ampoule T (°C)"
Range("S1").Value = "Panel 3 chemical"
Range("T1").Value = "Panel 3 flow (sccm)"
Range("U1").Value = "Panel 3 line T (°C)"
Range("V1").Value = "Panel 3 ampoule T (°C)"
Range("W1").Value = "Panel 4 chemical"
Range("X1").Value = "Panel 4 flow (sccm)"
Range("Y1").Value = "Panel 4 line T (°C)"
Range("Z1").Value = "Panel 4 ampoule T (°C)"
Range("AA1").Value = "Panel 1-1 flow (sccm)"
Range("AB1").Value = "Panel 1-2 flow (sccm)"
Range("AC1").Value = "Panel 1-3 flow (sccm)"
Range("AD1").Value = "Panel 1-4 flow (sccm)"
Range("C4").Value = "Rate (Å/s)"
Range("D4").Value = "Film thickness (kÅ)"
Range("E4").Value = "Substrate thickness (kÅ)"
Range("H4").Value = "Time"
Range("I4").Value = "Time"
Range("J4").Value = "Time (min)"

```

```

Range("K4").Value = "Time (s)"
Range("L4").Value = "Surface density (ng/cm2)"
Range("M4").Value = "Zero row number"

```

```

'Fill columnH with date
Range("A5").Select
Range(Selection, Selection.End(xlDown)).Copy 'Copy data from columnA
Range("H5").Select
ActiveSheet.Paste 'Paste data from columnA into columnH
Application.CutCopyMode = False
Selection.Replace What:="T", Replacement:=" ", LookAt:=xlPart, _
    SearchOrder:=xlByRows, MatchCase:=False, FormulaVersion:= _
    xlReplaceFormula2 'Replace T in pasted data with a space
Range("H5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnH and columnI
as date
Range("H:H").Columns.AutoFit

```

```

'Fill columnI with time
'Add milliseconds to first second of data
m = 4 'Row number of last filled row in columnI
n = 1 'Start with 1 point to check for equivalency of others
Cells((m + 1), "H").Select 'Select cell in columnH below the last filled row in
columnI
For j = 1 To 12 'Count number of equivalent points
    If ActiveCell.Offset(j, 0).Value = ActiveCell Then n = n + 1
Next
'Fill time with milliseconds for first second of data
For k = 1 To n 'For the number of equivalent points
    Cells((m + 1), "I").Select 'Select cell below the last filled row in columnI
    ActiveCell.FormulaR1C1 = "= RC[-1]+1/864000*" & 9 + k - n
    m = Cells(Rows.Count, "I").End(xlUp).Row 'Row number of last filled row in
columnI
Next
'Add milliseconds for remaining data
While m < t 'Repeat loop until end of data
    n = 1 'Reset used loop variable
    j = 1 'Reset used loop variable
    k = 1 'Reset used loop variable
    Cells((m + 1), "H").Select 'Select cell in columnH below the last filled row in
columnI
    For j = 1 To 12 'Count number of equivalent points
        If ActiveCell.Offset(j, 0).Value = ActiveCell Then n = n + 1
    Next
    'Fill time with milliseconds for remaining data
    For k = 1 To n 'For the number of equivalent points

```

```

Cells((m + 1), "I").Select 'Select cell below the last filled row in columnI
ActiveCell.FormulaR1C1 = "= RC[-1]+1/864000*" & k - 1
m = Cells(Rows.Count, "I").End(xlUp).Row 'Row number of last filled row in
columnI
Next
Wend
Range("I:I").Columns.AutoFit

```

```

'Fill columnJ with time (min) elapsed
Cells(5, "M").Value = 5
Range("J5:L" & t).Select
Selection.NumberFormat = "0.000" 'Format columnJ and columnK as number
Cells(5, "J").FormulaR1C1 = "=(RC[-1]-INDEX(R1C[-1]:R" & t & "C[-
1],R5C13))*1440" 'Calculate time elapsed
Range("J5:J" & t).FillDown 'Fill calculation for remaining rows
Range("A1").Select

```

```

'Fill columnK with time (s) elapsed
Cells(5, "K").FormulaR1C1 = "=(RC[-1])*60" 'Calculate time elapsed
Range("K5:K" & t).FillDown 'Fill calculation for remaining rows

```

```

'Fill columnL with surface density
Cells(5, "L").FormulaR1C1 = "=4.416915e14*(INDEX(R1C[-6]:R" & t & "C[-
6],R5C13)-RC[-6])/(INDEX(R1C[-6]:R" & t & "C[-6],R5C13)^2)" 'Calculate surface
density
Range("L5:L" & t).FillDown 'Fill calculation for remaining rows
ActiveWorkbook.Save 'Save xlsx file

```

```

'Plot frequency vs. time
'Plot creation requires x and y data to be in consecutive columns
Range("L5:L" & t).Select
Selection.Cut
Range("U5").Select
ActiveSheet.Paste 'Move surface density data to columnU
Range("F5:F" & t).Select
Selection.Cut
Range("L5").Select
ActiveSheet.Paste 'Move frequency data to columnL

```

```

'Create and format chart
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart
ActiveChart.SetSourceData Source:=Range("$K$5:$L$" & t) 'Select data
ActiveChart.Parent.Cut
Range("O4").Select
ActiveSheet.Paste 'Paste chart in O4

```

```

ActiveSheet.ChartObjects(1).Name = "Chart 1" 'Rename chart
ActiveSheet.ChartObjects(1).Height = 216 'Size chart
ActiveSheet.ChartObjects(1).Width = 360 'Size chart
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"F").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

'Rearrange data
Range("L5:L" & t).Select
Selection.Cut
Range("F5").Select
ActiveSheet.Paste 'Move frequency data back to columnF
Range("U5:U" & t).Select
Selection.Cut
Range("L5").Select
ActiveSheet.Paste 'Move surface density data back to columnL
Application.CutCopyMode = False

'Plot surface density vs. time
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart
ActiveChart.SetSourceData Source:=Range("$K$5:$L$" & t) 'Select data
ActiveChart.Parent.Cut
Range("O19").Select
ActiveSheet.Paste 'Paste chart in O19

```

```

ActiveSheet.ChartObjects(2).Name = "Chart 2" 'Rename chart
ActiveSheet.ChartObjects(2).Height = 216 'Size chart
ActiveSheet.ChartObjects(2).Width = 360 'Size chart
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"L").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

Range("A1").Select
ActiveWorkbook.Save 'Save xlsx file

End Sub

```

Module 7

```
Sub QCM_T_density_seconds()

Application.ScreenUpdating = False

Dim inFile As Variant, outFile As Variant
Dim inFile As Integer, outFile As Integer
Dim lineCount As Long
Dim fileLine As String, frequencyStr As String
Dim i As Long 'Loop to remove carriage return
Dim t As Long 'Count row number of last filled row in columnA data

'Rename sheet
ActiveSheet.Name = "Sheet1"

'Format sheet
Cells.Select 'Select all cells
Selection.Delete Shift:=xlUp 'Clear cells
With Selection.Font
    .Name = "Calibri"
    .Size = 12
    .Strikethrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ThemeColor = xlThemeColorLight1
    .TintAndShade = 0
    .ThemeFont = xlThemeFontMinor
End With
Selection.ColumnWidth = 10
Selection.RowHeight = 16
Range("A1").Select

'Create temporary txt file without carriage return in first line
inFilePath = Application.GetOpenFilename(".txt") 'Choose data file
outFilePath = Replace(inFilePath, ".txt", "_temp.txt") 'Create temporary file
If Dir$(inFilePath) = "" Then Exit Sub 'Confirm that path exists
inFile = FreeFile 'Assign file number
Open inFilePath For Input As #inFile 'Open file
outFile = FreeFile 'Assign file number
```

```

Open outFilePath For Output As #outFile 'Open file
lineCount = 0
Do Until EOF(inFile) 'Repeat loop command until end of file
    Line Input #inFile, fileLine
    lineCount = lineCount + 1 'Increase lineCount with each loop
    If lineCount > 1 Then
        Print #outFile, fileLine 'Print line2 to end into temporary file
    End If
Loop
Close #inFile 'Close file
Close #outFile 'Close file

'Copy txt file into Excel
Range("A4").Activate
Open outFilePath For Input As #outFile 'Open temporary file
lineCount = 0 'Reset lineCount
Do Until EOF(outFile) 'Repeat loop command until end of file
    Line Input #outFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
    ActiveCell.Offset(lineCount, 2).Value = LineItems(2) 'Fill xlsx column3 with txt
column3
    ActiveCell.Offset(lineCount, 3).Value = LineItems(3) 'Fill xlsx column4 with txt
column4
    ActiveCell.Offset(lineCount, 4).Value = LineItems(4) 'Fill xlsx column5 with txt
column5
    ActiveCell.Offset(lineCount, 5).Value = LineItems(5) 'Fill xlsx column6 with txt
column6
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #outFile 'Close file
Kill outFilePath 'Delete temporary file

'Remove carriage return from frequency column
i = 4 'First row of data
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
While i < t 'Repeat loop until end of data
    Cells(i, "F").Activate
    frequencyStr = ActiveCell.Value
    ActiveCell.Value = Left(frequencyStr, Len(frequencyStr) - 1) 'Remove
rightmost character from cell
    i = i + 1

```

Wend

'Save file As

Application.Dialogs(xlDialogSaveAs).Show

'Fill header information

Range("A1").Value = "Date"

Range("B1").Value = "Run #"

Range("C1").Value = "Precursor"

Range("D1").Value = "Co-reactant"

Range("E1").Value = "Co-adsorbate"

Range("F1").Value = "Carrier gas"

Range("G1").Value = "Process"

Range("H1").Value = "Sequence"

Range("I1").Value = "Crystal substrate"

Range("J1").Value = "Wafer substrate"

Range("K1").Value = "Furnace T (°C)"

Range("L1").Value = "Pressure (Torr)"

Range("M1").Value = "Total flow (sccm)"

Range("N1").Value = "z position (in)"

Range("O1").Value = "Panel 2 chemical"

Range("P1").Value = "Panel 2 flow (sccm)"

Range("Q1").Value = "Panel 2 line T (°C)"

Range("R1").Value = "Panel 2 ampoule T (°C)"

Range("S1").Value = "Panel 3 chemical"

Range("T1").Value = "Panel 3 flow (sccm)"

Range("U1").Value = "Panel 3 line T (°C)"

Range("V1").Value = "Panel 3 ampoule T (°C)"

Range("W1").Value = "Panel 4 chemical"

Range("X1").Value = "Panel 4 flow (sccm)"

Range("Y1").Value = "Panel 4 line T (°C)"

Range("Z1").Value = "Panel 4 ampoule T (°C)"

Range("AA1").Value = "Panel 1-1 flow (sccm)"

Range("AB1").Value = "Panel 1-2 flow (sccm)"

Range("AC1").Value = "Panel 1-3 flow (sccm)"

Range("AD1").Value = "Panel 1-4 flow (sccm)"

Range("C4").Value = "Rate (Å/s)"

Range("D4").Value = "Film thickness (kÅ)"

Range("E4").Value = "Substrate thickness (kÅ)"

Range("I4").Value = "Time"

Range("J4").Value = "Time (min)"

Range("K4").Value = "Time (s)"

Range("L4").Value = "Surface density (ng/cm²)"

Range("M4").Value = "Zero row number"

'Fill columnI with date

```

Range("A5").Select
Range(Selection, Selection.End(xlDown)).Copy 'Copy data from columnA
Range("I5").Select
ActiveSheet.Paste 'Paste data from columnA into columnI
Application.CutCopyMode = False
Selection.Replace What:="T", Replacement:=" ", LookAt:=xlPart, _
    SearchOrder:=xlByRows, MatchCase:=False, FormulaVersion:= _
    xlReplaceFormula2 'Replace T in pasted data with a space
Range("I5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnI as date
Range("I:I").Columns.AutoFit

```

```

'Fill columnJ with time (min) elapsed
Cells(5, "M").Value = 5
Range("J5:L" & t).Select
Selection.NumberFormat = "0.000" 'Format columnJ and columnK as number
Cells(5, "J").FormulaR1C1 = "=(RC[-1]-INDEX(R1C[-1]:R" & t & "C[-
1],R5C13))*1440" 'Calculate time elapsed
Range("J5:J" & t).FillDown 'Fill calculation for remaining rows
Range("A1").Select

```

```

'Fill columnK with time (s) elapsed
Cells(5, "K").FormulaR1C1 = "=(RC[-1]*60)" 'Calculate time elapsed
Range("K5:K" & t).FillDown 'Fill calculation for remaining rows

```

```

'Fill columnL with surface density
Cells(5, "L").FormulaR1C1 = "=4.416915e14*(INDEX(R1C[-6]:R" & t & "C[-
6],R5C13)-RC[-6])/(INDEX(R1C[-6]:R" & t & "C[-6],R5C13)^2)" 'Calculate surface
density
Range("L5:L" & t).FillDown 'Fill calculation for remaining rows
ActiveWorkbook.Save 'Save xlsx file

```

```

'Plot Frequency vs. Time
'Plot creation requires x and y data to be in consecutive columns
Range("L5:L" & t).Select
Selection.Cut
Range("U5").Select
ActiveSheet.Paste 'Move surface density data to columnU
Range("F5:F" & t).Select
Selection.Cut
Range("L5").Select
ActiveSheet.Paste 'Move frequency data to columnL

```

```

'Create and format chart
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart

```

```

ActiveChart.SetSourceData Source:=Range("$K$5:$L$" & t) 'Select data
ActiveChart.Parent.Cut
Range("O4").Select
ActiveSheet.Paste 'Paste chart in O4
ActiveSheet.ChartObjects(1).Name = "Chart 1" 'Rename chart
ActiveSheet.ChartObjects(1).Height = 216 'Size chart
ActiveSheet.ChartObjects(1).Width = 360 'Size chart
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"F").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

'Rearrange data
Range("L5:L" & t).Select
Selection.Cut
Range("F5").Select
ActiveSheet.Paste 'Move frequency data back to columnF
Range("U5:U" & t).Select
Selection.Cut
Range("L5").Select
ActiveSheet.Paste 'Move surface density data back to columnL
Application.CutCopyMode = False

'Plot surface density vs. time
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart

```

```

ActiveChart.SetSourceData Source:=Range("$K$5:$L$" & t) 'Select data
ActiveChart.Parent.Cut
Range("O19").Select
ActiveSheet.Paste 'Paste chart in O19
ActiveSheet.ChartObjects(2).Name = "Chart 2" 'Rename chart
ActiveSheet.ChartObjects(2).Height = 216 'Size chart
ActiveSheet.ChartObjects(2).Width = 360 'Size chart
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"L").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

Range("A1").Select
ActiveWorkbook.Save 'Save.xlsx file

End Sub

```

Module 8

```
Sub QCM_M_density_milliseconds()  
  
Application.ScreenUpdating = False  
  
Dim inFilePath As Variant, outFilePath As Variant  
Dim inFile As Integer, outFile As Integer  
Dim lineCount As Long  
Dim fileLine As String, frequencyStr As String  
Dim i As Long 'Loop to remove carriage return  
Dim t As Long 'Count row number of last filled row in columnA data  
Dim m As Long 'Count row number of last filled row for loop  
Dim n As Long 'Count number equivalent data points  
Dim j As Long 'Loop to count equivalent data points  
Dim k As Long 'Loop to fill equivalent data points  
  
'Rename sheet  
ActiveSheet.Name = "Sheet1"  
  
'Format sheet  
Cells.Select 'Select all cells  
Selection.Delete Shift:=xlUp 'Clear cells  
With Selection.Font  
    .Name = "Calibri"  
    .Size = 12  
    .Strikethrough = False  
    .Superscript = False  
    .Subscript = False  
    .OutlineFont = False  
    .Shadow = False  
    .Underline = xlUnderlineStyleNone  
    .ThemeColor = xlThemeColorLight1  
    .TintAndShade = 0  
    .ThemeFont = xlThemeFontMinor  
End With  
Selection.ColumnWidth = 10  
Selection.RowHeight = 16  
Range("A1").Select  
  
'Create temporary txt file without carriage return in first line  
inFilePath = Application.GetOpenFilename(".txt") 'Choose data file  
outFilePath = Replace(inFilePath, ".txt", "_temp.txt") 'Create temporary file
```

```

If Dir$(inFilePath) = "" Then Exit Sub 'Confirm that path exists
inFile = FreeFile 'Assign file number
Open inFilePath For Input As #inFile 'Open file
outFile = FreeFile 'Assign file number
Open outFilePath For Output As #outFile 'Open file
lineCount = 0
Do Until EOF(inFile) 'Repeat loop command until end of file
    Line Input #inFile, fileLine
    lineCount = lineCount + 1 'Increase lineCount with each loop
    If lineCount > 1 Then
        Print #outFile, fileLine 'Print line2 to end into temporary file
    End If
Loop
Close #inFile 'Close file
Close #outFile 'Close file

'Copy txt file into Excel
Range("A4").Activate
Open outFilePath For Input As #outFile 'Open temporary file
lineCount = 0 'Reset lineCount
Do Until EOF(outFile) 'Repeat loop command until end of file
    Line Input #outFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
    ActiveCell.Offset(lineCount, 2).Value = LineItems(2) 'Fill xlsx column3 with txt
column3
    ActiveCell.Offset(lineCount, 3).Value = LineItems(3) 'Fill xlsx column4 with txt
column4
    ActiveCell.Offset(lineCount, 4).Value = LineItems(4) 'Fill xlsx column5 with txt
column5
    ActiveCell.Offset(lineCount, 5).Value = LineItems(5) 'Fill xlsx column6 with txt
column6
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #outFile 'Close file
Kill outFilePath 'Delete temporary file

'Remove carriage return from frequency column
i = 4 'First row of data
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
While i < t 'Repeat loop until end of data
    Cells(i, "F").Activate

```

```

    frequencyStr = ActiveCell.Value
    ActiveCell.Value = Left(frequencyStr, Len(frequencyStr) - 1) 'Remove
rightmost character from cell
    i = i + 1
Wend

```

```

'Save file As
Application.Dialogs(xlDialogSaveAs).Show

```

'Fill header information

```

Range("A1").Value = "Date"
Range("B1").Value = "Run #"
Range("C1").Value = "Precursor"
Range("D1").Value = "Co-reactant"
Range("E1").Value = "Co-adsorbate"
Range("F1").Value = "Carrier gas"
Range("G1").Value = "Process"
Range("H1").Value = "Sequence"
Range("I1").Value = "Crystal substrate"
Range("J1").Value = "Wafer substrate"
Range("K1").Value = "Furnace T (°C)"
Range("L1").Value = "Pressure (Torr)"
Range("M1").Value = "Total flow (sccm)"
Range("N1").Value = "z position (in)"
Range("O1").Value = "Panel 2 chemical"
Range("P1").Value = "Panel 2 flow (sccm)"
Range("Q1").Value = "Panel 2 line T (°C)"
Range("R1").Value = "Panel 2 ampoule T (°C)"
Range("S1").Value = "Panel 3 chemical"
Range("T1").Value = "Panel 3 flow (sccm)"
Range("U1").Value = "Panel 3 line T (°C)"
Range("V1").Value = "Panel 3 ampoule T (°C)"
Range("W1").Value = "Panel 4 chemical"
Range("X1").Value = "Panel 4 flow (sccm)"
Range("Y1").Value = "Panel 4 line T (°C)"
Range("Z1").Value = "Panel 4 ampoule T (°C)"
Range("AA1").Value = "Panel 1-1 flow (sccm)"
Range("AB1").Value = "Panel 1-2 flow (sccm)"
Range("AC1").Value = "Panel 1-3 flow (sccm)"
Range("AD1").Value = "Panel 1-4 flow (sccm)"
Range("C4").Value = "Rate (µg.s/cm2)"
Range("D4").Value = "Film mass (µg/cm2)"
Range("E4").Value = "Substrate mass (µg/cm2)"
Range("H4").Value = "Time"
Range("I4").Value = "Time"
Range("J4").Value = "Time (min)"

```

```

Range("K4").Value = "Time (s)"
Range("L4").Value = "Surface density (ng/cm2)"
Range("M4").Value = "Zero row number"

```

```

'Fill columnH with date
Range("A5").Select
Range(Selection, Selection.End(xlDown)).Copy 'Copy data from columnA
Range("H5").Select
ActiveSheet.Paste 'Paste data from columnA into columnH
Application.CutCopyMode = False
Selection.Replace What:="T", Replacement:=" ", LookAt:=xlPart, _
    SearchOrder:=xlByRows, MatchCase:=False, FormulaVersion:= _
    xlReplaceFormula2 'Replace T in pasted data with a space
Range("H5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnH and columnI
as date
Range("H:H").Columns.AutoFit

```

```

'Fill columnI with time
'Add milliseconds to first second of data
m = 4 'Row number of last filled row in columnI
n = 1 'Start with 1 point to check for equivalency of others
Cells((m + 1), "H").Select 'Select cell in columnH below the last filled row in
columnI
For j = 1 To 12 'Count number of equivalent points
    If ActiveCell.Offset(j, 0).Value = ActiveCell Then n = n + 1
Next
'Fill time with milliseconds for first second of data
For k = 1 To n 'For the number of equivalent points
    Cells((m + 1), "I").Select 'Select cell below the last filled row in columnI
    ActiveCell.FormulaR1C1 = "= RC[-1]+1/864000*" & 9 + k - n
    m = Cells(Rows.Count, "I").End(xlUp).Row 'Row number of last filled row in
columnI
Next
'Add milliseconds for remaining data
While m < t 'Repeat loop until end of data
    n = 1 'Reset used loop variable
    j = 1 'Reset used loop variable
    k = 1 'Reset used loop variable
    Cells((m + 1), "H").Select 'Select cell in columnH below the last filled row in
columnI
    For j = 1 To 12 'Count number of equivalent points
        If ActiveCell.Offset(j, 0).Value = ActiveCell Then n = n + 1
    Next
    'Fill time with milliseconds for remaining data
    For k = 1 To n 'For the number of equivalent points

```

```

Cells((m + 1), "I").Select 'Select cell below the last filled row in columnI
ActiveCell.FormulaR1C1 = "= RC[-1]+1/864000*" & k - 1
m = Cells(Rows.Count, "I").End(xlUp).Row 'Row number of last filled row in
columnI
Next
Wend
Range("I:I").Columns.AutoFit

```

```

'Fill columnJ with time (min) elapsed
Cells(5, "M").Value = 5
Range("J5:L" & t).Select
Selection.NumberFormat = "0.000" 'Format columnJ and columnK as number
Cells(5, "J").FormulaR1C1 = "=(RC[-1]-INDEX(R1C[-1]:R" & t & "C[-
1],R5C13))*1440" 'Calculate time elapsed
Range("J5:J" & t).FillDown 'Fill calculation for remaining rows
Range("A1").Select

```

```

'Fill columnK with time (s) elapsed
Cells(5, "K").FormulaR1C1 = "=(RC[-1])*60" 'Calculate time elapsed
Range("K5:K" & t).FillDown 'Fill calculation for remaining rows

```

```

'Fill columnL with surface density
Cells(5, "L").FormulaR1C1 = "=4.416915e14*(INDEX(R1C[-6]:R" & t & "C[-
6],R5C13)-RC[-6])/(INDEX(R1C[-6]:R" & t & "C[-6],R5C13)^2)" 'Calculate surface
density
Range("L5:L" & t).FillDown 'Fill calculation for remaining rows
ActiveWorkbook.Save 'Save xlsx file

```

```

'Plot frequency vs. time
'Plot creation requires x and y data to be in consecutive columns
Range("L5:L" & t).Select
Selection.Cut
Range("U5").Select
ActiveSheet.Paste 'Move surface density data to columnU
Range("F5:F" & t).Select
Selection.Cut
Range("L5").Select
ActiveSheet.Paste 'Move frequency data to columnL

```

```

'Create and format chart
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart
ActiveChart.SetSourceData Source:=Range("$K$5:$L$" & t) 'Select data
ActiveChart.Parent.Cut
Range("O4").Select
ActiveSheet.Paste 'Paste chart in O4

```

```

ActiveSheet.ChartObjects(1).Name = "Chart 1" 'Rename chart
ActiveSheet.ChartObjects(1).Height = 216 'Size chart
ActiveSheet.ChartObjects(1).Width = 360 'Size chart
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"F").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

'Rearrange data
Range("L5:L" & t).Select
Selection.Cut
Range("F5").Select
ActiveSheet.Paste 'Move frequency data back to columnF
Range("U5:U" & t).Select
Selection.Cut
Range("L5").Select
ActiveSheet.Paste 'Move surface density data back to columnL
Application.CutCopyMode = False

'Plot surface density vs. time
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart
ActiveChart.SetSourceData Source:=Range("$K$5:$L$" & t) 'Select data
ActiveChart.Parent.Cut
Range("O19").Select
ActiveSheet.Paste 'Paste chart in O19

```

```

ActiveSheet.ChartObjects(2).Name = "Chart 2" 'Rename chart
ActiveSheet.ChartObjects(2).Height = 216 'Size chart
ActiveSheet.ChartObjects(2).Width = 360 'Size chart
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"L").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

Range("A1").Select
ActiveWorkbook.Save 'Save xlsx file

End Sub

```

Module 9

```
Sub QCM_M_density_seconds()

Application.ScreenUpdating = False

Dim inFile As Variant, outFile As Variant
Dim inFile As Integer, outFile As Integer
Dim lineCount As Long
Dim fileLine As String, frequencyStr As String
Dim i As Long 'Loop to remove carriage return
Dim t As Long 'Count row number of last filled row in columnA data

'Rename sheet
ActiveSheet.Name = "Sheet1"

'Format sheet
Cells.Select 'Select all cells
Selection.Delete Shift:=xlUp 'Clear cells
With Selection.Font
    .Name = "Calibri"
    .Size = 12
    .Strikethrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ThemeColor = xlThemeColorLight1
    .TintAndShade = 0
    .ThemeFont = xlThemeFontMinor
End With
Selection.ColumnWidth = 10
Selection.RowHeight = 16
Range("A1").Select

'Create temporary txt file without carriage return in first line
inFilePath = Application.GetOpenFilename(".txt") 'Choose data file
outFilePath = Replace(inFilePath, ".txt", "_temp.txt") 'Create temporary file
If Dir$(inFilePath) = "" Then Exit Sub 'Confirm that path exists
inFile = FreeFile 'Assign file number
Open inFilePath For Input As #inFile 'Open file
outFile = FreeFile 'Assign file number
```

```

Open outFilePath For Output As #outFile 'Open file
lineCount = 0
Do Until EOF(inFile) 'Repeat loop command until end of file
    Line Input #inFile, fileLine
    lineCount = lineCount + 1 'Increase lineCount with each loop
    If lineCount > 1 Then
        Print #outFile, fileLine 'Print line2 to end into temporary file
    End If
Loop
Close #inFile 'Close file
Close #outFile 'Close file

'Copy txt file into Excel
Range("A4").Activate
Open outFilePath For Input As #outFile 'Open temporary file
lineCount = 0 'Reset lineCount
Do Until EOF(outFile) 'Repeat loop command until end of file
    Line Input #outFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
    ActiveCell.Offset(lineCount, 2).Value = LineItems(2) 'Fill xlsx column3 with txt
column3
    ActiveCell.Offset(lineCount, 3).Value = LineItems(3) 'Fill xlsx column4 with txt
column4
    ActiveCell.Offset(lineCount, 4).Value = LineItems(4) 'Fill xlsx column5 with txt
column5
    ActiveCell.Offset(lineCount, 5).Value = LineItems(5) 'Fill xlsx column6 with txt
column6
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #outFile 'Close file
Kill outFilePath 'Delete temporary file

'Remove carriage return from frequency column
i = 4 'First row of data
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
While i < t 'Repeat loop until end of data
    Cells(i, "F").Activate
    frequencyStr = ActiveCell.Value
    ActiveCell.Value = Left(frequencyStr, Len(frequencyStr) - 1) 'Remove
rightmost character from cell
    i = i + 1

```

Wend

'Save file As

Application.Dialogs(xlDialogSaveAs).Show

'Fill header information

Range("A1").Value = "Date"

Range("B1").Value = "Run #"

Range("C1").Value = "Precursor"

Range("D1").Value = "Co-reactant"

Range("E1").Value = "Co-adsorbate"

Range("F1").Value = "Carrier gas"

Range("G1").Value = "Process"

Range("H1").Value = "Sequence"

Range("I1").Value = "Crystal substrate"

Range("J1").Value = "Wafer substrate"

Range("K1").Value = "Furnace T (°C)"

Range("L1").Value = "Pressure (Torr)"

Range("M1").Value = "Total flow (sccm)"

Range("N1").Value = "z position (in)"

Range("O1").Value = "Panel 2 chemical"

Range("P1").Value = "Panel 2 flow (sccm)"

Range("Q1").Value = "Panel 2 line T (°C)"

Range("R1").Value = "Panel 2 ampoule T (°C)"

Range("S1").Value = "Panel 3 chemical"

Range("T1").Value = "Panel 3 flow (sccm)"

Range("U1").Value = "Panel 3 line T (°C)"

Range("V1").Value = "Panel 3 ampoule T (°C)"

Range("W1").Value = "Panel 4 chemical"

Range("X1").Value = "Panel 4 flow (sccm)"

Range("Y1").Value = "Panel 4 line T (°C)"

Range("Z1").Value = "Panel 4 ampoule T (°C)"

Range("AA1").Value = "Panel 1-1 flow (sccm)"

Range("AB1").Value = "Panel 1-2 flow (sccm)"

Range("AC1").Value = "Panel 1-3 flow (sccm)"

Range("AD1").Value = "Panel 1-4 flow (sccm)"

Range("C4").Value = "Rate ($\mu\text{g}\cdot\text{s}/\text{cm}^2$)"

Range("D4").Value = "Film mass ($\mu\text{g}/\text{cm}^2$)"

Range("E4").Value = "Substrate mass ($\mu\text{g}/\text{cm}^2$)"

Range("I4").Value = "Time"

Range("J4").Value = "Time (min)"

Range("K4").Value = "Time (s)"

Range("L4").Value = "Surface density (ng/cm^2)"

Range("M4").Value = "Zero row number"

'Fill columnI with date

```

Range("A5").Select
Range(Selection, Selection.End(xlDown)).Copy 'Copy data from columnA
Range("I5").Select
ActiveSheet.Paste 'Paste data from columnA into columnI
Application.CutCopyMode = False
Selection.Replace What:="T", Replacement:=" ", LookAt:=xlPart, _
    SearchOrder:=xlByRows, MatchCase:=False, FormulaVersion:= _
    xlReplaceFormula2 'Replace T in pasted data with a space
Range("I5:I" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnI as date
Range("I:I").Columns.AutoFit

```

```

'Fill columnJ with time (min) elapsed
Cells(5, "M").Value = 5
Range("J5:L" & t).Select
Selection.NumberFormat = "0.000" 'Format columnJ and columnK as number
Cells(5, "J").FormulaR1C1 = "=(RC[-1]-INDEX(R1C[-1]:R" & t & "C[-
1],R5C13))*1440" 'Calculate time elapsed
Range("J5:J" & t).FillDown 'Fill calculation for remaining rows
Range("A1").Select

```

```

'Fill columnK with time (s) elapsed
Cells(5, "K").FormulaR1C1 = "=(RC[-1]*60)" 'Calculate time elapsed
Range("K5:K" & t).FillDown 'Fill calculation for remaining rows

```

```

'Fill columnL with surface density
Cells(5, "L").FormulaR1C1 = "=4.416915e14*(INDEX(R1C[-6]:R" & t & "C[-
6],R5C13)-RC[-6])/(INDEX(R1C[-6]:R" & t & "C[-6],R5C13)^2)" 'Calculate surface
density
Range("L5:L" & t).FillDown 'Fill calculation for remaining rows
ActiveWorkbook.Save 'Save xlsx file

```

```

'Plot Frequency vs. Time
'Plot creation requires x and y data to be in consecutive columns
Range("L5:L" & t).Select
Selection.Cut
Range("U5").Select
ActiveSheet.Paste 'Move surface density data to columnU
Range("F5:F" & t).Select
Selection.Cut
Range("L5").Select
ActiveSheet.Paste 'Move frequency data to columnL

```

```

'Create and format chart
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart

```

```

ActiveChart.SetSourceData Source:=Range("$K$5:$L$" & t) 'Select data
ActiveChart.Parent.Cut
Range("O4").Select
ActiveSheet.Paste 'Paste chart in O4
ActiveSheet.ChartObjects(1).Name = "Chart 1" 'Rename chart
ActiveSheet.ChartObjects(1).Height = 216 'Size chart
ActiveSheet.ChartObjects(1).Width = 360 'Size chart
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"F").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

'Rearrange data
Range("L5:L" & t).Select
Selection.Cut
Range("F5").Select
ActiveSheet.Paste 'Move frequency data back to columnF
Range("U5:U" & t).Select
Selection.Cut
Range("L5").Select
ActiveSheet.Paste 'Move surface density data back to columnL
Application.CutCopyMode = False

'Plot surface density vs. time
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart

```

```

ActiveChart.SetSourceData Source:=Range("$K$5:$L$" & t) 'Select data
ActiveChart.Parent.Cut
Range("O19").Select
ActiveSheet.Paste 'Paste chart in O19
ActiveSheet.ChartObjects(2).Name = "Chart 2" 'Rename chart
ActiveSheet.ChartObjects(2).Height = 216 'Size chart
ActiveSheet.ChartObjects(2).Width = 360 'Size chart
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"K").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create y-axis title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(4,
"L").Value 'Define y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move y-axis
label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0" 'Define
y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define y-axis origin
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 0.25
End With

Range("A1").Select
ActiveWorkbook.Save 'Save.xlsx file

End Sub

```

Module 10

```
Sub QCM_thickness_cycles_density()

Application.ScreenUpdating = False

Dim i As Long 'Loop for steps and cycles
Dim j As Integer 'Loop for steps
Dim k As Long 'Counter for steps
Dim n_steps As Integer 'Number of steps
Dim steps() 'Array of undefined length for number of steps
Dim n_cycles As Variant 'Number of cycles
Dim cycles() 'Array of undefined length for cycle time
Dim r As Long 'Count row number of last filled row in columnA
Dim max_d1 As Double 'Maximum density
Dim max_d2 As Variant 'Maximum density rounded
Dim min_d1 As Double 'Minimum density
Dim min_d2 As Variant 'Minimum density rounded
Dim off As Long 'Offset for chart placement

Range("A1").Activate

'Input for number of steps in the sequence
n_steps_restart: 'Reference for below
n_steps = Application.InputBox(Prompt:="Enter the number of steps in the
sequence", Type:=1) 'Numerical input only
If n_steps = 0 Then 'If user presses cancel
    GoTo n_steps_restart 'Display inputbox again
End If

'Define length of array for number of steps
ReDim steps(0 To n_steps)

'Inputs to fill steps array with time for each step
steps(0) = 0
For i = 1 To n_steps
    steps_restart: 'Reference for below
    steps(i) = steps(i - 1) + Application.InputBox(Prompt:="Enter the time in
seconds for step " & i, Type:=1) 'Numerical input only
    If steps(i) = 0 Then 'If user presses cancel
        GoTo steps_restart 'Display inputbox again
    End If
Next
```

```

'Input for number of cycles
n_cycles_restart: 'Reference for below
n_cycles = Application.InputBox(Prompt:="Enter the number of cycles", Type:=1)
'Numerical input only
If n_cycles = 0 Then 'If user presses cancel
    GoTo n_cycles_restart 'Display inputbox again
End If

'Define length of array for cycle time
ReDim cycles(0 To n_cycles)

'Fill cycles array with time for each cycle
cycles(0) = 0
cycles(1) = steps(n_steps)
For i = 2 To n_cycles
    cycles(i) = cycles(1) * i
Next

'Insert columns for step indicator line information
Columns("V:X").Select
Selection.Insert Shift:=xlToRight 'Insert columns
Range("V1:X2").Select
Selection.Delete Shift:=xlToLeft 'Delete gap in header

'Determine maximum and minimum density for step indicator lines
r = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
max_d1 = Application.WorksheetFunction.max(Range("L5:L" & r)) 'Find
maximum density
max_d2 = Application.WorksheetFunction.Ceiling_Precise(max_d1, 1) 'Round
maximum density up to nearest 5
min_d1 = Application.WorksheetFunction.Min(Range("L5:L" & r)) 'Find
minimum density
min_d2 = Application.WorksheetFunction.Floor_Precise(min_d1, 1) 'Round
minimum density down to nearest 5
If Abs(min_d2) < 1 Then
    min_d2 = 0
End If

'Prevent overlapping of plots and step indicator line information
If n_steps < 6 Then
    off = 15
Else
    off = n_steps * 2 + 4
End If

```

```

For i = 1 To n_cycles
  'Duplicate Chart 1 and format new charts
  ActiveSheet.ChartObjects("Chart 1").Activate
  ActiveChart.Parent.Copy
  Range("P4").Offset(i * off, 0).Activate
  ActiveSheet.Paste
  ActiveChart.Parent.Name = "Chart " & i + 100 'Rename chart
  ActiveChart.SetElement (msoElementChartTitleAboveChart) 'Create title
  ActiveChart.ChartTitle.Text = "Cycle " & i 'Change title
  ActiveChart.Axes(xlCategory).Select 'Change x-axis range
  ActiveChart.Axes(xlCategory).MinimumScale = cycles(i - 1)
  ActiveChart.Axes(xlCategory).MaximumScale = cycles(i)

  'Fill information for step indicator lines
  Range("V4").Offset(i * off + 1, 0).Activate
  ActiveCell.Offset(-1, 0).Value = "Time (s)"
  ActiveCell.Offset(-1, 1).Value = "Surface density (ng/cm2)"
  For j = 0 To n_steps
    ActiveCell.Value = cycles(i - 1) + steps(j)
    ActiveCell.Offset(0, 1).Value = min_d2
    ActiveCell.Offset(1, 0).Value = cycles(i - 1) + steps(j)
    ActiveCell.Offset(1, 1).Value = max_d2
    ActiveCell.Offset(2, 0).Activate
  Next

  'Add step indicator lines to chart
  ActiveSheet.ChartObjects("Chart 10" & i).Activate
  k = 1
  For j = 1 To n_steps
    With ActiveChart.SeriesCollection.NewSeries
      .XValues = ActiveSheet.Range(Range("V4").Offset(i * off + k, 0),
Range("V4").Offset(i * off + k + 1, 0))
      .Values = ActiveSheet.Range(Range("V4").Offset(i * off + k, 1),
Range("V4").Offset(i * off + k + 1, 1))
    End With
    ActiveChart.FullSeriesCollection(j + 1).Name = "Series" & j + 1 'Rename
Series
    k = k + 2
  Next

  'Change line weight of step indicator lines
  For j = 1 To n_steps
    ActiveChart.FullSeriesCollection(j + 1).Select
    With Selection.Format.Line
      .Visible = msoTrue
    End With
  Next

```

```
        .ForeColor.ObjectThemeColor = msoThemeColorText1
        .Weight = 0.25
    End With
Next
Next

Range("A1").Activate
ActiveWorkbook.Save 'Save xlsx file

End Sub
```

Module 11

```
Sub QCM_thickness_cycles_thickness()

Application.ScreenUpdating = False

Dim i As Long 'Loop for steps and cycles
Dim j As Integer 'Loop for steps
Dim k As Long 'Counter for steps
Dim n_steps As Integer 'Number of steps
Dim steps() 'Array of undefined length for number of steps
Dim n_cycles As Variant 'Number of cycles
Dim cycles() 'Array of undefined length for cycle time
Dim r As Long 'Count row number of last filled row in columnA
Dim max_t1 As Double 'Maximum thickness
Dim max_t2 As Variant 'Maximum thickness rounded
Dim min_t1 As Double 'Minimum thickness
Dim min_t2 As Variant 'Minimum thickness rounded
Dim off As Long 'Offset for chart placement
Dim rng As Range 'Starting range for chart duplication

Range("A1").Activate

'Input for number of steps in the sequence
n_steps_restart: 'Reference for below
n_steps = Application.InputBox(Prompt:="Enter the number of steps in the
sequence", Type:=1) 'Numerical input only
If n_steps = 0 Then 'If user presses cancel
    GoTo n_steps_restart 'Display inputbox again
End If

'Define length of array for number of steps
ReDim steps(0 To n_steps)

'Inputs to fill steps array with time for each step
steps(0) = 0
For i = 1 To n_steps
    steps_restart: 'Reference for below
    steps(i) = steps(i - 1) + Application.InputBox(Prompt:="Enter the time in
seconds for step " & i, Type:=1) 'Numerical input only
    If steps(i) = 0 Then 'If user presses cancel
        GoTo steps_restart 'Display inputbox again
    End If
```

Next

```
'Input for number of cycles
n_cycles_restart: 'Reference for below
n_cycles = Application.InputBox(Prompt:="Enter the number of cycles", Type:=1)
'Numerical input only
If n_cycles = 0 Then 'If user presses cancel
    GoTo n_cycles_restart 'Display inputbox again
End If
```

```
'Define length of array for cycle time
ReDim cycles(0 To n_cycles)
```

```
'Fill cycles array with time for each cycle
cycles(0) = 0
cycles(1) = steps(n_steps)
For i = 2 To n_cycles
    cycles(i) = cycles(1) * i
Next
```

```
'Determine maximum and minimum thickness for step indicator lines
r = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
max_t1 = Application.WorksheetFunction.max(Range("M5:M" & r)) 'Find
maximum thickness
max_t2 = Application.WorksheetFunction.Ceiling_Precise(max_t1, 0.5) 'Round
maximum thickness up to nearest 0.5
min_t1 = Application.WorksheetFunction.Min(Range("M5:M" & r)) 'Find
minimum thickness
min_t2 = Application.WorksheetFunction.Floor_Precise(min_t1, 0.5) 'Round
minimum thickness down to nearest 0.5
If Abs(min_t2) < 1 Then
    min_t2 = 0
End If
```

```
'Prevent overlapping of plots and step indicator line information
If n_steps < 6 Then
    off = 15
Else
    off = n_steps * 2 + 4
End If
```

```
'Determine starting range for chart duplication
If WorksheetFunction.CountA(Range("V4:V" & r)) = 0 Then
    Set rng = Range("V4")
Else
```

```

Set rng = Range("Y4")
End If

For i = 1 To n_cycles
'Duplicate Chart 2 and format new charts
ActiveSheet.ChartObjects("Chart 2").Activate
ActiveChart.Parent.Copy
rng.Offset(i * off, 0).Activate
ActiveSheet.Paste
ActiveChart.Parent.Name = "Chart " & i + 200 'Rename chart
ActiveChart.SetElement (msoElementChartTitleAboveChart) 'Create title
ActiveChart.ChartTitle.Text = "Cycle " & i 'Change title
ActiveChart.Axes(xlCategory).Select 'Change x-axis range
ActiveChart.Axes(xlCategory).MinimumScale = cycles(i - 1)
ActiveChart.Axes(xlCategory).MaximumScale = cycles(i)

'Fill information for step indicator lines
rng.Offset(i * off + 1, 6).Activate
ActiveCell.Offset(-1, 0).Value = "Time (s)"
ActiveCell.Offset(-1, 1).Value = "Thickness (Å)"
For j = 0 To n_steps
    ActiveCell.Value = cycles(i - 1) + steps(j)
    ActiveCell.Offset(0, 1).Value = min_t2
    ActiveCell.Offset(1, 0).Value = cycles(i - 1) + steps(j)
    ActiveCell.Offset(1, 1).Value = max_t2
    ActiveCell.Offset(2, 0).Activate
Next

'Add step indicator lines to chart
ActiveSheet.ChartObjects("Chart 20" & i).Activate
k = 1
For j = 1 To n_steps
    With ActiveChart.SeriesCollection.NewSeries
        .XValues = ActiveSheet.Range(rng.Offset(i * off + k, 6), rng.Offset(i * off +
k + 1, 6))
        .Values = ActiveSheet.Range(rng.Offset(i * off + k, 7), rng.Offset(i * off + k
+ 1, 7))
    End With
    ActiveChart.FullSeriesCollection(j + 1).Name = "Series" & j + 1 'Rename
Series
    k = k + 2
Next

'Change line weight of step indicator lines
For j = 1 To n_steps
    ActiveChart.FullSeriesCollection(j + 1).Select

```

```
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorText1
    .Weight = 0.25
End With
Next
Next

Range("A1").Activate
ActiveWorkbook.Save 'Save xlsx file

End Sub
```

Module 12

```
Sub QCM_pressure()  
  
Application.ScreenUpdating = False  
  
Dim inFilePath As Variant  
Dim inFile As Integer  
Dim lineCount As Long  
Dim secondsStr As String  
Dim i As Long 'Loop to remove carriage return  
Dim t As Long 'Count row number of last filled row in columnA data  
  
'Rename sheet  
ActiveSheet.Name = "Sheet1"  
  
'Format sheet  
Cells.Select 'Select all cells  
Selection.Delete Shift:=xlUp 'Clear cells  
With Selection.Font  
    .Name = "Calibri"  
    .Size = 12  
    .Strikethrough = False  
    .Superscript = False  
    .Subscript = False  
    .OutlineFont = False  
    .Shadow = False  
    .Underline = xlUnderlineStyleNone  
    .ThemeColor = xlThemeColorLight1  
    .TintAndShade = 0  
    .ThemeFont = xlThemeFontMinor  
End With  
Selection.ColumnWidth = 10  
Selection.RowHeight = 16  
Range("A1").Select  
  
'Copy txt file into Excel  
inFilePath = Application.GetOpenFilename(".txt") 'Choose data file  
If Dir$(inFilePath) = "" Then Exit Sub 'Confirm that path exists  
inFile = FreeFile 'Assign file number  
Open inFilePath For Input As #inFile 'Open file  
Range("A2").Activate  
lineCount = 0 'Reset lineCount
```

```

Do Until EOF(inFile) 'Repeat loop command until end of file
    Line Input #inFile, LineFromFile
    LineItems = Split(LineFromFile, vbTab) 'Assign delimiter as tab
    ActiveCell.Offset(lineCount, 0).Value = LineItems(0) 'Fill xlsx column1 with txt
column1
    ActiveCell.Offset(lineCount, 1).Value = LineItems(1) 'Fill xlsx column2 with txt
column2
    ActiveCell.Offset(lineCount, 2).Value = LineItems(2) 'Fill xlsx column3 with txt
column3
    lineCount = lineCount + 1 'Increase lineCount with each loop
Loop
Close #inFile 'Close file

'Remove carriage return
i = 2 'First row of data
t = Cells(Rows.Count, "A").End(xlUp).Row 'Row number of last filled row in
columnA
While i - 1 < t 'Repeat loop until end of data
    Cells(i, "C").Activate
    secondsStr = ActiveCell.Value
    ActiveCell.Value = Left(secondsStr, Len(secondsStr) - 1) 'Remove rightmost
character from cell
    i = i + 1
Wend

'Save file As
Application.Dialogs(xlDialogSaveAs).Show

'Fill header information
Range("A1").Value = "Time"
Range("B1").Value = "Pressure (Torr)"
Range("C1").Value = "Valve position (% open)"
Range("D1").Value = "Time (s)"

'Fill columnD with time (s) elapsed
Cells(2, "D").FormulaR1C1 = "=(RC[-3]-R2C1)*86400" 'Calculate time elapsed
Range("D2:D" & t).FillDown 'Fill calculation for remaining rows

'Format columns
Range("A2:A" & t).Select
Selection.NumberFormat = "m/d/yy h:mm:ss.0" 'Format columnA as date
Range("A:A").Columns.AutoFit
Range("B2:B" & t).Select
Selection.NumberFormat = "0.000" 'Format columnB as number
Range("B:B").Columns.AutoFit
Range("C2:C" & t).Select

```

```
Selection.NumberFormat = "0.00" 'Format columnC as number
Range("C:C").Columns.AutoFit
Range("D2:D" & t).Select
Selection.NumberFormat = "0.000" 'Format columnF as number
```

```
'Rearrange columns
Columns("D:D").Select
Selection.Cut
Columns("B:B").Select
Selection.Insert Shift:=xlToRight
ActiveWorkbook.Save 'Save xlsx file
```

```
'Plot pressure and valve position vs. time
ActiveSheet.Shapes.AddChart2(240, xlXYScatterLinesNoMarkers).Select 'Create
chart
ActiveChart.SetSourceData Source:=Range("$B$2:$D$" & t) 'Select data
ActiveChart.Parent.Cut
Range("F2").Select
ActiveSheet.Paste 'Paste chart in F2
ActiveSheet.ChartObjects(1).Name = "Chart 1" 'Rename chart
ActiveSheet.ChartObjects(1).Height = 216 'Size chart
ActiveSheet.ChartObjects(1).Width = 360 'Size chart
ActiveChart.FullSeriesCollection(2).AxisGroup = 2 'Create secondary y-axis for
Series2 data
ActiveChart.SetElement (msoElementChartTitleNone) 'Remove title
ActiveChart.SetElement (msoElementLegendNone) 'Remove legend
ActiveChart.Axes(xlCategory, xlPrimary).HasTitle = True 'Create x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).AxisTitle.Characters.Text = Cells(1,
"B").Value 'Define x-axis title
ActiveChart.Axes(xlCategory, xlPrimary).TickLabelPosition = xlLow 'Move x-
axis label outside of plot
ActiveChart.Axes(xlCategory, xlPrimary).TickLabels.NumberFormat = "0.0"
'Define x-axis label format
ActiveChart.Axes(xlCategory, xlPrimary).CrossesAt = 0 'Define x-axis origin
ActiveChart.Axes(xlValue, xlPrimary).HasTitle = True 'Create primary y-axis
title
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = Cells(1,
"C").Value 'Define primary y-axis title
ActiveChart.Axes(xlValue, xlPrimary).TickLabelPosition = xlLow 'Move primary
y-axis label outside of plot
ActiveChart.Axes(xlValue, xlPrimary).TickLabels.NumberFormat = "0.0000"
'Define primary y-axis label format
ActiveChart.Axes(xlValue, xlPrimary).CrossesAt = 0 'Define primary y-axis
origin
ActiveChart.Axes(xlValue, xlSecondary).HasTitle = True 'Create secondary y-
axis title
```

```

ActiveChart.Axes(xlValue, xlSecondary).AxisTitle.Characters.Text = Cells(1,
"D").Value 'Define secondary y-axis title
ActiveChart.Axes(xlValue, xlSecondary).AxisTitle.Orientation = xlDownward
'Define orientation of secondary y-axis title text
ActiveChart.Axes(xlValue, xlSecondary).TickLabelPosition = xlHigh 'Move
secondary y-axis label outside of plot
ActiveChart.Axes(xlValue, xlSecondary).TickLabels.NumberFormat = "0.0"
'Define secondary y-axis label format
ActiveChart.Axes(xlValue, xlSecondary).CrossesAt = 0 'Define secondary y-axis
origin
ActiveChart.Axes(xlValue, xlPrimary).AxisTitle.Select 'Change color of primary
y-axis title
With Selection.Format.TextFrame2.TextRange.Font.Fill
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .ForeColor.TintAndShade = 0
    .ForeColor.Brightness = 0
    .Transparency = 0
    .Solid
End With
ActiveChart.Axes(xlValue, xlSecondary).AxisTitle.Select 'Change color of
secondary y-axis title
With Selection.Format.TextFrame2.TextRange.Font.Fill
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent2
    .ForeColor.TintAndShade = 0
    .ForeColor.Brightness = 0
    .Transparency = 0
    .Solid
End With
ActiveChart.FullSeriesCollection(1).Select 'Change color and line weight of
Series1 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent1
    .Weight = 1#
End With
ActiveChart.FullSeriesCollection(2).Select 'Change color and line weight of
Series2 data
With Selection.Format.Line
    .Visible = msoTrue
    .ForeColor.ObjectThemeColor = msoThemeColorAccent2
    .Weight = 1#
End With

Range("A1").Activate

```

ActiveWorkbook.Save 'Save xlsx file

End Sub

Appendix F: Standard operating procedures for common lab tasks

Procedure: change mechanical pump oil

Mechanical pump oil must be changed regularly to optimize pump performance and reduce contamination. A change in oil color, especially a darkening, indicates that a pump oil change is required. This occurs when the oil becomes contaminated or begins breaking down. Operating a pump with contaminated oil can lead to increased internal pressure, which decreases the lifespan of the pump.

Following are two options: one for if the chamber is shut down, and one that includes a temporary shutdown procedure for if the pumps will be removed and replaced within the same day. Typically, pump oil in both pumps will be changed at the same time.

Option one: The chamber is shut down and under vacuum.

1. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed
 - e. M6 closed
 - f. M7 open
 - g. M8 closed
 - h. P24 closed

- i. P25 closed
 - j. Throttle valve set to 100% open
 - k. QCM in load lock
 - l. Crystal and wafer samples not loaded
 - m. Turbo pump off
 - n. Chiller off
 - o. All cylinders and valves downstream of regulators closed
2. Gather necessary items
 - a. Paper towels
 - b. Hex wrench or screwdriver to remove oil drain plug
 - c. Needle-nose pliers to remove oil filler plug, if tight
 - d. Designated pump oil funnel
 - e. Designated pump oil change bucket
 - i. Place bucket in sink all the way to one side
 - f. Flushing fluid
 - g. Pump oil that is compatible with pump
3. Prepare pump 1 for oil change
 - a. Identify appropriate support for exhaust line once pump and trap are removed
 - b. Remove clamp and O-ring from KF fitting between isolation valve and KF16-KF25 adapter, realizing that the chamber upstream of isolation valve remains under vacuum
 - c. Cover exposed isolation valve KF fitting with aluminum foil

- d. Place exhaust line on support
 - e. Remove clamp from KF fitting between pump inlet and KF16-KF25 adapter
 - f. Place trap (with two adapters) on a paper towel on counter
 - g. Blank pump inlet KF fitting
 - h. Run pump for 60 minutes
 - i. Turn off pump
 - j. Unplug pump
 - k. Remove clamp and O-ring from pump outlet KF fitting
 - l. Cover exposed exhaust line KF fitting with aluminum foil
 - m. Cover pump outlet KF fitting loosely with aluminum foil
 - n. Place pump on counter with oil drain plug facing sink, slightly overhanging pump into sink over bucket (this might require two people)
4. Drain used oil
- a. Remove oil filler plug
 - b. Remove oil drain plug and allow oil to drain into bucket, taking care not to drop plug into bucket or touch the hot oil
 - i. If the plug is tight, tap the hex wrench with a soft-headed hammer to loosen, ensuring the pump does not lift on one side
 - c. Gently tilt pump to maximize oil removal and gently place pump back on counter in a level position
 - d. Replace oil filler and drain plugs and tighten by hand
 - e. Turn on pump for 1 s to remove oil from pumping chamber
 - f. Remove oil filler plug

- g. Remove oil drain plug
 - h. Gently tilt pump to maximize oil removal and gently place pump back on counter in a level position
5. Flush used oil from pump
- a. Replace oil drain plug and tighten with tool
 - b. Place funnel in oil filler hole
 - c. Slowly fill oil reservoir to 70% with flushing fluid
 - d. Replace oil filler plug and tighten by hand
 - e. Turn on pump for 10 minutes
6. Drain flushing fluid
- a. Remove oil filler plug
 - b. Remove oil drain plug and allow flushing fluid to drain into bucket, taking care not to drop plug into bucket
 - c. Gently tilt pump to maximize fluid removal and gently place pump back on counter in a level position
 - d. Replace oil filler and drain plugs and tighten by hand
 - e. Turn on pump for 1 s to remove fluid from pumping chamber
 - f. Remove oil filler plug
 - g. Remove oil drain plug
 - h. Gently tilt pump to maximize fluid removal and gently place pump back on counter in a level position
7. Fill pump with new oil
- a. Replace oil drain plug and tighten with tool

- b. Place funnel in oil filler hole
 - c. Slowly fill oil reservoir to 70% with pump oil
 - i. Do not overfill, as this could saturate the oil mist filter during pump down and damage the pump
 - d. Replace oil filler plug and tighten by hand
 - e. Turn on pump for 30 s to ensure there are no issues, such as the oil level rising above the top of the sight glass
8. Check sieve in trap
- a. Remove clamps and O-rings from KF fittings between trap and KF16-KF25 adapters
 - b. Remove clamp on trap (requires 7/16 in wrench)
 - c. Separate trap and remove O-ring
 - d. Remove nut and washer on mesh cover (requires 1/4 in wrench)
 - e. Assess status of sieve (it must be replaced if there is a noticeable change in color or a buildup of any foreign material)
 - i. If replacing sieve, go to **step 9**, then skip **step 10** and go to **step 11**
 - ii. If not replacing sieve, skip **step 9** and go to **step 10**
9. Replace sieve and reassemble trap
- a. Empty used sieve completely
 - b. Clean trap, KF16-KF25 adapters, and all loose O-rings with Alconox laboratory soap
 - c. Rinse trap with DI water
 - d. Allow trap to air dry

- e. Fill mesh body 3/4 full
- f. Replace and secure mesh cover
- g. Coat O-ring with vacuum-safe lubricant and replace
- h. Secure clamp
- i. Attach dry KF16-KF25 adapters to trap

10. Reassemble trap

- a. Clean KF16-KF25 adapters and all loose O-rings with Alconox laboratory soap
- b. Replace and secure mesh cover
- c. Replace O-ring
- d. Secure clamp
- e. Attach dry KF16-KF25 adapters to trap

11. Return pump to chamber

- a. Clean entire pump using spray cleaner or soap to remove all pump oil residue and dust
- b. Replace pump on floor
- c. Remove blank from pump inlet KF fitting
- d. Remove aluminum foil from pump outlet KF fitting, exposed isolation valve KF fitting, and exposed exhaust line KF fitting
- e. Attach trap with KF16-KF25 adapters to pump inlet KF fitting
- f. Attach KF fitting between isolation valve and KF16-KF25 adapter
- g. Attach KF fitting to pump outlet
- h. Plug pump into power strip

12. Repeat steps 2–11 for pump 2
13. Bake traps to regenerate new and used sieve
 - a. Turn on pumps 1 and 2
 - b. Wrap traps with heating tape
 - c. Plug heating tape into variacs using extension cords, connecting like heating tape to the same variac
 - d. Set variac output to 50–60 V, depending on the width of the heating tape (thinner heating tape needs higher voltage)
 - e. Allow bake to proceed for 2 hours
 - f. Turn off variacs
 - g. Once cooled, unwrap heating tape from traps
 - h. Turn off pumps 1 and 2
14. Transfer used flushing fluid and oil for disposal
 - a. Place a funnel into an empty flushing fluid or pump oil bottle
 - b. Transfer used flushing fluid and oil from bucket into waste bottle
 - c. Dispose of used flushing fluid and oil in Olin Hall B56
15. Clean up
 - a. Clean all tools and bucket thoroughly with soap to remove all pump oil residue
 - b. Clean sink thoroughly with soap to remove all pump oil residue
 - c. Clean counters thoroughly with spray cleaner to remove all pump oil residue

Option two: Temporary shutdown of the chamber because the pumps will be removed and replaced within the same day.

1. Starting conditions:

- a. No flow
- b. All pneumatic valves on panels 1–4 closed
- c. All MFCs closed
- d. M5 closed
- e. M6 open
- f. M7 open
- g. M8 open
- h. P24 closed
- i. P25 closed
- j. Throttle valve set to 100% open
- k. QCM in load lock or furnace
- l. Crystal and wafer samples loaded or not loaded
- m. Turbo pump on
- n. Chiller on
- o. All cylinders and valves downstream of regulators closed

2. Temporarily shut down chamber

- a. Close M8
- b. Turn off turbo pump
- c. Turn off chiller

- d. Unplug solenoids for P26 and P27 to close isolation valves 1 and 2
3. Gather necessary items
 - a. Paper towels
 - b. Hex wrench or screwdriver to remove oil drain plug
 - c. Needle-nose pliers to remove oil filler plug, if tight
 - d. Designated pump oil funnel
 - e. Designated pump oil change bucket
 - i. Place bucket in sink all the way to one side
 - f. Flushing fluid
 - g. Pump oil that is compatible with pump
 4. Prepare pump 1 for oil change
 - a. Identify appropriate support for exhaust line once pump and trap are removed
 - b. Turn off pump
 - c. Unplug pump
 - d. Remove clamp and O-ring from pump outlet KF fitting
 - e. Cover exposed exhaust line KF fitting with aluminum foil
 - f. Cover pump outlet KF fitting loosely with aluminum foil
 - g. Remove clamp and O-ring from KF fitting between isolation valve and KF16-KF25 adapter, realizing that the chamber upstream of isolation valve remains under vacuum
 - h. Cover exposed isolation valve KF fitting with aluminum foil
 - i. Place exhaust line on support

- j. Remove clamp from KF fitting between pump inlet and KF16-KF25 adapter
 - k. Place trap (with two adapters) on a paper towel on counter
 - l. Blank pump inlet KF fitting
 - m. Place pump on counter with oil drain plug facing sink, slightly overhanging pump into sink over bucket (this might require two people)
5. Drain used oil
- a. Remove oil filler plug
 - b. Remove oil drain plug and allow oil to drain into bucket, taking care not to drop plug into bucket or touch the hot oil
 - i. If the plug is tight, tap the hex wrench with a soft-headed hammer to loosen, ensuring the pump does not lift on one side
 - c. Gently tilt pump to maximize oil removal and gently place pump back on counter in a level position
 - d. Replace oil filler and drain plugs and tighten by hand
 - e. Turn on pump for 1 s to remove oil from pumping chamber
 - f. Remove oil filler plug
 - g. Remove oil drain plug
 - h. Gently tilt pump to maximize oil removal and gently place pump back on counter in a level position
6. Flush used oil from pump
- a. Replace oil drain plug and tighten with tool
 - b. Place funnel in oil filler hole
 - c. Slowly fill oil reservoir to 70% with flushing fluid

- d. Replace oil filler plug and tighten by hand
 - e. Turn on pump for 10 minutes
7. Drain flushing fluid
- a. Remove oil filler plug
 - b. Remove oil drain plug and allow flushing fluid to drain into bucket, taking care not to drop plug into bucket
 - c. Gently tilt pump to maximize fluid removal and gently place pump back on counter in a level position
 - d. Replace oil filler and drain plugs and tighten by hand
 - e. Turn on pump for 1 s to remove fluid from pumping chamber
 - f. Remove oil filler plug
 - g. Remove oil drain plug
 - h. Gently tilt pump to maximize fluid removal and gently place pump back on counter in a level position
8. Fill pump with new oil
- a. Replace oil drain plug and tighten with tool
 - b. Place funnel in oil filler hole
 - c. Slowly fill oil reservoir to 70% with pump oil
 - i. Do not overfill, as this could saturate the oil mist filter during pump down and damage the pump
 - d. Replace oil filler plug and tighten by hand
 - e. Turn on pump for 30 s to ensure there are no issues, such as the oil level rising above the top of the sight glass

9. Check sieve in trap

- a. Remove clamps and O-rings from KF fittings between trap and KF16-KF25 adapters
- b. Remove clamp on trap (requires 7/16 in wrench)
- c. Separate trap and remove O-ring
- d. Remove nut and washer on mesh cover (requires 1/4 in wrench)
- e. Assess status of sieve (it must be replaced if there is a noticeable change in color or a buildup of any foreign material)
 - i. If replacing sieve, go to **step 10**, then skip **step 11** and go to **step 12**
 - ii. If not replacing sieve, skip **step 10** and go to **step 11**

10. Replace sieve and reassemble trap

- a. Empty used sieve completely
- b. Clean trap, KF16-KF25 adapters, and all loose O-rings with Alconox laboratory soap
- c. Rinse trap with DI water
- d. Allow trap to air dry
- e. Fill mesh body 3/4 full
- f. Replace and secure mesh cover
- g. Coat O-ring with vacuum-safe lubricant and replace
- h. Secure clamp
- i. Attach dry KF16-KF25 adapters to trap

11. Reassemble trap

- a. Clean KF16-KF25 adapters and all loose O-rings with Alconox laboratory soap
- b. Replace and secure mesh cover
- c. Replace O-ring
- d. Secure clamp
- e. Attach dry KF16-KF25 adapters to trap

12. Return pump to chamber

- a. Clean entire pump using spray cleaner or soap to remove all pump oil residue and dust
- b. Replace pump on floor
- c. Remove blank from pump inlet KF fitting
- d. Remove aluminum foil from pump outlet KF fitting, exposed isolation valve KF fitting, and exposed exhaust line KF fitting
- e. Attach trap with KF16-KF25 adapters to pump inlet KF fitting
- f. Attach KF fitting between isolation valve and KF16-KF25 adapter
- g. Attach KF fitting to pump outlet
- h. Plug pump into power strip
- i. Turn on pump

13. Repeat **steps 3–12** for pump 2

14. Bake traps to regenerate new and used sieve

- a. Wrap traps with heating tape
- b. Plug heating tape into variacs using extension cords, connecting like heating tape to the same variac

- c. Set variac output to 50–60 V, depending on the width of the heating tape (thinner heating tape needs higher voltage)
 - d. Allow bake to proceed for 2 hours
 - e. Turn off variacs
 - f. Once cooled, unwrap heating tape from traps
15. Open chamber to pumps 1 and 2
- a. Plug in solenoids for P26 and P27 to open isolation valves 1 and 2
 - b. Turn on turbo pump
 - c. Turn on chiller
 - d. Open M8
16. Transfer used flushing fluid and oil for disposal
- a. Place a funnel into an empty flushing fluid or pump oil bottle
 - b. Transfer used flushing fluid and oil from bucket into waste bottle
 - c. Dispose of used flushing fluid and oil in Olin Hall B56
17. Clean up
- a. Clean all tools and bucket thoroughly with soap to remove all pump oil residue
 - b. Clean sink thoroughly with soap to remove all pump oil residue
 - c. Clean counters thoroughly with spray cleaner to remove all pump oil residue

Procedure: standard clean for vacuum parts

Standard cleaning is required for equipment used in vacuum systems. Installation of contaminated equipment can lead to erroneous experimental results. Standard cleaning is a three-step process where the equipment is sonicated in solvents to remove various contaminants. If equipment is not stainless steel, confirm that material is compatible with required chemicals.

Use a respirator when exposure to trichloroethylene is possible: during **step 6** and while cleaning glass containers exposed to trichloroethylene. Immediately change gloves that are contaminated with trichloroethylene.

If equipment has not been exposed to sulfur-containing compounds, skip **step 5**.

1. Don laboratory coat
2. Remove sonicator from storage below the sink and place it in fume hood
3. Choose a glass container of an appropriate size for the equipment that is being cleaned (e.g., a 4 L beaker for a bubbler) and place it in fume hood
4. Place equipment in empty glass container, as equipment dropped into container full of solvent will break the glass (place a bubbler right-side up so solvent will fill the bubbler)
5. Clean with 50% nitric acid to remove sulfur
 - a. Bring nitric acid bottle from cabinet below fume hood into fume hood

- b. Carefully fill the glass container containing the equipment with solvent, using the minimum amount necessary
- c. Replace solvent bottle in cabinet below fume hood
- d. Place the container filled with equipment and solvent into the empty sonicator
- e. Carefully fill the sonicator with water up to the level of the solvent in the container, or to the top of the sonicator if the solvent level is higher
- f. Sonicate for 30 minutes
- g. If equipment is taller than a 4 L beaker (e.g., a bubbler), rotate and sonicate for 30 minutes
- h. If cleaning a bubbler, remove it from the solvent, taking care not to touch the solvent, and place it in a clean glass container in the fume hood
- i. Bring another clean glass container into the fume hood
- j. Carefully transfer the nitric acid to the empty container
- k. Remove any additional equipment from the original container and place it in the container with the bubbler
- l. Leave container used for nitric acid sonication in fume hood until cleaning
- m. Rinse equipment thoroughly with DI water in the sink
- n. Place container with rinsed equipment in fume hood
- o. If equipment still smells of sulfur, repeat sonication until smell is gone
 - i. Nitric acid can be reused for a second sonication on the same day
- p. Bring a compatible waste bottle (glass only for nitric acid $\geq 50\%$) into the fume hood

- q. Place a funnel into the waste bottle and carefully dispose of the nitric acid
 - r. Place equipment in a clean and dry glass container
6. Clean with trichloroethylene to remove hydrocarbons
- a. Bring trichloroethylene bottle from cabinet below fume hood into fume hood
 - b. Carefully fill the glass container containing the equipment with solvent, using the minimum amount necessary
 - c. Replace solvent bottle in cabinet below fume hood
 - d. Place the container filled with equipment and solvent into the empty sonicator (or sonicator already containing water, if nitric acid sonication was performed)
 - e. Carefully fill the sonicator (or ensure it is filled) with water up to the level of the solvent in the container, or to the top of the sonicator if the solvent level is higher
 - f. Sonicate for 30 minutes
 - g. If equipment is taller than a 4 L beaker (e.g., a bubbler), rotate and sonicate for 30 minutes
 - h. If cleaning a bubbler, remove it from the solvent, taking care not to touch the solvent, and place it in a clean glass container in the fume hood
 - i. Bring a compatible waste bottle (glass only for trichloroethylene) into the fume hood
 - j. Place a funnel into the waste bottle and carefully dispose of the trichloroethylene

- k. Remove any additional equipment from the original container and place it in the container with the bubbler
 - l. Leave container used for trichloroethylene sonication in fume hood until cleaning
 - m. Rinse equipment thoroughly with DI water in the sink
 - n. Place container with rinsed equipment in fume hood
 - o. Place equipment in a clean and dry glass container
7. Clean with acetone to remove hydroxyl groups (water)
- a. Bring acetone bottle from cabinet below fume hood into fume hood
 - b. Carefully fill the glass container containing the equipment with solvent, using the minimum amount necessary
 - c. Replace solvent bottle in cabinet below fume hood
 - d. Place the container filled with equipment and solvent into the sonicator
 - e. Ensure the sonicator is filled with water up to the level of the solvent in the container, or to the top of the sonicator if the solvent level is higher
 - f. Sonicate for 30 minutes
 - g. If equipment is taller than a 4 L beaker (e.g., a bubbler), rotate and sonicate for 30 minutes
 - h. If cleaning a bubbler, remove it from the solvent, taking care not to touch the solvent, and place it in a clean and dry glass container in the fume hood
 - i. Bring a compatible waste bottle (poly or glass for acetone) into the fume hood
 - j. Place a funnel into the waste bottle and carefully dispose of the acetone

10. Empty the sonicator and return it to storage below the sink
11. Clean the funnel and all containers thoroughly with Alconox laboratory soap
12. Request the next available pickup for generated hazardous waste
 - a. Refer to the Cornell EHS information as needed:
<https://ehs.cornell.edu/environmental-compliance/hazardous-materials-waste/chemical-hazardous-waste>

Procedure: cleave wafer samples

Wafer samples used in the QCM chamber are 1.15 x 0.35 in for compatibility with the sample holder used for XPS in the microreactor chamber. The following procedure is based on a starting sample in the shape of a quarter circle, for example.

Wafer holders have a sloped interior, where the outer edge is higher than the center. For this reason, samples are placed upside down in wafer holders, so the deposition area cannot be damaged by contact with the holder. However, this design works only when the wafer holder diameter and the sample length are approximately the same, so small wafer holders must be used for samples of this size.

1. Gather necessary items
 - a. Clean wipes
 - b. Wafer
 - c. Metal wafer tweezers
 - d. Designated ruler for measuring wafer samples
 - e. Diamond scribe
 - f. Wafer cleaving pliers
 - g. Small wafer holders
2. Clean tweezers, ruler, scribe and pliers with 2-propanol and place on a clean wipe
3. Place the wafer on a clean wipe (upside down if it is a metal-coated or patterned wafer, so the silicon side is scribed)

4. Cleave a rectangle of 1.15 in height from the wafer
 - a. Starting at the point created by the two straight sides, measure 1.15 in on one of the sides
 - b. Scribe the wafer using the diamond scribe, creating a single line from 2–3 mm in from the wafer edge to the wafer edge
 - c. Hold the pliers with the white line facing up
 - d. Place the wafer inside the pliers, lining the white line up with the scribe, and overlapping the pliers 3–4 mm onto the wafer
 - e. Keeping the wafer close to the counter, gently squeeze the pliers until the wafer cleaves
5. Cleave 1.15 x 0.35 in rectangles
 - a. Starting at the point created by one of the long, straight sides and the side of height 1.15 in, measure 0.35 in on the long side
 - b. Scribe the wafer using the diamond scribe, creating a single line from 2–3 mm in from the wafer edge to the wafer edge
 - c. Hold the pliers with the white line facing up
 - d. Place the wafer inside the pliers, lining the white line up with the scribe, and overlapping the pliers 3–4 mm onto the wafer
 - e. Keeping the wafer close to the counter, gently squeeze the pliers until the wafer cleaves
6. Repeat **step 5** for the length of the wafer fragment, or for however many samples are desired
7. For silicon samples, scribe an X on one side to indicate the bottom

8. Place samples upside down in wafer holders
9. Clean tweezers, ruler, scribe and pliers with 2-propanol and put away

Procedure: make chemical oxide on silicon wafer samples

When exposed to atmosphere, the surface of a Si(100) wafer becomes partially oxidized, creating what is called “native oxide.” The density of hydroxyl groups in native oxide is unknown and variable, so samples from silicon wafers are chemically modified to produce a hydroxyl-terminated silicon oxide surface with a density of $\sim 5 \times 10^{14}$ hydroxyl groups/cm². This process is completed in a chemistry hood in the Cornell NanoScale Science and Technology Facility (CNF) cleanroom.

1. Prepare workspace
 - a. Bring silicon wafer samples, safety glasses, and cleanroom notebook with procedure to the CNF
 - b. Retrieve two metal wafer tweezers from the group box in the cleanroom (one without holes and one with holes)
 - c. Bring samples, tweezers, and notebook to one of the chemistry hoods designated for acids
 - d. Sign in on clipboard with name, date, time, chemicals, and chemical quantities
 - e. Fill out 4 sticky notes with name, date, and chemical names (Nanostrip, BOE 6:1, DI water, DI water)
 - f. Bring 4 wipes to the hood
 - g. Bring 2 glass containers, 1 glass watch glass, 2 Teflon containers, and 2 Teflon watch glasses to the hood

- h. Bring a timer to the hood
 - i. Put on apron, face shield, and thick nitrile gloves
 - j. Bring a hot plate with thermometer attachment and ring stand with clamp to the left side of the hood, if not already present
 - k. Plug in hot plate and press button to start 15-minute power timer (press regularly to keep hot plate on)
 - l. Cover workspace with wipes
2. Prepare 1 container of Nanostrip (sulfuric acid and hydrogen peroxide)
 - a. Bring Nanostrip bottle from cabinet below hood into hood
 - b. Pour Nanostrip into 1 glass container, using the minimum amount necessary to cover the samples
 - c. Replace Nanostrip bottle in cabinet below fume hood
 - d. Place container of Nanostrip on hot plate
 - e. Use clamp to secure thermometer in a location where it is submerged in Nanostrip but not touching the bottom of the container
 - f. Set hot plate to 75 °C
 - g. Place Nanostrip sticky note label in front of hot plate
 3. Prepare 1 container of buffered oxide etch (BOE) 6:1 (hydrofluoric acid and buffering agent)
 - a. Bring BOE 6:1 bottle from cabinet below hood into hood
 - b. Pour BOE 6:1 into 1 Teflon container, using the minimum amount necessary to cover the samples
 - c. Replace BOE 6:1 bottle in cabinet below fume hood

- d. Cover container of BOE 6:1 with 1 Teflon watch glass
 - e. Place BOE 6:1 sticky note label on watch glass
4. Prepare 2 containers of DI water
 - a. Fill 1 glass container with DI water
 - b. Cover container of DI water with 1 glass watch glass
 - c. Place DI water sticky note label on watch glass
 - d. Fill 1 Teflon container with DI water
 - e. Cover container of DI water with 1 Teflon watch glass
 - f. Place DI water sticky note label on watch glass
5. Arrange workspace
 - a. The container of Nanostrip is on the hot plate on the left
 - b. The glass container of DI water is on a wipe to the right of the hot plate
 - c. The container of BOE 6:1 is on the next wipe to the right
 - d. The Teflon container of DI water is on the next wipe to the right
 - e. The last wipe on the right is used to place the wafer holders, the samples between processes, and the tweezers when not in use
6. Remove native oxide from silicon samples
 - a. Submerge sample in BOE 6:1 for 2 minutes
 - b. Using metal wafer tweezers without holes, remove sample from BOE 6:1
 - c. Rinse sample in the DI water in the Teflon container
 - d. Rinse sample with DI water spray gun into sink
 - e. Dry sample with N₂ blow gun over sink
 - f. Set sample down on wipe

- g. Dry tweezers with N₂ blow gun over sink
 - h. Pick up sample from the opposite end
 - i. Dry sample with N₂ blow gun over sink
 - j. Inspect sample to ensure it is completely dry and there are no water stains
 - i. If water stains are present, repeat steps 6d–6j
 - k. Repeat steps 6a–6j for all samples
 - l. Empty and refill the DI water in the Teflon container
7. Make chemical oxide on silicon samples
- a. Submerge sample in Nanostrip (at 75–80 °C) for 5 minutes
 - b. Using metal wafer tweezers with holes, remove sample from Nanostrip
 - c. Rinse sample in the DI water in the glass container
 - d. Rinse sample with DI water spray gun into sink
 - e. Dry sample with N₂ blow gun over sink
 - f. Set sample down on wipe
 - g. Dry tweezers with N₂ blow gun over sink
 - h. Pick up sample from the opposite end
 - i. Dry sample with N₂ blow gun over sink
 - j. Inspect sample to ensure it is completely dry and there are no water stains
 - i. If water stains are present, repeat steps 7d–7j
 - k. Repeat steps 7a–7j for all samples
 - l. Empty and refill the DI water in the glass container
8. Remove native oxide from silicon samples
- a. Submerge sample in BOE 6:1 for 2 minutes

- b. Using metal wafer tweezers without holes, remove sample from BOE 6:1
 - c. Rinse sample in the DI water in the Teflon container
 - d. Rinse sample with DI water spray gun into sink
 - e. Dry sample with N₂ blow gun over sink
 - f. Set sample down on wipe
 - g. Dry tweezers with N₂ blow gun over sink
 - h. Pick up sample from the opposite end
 - i. Dry sample with N₂ blow gun over sink
 - j. Inspect sample to ensure it is completely dry and there are no water stains
 - i. If water stains are present, repeat **steps 8d–8j**
 - k. Repeat **steps 8a–8j** for all samples
 - l. Empty and refill the DI water in the Teflon container
9. Make chemical oxide on silicon samples
- a. Submerge sample in Nanostrip (at 75–80 °C) for 15 minutes
 - b. Using metal wafer tweezers with holes, remove sample from Nanostrip
 - c. Rinse sample in the DI water in the glass container
 - d. Rinse sample with DI water spray gun into sink
 - e. Dry sample with N₂ blow gun over sink
 - f. Set sample down on wipe
 - g. Dry tweezers with N₂ blow gun over sink
 - h. Pick up sample from the opposite end
 - i. Dry sample with N₂ blow gun over sink
 - j. Inspect sample to ensure it is completely dry and there are no water stains

- i. If water stains are present, repeat steps 9d–9j
- k. Repeat steps 9a–9j for all samples

10. Shut down

- a. Turn off hot plate
- b. Remove container of Nanostrip from hot plate
- c. Place samples upside down in wafer holders
- d. Rinse tweezers with DI water spray gun into sink

11. Dispose of used DI water

- a. Remove Teflon watch glass covering Teflon container of DI water
- b. Dispose of sticky note label
- c. Rinse thoroughly with city water
- d. Empty Teflon container of DI water into sink
- e. Rinse thoroughly with city water
- f. Remove glass watch glass covering glass container of DI water
- g. Dispose of sticky note label
- h. Rinse thoroughly with city water
- i. Empty glass container of DI water into sink
- j. Rinse thoroughly with city water
- k. Place containers and watch glasses in rack by dishwashers

12. Dispose of BOE 6:1

- a. Remove Teflon watch glass covering container of BOE 6:1
- b. Dispose of sticky note label
- c. Rinse thoroughly with city water

- d. Place BOE waste bottle into sink
- e. Remove pressure-relief cap
- f. Place a funnel into the waste bottle and carefully dispose of the BOE
- g. Remove funnel from waste bottle and place in sink
- h. Replace pressure-relief cap
- i. Remove waste bottle from sink
- j. Thoroughly rinse the funnel
- k. Thoroughly rinse the Teflon container
- l. Place container and watch glass in rack by dishwashers

13. Dispose of Nanostrip

- a. Dispose of sticky note label
- b. Place Nanostrip waste bottle into sink
- c. Remove pressure-relief cap
- d. Place a funnel into the waste bottle and carefully dispose of the Nanostrip
- e. Remove funnel from waste bottle and place in sink
- f. Replace pressure-relief cap
- g. Remove waste bottle from sink
- h. Thoroughly rinse the funnel
- i. Thoroughly rinse the glass container
- j. Place container in rack by dishwashers

14. Continue shut down

- a. Wet one of the wipes from under the containers with DI water
- b. Use wipe to clean thermometer

- c. Dispose of all wipes
- d. Dispose of thick nitrile gloves
- e. Remove face shield and apron
- f. Return two metal wafer tweezers to the group box in the cleanroom
- g. Return silicon wafer samples, safety glasses, and cleanroom notebook to lab

When making several samples, it saves time to immerse multiple samples in the Nanostrip at one time. Because the BOE step is only 2 minutes, it is not recommended to immerse more than one sample at a time, because rinsing and drying a sample can take multiple minutes to complete. An example of timing for 5 samples is below. In all steps, the last sample is removed with sufficient time to complete rinsing and drying the sample before the timer runs out.

1. BOE 6:1, 2 minutes
 - a. 25 minutes, in sample 1
 - b. 23 minutes, out sample 1
 - c. 21 minutes, in sample 2
 - d. 19 minutes, out sample 2
 - e. 17 minutes, in sample 3
 - f. 15 minutes, out sample 3
 - g. 13 minutes, in sample 4
 - h. 11 minutes, out sample 4
 - i. 9 minutes, in sample 5

- j. 7 minutes, out sample 5
2. Nanostrip, 5 minutes
- a. 25 minutes, in sample 1
 - b. 21 minutes, in sample 2
 - c. 20 minutes, out sample 1
 - d. 17 minutes, in sample 3
 - e. 16 minutes, out sample 2
 - f. 13 minutes, in sample 4
 - g. 12 minutes, out sample 3
 - h. 9 minutes, in sample 5
 - i. 8 minutes, out sample 4
 - j. 4 minutes, out sample 5
3. BOE 6:1, 2 minutes
- a. 25 minutes, in sample 1
 - b. 23 minutes, out sample 1
 - c. 21 minutes, in sample 2
 - d. 19 minutes, out sample 2
 - e. 17 minutes, in sample 3
 - f. 15 minutes, out sample 3
 - g. 13 minutes, in sample 4
 - h. 11 minutes, out sample 4
 - i. 9 minutes, in sample 5
 - j. 7 minutes, out sample 5

4. Nanostrip, 15 minutes
 - a. 40 minutes, in sample 1
 - b. 35 minutes, in sample 2
 - c. 31 minutes, in sample 3
 - d. 26 minutes, in sample 4
 - e. 25 minutes, out sample 1
 - f. 21 minutes, in sample 5
 - g. 20 minutes, out sample 2
 - h. 16 minutes, out sample 3
 - i. 11 minutes, out sample 4
 - j. 6 minutes, out sample 5

Procedure: shut down chamber

To shut down the chamber from vacuum, it is unnecessary to vent all lines to the cylinders. The chamber can be left under vacuum, without being pumped, for extended periods, which minimizes exposure to water and other contaminants. In the event of unexpected venting to atmospheric pressure, the QCM must be in the load lock to prevent damage to the translator bellows.

All electronics must be shut down if the chamber will not be used for an extended period. Before turning off electronics, ensure that all equipment is in the desired configuration for shutdown (pneumatic valves closed, MFCs closed, throttle valve open, etc.). The lab must also be left in a safe and energy-saving condition if it will not be used for an extended period.

After this procedure, the chamber is isolated in dead volume from downstream of panels 2–4, to P24, to P25, to M8 and M5, through the translator and QCM backside purge to M6. Other smaller areas of dead volume exist, such as from downstream of P3, P5, and P7 on panel 1 to P24, and from M1 to M5 and M6. Because KF flanges are not leak-tight, the forelines up to P25 and M8 will increase in pressure over time. However, the chamber should not increase significantly in pressure because it is closed from atmosphere by gate valves. There could be a small increase in chamber pressure because there is a short section of KF tubing upstream of the throttle valve. Because MFCs are not on-off valves,

some gas will pass through MFCs E, F, and G, causing a pressure increase upstream of P3/P4, P5/P6, and P7/P8.

1. Starting conditions:

- a. No flow
- b. All pneumatic valves on panels 1–4 closed
- c. All MFCs closed
- d. M5 closed
- e. M6 open
- f. M7 open
- g. M8 open
- h. P24 closed
- i. P25 closed
- j. Throttle valve set to 100% open
- k. QCM in furnace
- l. Crystal and wafer samples not loaded
- m. Turbo pump on
- n. Chiller on
- o. All cylinders and valves downstream of regulators closed

2. Switch process pump

- a. Close M8
- b. Turn off turbo pump
- c. Turn off chiller

- d. Open P25
3. Remove controller BNC cable from QCM
4. Move QCM to position 0.75" on translator (moving to position 0" would catch QCM sensor clamps on load lock flange and cause damage)
5. Evacuate all gas up to P1, P3/P4, P5/P6, P7/P8 and send to pump
 - a. Open P24
 - b. Open P4, P6, P8, P9, P13, P14, P18, P19, P23
 - c. Open P10, P11 if a bubbler is attached to panel 2 (ensure manual valves on bubbler are closed)
 - d. Open P15, P16 if a bubbler is attached to panel 3 (ensure manual valves on bubbler are closed)
 - e. Open P20, P21 if a bubbler is attached to panel 4 (ensure manual valves on bubbler are closed)
 - f. Open M5
 - g. Set MFCs A, B, C, D to open
 - h. Allow lines to be pumped for 10 minutes
 - i. Close MFCs A, B, C, D
 - j. Close M1, M2, M3, M4
 - k. Close M5, M6
 - l. Close P10, P11, P15, P16, P20, P21
 - m. Close P4, P6, P8, P9, P13, P14, P18, P19, P23
 - n. Close P24
6. Close P25 to isolate chamber

7. Place a support under the bellows of the translator in case of unexpected vent
8. Shut down powered equipment
 - a. Unplug solenoids for P26 and P27 to close isolation valves 1 and 2
 - b. Turn off pumps 1 and 2
 - c. Turn off tube furnace by switch on front and switch on back, and unplug
 - d. Turn off chiller by button on front and switch on front, and unplug
 - e. Unplug plasma generator
 - f. Turn off MFC controllers 1 and 2 by switch on front
 - g. Turn off throttle valve/Baratron controller by switch on back
 - h. Turn off thermocouple gauge 1 and 2 displays by switch on front
 - i. Turn off computer
 - j. Unplug all power strips, placing plugs in an elevated location
 - k. Ensure no electrical cords or plugs are directly on the floor in case of unexpected flooding
9. Shut down lab
 - a. Dispose of all hazardous waste
 - b. Ensure fume hood is empty and closed completely
 - c. Put away all glassware on the drying rack
 - d. Close door between 310 and 312
 - e. Close window blinds
 - f. Turn heat to lowest setting
 - g. Turn off lights

Procedure: vent chamber

If the chamber needs to be vented to atmosphere, such as for maintenance, the surface area exposed to air should be minimized. The following is an option to slowly open the leak valve on the turbo pump to vent using air. An option also exists to vent using inert gas, but this process is slow and does not prevent contamination once the chamber is exposed to air. The QCM must be in the load lock to prevent damage to the translator bellows.

After completing this procedure, the chamber will be vented from downstream of panels 2–4, to P24, to P25, to M8 and M5, through the translator and QCM backside purge to M6. P25, M8, P26, and P27 remain in a closed position so the pumps are not overloaded when turned back on, because the chamber is too large of a volume for the pumps to evacuate at once.

If the vent is temporary, and not to shut down the lab for an extended period, skip steps 5j, 9, and 10.

1. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed

- e. M6 open
 - f. M7 open
 - g. M8 open
 - h. P24 closed
 - i. P25 closed
 - j. Throttle valve set to 100% open
 - k. QCM in furnace
 - l. Crystal and wafer samples not loaded
 - m. Turbo pump on
 - n. Chiller on
 - o. All cylinders and valves downstream of regulators closed
2. Switch process pump
 - a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
 3. Remove controller BNC cable from QCM
 4. Move QCM to position 0.75" on translator (moving to position 0" would catch QCM sensor clamps on load lock flange and cause damage)
 5. Evacuate all gas up to P1, P3/P4, P5/P6, P7/P8 and send to pump
 - a. Open P24
 - b. Open P4, P6, P8, P9, P13, P14, P18, P19, P23

- c. Open P10, P11 if a bubbler is attached to panel 2 (ensure manual valves on bubbler are closed)
 - d. Open P15, P16 if a bubbler is attached to panel 3 (ensure manual valves on bubbler are closed)
 - e. Open P20, P21 if a bubbler is attached to panel 4 (ensure manual valves on bubbler are closed)
 - f. Open M5
 - g. Set MFCs A, B, C, D to open
 - h. Allow lines to be pumped for 10 minutes
 - i. Close MFCs A, B, C, D
 - j. Close M1, M2, M3, M4
 - k. Close M5, M6
 - l. Close P10, P11, P15, P16, P20, P21
 - m. Close P4, P6, P8, P9, P13, P14, P18, P19, P23
 - n. Close P24
6. Close P25 to isolate chamber
7. Place a support under the bellows of the translator
8. Vent chamber
- a. Unplug solenoids for P26 and P27 to close isolation valves 1 and 2
 - b. Turn off pumps 1 and 2
 - c. Open M8
 - d. Slowly and incrementally open the leak valve on the turbo pump until the pressures equilibrate

- e. Close the leak valve
 - f. Close M8
9. Shut down powered equipment
- a. Unplug solenoids for P26 and P27 to close isolation valves 1 and 2
 - b. Turn off pumps 1 and 2
 - c. Turn off tube furnace by switch on front and switch on back, and unplug
 - d. Turn off chiller by button on front and switch on front, and unplug
 - e. Unplug plasma generator
 - f. Turn off MFC controllers 1 and 2 by switch on front
 - g. Turn off throttle valve/Baratron controller by switch on back
 - h. Turn off thermocouple gauge 1 and 2 displays by switches on front
 - i. Turn off computer
 - j. Unplug all power strips, placing plugs in an elevated location
 - k. Ensure no electrical cords or plugs are directly on the floor in case of unexpected flooding
10. Shut down lab
- a. Dispose of all hazardous waste
 - b. Ensure fume hood is empty and closed completely
 - c. Put away all glassware on the drying rack
 - d. Close door between 310 and 312
 - e. Close window blinds
 - f. Turn heat to lowest setting
 - g. Turn off lights

Procedure: restart chamber after vent

When the chamber is restarted after being vented, it must be opened to the mechanical pumps incrementally because the chamber is too large of a volume for the pumps to evacuate at once. First, the pumps are turned on and they pump up to the isolation valves. After opening the isolation valves, P25 is opened so pump 1 pumps up to P24 and panels 2–4, and pump 2 pumps up M8. Then, any further sections exposed to atmosphere are pumped down.

1. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed
 - e. M6 closed
 - f. M7 open
 - g. M8 closed
 - h. P24 closed
 - i. P25 closed
 - j. Throttle valve set to 100% open
 - k. QCM in load lock
 - l. Crystal and wafer samples not loaded
 - m. Turbo pump off

- n. Chiller off
 - o. All cylinders and valves downstream of regulators closed
2. Pump down chamber
 - a. Turn on pumps 1 and 2
 - b. Wait 15 minutes for pumps to warm up
 - c. Plug in solenoids for P26 and P27 to open isolation valves 1 and 2
 - d. Wait for pressure, as measured by the thermocouple gauges, to drop
 - e. Open P25
 - f. If upstream of P24 was vented, open P24 and wait for pressure to drop
 - g. If upstream of M5 and M6 was vented, open M5 and wait for pressure to drop
 - h. If panels were vented, incrementally open valves from downstream to upstream and wait for pressure to drop
 3. Switch process pump
 - a. Close P25
 - b. Open M8
 - c. Turn on turbo pump
 - d. Turn on chiller
 4. Bake sections exposed to atmosphere according to "Procedure: bake chamber, option one"

Procedure: after power outage

The main concern of a power outage occurring while the chamber is under vacuum is that the pumps will be damaged by exposure to atmospheric pressure while operating, especially the turbo pump. The translator bellows could also be damaged by venting of the chamber if the QCM is positioned in the furnace. Because the isolation valves close at a loss of power, no vent to atmosphere should occur and the vacuum conditions in the chamber should be preserved, but understanding what happens when the power goes out helps for a quick response to resolve any potential issues.

An unexpected power outage is most likely to occur while an operator is not in lab, and while there is no gas flow through the chamber. However, it is possible that a power outage will occur while an operator is not in lab and while gas is flowing, such as during an overnight bake. In any case, it is important to go to lab as soon as possible. One issue is that, if flow is on when the power goes out, the pneumatic valves controlled by the DAQ will not reopen once the power turns back on, but the MFCs will return to their setpoints, which would result in a pressure buildup downstream of the MFCs.

Following are three scenarios: one for if there is no gas flowing, one for if there is gas flowing to the pump from cylinders 1–4, and one for if there is gas flowing to the reactor from cylinders 1–4.

Scenario one: No flow.

1. Starting conditions:

- a. No flow
- b. All pneumatic valves on panels 1–4 closed
- c. All MFCs closed
- d. M5 closed
- e. M6 open
- f. M7 open
- g. M8 open
- h. P24 closed
- i. P25 closed
- j. Throttle valve set to 100% open
- k. QCM in load lock or furnace
- l. Crystal and wafer samples loaded or not loaded
- m. Turbo pump on
- n. Chiller on
- o. All cylinders and valves downstream of regulators closed

2. Results of a power outage:

- a. DAQ and DAQ power supply are turned off, but solenoids for P1–P23 are already deactivated, so no change
- b. Solenoid for P24 is already deactivated, so no change
- c. Solenoid for P25 is already deactivated, so no change
- d. Solenoid for P26 is deactivated, closing isolation valve 1

- e. Solenoid for P27 is deactivated, closing isolation valve 2
 - f. Pump 1 is turned off
 - g. Pump 2 is turned off
 - h. Turbo pump controller is turned off, stopping turbo pump
 - i. Plasma generator is turned off, if it is plugged in
 - j. Furnace is turned off
 - k. Chiller is turned off, stopping water circulation
 - l. MFC controllers 1 and 2 are turned off, but all MFCs are already closed, so no change
 - m. Throttle valve/Baratron controller is turned off, halting throttle valve in position at time of power outage
 - n. Thermocouple gauge display is turned off
 - o. Heating cord controllers 1 and 2 are turned off
 - p. Translator is turned off
 - q. Computer and monitor are turned off, but solenoids for P1–P23 are already deactivated, so no change (does not affect other controllers)
 - r. Any variacs in use are turned off
 - s. Any heating baths in use are turned off
3. When power returns:
- a. DAQ and DAQ power supply are turned on, but solenoids for P1–P23 are not activated, so all valves on panels remain closed
 - b. Solenoid for P24 is already deactivated, so no change
 - c. Solenoid for P25 is already deactivated, so no change

- d. Solenoid for P26 is activated, opening isolation valve 1
- e. Solenoid for P27 is activated, opening isolation valve 2
- f. Pump 1 is turned on
- g. Pump 2 is turned on
- h. Turbo pump controller is turned on, returning turbo pump to setpoint from before power outage
- i. Plasma generator is turned on, if it is plugged in
- j. Furnace is turned on
 - i. If no program is on, furnace returns to manual setpoint
 - ii. If program is on, furnace returns to program and restarts step in action at time of power outage
- k. Chiller is turned on, restarting water circulation
- l. MFC controllers 1 and 2 are turned on, but all MFCs are already closed, so no change
- m. Throttle valve/Baratron controller is turned on, returning throttle valve to setpoint from before power outage
- n. Thermocouple gauge display is turned on
- o. Heating cord controllers 1 and 2 are turned on, returning to setpoints from before power outage
- p. Translator is turned on
- q. Computer and monitor are turned on, but solenoids for P1–P23 are not activated, so all valves on panels remain closed (does not affect other controllers)

- r. Any variacs in use are turned on, returning to setpoints from before power outage
 - s. Any heating baths in use are turned on, returning to setpoints from before power outage
4. What needs to be checked:
- a. Status of P1–P23
 - b. P26 and P27, isolation valves 1 and 2
 - c. Pumps 1 and 2
 - d. Turbo pump
 - e. Plasma generator, if it is plugged in
 - f. Furnace
 - g. MFC setpoints
 - h. Throttle valve position
 - i. Heating cords, if in use
 - j. Any variacs in use
 - k. Any heating baths in use

Scenario two: Flow to pump from cylinders 1–4.

1. Starting conditions:
- a. Flow on
 - b. P1, P4, P6, P8, P9, P13, P14, P18, P19, P23 open
 - c. MFCs B, C, D, E, F, G at a setpoint

- d. M5 closed
 - e. M6 open
 - f. M7 open
 - g. M8 closed
 - h. P24 closed
 - i. P25 open
 - j. Throttle valve set to 100% open
 - k. QCM in load lock or furnace
 - l. Crystal and wafer samples loaded or not loaded
 - m. Turbo pump off
 - n. Chiller off
 - o. All cylinders and valves downstream of regulators open
2. Results of a power outage:
- a. DAQ and DAQ power supply are turned off, deactivating solenoids for P1–P23, closing all valves on panels
 - b. Solenoid for P24 is already deactivated, so no change
 - c. Solenoid for P25 is deactivated, closing gate valve downstream of throttle valve
 - d. Solenoid for P26 is deactivated, closing isolation valve 1
 - e. Solenoid for P27 is deactivated, closing isolation valve 2
 - f. Pump 1 is turned off
 - g. Pump 2 is turned off
 - l. Turbo pump controller is turned off, but turbo pump is not on, so no change

- h. Plasma generator is turned off, if it is plugged in
 - i. Furnace is turned off
 - j. Chiller is turned off, stopping water circulation
 - k. MFC controllers 1 and 2 are turned off, closing all MFCs
 - l. Throttle valve/Baratron controller is turned off, halting throttle valve in position at time of power outage
 - m. Thermocouple gauge display is turned off
 - n. Heating cord controllers 1 and 2 are turned off
 - o. Translator is turned off
 - p. Computer and monitor are turned off, deactivating solenoids for P1–P23, closing all valves on panels (does not affect other controllers)
 - q. Any variacs in use are turned off
 - r. Any heating baths in use are turned off
3. When power returns:
- a. DAQ and DAQ power supply are turned on, but solenoids for P1–P23 are not activated, so all valves on panels remain closed
 - b. Solenoid for P24 is already deactivated, so no change
 - c. Solenoid for P25 is activated, opening gate valve downstream of throttle valve
 - d. Solenoid for P26 is activated, opening isolation valve 1
 - e. Solenoid for P27 is activated, opening isolation valve 2
 - f. Pump 1 is turned on
 - g. Pump 2 is turned on

- h. Turbo pump controller is turned on, but turbo pump was not on, so no change
- i. Plasma generator is turned on, if it is plugged in
- j. Furnace is turned on
 - i. If no program is on, furnace returns to manual setpoint
 - ii. If program is on, furnace returns to program and restarts step in action at time of power outage
- k. Chiller is turned on, restarting water circulation
- l. MFC controllers 1 and 2 are turned on, returning all MFCs to setpoints from before power outage
- m. Throttle valve/Baratron controller is turned on, returning throttle valve to setpoint from before power outage
- n. Thermocouple gauge display is turned on
- o. Heating cord controllers 1 and 2 are turned on, returning to setpoints from before power outage
- p. Translator is turned on
- q. Computer and monitor are turned on, but solenoids for P1–P23 are not activated, so all valves on panels remain closed (does not affect other controllers)
- r. Any variacs in use are turned on, returning to setpoints from before power outage
- s. Any heating baths in use are turned on, returning to setpoints from before power outage

4. What needs to be fixed:
 - a. Open P1, P4, P6, P8, P9, P13, P14, P18, P19, P23
5. What needs to be checked:
 - a. P25, gate valve downstream of throttle valve
 - b. P26 and P27, isolation valves 1 and 2
 - c. Pumps 1 and 2
 - d. Turbo pump
 - e. Plasma generator, if it is plugged in
 - f. Furnace
 - g. MFC setpoints
 - h. Throttle valve position
 - i. Heating cords, if in use
 - j. Any variacs in use
 - k. Any heating baths in use

Scenario three: Flow to reactor from cylinders 1–4.

1. Starting conditions:
 - a. Flow on
 - b. P1, P3, P5, P7, P9, P12, P14, P17, P19, P22 open
 - c. MFCs B, C, D, E, F, G at a setpoint
 - d. M5 closed
 - e. M6 open

- f. M7 open
 - g. M8 closed
 - h. P24 open
 - i. P25 open
 - j. Throttle valve set to 100% open
 - k. QCM in furnace
 - l. Crystal and wafer samples not loaded
 - m. Turbo pump on
 - n. Chiller on
 - o. All cylinders and valves downstream of regulators open
2. Results of a power outage:
- a. DAQ and DAQ power supply are turned off, deactivating solenoids for P1–P23, closing all valves on panels
 - b. Solenoid for P24 is deactivated, closing gate valve downstream of plasma generator
 - c. Solenoid for P25 is deactivated, closing gate valve downstream of throttle valve
 - d. Solenoid for P26 is deactivated, closing isolation valve 1
 - e. Solenoid for P27 is deactivated, closing isolation valve 2
 - f. Pump 1 is turned off
 - g. Pump 2 is turned off
 - h. Turbo pump controller is turned off, stopping turbo pump
 - i. Plasma generator is turned off, if it is plugged in

- j. Furnace is turned off
 - k. Chiller is turned off, but chiller is not on, so no change
 - l. MFC controllers 1 and 2 are turned off, closing all MFCs
 - m. Throttle valve/Baratron controller is turned off, halting throttle valve in position at time of power outage
 - n. Thermocouple gauge display is turned off
 - o. Heating cord controllers 1 and 2 are turned off
 - p. Translator is turned off
 - q. Computer and monitor are turned off, deactivating solenoids for P1–P23, closing all valves on panels (does not affect other controllers)
 - r. Any variacs in use are turned off
 - s. Any heating baths in use are turned off
3. When power returns:
- a. DAQ and DAQ power supply are turned on, but solenoids for P1–P23 are not activated, so all valves on panels remain closed
 - b. Solenoid for P24 is activated, opening gate valve downstream of plasma generator
 - c. Solenoid for P25 is activated, opening gate valve downstream of throttle valve
 - d. Solenoid for P26 is activated, opening isolation valve 1
 - e. Solenoid for P27 is activated, opening isolation valve 2
 - f. Pump 1 is turned on
 - g. Pump 2 is turned on

- h. Turbo pump controller is turned on, returning turbo pump to setpoint from before power outage
- i. Plasma generator is turned on, if it is plugged in
- j. Furnace is turned on
 - i. If no program is on, furnace returns to manual setpoint
 - ii. If program is on, furnace returns to program and restarts step in action at time of power outage
- k. Chiller is turned on, but goes to standby mode
- l. MFC controllers 1 and 2 are turned on, returning all MFCs to setpoints from before power outage
- m. Throttle valve/Baratron controller is turned on, returning throttle valve to setpoint from before power outage
- n. Thermocouple gauge display is turned on
- o. Heating cord controllers 1 and 2 are turned on, returning to setpoints from before power outage
- p. Translator is turned on
- q. Computer and monitor are turned on, but solenoids for P1–P23 are not activated, so all valves on panels remain closed (does not affect other controllers)
- r. Any variacs in use are turned on, returning to setpoints from before power outage
- s. Any heating baths in use are turned on, returning to setpoints from before power outage

4. What needs to be fixed:
 - a. Open P1, P3, P5, P7, P9, P12, P14, P17, P19, P22
5. What needs to be checked:
 - a. P25, gate valve downstream of throttle valve
 - b. P26 and P27, isolation valves 1 and 2
 - c. Pumps 1 and 2
 - d. Turbo pump
 - e. Plasma generator, if it is plugged in
 - f. Furnace
 - g. Chiller
 - h. MFC setpoints
 - i. Throttle valve position
 - j. Heating cords, if in use
 - k. Any variacs in use
 - l. Any heating baths in use

Procedure: helium leak check

Helium leak checking is used to confirm that a vacuum system is leak-tight, or to identify the location of a known leak. The Cornell Center for Materials Research (CCMR) has a Varian 979 Helium Leak Detector that is available for users to rent. The leak detector includes a turbo pump with a rotary vane backing pump, and serves as the sole pumping configuration when connected to the chamber. Once the chamber is pumped down using the leak detector, a calibration is completed on the smallest volume possible, before opening the leak detector to the whole chamber. Helium is then sprayed around the outside of the chamber to determine if any leaks exist. A complete operating manual for the leak detector can be found online.

To leak check all the way up to the cylinders, complete steps 1–6, skip step 7, and continue with step 8. To leak check up to P1, complete steps 1–5, skip step 6, continue with step 7, then skip steps 15c–k and steps 16m–n so P1, P3/P4, P5/P6, P7/P8 are not opened.

Pumping down and calibrating the leak detector can take over an hour. Then, testing the entire system can take many hours, especially if a leak is discovered, so a full day is recommended. The leak detector must be logged in and accruing charges while away from CCMR, including if it is kept overnight, so it is best to retrieve and return it on the same day. The user must have CCMR card access to return equipment after business hours. Steps 1–7 can be completed in advance of the day leak testing will be performed.

1. Reserve leak detector on CCMR online tool manager
2. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed
 - e. M6 open
 - f. M7 open
 - g. M8 open
 - h. P24 closed
 - i. P25 closed
 - j. Throttle valve set to 100% open
 - k. QCM in furnace
 - l. Crystal and wafer samples not loaded
 - m. Turbo pump on
 - n. Chiller on
 - o. All cylinders and valves downstream of regulators closed
3. Switch process pump
 - a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
4. Remove controller BNC cable from QCM

5. Move QCM to position 0.75" on translator (moving to position 0" would catch QCM sensor clamps on load lock flange and cause damage)
6. Evacuate all gas up to regulators and send to pump
 - a. Open P24
 - b. Open P4, P6, P8, P9, P13, P14, P18, P19, P23
 - c. Open P10, P11 if a bubbler is attached to panel 2 (ensure manual valves on bubbler are closed)
 - d. Open P15, P16 if a bubbler is attached to panel 3 (ensure manual valves on bubbler are closed)
 - e. Open P20, P21 if a bubbler is attached to panel 4 (ensure manual valves on bubbler are closed)
 - f. Open P1
 - g. Set all MFCs to open
 - h. Open M5
 - i. Allow lines to be pumped for 10 minutes
 - j. Close all MFCs
 - k. Close M1, M2, M3, M4
 - l. Close M5, M6
 - m. Close P10, P11, P15, P16, P20, P21
 - n. Close P4, P6, P8, P9, P13, P14, P18, P19, P23
 - o. Close P24
7. Evacuate all gas up to P1 and send to pump
 - a. Open P24

- b. Open P9, P13, P14, P18, P19, P23
 - c. Open P10, P11 if changing bubbler attached to panel 2 (ensure manual valves on bubbler are closed)
 - d. Open P15, P16 if changing bubbler attached to panel 3 (ensure manual valves on bubbler are closed)
 - e. Open P20, P21 if changing bubbler attached to panel 4 (ensure manual valves on bubbler are closed)
 - f. Set MFCs A, B, C, D to open
 - g. Open M5
 - h. Allow lines to be pumped for 10 minutes
 - i. Close MFCs A, B, C, D
 - j. Close M1, M2, M3, M4
 - k. Close M5, M6
 - l. Close P10, P11, P15, P16, P20, P21
 - m. Close P9, P13, P14, P18, P19, P23
 - n. Close P24
8. Prepare helium
- a. Bring a helium gas cylinder into lab
 - b. Affix the helium regulator with attached plastic tubing and needle valve to the helium gas cylinder
9. Retrieve leak detector
- a. Go to CCMR

- b. Log in to leak detector on CCMR online tool manager to start accruing charges
 - c. Carefully bring leak detector to Olin Hall, choosing a route that avoids stairs (having two people might be useful, as the cart is heavy)
10. Isolate chamber
 - a. Close M7
 - b. Close P25
11. Attach the leak detector to the chamber
 - a. Unplug solenoid for P26 to close isolation valve 1
 - b. Turn off pump 1
 - c. Separate the exhaust line to pump 1 between the thermocouple gauge and isolation valve
 - d. Loosen KF fittings in exhaust line downstream of P25, realizing that the chamber upstream of gate valve remains under vacuum
 - e. Reconfigure exhaust line from P25 to the thermocouple gauge and connect to leak detector inlet, possibly utilizing spare KF tubing
 - f. Cover the exposed KF fitting with aluminum foil
12. Start up the leak detector
 - a. Plug in leak detector
 - b. Turn on leak detector by switch on back
 - c. Wait until the screen shows "System Ready" and the test port pressure is at one light

- d. Press the "Test" button to put the system in test mode and wait until the test port pressure is at one light
- e. Press the "Calibrate" button to perform an automated calibration of the system and wait until the system returns to test mode
- f. Press the "Read Standard Leak" button and compare the displayed leak rate value to the calibrated leak rate value
- g. Press the "Read Standard Leak" button again to return to test mode and wait until the test port pressure is at one light

13. How to operate the leak detector

- a. Press the "Hold" button when in test mode to isolate the test port, and any volume of the chamber not isolated from the test port, from the mass spectrometer, which is necessary to protect the mass spectrometer and turbo pump if there is a rise in pressure in the chamber
- b. Press the "Vent" button to isolate the test port from the mass spectrometer and vent the test port, and any volume of the chamber not isolated from the test port, to the atmosphere
- c. Press the "Zero" button to subtract the background pressure from the displayed leak rate, but only when there can be no helium in the chamber
- d. If a leak is observed at any time, identify the exact location of the leak and resolve it, putting the leak detector into hold mode if necessary

14. Incrementally leak check the chamber

- a. Spray all fittings up to P25 and observe the displayed leak rate value for any increase

- b. Open P25 and wait until the test port pressure is at one light
- c. Spray all fittings from downstream of panels 2–4, to P24, to M7 and observe the displayed leak rate value for any increase
- d. Open M7 and wait until the test port pressure is at one light
- e. Spray all fittings from M7, to M5, to M8, through the translator and QCM backside purge to M6 and observe the displayed leak rate value for any increase
- f. Open M5 and wait until the test port pressure is at one light
- g. Spray all fittings from M1 to M6 and observe the displayed leak rate value for any increase
- h. Close M5
- i. Close M7

15. Incrementally leak check upstream of the plasma generator

- a. Open P24 and wait until the test port pressure is at one light
- b. Spray all fittings from downstream of P3/P4, P5/P6, P7/P8 to P24 and observe the displayed leak rate value for any increase
- c. Open P3 and MFC E and wait until the test port pressure is at one light
- d. Spray all fittings from regulator of cylinder 2 to P3/P4 and observe the displayed leak rate value for any increase
- e. Close P3 and MFC E
- f. Open P5 and MFC F and wait until the test port pressure is at one light
- g. Spray all fittings from regulator of cylinder 3 to P5/P6 and observe the displayed leak rate value for any increase

- h. Close P5 and MFC F
- i. Open P7 and MFC G and wait until the test port pressure is at one light
- j. Spray all fittings from regulator of cylinder 4 to P7/P8 and observe the displayed leak rate value for any increase
- k. Close P7 and MFC G
- l. Close P24

16. Incrementally leak check the panels

- a. Open P9, P10, P11, P12 and wait until the test port pressure is at one light
- b. Spray all fittings from M2 to P12/P13 and observe the displayed leak rate value for any increase
- c. Close P9, P10, P11, P12
- d. Open P14, P15, P16, P17 and wait until the test port pressure is at one light
- e. Spray all fittings from M3 to P17/P18 and observe the displayed leak rate value for any increase
- f. Close P14, P15, P16, P17
- g. Open P19, P20, P21, P22 and wait until the test port pressure is at one light
- h. Spray all fittings from M4 to P22/P23 and observe the displayed leak rate value for any increase
- i. Close P19, P20, P21, P22
- j. Open P9, P12, M2, and MFCs A, B, C, D and wait until the test port pressure is at one light
- k. Spray all fittings from P1 to P2, to M1, to M2, to M3, to M4 and observe the displayed leak rate value for any increase

- l. Close MFCs A, C, D
 - m. Open P1 and wait until the test port pressure is at one light
 - n. Spray all fittings from regulator of cylinder 1 to P1 and observe the displayed leak rate value for any increase
 - o. Close P1, P9, P12, M2, MFC B
17. Remove the leak detector from the chamber
- a. Close P25
 - b. Press the "Hold" button
 - c. Press the "Vent" button
 - d. Turn off leak detector by switch on back
 - e. Unplug leak detector
 - f. Disconnect KF tubing from leak detector inlet and reconnect exhaust line to pump 1, ensuring all KF fittings are fully tightened
18. Open chamber to pumps 1 and 2
- a. Turn on pump 1
 - b. Wait 15 minutes for pump to warm up
 - c. Plug in solenoid for P26 to open isolation valve 1
 - d. Open M7
 - e. Open M8
 - f. Turn on turbo pump
 - g. Turn on chiller
19. Return leak detector

- a. Carefully bring leak detector to CCMR, choosing a route that avoids stairs
(having two people might be useful, as the cart is heavy)
 - b. Log out of leak detector on CCMR online tool manager
20. Remove the helium gas cylinder from lab, removing the regulator if necessary

Procedure: change gas cylinder

Changing a gas cylinder is required if a cylinder is emptied, or if a new gas is desired. Complete steps 1–3; choose step 4, 5, 6, or 7 depending on which cylinder is being replaced; then complete steps 8–14.

1. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed
 - e. M6 open
 - f. M7 open
 - g. M8 open
 - h. P24 closed
 - i. P25 closed
 - j. Throttle valve set to 100% open
 - k. QCM in load lock or furnace
 - l. Crystal and wafer samples not loaded
 - m. Turbo pump on
 - n. Chiller on
 - o. All cylinders and valves downstream of regulators closed
2. Switch process pump

- a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
3. Bring new cylinder to lab on designated cylinder cart
 4. Evacuate all gas up to cylinder 1 and send to pump
 - a. Open P1, P9, P13, P14, P18, P19, P23
 - b. Set MFCs A, B, C, D to open
 - c. Open valve downstream of regulator on cylinder 1
 - d. Open regulator on cylinder 1
 - e. Allow lines to be pumped for 10 minutes
 - f. Close regulator on cylinder 1
 - g. Close valve downstream of regulator on cylinder 1
 - h. Close MFCs A, B, C, D
 - i. Close P1, P9, P13, P14, P18, P19, P23
 5. Evacuate all gas up to cylinder 2 and send to pump
 - a. Open P24
 - b. Open P4
 - c. Set MFC E to open
 - d. Open valve downstream of regulator on cylinder 2
 - e. Open regulator on cylinder 2
 - f. Allow lines to be pumped for 10 minutes
 - g. Close regulator on cylinder 2

- h. Close valve downstream of regulator on cylinder 2
 - i. Close MFC E
 - j. Close P4
 - k. Close P24
6. Evacuate all gas up to cylinder 3 and send to pump
- a. Open P24
 - b. Open P6
 - c. Set MFC F to open
 - d. Open valve downstream of regulator on cylinder 3
 - e. Open regulator on cylinder 3
 - f. Allow lines to be pumped for 10 minutes
 - g. Close regulator on cylinder 3
 - h. Close valve downstream of regulator on cylinder 3
 - i. Close MFC F
 - j. Close P6
 - k. Close P24
7. Evacuate all gas up to cylinder 4 and send to pump
- a. Open P24
 - b. Open P8
 - c. Set MFC G to open
 - d. Open valve downstream of regulator on cylinder 4
 - e. Open regulator on cylinder 4
 - f. Allow lines to be pumped for 10 minutes

- g. Close regulator on cylinder 4
 - h. Close valve downstream of regulator on cylinder 4
 - i. Close MFC G
 - j. Close P8
 - k. Close P24
8. Remove regulator from old cylinder at the CGA fitting (this will require two people, as someone needs to hold the regulator during the cylinder exchange)
 9. Remove new cylinder from cart
 10. Place old cylinder on cart
 11. Securely strap new cylinder into wall support
 12. Attach regulator to new cylinder
 13. Properly store or dispose of old cylinder
 14. Bake according to "Procedure: bake chamber, option two"
 15. If desired, leak check according to "Procedure: helium leak check"

Procedure: change bubbler

This procedure is for a bubbler with a 1/2 in VCR filling port, but it can be easily modified for bubblers of a different type.

It is important to clean the flexible tubing upstream of a bubbler when the bubbler is cleaned. The flexible tubing is exposed to the chemical in the bubbler during experiments, and would be contaminated by air exposure when the bubbler is removed. The flexible tubing should always be installed upstream of the bubbler, to minimize internal surface area downstream of the bubbler and distance that the chemical must travel from the bubbler to the reactor.

1. Reserve glovebox on CCMR online tool manager
2. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed
 - e. M6 open
 - f. M7 open
 - g. M8 open
 - h. P24 closed
 - i. P25 closed

- j. Throttle valve set to 100% open
 - k. QCM in furnace
 - l. Crystal and wafer samples not loaded
 - m. Turbo pump on
 - n. Chiller on
 - o. All cylinders and valves downstream of regulators closed
3. Switch process pump
- a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
4. Evacuate all gas up to P1 and send to pump
- a. Open P9, P13, P14, P18, P19, P23
 - b. Open P10, P11 if changing bubbler attached to panel 2 (ensure manual valves on bubbler are closed)
 - c. Open P15, P16 if changing bubbler attached to panel 3 (ensure manual valves on bubbler are closed)
 - d. Open P20, P21 if changing bubbler attached to panel 4 (ensure manual valves on bubbler are closed)
 - e. Set MFCs A, B, C, D to open
 - f. Allow lines to be pumped for 10 minutes
 - g. Close MFCs A, B, C, D
 - h. Close P10, P11, P15, P16, P20, P21

- i. Close P9, P13, P14, P18, P19, P23
5. Remove bubbler from panel
 - a. Use jack stand to support bubbler
 - b. Undo VCR fitting below P10, P15, or P20 to flexible tubing
 - c. Undo VCR fitting below P11, P16, or P21 to bubbler
 - d. While holding bubbler, lower jack stand to remove bubbler from panel
 - e. Undo VCR fitting(s) on flexible tubing to bubbler, so all pieces are separated
6. Empty bubbler
 - a. Place bubbler on a wipe in fume hood
 - b. Bring a small container to fume hood to dispose of any chemical remaining in bubbler
 - c. Undo VCR fitting on bubbler filling port
 - d. Pour any chemical remaining in bubbler from filling port into waste container
 - e. Request the next available pickup for generated hazardous waste
7. Clean equipment
 - a. Move manual valves on bubbler to the open position
 - b. Disassemble manual valves on bubbler and dispose of used valve parts
 - c. Clean bubbler, 1/2 in filling port cap, 1/4 in VCR cap, and flexible tubing according to "Procedure: standard clean for vacuum parts"
8. Prepare bubbler for bake
 - a. Reassemble manual valves on bubbler with replacement valve kits
 - b. Attach 1/2 in VCR cap to filling port

- c. Attach 1/4 in VCR cap to bubbler inlet
 - d. Attach 1/4 in VCR female-female adapter and VCR-KF25 adapter combo to bubbler outlet
 - e. Open bubbler manual valves
9. Switch process pump
- a. Close P25
 - b. Open M8
 - c. Turn on turbo pump
 - d. Turn on chiller
10. Prepare pump 1 for bake
- a. Unplug solenoid for P26 to close isolation valve 1
 - b. Turn off pump 1
 - c. Separate the exhaust line to pump 1 upstream of the thermocouple gauge tee
 - d. Move pump 1 slightly away from the exhaust line
 - e. Cover the exposed KF fitting downstream of the throttle valve with aluminum foil
11. Bake bubbler
- a. Wrap bubbler with heating tape
 - b. Wrap bubbler with aluminum foil
 - c. Lay bubbler on its side on a counter near pump 1
 - d. Attach KF adapter on bubbler to thermocouple gauge tee upstream of pump 1, possibly utilizing spare KF tubing

- e. Turn on pump 1
 - f. Plug in solenoid for P26 to open isolation valve 1
 - g. Plug heating tape into variac using extension cord
 - h. Set variac output to 50–60 V, depending on the width of the heating tape (thinner heating tape needs higher voltage)
 - i. Allow bake to proceed for at least 18 hours
12. Turn off bake
- a. Close bubbler manual valves
 - b. Turn off variac
 - c. Unwrap aluminum foil and heating tape from bubbler
13. Return pump 1 to chamber
- a. Unplug solenoid for P26 to close isolation valve 1
 - b. Turn off pump 1
 - c. Disconnect KF tubing from pump to bubbler
 - d. Reconnect exhaust line to pump 1, ensuring all KF fittings are fully tightened
 - e. Turn on pump 1
 - f. Plug in solenoid for P26 to open isolation valve 1
14. Prepare to load new chemical
- a. Remove 1/4 in VCR female-female adapter and VCR-KF25 adapter combo from bubbler outlet
 - b. Cover bubbler outlet with aluminum foil
 - c. Gather items to bring to CCMR in a box

- i. Bubbler
- ii. Container of new chemical
- iii. 15/16 and 1-1/16 in wrenches
- iv. 1/2 in VCR gasket (open before loading into antechamber)
- v. Funnel with small tip
- vi. Wipes
- vii. Safety glasses
- viii. Gloves

15. Load new chemical

- a. Go to CCMR
- b. Log in to glovebox on CCMR online tool manager
- c. Put on safety glasses and gloves
- d. Following CCMR procedure, load all other items into the glovebox through the large antechamber, keeping the bubbler upright at all times
- e. Cover workspace with wipes
- f. Undo VCR fitting on bubbler filling port, taking care not to touch the VCR fitting or inside of the cap with the glovebox gloves
- g. Set used 1/2 in VCR gasket aside for disposal
- h. Place funnel into bubbler filling port without touching the inside that will come into contact with the chemical
- i. Carefully pour new chemical into bubbler
- j. Remove funnel

- k. Drop new gasket into 1/2 in VCR cap directly from packaging, taking care not to touch the gasket with the glovebox gloves
 - l. Attach 1/2 in VCR cap to filling port
 - m. Ensure bubbler manual valves are closed
 - n. Following CCMR procedure, remove all items from the glovebox through the large antechamber, keeping the bubbler upright at all times
 - o. Log out of glovebox on CCMR online tool manager
16. Attach bubbler to panel
- a. Loosely assemble VCR fittings on clean flexible tubing to bubbler
 - b. Using jack stand to support bubbler, loosely attach bubbler outlet to VCR fitting below P11, P16, or P21
 - c. Loosely attach flexible tubing to VCR fitting below P10, P15, or P20
 - d. Tighten VCR fitting below P11, P16, or P21 to bubbler outlet
 - e. Tighten remaining VCR fittings through flexible tubing to VCR fitting below P10, P15, or P20 in an order that reduces torsion and tension in the line
17. Switch process pump
- a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
18. Bake lines according to "Procedure: bake chamber, option two"

Procedure: bake chamber

A bake is used to remove contaminants from the chamber, especially after exposure to air, but also if the base pressure is higher than desired. Following are two options: baking with gas flowing through the chamber, to be used when the chamber itself is vented; and baking with gas flowing from the panels directly to the pump, to be used when air exposure only occurs upstream of P3/P4, P5/P6, P7/P8, P12/P13, P17/P18, and/or P22/P23, such as when changing a gas cylinder or a bubbler. For option one, the QCM is kept in the load lock, which is pumped with pump 2 to prevent dead volume.

A common chamber configuration is for M7 to be closed with P25 and M8 open, so pumps 1 and 2 are pumping on different sections of the chamber. Pump 1 pumps on the main reactor section from M7 to P24 (or the three-way valves on panel 1 if P24 is open) to the three-way valves on panels 2–4. Pump 2 pumps on the load lock from M7 to M5 and M6 (both closed). Pumps 1 and 2 will achieve different ranges of vacuum, so M8 and P25 must be closed to isolate the reactor sections under dead volume before opening M7 to open the load lock to the rest of the chamber. If, for example, pump 1 achieves a higher vacuum range than pump 2 and M7 is opened without isolating the sections under dead volume first, then the higher pressure from the section pumped by pump 2 will flow into the section pumped by pump 1 to equilibrate and potentially result in backstreaming of oil from pump 2, which would contaminate the chamber. By isolating the reactor sections under dead volume first, the pressure can equilibrate under dead volume when M7 is

opened, preventing potential backstreaming from occurring. Then M8 is opened so the reactor is pumped by pump 2.

Option one: Bake with gas flowing through the chamber. If not baking lines upstream of plasma generator, see the modified procedure below.

1. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed
 - e. M6 open
 - f. M7 open
 - g. M8 open
 - h. P24 closed
 - i. P25 closed
 - j. Throttle valve set to 100% open
 - k. QCM in furnace
 - l. Crystal and wafer samples not loaded
 - m. Turbo pump on
 - n. Chiller on
 - o. All cylinders and valves downstream of regulators closed
2. Remove controller BNC cable from QCM

3. Move QCM to position 0.75" on translator (moving to position 0" would catch QCM sensor clamps on load lock flange and cause damage)
4. Isolate load lock from rest of chamber
 - a. Close M7
 - b. Open P25
5. Set up for bake
 - a. Set up heating tape covered with aluminum foil on lines that were exposed to air, ensuring that the ends of the tape are close enough to be plugged in together
 - b. Plug heating tape into variacs using extension cords, connecting like heating tape to the same variac
 - c. Set variac output to 50–60 V, depending on the width of the heating tape (thinner heating tape needs higher voltage)
 - d. Set heating cords to desired setpoint
6. Start gas flow
 - a. Open all cylinders and valves downstream of regulators
 - b. Open P24
 - c. Open P1, P3, P5, P7, P9, P12, P14, P17, P19, P22
 - d. Set all MFCs to 5 sccm
7. Allow bake to proceed for at least 18 hours
 - a. Turn off variacs
 - b. Turn off heating cords
8. Turn off bake

- a. Close P1
 - b. Close all MFCs
 - c. Close P3, P5, P7, P9, P12, P14, P17, P19, P22
 - d. Close P24
 - e. Close all cylinders and valves downstream of regulators
9. Open load lock to rest of chamber
- a. Close M8
 - b. Close P25
 - c. Open M7
 - d. Open M8
 - e. Turn on turbo pump
 - f. Turn on chiller

Modifications:

- 6a. Open cylinder 1
- 6b. Skip to keep P24 closed
- 6c. Open P1, P9, P12, P14, P17, P19, P22
- 6d. Set MFCs B, C, D to 5 sccm
- 8b. Close MFCs B, C, D
- 8c. Close P9, P12, P14, P17, P19, P22
- 8d. Skip
- 8e. Close cylinder 1

Option two: Bake with gas flowing from the panels directly to the pump. If not baking lines upstream of plasma generator, see the modified procedure below.

1. Starting conditions:

- a. No flow
- b. All pneumatic valves on panels 1–4 closed
- c. All MFCs closed
- d. M5 closed
- e. M6 open
- f. M7 open
- g. M8 closed
- h. P24 closed
- i. P25 open
- j. Throttle valve set to 100% open
- k. QCM in load lock or furnace
- l. Crystal and wafer samples not loaded
- m. Turbo pump off
- n. Chiller off
- o. All cylinders and valves downstream of regulators closed

2. Set up for bake

- a. Set up heating tape covered with aluminum foil on lines that were exposed to air, ensuring that the ends of the tape are close enough to be plugged in together

- b. Plug heating tape into variacs using extension cords, connecting like heating tape to the same variac
 - c. Set variac output to 50–60 V, depending on the width of the heating tape (thinner heating tape needs higher voltage)
 - d. Set heating cords to desired setpoint
 3. Start gas flow
 - a. Open all cylinders and valves downstream of regulators
 - b. Open P4, P6, P8, P9, P13, P14, P18, P19, P23
 - c. Open P10, P11 if baking a bubbler attached to panel 2 (ensure manual valves on bubbler are closed)
 - d. Open P15, P16 if baking a bubbler attached to panel 3 (ensure manual valves on bubbler are closed)
 - e. Open P20, P21 if baking a bubbler attached to panel 4 (ensure manual valves on bubbler are closed)
 - f. Open P1
 - g. Set MFCs B, C, D, E, F, G to 5 sccm
 4. Allow bake to proceed for at least 18 hours
 - a. Turn off variacs
 - b. Turn off heating cords
 5. Turn off bake
 - a. Close P1
 - b. Close MFCs B, C, D, E, F, G
 - c. Close P10, P11, P15, P16, P20, P21

- d. Close P4, P6, P8, P9, P13, P14, P18, P19, P23
- e. Close all cylinders and valves downstream of regulators

Modifications:

- 3a. Open cylinder 1
- 3c. Open P9, P13, P14, P18, P19, P23
- 3g. Set MFCs B, C, D to 5 sccm
- 5b. Close MFCs B, C, D
- 5d. Close P9, P13, P14, P18, P19, P23
- 5f. Close cylinder 1

Procedure: change QCM crystal and wafer samples

All MFCs are calibrated for nitrogen. Because other gases are used instead of nitrogen, the rated full scale of each MFC is multiplied by a gas conversion factor, which is determined by the thermal properties of the gas that is actually delivered by the MFC. These conversions are programmed into the MFC controller channel settings for each MFC in use. MFC A has a nitrogen full scale of 150 sccm, and argon has a gas conversion factor of 1.39, so the argon full scale is ~209 sccm. This allows MFC A to be set to 200 sccm in **step 4h** when venting the load lock, despite the MFC part number indicating a full scale of 150 sccm.

A common chamber configuration is for M7 to be closed with P25 and M8 open, so pumps 1 and 2 are pumping on different sections of the chamber. Pump 1 pumps on the main reactor section from M7 to P24 (or the three-way valves on panel 1 if P24 is open) to the three-way valves on panels 2–4. Pump 2 pumps on the load lock from M7 to M5 and M6 (both closed). Pumps 1 and 2 will achieve different ranges of vacuum, so M8 and P25 must be closed to isolate the reactor sections under dead volume before opening M7 to open the load lock to the rest of the chamber. If, for example, pump 1 achieves a higher vacuum range than pump 2 and M7 is opened without isolating the sections under dead volume first, then the higher pressure from the section pumped by pump 2 will flow into the section pumped by pump 1 to equilibrate and potentially result in backstreaming of oil from pump 2, which would contaminate the chamber. By isolating the reactor sections under dead volume first, the pressure can equilibrate under dead volume when M7 is

opened, preventing potential backstreaming from occurring. Then M8 is opened so the reactor is pumped by pump 2.

If changing a crystal but not removing or loading wafer samples, skip steps 4d, 4h, 4i, 8, and 10.

1. Starting conditions:

- a. No flow
- b. All pneumatic valves on panels 1–4 closed
- c. All MFCs closed
- d. M5 closed
- e. M6 open
- f. M7 open
- g. M8 open
- h. P24 closed
- i. P25 closed
- j. Throttle valve set to 100% open
- k. QCM in furnace
- l. Crystal and wafer samples loaded
- m. Turbo pump on
- n. Chiller on
- o. All cylinders and valves downstream of regulators closed

2. Switch process pump

- a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
3. Move QCM to load lock and vent load lock
- a. Remove controller BNC cable from QCM
 - b. Move QCM to position 0.75" on translator (moving to position 0" would catch QCM sensor clamps on load lock flange and cause damage)
 - c. Close M7
 - d. Close M6
 - e. Open M5
 - f. Open cylinder 1 and valve downstream of regulator
 - g. Open P1
 - h. Set MFC A to 200 sccm
 - i. Wait ~17 minutes for load lock to reach atmospheric pressure (do not over-pressurize, as this will damage the bellows)
 - j. Once load lock reaches atmospheric pressure, close P1
 - k. Quickly close MFC A
 - l. Quickly close M5
4. Gather necessary items
- a. Clean wipes
 - b. Crystal snatcher
 - c. Plastic tweezers, for handling crystals

- d. Metal wafer tweezers, for handling wafer samples
 - e. Long metal tweezers, for securing locking handle on QCM sensor head
 - f. 2 small wafer holders, for used crystal and wafer samples
 - g. New crystal
 - h. Chemical oxide wafer sample
 - i. Metal-coated wafer sample
5. Clean all tweezers, crystal snatcher, and wafer holders with 2-propanol and place on a clean wipe
 6. Prepare QCM for crystal change
 - a. Don laboratory coat
 - b. Don laboratory gloves
 - c. Standing on the west side of the chamber, open load lock door
 - d. Carefully lift QCM from below the sensor body
 - e. Move QCM to position 0" on translator
 7. Remove used crystal
 - a. Release locking handle on sensor body
 - b. Lift crystal holder from sensor body and place upside down on a clean wipe
 - c. Remove the ceramic retainer using the tapered end of the crystal snatcher, leaving the ceramic retainer on the crystal snatcher
 - d. Invert the crystal holder over the first wafer holder to remove the used crystal
 8. Remove used wafer samples from sample holder

- a. Using wafer tweezers, carefully rotate samples from north-south position to east-west position
 - b. Carefully remove the sample on the north side of the sample holder and place in the second wafer holder
 - c. Carefully remove the sample on the south side of the sample holder and place in the second wafer holder
9. Load new crystal
- a. Clean the crystal holder with 2-propanol and place upside down
 - b. Using plastic tweezers, place the new crystal into the crystal holder with the electrode facing up
 - c. Replace the ceramic retainer using the crystal snatcher, avoiding rotation once seated to prevent scratches on the crystal electrode
 - d. Use the non-tapered end of the crystal snatcher to ensure the ceramic retainer is completely seated
 - e. Replace crystal holder in sensor body
 - f. Use left hand to support sensor body from below while gently pressing crystal holder down with left thumb and forefinger
 - g. Use metal tweezers in right hand to squeeze pins inside locking handle on sensor body
 - h. Use left thumb to press locking handle down
 - i. Remove metal tweezers
 - j. Use left hand to support sensor body from below while using left thumb to ensure handle is fully locked

10. Load new wafer samples
 - a. Carefully place the metal-coated sample on the east side of the sample holder, in a north-south position
 - b. Carefully place the chemical oxide sample on the west side of the sample holder, in a north-south position
11. Pump down load lock
 - a. Attach controller BNC cable to QCM to ensure crystal operates properly
 - b. Close and tighten load lock door
 - c. Open M8 and allow load lock to be evacuated
 - d. Open and quickly close M5 to evacuate up to MFC A
 - e. Turn on turbo pump for at least 30 minutes
 - f. Turn on chiller
12. Open load lock to rest of chamber and move QCM to furnace
 - a. Close M8
 - b. Close P25
 - c. Open M7
 - d. Open M8
 - e. Open M6
 - f. Move QCM to position 24" on translator, guiding the BNC controller cable and ensuring that the sample holder properly guides the QCM into the reactor tube
13. Clean all tweezers and crystal snatcher with 2-propanol and put away

Procedure: anneal QCM crystal and wafer samples

An anneal can be a necessary step before an experiment to achieve the desired starting surface. For example, it was determined that a 1 hour anneal at 180 °C with flowing inert gas was needed to remove oxide sites from copper substrates. Other temperature and time conditions would need to be explored for different substrates.

1. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed
 - e. M6 open
 - f. M7 open
 - g. M8 open
 - h. P24 closed
 - i. P25 closed
 - j. Throttle valve set to 100% open
 - k. QCM in furnace
 - l. Crystal and wafer samples loaded
 - m. Turbo pump on
 - n. Chiller on
 - o. All cylinders and valves downstream of regulators closed

2. Set furnace to desired anneal setpoint and wait
3. Switch process pump
 - a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
4. Start gas flow
 - a. Open cylinder 1 and valve downstream of regulator
 - b. Open P1, P9, P12, P14, P17, P19, P22
 - c. Set MFCs A, B, C, D to 10 sccm
5. Allow anneal to proceed for 1 hour
6. Set furnace to desired experimental setpoint

Procedure: experiment with delivery of reactants from panels 2–4

When using a QCM, stabilization of frequency is crucial. The frequencies at the beginning and end of the experiment are compared to calculate the total change in thickness. To ensure an accurate starting value, data collection should be turned on at least 2 minutes prior to introduction of the first reactant and turned off at least 2 minutes after the end of the final cycle.

Before an experiment, the headspaces of bubblers containing chemicals with high vapor pressure are cleared to ensure a consistent dose of chemical throughout the experiment. In **step 5** of this procedure, panel 2 is used as an example, but analogous versions of this step should be completed one at a time for all panels that have a bubbler with a high vapor pressure chemical.

1. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed
 - e. M6 open
 - f. M7 open
 - g. M8 open

- h. P24 closed
 - i. P25 closed
 - j. Throttle valve set to 100% open
 - k. QCM in furnace, and furnace is at desired experimental setpoint
 - l. Crystal and wafer samples loaded and annealed, if necessary
 - m. Turbo pump on
 - n. Chiller on
 - o. All cylinders and valves downstream of regulators closed
2. Switch process pump
- a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
3. Start gas flow
- a. Open cylinder 1 and valve downstream of regulator
 - b. Open P1, P9, P12, P14, P17, P19, P22
 - c. Set MFCs A, B, C, D to setpoint
 - d. Set pressure to setpoint
 - e. Allow crystal to equilibrate until frequency fluctuations are within ~1 Hz over 5 minutes
4. Set up for experiment
- a. Set up heating/ice bath(s) for bubbler(s) at least 30 minutes before start of experiment

- b. Set heating cords to setpoints
 - c. Set up experiment in LabVIEW automatic program
 - d. Set up data collection settings in STM-2 program
5. Clear panel 2 bubbler headspace
 - a. Close P12 and open P13
 - b. Close P9 and open P10, P11 for 10 seconds
 - c. Close P10, P11 and open P9
 - d. Wait at least 1 minute
 - e. Close P13 and open P12
6. Start experiment
 - a. Open bubblers
 - b. Start collecting data in STM-2 program
 - c. Start LabVIEW automatic program
7. Conclude experiment
 - a. Close bubblers
 - b. Stop LabVIEW automatic program
 - c. Stop collecting data in STM-2 program
 - d. Turn off heating cords
 - e. Turn off heating bath(s) and empty ice bath(s)
8. Turn off gas flow
 - a. Set throttle valve to 100% open
 - b. Close P1
 - c. Close MFCs A, B, C, D

- d. Close P9, P12, P14, P17, P19, P22
 - e. Close cylinder 1 and valve downstream of regulator
9. If removing samples, skip step 10 and complete "Procedure: change QCM crystal and wafer samples"
10. If not removing samples, switch process pump
- a. Close P25
 - b. Open M8
 - c. Turn on turbo pump
 - d. Turn on chiller

Procedure: experiment with delivery of reactants from panels 1–4

When using a QCM, stabilization of frequency is crucial. The frequencies at the beginning and end of the experiment are compared to calculate the total change in thickness. To ensure an accurate starting value, data collection should be turned on at least 2 minutes prior to introduction of the first reactant and turned off at least 2 minutes after the end of the final cycle.

Before an experiment, the headspaces of bubblers containing chemicals with high vapor pressure are cleared to ensure a consistent dose of chemical throughout the experiment. In **step 5** of this procedure, panel 2 is used as an example, but analogous versions of this step should be completed one at a time for all panels that have a bubbler with a high vapor pressure chemical.

Because MFCs are not on-off valves, some gas will pass through MFCs E, F, and G between uses, causing a pressure increase upstream of P3/P4, P5/P6, and P7/P8. This area of high pressure must be cleared to the pump to avoid a pressure spike in the reactor. To achieve this, P4 is opened during **step 3c** rather than P3. Once MFC E reaches the desired setpoint, P4 is closed and P3 is opened in **step 3e**. P6 and P8 to flow oxidizing and reducing gases, respectively, are not opened until the experiment is about to begin, so as to not waste the process gases. During an experiment, MFCs F and G are continuously flowing oxidizing and reducing gases, respectively. For most of the experiment, the gases

are sent directly to the pump. When the gases are being dosed, the three-way valves downstream of the MFCs switch the flow of the gases into the chamber. If the time between doses is very long, the MFCs could be closed and later reopened, as long as there is sufficient time for the MFC to stabilize at the setpoint while flowing to the pump before dosing begins.

1. Starting conditions:

- a. No flow
- b. All pneumatic valves on panels 1–4 closed
- c. All MFCs closed
- d. M5 closed
- e. M6 open
- f. M7 open
- g. M8 open
- h. P24 closed
- i. P25 closed
- j. Throttle valve set to 100% open
- k. QCM in furnace, and furnace is at desired experimental setpoint
- l. Crystal and wafer samples loaded and annealed, if necessary
- m. Turbo pump on
- n. Chiller on
- o. All cylinders and valves downstream of regulators closed

2. Switch process pump

- a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
3. Start gas flow
- a. Open all cylinders and valves downstream of regulators
 - b. Open P24
 - c. Open P1, P4, P9, P12, P14, P17, P19, P22
 - d. Set MFCs A, B, C, D, E to setpoint
 - e. Close P4 and open P3
 - f. Set pressure to setpoint
 - g. Allow crystal to equilibrate until frequency fluctuations are within ~1 Hz over 5 minutes
4. Set up for experiment
- a. Set up heating/ice bath(s) for bubbler(s) at least 30 minutes before start of experiment
 - b. Set heating cords to setpoints
 - c. Set up experiment in LabVIEW automatic program
 - d. Set up data collection settings in STM-2 program
5. Clear panel 2 bubbler headspace
- a. Close P12 and open P13
 - b. Close P9 and open P10, P11 for 10 seconds
 - c. Close P10, P11 and open P9

- d. Wait at least 1 minute
 - e. Close P13 and open P12
 6. Start experiment
 - a. Open P6, P8
 - b. Set MFCs F, G to setpoint
 - c. Open bubblers
 - d. Start collecting data in STM-2 program
 - e. Start LabVIEW automatic program
 7. Conclude experiment
 - a. Close bubblers
 - b. Stop LabVIEW automatic program
 - c. Stop collecting data in STM-2 program
 - d. Turn off heating cords
 - e. Turn off heating bath(s) and empty ice bath(s)
 8. Turn off gas flow
 - a. Set throttle valve to 100% open
 - b. Close P1
 - c. Close all MFCs
 - d. Close P3, P6, P8, P9, P12, P14, P17, P19, P22
 - e. Close P24
 - f. Close all cylinders and valves downstream of regulators
 9. If removing samples, skip step 10 and complete "Procedure: change QCM crystal and wafer samples"

10. If not removing samples, switch process pump

- a. Close P25
- b. Open M8
- c. Turn on turbo pump
- d. Turn on chiller

Procedure: measure pressure rise of reactant in bubbler, with flow from panels 2–4

The partial pressure of a reactant is an important variable in a deposition experiment. In a pressure-controlled experiment, the pressure is fixed and the throttle valve position is variable. When reactants are introduced, the pressure would increase, but the throttle valve opens to maintain the pressure at the setpoint. By fixing the throttle valve position and allowing the pressure to be variable, the pressure rise due to introduction of a reactant can be measured.

Before an experiment, the headspace of bubblers containing chemicals with high vapor pressure are cleared to ensure a consistent dose of chemical throughout the experiment. In **step 6** of this procedure, panel 2 is used as an example, but an analogous version of this step should be completed for panel 3 or 4, depending on which bubbler contains the chemical of interest.

1. Starting conditions:
 - a. No flow
 - b. All pneumatic valves on panels 1–4 closed
 - c. All MFCs closed
 - d. M5 closed
 - e. M6 open
 - f. M7 open

- g. M8 open
 - h. P24 closed
 - i. P25 closed
 - j. Throttle valve set to 100% open
 - k. QCM in furnace, and furnace is at desired experimental setpoint
 - l. Crystal and wafer samples not loaded
 - m. Turbo pump on
 - n. Chiller on
 - o. All cylinders and valves downstream of regulators closed
2. Switch process pump
- a. Close M8
 - b. Turn off turbo pump
 - c. Turn off chiller
 - d. Open P25
3. Start gas flow
- a. Open cylinder 1 and valve downstream of regulator
 - b. Open P1, P9, P12, P14, P17, P19, P22
 - c. Set MFCs A, B, C, D to setpoint
 - d. Set pressure to setpoint
4. Determine valve position
- a. Wait 15 minutes after setting pressure to setpoint
 - b. Record pressure and throttle valve position for 1 minute
 - c. Average valve position values

- d. Set valve position to averaged setpoint
5. Set up for experiment
 - a. Set up heating/ice bath for bubbler at least 30 minutes before start of experiment
 - b. Set heating cords to setpoints
 - c. Set up experiment in LabVIEW automatic program
6. Clear panel 2 bubbler headspace
 - a. Close P17 and open P18
 - b. Close P14 and open P15, P16 for 10 seconds
 - c. Close P15, P16 and open P14
 - d. Wait at least 1 minute
 - e. Close P18 and open P17
7. Start experiment
 - a. Open bubbler
 - b. Start recording pressure and throttle valve position
 - c. Start LabVIEW automatic program
8. Conclude experiment
 - a. Close bubbler
 - b. Stop LabVIEW automatic program
 - c. Stop recording pressure and throttle valve position
 - d. Turn off heating cords
 - e. Turn off heating bath or empty ice bath
9. Turn off gas flow

- a. Set throttle valve to 100% open
- b. Close P1
- c. Close MFCs A, B, C, D
- d. Close P9, P12, P14, P17, P19, P22
- e. Close cylinder 1 and valve downstream of regulator

10. Switch process pump

- a. Close P25
- b. Open M8
- c. Turn on turbo pump
- d. Turn on chiller

An example of timing for an experiment is below. In the ALD experiment being used as a reference, the cycle time is 2 minutes and the sequence is 15 s 4-octyne, 30 s TEMAZ/4-octyne, 5 s 4-octyne, 10 s purge, 3 s water, 57 s purge. To study only 4-octyne, 4-octyne is dosed for 50 seconds, followed by a 70 second purge. The cycle is repeated 5 times to determine whether delivery of the reactant is consistent over time.

1. 00:00 start timer
2. 01:00 start recording pressure
3. 02:00 4-octyne on 1
4. 02:50 4-octyne off 1
5. 04:00 4-octyne on 2
6. 04:50 4-octyne off 2

7. 06:00 4-octyne on 3
8. 06:50 4-octyne off 3
9. 08:00 4-octyne on 4
10. 08:50 4-octyne off 4
11. 10:00 4-octyne on 5
12. 10:50 4-octyne off 5
13. 13:00 stop recording pressure

This experiment must be repeated to measure the pressure over time with and without 4-octyne, and with varying any experimental conditions that are being investigated. An example of a sequence of experiments for studying four different flow conditions is below. In all cases, the total flow rate is the same, and the flow rate ratio between the panels is differed to study how flow rate through the bubbler affects partial pressure. The order in which the flow conditions are studied is randomized and there must be a sufficient purge between experiments to prevent hysteretic effects.

1. No 4-octyne, flow conditions 3
2. No 4-octyne, flow conditions 1
3. No 4-octyne, flow conditions 2
4. No 4-octyne, flow conditions 4
5. 4-octyne 0 °C, flow conditions 2
6. 4-octyne 0 °C, flow conditions 1
7. 4-octyne 0 °C, flow conditions 4

8. 4-octyne 0 °C, flow conditions 3

Appendix G: Resume

Colleen Lawlor

Education

Cornell University – Ithaca, NY

August 2016 – December 2021

Doctor of Philosophy in Chemical and Biomolecular
Engineering

Concentrations in Surface Science and Theoretical Chemistry

GPA 3.65/4.30, Professional GPA 3.65/4.30

Rochester Institute of Technology – Rochester, NY

September 2011 – May 2016

Bachelor of Science in Chemical Engineering

Minor in Chemistry, Concentration in Spanish Language

Graduated summa cum laude

GPA 3.88/4.00, Professional GPA 3.98/4.00

Research and Work Experience

Pall Corporation – Cortland, NY

Research and Development Leadership Program Associate

September 2021 – Present

Completion of four six-month rotations within different research and development groups throughout the company, including participation in the advancement of novel separation devices and processes during each rotation; collaboration with the other RDLP associates in leadership development training opportunities; application of Danaher Business System tools to all job responsibilities.

Cornell University – Ithaca, NY

PhD Candidate, Adviser: Professor James Engstrom

August 2016 – December 2021

Designed and fabricated a custom quartz crystal microbalance vacuum chamber for real-time study of adsorption and desorption behavior during atomic layer deposition; identified and interpreted fundamental aspects of deposition, with emphasis on area-selective atomic layer deposition; investigated the impact of reactant delivery method on the substrate-dependent adsorption behavior.

Lam Research Corporation – Tualatin, OR

Engineering Intern

June 2017 – September 2017

Investigated the dynamic behavior of atomic layer deposition of silicon oxide under varying process conditions toward achieving area selective deposition, maintained and operated the vacuum deposition chamber, assisted in analyzing data and determining future experiments, presented results to colleagues in the company and in the academic research group at Cornell.

NanoPower Research Labs, Rochester Institute of Technology – Rochester, NY

Student Researcher

May 2013 – July 2016

Developed techniques to purify carbon nanotube (CNT) materials, fabricated conductive CNT wires with multifunctional properties, investigated chemical dopants to increase the bulk electrical conductivity of CNT materials, measured current carrying capacity of densified CNT wires, managed and instructed novice undergraduates.

Keurig Green Mountain – Burlington, MA

Quality Engineer (Co-op)

January 2015 – June 2015

Performed quality testing on all varieties of Keurig pods, worked with technicians who assembled preliminary versions of Kold pods, generated and distributed a comprehensive weekly report of quality testing results, worked with the research and development team on the design of Kold pod revisions, prepared for the launch of Keurig Kold products.

New York State Pollution Prevention Institute – Rochester, NY

Assistant Pollution Prevention Engineer (Co-op)

April 2014 – August 2014

Completed on-site evaluations of clients across New York State, performed engineering analyses of client operations, researched viable process and product alternatives to improve sustainability, assessed the economic and sustainability impacts of modifications to the system, delivered results to clients in both report and presentation form.

Publications

- Rossi, J. E., Schauerman, C. M., Lawlor, C. C., Cress, C. D., Ganter, M. J., Bucossi, A. R., Landi, B. J. (2021). Carbon Nanotube Survivability in Biofouling Marine Environments. Manuscript submitted for publication.
- Soule, K. J., Lawlor, C. C., Bucossi, A. R., Cress, C. D., Puchades, I., Landi, B. J. (2019). Sustaining Enhanced Electrical Conductivity in KAuBr₄-Doped Carbon Nanotube Wires at High Current Densities. *ACS Applied Nano Materials*, 2(11), 7340–7349.
- Cress, C. D., Ganter, M. J., Schauerman, C. M., Soule, K., Rossi, J. E., Lawlor, C. C., Puchades, I., Ubnoske, S., Bucossi, A. R., Landi, B. J. (2017). Carbon nanotube wires with continuous current rating exceeding 20 Amperes. *Journal of Applied Physics*, 122(2), 25101.
- Puchades, I., Lawlor, C. C., Schauerman, C. M., Bucossi, A. R., Rossi, J. E., Cox, N. D., Landi, B. J. (2015). Mechanism of chemical doping in electronic-type-separated single wall carbon nanotubes towards high electrical conductivity. *Journal of Materials Chemistry C*, 3(39), 10256–10266.
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Patents

- Hausmann, D. M., Fox, A. R., Lawlor, C. C. (2020). *Selective growth of SiO₂ on dielectric surfaces in the presence of copper* (U.S. Patent No. 10,825,679). U.S. Patent and Trademark Office.
- Hausmann, D. M., Fox, A. R., Lawlor, C. C. (2019). *Selective growth of SiO₂ on dielectric surfaces in the presence of copper* (U.S. Patent No. 10,460,930). U.S. Patent and Trademark Office.
- Hausmann, D. M., Fox, A. R., Lawlor, C. C. (2018). *Method to increase deposition rate of ALD process* (U.S. Patent Application No. 16/056301). U.S. Patent and Trademark Office.
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Presentations and Posters

- | | |
|---|-------------------|
| Presentation at the Cornell CBE Graduate Research Symposium, virtual | January 20, 2021 |
| Poster at the Semiconductor Research Corporation Nanomanufacturing Materials & Processes Annual Review, virtual | November 19, 2020 |
| Poster at the Lam Research University Collaboration Showcase, Fremont, CA | August 9, 2019 |
| Poster at the Cornell CBE Graduate Research Symposium, Ithaca, NY | January 17, 2019 |
| Poster at the Lam Research University Collaboration Showcase, Tualatin, OR | August 9, 2018 |
| Presentation at the AIChE Annual Meeting, Salt Lake City, UT | November 9, 2015 |
| Poster at the AIChE Annual Student Conference, Atlanta, GA | November 17, 2014 |
| Presentation at the RIT Undergraduate Research Symposium, Rochester, NY | August 8, 2014 |
| Presentation at the RIT Undergraduate Research Symposium, Rochester, NY | August 2, 2013 |
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Awards and Honors

Semiconductor Research Corporation Aspire Program	<i>Cornell spring 2021</i>
Best Oral Presentation, CBE Graduate Research Symposium	<i>Cornell 2021</i>
Center for Teaching Innovation Graduate Teaching Fellowship	<i>Cornell 2020 – 2021</i>
Colman Leadership Program	<i>Cornell June 2019</i>
Graduate Student Organization of the Year Award, for the Chemical and Biomolecular Engineering Graduate Women's Group (CBE Women)	<i>Cornell 2019</i>
McMullen Graduate Fellowship	<i>Cornell fall 2016</i>
Outstanding Undergraduate Scholar Award	<i>RIT 2016</i>
Nathaniel Rochester Society Scholarship	<i>RIT 2014 – 2016</i>
Presidential Scholarship	<i>RIT 2011 – 2016</i>
Honors Engineering Program	<i>RIT 2011 – 2016</i>
Dean's List Honors each academic quarter/semester	<i>RIT 2011 – 2016</i>

Graduate Teaching Assistantships

Air Pollution Control	<i>Spring 2020</i>
Chemical Engineering Thermodynamics	<i>Fall 2019</i>
Intro to Process Dynamics and Control	<i>Spring 2017, 2018, 2019</i>
Microchemical and Microfluidic Systems	<i>Fall 2017</i>
Responsibilities: graded homework, exams, and projects; scheduled and attended office hours; guided students through questions about problem sets and study techniques; managed online learning management system content; assisted with delivery of course content during transition to online in spring 2020	

Graduate Leadership Activities

Website Manager for research group	<i>September 2017 – August 2021</i>
Parent Program Lead for the Chemical and Biomolecular Engineering Graduate Women's Group (CBE Women) WOMEN outreach event (virtual)	<i>March 2021</i>
Lab Safety Officer for research group	<i>January 2019 – February 2021</i>
Publicity Coordinator for CBE Women	<i>May 2019 – May 2020</i>
Symposium Chair for the Chemical and Biomolecular Engineering Graduate Student Association (ChEGSA)	<i>May 2019 – May 2020</i>
Parent Program Lead for the CBE Women WOMEN outreach event (virtual)	<i>May 2020</i>
President for CBE Women	<i>May 2018 – May 2019</i>
Organizer for 2019 CBE Graduate Alumni Reunion	<i>June 2019</i>
Parent Program Lead for the CBE Women WOMEN outreach event	<i>March 2019</i>
Vice President for CBE Women	<i>May 2017 – May 2018</i>
Organizer for inaugural 2018 CBE Graduate Alumni Reunion	<i>June 2018</i>
Parent Program Lead for the CBE Women WOMEN outreach event	<i>March 2018</i>
First Year Representative for CBE Women	<i>October 2016 – May 2017</i>
Parent Program Co-Lead for the CBE Women WOMEN outreach event	<i>March 2017</i>

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