SILVER ON SILICON (111): SURFACE STRUCTURAL TRANSFORMATIONS
AND TRACE CONTAMINANT EFFECTS AT SUBMONOLAYER COVERAGE

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by
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The structural details for the formation of the (\(\sqrt{3} \times \sqrt{3}\))R30° Silver on Silicon (111) system have eluded definitive resolution for 40 years. Wildly conflicting evidence, gathered by every available surface science technique and theoretical method, is beyond the scale customary for this field. In order for this system to progress, a comprehensive review of the state-of-the-field, a newly constructed surface structure diagram, a new set of experimentally determined atomic positions and the quantitative effects minor contaminants are presented for Ag/Si(111).

From careful data mining and analysis of the nearly 600 papers in the literature database, a comprehensive Ag-(\(\sqrt{3} \times \sqrt{3}\))R30°/Si(111) surface structure diagram has been constructed. It includes a new \(\beta-(\sqrt{3} \times \sqrt{3})\)R30° phase; a two atom per unit cell proto-cluster variation of the SAV structure, and also a \(\gamma-(\sqrt{3} \times \sqrt{3})\)R30° phase; with structure similar to a later variant of the HCT model.

Atomic positions for Ag in the \(\sqrt{3} \times \sqrt{3}\)R30° and the (3x1) structural conformations have been determined by a number of complementary techniques; X-ray Standing Wave (XSW), Surface Extended X-ray Absorption Fine Structure (SEXAFS), Auger Electron Spectroscopy (AES), Rutherford Backscattering Spectroscopy (RBS), Low Energy Electron Diffraction (LEED) and Isothermal Desorption Spectroscopy (ITDS).
Three “second order” influences were also evaluated; boron, surface steps and carbon. It was found that boron contamination and low surface steps densities have insignificant influences on the $\sqrt{3}$ or (3x1) structures. Minor carbon contamination, however, caused dramatic effects. First, tenth ML levels of carbon completely inhibit the formation of the Ag-(3x1)/Si(111) phase. Second, at low C contamination levels, the Ag-($\sqrt{3}$x$\sqrt{3}$)R30° layer is comprised of dual, Ag-Si bond lengths (2.2Å and 2.6Å); Ag-Ag bond lengths of 3.2Å; and Ag locations 0.97Å below the extension of bulk Si(111) planes inferring a Si surface contraction of 0.2Å. Finally, carbon promoted a high degree of Ag surface order and surface relaxation.

The existence of the $\beta$-($\sqrt{3}$x$\sqrt{3}$)R30° and $\gamma$-($\sqrt{3}$x$\sqrt{3}$)R30° phases is fully consistent with quantitative literature citations and helps explain the decades-long debate over model and critical coverage inconsistencies. The profound influence of C, a ubiquitous contaminant in even the best experimental systems, helps explain surface position, relaxation and coverage discrepancies.
BIOGRAPHICAL SKETCH

Gary Navrotsky was born on July 4, 1954 in Canonsburg, Pennsylvania to Edwin Joseph Navrotsky and Cecelia Bober Navrotsky. He graduated from Canon-McMillan Senior High School there in 1972. His undergraduate training in physics was completed at Case Institute of Technology of Case Western Reserve University with a B.S. in 1976. In 1978, he completed an M.S. degree in Materials Science specializing in the area of high temperature creep of metallic materials, while working at NASA Langley Research Center through the Joint Institute for the Advancement of Flight Sciences (JIAFS) and George Washington University. He spent four years as a staff scientist working on surface chemistry and aluminum alloy development then three years as a senior scientist working on superplasticity and fatigue research at Reynolds Metals Company, Corporate Research and Development labs in Richmond, Virginia while earning his Professional Engineer's license in Materials Engineering in 1982. Marrying the former Sarah Ellen Simonson in April 1984, he then returned for doctoral study in Materials Science at Cornell University in September of 1985. During their time at Cornell, they were blessed with two children, Alexander Edwin and Emily Irene. While compiling and analyzing the data presented here, he worked as a freelance engineer and then, in late 1994, was employed by the University of Chicago as the Project Engineer for x-ray optics, facilities and beamline design for the BioCARS sector located at the Advanced Photon Source near Chicago, Illinois. He returned to private engineering practice in 2003 where completed the remainder of the compilation, analysis and writing of this dissertation.
to

Sarah, Alex and Emily
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LIST OF ACRONYMS

Glossary of Surface Science Experimental Method Acronyms

2PPE Two-Photon PhotoEmission Spectroscopy
AED (µAED) Auger Electron Diffraction (micro AED)
AES (µAES) Auger Electron Spectroscopy (micro AES)
AFM Atomic Force Microscopy
AR-Imaging Angularly Resolved Imaging (with AR-Electron Spectroscopy)
ARUPS Angle-Resolved Ultraviolet Photoelectron Spectroscopy ( = ARPES)
ARPES Angle-Resolved Photo-Emission Spectroscopy ( = ARUPS)
AST Auger Signal-Time (plots)
b-SEI biased Secondary Electron Imaging
BE Binding energy
BIS Bremsstrahlung Isochromat Spectroscopy (=IPE, e⁻ in/X-ray out)
CAICISS Coaxial Impact Collision Ion Scattering Spectroscopy
CL CathodoLuminescence
CPD Contact Potential Difference (from SKPM)
CTR Crystal Truncation Rod (X-ray surface diffraction)
CV Cyclic Voltammetry
DFT Density Functional Theory
DOS Density of states
DR Differential Reflectance ( = Photoreflectance)
DRS DR Spectroscopy
EDC Energy distribution curve
EELS Electron-Energy-Loss Spectroscopy (=ELS)
ELEED Elastic Low Energy Electron Diffraction
ELS Electron-energy Loss Spectroscopy (=EELS)
EMSS Electromigration on Semiconductor Surfaces
ERDA Elastic Recoil Detection Analysis (= FRES)
ESCA Electron Spectroscopy for Chemical Analysis (=XPS)
ESD Electron Stimulated Desorption
FE-SEM Field Emission (source) SEM
FIM Field Ion Microscopy
FRES Forward Recoil Elastic Spectrometry (= ERDA)
FPC First Principles Calculations
GIXD Grazing Incidence X-ray Diffraction
GIXRD Grazing Incidence X-ray Diffraction
GIXRF Grazing Incidence X-ray Fluorescence
HR- High-Resolution (as in HREELS, HR-PES, HR-LEED )
ICB Ionized Cluster Beam
ICISS Impact Collision Ion Scattering Spectroscopy
IID Ion Impact Desorption
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPE</td>
<td>Inverse Photoemission Current (=BIS, =UVIS)</td>
</tr>
<tr>
<td>IPES</td>
<td>Inverse Photoemission Spectroscopy</td>
</tr>
<tr>
<td>ISS</td>
<td>Ion scattering spectroscopy</td>
</tr>
<tr>
<td>ITCS</td>
<td>Isothermal Condensation Spectroscopy</td>
</tr>
<tr>
<td>ITDS</td>
<td>Isothermal Desorption Spectroscopy</td>
</tr>
<tr>
<td>IV</td>
<td>Intensity-Voltage (LEED) or Current-Voltage (electrical conductivity)</td>
</tr>
<tr>
<td>KMC</td>
<td>Kinetic Monte-Carlo calculations</td>
</tr>
<tr>
<td>KRIPS</td>
<td>K (momentum) Resolved Inverse Photoelectron (-emission) Spectroscopy</td>
</tr>
<tr>
<td>LCAO</td>
<td>Linear combination of atomic orbitals</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation (as in LDA-LDF or LDA-DFT theory)</td>
</tr>
<tr>
<td>LDF</td>
<td>Linear Density Functional theory (Band Structure Calculations)</td>
</tr>
<tr>
<td>LEED</td>
<td>Low-Energy Electron Diffraction</td>
</tr>
<tr>
<td>LEED/CMTA</td>
<td>LEED Constant Momentum Transfer Averaging</td>
</tr>
<tr>
<td>LEEM</td>
<td>Low Energy Electron Microscopy</td>
</tr>
<tr>
<td>LEIS</td>
<td>Low Energy Ion Scattering (Spectroscopy)</td>
</tr>
<tr>
<td>LEISS</td>
<td>LEIS Spectroscopy</td>
</tr>
<tr>
<td>LNT</td>
<td>Liquid-nitrogen temperature</td>
</tr>
<tr>
<td>MC</td>
<td>Monte-Carlo calculations</td>
</tr>
<tr>
<td>MCS</td>
<td>Monte-Carlo Simulations</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics (Simulations)</td>
</tr>
<tr>
<td>MEED</td>
<td>Medium Energy Electron Diffraction</td>
</tr>
<tr>
<td>MEES</td>
<td>Medium Energy quasi-Elastic Scattered electrons</td>
</tr>
<tr>
<td>MEIS</td>
<td>Medium Energy Ion Scattering</td>
</tr>
<tr>
<td>MEISS</td>
<td>MEIS Spectroscopy</td>
</tr>
<tr>
<td>MSC</td>
<td>Multiple Scattering Cluster calculations</td>
</tr>
<tr>
<td>NC-</td>
<td>Noncontact (as NC-AFM)</td>
</tr>
<tr>
<td>NE-</td>
<td>Near Edge (as NEXAFS = XANES)</td>
</tr>
<tr>
<td>NRA</td>
<td>Nuclear Reaction Analysis</td>
</tr>
<tr>
<td>OSHG</td>
<td>Optical Second Harmonic Generation</td>
</tr>
<tr>
<td>PAX</td>
<td>Photoemission of Adsorbed Xenon</td>
</tr>
<tr>
<td>PED</td>
<td>Photoelectron Diffraction</td>
</tr>
<tr>
<td>PEEM</td>
<td>Photoemission Electron Microscopy</td>
</tr>
<tr>
<td>PES</td>
<td>PhotoEmission Spectroscopy ( = UPS)</td>
</tr>
<tr>
<td>Photoreflectance</td>
<td>( = DRS)</td>
</tr>
<tr>
<td>PIXE</td>
<td>Proton Induced X-Ray Emission</td>
</tr>
<tr>
<td>PSD</td>
<td>Photon Stimulated Desorption</td>
</tr>
<tr>
<td>QKLEED</td>
<td>Quasi-Kinematical LEED</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Back Scattering or Rutherford Backscattering Spectroscopy</td>
</tr>
<tr>
<td>REM</td>
<td>Reflection Electron Microscopy</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection-High-Energy Electron Diffraction</td>
</tr>
<tr>
<td>RHEED-TRAXS</td>
<td>RHEED Total Reflection Angle X-ray Spectroscopy</td>
</tr>
<tr>
<td>RHEPD</td>
<td>Reflection High-Energy Positron Diffraction</td>
</tr>
<tr>
<td>RNRA</td>
<td>Resonant Nuclear Reaction Analysis</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>SAM</td>
<td>Scanning Auger Microscopy</td>
</tr>
<tr>
<td>SBH</td>
<td>Schottky Barrier Height</td>
</tr>
<tr>
<td>SEE</td>
<td>(angle scanned) Secondary Electron Emission</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SEXAFS</td>
<td>Surface Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SKPM</td>
<td>Scanning Kelvin Probe Microscopy (produce CPD Maps)</td>
</tr>
<tr>
<td>SPA-LEED</td>
<td>Spot Profile Analysis of LEED</td>
</tr>
<tr>
<td>SPEM</td>
<td>Scanning Photoemission Microscopy</td>
</tr>
<tr>
<td>SRS</td>
<td>Surface Reflectance Spectroscopy</td>
</tr>
<tr>
<td>SSC</td>
<td>Single Scattering Cluster calculations</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transition Electron Microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>STM-LE</td>
<td>Scanning Tunneling Microscopy (stimulated) Light Emission</td>
</tr>
<tr>
<td>STS</td>
<td>Scanning Tunneling Spectroscopy</td>
</tr>
<tr>
<td>TDS</td>
<td>Thermal Desorption Spectroscopy</td>
</tr>
<tr>
<td>TED</td>
<td>Transmission Electron Diffraction ( = THEED)</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>THEED</td>
<td>Transmission High Energy Electron Diffraction ( = TED)</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high vacuum</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy ( = PES)</td>
</tr>
<tr>
<td>UVIS</td>
<td>UV Isochromat Spectroscopy (=IPE, e⁻ in/UV out)</td>
</tr>
<tr>
<td>XAFS</td>
<td>X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Structure ( = NEXAFS)</td>
</tr>
<tr>
<td>XePES</td>
<td>Xenon PhotoEmission Spectroscopy (= PAX)</td>
</tr>
<tr>
<td>XPD</td>
<td>X-ray Photoelectron Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron (or Photoemission) Spectroscopy (=ESCA)</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRD-CTR</td>
<td>Crystal Truncation Rod scans/analysis</td>
</tr>
<tr>
<td>XSW</td>
<td>X-ray Standing Wave</td>
</tr>
</tbody>
</table>

**Glossary of Surface Science Theoretical/Calculational Method Acronyms**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCAO</td>
<td>Linear Combination of Atomic Orbitals</td>
</tr>
<tr>
<td>DV</td>
<td>Discrete variational</td>
</tr>
<tr>
<td>HFS</td>
<td>Hartree-Fock-Slater equations</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LDF</td>
<td>Local Density Functional</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>NL</td>
<td>Non-Linear (Response Theory)</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
</tbody>
</table>
MDS | MS Simulations  
---|---  
MC | Monte Carlo  
SCF | MC-SCF? (231) like MO-SCF calculations  
TLK | Thermodynamics and Kinetics (hopping frequency) calculations  

**Surface Science Nomenclature:**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>Two Dimension(al)</td>
</tr>
<tr>
<td>2DAG</td>
<td>Two-Dimensional Adatom Gas</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimension(al)</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction-Band Minimum</td>
</tr>
<tr>
<td>DAS</td>
<td>Dimer-Adatom-Stacking fault</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi energy</td>
</tr>
<tr>
<td>F-M</td>
<td>Frank-van der Merwe (layer by layer) growth mode</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HCT</td>
<td>Honeycomb-Chained Triangles</td>
</tr>
<tr>
<td>ML</td>
<td>Mono Layer (Monolayer)</td>
</tr>
<tr>
<td>MESFET</td>
<td>Metal-Semiconductor Field-Effect Transistor</td>
</tr>
<tr>
<td>MISFET</td>
<td>Metal-Insulator-Semiconductor Field-Effect Transistor</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>SBH</td>
<td>Schottky barrier height</td>
</tr>
<tr>
<td>S-K</td>
<td>Stranski-Krastanov (layer + island) growth mode</td>
</tr>
<tr>
<td>TV</td>
<td>Television</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence-Band Maximum</td>
</tr>
<tr>
<td>V-W</td>
<td>Volmer-Webber (island) growth mode</td>
</tr>
</tbody>
</table>
CHAPTER ONE:
INTRODUCTION

1.1 Preface

The study of the chemical, electronic and physical nature of metal-silicon interfaces is of fundamental scientific interest as well as practical technological importance. More specifically, Schottky barrier formation in a high-electrical conductivity metallization, stable at elevated temperatures is important for current VLSI circuit technologies. Modern semiconductor electronic devices often use thin metal films deposited on their surfaces as ohmic and rectifying (or Schottky) contacts and interconnections as shown in Figure 1.1. The fabrication of these devices requires good thin-film adhesion properties and interfacial thermal stability for practical application of this technology. In all aspects, the operation of these devices depends critically on an understanding of the micro-chemical, electronic and crystallographic nature of the interface formed between the metal and the underlying semiconductor material.

Figure 1.1 - Schematic illustration of the interrelation between state-of-the-art VLSI devices and Schottky barriers. Clockwise from left, motherboard level, CPU level, VLSI microprocessor level, interconnect level, device level, atomic level.
Due to this immense technical importance, there has been a strong force driving scientific investigation in this field. Numerous theoretical and experimental studies of the formation of these Schottky barriers have been undertaken. We present here new experimental results in combination with 40 years of literature study for one specific interface; silver on silicon(111).

Silver is the best elemental electrical conductor known, has superlative resistance to electromigration, develops a sharp, stable, non-silicide-forming interface with Si(111) and has unproblematic epitaxy. Since so much is known about the system, it has also become a test-bed for low-dimensional physics. For example, under some conditions it exhibits behavior that is the electronic equivalent of a two-dimensional free electron gas while under others, provides a framework for organizing single, detachable, widely-spaced atoms, localized at 16Å spacing grid points. This well documented and easily produced system has the potential to become a nanotechnology design test surface and the ultimate limit in current device technology; single atom line-width interconnects of the highest conductivity metal on silicon.

The course of this treatise will proceed as follows. The remainder of Chapter 1 is dedicated to a general overview of the field of Ag/Si(111) and of the specific analytical techniques used in this study. Chapter 2 attempts to clarify, compare and present in a practical and historical manner the voluminous literature-base available. This has not been attempted since 1983 and is urgently needed for further progress in the sub-field. Chapters 3 and 4 detail the theoretical and experimental basis, respectively, behind the synchrotron x-ray and surface science techniques employed in this study. Chapter 5 presents the original results of this study, compared and contrasted with information in the literature. Chapter 6 summarizes, attempts to unify and concludes this study. Minute technical details relating individual literature
contributions to the field, to the construction of scientific apparatus for this study by the author and to other compilations of data are relegated to future publications.

1.2 Historical Introduction to Silver on Silicon(111)

As traditionally classified, there are three growth modes for films on substrates; the island or Volmer-Weber (V-W) growth model, the layer-by-layer or Frank-Van der Merwe (F-M) growth model and the layer-plus-island or Stranski-Krastanov (S-K) growth model. The mode exhibited by any pair of layer and substrate depends on surface free-energy terms and the lattice mismatch between the two species. The F-M and V-W growth models can be easily understood based on macroscopic wetting arguments. The S-K growth model, however, requires the additional complication of elastic strain accommodation required to lattice mismatch sequentially the substrate, first layer and subsequent “bulk like” island crystalline lattices. Ag on Si(111) strongly favors S-K growth dynamics, even at the lowest temperatures where the lines between S-K and F-M mechanisms blur. It is in the formation of the first monolayer of the S-K process, the Ag-(\sqrt{3}x\sqrt{3})R30° structure, where the mystery of Ag/Si(111) lies.

In 1967, K. Spiegel was probably pragmatically motivated to be the first to study monolayers of silver atoms on a silicon surface. At that time, the nature of ohmic and Schottky interfaces was poorly understood. First proposed by Schottky in (1938), the original conjecture was that the barrier height, \( \phi_B \) was proportional to the applied metal work function, \( \phi_M \) and the electron affinity of the underlying semiconductor material, \( \chi \) by the linear relationship:

\[
\phi_B = \phi_M - \chi
\]
It was quickly discovered that, experimentally, this did not hold true. Bardeen\(^5\) (1947) modified the Schottky theory to include an interfacial layer and band-bending to explain the apparent independence of $\phi_B$ and $\phi_M$. (Thanailakis\(^6\) later showed that the Bardeen model reduces to the Schottky model in the limit when the proposed interfacial layer thickness approaches zero). Heine\(^7\) (1965) and Inkson\(^8\) (1973) added a proposed effect of the surface/interface states to modify the band interactions. That is, if the semiconductor Fermi level is shifted or pinned due to extrinsic or intrinsic surface band bending effects, the resultant change in the interfacial dipole is correspondingly modified resulting in a shifted barrier height. Cowley\(^9\) added the temperature dependence of the interfacial states to the interfacial model.

During this theoretical development, a simple model system was needed where atomic structure was known so that electronic structure could be calculated and measured in order for current theory to be tested. Of the d-metal to silicon interfaces, there was only one system that did not form a complicating silicide structure; only one combination of overlayer and substrate that bulk studies had unambiguously shown not to intermix\(^10\); that was the Ag on Si(111) system. Spiegel conducted the first Low Energy Electron Diffraction (LEED) studies and concluded that it took 1/3 of a monolayer (1 Ag atom for every 3 Si atoms in the surface unit cell) to cover the surface before subsequent Ag deposits produced crystalline Ag islands on top of this adlayer and began S-K growth. The Ag/Si(111) interface was thus modeled as Ag atoms sitting in hollows formed by three Si surface atoms and making a centered-hexagonal network on the surface.

At the time of this writing, 40 years later, this simple non-silicide forming non-intermixing non-reactive system of silver atoms on a Si(111) surface has been repeatedly tested by every available surface science technique. Despite the abundance of data, we have not confirmation or refinement of the original findings, but a wide
and divergent range of proposals for the structure. Nearly 600 different papers with contributions from over 800 individual authors have proposed at least twenty seven different surface structural models or model variants for this system. Unfortunately, there is only a tentative, model dependant, consensus as to how many Ag atoms per Si surface unit cell constitutes a single monolayer and similar consensus as to whether the Ag atom sits above the Si surface, embeds itself in the top surface double layer, sits on, under or between a Si self-adlayer structure.

Currently, the theoretical interest in Ag/Si(111) as a model system has long been forgotten. The applied interest in understanding Ag/Si as a Schottky barrier has been supplanted by experience and engineering solutions to technical difficulties. To surface scientists, Ag on Si(111) has become a challenge to our wide array of analytical, computational and theoretical tools. It has become one of the test cases by which we measure the effectiveness of our methodology. As of the time of this writing, there seems to have been a convergence toward an agreed upon model for the $\sqrt{3}\times\sqrt{3}R30^\circ$ surface although the field has seen numerous similar declarations of victory in the past.

The study of Ag in Si(111) is a “milicosm” of the field of surface science and a microcosm of the scientific research process itself. In it, one finds the spectrum of personalities, experimental and theoretical approaches, large lab and single author efforts. With the solution of its structure, we can, hopefully, begin to understand the interaction between the crystallographic, electronic and micro-chemical structures in this enigmatic and fascinating system.
1.3 Thesis Statement

The objective of this research has evolved over the course of the project from “What is the right answer to the solution of this $\sqrt{3}\times\sqrt{3}R30^\circ$ Ag/Si(111) structure?” to the question of “Why are there so many answers?”. The research described here attempts to help answer the basic question of how so many different researchers can come to such fundamentally different conclusions about the surface structure of such a 'simple' system. The underlying premise of this research is an assertion that the structure Ag on Si(111) is extremely sensitive to the effects of patterning or processing caused by unintended and unnoticed experimental effects, especially surface preparation effects. The kinetics of the problem rather than the equilibrium structure are the controlling as well as the bewildering factor in the study of this system. It is the intent of this study to actively examine the patterning effect by clarifying the role of three minor experimental variables on the resultant Ag/Si(111) structure. The effects studied include; i) minor boron contamination, ii) minor carbon contamination and iii) surface step structure. It is also the intent of this study to passively understand the proposed processing effect by correlating previously reported research in new ways.

Regarding the patterning effects actively studied, first, boron contamination at 1/3 monolayer ($2.6 \times 10^{14}$ atoms/cm$^2$) levels are known to cause a complete $\sqrt{3}\times\sqrt{3}R30^\circ$ reconstruction of the Si(111) surface identical to those produced by Ag under the majority of temperature and coverage conditions. This boron contaminant is thought to substitute for a Si atom occupying the lower half of the Si(111) double layer, as shown in Figure 1.2, thus creating the $\sqrt{3}$ reconstruction while presenting an all Si surface to later adsorbates. Contamination at these levels has been demonstrated by numerous paths including transport through HEPA filtered (borosilicate glass) air, introduction into both glass and metal vacuum systems containing Pyrex™ (borosilicate glass) or during the wet chemical processing of
the Si prior to vacuum introduction. Alternately, researchers using p-type, B doped, Si(111) substrates for their research may unintentionally be surface segregating B contaminants through their surface chemical and thermal processing.\textsuperscript{22, 23}

![Figure 1.2 - B/Si(111)-(√3x√3)R30° structure. (After Headrick\textsuperscript{11,15})](image)

Second, carbon is a ubiquitous element, found in even the best ultra-high vacuum environments. Tungsten filaments used in most electron producing surface analysis instruments are known to be an infinite source of carbon from deposits inherent to the microstructure. Carbon has a wide and adaptable array of bonding configurations available. Its presence on an ultra-clean surface as checked using the most commonly available method, Auger electron spectroscopy, would be masked by satellites of a silver deposit (Illustrated later in Figure 3.8). Additionally, carbon on silicon is known to form SiC particulates when exposed to the high temperatures typical of many surface cleaning procedures.

Finally, surface steps, as lower energy, higher coordination bonding sites, are well documented as sites for selective adsorption and phase nucleation. Assuming a random Ag adsorption pattern, the miscutting of an atomically flat Si(111) surface by $1/2^\circ$ from ideal (typical of the precision of commonly used Laue x-ray crystal orienting techniques) results in about 1\% of the adsorbate atoms being at step sites\textsuperscript{24}. 

7
Adsorption on dislocation terminations\textsuperscript{25} would have an effect of the same magnitude if it were not for the high mobility of Ag on this surface and documented selective adsorption and exceptionally high Ag transport along step edges.

These three minor experimental variables were judged to be easily overlooked, rarely reported in the literature and potentially crucial as unintentional patterning influences on Ag/Si surface structure. There are also a number of other important uncontrolled experimental variables who’s study was beyond the scope of available resources and time. Of these, literature evidence is presented that the most important are that of processing temperature and manner of surface cleaning. This author has seen evidence for residual surface stress effects on ($\sqrt{3}\times\sqrt{3}$)R30°-Ag morphology directly attributable to high temperature cleaning. (Only lower temperature, $<900^\circ\text{C}$, cleaning cycles were used on the surfaces studied in this program.) Vicinal Si(111) surfaces, when taken to high temperature are known to decompose into multi-bunch steps\textsuperscript{26} separated by flat (111) terraces. Considering that the known pinning\textsuperscript{27} ($T < 450^\circ\text{C}$) or rapid transport\textsuperscript{28} ($T > 500^\circ\text{C}$) of Ag along step edges can affect morphology and indicated surface uptake, surface areal averaging analysis techniques can be unintentionally affected.

Determination of the Ag on Si(111) structure has been a problem of the highest class. It has also been a plaguing problem that daunts surface science and reminds us of our limited abilities to both prepare and probe the atomic dimensions of surfaces. The author will not only attempt to answer the question of what structural model is “right” insofar as it is consistent with the given data, but will also provide arguments that Ag/Si(111) is multi-structural, that is, can take on numerous forms critically depending on its processing and the substrate’s processing histories.
1.4 Introduction to Experimental Methods

Reported here are studies of the atomic arrangement of submonolayers of Ag (adsorbate) on the Si(111) (surface) using the X-ray Standing Wave (XSW) and polarization dependant Surface Extended X-ray Absorption Fine Structure (SEXAFS) synchrotron x-ray techniques. These results, supported by additional Rutherford Backscattering (RBS), Low Energy Electron Diffraction (LEED), Isothermal Desorption Spectroscopy (ITDS) and Quantitative Auger Electron Spectroscopy (AES) surface science techniques, present some new insights into this complicated adsorption system.

The coherent interference between two x-ray wave fields of similar intensity, results in the generation of an X-ray Standing Wave (XSW). This XSW is a spatially modulated x-ray interference field and is normally generated by diffraction or total external reflection processes. It is spatially movable in the direction of the scattering vector by changing the relative angle between the incoming and outgoing wave vectors as shown in Figure 1.3. By moving this interference field, one can scan the nodes (areas of zero electromagnetic field intensity) and anti-nodes (areas of double electromagnetic field intensity) across the locations of foreign substitutional, interstitial, surface or above-surface atoms. Since these foreign atoms respond to high field intensities by emitting characteristic fluorescence, Auger or photoelectrons, their positions can be determined on a few hundredths Å scale, by coincidentally watching for this characteristic emission while scanning the interference field.

What must be realized with XSW measurements is that this positional determination is measured as a perpendicular distance from an imaginary extension of the bulk-crystal diffraction planes. In order to locate an atom in 3 dimensions, three independent XSW measurements must be made, referenced to three diffraction planes not all in the same crystallographic zone. This is not easily done in ultra-high vacuum
so, typically, two or three measurements in the same zone are made and then
symmetry or other arguments are made to limit the positional possibilities for the
foreign atom. Even then, the XSW measurement tells you nothing of the position of
the foreign atoms of interest with respect to the actual surface of the material. One can
assume a bulk-like termination for the surface, but nature is rarely so kind; surface
contractions, reconstructions, defects, steps and expansions are the norm for real
surfaces.

Figure 1.3 - Schematic illustration of coherent interfering wave fronts producing a
movable standing wave pattern.

To overcome this inherent surface-reconstruction insensitivity by the XSW
technique, a second synchrotron x-ray technique was used on the same surface to
determine bond lengths between Ag and its nearest neighbors. The Surface Extended
X-ray Absorption Fine Structure (SEXAFS) technique takes advantage that each
element will anomalously diffract (absorb) x-rays at characteristic energies. When an
x-ray photon is absorbed, a core-level (for hard x-rays used in this study)
photoelectron is emitted. Part of this emitted photoelectron wavefunction can be
backscattered by near neighbor atoms, coherently interfering with the outgoing
wavefunction and modifying that absorption process. By fitting the known
backscattering strengths and phase shifts of the nearest neighbor species, a measure of
the distance between the two atoms, the bond length, can be measured. Additionally,
the inherent polarization of synchrotron x-rays can be used to determine in-plane and
out-of-plane projections for these bond lengths. There are also weaknesses in the SEXAFS technique, mainly due to the complexity of the calculations of emitter and backscattering phase shifts, curved photoelectron wave function corrections and large number of degrees-of-freedom available in the fitting process.

By combining the two techniques, it is felt that the complementary strengths of each method can provide a better overall picture of the surface crystallography. It is crucially significant that these experiments were done consecutively, on the same sample, in the same few hours. Comparison of results from different researchers, with different sample preparation methods have already been done and have added nothing but conflicting information about the Ag/Si(111) structure.

To summarize, complementary XSW and SEXAFS have been done on these surfaces concurrently with LEED, RBS, AES and ITDS, providing information that takes account of absolute coverage and surface contraction effects. Additionally, we have studied the rare 3x1 to $\sqrt{3}\times\sqrt{3}R30^\circ$ phase transition in order to gain insight into the Ag surface placement in this perplexing system.

### 1.5 Conventions

- Extensive use is made of common surface and x-ray science acronyms. A list is included in the preliminary pages. This dissertation is written for practitioners "skilled in the art" of surface and synchrotron x-ray science. Introductory materials will be presented on a limited basis as needed but, for the most part, the casual reader will be directed to relevant introductory readings at the beginning of each chapter.

- One monolayer (1ML) is defined here as $7.83 \times 10^{14}$ Ag atoms/cm$^2$. There are three main conventions used by surface scientists to define a "monolayer". The first defines 1 ML as the number of atoms in one atomic layer of the bulk elemental
material as calculated from the atomic/molecular weight and bulk density. The second convention, especially for layer-by-layer growth modes, is to watch the uptake of adsorbate atoms by AES, RHEED, etc. and define the endpoint of a completed surface coverage as one "monolayer". The third, defines the areal density of the underlying substrate to define a "monolayer" so that one adsorbate atom for each surface atom would be a single monolayer. The last convention is used in this paper and, to a large extent, is followed for papers published in the last 10 years. Care has been taken to convert other conventions used in the literature references into this definition of ML.

• Nomenclature and coordinate system. The terms ($\sqrt{3}\times\sqrt{3}$)R30°, $\sqrt{3}\times\sqrt{3}$R30° and $\sqrt{3}$ are used interchangeably. The relationship between the ($\sqrt{3}\times\sqrt{3}$)R30° or 3x1 superlattices and the Si(111) 1x1 bulk lattice follows a right hand rule convention with positive z coordinate defined as perpendicular outward from the surface. This is not a universal convention and the reader must be careful when analyzing literature sources. In fact, the most extensive surface structural database compilation29 defines +z as pointing into the surface creating a de facto left-handed coordinate system.

• Literature citations are made using the first author's name exclusively. With such a large literature database and multiple collaborative efforts of 3 to 6 authors the norm and 13 authors at the extrema30, practical considerations require this limitation. The American Institute of Physics guidelines for the complete reference citation are followed at the end of each chapter.

• Negative inter-comparisons in the literature database are avoided. There is extensive, and confusing, cross-reference structure in the literature. Since cross-comparisons for each paper expand roughly as $2^n$ where n is the number of literature studies, only positive correlations will be reported to simplify the process.
1.6 References – Chapter One

1. E. Bauer, Z. Kristallogr. 110, 372 (1958)


CHAPTER TWO:
LITERATURE ANALYSIS

2.1 Literature Compilation

2.1.1 Introduction

The study of Ag on Si(111) has consumed a disproportionate share of the resources available to surface science over the past 40 years with very available surface science technique and theoretical method utilized. Over 800 individuals, as authors and co-authors, have published almost 600 papers (Figure 2.1) in all major research journals (Figure 2.2) in addition to countless minor symposia and oral presentations. Historically averaged it took 3.7 authors to prepare an Ag/Si(111) paper at a conservatively estimated total research cost of over $76M ($US - year 2002 adjusted constant dollars)*. From that effort, 38 different atomic surface models have been adapted or proposed for the eight different Ag/Si phases with 77% of this effort devoted to the Ag-(√3x√3)R30°, Ag-(3x1) and Ag-3D island structures. Ag/Si(111) has been called everything from, a “…mysterious surface” to “…the most thoroughly investigated metal-semiconductor system”. Even after such an exhaustive and lengthy study process, one of the most prominent leaders in this field of research declared in 2000 that “… this surface is still a challenging target in surface physics”.

With such an enormous literature background to review, the author will take the opportunity to present an ‘ensemble average’ review, analysis and summary of the literature in this chapter and reserve the more traditional, highly detailed, paper-by-paper review for a later, more voluminous publication.

* See addendum 1.
† These CNxxx numbers denote a “Chronological Numbering” system used in the reference list located at the end of this chapter to manage literature referrals.
Figure 2.1 - Annual and cumulative Ag/Si(111) publication history.

Figure 2.2 - Distribution of Ag/Si(111) papers by publication source.
2.1.2 Chronological listing

Electronic literature searching methods have become a tremendous time saving asset for current researchers. Search accuracy and completeness is almost a guarantee. Unfortunately, there is a paucity of electronic database information before 1994 but a wealth of Ag/Si information there. As an aid to future research, the reference list presented at the end of this chapter is in the form of a chronological bibliography in comprehensive citation format. All papers were back reviewed for their citations and citation accuracy. Database papers were also forward traced to their future citing sources using the ISI Science Citation Index and cross-collated with previous listings. To fully appreciate the enormity and evolution of the Ag/Si(111) problem, the serious researcher must put each nugget of information into it’s proper historical context.

Chronological assignment was done using paper *submittal* date (not acceptance date) when listed. Books and journal articles without definitive submittal information were indexed using January of the publication year. This 01 January assumption conservatively accounts for long book lead times and approximates accuracy “on average” for journal articles with typical 3-5 month lead times. Conferences were sorted using the first conference date.

The author realizes that this type of chapter is an unusual inclusion for a scientific paper. If, however, this kind of information had been available it would have saved literally months of time roaming library stacks and reading irrelevant papers while chasing misleading and often mis-transcribed citations present in the literature record. As a further aid to researchers, Tables 2.1 and 2.2 present the body of Ag/Si(111) literature categorized by experimental and calculational techniques respectively.
2.1.3 Instrumental technique listing

Each citation from the compilation above is re-categorized by major experimental technique in this section.

<p>| Table 2.1 - Ag/Si(111) Papers Categorized by Primary Experimental Technique |
|-------------------|--------------------------------------------------|
| 2PPE              | Cinchetti [CN518], Cinchetti [CN545]             |
| µ-AED             | Kono [CN267]                                      |
| µ-AES             | Hanbücken [CN72], Tokutaka [CN99], Kono [CN154], Boutaoui [CN172], Raynerd [CN209], Watanabe [CN349] |
| AES               | Bauer [CN4], Wehking [CN9], Rhead [CN11], Housley [CN13], Le Lay [CN15], McKinley [CN19], Dufour [CN38], Bolmont [CN40], Cros [CN41], Le Lay [CN44], Gotoh [CN46], Tokutaka [CN48], Hanbücken [CN50], Cros [CN52], Horio [CN64], Horio [CN82], Zhu [CN92], Aristov [CN93], Kohmoto [CN117], Grazulis [CN118], Chambers [CN147], Fan [CN148], Venables [CN159], Fan [CN161], Borensztein [CN170], Inoue [CN196], Yasunaga* [CN204], Raynerd [CN214], Yuhara [CN262], Saranin [CN269], Saranin [CN271], Gavriljuk [CN273], Weitering [CN283], Fukuda [CN299], Ishigami [CN303], Yuhara [CN311], Yuhara [CN317], Ichimiya [CN321], Ishikawa [CN334], Ishikawa [CN338], Ishikawa [CN340], Watanabe [CN357], Yuhara [CN363], Yuhara [CN380], Takagi [CN467], Müller [CN484], Zhachuk [CN531] |
| *(scanning AES)   | AFM Minobe [CN399], Sugawara [CN401], Kitamura [CN402], Sasaki [CN448], Hirayama [CN455], Morita [CN462.5], Müller [CN484], Márquez [CN486], Aswal [CN504], Goto [CN514], Honda [CN548], Tokuda [CN562], Aseev [CN564] |
| AFM               | AR-EELS Horioka [CN62], Horioka [CN70]           |
| ARPES             | Shapiro [CN100], Shapiro [CN127], Johansson [CN223], Sakamoto [CN452], Zhang [CN459], Arranz [CN462], Sánchez-Royo [CN462.2], Arranz [CN464], Crain [CN473], Matsuda [CN505], Zhang [CN527], Hirahara [CN532], Matsuda [CN552], Crain [CN555] |</p>
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2.1.4 Theoretical/computational technique listing

Table 2.2 - Ag/Si(111) Papers Categorized by Primary Theoretical Technique

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2.2 Ag/Si(111) surface phase diagram reconstruction

2.2.1 Overview

By scouring the literature for references to specific Ag/Si(111) phase observations and correlating that with the corresponding surface preparation technique, a new 2D surface phase diagram for the system has been constructed as shown in the slightly idealized form of Figure 2.3.

![Figure 2.3 - Idealized surface structure diagram for Ag/Si(111).](image)

In this phase diagram format with surface structural regions plotted on standard temperature vs. coverage axes, the reader should note the following. To the right of the figure are defined temperature “regimes” of cryogenic, low, ambient, elevated, high, desorption and flash that will aid future discussions. In the lower left of the
figure, low Ag coverage at temperatures below 200°C, Ag on Si(111)-(7x7) deposits in a disorganized fashion. As temperature increases to near 200°C and Ag coverage approaches 1 ML, there is a complex and mixed attempt to organize into Ag-(1x1) or Ag(111) crystallites. Moving into the lower right portion of the diagram, as coverage increases in these cryogenic, low and ambient temperatures, Ag grows in layer-by-layer, Frank-van der Merwe fashion only at cryogenic temperatures. Increasing temperature at high coverages initiates what has been termed, “pseudo F-M” growth. In this mode, Ag atoms reaching the low and ambient temperature surface have sufficient energy to migrate and the overlayer grows by an island growth and coalescence mode with temperature determining the island size, distribution and growth rates. These pseudo-F-M Ag(111) islands grow with two, twin-related orientations until about 100°C where the Ag <110> || Si <110> orientation dominates.

As we move to the upper two thirds of Figure 2.3, temperatures above 200°C and low Ag coverage, there is the appearance of the Ag-(√3x√3)R30° phase in β- and γ- forms. As temperatures further increase into the desorption regime, Ag atoms emanate from the surface leaving the Ag-(3x1) phase before transitioning to the clean Si(111)-(7x7) then Si(111)-(1x1) phases. For high coverages, the √3-Ag phase forms first and additional Ag grows in classic layer-plus-island, Stranski-Krastanov (S-K) mode until a temperature of about 450°C. Above this temperature, the sticking coefficient for new Ag atoms onto the √3-Ag surface is zero and any existing Ag(111) islands desorb at known temperature-dependant rates.

2.2.2 Low coverage, low temperature region

To support the features of this new surface phase diagram, it is necessary to look at each quadrant of Figure 2.3 in detail. Starting with the low coverage, low temperature portion, an expanded and annotated view is presented as Figure 2.4. At
the lowest coverage and temperature, the series of open circles indicate the onset of surface conductivity. These measurements in and of themselves, do not aid with phase identification. However, percolation theory predicts that the perfect random placement of conductors on a surface will create a conduction path at a coverage of 0.5 ML. Thus doubling the coverage determined by conduction experiments can place the monolayer coverage boundary at these low temperatures. This procedure produces a 1 ML boundary line is excellent agreement with four other conductivity and RHEED measurements of complete coverage at cryogenic temperatures, solid circles in the figure. How is the shallow slope of the boundary explained? This author proposes the following. First, there is a point at -188°C where surface conductivity is complete at 0.5 ML where Ag/Si(111) behaves as an ideal percolation model material. At temperatures below this ideal point, lateral movement of an incoming Ag atom becomes increasingly restricted. Those atoms that find themselves deposited atop previous Ag adsorbates remained trapped away from the surface and unable to contribute to the conduction link. At temperatures above this ideal point, Ag adsorbates easily ‘climb down’ from deposited positions atop Ag islands and can migrate with increasing ease to larger and larger island groups.

Moving into the low and ambient temperature range from roughly -150°C to +100°C, knowledge of the surface dynamics comes increasingly from STM and RHEED observations. Even at -123°C, Ag atoms arriving at a surface with typical 2-3 eV thermal energies have a radius of non-thermal migration greater than 50 Å.
Summary of Growth Structures
Ag/Si(111)-(7x7)

Details: Low Coverage, Low Temperature Quadrant

Figure 2.4 - Low coverage, low temperature quadrant of the Ag/Si(111)-(7x7) surface structure diagram
As room temperature approaches, the long thermal diffusion lengths allow Ag atom placement to evolve from random to a more organized but not yet crystalline structure. At the lowest coverages, < 0.1 ML, Ag is not imaged but its effect on the underlying Si(111)-(7x7) structure is noted. The Ag is thought to initially drop into the Si(111)-(7x7) corner holes. Shibata\textsuperscript{CN282} calls this the "first stage $\alpha$-island" structure. Increasing Ag coverage produces a "second stage $\alpha$-island" structure imaged in STM as a bright-spot, empty-state located at the center of the (7x7) faulted half. Further condensation produces a third stage $\alpha$-island structure consisting of a ring-like shape on the faulted (7x7) half. Further growth at R.T. consists of coalescence of these $\alpha$-island structures to form a smooth uniform structure. The critical coverage at near-room temperatures is ill-determined as seen by the six solid circle determinations indicated in the figure. Above 0.5 ML, the surface is in concurrent transition between a continued random, organized, Ag-(1x1), Ag(111) or 3D Ag crystallite ending phase. This is an unfortunate happenstance of this surface system since room-temperature structures are, by definition, the simplest and most widely probed. This fundamental characteristic of the system has contributed greatly to the overall complexity and confusion about the physics of Ag/Si(111).

2.2.3 High coverage, low temperature region

An expanded and annotated view of the lower right quadrant of Figure 2.3 is shown in Figure 2.5. (Note the 10X increase in the horizontal scale factor.) At the lowest, cryogenic temperatures, it is agreed that Ag grows in F-M fashion denoted as the $\alpha$-Ag(111) growth region. The upper limit on this F-M growth mode ranges from -183°C\textsuperscript{CN135} upward\textsuperscript{CN458} to -117°C\textsuperscript{CN289} depending on technique with reports that the transition is coverage but not temperature dependant starting at 6 ML\textsuperscript{CN351} and contradictory reports that the transition is temperature but not coverage.
dependant\textsuperscript{CN309, CN135}. This author asserts that this is a continuum transition, with inhibited micro-island nucleation, growth and coalescence as the growth mechanism, and assigns the transition temperature of -188°C discussed in the previous section. Even at these low temperatures, Ag(111) forms parallel to Si(111), loosing epitaxy only after deposit thicknesses greater than 1000 Å.

Above this $\alpha$-Ag(111) region, denoted the $\beta$-Ag(111) pseudo F-M region. Ag(111) forms epitaxially with two, twin related orientations of $\text{Ag}(111) \parallel \text{Si}(111)$ and $\text{Ag}<110> \parallel \text{Si}<110>$ as well as $\text{Ag}<1\overline{1}2> \parallel \text{Si}<1\overline{1}0>$. This region has S-K as well as F-M like characteristics depending on technique used to probe it. At even higher temperatures the $\gamma$-Ag(111) pseudo F-M growth region begins at roughly 130°C (depending on deposition rate). This $\gamma$-Ag(111) continues to form epitaxially but only in the ideal $\text{Ag}(111) \parallel \text{Si}(111)$ and $\text{Ag}<110> \parallel \text{Si}<110>$ orientation. As indicated with the dash-dot line in Figure 2.5, this pseudo F-M phase can be moved to substantially higher temperatures with sufficiently rapid Ag deposition rates. The low coverage portion of this region, from 1 to 3 ML is labeled “proto” since the great majority of papers defer phase definition until unambiguous LEED or RHEED patterns appear.

There is a critical and fundamental transition at approximately 200°C the upper portion of Figure 2.5 traversing all coverages as seen previously in the overview of Figure 2.3 and detail of Figure 2.4. Estimates for this transition range from 190°C at the low end\textsuperscript{CN297} to 290°C at the high\textsuperscript{CN114}. It is essential that the reader understand that this transition is due to the tertiary interactions of Ag, Si(111)-(7x7) adatoms and Si(111)-(7x7) dimer-stacking fault substrate. That is, the Si self-adatoms in the presence of Ag acting as a surfactant, can restructure to allow an Ag to Si(substrate) coupling. This line establishes the great divide between lower temperature, weakly-interacting Ag/Si and the higher temperature, much stronger bonding Ag-$\sqrt{3}$ and Ag S-K growth dichotomy.
Figure 2.5 - High coverage, low temperature quadrant of the Ag/Si(111)-(7x7) surface structure diagram
2.2.4 Low coverage, high temperature region

Figure 2.6 expands and annotates the upper left quadrant, the high temperature low coverage portion, of Figure 2.3. This is the region wherein lies the greatest controversy about the structure of the Ag-(\(\sqrt{3}\times\sqrt{3}\))R30° phase. As noted in the paragraph above, the Ag-\(\sqrt{3}\) phase is able to form at temperatures above \(\sim 200^\circ C\) where sufficient thermal energy exists, in connection with Ag adatoms, to reorder the Si self-adatoms of the Si(111)-(7x7) DAS surface. It is the movement, incorporation and segregation of these Si atoms by or into the \(\sqrt{3}\) structure that this author considers to be one of the outstanding unanswered questions in surface science today.

There is no dispute that Ag/Si(111) forms the \(\sqrt{3}\) structure for all Ag coverages at temperatures of 200\(^\circ\)C and above (until desorption). Presented here instead, is the first compilation of observations and anecdotal evidence supporting the concept of multiple forms of the phase, christened \(\beta\)-\(\sqrt{3}\) and \(\gamma\)-\(\sqrt{3}\) for the 2/3 and 1 ML versions respectively. Determination of a complete monolayer coverage in the \(\beta\)- and \(\gamma\)-regions have been attempted in nineteen papers as shown by the open circles in Figure 2.6. The most complete study delineated by the dash-dot-dash connecting line is by Raynerd\(^{CN209}\) using \(\mu\)-AES. Their data provides a convenient outer envelope for all other determinations with the exception of one outlyer.\(^{CN088}\) The combined result is conceptually similar to that proposed in 1981 by LeLay\(^{CN044}\) followed closely by Julg\(^{CN056}\) in 1982, where the \(\sqrt{3}\) layer is initially formed with 2 Ag atoms per surface unit cell (2/3 ML coverage) until additional thermal energy of 0.1 eV is available to allow a third Ag atom (1 ML coverage total) to traverse an activation barrier to complete the phase.
Figure 2.6 - Low coverage, high temperature quadrant of the Ag/Si(111)-(7x7) surface structure diagram
In addition to the data points plotted above, there have been numerous other citings of an anecdotal nature detailing the variability of Ag/Si(111) critical coverage. Le Lay\textsuperscript{CN044} noted that $\theta_c$ increases as $T_{\text{substrate}}$ increases ($\theta_c$ varies from 0.8 to 1.0 at 500°C) and $\theta_c = 2/3$ at 200°C. Raynerd\textsuperscript{CN236} demonstrated that $\theta_c$ is deposit path dependant and can be $2/3$ or 1. Hasegawa\textsuperscript{CN105} and later Ino\textsuperscript{CN242} showed critical coverage temperature dependency with; $\theta_c = 0.8 \pm 0.1$ ML for Ag-$\sqrt{3}$ produced at 480°C and $\theta_c = 0.9 \pm 0.1$ ML for Ag-$\sqrt{3}$ produced at 440°C. Ishigami\textsuperscript{CN303} conjectured that Ag forms two different $\sqrt{3}$ structures, one for Ag coverage $>0.5$ML and another for coverage $<0.5$ML. In all, the concept that critical coverage can be a changing function has been independently observed by a number of researchers but ignored by the sub-field in general while searching for \textit{the} one correct solution to the structure of Ag-($\sqrt{3} \times \sqrt{3}$)R30° on Si(111).

The assertion by this author that there exists $\beta$- and $\gamma$- forms of the Ag-$\sqrt{3}$ structure comes not only from the experimental results presented later in Chapter 5 and the unusual 2/3 to 1 ML transition in the surface structure diagram of Figure 2.6 but also the following anecdotal evidence from the extensive literature database. The earliest unaccounted indication of a multi-conformal $\sqrt{3}$ phase was noted in the ITDS results of Hasegawa.\textsuperscript{CN105} Isothermally desorbing $\sqrt{3}$ phase created at 440°C shows a break-point between the $\sqrt{3}$ and (3x1) phases. In contrast, $\sqrt{3}$ phase created at a higher 480°C temperature showed no such feature. Later, Ino\textsuperscript{CN112} while isothermally desorbing Ag$\sqrt{3}$ at temperatures between 560° and 585°C noted three independent break points at 1, 2/3 and 1/3 ML respectively corresponding, this dissertation’s author believes, to the $\gamma$-, $\beta$- and (3x1) phases. Raynerd\textsuperscript{CN214} pinned this unknown transition temperature at 427°C, echoing Julg’s idea\textsuperscript{CN056} [sic. LeLay\textsuperscript{CN044}] of a 2/3 ML Ag-$\sqrt{3}$ phase extended by an additional 1/3 ML after an activation barrier is traversed.
At the upper portion of the diagram, in the desorption region above 550°C lies the Ag-(3x1) metastable phase. Two important points must be emphasized. First, any Ag phase on Si(111) held at temperatures above 550°C will desorb, so if the reader is thinking of these structural diagrams as traditional phase diagrams, these Ag-(3x1) and Ag-(√3x√3) are not there. There are no stable phases at these temperatures, Ag completely desorbs leaving bare Si(111) with a residual 0.02ML equivalent of 2D delocalized Ag adatom gas present at pressures below 3 x 10⁻⁸ torr. Desorption rates for Ag/Si(111) phases are well documented even in the earliest literature by ITDS. Second, it is this author’s contention that coverage declarations in the literature are suspect if measurements are made or samples prepared by transitioning into desorption region or above unless careful notations of time at temperature are included. The sloping upper boundary does not specify an exact transition but rather connotes the general idea that phases are shorter lived as temperatures increase.

Understanding the metastable nature of all Ag phases at this temperature, the reader can appreciate that a high coverage S-K growth of Ag(111) islands on Ag-√3 on Si(111) taken into the desorption regime will transition first from S-K to Ag-√3 by desorption of Ag islands. Next the Ag-√3 phase will desorb at a slower rate, leaving Ag-(3x1) phase. Finally, the Ag-(3x1) phase desorbs at a much slower rate yet, leaving bare Si(111). Although the different phase desorption is considered to be consecutive, STM images taken after high temperature exposure or in the proximity of surface defects show simultaneous existence of Si(111)-(7x7), Ag-(3x1) and Ag-√3 phases.

Uppermost in the diagram is shown the broad Si(111)-(7x7) region that remains after complete Ag desorption. Interestingly, a faint 0.02ML equivalent of 2D Ag adatom gas remains as determined by electrical conductivity measurements. Finally, above 830°C, Si(111)-(7x7) transforms into a Si(111)-(1x1) structure that
includes a faint 0.25 ML equivalent of Si(√3x√3) superstructure. RHEED experiments\textsuperscript{CN155} suggest a first-order transformation with increasing temperature rather than an order-disorder one. REM observations\textsuperscript{CN130} suggest a step-edge-effect dominated second-order reverse transformation.

### 2.2.5 High coverage, high temperature region

Finally, the upper right quadrant of the surface structural diagram Figure 2.3 has been expanded and annotated in Figure 2.7 below. At all temperatures above 200°C and coverages greater than $\theta_C$, the dominant feature of this surface is an Ag-(√3x√3) structure dotted with Ag(111) islands of varying size and areal density. This is a prototypical Stranski-Krastanov system were the initial Ag deposit forms a $\sqrt{3}$ barrier layer and subsequent Ag deposits do not “wet” this interface, but rather, cluster into a few large islands. The effect is dramatic at higher temperatures with deposits of 60 ML forming a surface with projected area of 80% Ag-$\sqrt{3}$ and only 20% Ag-island structure.

Above 450°C Ag islands no longer nucleate\textsuperscript{CN085} on this solid-state equivalent of an Ag-$\sqrt{3}$ Leidenfrost layer. Measured sticking coefficients\textsuperscript{CN105, CN112} of $\Sigma_{440^\circ C} = 1/3$ and $\Sigma_{480^\circ C} = 0$ quantitatively confirm this dramatic effect. In this regime, a complex behavior\textsuperscript{CN016} of small island Ag desorption and Oswald ripening acts upon the islands until temperatures increase fully into the desorption range. Looking back upon the low-coverage $\beta$-$\sqrt{3}$ to $\gamma$-$\sqrt{3}$ transition proposed at ~400°C in the previous section and the strong break-point at 450°C in this high-coverage region, the author conjectures here that an Ag catalyzed rearrangement of the Si(111)-(7x7) surface stacking fault defect is the underlying effect driving this $\beta$- to $\gamma$- transition.

Once temperatures are well above 550°C, Ag desorbs selectively from island edges, leaving the Ag-$\sqrt{3}$ layer undisturbed, until all island features vanish.
Researchers can balance and in some cases overwhelm this desorption path by surface dosing at high rates but only transiently. At the highest temperatures the concept of high Ag surface coverage becomes moot and the Si(7x7) and Si(111) behavior described in the previous section applies.

### 2.2.6 Special case: deposition on Si(111)-(2x1)

A clean Si(111) surface created by cleaving rather than the more prevalent chemical and thermal techniques, will form a characteristic Si(111)-(2x1) surface structure. As seen in Figure 2.8, this clean (2x1) surface will convert into the Si(111)-(7x7) structure at temperatures between 210° and 425°C depending upon cleavage surface step density. If Ag is deposited on this Si(111)-(2x1) surface, two unique phases, different than those previously discussed can form, both at ambient temperatures.

Following the development used in the previous sections, examining Ag deposition on Si(111)-(2x1) from low to high temperatures and low to high coverages, the following changes occur. At the lowest temperatures, Ag randomly decorates the Si(111)-(2x1) surface until Ag(111) F-M growth takes over at high coverages. This is similar to the response on the Si(111)-(7x7) surface. There are a series of experiments that determine the temperature and coverage points where random Ag/Si(111)-(2x1) transitions to Ag(1x1)/Si(111)-(2x1) and at higher coverages to Ag(111) S-K growth. This behavior again parallels the Ag/Si(111)-(7x7) growth case.

Near room temperature however, phase behavior on Si(111)-(2x1) ceases to model the behavior on Si(111)-(7x7). Ag coverage above 0.3 ML produces a unique Ag($\sqrt{7}x\sqrt{7}$)R19.1° structure on Si(111)-(2x1). It is noted that the formation of this phase is sensitive to “vacuum conditions” in much the same way that
the formation of the high temperature, low coverage Ag(3x1)/Si(111)-(7x7) phase has been found to be in this dissertation. As coverage increases, some Ag(111)-(1x1)/Si(111)-(2x1) growth is already apparent and the Ag(√7x√7)R19.1° structure continues to form. It is asserted that this Ag-√7 structure becomes complete at 6/7 ML. Continuing to increase coverage, Ag(111) island growth increases on Si(111)-(2x1), the Ag-√7 LEED pattern still persists to 2 ML and a new additional Ag(3x1)/Si(111)-(2x1) phase emerges at 1.5 ML. Above 2.5 ML, the Ag-√7 phase has faded leaving the Ag(111) and Ag(3x1) phases which catalyze a Si(111)-(2x1) to Si(111)-(1x1) substrate change.

At higher than ambient temperatures there is a transition from these Si(111)-(2x1) specific phases to the standard Ag-√3 and S-K growth on Si(111)-(7x7) phases. The exact temperature and coverage transitions have not yet been explored in detail. Certainly, at temperatures above 200°C for >1 ML coverages the transition has occurred. At 400°C, it is known that even 0.1 ML Ag coverage will readily catalyze the Si(2x1) to Si(7x7) transition. Once this transition occurs, the surface structural diagram for all practical purposes is equivalent to those previously presented in Figure 2.6 and Figure 2.7.

There are many studies that prepare clean initial surfaces by cleaving at room temperature then deposit Ag at elevated temperatures where the Si(111)-(2x1) surface character is lost. The results of these studies have been included with the results produced by Ag on Si(111)-(7x7) surfaces. It is recommended that the two preparation methods be separated in future studies to determine if they have an effect on coverage or surface structure findings.
Summary of Growth Structures
Ag/Si(111)-(7x7)

Details: High Coverage, High Temperature Quadrant

Figure 2.7 - High coverage, high temperature quadrant of the Ag/Si(111)-(7x7) surface structure diagram
Summary of Growth Structures
Ag/Si(111)-(2x1)

Figure 2.8 - Special case: surface structure diagram, Ag on cleaved Si(111)-(2x1)
2.2.7 Special case: over-deposition onto existing Ag-(√3x√3)R30°/Si(111)

A special processing case for Ag/Si(111)-(7x7), has yielded interesting results including three additional new phases. Shown in Figure 2.9 are the cumulative results for these special case surfaces produced by, first, creating a complete Ag-(√3x√3)R30°/Si(111) surface at elevated temperatures then, second, over-depositing Ag at cryogenic or low temperatures. It must be made perfectly clear that in this Section 2.2.7, the starting surfaces already have an unknown quantity of Ag deposited forming a base Ag-√3 structure. The Ag coverage plotted on Figure 2.9’s abscissa represents the controlled amount in addition to the amount which was required to form the Ag-√3 surface. It is the two step processing path, a high temperature step followed by a low temperature step, that differentiates these surfaces from the other single preparation results previously presented.

At the very lowest cryogenic temperatures and coverages Ag randomly nucleates on the Ag-√3 surface. At low excess coverages and temperatures below -175°C and after some short-range ordering of Ag upon initial deposit, a new Ag(6x6) phase emerges\(^{CN356}\), stable only from roughly 0.2 to 0.5 ML before giving way to Ag 3D island growth with S-K characteristic.

Moving higher in temperature, -100 to -175°C, initial deposits show no, or at best short range order, before organizing briefly into a Ag(√21x√21)R10.9° configuration. Further deposits result in the brief appearance of the Ag(6x6) phase before both are slowly replaced by Ag(111) 3D growth above 1ML excess coverage. The Ag-√21 phase remains visible up through 2.5ML coverage and the Ag(6x6) phase if formed remains until quenched at 1.75ML. Also in this temperature zone is an important displacive transition in the underlying Ag-(√3x√3)R30° structure.\(^{CN490}\) Literature momentum suggest the elevated temperature Ag-√3 structure is best described by one of the HCT or Honeycomb Chained Triangle models. Throughout
this dissertation, this author has labeled this the $\beta-(\sqrt{3}\times\sqrt{3})R30^\circ$ structure. At -123°C, this underlying $\beta-\sqrt{3}$ makes a displacive transition to an $\alpha-(\sqrt{3}\times\sqrt{3})R30^\circ$ structure currently thought to match IET or Inequivalent Triangle model parameters. Both models are explained generally in Section 2.4.3.

As temperature generally increases further, -100 to 0°C, the Ag-$\sqrt{21}$ and $\beta-\sqrt{3}$ structures dominate until S-K growth takes over. Above -75°C there is only a very narrow low-coverage region of Ag-$\sqrt{21}$ stability, the remainder of growth looks exactly like prototypical Ag(111) S-K growth covered in all previous Ag/Si(111)-(7x7) diagrams. Also at these temperatures, the very lowest Ag deposits, <0.03ML are known to be delocalized, forming a highly conductive 2D Ag atom gas. Higher deposit amounts cause this delocalized layer to condense as the nuclei for 3D Ag island growth.
Figure 2.9 - Special case: surface structure diagram, Ag on a pre-formed Ag-(√3x√3)/Si(111) surface.
2.3 Critical surface coverage determination for Ag-(√3x√3)R30°/Si(111)

One of the key points of contention in the search for a Ag-(√3x√3) model has been the determination of the saturation, critical or completion coverage, denoted equivalently as \( \theta_S \) or \( \theta_C \). With the new evidence presented in the previous section, this author has hoped to convince the reader that the Ag-√3 phase can accommodate both two or three atoms per unit cell depending on preparation temperature, corresponding to 2/3 and 1 monolayer \( \theta_C \) respectively. The overwhelming majority of the research however, has focused on finding the one correct model and thus the corresponding one correct critical coverage. Historically shown in Figure 2.10, there raged a fierce rivalry between 2/3 and 1 ML solutions during the years from 1975 to 1995.

![Figure 2.10 - Historical trend: Ag-(√3x√3) phase critical surface coverage, \( \theta_C \).](image)

With the emergence of a dominant model, the Honeycomb Chained Triangle or HCT model, those papers expressly supporting a particular \( \theta_C \) tended toward the 1 ML solution based upon the HCT model’s structural requirements rather than explicit measurement. Overwhelmingly, the data points of Figure 2.10 which lie exactly on
the 2/3 or 1 ML range-values are specifically due to the support for one particular model over another. Those data points lying between 1/3, 2/3 and 1 ML coverages, especially those including error bars, are a result of experimental measurements of $\theta_C$ rather than model dependant arguments.

To compliment the historical data analysis above, analyses of $\theta_C$ versus Si(111) substrate properties; specifically substrate type, substrate dopant, substrate resistivity and clean surface preparation temperature, were made but yielded limited correlations. Results are shown in Figure 2.11. It was initially conjectured that boron, a known delta-dopant and subsurface $\sqrt{3}$ forming element, could pattern the surface for subsequent Ag-(\$\sqrt{3}x\sqrt{3}$) phase formation. The top two Figure 2.11 graphs were a check of that conjecture. Most authors report their substrates as p-type (including B) or n-type. The 1:1 split between a $\theta_C$ of 1 and 2/3 ML for p-type as compared with a 2:1 ratio for n-type seemed to support that stance. Looking, however, at the smaller subset of authors who actually reported the dopant element; B, P, As, Sb, etc. shows a 1:1 ratio for both p-type boron and n-type phosphorous substrates. Although the sample set is small, only five total data points in the literature, this information plus the experimental evidence to be presented in Chapter 5 indicates that trace B on Si(111) does not influence Ag/Si(111) structure. Perhaps the discrepancy can be explained by the influence of the quantity of dopant in addition to the type. This is tracked in the figure’s lower left graph of critical coverage versus substrate resistivity, where low resistivity means high dopant density and high resistivity indicates low dopant density. It is shown that low resistivities (high dopant level) below 1 $\Omega$-cm show 1:2/3 ML ratio of $\sim$2:1 where high resistivities revert to the 1:1 level tentatively suggesting that high dopant levels influence structure. Of equal interest was the provisional-correlation with clean Si(111) substrate preparation temperature shown in the final, lower right graph of Figure 2.11. This author’s experience with high
temperature flashing of Si(111) wafer samples, presented later in Chapter 5, showed optical indications of surface faceting and RBS indications of subsequent subsurface Ag migration. It is still considered by this author, that surface flashing to temperatures greater than 1000°C reformulates surface C into SiC and other surface phase influencing impurities, defects and structures. Taking all data points at 1000°C and below there appears to be a 1:1 split between $\theta_C$ of 1 and 2/3 ML. Summing points above 1000°C gives the more normal 2:1 ratio seen in all other non-correlations. It is tempting to count the discrepancy in favor of the stated bias toward low-temperature surface cleaning cycles. Obviously, the two parameter correlation space used in the figures are too simplistic and tenuous arguments given suggests further analysis is appropriate.

Similar checks were made of Ag overlayer preparation methods. Re-analyzing the literature data in terms of critical coverage against highest Ag covered surface processing temperature lead to the construction of the surface structural diagram of Figure 2.3 after all measured values $\theta_C$ were plotted and model determined values were eliminated. Two other fascinating correlations emerged. The first, shown in Figure 2.12, correlates critical coverage with the method for surface dosing with Ag. As introduced in the thesis statement of Section 1.3, the effect carbon contamination on subsequent Ag/Si structures was one of the three primary foci of this dissertation. Not only are trace C contamination Auger peaks masked by Ag Auger satellites, but C can easily co-deposited with Ag after clean surface preparation. One of the stealth sources of contamination comes from carbon emitted from W filaments. Figure 2.12 shows the usual support of $\theta_C$ ratios 1ML:2/3ML of 2:1 for the unspecified Ag deposition sources at far left and general source categories at far right. For those authors who specify W filaments, wires, boats, coils, etc. the ratio becomes ~3:1.
Figure 2.11 - Null correlations; critical coverage vs. substrate type & dopant. Provisional correlations; resistivity & surface temp.
Figure 2.12 - Provisional correlation; critical coverage vs. Ag deposition source.
Figure 2.13 - Correlation; critical coverage vs. experimental method
Those specifying Ta or Mo filaments and crucibles, the ratio becomes 1:1 although the sample size makes quantitation meaningless. The correlation for C contamination from hot W deposition sources has been determined to be provisional. The second quite surprising correlation is illustrated in Figure 2.13. This complicated plot correlates critical coverage on the vertical axis against surface science experimental method on the horizontal axis. The experimental methods are arranged first, by primary incoming probe; electron, photon, ion then sub-categorized by outgoing detection channel; electron, photon or ion as delineated on the top horizontal axis. The electron probe techniques (AES, EELS, LEED, RHEED, SEM, etc.) have a 1ML:2/3ML support ratio of ~2:1 as in all other uncorrelated comparisons. Ion probe techniques drop to a 1:1 support ratio and photon techniques almost exclusively support the 1ML option. How can such a bias come about? Why would the non-particle, photon in/ photon out, techniques exclusively favor the 1ML surface models? The physical basis behind such a correlation eludes this author but is fascinating none the less.

2.4 Surface model determination for Ag-(√3x√3)R30°/Si(111)

For the Ag-√3 phase alone, there have been eighteen distinct models proposed with numerous variants within each model class. To simplify presentation and analysis, these models will be categorized as; i) Ag independent, ii) Ag embedded or iii) Ag on-top. In the first category, two models have been developed that either have Ag atoms present strictly as a catalyst without primary organization or do not require Ag atoms at all. Both produce the √3 structure via a organized Si reconstruction and both are minor mentions in the structural development of Ag/Si(111), included for completeness. In the second category, Ag embedded, the center of the Ag adsorbate is
at or below the center plane of the topmost Si atoms. Typically, large Si substrate atom movement and strains are required. In the final category, Ag on-top, adatoms decorate an in-tact or rearranged Si substrate in the more classic balls-on-a-Chinese-checkerboard fashion.

From the literature database there have been 175 declarations of a favored model. Of those, 2% favor the Ag independent, 35% favor the Ag embedded and 63% prefer the Ag on-top models. What follows is a brief synopsis of each model. The complex development, mutation and support for each model will be presented with historical and contextual references in a future, more voluminous publication.

One of the problems with the model systems discussed below is the fact that there is no ‘standard’ nomenclature system used to describe surface models. Model naming has historically been left to the imagination of the model’s creator and, especially in the Ag/Si(111) system, tremendous confusion has been purveyed when one of two things happen. First, if the model anagram (ex. HCT = Honeycomb Chained Trimer and Honeycomb Chained Triangle models) is not distinct confusion is common. Second and more commonly, when an author makes a slight structural change to an existing model and gives it a completely new moniker the historical link is often lost. In addition, a model developed for one system is often applied to another system and renamed by the author(s) for application in the new system and again, the historical link is unobvious.

2.4.1 Ag independent models,

- **D-Ag/Si V Model** (Disordered Ag adsorbate / Stabilized Silicon Vacancy): In this model the concept of $\Theta_C$ is inapplicable but disordered Ag is required. It was first proposed by Yang$^{CN087}$ in 1986, suggesting that
the $\sqrt{3}$ structure was due to a Silicon reconstruction with disordered adsorbates of Ag or Ta catalyzing the transformation.

- **SSV Model** (Stabilized Silicon Vacancy): No adsorbate is needed at all, therefore $\Theta_c = 0$ML. Introduced by Fan\textsuperscript{CN148} after observing that fast 1000°C flash cleaning and cooling can create a $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure on Si(111) without the presence of adatoms. LEED I-V measurements of this $\sqrt{3}$ silicon vacancy structure are nearly identical to I-V measurements of a 0.6ML Ag-$(\sqrt{3}\times\sqrt{3})$/Si(111)-(7x7) surface.

### 2.4.2 Ag embedded models

- **E** (Embedded – general): There are many studies that have made measurements of a general nature supporting an embedded vs. an atop model so this category has been added to the following analyses.

- **EH Model** (Embedded Honeycomb): Saitoh\textsuperscript{CN029, CN031} first proposed embedding Ag below the Si(111) surface, between the two layers that make up the surface double-layer with $\Theta_c = 2/3$ ML.

- **ET Model** (Embedded Trimer): With $\Theta_c = 1$ML, this embedded model was first proposed by van Loenen\textsuperscript{CN104}. Features include embedded Ag trimers between the surface double-layers with 1/3 of the top surface Si atoms per $\sqrt{3}$ unit cell removed forming an open Si honeycomb structure on top of the embedded Ag structure. It’s construction is similar to the Missing Top Layer model series later proposed so, for purposes of
analysis, the ET model is considered the first iteration in the MTL model series and thus denoted equivalently, MTL-1.

• **MTL Model** (Missing Top Layer): This model with $\Theta_C = 2/3$ ordered Ag + 1/3ML dilute Ag was proffered by Kono\textsuperscript{CN088} who refined calculated positions for the Ag atoms as $(0.15 \pm 0.10)\text{Å}$ below the outermost Si layer with a compression of the topmost Si 3-fold (H$_3$) triangle from 3.84Å to $(2.7 \pm 0.2)\text{Å}$. This model is the first to propose that Ag sits *above* the Si(111) double-layer but maintains an embedded Ag honeycomb orientation by sitting above 3-fold, H$_3$, double-layer sites of the bulk but below a trimer Si structure made, presumably, of Si adatoms. This is equivalent to AEH Model (Adatom Embedded Honeycomb) model nomenclature sometimes used in the literature.

• **SHCT Model** (Silver Honeycomb Chained Trimer): $\Theta_C = 1$ML. Within four months of Takahashi's HCT-1 model\textsuperscript{CN126} journal submission detailed below, Vlieg\textsuperscript{CN137} was the first to propose the SHCT model with similar plan-view features but with Si adatoms sitting in the H$_3$ sites created by Ag trimers.

• **ST Model** (Substitutional Trimer): $\Theta_C = 1$ML by Horio\textsuperscript{CN082} who was first to propose substituting Ag trimers for 1/3 missing top layer of the surface double-layer Si atoms thus forming the $\sqrt{3}$ structure.
2.4.3 Ag on top models

- **AST Model** (Atop Sylil Trimer): $\Theta_C = 1\text{ML}$ by Williams\textsuperscript{CN145} used the Ag-triangle idea\textsuperscript{CN126} to create the AST model based on a chemically intuitive Sylil Group (SiAg\textsubscript{3}) placed at atop sites on the Si(111) surface.

- **AT Model** (Atop Trimer): With $\Theta_C = 1\text{ML}$ Wehking, et.al.\textsuperscript{CN016} was the first to apply Lander and Morrison's\textsuperscript{*} Trimer model proposed for Al/Si(111) to the Ag/Si(111) system. They indicate that the Ag in the trimers has near ionic diameter (2.52Å) when bonded to Si(111)\textsuperscript{CN126} for this structure. The AT nomenclature was used before 1985 and is equivalent to this author’s HCT-0 designation.

- **CH Model** (Centered Hexagon): With $\Theta_C = 1/3\text{ML}$, Spiegel\textsuperscript{CN001} placed Ag residing at a hollow site in a centered hexagon configuration with Ag-Ag nearest-neighbor distance of 6.6Å.

- **HCT Model** (Honeycomb Chained Trimer): Prior to 1985, this model series was known as the AT or Atop Trimer Model. There was a period of indiscriminate interchanging of the words “Trimer” and “Triangle” in the HCT-type models much to everyone’s confusion. This AT or HCT model is re-branded the HCT-0 model for this dissertation. As of the writing of this dissertation, this model has emerged as the pre-eminent favorite for the final structure of Ag/Si(111) so with historical hindsight, it was possible to break out the sub-models into the HCT-x series listed below.

• **HCT-x Models** (Honeycomb Chained Triangle): With $\Theta_C = 1$ML, Takahashi\textsuperscript{CN126} was the first to propose this major variation of the Honeycomb Chained Trimer model. This model also has characteristics in common with the MTL series of models in that a final complete bulk-like Si(111) double-layer is covered with a layer of Si atoms followed by a layer of Ag atoms. It is also similar to the AT/HCT-0 model in the appearance of Ag atoms in triangular formation bonded to a Si base-layer. In the HCT-1 model, as we will designate this original Takahashi proposal\textsuperscript{CN126}, the ratio of the Ag triangle half-height to the $\sqrt{3}$ unit cell side, $x/a$ ratio, was calculated to be $(0.44 \pm 0.01)$ with the Ag atoms placed $z_{Ag} = (2.9 \pm 0.1)$Å above the in-tact surface double-layer. A Si-adatom layer is proposed between the Ag and Si double-layer at a position 1Å below the Ag layer.

• **IET Model** (Inequivalent Triangle): $\Theta_C = 1$ML. Building on the HCT-x series of models, Aizawa\textsuperscript{CN411} was the first to modify the Ag triangle configuration and break the p31m surface symmetry by counter-rotating the Ag triangles like in Over’s\textsuperscript{CN275} HCT-9R model, then also counter-rotating the next layer Si triangles in the opposite direction and making one of the two triangles in the surface unit cell larger than the other.

• **q-HC Model** (quasi-Honeycomb): $\Theta_C = 1$ ML. Kono, et.al.\textsuperscript{CN162} were the first to propose a quasi-honeycomb model in which 1/3 of the Ag atoms in the unit cell were displaced by 0.45Å into the surface and inter-Ag atomic distances $\alpha_1=4.4$, $\alpha_2=3.6$ and $\beta=3.1$ Å.
• **RCH Model** (Rumpled Centered Hexagon): $\theta_C = 2/3$ and 1 ML. LeLay\textsuperscript{CN012} proposed early in the model discovery history, that the Ag-$\sqrt{3}$ phase initially forms from a simple hexagonal (SH) network, completed at 2/3 ML, and upon further deposition, excess Ag atoms center the hexagon with Ag atom at $z = -0.3\text{Å}$.

• **SAV Model** (Silicon Adatom Vacancy): $\theta_C = 1$ ML. Copel and Tromp\textsuperscript{CN149} insisted on model structures with large Si surface displacements and $\theta_C = 1$ML coverages. This SAV model features a layer of Si adatoms nearly co-planar with an array of Ag trimers. The top half of the Si double-layer is distorted by the presence of vacancies in the bottom half of the surface double-layer and by the Ag adatoms. The equivalent of 2ML of surface Si is displaced laterally and 1ML of surface Si is displaced vertically in this model.

• **SH Model** (Simple Hexagon/Honeycomb) or **HC** (Honeycomb): $\theta_C = 2/3$ ML by Kern and LeLay\textsuperscript{CN012} from ITDS measurements.

• **SHST Model** (Silver Honeycomb Silver Trimer): $\theta_C = 1$ML. Wilson and Chiang\textsuperscript{CN108} were the first and only authors to mention the viability of a model that combined Ag trimers and inequivalent Ag atoms at the honeycomb centers of those triangular arrangements.

• **TMTL Model** (Twisted Missing Top Layer): $\theta_C = 1$ ML. Building on Kono's MTL\textsuperscript{CN088} idea of Si and Ag trimers, Ichimiya\textsuperscript{CN142} first proposed a MTL-like model with the following differences. First, Ag trimers are
uppermost at (2.95 ± 0.05)Å above the bulk-like Si(111) surface double-layer and are chained to make a honeycomb structure. Secondly, a trimerized Si layer is present at (2.2 ± 0.1)Å above the surface double-layer and is twisted by ±20° about the surface normal.

The long, non-linear development path for the various Ag-(√3x√3)R30° models is illustrated in Figure 2.14. The earliest CH model, first proposed by Spiegel in 1967, was followed by languished development through 1985. Rapid model evolution and development followed until 1999 with the HCT and IET models emerging as de-facto favorites.

![Figure 2.14 - Ag-√3 model historical development timeline.](image)

As was the case with critical coverage θC associations of Section 2.3, the question was asked, “Can any ensemble average correlations be drawn between model results and literature cited sample, preparation or experimental method?” Figure 2.15 and Figure 2.16 show the answers to those questions regarding the influence of Si(111) substrate. There is a null correlation reached when individual models as grouped into Ag independent, Ag embedded or Ag on-top categories are plotted against substrate type (p-type or n-type) and substrate dopant element. In the first plot, there is an approximately even split between Ag embedded and Ag on-top models for both p-type and n-type substrates.
Figure 2.15 - Null correlation; model vs. substrate type.
Null Correlation: Model vs Substrate Doping

Figure 2.16 - Null correlation; model vs. substrate dopant.
The second of the two plots, Figure 2.16, has small data sets with no conclusive trends favoring any model or above/below surface orientation for the individual dopants reported of boron, phosphorous or antimony.

In similar fashion, tests of dopant quantity as indicated by substrate resistivity were made as shown in Figure 2.17. High resistivities above 1 Ω-cm (low dopant levels) favored Ag embedded models where low resistivities (high dopant levels) switched to favoring Ag on-top models. The observed 15% swing in correlation from low-dopant-levels favor embedded to high-dopant-levels favor on-top is enough to classify this as a provisional correlation.

Unlike the case of a provisional correlation between critical coverage and substrate preparation (flash) temperature shown in Section 2.3, there exists no such correlation with model as seen in Figure 2.16. Surface preparation and cleaning at temperatures below 1000°C, considered by this author to provide superior strain and defect free surfaces, correlates similarly with embedded or on-top surface Ag models. Elevated temperature cleaning at temperatures above 1000°C shows a slight but statistically insignificant shift to on-top model support.

When cross comparing model against Ag-√3 phase surface preparation temperature, one would expect a correlation if the assertions made by the new surface structural phase diagram in Figure 2.3 are correct. Those literature points are plotted in Figure 2.17. If during surface preparation, maximum temperatures between 200°C and 400°C were used, 73% favored Ag on-top and 27% favored Ag embedded models. If temperatures greater than 420°C were used to prepare the surface phase, there is a 13% shift toward favoring embedded models. Again, this shift is listed as a provisional correlation.

Just as interesting is the correlation between deposition source material and model shown in Figure 2.20. Of those papers specifying support for a particular
model but not declaring deposition method, 74% favor Ag on-top models and 26% favor Ag embedded models. For those papers specifying both a model and a W-based deposition method (W wire, W filament, W basket, etc.) the same ratio exists; 73% favor Ag on-top, 23% favor Ag embedded. In other words, hot tungsten deposition sources, a known carbon crypto-contaminant source, favors Ag on-top over Ag embedded by a >3:1 ratio. It is exactly this trace C contamination’s effect on structure that is one of the foci of this dissertation. Specific data for other deposition source equipment materials; B, C, Ta and Mo are too sparse to draw any conclusions. If however, the reader looks at the experimenters who declared both a preferred model and a Knudsen effusion source, the ratio changes by over 12%. That is, ~60% favor Ag on-top models and 40% now support Ag embedded models. The ratio swings even further toward embedded models if Knudsen sources in all other categories are included.

Model correlations versus experimental method also show interesting trends. As seen in Figure 2. 19, different experimental methods favor Ag on-top to Ag-embedded models by the ratios; ~1.5:1 for photon techniques, 2:1 for electron techniques, 2.5:1 for ion techniques and a surprising ratio of >6:1 for theoretical techniques. As was the case for critical coverage correlations, the photon-in / photon-out techniques overwhelmingly favor Ag on-top models.

As has been shown, none of the correlations or provisional correlations for critical coverage or surface model have been unequivocal. Even with such a large literature database, creating two parameter correlations is difficult due to the fact that all authors in all papers do not report all experimental, technical, analytical facts needed to formulate new knowledge.
Figure 2.17 - Provisional correlation; model vs. substrate resistivity.
Figure 2.18 - Null correlation; model vs. substrate preparation temperature.
Figure 2.19 - Provisional correlation; model vs. sample preparation temperature.
Figure 2.20 - Provisional correlation; model vs. deposition source material.
Figure 2.21 - Correlation; model vs. experimental method.
2.4.4 Critical model parameters

Of the 564 papers analyzed, 104 present some type of model detail. This information can be as simple as supporting a T₄ adsorption site, for example, or as complex as a detailed mapping of adsorbate and substrate atoms down to the seventh in-tact Si(111) double layer below the surface. This information was used to build accurate models for all variations. Rather than present a confusing array of atomic coordinates for each system, the three parameters that can be directly compared with experimental results of Chapter 5; Ag-Ag bond length, Ag-Si bond length and Ag-bulk Si(111) plane spacing, are compiled in Table 2.3. As in previous figures, models are grouped into Ag independent, Ag embedded and Ag on top categories then alphabetized within those groups.

Figure 2.22 helps to visualize the data presented in the table. To the left of the figure is an ideally truncated Si(111) crystal shown five double-layers deep, d₁ through d₅. No bulk Si rearrangements, Si(B), are shown and selvage double-layers maintain perfect bulk Si(111) d-spacing. On top is a potential reconstructed Si surface layer made up of Si(S) atoms, an ordered Ag adsorbed layer and another potential but not required Si adatom layer, Si(A). The bonding style illustrates a single Ag-Ag nearest neighbor bond length and two Ag-Si near-neighbor bond lengths, Ag-Si₁ and Ag-Si₂. To the right of Figure 2.21 is an exact proposed model for the HCT-6 (sixth variation of the basic HCT structure) model. This model includes bulk Si(111) atomic rearrangements down to the fourth double layer, bulk d-spacing contractions, a surface contraction between the top in-tact double-layer, d₁ and a surface Si layer, Si(S) and an Ag surface adlayer. Note that, with respect to an extension of the bulk Si(111) atomic planes assumed here to start at double-layer d₅ and indexed by the Φₑ scale to the left of each figure, the Ag atoms seem to sit only 0.1d_{Si(111)} above bulk extended planes. This is what the XSW technique measures, positions relative to the bulk.
Table 2.3 - Summary of bond lengths and bulk registry for Ag/Si(111) models.

<table>
<thead>
<tr>
<th>Model</th>
<th>(reference)</th>
<th>Ag-Ag n-n (Å)</th>
<th>Ag-Si 1st n-n (Å)</th>
<th>Ag-Si 2nd n-n (Å)</th>
<th>Ag to 1st in-tact DL (Å)</th>
<th>Ag to bulk registry d-Si(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ag independent models</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-Ag/Si V</td>
<td>(CN087)</td>
<td>random</td>
<td>undetermined</td>
<td>undetermined</td>
<td>1.38*</td>
<td>+0.31*</td>
</tr>
<tr>
<td>SSV</td>
<td>(CN148)</td>
<td>random</td>
<td>undetermined</td>
<td>undetermined</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ag embedded models</strong></td>
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<tr>
<td>EH</td>
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<td>2.174</td>
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<td>2.876</td>
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<td></td>
<td>(CN043)</td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>MTL</td>
<td>(CN104)</td>
<td>3.8402</td>
<td>2.65</td>
<td>-</td>
<td>3.135</td>
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<tr>
<td>SHCT</td>
<td>(CN088)</td>
<td>3.3602</td>
<td>2.593</td>
<td>2.608 2.730</td>
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<td></td>
</tr>
<tr>
<td>ST</td>
<td>(CN137)</td>
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<td>2.147</td>
<td>2.540</td>
<td>0.392</td>
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<td><strong>Ag on-top models</strong></td>
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<td>AST</td>
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<td>1.9919</td>
<td>3.441 4.1775</td>
<td>3.29</td>
<td>+0.05^</td>
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<td></td>
<td>(CN126)</td>
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<td>4.084</td>
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<td>3.5432</td>
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<td>HCT</td>
<td>(CN016)</td>
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<td>2.512</td>
<td>3.304</td>
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<td>HCT-1</td>
<td>(CN126)</td>
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<td>2.68</td>
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<td>HCT-3</td>
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<td>2.63</td>
<td>3.342</td>
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<td>2.54</td>
<td>2.60</td>
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<td>3.292</td>
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<tr>
<td>HCT-8</td>
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<td>2.596</td>
<td>3.055</td>
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<td>2.41</td>
<td>?</td>
<td>3.392</td>
<td>+0.96</td>
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<td>IET</td>
<td>(CN411)</td>
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<td>2.54</td>
<td>2.60</td>
<td>3.342</td>
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<td></td>
<td></td>
<td>3.89</td>
<td></td>
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<td>q-HC</td>
<td>(CN154)</td>
<td>2.558</td>
<td>2.972</td>
<td>3.543</td>
<td>2.072 &amp; 2.372</td>
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<tr>
<td></td>
<td>(CN162)</td>
<td>3.840</td>
<td>2.972</td>
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<td>2.072</td>
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<td>1.838</td>
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<td>4.249</td>
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<td>5.38</td>
<td>2.2693</td>
<td>&gt;3</td>
<td>3.342</td>
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* Ag, H₃ site and covalent radius assumed
^ from estimates of CN191
Figure 2.22 - Left: ideal surface cross section. Right: exact HCT-6 model with bulk rearrangement, surface contraction & adlayers.
2.5 Conclusion

This chapter is the result of an applied study of the question, “Can knowledge be generated by re-examining and correlating old information in new ways?” The question is key to future scientific endeavor where easy access to a vast electronic library should allow computer aided ‘data mining’. As one who has spent an inordinate amount of time wandering the stacks of numerous libraries, searching for relevant information in standard publications as well as obscure conference proceedings, this author can not wait for the day when it is possible to direct a web-based system to search for relevant papers by keyword, read them and report back with correlations based on requested parameters.

From this author’s human driven data mining of the Ag/Si(111) literature base of almost 600 major papers, the short answer to the question is yes, new knowledge can be generated. The surface structure diagrams and provisional correlations presented in this chapter are proof. The practical answer however, is that the majority of the questions asked will be answered with the phrase, “insufficient information to complete request”. For every new nugget of knowledge mined from previous research there are scores of inconclusive, null or insufficient information dead-ends. This author fears that it will always be more cost effective to generate new information in a freshly tailored and controlled study if not already researched, rather than try to extract it from experiments not specifically designed for the question at hand.

In order for the ‘data mining’ concept to be successful, surface scientists must develop and improve upon the highly successful efforts used in the biological community; specifically the human genome project and the worldwide protein data bank, for reporting, storing and accessing surface information. This can only be accomplished if all surface scientists complete their publication cycle with a “data reporting” step, wherein extensive, exact and specific details on experimental and
theoretical technique are catalogued along with resultant structures or findings. An excellent start to this process has been made by the Surface Crystallographic Information Service* in that they require specific experimental and structural details for an entry to be accepted and catalog the information in a standard format.

As scientists in general, we seem to have forgotten that a publication is not only a communication with peers, but more importantly is also a “note in a bottle” sent forward in time to future researchers. Every error and omission profoundly affects others not yet in the field. For example, looking specifically at the way in which we acknowledge reference trails, one must acknowledge that each missed or erroneous reference, each “to be published”, each inclusion of an unrelated publication merely because it contains your name, wastes the valuable time and talent of scores of others. The practices are commonplace and yet they must cease. We must imbue ourselves with the higher ideal of communicating scientific information clearly and concisely and we must reward the same. Currently, it seems that only the number of referrals or publications with ones name is the figure of merit and it must also cease.

The success of this endeavor to mine data is shown in the new surface structural diagram of Figure 2.3 where the ensemble average plot, with all inconsistencies and ambiguities included, can be used by a scientist skilled in the art, to surmise new conclusions. The reality of this effort is shown in the correlations of Sections 2.3 and 2.4 where only inferences rather than solid conclusions are possible. Inferences may be key but a solid and specific study is still required to firmly link cause and effect.

2.6 References – Chapter Two: a chronological record of Ag/Si(111) publications

[CNxxx] denotes this author’s ‘Chronological Numbering’ index system

1967

1969

1971

1972

1975


1976


1977


1978


1979


1980


1981


1982


1983


1984


1985


1986


1987


1988


1989


1990


1991


1992


1993


1994


1995


1996


[CN342] A. Natori, M. Murayama, H. Yasunaga, "Atomic Structures of Ag on √3x√3 Ag/Si(111) and on 7x7 Si(111)," Surf. Sci. 357, 47-50 (1996).


1997


[CN364] K. Kempa, D.A. Broido, H.H. Weitering, "Correlational switching between 3 x 1 and 6 x 1 surface reconstructions on Si(111) with submonolayer Ag adsorption," Physica B 230, 800-802 (1997).


1998


[CN383] B. Cvikl, D. Korosak, Zs.J. Horváth, "Comparative study of I-V characteristics of the ICB deposited Ag/n-Si(111) and Ag/p-Si(100) Schottky junctions," Vacuum 50, 385-393 (1998).


1999


2000


2001


2002


[CN461.2] N. Kishi, K. Morita, "Differential scattering cross-sections, inelastic energy losses and ion fractions in backscattering of keV He+ ions from monolayer


2003


2004


2005


**Addendum 1: Ag/Si(111) research expenditure estimate**

1) \((3.74 \text{ Authors / paper}) \times (573 \text{ papers}) / (4 \text{ papers/year}) = 535.755 \text{ FTE – years total}\)

2) Average of 80% Academic and 20% Commercial/Gov’t. Salaries ($84,000/yr) + 30% overhead costs – Academic + 0% overhead commercial/govt. = ($24,000/yr) + $500,000 facility equipment (amortized 15 years) = (~$33,000/yr) = ($142,000)

Ag/Si(111) Research Expenditure Estimate = $142,000 \times 535.755 = $76.1M

---

**Median salary and age for major employment sectors, PhDs 2002. (a)**

<table>
<thead>
<tr>
<th>Median</th>
<th>Salary</th>
<th>Age</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Academic Sector</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>University 9-10 Month Salary</td>
<td>$72,000</td>
<td>48</td>
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<tr>
<td>University 11-12 Month Salary</td>
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<tr>
<td>4 Year College 9-10 Month Salary</td>
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<tr>
<td><strong>Non-Academic Sector</strong></td>
<td></td>
<td></td>
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<tr>
<td>Hospital, medical services</td>
<td>$108,000</td>
<td>49</td>
</tr>
<tr>
<td>FFR&amp;DC (b)</td>
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<td>48</td>
</tr>
<tr>
<td>Industry, self-employed</td>
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<tr>
<td>Government</td>
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<tr>
<td>Nonprofit</td>
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</tr>
<tr>
<td>UARI (b)</td>
<td>$82,000</td>
<td>45</td>
</tr>
</tbody>
</table>


(a) Employed U.S. resident members only. Post-doctorates not included.

(b) FFR&DC = Federally-Funded Research and Development Center

UARI = University-Affiliated Research Institute or Observatory.
CHAPTER THREE:
THEORETICAL BACKGROUND

3.1 X-Ray Standing Waves (XSW)

As in all wave phenomena, if two coherently related waves cross, a standing wave or "beat pattern" results. As applied to electromagnetic waves and X-rays in particular, the process of Bragg diffraction or of total external reflection, among others, can produce two (or more) such coherently related wave-fronts of similar intensities. In the region of overlap between the incoming, $k_o$, and the outgoing, $k_R$, coherently related X-ray plane waves the interference field generated is an X-ray Standing Wave (XSW) as illustrated in Figure 3.1.

![Figure 3.1 - X-ray Standing Wave (XSW) formation by coherent interference between incident and outgoing X-ray plane waves.](image)

The underlying physics of X-ray standing waves are framed upon theoretical foundations of dynamical diffraction established by von Laue $^{31,32,33,34}$ and Batterman and Cole $^{35}$. These principles were first applied to Laue-case anomalous transmission
in perfect crystals by Borrmann\textsuperscript{36} and to symmetric Bragg-case diffraction by Batterman\textsuperscript{37, 38, 39}. Since then, the technique has been thoroughly reviewed and improved\textsuperscript{40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53}, applied both toward finding atomic and impurity positions both within bulk highly-crystalline materials and also to a large number of adsorbate/substrate system combinations as outlined in Table 3.1. The reader is referred to papers by Bedzyk\textsuperscript{53} or Andersen, Golovchenko and Mair\textsuperscript{54} for a good general overview of the technique and by Koval’chuk and Kohn\textsuperscript{51}, Authier\textsuperscript{52} or Bedzyk\textsuperscript{55} for detailed discussions of the theory involved.

An X-ray Standing Wave (XSW) experiment is a coincidence measurement of the incoming and outgoing wave-vector intensities from some highly crystalline material along with some external signal unique to the surface or near-surface atomic species of interest while varying the probe X-ray’s angle of incidence. The external signal can be any channel proportional to the electromagnetic (X-ray) field strength at the center of the atom, in the dipole approximation. Auger, photoelectron or fluorescence yields are most commonly chosen as this external signal although use of other channels such as Compton or thermal diffuse scattering yield can be envisioned. The discussion that follows will specifically address Bragg diffraction as the source of outgoing wave-vector generation and atomic fluorescence as the external signal resulting from the change in $\vec{E}$ field intensity at the adatom position. The basic ideas behind the experiment for, as an example, total external reflection as the standing wave field generator and photoelectrons as the external signal channel remain, although the formalisms of the analytical equations change appropriately.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Adsorbate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(111)</td>
<td>O\textsuperscript{56}</td>
</tr>
<tr>
<td>CdMnTe(111)</td>
<td>bulk\textsuperscript{37}</td>
</tr>
<tr>
<td>Cu(111)</td>
<td>Cl\textsuperscript{38,39}, Cu\textsuperscript{60}, Tl\textsuperscript{61}</td>
</tr>
<tr>
<td>GaAs(111)</td>
<td>bulk\textsuperscript{55,62,63,64,65], CaSrF\textsuperscript{66}, S\textsuperscript{67}, Sb\textsuperscript{68}}</td>
</tr>
<tr>
<td>Ge(111)</td>
<td>bulk\textsuperscript{55,69,70,71}, Au\textsuperscript{71,72}, Br\textsuperscript{73,74,75}, I\textsuperscript{76}}</td>
</tr>
<tr>
<td>Ge(220)</td>
<td>bulk\textsuperscript{58,77,78,79}</td>
</tr>
<tr>
<td>InP</td>
<td>bulk\textsuperscript{50}</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>Cl\textsuperscript{81}</td>
</tr>
<tr>
<td>Si(100)</td>
<td>As\textsuperscript{82}, Ga\textsuperscript{83}, Ge\textsuperscript{84}</td>
</tr>
<tr>
<td>Si(220)</td>
<td>bulk\textsuperscript{39,54], As\textsuperscript{85}, Bi\textsuperscript{86}, Br\textsuperscript{87}, Se\textsuperscript{88}}</td>
</tr>
<tr>
<td>Si(111)</td>
<td>bulk\textsuperscript{71,89,90], Ag\textsuperscript{91,92}, Au\textsuperscript{71,93,94,95,96}, Br\textsuperscript{97,98,99,100,101,102,103,104}, Cs\textsuperscript{105}, Ga\textsuperscript{106,107}, GaAs\textsuperscript{108}, Ge\textsuperscript{109,110,111,112}, In\textsuperscript{113}, LiBr\textsuperscript{114}, NiSi\textsubscript{2}\textsuperscript{115,116,117,118,119,120}, Pb\textsuperscript{121}, RbBr\textsuperscript{122}, Se\textsuperscript{88}, Si\textsuperscript{120,123}, SiO\textsubscript{2}\textsuperscript{124}}</td>
</tr>
<tr>
<td>Si(211)</td>
<td>Br\textsuperscript{125}</td>
</tr>
<tr>
<td>Pt/C LSM (layered synthetic multilayer)</td>
<td>Cu\textsuperscript{126}, I\textsuperscript{126}, Hf\textsuperscript{127}}</td>
</tr>
<tr>
<td>Au/Cr/Glass</td>
<td>Langmuir-Blodgett Films\textsuperscript{128,129}</td>
</tr>
</tbody>
</table>
For the series of experiments described here, Ag atoms are adsorbed at an unknown position above or within the surface selvage of a Si(111) substrate as illustrated in Figure 3.2A. Introducing truly monoenergetic X-rays with energy $E$ at an angle $\theta_1$ sufficiently below the Bragg angle, $\theta_B$, (ignoring for the present refractive index effects) resulting in the fluorescence from the Ag atoms with normalized intensity proportional to the number of Ag atoms in the beam and attenuated transmission of the X-ray beam as shown in Figure 3.2B. As the angle of incidence is increased to slightly greater than one half Darwin width, $\frac{1}{2} \delta\theta_D$, from the Bragg angle, $\theta_2$, dynamical diffraction effects start as shown in Figure 3.2C. As the angle increases to $\theta_3 = (\theta_B - \frac{1}{2} \delta\theta_D)$, the generation of a strongly diffracted X-ray is complete and a standing X-ray field has been generated. The periodicity of the standing wave, $D$, is equal to the periodicity of the underlying crystal diffraction planes generating the diffraction; $d_{Si(111)}$ in this case. The standing wave pattern not only pervades the bulk of the diffracting crystal but also extends to hundreds of nanometers above the crystal surface as illustrated in Figure 3.2D. This is known as the "low angle" side of the diffraction curve and is characterized by a standing wave pattern with nodes in the $\vec{E}$ field located at the positions of the diffraction planes and anti-nodes directly between. As we continue to increase the diffraction angle, the standing wave shifts inward by $\frac{1}{2} D$ continuously as the relative phase between $k_o$ and $k_R$ changes between $0$ and $\pi$ until we reach $\theta_4 = (\theta_B + \frac{1}{2} \delta\theta_D)$ shown in Figure 3.2E. This is known as the "high angle" side of the diffraction curve. Continued increase in $\theta$ to $\theta_5$ results in loss of diffraction and fluorescence/transmission conditions equivalent to $\theta_1$ as shown in Figure 3.2F.
Figure 3.2 - A) Prototype Ag/Si(111) surface. B) Incident X-Ray plane-wave not yet in the Bragg diffraction condition. Incident wavevector, $k_0$, and transmitted wavevector, $k_t$. Ag AES (Auger Electron), Pe- (photoelectron production) and Flu. (fluorescence) proportional to Ag atom density. C) Just entering diffraction condition. AES, Pe- and Flu. decreasing due to destructive interference.
Figure 3.2 - D) Dynamical diffraction fully formed. An X-ray Standing Wave field has been generated, “low angle” side, with periodicity D, equal to $d_{\text{Si(111)}}$ and nodes (no $\vec{E}$ field intensity) at the positions of the diffracting planes thus no Ag fluorescence. E) XSW field at the “high angle” side of the diffraction. The field has moved inward by $\frac{1}{2}d_{\text{Si(111)}}$ due to the $\pi$ phase shift between $k_o$ and $k_R$. Fluorescence = 4X the off Bragg. F) Out of diffraction, high angle side.
The atomic position of the Ag adsorbate atoms is deduced by coincidentally matching the fluorescence signal with the phase of the standing wave induced by the (111) Fourier component of the diffracting Si crystal's charge density. As in the example of Figure 3.2, Ag atoms at the position indicated exhibit no fluorescence on the low angle side of the rocking curve, 4X fluorescence at the high angle side as normalized to unity fluorescence off-Bragg.

Conversely, if Ag atoms were located at a position of $1/2 \, d_{\text{Si(111)}}$ (i.e. between the Si double layers or above the surface at a spacing of $1/2 \, D$) there would be a maximum in the fluorescence at the low angle side of the diffraction and no fluorescence at the high angle side.

A continuum of solutions exists between these two extremes as illustrated in Figure 3.3.

![Figure 3.3](image-url)

Figure 3.3 - Calculated fluorescence curves for a perfectly coherent assemblage of atoms at different coherent positions, Fe excited by an XSW field.
The strength of X-ray photoabsorption and the intensity of the subsequent shake-down process depends on the local $E$ amplitude. The shape of the Ag K$_\alpha$ or L$_{\alpha\beta}$ fluorescence yield, $Y(\theta)$, used in this study, can be modeled in general form by:

$$Y(\theta) = 1 + R(\theta) + 2P\sqrt{R(\theta)} F_c \cos[\nu(\theta) - 2\pi \Phi_c] e^{i\nu z}$$  \hspace{1cm} (1)

where:

- $R(\theta) = \text{Reflectivity (}I_R/I_0\text{)}$  
- $P = \text{Polarization constant: i.e. 1 for } \sigma \text{ polarization; } \cos 2\theta \text{ for } \pi \text{ polarization}$ 
- $F_c = \text{Coherent fraction}$  
- $\Phi_c = \text{Coherent position}$  
- $\nu = \text{relative phase between incoming and diffracted waves}$  
  $= \tan^{-1}[\text{Im}(E_R/E_0)/\text{Re}(E_R/E_0)]$  
- $z = \text{average photoelectron depth}$  
- $\mu(\theta) = \text{effective linear absorption coefficient}$  
  $= [1 + P \sqrt{R(FH' \sin \nu + FH'' \cos \nu)/F_0'']} (\mu_0/\sin \theta_B)$

The phase factor, $\nu$ and the reflectivity, $R$, are computed from the measured reflectivity as a function of reflection angle, $\theta$. The only two free parameters of coherent fraction $F_c$ and coherent position, $\Phi_c$ are determined* by a Fumili least-squares fitting techniques. The $F_c$ and $\Phi_c$ are simply the amplitude and phase fitting parameters and are related to atomic positions in the unit surface cell by:

$$F_c e^{2\pi i \Phi_c} = \frac{I}{N} \sum_j e^{2\pi i (H \cdot r_j)}$$  \hspace{1cm} (2)

with $H$ a reciprocal lattice vector, $N$ the number of atoms in the unit cell and $r_j$ the position of the $j$-th atom in that unit cell.

Since the Si(111) "planes" lie at the midpoint of the Si(111) bilayer, the coherent fraction, $F_c$, is equal to $\cos(\pi b/a_{111})$ where $b$ is the Si(111) bilayer spacing of 0.784 Å and $a_{111}$ is the Si(111) lattice constant of 3.1354 Å.

If one would have a mono-planar array of atoms probed with a standing wave field, $F_c$ should be unity and deviations could be attributed to thermal vibration effects as:

$$F_c = F e^{-M}$$

where:

$$M = 8\pi^2 \langle u^2 \rangle \frac{\sin^2 \theta}{\lambda^2}$$

$\langle u^2 \rangle$ = mean square atomic displacement

For a gaussian distribution of atomic displacements and realizing that the XSW measurement only probes one Fourier component of that displacement volume, we can model:

$$F_c = e^{-2\pi^2 \langle u^2 \rangle / \Delta^2} = e^{-2\pi^2 \Delta d^2 / d^2}$$

and thus determine experimentally thermal vibration displacement components.

It is important to clarify the strengths and weaknesses of the XSW technique. The strongest feature of the technique is that the standing wave is self-phasing. The relative phases for the two beam case outlined above are well understood and provide an interferometric reference. Also, by using characteristic fluorescence lines in this case, the XSW technique provides an element specific structural characterization. The fits to amplitude and phase, lock the atomic density along the Fourier component studied.

On the other hand, there is an inherent ambiguity in the positional determinations since $F_c$ is by definition determined per modulo-$d_{Si(111)}$. Stated another way, atomic positions can only be determined with respect to an extension of the bulk reference planes, independent of actual surface position and only in the direction of
the diffraction vector $\mathbf{H}$. Also, the determined positions must be understood to be the median, ensemble average plane of the target species with the implicit assumption that, atoms located off of that median plane are arranged randomly.

These points are most easily illustrated by means of the examples shown in Figure 3.4. Figures A-E represent Ag atoms positioned on extensions of the bulk Si(111) atomic planes that would produce coherent positions, $\Phi_c = 1$ and coherent fractions, $F_c = 1$ even though distributed at a position $d_{\text{Si}(111)}$ above the bulk terminated surface (A), in a $T_4$ hollow site of the bulk terminated surface (B), on an atop position of a contracted surface (C), distributed at some modulo-$d_{\text{Si}(111)}$ positions including positions interior to the bulk of the crystal (D) or across a Si(111) double-layer step (E). In like manner, continuing in Figure 3.5, we explore variations in $F_c$. Ag atoms distributed at $\Phi_c = 0.5$ and $F_c = 1$ are shown in (A), reducing 30% of the atoms to random positions gives $\Phi_c = 0.5$ and $F_c = 0.7$ (B). The same position and yield can be managed by symmetrically distributing the electron density, split by $\pm 1/8 \ d_{\text{Si}(111)}$ on either side of the $\Phi_c = 0.5$ median position (C). Following the logical progression from panels (A) and (B) a $F_c = 0$ is achieved by randomly distributing the Ag atoms with respect to the diffraction planes. $\Phi_c$ is meaningless in this case. Unfortunately, following the progression of panels (A) and (C), we can likewise achieve an $F_c = 0$ by positioning equivalent numbers of atoms exactly $\pm 1/4 \ d_{\text{Si}(111)}$ on either side of the $\Phi_c = 0.5$ position. As the standing wave field passes through the adsorbate, the amplitude and phases of the fluorescence signal is $\pi/2$ out of phase with itself and creates a signal identical with that of panel (D).

XSW measurement gives position on a plane. A double XSW measurement or any number of measurements using diffraction planes of the same zone localize the atoms to a line. Only a triangulation, with three standing wave measurements, not all in the same crystallographic zone can reduce positional uncertainty to a point location.
Figure 3.4 A-E (see text): Examples of atomic arrangements of Ag (filled circles) on Si(111) (open circles) that would give the same coherent position, $\Phi_c = 1$, and coherent fraction, $F_c = 1$, from a Si(111) X-ray Standing Wave experiment series.
Figure 3.5 A-E (see text): Examples of the effect of atomic arrangements of Ag (filled circles) on Si(111) (open circles) that alter the coherent fraction parameter, $F_c$. 

$\phi_c = 0.5 \quad F_c = 1$

$\phi_c = 0.5 \quad F_c = 0$

$\phi_c = N/A \quad F_c = 0$

$\phi_c = N/A \quad F_c = 0$

$\phi_c = N/A \quad F_c = 0$
Even then, the position is known with reference to the bulk atomic planes with no information on the surface reconstruction. It is the intent of this work to utilize the strengths of the XSW techniques without succumbing to its limitations by pairing it with other complementary techniques for atom location.

### 3.2 Surface Extended X-Ray Absorption Fine Structure (SEXAFS)

#### 3.2.1 Introduction

Extended X-Ray Absorption Fine Structure (EXAFS) and the sub-specialty of Surface EXAFS (SEXAFS) have been well described in the literature since Kronig's\textsuperscript{130} initial explanation of the phenomena in 1931-1932. The reader is referred to the following works for development of the subject. For introductory material, Ertl and Küppers\textsuperscript{131}, Feldman and Mayer\textsuperscript{132}, Zangwill\textsuperscript{133}, and Stöhr\textsuperscript{134} are well written and easily understandable. For an intermediate level primer, the three part series by Stern\textsuperscript{135,136} or Stern, Lytle and Sayers\textsuperscript{137} is recommended. Detailed discussions are found in Lee, Citrin, Eisenberger and Kincaid's landmark review\textsuperscript{138} and in the monograph by Koningsberger and Prins\textsuperscript{139}. Only an overview, based on the aforementioned references, is presented here.

#### 3.2.2 Basic EXAFS physics

To understand EXAFS, a review of the quantum principles involved in x-ray absorption is necessary. X-rays are absorbed in matter by two main processes, photo emission and Compton scattering. For incident photon energies in the tens of keV and low to moderate Z elements, the Compton process is small and can be neglected. It follows that the probability for absorption of an X-ray photon, $\mu$ equals, invoking Fermi's "Golden Rule":

\[ \mu = \text{Fermi's "Golden Rule"}. \]
\[ \tilde{\mu} = \frac{4\pi^2 N_o e^2 \omega}{c} \left\langle \left| \bar{\Psi}_f \cdot \bar{\widetilde{e}} \right| \right\rangle^2 \rho(E_f) \]

where:

- \( N_o \) = number of atoms/unit volume
- \( \omega \) = photon frequency

\[ |\bar{k}| = \sqrt{\frac{2mE_f}{\hbar^2}} \]

\[ E_f = (E_x - E_{\text{bind}}) \]

\( \rho(E_f) \) = density of state at the final state energy \( E_f \) per unit energy

\( \bar{\widetilde{e}} \) = polarization vector

\[ \bar{\mu} \propto \left\langle \left| \bar{\Psi}_f \cdot \bar{\widetilde{e}} \right| \right\rangle^2 \]

\[ \bar{\mu} \propto \left| \left\langle \bar{\Psi}_{\text{out}} \cdot \bar{\widetilde{e}} \right| \Psi_i \right\rangle^2 + \left| \left\langle \bar{\Psi}_{\text{return}} \cdot \bar{\widetilde{e}} \right| \Psi_i \right\rangle^2 \]

\( \Psi_i \) = initial state wave function

\( \Psi_{\text{out}} \) = direct outwardly propagating photoelectron

This superposition and “interference” of outgoing and backscattered wavefunctions is often illustrated as shown in Figure 3.6.

![Figure 3.6](image-url)

Figure 3.6 - Schematic illustration of an outgoing electron wavefunction, \( \psi_1 \), interfering with coherent wavefunction \( \psi_f \) backscattered from four near neighbors.
\[ \Psi_{\text{back}} = \Psi_{\text{out}} e^{i\delta_i} \cdot \frac{e^{ikR}}{R} \cdot \left| f(k, \pi) \right| e^{i\delta_f} \cdot e^{ikR} \]

where:
- \( e^{i\delta_i} \) = the phase shift associated electron wavefunction departing the potential well of the originating atom
- \( \frac{e^{ikR}}{R} \) = the phase shift due to travel of distance \( R \) between originating and backscattering atoms
- \( \left| f(k, \pi) \right| e^{ikR} \) = backscattering function
- \( e^{i\delta_f} \) = phase shift at backscatter potential well
- \( e^{i\delta_i} \) = phase shift due to backscattered electron re-influenced by return to the originating atom scattering potential.

by combining terms in the exponentials we simplify as:

\[ = \Psi_{\text{out}} \cdot \frac{e^{i(2kR+2\delta_i+\delta_f)}}{kR^2} \cdot \left| f(k, \pi) \right| \]

\[ = \Psi_{\text{out}} \cdot \frac{e^{i(2kR+\Psi_j(k))}}{kR^2} \cdot \left| f(k, \pi) \right| \]  \( (9) \)

and define:
- \( \Psi_j(k) \equiv \) the total phase shift

The absorption can thus be decomposed into terms related to phase shifts associated with the originating and scattering atoms as well as scattering amplitude factors. Since, for practical purposes, one is not usually interested in calculation of the absolute absorption properties of an atomic species, but rather in the information on nearest neighbor distance and coordination in atomic systems, it is common to deconvolute the “free atom” portion of the absorption process from the “near neighbors interference” portion by defining:
\[ \mu = \mu_0(E)[1 - \chi(E)] \]

where:
\[ \chi(E) = \frac{\Delta \mu}{\mu_0} \equiv \text{the EXAFS function} \]

All that remains is to formalize the discussion above into quantifiable and calculable form, sum contributions from all atoms at distance \( \vec{R}_j \) and determine an analysis strategy.

### 3.2.3 Assumptions and corrections to the basic EXAFS physics

There are inherent and implicit assumptions in such a treatment. First, it is assumed that the initial state wavefunction, \( \Psi_i \), dimensionality is << than the distance between absorber and scatterer, \( \vec{R} \) in order to invoke plane wave scattering factors, \(|f(k, \theta)|\) (i.e. \( r << R \) or \( kR_j << 1 \)). State of the art analysis techniques are currently advanced to the point of using “curved wave” analysis formalisms. Secondly, for EXAFS analysis used in this analysis, it is assumed that the outgoing photoelectron has kinetic energy > 50 eV. This allows the backscattering factor, \(|f(k, \theta)|\) to be dominated by terms arising from core potential scattering. This simplifies calculation of the backscattering amplitude indicated as \(|f(k, \pi)|\) above. Third, it is assumed that the central atom excited state lifetime (~ 10^{-15} sec) is greater than the propagation time for the forward and backscattered wavefronts making the waves self coherent. Finally, partial wave scattering theory is invoked to allow symmetry arguments between the outgoing wave scattering and phase shift and the returning wave scattering and phase shifts \( e^{i\delta} \) in the muffin-tin atomic potential region.

Three other correction factors, typical of X-ray, electron and particle techniques are added. First, to compensate for static thermal disorder (in the harmonic approximation) a Debye-Waller-like factor is provided. The outgoing photoelectrons are modified by an inelastic scattering factor to introduce an electron mean free path.
coherence correction. Finally, understanding that our photon excitation source comes
from the bending magnet of a synchrotron, we understand that the X-rays are highly
polarized. This polarization causes directed photoemission that goes as \( \cos^2 \) of the
angle between the polarization vector of the exciting X-ray photon and the directed
distance \( \vec{r}_j \) to the scattering atom.

Inserting all factors outlined above brings us to the “EXAFS Function”,
equation 11 (next page).

3.2.4 SEXAFS Analysis Procedures

The SEXAFS signal must be extracted from the raw x-ray fluorescence
absorption spectrum, Figure 3.7a, through a series of steps, as detailed below. The raw
signal is adjusted by first subtracting out the pre-edge background slope by fitting a
Victoreen function of the form \( A\lambda^2 + B\lambda^4 \) then defining the absorption edge, the first
derivative inflection point at the edge jump, as the zero point of the energy scale
(Figure 3.7b). Experimental fluorescence spectra were normalized to incident number
of photons during data collection. During analysis they were re-normalized such that a
point 52 eV above the edge at the position of the spline background fit was set to a
relative intensity of 1 per suggestions of Sayers and Bunker\textsuperscript{140}. 
The EXAFS Function:

\[
\chi(\tilde{k}) = -3 \sum_i \sum^{}_{shellj} \cos^2 \alpha_{ij} \frac{N_j}{k^2 r_j^2} \left| f_j(\tilde{k}, \pi) \right| \sin \left[ 2kr_j + \psi_j(\tilde{k}) \right] e^{2\sigma_j^2 k^2} \frac{-2\sigma_j^2}{\lambda_j \rho_j} \tag{11}
\]

WHERE:

\[
\chi(\tilde{k}) = \frac{\Delta \mu}{\mu_0} = \text{the EXAFS modulation}
\]

\[
\Delta \mu = \text{differential absorption}
\]

\[
\mu_0 = \text{free atom absorption}
\]

\[
\sum_i = \text{a sum over atoms of equal } Z \text{ at the same } R_i \text{ from the adsorbing atom}
\]

\[
\alpha_{ij} = \angle \text{between x-ray polarization vector and the interatomic distance, } r_{ij}
\]

\[
\sum^{}_{shellj} = \text{a sum over coordination shells}
\]

\[
N_j = \text{Number of scattered distance } \tilde{r}_j
\]

\[
\tilde{k} = \left[ \frac{2m(\hbar \omega - E_0)}{\hbar^2} \right]^2
\]

\[
f_j = \text{electron back-scattering amplitude} \quad (\theta = \pi) \text{ at } j^{th} \text{ atom}
\]

\[
\sin \left[ 2kr_j + \psi_j(\tilde{k}) \right] = \text{electron wave function interference term}
\]

\[
\psi_j(\tilde{k}) = \text{phaseshift} = \phi_j(\tilde{k}) + 2 \delta_r(\tilde{k})
\]

\[
\phi_j(\tilde{k}) = \text{backscattering phaseshift from } j^{th} \text{ atom}
\]

\[
\delta_r(\tilde{k}) = \text{phaseshift at central atom (primed denotes photo-excited central atom)}
\]

\[
e^{-2\sigma_j^2 k^2} = \text{Debye-Waller-like factor (harmonic approximation)}
\]

\[
\sigma_j = \text{mean rms thermal fluxuation or static disorder}
\]

\[
e^{-2\sigma_j^2 k^2} e^{-2\sigma_j^2 / \lambda_j \rho_j} = \text{inelastic scattering factor}
\]

\[
\lambda_j = \text{electron mean free path}
\]
Next, the oscillatory part of the spectrum due to photoelectrons with energies greater than 50 eV is stripped from the data set. The data is transformed into wavenumber, \( k \) space as \( k = \sqrt{2m(E-E_{\text{bind}})/\hbar^2} \). The non-oscillatory background component of the spectrum due to an equivalent “free atom” absorption effect is removed by fitting a five-knot cubic spline function as shown in Figure 3.7c. The resulting \( \chi(k) \) function, Figure 3.7d is \( k^n \) weighted (where \( n=3 \) for periods 1,2,3,4, \( n=2 \) for period 5 and \( n=1 \) for periods 6+) to compensate for \( k \) dependences in the scattering potentials as a function of Z. Normally, upon transformation from energy to \( k \) space, elements such as Ag, from the fourth period are commonly \( k^2 \) weighted to symmetrize the peaks in the Fourier transform by selective weighting the higher \( k \) contributions. Aebi, et.al.\(^{141}\) has argued that \( k^2 \) weighting contributes unnecessarily to a loss of low-\( k \) information detrimental to low-Z backscatters like Si whose backscattering amplitude peaks at near 1 Å\(^{-1}\) and suggests \( k^1 \) weighting. Following this advice, all experimental \( \chi(k) \) data is \( k^1 \) weighted, at variance with pre-1995 common practice, Figure 3.7e.

The resulting \( k \cdot \chi(k) \) function is Fourier transformed producing a first approximation to the radial distribution function as shown in Figure 3.7f. In this example an Ag nearest-neighbor distance of 2.575 Å is found, within 11% of the textbook value of 2.889 Å. To further refine this radial distribution function, phase shifts must be adjusted, normally by comparison with reference standards containing the same absorber-nearest neighbor atom pairs but with known bond lengths. As shown in Figure 3.7f, the first approximation radial distribution function is fit with an Hanning window to select individual atom pair contributions to the spectrum.

This filtered spectrum is then back-Fourier transformed, shown in Figure 3.7g with the additional advantage that the multivariate problem of Equation 11 is now reduced to roughly seven degrees of freedom. The resulting back transformed
wavefunction, has an amplitude envelope, \( A(\vec{k}) \) containing information on the number of nearest neighbors, and an oscillatory component, \( \sin \varphi(\vec{k}) \), containing the information on the scattering pairs and inter-atomic distances.

The \( \sin \varphi(\vec{k}) \) component, which from Equation 11 is composed of two terms, 
\[
\sin \left[ 2 kr_j + \psi_j(\vec{k}) \right],
\]
is fit with appropriate amplitude and phase parameters. Using the interatomic distances of the known standard and assuming that chemical transferability is not dependant on binding energies, the unknown backscattering phase shift parameter, \( \psi_j(\vec{k}) \) is determined to be back transferred to the unknown spectrum as shown in Figure 3.7h.

The resulting filtered and phase adjusted spectra is again Fourier transformed. The real and imaginary forward transformed components are combined, Figure 3.7i, creating a \(|\text{FT}|\) magnitude envelope with the closest determination of the actual radial distribution function for that pair’s atomic distance and nearest neighbor information.

In the case of our example using an ideal Ag standard material and excellent experimental counting statistics, we find an Ag-Ag bond length of \( 2.878 \pm 0.010 \text{ Å} \); a result within 1\% of handbook values of 2.889 Å.
Figure 3.7a - Raw absorption data, 25 micron Ag foil

Figure 3.7b - Absorption spectrum, background removed, normalized to electron kinetic energy zero-point, $E_0$ at edge jump inflection.
Figure 3.7c - Spline fit to remove "free atom" contribution to the XFS oscillations

Figure 3.7d - The "Chi Function", $\chi(k)$
Figure 3.7e - k weighted wavefunction

Figure 3.7f - Fourier transformed "1st approximation" radial distribution function with Hanning isolation window function.
Figure 3.7g – Back-transformation of the filtered radial distribution function showing amplitude envelope and oscillatory components.

Figure 3.7h - Phase matching to known reference standard.
Figure 3.7i - Back-transformation of filtered and phase adjusted wavefunction showing real (solid) and imaginary (dashed) components of the Fourier transformation.

Figure 3.7j - Final single-pair radial distribution function solved, $d_{N-N} = 2.878 \, \AA$. 
3.3 Quantitative Auger Electron Spectroscopy (AES)

In most surface studies, it is desirable to find the quantity of a surface element or surface contamination using Auger Electron Spectroscopy (AES). In the case of Ag/Si(111), critical differences between 2/3 and 1 ML coverages influences model choices. Of equal importance is the determination of surface cleanliness levels. As we shall discuss later, carbon contamination plays a crucial role in surface structure formation so accurate quantitation is imperative. Many studies cite the misinformed notion that they obtained a clear Si(111)-(7x7) pattern with LEED therefore the surface must be clean. Numerous observations during this series of experiments have shown that clear Si-(7x7) LEED patterns can be obtained with 30% C contamination levels where C contamination levels of under 3% drastically influence surface structure and suppress Ag-(3x1) formation.

Quantification of raw deposition amounts often rely on reference to an external quartz crystal oscillator thickness monitor\textsuperscript{142}. In-situ surface adsorbate measurements require AES quantitation. It is most common to find reference in the literature to coverages determined by the method of standards, by the method of Elemental Sensitivity Factors\textsuperscript{143,144} or by a thin layer simplification of for the Ag/Si p-p ratio\textsuperscript{145}. Even using the most complete first principles calculations for this study, AES coverage determinations for submonolayer deposits were estimated high by up to a factor of 10x compared with rigorous RBS measurements.

In the vast majority of studies including this one, AES spectra are measured as differential, dN(E)/dE vs. Auger electron energy as shown in Figure 3.8. The peak-to-peak height for the characteristic substrate and overlayer elements are used to calculate relative abundances.
Figure 3.8 - CMA measured Auger electron spectra for Si, Ag and C. (After Davis\textsuperscript{144}) Ag MNN peaks identified by Housley, Heckingbottom and Todd\textsuperscript{146} and Si LVV peaks in LeLay notation where $V_2$ represents a lower 3s-like final state and $V_4$ indicates an 3p-like final state.
3.3.1 Quartz oscillator crystal measurements

Direct measurement of Ag deposition rate is most easily accomplished by allowing an AT-cut quartz crystal slice to intercept the incoming Ag stream at the position of the substrate. The increase in mass of this crystal, vibrating in the MHz frequency range, as Ag adsorbs causes an easily measurable shift of its resonance frequency. From this frequency shift, the mass increase and therefore deposit thickness can be calculated in a straightforward manner. An excellent primer on the quartz crystal technique can be found in Ashworth and Shacklette\textsuperscript{142} and frequency shift to mass calculations can be found in Ridgway and Haneman\textsuperscript{147}. Pre-packaged commercial units can be purchased that calculate deposition amounts and rates in real-time. One must remember that unless the quartz monitor head is in the same position as the sample, there is a $1/r^2$ distance effect that many do not take into account.

3.3.2 AES standards and sensitivity factor methods

To zeroth-order, if one measures the AES p-p (peak-to-peak) height of a pure standard then a dilute surface deposit of the same element with the same instrument under the same experimental conditions, the concentration of the dilute element is directly proportional to the ratio of the AES p-p height of the standard. To avoid the experimental complications of mounting and preparing numerous pure standards, using one standard with a high sensitivity factor to scale your experimental conditions has become common. That standard element happens to be silver and the relative sensitivity for Auger emission of all elements against that standard under various excitation conditions is well known. Experimental determination of a dilute concentration of any element measured relative to a Ag standard can be simply calculated using scaling factors for that element vs. silver although accuracy is necessarily sacrificed over the method of pure standards.
If a standard is not included in AES measurements, good estimates of relative concentration can be made by measuring the major and minor component AES response, adsorbate and substrate in our case, and scaling their p-p heights using the same sensitivity factors. (See Davis\textsuperscript{144}) Again, accuracy suffers over the Ag standard method.

In all cases, these experimental (quartz oscillator) and computational (standards and sensitivity factor) methods work well for high concentrations and thick adsorbate layers. It will be shown in the experimental section of Chapter 5 that each of the techniques becomes less and less reliable when applied to vanishingly small quantities, tenths of monolayers, on surfaces as studied in this dissertation. Even thin film approximations\textsuperscript{145} and first principles calculations have difficulties with these extremely dilute systems.

### 3.3.3 AES first principles calculations

The experimentally detected surface Auger signal, $I_{\alphaXYZ}$ arising from some distribution of $N$ atoms is a function of the incident probe flux $J$, an interaction cross-section, $\sigma$, between the probe beam and the surface atoms, the Auger yield per interaction, $\omega$, and a detector efficiency factor, $f$ as:

$$I_{\alphaXYZ} = fNJS\omega$$

These factors are customary expanded to the form:

$$I_{\alphaXYZ} = \frac{1}{4\pi} \int d\Omega \int_{E_x}^{E_p} dE \int_0^{\infty} n_\alpha(t) \sigma_\alpha(E_x, E_p) \gamma_{\alphaXYZ} r^*_R e^{-\frac{t}{\lambda_\alpha}} dt$$

where the first integral is over the detector solid angle, the second integral is over the energy range between Auger electron energy and the primary electron beam energy and the third integral is over penetration depth into the probed solid.
Three simplifying assumptions are usually made at this time. First, the sample composition is assumed to be homogeneous over the probed volume. This allows the $n_\alpha(t)$, atomic distribution, and $\gamma_\alpha$, Auger yield to be pulled from the integrals. Secondly, since the Auger electrons come from such a thin surface layer, the probe current, $I_p$, is assumed constant, the probe energy, $E_p$, is assumed constant and thus the backscattering coefficient, $R^*$, can be pulled out of the energy and thickness integrals. Finally, since the majority of the Auger excitations are produced by the direct probe beam or by secondary electrons, both with energy near that of the probe beam, $E_p$, the ionization cross-sections can be approximated by one at energy $E_p$ for core-hole excitations of energy $E_\alpha$. The remaining integral over the detector solid angle, probe angle and sample roughness are condensed into a transmission function, $T$. These detector dependant factors are different for an electrostatic $127^\circ$ sector analyzer, a retarding field analyzer (RFA), an angular resolved secondary electron spectrometer (ARSES) or a cylindrical mirror analyzer (CMA) instrument. Finally, the roughness factor, $r^*$, and is considered a constant for a given experimental set-up.

With these simplifying but reasonable assumptions, Palmberg showed that a first principles calculation of Auger peak intensity involves a function of the form:
Equation 12 is the usual starting point for Auger quantitation calculations.
Calculating these components is fraught with uncertainty and experimental variability.

For the particular example of this research, we are primarily concerned with Ag M4,5N4,5N4,5 and Si L2,3VV Auger electrons as indicators of surface coverage. The ionization cross-sections, \( \sigma_{\alpha}(x, E_p) \) can be estimated from Worthington and Tomlin\textsuperscript{152} calculations for K and L shells. A better approximation with no free parameters and with some hope for M and N shell applicability is the semi-classically derived Gryzinski\textsuperscript{153} formulation. The Auger Yield term, \( \gamma_{\alpha xyz} \), is well approximated by Siegbahn’s\textsuperscript{154} polynomial for K electrons. Formalism for L, M and higher shell Auger yields are similar but less accurately predicted.
To remove these two poorly understood terms from the quantitation process, analysis is done with reference to pure, infinitely thick standards of the component elements. For the particular system under study, Ag/Si(111) represents a simple thin film overlayer on bulk substrate system, the simplest binary system. By normalizing the Auger intensities of equation 12 to reference standards and canceling factors we have:

\[
\frac{I_{\alpha,xyz}}{I_{\beta,xyz}} = \frac{[I + R^\alpha_n(E_p, E_\alpha)] n_\alpha \lambda_\alpha^\beta \cdot [I + R^\beta_n(E_p, E_\beta)] n_\beta \lambda_\beta R^\alpha_R(\beta)}{[I + R^\beta_n(E_p, E_\beta)] n_\beta \lambda_\beta \cdot [I + R^\alpha_n(E_p, E_\alpha)] n_\alpha \lambda_\alpha R^\beta_R(\alpha)}
\]

(15)

thus removing a few analytical, experimental and instrumental uncertainties.

Further, one can approximate:

\[
\lambda_M = 0.41 \cdot a_M^{1.5} \cdot E_M^{0.5}
\]

(16)

where:

\[a_M\] = atomic size of the M element
\[E_M\] = the Auger electron kinetic energy

from the Seah and Dench\textsuperscript{155,156} relationship for electron inelastic mean free paths.

Furthermore, following arguments of Seah\textsuperscript{157}, we can simplify the complicated \(\alpha/\beta\) matrix interaction effects\textsuperscript{158} by realizing that, for Ag/Si(111) we have a thin overlayer of non-buried adsorbate “contamination” on an infinitely thick Si substrate. By defining \(\phi_{Ag}\) as the fractional monolayer coverage, we derive the Auger intensity of the substrate Si Auger electrons as the \((1 - \phi_{Ag})\) part from the uncovered surface and \(\phi_{Ag}\) part attenuated by Ag. Thus:

\[I_{Si} = I_{Si}^\infty \{1 - \phi_{Ag}\} + \phi_{Ag} e^{-a_{Ag}/\lambda_{Ag}(E_{agXYZ})\cos\theta}\}

and

\[I_{Ag} = \phi_{Ag} I_{Ag}^\infty \left[\frac{1 + R_{Si}^\alpha_n(E_p, E_{Ag})}{1 + R_{Ag}^\beta_n(E_p, E_{Ag})}\right] \{1 - e^{-a_{Ag}/\lambda_{Ag}(E_{agXYZ})\cos\theta}\}\]

(17)
Combining the measured, calculated and experimental terms of equation 15 gives the AES quantitation form used for this experimental work:

\[
\frac{\phi_{Ag}}{[1 - \phi_{Ag}]} = \left\{ \frac{1 - e^{-\theta_{Ag} / \lambda_{Ag}(E_{XYZ}) \cos \theta}}{1 - e^{-\theta_{Ag} / \lambda_{Ag}(E_{XYZ}) \cos \theta}} \right\} \left[ \frac{I + R_{Ag}(E_p, E_{Ag})}{I + R_{Si}(E_p, E_{Ag})} \right] \frac{I_{Ag_{XYZ}} / I_{Ag_{XYZ}^*}}{I_{Si_{XYZ}} / I_{Si_{XYZ}^*}} \tag{18}
\]

where we solve for surface coverage, \( \phi_{Ag} \), by computing the first bracketed term from known constants and instrumental parameters, the second term from backscattering factors calculated from the data of Shimizu\textsuperscript{159} and Ichimura\textsuperscript{160} and the third terms from experimentally measured Auger peak-peak (p-p) heights of sample and standards.
3.4 Rutherford Backscattering Spectroscopy (RBS)

As in the more general field of Ion Scattering Spectroscopy (ISS), the sub-field of Rutherford Backscattering Spectrometry involves “hard sphere” collisions between incident particles and subject materials as schematically illustrated in Figure 3.9. For introductory material, the reader is directed to the texts by Chu, Nicolet and Mayer\textsuperscript{161} or Feldman and Mayer\textsuperscript{132} and the review article by Nicolet, et. al.\textsuperscript{162}

Figure 3.9 - Schematic of RBS analysis of Ag/Si(111). A 2.7 MeV He\textsuperscript{++} ion with initial kinetic energy and momentum recoils elastically after collision with a surface atom.

The scattered or channeled probe particles are analyzed for scattering angle and residual kinetic energy. Calculations of the energy transfer kinematics are well understood resulting in compositional analysis of the target substance. Starting with the assumption of non-relativistic velocities and elastic scattering we proceed using
classical mechanics and write the equations for the conservation of energy, $E$, and momentum, $\vec{p}$:

\[
\sqrt{\frac{1}{2} M_o v_o^2} = \sqrt{\frac{1}{2} M_{o_1} v_{o_1}^2 + \frac{1}{2} M_2 v_2^2} \quad \text{E conservation}
\]

\[
M_o v_o = M_{o_1} v_{o_1} \cos(\vartheta) + M_2 v_2 \cos(\varphi) \quad \text{p conservation} \tag{20}
\]

\[
0 = M_{o_1} v_{o_1} \sin(\vartheta) + M_2 v_2 \sin(\varphi)
\]

Combining the two $\vec{p}$ conservation equations and substituting into the $E$ equation we define $K$, the kinematic factor as:

\[
K = \left( \frac{v_2}{v_o} \right)^2 = \frac{E_2}{E_o} = \left[ \frac{x \cos(\vartheta) + \sqrt{1 - x^2 \sin^2(\vartheta)}}{1 + x} \right]^2 \tag{21}
\]

where:

\[
x = \frac{M_o}{M_2}
\]

For surface scattering, the final energy of the scattered He$^{++}$ ion equals:

\[
E_1 = K E_o \tag{22}
\]

independent of the initial kinetic energy of the He$^{++}$ ion and only modified by the scattering angle and mass ratio of the elements.

For areal quantitation we also need the collision cross-section between the incident $M_o$ particle and the surface target, $M_2$. Using classical electrostatics, Rutherford$^{163}$ determined that the differential cross-section can be represented as:

\[
\frac{d\sigma}{d\Omega} \propto \frac{(Z_o Z)^2}{E_o^2} \left[ \frac{4(\cos(\vartheta) + \sqrt{1 - x^2 \sin^2(\vartheta)})^2}{\sin^4(\vartheta)\sqrt{1 - x^2 \sin^2(\vartheta)}} \right] \tag{23}
\]

Entering the appropriate proportionality factors for units of $\text{Å}^2$/steradian, making the reasonable assumption that the He$^{++}$ atom is much less massive than the target atoms,
x< ½ and performing appropriate trigonometric manipulation, we derive a form for the
differential scattering cross section for Coulomb scattering/unit solid angle of:

\[ \frac{d\sigma}{d\Omega} = \frac{12.96 (Z_a Z_2^2)}{E_o^2} \left[ 1 - 2x^2 \sin^2(\theta/2) \right] \sin^4(\theta/2) \]  

(24)

Now repeating the logic used in Auger quantitation, Equation 10 we have:

\[ I_{RBS} = f N J \sigma \omega \]

where:
- \( I_{RBS} \) = measured RBS signal rate
- \( f \) = fractional collection (detector solid angle, \( d\Omega \))
- \( N \) = number of scattering atoms (areal density)
- \( J \) = incident beam current density
- \( \sigma \) = scattering cross-section (from equation 22)
- \( \omega \) = backscattering yield

an equation that gives quantitative measurement of atom specific surface density with
no free parameters. Detected signal, \( I_{RBS} \) is subject to counting statistics. Detector
solid angle and take-off angle can be precisely determined, incident beam current can
be measured as a sample current with precision pico-ammeters, scattering cross
section has no free parameters and backscattering yield, as a primary process, is unity.
Fits using equations 19 and 20 determine atom specificity. Fits using equations 22
and 23 with calibrated detectors and electronics determine atomic quantities for those
surface atoms.

In the specific instrument used for this work, 2.7 MeV \(^4\)He\(^{++}\) ions were
extracted from the Cornell MSC Tandetron after separation from other ions using a
15° sector magnet and collimated with standard slit systems. These ions were directed
at Ag/Si and reference standard materials. The 7° tilt indicated in Figure 3.7 is
necessary to avoid ion channeling effects. Ions backscattered at 170° were analyzed to
determine quantitatively, the areal density of Ag atoms (high Z) on Si (low Z).
Analysis was done using the computer program RUMP and fitting algorithms developed by Doolittle\textsuperscript{164, 165}.

RBS is unique in its ability to detect at the $\sim 10^{10}$ atoms/cm$^2$ for heavy elements on light element substrates. This sensitivity level far greater than needed to distinguish a single Ag/Si(111) monolayer coverage of $7.83 \times 10^{14}$ atoms/cm$^2$ and is unique in providing absolute coverage quantitation.
3.5 References - Chapter Three


130. R. Kronig, Z. Phys. 70, 317 (1931); Z. Phys. 75, 475 (1932); Z. Phys. 76, 468 (1932).


163 E. Rutherford, Phil. Mag. 21 669 (1911).


CHAPTER FOUR:
EXPERIMENTAL METHODS

4.1 Ultra-high Vacuum System

As mentioned, two of the three experimental variables studied in this experiment involve control of traditional "surface contaminants". This study required a contamination free, especially boron and carbon contamination free, ultra-high vacuum system (UHV). The system, constructed by the author, can be thought of as two vacuum subsystems, a lower pumping well and an upper twenty inch diameter spherical analysis chamber. The vacuum unit, accompanied by control electronics and ancillary control systems, was portable and adjustable for use "off line" as a fully functioning surface preparation and analysis system or "on line" in the synchrotron X-ray beamline for XSW and SEXAFS measurements as illustrated in Figure 4.1. Details of specialized equipment developed for these measurements are deferred for publication at a later date.

The pumping well, separated from the analysis chamber by a poppet-type gate valve, was adapted from an experimental system used previously in our group.\textsuperscript{166, 167} Rough pumping, from atmospheric to $10^{-6}$ torr, was accomplished by connecting an ancillary Balzers turbomolecular and mechanical pump cart, via a liquid nitrogen filled cryo-trap\textsuperscript{*}, to the pumping well. Primary pumping at pressures below $10^{-6}$ torr was handled by a Perkin-Elmer TNB-X 200 l/sec diode ion pump, a titanium sublimation pump (TSP) and a LN$_2$ cryo-pump if needed.

\textsuperscript{*} On loan courtesy of Newman Lab accelerator physics group.
Figure 4.1 - Experimental vacuum system in place at CHESS D-line. Left, photo showing spherical vacuum chamber and pumping well outfitted with: 1) stepping motor manipulator control, 2) manipulator, 3) upper TSP, 4) CMA, 5) ion source, 6) RGA, 7) 200 l/s pumping well, 8) rotation/translation base, 9) final x-ray slit, 10) x-ray flight tube, 11) Be entrance window, 12) Si(Li) fluorescence detector and 13) surface science instrumentation control electronics.

The upper analysis chamber consisted of a specially designed Perkin-Elmer double-walled spherical stainless steel chamber* with twenty-three flanges oriented toward either of two focal points. Fourteen of the ports were aimed at the sphere's center, the focal point for X-ray measurements. The remaining ports were directed at a focal point offset two inches from the sphere center, the focal point for various surface analysis instruments. A schematic equatorial cross-sectional view of the analysis chamber with surface analysis instruments are shown in Figure 4.2. The available surface analysis instruments include Auger Electron Spectroscopy (AES)/ X-ray Photoelectron Spectroscopy (XPS) using a retractable† Phi 15-255GAR double-pass cylindrical mirror analyzer (CMA), a Phi 15-120Low Energy Electron Diffraction (LEED) apparatus, a silver deposition source consisting of a water cooled graphite Knudsen

* Courtesy of Cornell University, Material Science Center purchase #870554
† Designed and fabricated by author.
cell from Microscience model WJC-2G with crystal thickness monitor and shutter system†. A re-entrant, Be window snout† was developed for placement of a 205 eV resolution Si(Li) detector's active face near the sphere center subtending a maximum of 0.5 radians solid angle. Auxiliary equipment necessary for surface science included, an Phi ion gun for surface sputtering, a Phi residual gas analyzer system, a multifilament nude ionization gauge, various precision gas leak valves, an auxiliary sample heater†, an auxiliary water cooled TSP numerous commercial and in-house fabricated Be windows. Critical to quick sample turn-around was an in-house fabricated sample introduction and load lock system based on a UHV Instruments magnetic linear translation device and plug-in sample holder.

Figure 4.2 - Cross-section of experimental UHV chamber, in plane of incident X-rays. Surface analytical instrumentation and their respective foci are shown.

* Winner, American Vacuum Society, 1995 “Shop Note” award.
The factory cleaned and in-house assembled chamber was blind-baked before instrument installation to a base pressure in the low $10^{-12}$ torr range, well below the x-ray threshold reading reliability of the nude ionization gauges used to measure pressure and well into the XHV (Extreme High Vacuum) regime. To keep the virgin system free of boron contamination, all Pyrex (borosilicate glass) view ports were boiled in high purity liquid chromatography (HPLC) water for 19½ hours to remove the soluble B rich surface layer of the glass, formed during high temperature fabrication. All components were then cleaned, installed and conditioned with numerous and extensive high temperature bake-outs using conventional resistive heating tapes and block heaters as well as with much more effective Huntington in-vacuum infrared heating elements.

In-vacuum manipulation of samples for surface analysis as well as X-ray goniometry was accomplished using a novel manipulator design*† attached to a standard Huntington Model PM-600 XYZθ feedthrough. This complex sample manipulation was necessary for two main reasons. First, the combination of chamber flange multiple focal point aiming, analysis instrument housing interferences and individual instrument focal distance requirements made flexible sample positioning a necessity as illustrated by the "X's" of Figure 4.2. Secondly, precision relative angular positioning at arc-second (micro radian) levels and translational positioning at sub-millimeter levels was necessary to chase the synchrotron X-ray and re-direct the diffracted beams at a given energy for the XSW work.

Control of sample temperature was critical to the success of this study. Careful cross-calibrations of sample furnace power, a W-5Re/W-26Re sample thermocouple readout system and optically measured (AcuFiber Optical Pyrometer Model 10,

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† Designed and fabricated by author.
temperatures were made. This sample furnace power was carefully controlled in current lock mode by a H-P 9850 regulated power supply.

The oxide protected Si samples could be interchanged quickly through a load-lock assembly while maintaining the pressure in the analysis chamber at an overall $10^{-10}$ torr base pressure. The sample holder also carried a sample thermocouple and the sample heating filament, two components that frequently fail during experimentation.

Samples were always radiatively heated from the rear by a Ta filament assembly allowing all surface species to desorb into vacuum without reflection, containment and recontamination by nearby chamber surfaces. This manner of heating not only avoids front surface contamination but also eliminates electromigration and surface reconstruction effects known for many metal/semiconductor systems. Specifically, for Ag/Si(111), heated by direct current methods it is known that Ag preferentially migrates toward the cathodic terminal. It is also known from RHEED observations that surface step agglomeration occurs with direct current heating on clean Si(111) surfaces.

4.2 Samples and Sample Preparation

For studying surface step effect, two kinds of samples were prepared; one with a flat Si(111), $0^\circ$ miscut surface and another with an intentional vicinal mis-orientation of $0.5^\circ$ toward the [112] pole. Both types were prepared from a single Si(111) slice. Specifically, samples used in this experiment were cut from a single 3 inch by (0.100±0.020) inch wafer of n-type (P-doped, 7000-8000 $\Omega$-cm) Si(111). The wafer was attached to an Bond barrel-holder with commercial "Crystalbond" adhesive and initially oriented using the existing $<110>$ flat provided by the manufacturer and a real-time Laue orientation facility available at Cornell's Materials Science Center.
facilities. Final orientation was done using a GE x-ray goniometer capable of 0.001°
arbitrary resolution and Ni filtered Cu Kα radiation giving an exact (111) orientation to
within 0.006° (1σ) when rotated 360° about the <111> pole. The sample was ground
and mirror polished using a grinding-bell fixture with a measured, worst case, static
mis-orientation tolerance of 0.012°. (The actual mis-alignment contribution from the
grinding-bell would be less since the barrel-holder is allowed to freely rotate within
this fixture, ideally averaging out this mis-alignment contribution.) This orientation,
grinding and polishing protocol was quite tedious and took three weeks to accomplish.

The single wafer, now polished to within ±0.018°(3σ) of (111) and protected
with a thick polymer covering ("Crystalbond") was now cut in half along a diameter.
Five 10mm² samples, designated as 0° misorientation, were prepared from this half-
wafer.

The remaining half wafer was similarly re-oriented with a 0.498° ± 0.012°
mis-cut rotated about <110> toward [001] or, as stated another way, mis-cut rotating the
<111> pole by 0.498° toward the [112]. This particular vicinal surface is known to
form a parallel stable single step structure up to 860°C. This re-oriented, re-ground
and re-polished half-wafer was subject to the same protocol of the 0° oriented surface.
Samples were cut from this half-wafer and designated as 0.5° vicinal surfaces. Such a
miscut should provide a step density of ~27/μm with terrace length of about 350 Å.

Laue patterns from the 0° and 0.5° samples after polishing are presented in
Figure 4.4 to illustrate not a difference in the patterns, but rather that, even a
technologist with 23 years of x-ray orientation experience, can not tell the difference
between the flat and vicinal surfaces with this standard technique.
Figure 4.3- a) (111) pole figure for the diamond cubic structure; b) Laue photograph of 0° flat surface sample wafer; c) 0.5° vicinally cut sample wafer.
Atomically clean Si(111) surfaces are typically prepared in a number of ways. The most common and straightforward method is to 'flash' surface adsorbates away by heating the Si to the 1200°C temperature range. This cleans the surface by a combination of solid state diffusion and desorption of all surface contaminants, including the ubiquitous carbon contaminants, but is known to form β-SiC "protuberances" \(^{173,174}\) on the surface, later identified by STM as triangular pyramids with a (111) base plane and \{110\} faces\(^{175}\). It is also known that flashing to temperatures this high induce surface faceting and large scale surface roughening\(^{176,177}\) limited by surface carbon contamination\(^{178}\), ultra-high vacuum base-pressure and total accumulated time at temperature.\(^{179,180}\) Lowering the flash cleaning temperature into the 900 - 1100°C temperature range reduces surface roughening but is known\(^{181}\) to produce cubic phase, epitaxially oriented SiC particles, stable at these temperatures. Except for the earliest experiments by this author, where evidence of this faceting and subsequent RBS indications that Ag can move subsurface were seen, flash cleaning of samples was avoided.

The second method used universally to clean surfaces is inert gas sputtering followed by sample annealing cycles to repair the surface damage. Unfortunately, the annealing cycles are in the 1000 to 1250°C temperature range raising the same concerns about SiC formation as above. RHEED experiments by Fan\(^{177}\) also confirm that sputter cycles on Si(111) result in increased surface roughness not removed by 1200°C annealing. They are able to fit phase and intensity RHEED oscillations to a model of random surface steps created by the sputter/anneal cycles.

The third method, specifically tailored for Si, is cleaning by wet chemical methods. There are a number of chemical cleaning and acid etching protocols that have been used for Si. Some researchers contend that solvent cleaning of a sample
The wet chemical technique used in this set of experiments follows a chemical formulation initially proposed by Henderson\textsuperscript{176} and improved by Ishizaka and Shiraki\textsuperscript{182}. In this process, a surface oxide which traps surface impurities is created then, using an HF dip, one strips that oxide removing the impurities with the oxide. The process is repeated multiple times finishing with a protective capping oxide. Once this capped sample is in vacuum, the oxide can be thermally desorbed at a relatively low temperature, 750 to 900°C. (A temperature far below the SiC formation temperature). The silicon surfaces for this study were prepared using this low temperature cleaning technique (Ishizaka and Shiraki) in which a thin protective oxide layer formed on a cleaned silicon surface is removed by subsequent desorption at 850°C in the UHV system.

The 0° and 0.5° samples were chemically cleaned using this Ishizaka and Shiraki etch protocol\textsuperscript{182} and stored, covered, in highly cleaned quartz or pyrex glassware under HPLC water. It was discovered that the amount of carbon present on the oxide protected Si surface had direct correspondence with the hold time in this high purity water. This is presumably due to the growth of organics on the surface that are pyrolized either by the electron analysis beams or during the high temperature surface oxide desorption step. Holding time at room temperature could be extended up to seven days after chemical oxidation without detriment. A general rule of thumb was developed to reliably predict the success of a chemical treatment to produce a clean, carbon free surface. If the AES spectra of the oxidized surface showed a 3:1 O KLL to C KLL ratio or greater, low temperature flashing would produce pristine C free surfaces. Ratios between 3:1 and 2:1 O:C usually showed minimum detectable C
contamination levels (~4% by Seah equation 3.16). Ratios less than 2:1 O:C showed higher C contamination inversely proportional to that O:C ratio.

Upon loading of a chemically cleaned Si sample and estimating the degree of C contamination that would remain after low temperature flashing, an Auger spectra of the 6--9's Ag reference standard would be taken. The Ag reference would be sputter cleaned, if necessary, and all system filaments as well as deposition source and sample furnaces would be degassed. Both titanium sublimation pumps (TSP's) would be refreshed prior to the oxide flash-off procedure. When a clean Ag reference spectra was in hand, the sample would be flashed to 850°C to remove the protective oxide coating and contaminants. Sample temperature was lowered to 400°C and a quick Auger spectra taken of the clean Si (now a reference spectra). The LEED pattern was checked to insure that a sharp 7x7 pattern was observed. The presence of sharp 7th order LEED spots in no way insures one that the surface is contamination free. To the contrary, perfectly acceptable 7x7 patterns were observed on even the 1/3 ML C contaminated surfaces even though literature reference to sharp 7x7 patterns, without spot profile analysis, is made in the context of assuring the reader of contamination free surfaces.

It is critical to keep the time between oxide surface flash off and Ag deposition to a minimum. It is also critical to keep the time in the LEED and AES electron beams at a minimum since it is well known that these are sources of C contamination, both from desorption of contaminants from the instruments, especially the W filaments, to the clean surface and from cracking of the residual gasses by the electron beams. Holding the sample at 400°C decreases the sticking coefficient significantly, however and helps maintain a contamination free surface.

During these critical oxide removal, clean surface analysis and deposition phases, a period of up to 1 hour, the lowest base pressure possible was attained by
filling the interstitial space of the double walled, 20" spherical vacuum chamber, with liquid nitrogen thus creating a tremendous cryo-pumping surface area and, along with the ion and TSP pumping, pulling the base pressure well into the mid-10^{-10} torr range.

Submonolayer coverages of silver were deposited as follows. Immediately after the protective Ishizaka/Shiraki oxide layer was thermally desorbed at 850°C for 10 minutes, the sample was cooled to 400°C and checked with Auger Electron Spectroscopy (AES) for surface cleanliness and LEED for surface structure. The sample was then positioned at a point 10 cm from the front of a graphite-crucible, water-jacket cooled and temperature stabilized Knudsen effusion source. Ultra-pure silver shot of 6-nines (99.9999 atomic %) purity with certified composition was purchased and purity was re-checked in-house to assure no B, C or √3 producing metal contaminants were present. (The shot had been ultrasonically cleaned in solvents, loaded into a thoroughly baked, graphite crucible, water shielded Knudsen effusion source and de-gassed at 250°C for 24 hours.) Before deposit, the Knudsen source and 6-9's Ag was temperature stabilized at 700°C for 30 minutes before Ag was thermally sublimed at 730°C giving a calibrated deposition rate of 0.03 Å/min as monitored by pre- and post-insertion of a quartz crystal oscillator. Most deposits were made onto a 400°C temperature stabilized Si(111) sample where it is known that there is still unity sticking coefficient for Ag on clean Si(111)\(^{183}\). Absolute coverage was determined by another, post-deposition AES knowing the AES to RBS coverage calibration for this CMA analysis system. Again, a check of the surface structure with LEED was needed to confirm that the expected √3×√3 R 30° or 3x1 starting surface structure.

After XSW or SEXAFS experiments were complete, a post-mortem check of surface coverage and contamination is done as well as a final surface structure check.
4.3 X-ray Beamline, Optics and Beam Characteristics

Experiments were conducted using hard synchrotron x-radiation produced at the Cornell High Energy Synchrotron Source (CHESS) facility’s D-Line as shown schematically in Figure 4.4. The critical optical components for the beamline are listed in the included table. These positions, types and sizes of the indicated apertures, filters and optical elements are critical to the calculation of X-ray spectra and flux. The radiation source was a swath, 4.5 milliradians wide of positron produced hard bend synchrotron dipole magnet radiation. After aperturing, the radiation was directed onto a Si(111) or a Si(220) four-bounce non-dispersive (+−+− orientation) monochromator* at the 10.8 meter point. The resulting monochromatic beam was directed into the experimental hutch and onto the in-situ prepared samples inside the vacuum sphere at the 14.4 meter point.

Figure 4.4 - Schematic illustration of CHESS D-line synchrotron radiation line, Si(111) monochromator and UHV experimental system

* Designed and fabricated by author.
The X-ray monochromator, is a critical component of the beamline since it needs to provide X-rays at the right energy with appropriate band pass and stability for the experimental requirements. Figure 4.5 illustrates and summarizes the capabilities of the monochromator optics built for this experiment. For XSW experiments it is important to measure the full Darwin width, $\delta \theta_D$, of the sample crystal by probing with an X-ray collimated to a known intrinsic width. The convolution (summing in quadrature) of the two Darwin widths becomes the measured reflectivity. For SEXAFS, it is important have the capability of exciting Ag.
absorption edges, especially the K edge at 25.514 keV and the L_{III} edge at 3.351 keV and simple energy tunability.

Figure 4.5 - Schematic illustration of Si(111) and (220) monochromators in limit design configurations.

XSW experiments were conducted with the Si(111) Bragg reflection at 5.2, 13 or 15 keV and SEXAFS experiments were done at the Ag K edge, 25.5 keV.

Especially important to the step density variable portion of the experiments is the coherence length of the probe X-rays.

Longitudinal coherence, $l_c$:

$$ l_c = \frac{\lambda^2}{\Delta \lambda} = \frac{\lambda}{\Delta \theta} \cot(\theta_B) $$

$l_c$ (13 keV) = 0.275 µm

where:

$\Delta \theta$ = beam vertical divergence = 53 µradians
$\lambda$ = X-ray wavelength (Å) = 12.39854/E(keV)
$\theta_B$ = Bragg diffraction angle

Transverse coherence, $l_t$:

$$ l_t = \frac{R \lambda}{d_s} $$

where:

$R$ = ring radius = 31.75 meter dipole bend radius
$d_s$ = source size ~ 2mm.

$l_t$ (31.75 m, 0.95 Å, 2 mm) = 1.508 µm
4.4 Ancillary Experimental Apparatus

These series of experiments would not have been possible without the extensive surface characterization, sample analysis, materials preparation and machining facilities available at Cornell University, which the author used on a service basis. The Rutherford backscattering calibrations were done using the Material Science Center's 2.8 MeV Tanditron as an external user. Initial instruction by Mr. Nick Szabo was greatly appreciated. The He\(^{++}\) beam was directed at 7° from the normal <111> channeling direction at a nominal 10\(\mu\)C fluence for each spectral measurement. Analysis was completed by the author as described in Chapter 3.

For sample and monochromator fabrication, the crystal orientation and cutting facilities of Professor B. Batterman were used and initial instruction by Mr. John Hart is acknowledged. Other materials preparation facilities under the direction of Ms. Margaret Rich and Mr. Bud Addis were made available for crystallographic polishing, orientation, photography, powder and single crystal diffraction.

Machine shop facilities at CHESS as well as Kimball, Clark, Newman and Snee Halls were used by the author and under the author's direction to fabricate numerous experiment components necessary for these series of experiments. Special thanks the professional machinists in those shops, especially Stanley Carpenter, Walter Protas, Basil Blank and Chuck Henderson for fabrication instruction and advice. Coating, electroplating, electropolishing, evaporating and vacuum leak checking facilities under the watchful eye of Mr. Ron Kemp were used for UHV component preparation.
4.5 References - Chapter Four


CHAPTER FIVE:

EXPERIMENTAL RESULTS AND ANALYSIS

5.1 Ag Coverage Quantitation

5.1.1 Literature database

As should be clear from Chapter 2, absolute determination of Ag surface coverage, especially at low coverage, is a crucial factor for this research area. There are so many model dependent structural features that rely on a 2/3 or 1 Ag atom occupancy per surface unit cell that the researcher, working with area averaging techniques, must be precise when describing exact surface under study. A close look at the Auger Electron Spectroscopy (AES) literature for Ag coverage quantitation at room temperatures yields no generally agreed upon correlations as shown in Figure 5.1. The same holds for elevated temperature deposits where it is well understood that the Stranski-Krastanov growth model holds. This adsorbate-substrate system, produced at ambient and lower temperatures, is exceedingly dose-rate dependant. In addition, Auger quantitation is, in general, instrument dependant. At one extreme, Wehking\textsuperscript{184} reports 10ML Ag/Si(111) at 50°C gives an AES Ag:Si p-p ratio of 10:1 and Bolmont\textsuperscript{185} shows 2 ML gives a Ag:Si = 6:1 ratio. At the other extreme, Grazhulis\textsuperscript{186} shows for 2 ML only a Ag:Si = 0.3 ratio.

Readers in this subject must be aware that the preponderance of surface coverage determinations are done using AES quantitation evidence or quartz crystal thickness monitoring of deposition mass. The former has been shown to be difficult to accomplish successfully and the latter is fraught experimental uncertainties and useless for the desorption induced structures, i.e. the 3x1 or the elevated temperature $\sqrt{3}$x$\sqrt{3}$R30° structures.
After discovering the disparity in literature results, both at elevated and at ambient temperatures and an inability to closely match coverage determinations based on different standards and calculational techniques, it was necessary to undertake a program of careful calibrations of the equipment used for this study. A series of deposition standards were prepared. AES calibration spectra, taken under closely controlled excitation and analyzer conditions along with a clean silver standard, were
made for a large range of Ag/Si(111) deposits*. The samples were then taken to the Cornell MSC RBS facility and absolute Ag coverages were determined. From these measurements, a linear cross-correlation between AES p-p ratio and absolute Ag coverage for low coverages was made.

Figure 5.2 - Compilation of literature Auger vs Coverage calibrations for elevated temperature deposits of Ag on Si(111)

* Participation of Undergraduate Research Experience student, Eunme Park, is gratefully acknowledged.
5.1.2 AES/RBS quantitation calibrations

Prior to RBS experiments, calculations of sputtering rates for Ag by 2.7 MeV He\(^{++}\) were determined. Insignificant (<0.1%) loss of target Ag atoms over 20 µCoulomb dose were expected. This is a number well within expected computational fitting errors. Due to minor uncertainties in the values for sputtering yield this loss was experimentally cross-checked. Reproducibility and dose rate effects (sputtering effects) of RBS measurements* undertaken in this study are shown in Fig. 5.3.

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* Results independently verified by Dr. Peter Revez, Cornell University MSC, 21 Feb 1994.
It was not expected that Ag would be lost from the surface upon exposure to atmosphere during the AES to RBS chamber transfer. Incidentally, Cro$^{197}$ reports an ARUPS confirmation that a $\sqrt{3}\times\sqrt{3}R30^\circ$-Ag layer prevents Si oxidation upon RT exposure.

Shown in Figure 5.4 are 12 separate AES vs RBS experiments over the 0 to 1.5 ML range. Correlation of AES and RBS agrees with Weitering$^{224}$ (elevated temperature) and Bolm$^{139}$ (room temperature) measurements (See Figures 5.1 and 5.2) rather than pre-1985 publications. Quantitative analysis presented here is also consistent with published RBS spectra for the Ag/Au/Si(111) by Yuhara, Inoue and Morita.$^{198}$

Figure 5.4 - Experimental determinations of Auger vs Coverage calibration by various AES quantitation methods and by RBS direct quantitation.
5.1.3 AES results and RBS correlation

Thus, it has been carefully established that the calibration for this particular CMA analyze under 3 keV incident electron excitation conditions with the particular electronics configuration and setting used for this study, that coverage quantitation can be validly described in the 0 to 1.5 M.L. range by the linear relationship:

$$\Theta(M.L.) = 19.9795 \left[ \frac{AgM_{4.5}N_{4.5}p-p}{SiL_{2,3}VVp-p} - 0.0392 \right]$$

(26)

5.2 XSW Positional Calculations

As detailed previously in Chapter 3, the X-ray Standing Wave (XSW) technique can be used to locate atomic positions for the Ag adsorbate atoms relative to a periodic extension of the bulk diffraction planes as predicted by dynamical diffraction theory. The Ag atoms fluoresce characteristically (22.16, 21.99, 24.94 keV for the $K_{\alpha 1}$, $K_{\alpha 2}$, and $K_{\beta}$ lines; 2.98, 3.15, 3.35 and 3.52 keV for the $L_{\alpha}$, $L_{\beta 1}$, $L_{\beta 2}$ and $L_{\gamma}$ lines respectively) in proportion to the square of the electromagnetic field amplitude at the Ag atom center, in the dipole approximation. Thus, a coincidence experiment monitoring the sample x-ray reflectivity and the Ag fluorescence yield simultaneously, provides all the relevant raw data to fit the amplitude and phase of a particular Fourier component of electron density.

Experimentally, the fluorescence spectrum is represented as a histogram of counts, normalized to the incident beam vs. energy, shown in Figure 5.5. For this study a spectrum like that shown is taken for each of 32 points along a complete Darwin reflectivity curve. Included in the spectrum is a peak artificially generated by a pulse generator set to random interval with known average frequency and constant
pulse height. This "pulser" peak along with a known timing signal is used to correct for Si(Li) detector dead-time effects. Also shown in the spectrum are peaks from thermal diffuse scattering (TDS), Compton scattering, Si Kα fluorescence, low energy noise and occasionally Fe fluorescence from the sample holder.

Figure 5.5 - Example Fluorescence Spectra. Complete spectra such as this, were recorded for each of 32 points along the Darwin reflectivity curve during the XSW experimental scans.

Spectra are generated by multiple passes through the Darwin reflectivity curve at rates of approximately 1 sec per spectrum per each of 32 points spanning the curve. To accumulate sufficient total fluorescence counts for greater than 3% statistical accuracy, this process was repeated roughly 30 times and summed in hardware memory for speed. Software tracking and centering of the reflectivity curve made it possible to repeatedly scan and sum these spectra, accounting for slow thermal or
beam position drifts. There were additional dead-time and beamline optics stabilization effects which made it possible to collect only two full data sets per each 1 hour synchrotron fill. A problem with this efficient hardware summing technique was that X-ray beam position or control electronics glitches could invalidate an entire data set. For low coverage, 0.1ML levels, six complete data sets were needed for sufficient counting statistics while high coverage, >1ML, necessitated only one or two complete data sets for accurate analysis. Slight smearing of rocking curves and fluorescence spectra from the thermal drift compensation software as well as from the alignment and summation protocol of many different data sets could contribute to data inaccuracies but not in a significant way.

Quantitative analysis of the data required turning each Ag fluorescence and pulser peak into background subtracted integrated intensities. Dead-time effects were calculated from pulser and timing data and applied to the Ag fluorescence signal. Using a phase factor determined by reflectivity fits, fluorescence yield data was fit by least squares techniques to the theory of equation 3.1 yielding coherent fraction, $F_c$ and coherent position, $\Phi_c$, information.

To deconvolute the effects of carbon, boron and step density on the structure of $\sqrt{3}\times\sqrt{3}R30^\circ$-Ag and 3x1-Ag, a standard three variable Plackett-Berman experimental screening test matrix was planned as shown in Figure 5.6. Testing nodes $S \rightarrow Z$, representing combinations of the three major variables, will be used to identify and coordinate the presentation of experimental results and analysis in the following sections.

Due to limited experimental time, not all combinations of experiments (XSW, SEXAFS), temperatures (R.T. to 600°C) and structures ($\sqrt{3}$, 3x1 and combinations) could be completed at all testing nodes. Valid conclusions can however, be drawn from the testing configurations completed.
Figure 5.6- Statistical Experimental Design screening test matrix used for the study of minor variables on the structure of Ag/Si(111)

5.2.1 Node-S testing: C free, B exposed, Flat Si(111)

XSW results obtained under Node-S conditions are presented in Figures 5.7. (The remainder of the XSW results will be presented in exactly the same format.)

This testing configuration, consisting of a flat Si(111) surface, cleaned using standard "wet" analytical chemistry techniques in Pyrex glassware and showing no trace of carbon contamination, represents a base-line against which other experiments are compared. Sample preparation, surface observations and processing path are noted in Figure 5.7a, resultant fluorescence yields, reflectivity and theoretical fits are presented in Fig 5.7b.

After surface preparation by flashing the Ishizaka-Shiraki oxide for 5 minutes at 850°C, a good 7x7 pattern was observed with carbon Auger signal below detection limits and a Si:Ag AES ratio of 53.3:9. Ag deposit at 400°C produced a sharp Ag-
(\sqrt{3}\times\sqrt{3})R30^\circ \text{ LEED pattern at 57 eV with no trace of the 7x7 spots remaining. For 2.58 ML coverage at 400^\circ C, Ag atoms are found from this measurement to be well ordered at a position, } \Phi_c = (0.79 \pm 0.02) \text{ modulus-d}_{111}. \text{ Considering only the three possibilities of; Ag included in the Si(111) double-layer, on the surface or in the next 1 d-spacing above the surface gives a } z\text{-Ag position of } -0.66, +2.48 \text{ or even } +5.61\text{Å (if situated above an intermediate adsorbate layer) as referenced to the center of a bulk-like terminated Si(111) surface double layer as shown in Figure 5.7c.}

**Ag/Si(111) Schematic of Growth Structures**

![Figure 5.7a](#)

**Figure 5.7a - Path-dependant XSW measurement locations. Open circles depict coverage and temperatures of XSW measurements of Figure 5.7b and 5.8a, b, c respectively (see text). Coverage range on data taken at 560^\circ C is due to ongoing Ag desorption at that temperature.**

After the completion of Node S testing, the sample temperature was increased to 560^\circ C to allow Ag to desorb from the surface. Measurements were made during this desorption process as shown on the surface structure diagram of Figure 5.7a. The \( F_c \) and \( \Phi_c \) fits to this data should not be taken with the same degree of confidence as
for any other XSW fit shown in this paper for the following reason. As mentioned previously in this chapter, for 3% error limits, one to two hours of counting are necessary for statistical accuracy but, even at this low desorption temperature, Ag is completely removed in 2 hours. XSW scans were accumulated in 15 minute slices in order to determine Ag positions during $\sqrt{3} \rightarrow 3\times1$ transformation and at desorption temperature. Figures 5.8 a, b and c are fits to the raw Ag integrated intensities without dead-time or background corrections. Rigorous propagation of errors (normally done during the analysis process) associated with these background and dead-time corrections on such short data sets create large error bars and create conditions of non-convergence of the fitting procedure.

An incomplete attempt at an additional, lower coverage XSW measurement is shown in Figures 5.9. A new node S sample was prepared and measured with 0.82 ML Ag/Si(111) at 250°C. Problems with Si(Li) detector electronics made detection of the weak Ag L$_{\alpha\beta\gamma}$ fluorescence signal difficult. The combination of ~50% losses of the L radiation in the detector and vacuum Be windows with the lower L fluorescence intensity coupled with detector electronics noise caused measured count-rates to be intolerably low. Before the onset of surface contamination and mindful of limited available X-ray beam time, the sample was reconfigured for measurement at 26.8 keV, above the Ag K edge. XSW results, although noisy from detector problems and difficult to fit due to the narrow Darwin reflectivity width at this energy, are presented in Figure 5.9 for completeness. A rough coherent position, $\Phi_c$ of 0.197 with good fit coherent fraction, $F_c$, but poor $\chi^2$ statistical convergence was found by the Fumili steepest descents fitting method.
Figure 5.7b - XSW results, Node S testing, 2.58 ML Ag/Si(111). Top curve, fluorescent yield, symbols and error bars and theoretical fit. Bottom symbols and curve, measured and fit reflectivity. $\Phi_c = 0.79$
Figure 5.7c - Node S testing. Possible locations (Ag₁, Ag₂ or combination) for Ag relative to Si(111) diffraction planes.

Figure 5.8a shows Ag positions after initial stabilization at 560°C with only the $\sqrt{3}\times\sqrt{3}R30^\circ$-Ag structure present. (The small number of Ag islands quickly desorb at this temperature. After 45 minutes at temperature, the $\sqrt{3}$ and 3x1 phases should be present in roughly the same proportions per thermal desorption formulae presented in Kern¹⁹⁹.°. The yield and calculated $\Phi_c$ positions are presented in Figure 5.8b. After 100 minutes at 560°C, only the 3x1 phase should be present and data are presented in Figure 5.8c. In all four cases, 400°C and the three 560°C tests, the Ag atom positions during desorption are found to be essentially unchanged.

* Translation from French by G. Navrotsky and J.M. Blakely, Accepted and filed by The International Translation Center, Schuttersveld 2, NL-2611 WE Delft, The Netherlands. ( itc@library.tudelft.nl or http://www.library.tudelft.nl/itc/ )
Figure 5.8a - XSW position, Node S testing, ~0.9 ML, 560° C (Beginning of desorption and 3x1 formation). √3x√3R30° Ag/Si(111) only, Φc = 0.78
Figure 5.8b - XSW position, Node S testing, ~0.5 ML, 560° C (Middle of desorption and 3x1 formation process). $\sqrt{3}R30^\circ + (3x1)$ Ag/Si(111), $\Phi_c = 0.78$.
Figure 5.8c - XSW position, Node S testing, ~0.1 ML, 560° C (End of desorption of 3x1 phase), 3x1 Ag/Si(111), Φc = 0.79
Figure 5.9 - XSW results, Node S testing, 0.82 ML Ag/Si(111) at 250°C. Top curve, fluorescent yield, symbols and error bars and theoretical fit. Bottom symbols and curve, measured and fit reflectivity.
5.2.2 Node-T testing: C exposed, B exposed, Flat Si(111)

After Node-S testing, all surface Ag had been desorbed as confirmed by AES. The sample was removed from vacuum, re-Ishizaka/Shiraki etched to create a newly oxidized surface and re-introduced into vacuum and oxide removal by a 5 minutes at 850°C flash. Numerous attempts were made to create a strictly 3x1 covered surface at \( \Theta < 0.3 \) ML. During the process, Ag was deposited and completely desorbed twice before a good 0.12 ML \( \sqrt{3} \)-Ag surface, as measured by LEED at 27 and 42 eV, was created at 400°C with a measured value of 19.6% carbon (Chapter 3, Equation 18) or roughly \( 1.5 \times 10^{14} \) C/cm\(^2\) (Figure 5.10a). It was noted that the 3x1 structure was completely inhibited by any presence of carbon on the surface. XSW tests were completed on this surface as shown in Figure 5.10b and surprisingly, the coherent fraction, \( F_c \), was still quite high but the coherent position, \( \Phi_c \), for this prototype surface was quite different than that found for the high coverage prepared surface of Node-S testing.

![Ag/Si(111) Schematic of Growth Structures](image)

Figure 5.10a - Path-dependant XSW measurement, Node T testing. Open circle shows coverage and temperature of sample preparation and measurement reported in Figure 5.10b.
X-Ray Standing Wave Results: Ag/Si(111)
\( \sqrt{3} \times \sqrt{3}R30^\circ, 400^\circ C, 0.1ML \)

Node T

Coherent Fraction \( f_c \)
1.01±0.06

Coherent Position \( \theta_c \)
0.69±0.01

Normalized Yield vs. Angle \( \Theta - \Theta_{Bragg} \) (\( \mu \text{rad} \))

Reflectivity

Ag L\(_{\text{agg}}\)

E=15,333 keV

Figure 5.10b - XSW Results, Node T testing, 0.13 ML Ag/Si(111). Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
5.2.3 Node-U testing: C exposed, B free, Flat Si(111)

Figure 5.11 presents results identical to Node-T testing in terms of coverage and temperature, obtained from a separately prepared sample cut from a different portion of the Si(111) sample boule. Carbon levels on this surface were at 0.299 ML (2.34 x 10^{14} C/cm^2) with 0.11 ML Ag coverage. Ag coverage was obtained by overdosing to 1.96 ML at 400°C then desorbing back to 0.11 ML by holding at 560-600°C. Again good √3 structure could be seen but 3x1 structure could not be formed in the presence of this level of carbon contamination.

![Ag/Si(111) Schematic of Growth Structures](image)

Figure 5.11a - Path-dependant XSW measurement, Node U testing. Open circle shows coverage and temperature of sample preparation and measurement reported in Figure 5.11b
Figure 5.11b - XSW Results, Node U testing, 0.11 ML Ag/Si(111). Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured reflectivity.
5.2.4 Node-V testing: C free, B free, Flat Si(111)

Figure 5.12 shows the available data for this configuration. Seen in Figure 5.12a, a carbon free surface with sharp 7x7 LEED structure was produced by Ishizaka/Shiraki oxide removal for five minutes at 920°C. 1.33ML of Ag was deposited at 400°C and flashed for 11 minutes at 650°C to remove coverage to 0.51 ML with a sharp √3 + faint 3x1 LEED structure. Synchrotron problems allowed only a few complete XSW and SEXAFS data sets to be taken, as seen by the large error bars of Figure 5.12b. Additional X-ray flux from the synchrotron source to increase counting statistics did not become available until after measurable surface contamination occurred.

With the previously gained knowledge of the profound effect of even slight carbon contaminations in mind, further work on this sample was abandoned. The results are included here for completeness along with forced fits for a totally random array of Ag atoms and a best estimate "χ by eye" fit.

![Ag/Si(111) Schematic of Growth Structures](image)

Figure 5.12a - Path-dependant XSW measurement, Node V testing. Open circle shows coverage and temperature of sample preparation and measurement reported in Figure 5.12b
Figure 5.12b - XSW Results, Node V testing, 0.5 ML Ag/Si(111). Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity. Insufficient data for meaningful statistical fits. Dashed theoretical fits are intended as baseline references.
5.2.5 Node-W testing: C free, B exposed, 0.5° miscut Si(111)

Results on stepped surfaces were of special interest in light of recent conjectures that both $\sqrt{3}$ and 3x1 structures require step edge reconstructions to form or, in absence of these, create hole-island pairs (essentially an artificial, 1 double-layer high step). Figures 5.13 show the effect of roughly 30 steps in our experimental coherence width on surfaces prepared of the same material and using the same techniques as for Node-S, T, U and V testing.

Surface was prepared by Ishizaka/Shiraki oxide desorption at 890°C for five minutes producing a sharp 7x7 structure. Ag was deposited on the surface held at 400°C to 0.15-0.2 ML coverage. LEED patterns showed easily attained and sharp Ag-($\sqrt{3} \times \sqrt{3}$)R30° and Ag-(3x1) patterns at 78 eV. XSW results show a striking difference from the flat Si(111) surfaces. Figures 5.13 b. c and d illustrate results at 400°C, 30°C and 500°C for a combination of $\sqrt{3}$ and (3x1)-Ag structures at 0.15 ML coverage. Coherent fractions, $F_c$, are roughly half of values previously seen at coherent positions, $\Phi_c$, of between 0.3 and 0.4. Further tests were conducted at 550°C in an attempt to determine $F_c$ and $\Phi_c$ for the 3x1 phase alone. Total desorption of 0.2ML occurs in 15 minutes at this temperature so, once again, only a low completeness data set was collected as shown in Figure 5.13e. By restricting $\Phi_c$ to values between 0.3 and 0.4, a convergence was forced with a fit $F_c$ in agreement with results at other temperatures. After over two hours at 550°C the spectra of Figure 5.13f was taken showing that a small random distribution of Ag atoms remains trapped most likely at step and defect sites as previously noted in the literature. A post-mortem examination of the surface showed no detectable Ag or carbon contamination.
Figure 5.13a - Path-dependant XSW measurement, Node W testing. Open circle shows coverage and temperature of sample preparation and measurement reported in Figure 5.13b, c, d, e, f.
X-Ray Standing Wave Results: Ag/Si(111)
$\sqrt{3X/\sqrt{R30^\circ} + (3X1)}$, 400°C, 0.2ML

<table>
<thead>
<tr>
<th>Node W</th>
<th>Coherent Fraction $f_c$</th>
<th>Coherent Position $\phi_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.29±0.11</td>
<td>0.49±0.05</td>
</tr>
</tbody>
</table>

Figure 5.13b - XSW Results, Node W testing, 0.2 ML Ag/Si(111), 400°C. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
Figure 5.13c - XSW Results, Node W testing, 0.2 ML Ag/Si(111), 30°C. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
Figure 5.13d - XSW Results, Node W testing, 0.2 ML Ag/Si(111), 500°C. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
Figure 5.13e - XSW Results, Node W testing, 0.2 ML Ag/Si(111), 550°C. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
Figure 5.13f - XSW Results, Node W testing, 0 ML Ag/Si(111), 550°C. (after desorption) Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity
5.2.6 Node-X and Y testing: (XSW not done)

5.2.7 Node-Z testing: C free, B free, 0.5° miscut Si(111)

Results from a new sample, prepared exactly as for Node-W testing with the exception of having wet-chemical cleaning and oxidizing done in borosilicate glassware is presented in Figures 5.14. Figure 5.14a outlines the preparation path for the surface at 400°C. LEED showed good $\sqrt{3}$, 3x1 and 1x1 spots with faint 7x7 spots remaining. Figure 5.14c is a duplication of the XSW results under the same conditions as for 5.14b with changes made in x-ray scattering protection and with the probe beam subtending 4.5X more surface area. The two figures can be considered indicative of the test-to-test variability of the method if it is assumed that no time dependent change in surface structure occurs. Further results at 30°C and 500°C are shown in Figures 5.14d and 5.14e confirming general observations that Ag atomic positions, $\Phi_c$ do not vary much as a function of temperature once the structure is formed. Slight increases in coherent fraction, $F_c$, are seen as temperature decreases, as expected from Debye-Waller effects.

![Ag/Si(111) Schematic of Growth Structures](image)

Figure 5.14a - Path-dependant XSW measurement, Node Z testing. Open circles show coverage & temperature of sample preparation & testing
X-Ray Standing Wave Results: Ag/Si(111)
\[ \sqrt{3}x\sqrt{3}R30° + (3\times1), 400°C, 0.25\text{ML} \]

Figure 5.14b - XSW Results, Node Z testing, 0.25 ML Ag/Si(111), 400°C. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
Figure 5.14c - XSW Results, Node Z testing, 0.25 ML Ag/Si(111), 400°C. Same conditions as 5.14b with changes in beam conditions. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
Figure 5.14d - XSW Results, Node Z testing, 0.25 ML Ag/Si(111), 30°C. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
Figure 5.14e - XSW Results, Node Z testing, 0.25 ML Ag/Si(111), 500°C. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
REM observations by Yagi\textsuperscript{200} and STM observations by Wilson and Chiang\textsuperscript{201} both confirm that $(\sqrt{3}\times\sqrt{3})R30^\circ$-Ag selectively forms at step edges. Calculations by Tong and Huang\textsuperscript{202} show readily that the $(7\times7) \rightarrow (\sqrt{3}\times\sqrt{3})$ transformation is greatly facilitated by the presence of a Si(111) double-layer step accommodating the Si self-adatoms of the $7\times7$ into an extension of the step edge. It is no surprise that Ag atoms remain trapped at step defects, Figure 5.13f, even after the remainder of the surface is Ag free.

5.2.8 Testing of Ag-$\sqrt{3}$ structures at atmospheric pressures

Tests of $(\sqrt{3}\times\sqrt{3})R30^\circ$-Ag/Si(111) structures with 31.6, 9.31, 2.16 and 0.48 ML coverages were done at atmosphere pressure under 99.997\% pure He cover gas. (The cover gas is essential since the three strongest Ag L$_{\alpha1}$, L$_{\alpha2}$ and L$_{\beta1}$ fluorescence lines are easily masked by Ar K$_{\alpha1}$, K$_{\alpha2}$ and K$_{\beta1}$ fluorescence lines from the 0.93 vol.\% Ar present in air.) As shown in Figures 5.15, the $\sqrt{3}$ structure is not preserved once exposed to the atmosphere, consistent with later findings of Schmitsdorf\textsuperscript{203} that surface passivation to oxidation does not hold at greater than $10^6$ Langmuir O$_2$ exposures. Additionally, the $\sqrt{3}$ Ag/Si(111) surface has been found not to be preserved when covered with other atmospheric gas layers such a H\textsuperscript{204} and NO\textsuperscript{205} at room temperature. In all cases, only a random distribution of Ag atoms were found with XSW for these air exposed Ag-(\sqrt{3}\times\sqrt{3})/Si(111) surfaces.
X-Ray Standing Wave Results: Ag/Si(111)

Sample BTL F.Z. Test A, R.T., 31.6 ML

Figure 5.15a - XSW Results, Post-mortem bench testing, 31.6 ML Ag/Si(111), R.T. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity
X-Ray Standing Wave Results: Ag/Si(111)

Sample C2 Test A, R.T., 9.3 ML

FIGURE 5.15b - XSW Results, Post-mortem bench testing, 9.3 ML Ag/Si(111), R.T.

Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
Figure 5.15c - XSW Results, Post-mortem bench testing, 2.16 ML Ag/Si(111), R.T. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity.
Figure 5.15d - XSW Results, Post-mortem bench testing, 0.48 ML Ag/Si(111), R.T. Top curve, fluorescent yield, measured values, error bars and theoretical fit. Bottom symbols and curve, measured values and theoretical fit to reflectivity
5.2.9 Summary of XSW results

XSW results are tabulated, along with reduced $\chi^2$ indications of goodness of fit in Table 5-1.

Table 5.1 - Summary of XSW findings for Ag/Si(111)

<table>
<thead>
<tr>
<th>Node</th>
<th>Figure</th>
<th>$\Theta$</th>
<th>Temp. $^\circ\text{C}$</th>
<th>$F_c$</th>
<th>$\Phi_c$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>5.7b</td>
<td>2.58</td>
<td>400</td>
<td>1.09 ± 0.33</td>
<td>0.79 ± 0.02</td>
<td>0.40</td>
</tr>
<tr>
<td>S</td>
<td>5.9</td>
<td>0.82</td>
<td>250</td>
<td>0.94 ± 0.17</td>
<td>0.20 ± 0.02</td>
<td>75.4</td>
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<tr>
<td>T</td>
<td>5.10b</td>
<td>0.13</td>
<td>400</td>
<td>1.01 ± 0.06</td>
<td>0.69 ± 0.01</td>
<td>2.40</td>
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<tr>
<td>U</td>
<td>5.11b</td>
<td>0.11</td>
<td>400</td>
<td>0.97 ± 0.15</td>
<td>0.69 ± 0.02</td>
<td>0.68</td>
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<tr>
<td>V</td>
<td>5.12b</td>
<td>0.5</td>
<td>400</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>W</td>
<td>5.13b</td>
<td>0.2</td>
<td>400</td>
<td>0.29 ± 0.11</td>
<td>0.40 ± 0.05</td>
<td>0.20</td>
</tr>
<tr>
<td>W</td>
<td>5.13c</td>
<td>&quot;</td>
<td>30</td>
<td>0.51 ± 0.18</td>
<td>0.37 ± 0.04</td>
<td>0.22</td>
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<tr>
<td>W</td>
<td>5.13d</td>
<td>&quot;</td>
<td>500</td>
<td>0.46 ± 0.14</td>
<td>0.30 ± 0.03</td>
<td>0.44</td>
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<tr>
<td>W</td>
<td>5.13c</td>
<td>&quot;</td>
<td>550</td>
<td>0.45 ± 0.52</td>
<td>0.38 ± 0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>Z</td>
<td>5.14b</td>
<td>0.25</td>
<td>400</td>
<td>0.82 ± 0.18</td>
<td>0.33 ± 0.02</td>
<td>0.21</td>
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<tr>
<td>Z</td>
<td>5.14c</td>
<td>&quot;</td>
<td>400</td>
<td>0.83 ± 0.09</td>
<td>0.36 ± 0.01</td>
<td>0.64</td>
</tr>
<tr>
<td>Z</td>
<td>5.14d</td>
<td>&quot;</td>
<td>30</td>
<td>1.00 ± 0.12</td>
<td>0.37 ± 0.01</td>
<td>0.59</td>
</tr>
<tr>
<td>Z</td>
<td>5.14e</td>
<td>&quot;</td>
<td>500</td>
<td>0.50 ± 0.12</td>
<td>0.39 ± 0.03</td>
<td>0.24</td>
</tr>
</tbody>
</table>
5.3 SEXAFS Bond Length Measurements

As outlined in Chapter 3, the Surface Extended X-ray Absorption Fine Structure (SEXAFS) technique can be used, as a first approximation, to determine atom-pair-specific bond lengths to within 4% and nearest-neighbor coordination to within 20%. Bond length results reported here can be confidently inter-compared since all contain the same error contributions from experimental and analytical methods. For absolute bond length measurements, careful propagation of errors indicates \( \pm 0.05 \) Å accuracy level. In this research, no attempt was made to determination coordination number and second nearest neighbor bond lengths.

X-ray Fine Structure (XFS) analysis in the Ag/Si system suffers from the lack of a reference material with known Ag-Si bond length to be used for the backscattering amplitude and phasing correction components of the data analysis. Following suggestions of Stöhr and Jaeger\(^{206}\), the experimentally determined corrections were taken from Pd\(_2\)Si as a model compound. It was hoped that the electronic structure of Pd, being only one 5s\(^1\) electron different than Ag, would provide the same correction factors since the core-potentials, the essential component for electron backscattering effects, should be for all purposes the same. One great advantage of this work over that of Stöhr and Jaeger’s comes from the ability to study K-edge absorption structure rather than L\(_{\text{III}}\) edge. Curved-wave electron wavefront propagation analysis and scattering is difficult enough for electrons with s-like character. Introducing p- and d- like character to the outwardly propagating wave can not yet be taken into account and is such complexity is usually ignored.

Experimentally, the sample fluorescence signal, Ag K\(\alpha_1\) and K\(\alpha_2\) at 22.163 and 21.990 keV respectively (K\(\alpha_{\text{ave}}\)=22.104 keV) is monitored through the re-entrant Be window snout with a Si(Li) detector. The electronic signal is amplified and
windowed to produce a signal to background count coincident with scanning of the incident X-ray energy through the Ag K absorption edge at 25.514 keV.

An inherent problem with Ag K edge XFS (X-ray Fine Structure) comes about due to interference by Compton scattered X-rays. First, the relatively high energy of the edge, 25.514 keV, and correspondingly short wavelength increases the Compton shift. Secondly, it is desirable to look along the polarization vector of the incident synchrotron bending magnet beam and there are constraints of the vacuum system such that the fluorescence signal is detected at 90° from the incident X-ray beam. The magnitude of the problem is illustrated in Figure 5.16 where Compton shifts at various incident energies are plotted over the energy range of a typical XFS scan. It can be seen by the figure to the right, that the Ag Kα signal from 1 ML in σ polarization geometry has a signal/noise ratio of only about 0.1 making counting times at X-ray fluxes of $10^{11}$ photons/sec incident, quite long for even 5% counting statistics.

An additional difficulty arises due to the peculiar behavior of small signals on sloping backgrounds. In the experimental case here, a narrow electronic window was placed around the Ag Kα1,2 peak and additional windows are placed above and below that signal window for background measurement and subtraction. In practice, the “signal” window is set by fluorescing the Ag standard, a strong signal, and setting windows to capture the appropriate signal and background channels. When measurements are made with a weak signal on a strongly sloping signal, the apparent signal maximum moves “up hill” from its “true” position. This shift is proportional to the signal (FWHM)$^2$ x (Background slope) and inversely proportional to the signal strength$^{207}$. In essence, useful signal is pushed into the upper background signal window and lost.
Experimental difficulties notwithstanding, SEXAFS data was taken on a number of coverage and temperature combinations in conjunction with XSW measurements in an attempt to locate Ag atoms with respect to the relaxed surface structures.

### 5.3.1 Node-S testing: C free, B exposed, Flat Si(111)

Sample preparation is as described in section 5.2.1. SEXAFS measurements in \( \sigma \) polarization orientation was performed immediately prior to XSW measurements of Figure 5.7b. The Figure 5.17a, below, indicates that this testing was done with 2.58 ML of Ag/Si(111) prepared and tested at 400°C, showing good \( \sqrt{3} \) LEED spots only.
As shown in Figure 5.17b, each of the three peaks A', A and B were filtered, transformed and phase adjusted using the Pd$_2$Si reference standard and using FEFF$^{208}$ or McKale$^{209}$ theory. Differences in predictions were within experimental variances. From McKale theory, dual distances for Ag-Si bond lengths of 2.2 and 2.5Å were determined for peaks A' and A respectively. Stöhr and Jaeger$^{206}$ found a similar A-A' pair and explained it as a splitting due to a Ramsauer-Townsend resonance in the backscattering amplitude as explained in Mott and Massey.$^{210}$ An Ag-Ag bond length of 3.27Å was determined for peak B, a value 13% larger than the bulk Ag-Ag distance of 2.9Å. Peak X appears in all of the fluorescence measurements and is a systematic artifact of the background fitting and subtraction method used for all data analysis.
Figure 5.17b - Node S SEXAFS measurement, 2.58 ML Ag/Si(111)- 400 °C (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window.
5.3.2 Node-T testing: C exposed, B exposed, Flat Si(111)

Sample preparation is as described in section 5.2.2. SEXAFS measurements in \(\sigma, 45^\circ\) and \(\pi\) polarizations were performed immediately concurrent with XSW measurements of Figure 5.10b. The Figure 5.18a, below, indicates that this testing was done with 0.12 ML of Ag/Si(111) prepared and tested at 400°C, showing good \(\sqrt{3}\) LEED spots only and a measured 19.3% C contamination. Numerous anneal cycles from 400°C to 600°C and back were done in an attempt to create a 3x1 structure. An anecdotal reference later discovered in the literature and confirmed by this research confirms that the Ag-(3x1)/Si(111) structure will not form in the presence of measurable carbon contamination even though the Si(111) surface prior to Ag deposition shows good 7x7 structure.

**Ag/Si(111) Schematic of Growth Structures**

![Diagram showing growth structures of Ag on Si(111)]

Figure 5.18a - Sample preparation, coverage and phase for Node-T SEXAFS measurements. Open circle depicts coverage and temperatures of duplicate measurements shown in Figure 5.18b and 5.18c.

Results from \(\sigma\) polarization tests indicate a 2.1 to 2.2Å Ag-Si bond length, peak \(A'\). Lengths for the \(A\) peak, Ag-Si bond as fit to 2.6. Peak \(C\) fits, modeled by phase shifts of an Ag-Ag bond pair, refines to an interatomic distance of 3.1Å assumed to be an in-plane second-nearest neighbor vector.
Figure 5.18b - Node T SEXAFS measurement, 0.12 ML Ag/Si(111)- 400 °C Wide slits (.5mm v x 5mm h) for large surface area averaging. Curves (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window
Figure 5.18c - Node T SEXAFS measurement, 0.12 ML Ag/Si(111)- 400 °C Narrow slits (.5mm v x 1mm h) for small surface area averaging. Curves; (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window
5.3.3 Node-U testing (No SEXAFS testing done)

5.3.4 Node-V testing: C free, B free, Flat Si(111)

Sample preparation, detailed in Section 5.2.4, producing a sharp $\sqrt{3}$ structure only at 0.51 ML coverage is illustrated in Figure 5.19a. SEXAFS data in $\sigma$ and $\pi$ polarizations were taken immediately after the XSW data of Figure 5.12b at $400^\circ$C.

Ag/Si(111) Schematic of Growth Structures

Figure 5.19a - Path-dependant SEXAFS measurement, Node V testing. Starting at 1.33 ML dose, sample preparation is shown by solid line. Open circle shows coverage and temperature of measurement reported in Figure 5.19b,c.

The dominant $A'$ peak in the $\pi$ “surface normal direction” polarization, Figure 5.19b, is fit with McKale theory to 1.4Å Ag-Si distance. Data for the $\sigma$ “in plane” polarization, Figure 5.19c, is either of too poor a quality to analyze (see section 5.2.4 for description of synchrotron problems) or actually has multiple, amorphous like, multi bond-length distances without a dominant first near-neighbor.
Figure 5.19b - Node V SEXAFS measurement $\pi$ polarization, 0.51 ML Ag/Si(111)-400 °C (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window
Figure 5.19c - Node V SEXAFS measurement $\sigma$ polarization, 0.51 ML Ag/Si(111)-400 °C (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window
5.3.5 Node-W testing: C free, B exposed, 0.5° miscut Si(111)

Immediately following the XSW measurements of Section 5.2.5, the sample surface remained carbon free and showed slight residual random located Ag (Figure 5.13f). This remaining adsorbate was removed by a five minute, 800°C flash then redeposition with Ag to 1.35ML coverage at 400°C. SEXAFS measurements were made at this high coverage (√3 structure only) then at 0.15 ML coverage (both √3 and 3x1 structures) produced by multiple annealing cycles to 700°C as outlined in Figure 5.20a.

\[ \text{Ag/Si(111) Schematic of Growth Structures} \]

![Graphical representation of growth structures](image)

Figure 5.20a - Path-dependant SEXAFS measurement, Node W testing. Starting at 1.33 ML dose, sample preparation is shown by solid line. Open circle shows coverage and temperature of measurement reported in Figure 5.20b,c.

Results of π polarization measurements, Figure 5.20b, shows a dominating A peak at 2.0 Å. Equivalent σ measurement, Figure 5.20c shows the amorphous-like, multi-peaked radial distribution function as in the previous section.
Figure 5.20b - Node W SEXAFS measurement π polarization, 1.35 ML Ag/Si(111)-400 °C (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window
Figure 5.20c - Node W SEXAFS measurement $\sigma$ polarization, 0.15 ML Ag/Si(111)-400 °C (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window
5.3.6 Node-X and Y testing: (SEXAFS not done)

5.3.7 Node-Z testing: C free, B free, 0.5° miscut Si(111)

Immediately before and after the XSW testing of Section 5.2.7, Figures 5.14b,c,d,e, SEXAFS measurements were taken. Initially, a coverage of 0.25 ML, good \( \sqrt{3} \) and (3x1) along with (1x1) and faint (7x7) LEED spots indicated, shown in Figure 5.21a, provided the radial distribution functions of Figure 5.21b with Ag-Si distance, peak B, of 2.8 Å.

\[
\text{Ag/Si(111) Schematic of Growth Structures}
\]

Figure 5.21a - Path-dependant SEXAFS measurement, Node Z testing. Starting at 0.6 ML dose, sample preparation is shown by solid line. Dashed line indicates structure and coverage change after 24 hour hold in UHV. Open circle shows coverage and temperature of measurement reported in Figure 5.21b,c and d.

The synchrotron x-ray source experienced an unplanned down period. After holding the sample at 400°C for 24 hours, minimum detectable carbon contamination of 0.02ML was found with loss of the 3x1 LEED pattern and apparent desorption, or redistribution, of Ag to the 0.1 ML level. SEXAFS measurements after this minuscule surface contamination in both\( \pi \) and \( \sigma \) geometries are presented in Figures 5.21c and d respectively.
Figure 5.21b - Node Z SEXAFS measurement $\pi$ polarization, 0.25 ML Ag/Si(111)-400 °C (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window.
Figure 5.21c - Node Z SEXAFS measurement $\pi$ polarization, 0.1 ML Ag/Si(111)- 400 °C (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window
Figure 5.21d - Node Z SEXAFS measurement $\sigma$ polarization, 0.1 ML Ag/Si(111)- 400 $^\circ$C (top) fluorescence signal, (middle) Chi function and fit from atom-pair shown in (bottom) radial distribution function with Hanning filter window.
5.3.8 Summary of SEXAFS results

Ag-Si and Ag-Ag bond length results from Figures 5.17 thru 5.21 are compiled in Table 5.2 below. In many cases, the individual single-shell filtered, back-transformed and fit results using either a Pd₂Si reference standard or theoretical spherical wave amplitude and phase shift functions calculated by Rehr’s FEFF²⁰⁸ method or McKale’s²⁰⁹ method are included. Clearly, bond lengths from π polarization measurements which enhance surface normal bond orientations, are much shorter than the σ or in-plane measurements.
Table 5.2: Summary of SEXAFS findings for Ag/Si(111)

All data at 400°C

A’, A = Ag-Si nearest neighbor bond lengths;
B= second nearest neighbor bond length (Ag-Ag or Ag-Si)

<table>
<thead>
<tr>
<th>Node</th>
<th>Figure</th>
<th>Θ</th>
<th>Pol.</th>
<th>Peak A’</th>
<th>Peak A</th>
<th>Peak B</th>
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</thead>
<tbody>
<tr>
<td>S</td>
<td>5.17b</td>
<td>2.58</td>
<td>σ</td>
<td>2.2 Å</td>
<td>2.5 Å</td>
<td>3.3 Å (Ave.)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>2.97 ± 0.04 Pd2Si</td>
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<td></td>
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<td></td>
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<td></td>
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<td>3.46 ± 0.02 FEFF</td>
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<td></td>
<td>3.38 ± 0.01 McKale</td>
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<tr>
<td>T</td>
<td>5.18b</td>
<td>0.12</td>
<td>σ</td>
<td>2.2 Å (Ave.)</td>
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<td>3.1 Å</td>
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<td>σ</td>
<td>2.1 Å (Ave.)</td>
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<td>V</td>
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<td>2.8 Å and 3.4 Å</td>
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<tr>
<td>Z</td>
<td>5.21c</td>
<td>0.10</td>
<td>π</td>
<td>1.5 Å (Ave.)</td>
<td>2.1 Å</td>
<td>2.8 Å</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1.28 ± 0.03 Pd2Si</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1.72 ± 0.04 FEFF</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.63 ± 0.04 McKale</td>
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<tr>
<td>Z</td>
<td>5.21d</td>
<td>0.10</td>
<td>σ</td>
<td>1.4 Å</td>
<td>2.0 Å</td>
<td>2.8 Å (Ave.)</td>
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<td></td>
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<td>2.98 ± 0.01 FEFF</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>2.87 ± 0.01 McKale</td>
</tr>
</tbody>
</table>
5.4 References - Chapter Five


207 A.H. Benade, Reference notes on the collection and treatment of data, Case Western Reserve University, Department of Physics, 1968.


CHAPTER SIX:
SUMMARY AND CONCLUSIONS

6.1 Summary Compilation of Results

6.1.1 Overview

The full three variable Plackett-Berman test matrix of Figure 5.6 was not completed but valid conclusions can be drawn from data comprising the six available test nodes shown in Figure 6.1. Sample parameters and corresponding XFS and SEXAFS data from Tables 5.1 and 5.2 are recompiled in Table 6.1 below for ease of comparison. As indicated by the half-circles on the diagram, valid Node U XSW but not SEXAFS and valid Node V SEXAFS but not XSW measurements were completed.

Figure 6.1 - Completed nodes of the three-level statistical screening experiment design. (Half symbol at Nodes U and V indicate only XSW or SEXAFS results available respectively.)
Table 6.1: Summary of Sample Preparation, XSW and SEXAFS findings for Ag/Si(111)

<table>
<thead>
<tr>
<th>Sample Parameters</th>
<th>XSW</th>
<th>SEXAFS</th>
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<tr>
<td></td>
<td>F_c (fraction)</td>
<td>Φ_c (position)</td>
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<tr>
<td>Node</td>
<td>B</td>
<td>C* (ML)</td>
</tr>
<tr>
<td>S</td>
<td>Y</td>
<td>0</td>
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<tr>
<td></td>
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<tr>
<td>T</td>
<td>Y</td>
<td>.19</td>
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<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>N</td>
<td>.30</td>
</tr>
<tr>
<td>V</td>
<td>N</td>
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<tr>
<td>W</td>
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<td>N</td>
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</table>

Notes: * Minimum carbon detection limit, 3.0 \times 10^{13} \text{C/cm}^2 or 0.038 ML
3D = 3D Ag islands on Ag-(√3x√3) σ, π = in-plane or out-of-plane polarization measurement states
Values in ( ) are general indications only and not strictly statistically valid
The following general observations can be made from the Table 6.1 for the clean surfaces. First, at low-elevated temperatures, 250°C and a capping coverage of 0.82 ML (Node S) Ag sits deeply embedded among the Si(111)-(7x7) self-adatoms at coherent position of $\Phi_c = 0.20$. In the high-elevated temperature regime, 400°C, and at low coverage, 0.2 ML (Node W & Z), Ag atoms begin to replace the Si self-adatoms. Since Ag atoms are insufficient in number to satisfy surface reconstruction needs, Si self-adatoms remain essential to the surface structure placing Ag at coherent position of $\Phi_c = -0.37$. Processing by over deposition and desorption back to low coverages increases coherent fraction (aligns Ag atoms better) than deposition at the exact 0.2 ML coverage studied but does not change the Ag atom locations.

Under the same elevated temperature conditions, 400°C, either C contamination or fully saturated Ag coverage satisfies surface dangling bonds allowing Ag to sit at a coherent position $\Phi_c = 0.69$ (C) or $\Phi_c = 0.79$ (Ag) from surface. Both scenarios produce well ordered Ag-$\sqrt{3}$ layers with high coherent fraction.

**6.1.2 Boron Exposure**

There is no effect from boron contamination by chemical processing in borosilicate (Pyrex™) glassware. (The reader is reminded that all other sources of B contamination; vacuum system viewports, boron nitride vacuum components, borosilicate glass insulators, etc. were all systematically eliminated as contributing factors.) Figure 6.2 compares node W and node Z XSW results (0.5° vicinal surfaces, C free, ~0.2 ML Ag at 30°C) with and without B exposure. No statistically significant differences in coherent position, $\Phi_c$ is seen. There is, however, significant difference in the coherent fraction, $F_c$, with the boron free surface exhibiting almost unity coherence. This is thought to be a path dependant surface preparation effect rather than a boron effect as will be elaborated on later. Similar results can be seen by
comparing like node W and Z results at 400°, 500° and 550°C. Bond lengths for the low coverage, low coherent fraction, node W experiments were not quantifiable and, in fact, seemed amorphous like. The node W, 1.35 ML, high coverage π polarization measurement shows the predominant 2.2 Å Ag-Si bond length. Comparable node Z bond lengths repeated the 2.2 Å length in addition to an almost unphysical 1.4 – 1.8 Å Ag-Si length and a 2.8Å Ag-Ag length.

Likewise, test nodes T and U can be directly compared as shown in Figure 6.3. No B effect is seen in these samples, both are flat surfaces, C contaminated (0.3 and 0.2 ML C respectively), ~0.2 ML Ag at 400°C. Node T Ag-Si bond lengths are consistently of 2.2 and 2.6 Å with an additional Ag-Ag length of ~3.2 Å. These are distances that will be shown to characteristically repeat for surfaces where the surface dangling bonds are satisfied by methods such as complete, ~ 1 ML Ag coverage or high, >.2 ML, carbon contamination.

As an aside, both moderate coverage, 0.8 and 0.5 ML nodes S and V (respectively) XSW tests, although statistically invalid, show indications of roughly the same Ag atomic positions at Φe =0.2.
Figure 6.2 - XSW measurement; effect of B exposure on nominal positions of $3\times 1 + \sqrt{3}\times \sqrt{3}R30^\circ$ Ag/Si(111) phases. Filled symbols, Node W (from Figure 5.13c). Open symbols, Node Z (from Figure 5.14d). Solid lines, theoretical fits to Rocking Curve and Coherent Position.
Figure 6.3 - XSW measurement; effect of B exposure on nominal positions of $\sqrt{3} \times \sqrt{3}$R30° Ag/Si(111) phase. Filled symbols, Node T (from Figure 5.10b). Open symbols, Node U (from Figure 5.11b). Solid lines, theoretical fits to Rocking Curve and Coherent Position.
With a null result for the Boron variable, we can straightforwardly reduce the dimensionality of the experimental matrix in a way that would have been done statistically if experimental results were available for all test nodes. That is, the test matrix can now be represented by the planar projection of the full test matrix along the boron axis into the two variable system of Figure 6.4.

![Reduced Dimensionality Three Level Plackett-Berman Statistical Screening-Experiment Design](Image)

Figure 6.4 - Reduced dimensionality test matrix removing Boron null test result.

### 6.1.3 Evaluation of the reduced test matrix

It is immediately apparent from Figures 6.2 and 6.3 that there is a major outward shift in Ag atomic positions of approximately 0.32 \(d_\text{Si(111)}\), almost 1Å, in the \(<111>\) direction between the, C free, flat surface, regardless of B, and the C contaminated, 0.5° vicinal surface, regardless of B. It is also apparent that there is an associated bond length change, speaking roughly; from the range of 1.4 -1.8Å to 2.2 Å for the \(A'\) peak, from 2.1 Å to 2.5Å for the \(A\) peak, and from 2.8 Å to 3.2 Å for the
B peak as schematically illustrated in Figure 6.5. So the immediate question becomes, which variable or variable combination is dominant?

![Figure 6.5 - Schematic model illustration of atomic arrangements in A) Node W or Z \( \Phi_c \) and bond lengths and B) Node T or U \( \Phi_c \) and bond lengths.]

First, the reader must be careful to compare only like-results from summary Table 6.1, above. Reliable node S, XSW and SEXAFS results are only available for high, 2.58 ML coverage. Node W SEXAFS results are only available, again, for high 1.35 ML coverage. Both sets of results must be excluded from the discussion to ascertain which, or what combination of carbon and boron are responsible for the surface shifts for the following reason. It is conjectured that the profound changes that accompany the transformation of the clean Si(111)-(7x7) DAS surface to the Ag-\( \beta \)-(\( \sqrt{3} \times \sqrt{3} \))R30°/Si(111) surface are complete at the 2/3 ML Ag deposition levels for temperatures between 200° and 400°C. It is also conjectured that the profound changes that accompany the transformation of this surface to the Ag-\( \gamma \)-(\( \sqrt{3} \times \sqrt{3} \))R30°/Si(111) surface are complete at the 1 ML Ag deposition levels for temperatures above 400°C. It is known, that these changes include the mass rearrangement of the 7x7 “self-adatoms” above 200°C, satisfaction of the bulk-like 1x1 surface dangling bonds and possibly the correction of the surface stacking fault at temperatures above 400°C.
as schematically illustrated in Figure 6.6. The atomistic processes associated with these atomic rearrangements, however, are not fully accounted for. Nevertheless, it is clear that the surface containing 0.1 ML Ag and the surface containing 1 ML Ag may be quite different with respect to the Si selvage atoms.

Figure 6.6 - Four layer model illustration of A) Takayanagi model of the Si(111) 7x7 surface and B) bulk-like Si(111) terminated surface.

6.1.4 0.5° Vicinal Surface Effects

Following the line of reasoning above, we can compare the bond length measurements from the two > 1 ML coverage experiments, nodes S and W, where the only free variable is surface miscut. Both indicate a shortest Ag-Si bond of 2.2 Å . If step edge patterning were a significant factor for the vicinal surface, there perhaps would not be as strong of a node S to node W bond length match. In this case there does not seem to be a measurable miscut effect. In like manner, also along the miscut axis, a comparison of node V and node Z bond lengths shows relatively short Ag-Si bond lengths. As compared to the large bond length shift of the C contaminated or the
high coverage surfaces, again, a minimal miscut effect. For these reasons, surface steps at this density level is thought to play a minor roll, if any, in the positioning of Ag $\sqrt{3}$ or 3x1 phases.

Most likely, it is not the fact that low step density ($0.5^\circ$ miscut) versus flat ($0^\circ$ miscut) shows no effect but rather that Ag deposits create pseudo-steps in the form of hole-island groups when natural step imperfections are not present. The act of sweeping Si(111)-(7x7) self-adatoms away by Ag deposits creates sinks to store these displaced Si atoms in lieu of insufficient storage space at naturally occurring defect sites.

6.1.4 Carbon Effect

Carbon is supremely good at modifying the 7x7 surface and satisfying dangling bonds better than Si or Ag adatoms. Silver, on the other hand, is a very weakly bonding species and for most intents and purposes is must be available in large, almost 1:1 quantities with the Si atoms to achieve the same surface modification effects. The effect of 0.2 ML C (as calculated by the conservative Seah equation, Chapter 3 equation 18) is equivalent to that of nearly a complete monolayer of Ag.

Supporting this assertion is anecdotal evidence presented in Chapter 5 as well as in the literature that the Ag-(3x1) structure can not be formed in the presence of C contamination. Additionally, others have quantified profound changes in the S-K growth mode and Ag(111) crystallite morphology at extremely high (hundreds of Å) coverage levels as a correlated with surface C contamination. All of these clues point to a C effect rather than a step effect as dominant.

Unfortunately, inexorably linked to this carbon effect is the mixed structure effect. That is, at low coverage, one can not form $\sqrt{3} + (3x1)$ mixed phase with C contamination and, conversely, one can not avoid forming this mixed phase on clean
surfaces by the desorption processing technique used in this study. Low and intermediate coverage deposits at temperatures less than 500°C, where only $\sqrt{3}$ structure is created, were not quantitatively successful within the experimental time available.

Carbon is an excellent Si(111) surfactant. As surface scientists we eschew C on the surface as contamination and have spent considerable effort to find suitable surfactants like Sb and Br that promote F-M, layer-by-layer growth. The role of C must be explored.

6.1.5 Surface Coverage / Surface Effect

An unexpectedly dominant effect proposed here as controlling the Ag-Si bond length as well as ensemble average position is total surface coverage. The higher the deposited Ag surface coverage, the more the Si(111)-(7x7) self-adatom layer is modified and bulk-like Si surface dangling bonds are satisfied.

This effect is implied by the following observations. Differences in the coherent fraction, $F_c$ but not position, $\Phi_c$ between results of node W and node Z (B vs. no-B) can be explained as proposed, by surface coverage effects. The preparation methods used to get to the same 0.2 ML Ag/Si test point were different illustrating the path dependence of this surface structure. For the node W surface, Ag was deposited on clean Si-(7x7) surface at exactly the 0.2 ML test coverage. Coherent fractions were low although coherent positions, $\Phi_c$ were equivalent to node Z tests. The node Z surface started with Ag depositions at a higher coverage, 0.6 ML, before reducing Ag to the 0.25 ML test coverage via surface desorption. The initial 7x7 adatom structure at least on the faulted half of the DAS 7x7 structure was swept away by this process before being re-formed in the desorption/rearrangement process.
6.1.6 Comparison to existing structural models

If we compare the experimental results of Table 6.1 with the model structure parameters of Table 2.3 we can make the correlations summarized in Table 6.2. First, for a fully developed, $\geq 1$ ML Ag-(\(\sqrt{3}\times\sqrt{3})\) R30°/Si(111) structure or a surface contaminated with C, both of which completely replace Si self-adatoms to satisfy surface dangling bonds, the three indicators of surface contraction, multiple Ag-Si bond lengths and Ag-Ag bond lengths are fully consistent with the HCT-8 model of Takahashi (CN252). In this model, Ag-Si bond length in the radial and side directions, as referenced to the Si trimer group are 2.57 ± 0.03 Å and 2.60 ± 0.01 Å respectively giving an Ag-Ag bond distance of 3.44Å. (The sum of non-bonding van der Waals radii for Ag-Ag is 3.44Å.) The Ag-Ag and Ag-Si bond lengths also fit the HCT-1, HCT-3, HCT-4, and SHCT variants of the model although model surface contraction information is unavailable. It is clear that only models containing Si and Ag trimers has the complexity of bond lengths seen in the experimental spectra.

Secondly, when examining the incipient [Ag-(\(\sqrt{3}\times\sqrt{3})\) R30°+Ag-(3x1)]/Si(111)-(7x7) surface, that is, a highly under-saturated Ag/Si surface where Si self-adatoms still play a significant role in surface dangling bond satisfaction; the SAV model (CN149) is the most consistent in the Ag-Ag and Ag-Si bond lengths but not surface contraction parameters.

The experimental data presented does not completely match all parameters of any of the models. This is not surprising and is, in fact, the problem that the collective Ag/Si research community has faced for almost forty years and is the reason for the numerous variations available for all models. This dissertation has chosen to track the HCT-x variations (0 through 11) specifically but adjustments to bond lengths, bond angles, adsorption sites, Si adatom inclusion, surface distortions and subsurface contractions are part of every model’s development. Bond length inconsistencies do
not trouble this author since a large variety can be accommodated with expansions and
rotations of the basic Si and Ag trimer units that make up the supported models. The
lack of agreement between this paper’s most concrete evidence, the coherent position
Φ_c and the available model-parameters is the most troubling but perhaps not
unexpected. The goal of the vast majority was to solve the Ag-√3 structure. The
result of this study provides an indication of the Ag incorporation process in action.
Coherent positions for the under saturated experiments match bond lengths of the
SAV model with the positions more typical of covalently bonded, simple H_3 site
adsorption.

Table 6.2 - Summary comparison of experimental and surface model matches.

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<tr>
<th>Model</th>
<th>(ref.)</th>
<th>Ag-Ag n-n (Å)</th>
<th>Ag-Si 1st n-n (Å)</th>
<th>Ag-Si 2nd n-n (Å)</th>
<th>Ag to 1st in-tact DL (Å)</th>
<th>Ag to bulk registry d-Si(111)</th>
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<tr>
<td><strong>Saturated surfaces (fully developed Ag-√3 phase coverage &gt;1 ML or C contamination)</strong></td>
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<tr>
<td>This Dissertation</td>
<td>Experimental Range</td>
<td>3.1 to 3.3</td>
<td>2.1 to 2.2</td>
<td>2.5 to 2.6</td>
<td>--</td>
<td>0.69 to 0.79</td>
</tr>
<tr>
<td>Ag on-top models</td>
<td>HCT-8 (CN252)</td>
<td>3.426, 4.938</td>
<td>2.593</td>
<td>2.596</td>
<td>3.055</td>
<td>+0.90</td>
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<td>IET (CN411)</td>
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<td>2.54</td>
<td>2.60</td>
<td>3.342</td>
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<td></td>
<td>HCT-1 (CN126)</td>
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<td>2.54</td>
<td>2.68</td>
<td>3.342</td>
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<td>HCT-3 (CN178)</td>
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<td>2.54</td>
<td>2.63</td>
<td>3.342</td>
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<td>HCT-4 (CN185)</td>
<td>3.3742, 5.1</td>
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<td>2.721</td>
<td>3.292</td>
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<td>Ag embedded models</td>
<td>SHCT (CN088) (CN137)</td>
<td>3.3602</td>
<td>2.593 (to Si overlayer)</td>
<td>2.608 2.730 2.778</td>
<td>2.6</td>
<td>+0.96^</td>
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<td>^ from estimates of CN191</td>
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<td>1.4 to 1.8</td>
<td>2.0 to 2.2</td>
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<td>0.3 to 0.4</td>
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<td>Ag on-top models</td>
<td>SAV (CN149)</td>
<td>2.88</td>
<td>1.838</td>
<td>2.540 2.985</td>
<td>4.31</td>
<td>+0.93 +0.81^</td>
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6.2 Conclusions

This is the first paper to show that there is no effect on the Ag/Si(111) structure from boron contamination by chemical processing in borosilicate (Pyrex™) glassware combine with low-temperature oxide removal used in this study. This is at variance with long standing and commonly accepted assertions about the ease of B surface contamination. The lower temperature oxide removal used in this study may be responsible for B desorption rather than commonly seen delta-doping effects.

This the first paper to actively examine carbon’s role in Ag/Si(111) structure formation. Carbon is found to produce three dramatic effects. First, carbon coverage at tenth ML levels was found to completely inhibit the formation of the Ag-(3x1)/Si(111) phase. Secondly, it is found that, at these C contamination levels, the Ag-(√3x√3)R30° layer is comprised of dual, Ag-Si bond lengths of 2.2 Å and ~2.6 Å, Ag-Ag bond lengths of 3.2 Å located at \( \Phi_c = 0.69 \) or equivalently 0.97 Å below the extension of bulk Si(111) planar positions in the <111> direction. From these numbers, a Si surface contraction of 0.2Å can be deduced based on an HCT type model. Finally, carbon is found to promote a very high degree of Ag surface order and surface relaxation in the low coverage Ag-√3 layer almost equivalent to that of a full monolayer Ag coverage. This is the first paper to quantify the magnitude of the effect of small amounts of surface carbon contamination on resulting structure and the first paper to provide direct measurement of the Si surface relaxation during the Si 7x7 to (Si + adatom) structural transition. We propose that since C is an excellent surface stabilizer and surfactant, it should be exploited when using Ag as a surface template for nanosciences and explored by device makers requiring better F-M layering.
This paper is the first to show, through XSW measurements during thermal desorption, that there is only one type of bonding site common to the Ag-$\sqrt{3}$ and Ag-(3x1) structures at desorption temperatures. Model proposals for the Ag-(3x1) structure must take this into consideration.

This paper is the first to show a new complex surface structural phase diagram built from the vast literature database. It is strongly asserted that the Ag-$\sqrt{3}$ phase does not consist of one static model structure, but rather, changes subtly at various critical coverages and temperatures into the final HCT-like model supported to-date. At low coverages and temperatures, a weak Ag$_2$Si-like agglomeration is proposed. These proposed Ag$_2$Si proto-clusters are formed from low coverage Ag and Si DAS adatoms and are consistent with observed low coherent fraction and “amorphous like” Ag-Si radial distribution function measurements. These are supplanted by a more ordered phase if adatoms had been previously swept to sinks or a more ordered, less tightly bound Ag phase at high coverage.

This is the first paper to propose the existence of $\beta$-(\sqrt{3}x\sqrt{3})R30° and $\gamma$-(\sqrt{3}x\sqrt{3})R30° forms based on the new surface structure diagram details and upon measurements of unsaturated, low-coverage measurements and saturated, high-coverage measurements of structural parameters. The $\beta$-$\sqrt{3}$ form is proposed to have many features in common with the SAV class of models including an in-tact although highly strained surface double layer and slightly embedded Ag atoms. The SAV class of models must be modified to allow a variable critical coverage down to, on average, a lower temperature limit of $\theta_c = 2/3$ ML. The $\gamma$-$\sqrt{3}$ form is proposed to conform with the HCT class of models where the equivalent of the top half of the former Si double layer has been sloughed off, Ag atoms trimerize and expand while Si surface atoms trimerize and contract effectively lifting the Ag atoms from their formerly cramped positions. The proposed $\beta$- and $\gamma$- forms are illustrated generally in Figure 6.7.
This paper confirms that the exposure of \( (\sqrt{3} \times \sqrt{3})R30^\circ \) Ag/Si(111) surface to atmosphere randomizes Ag atomic positions, but does not eliminate Ag from the surface. This is in agreement with other studies that show exposure to H\(_2\), O\(_2\), Ag, etc. causes disruption of the \( \sqrt{3} \) structure and pile-up of Ag into 3D crystallite forms.

Why are there so many conflicting models for Ag/Si(111)? Simply put, because there actually are a continuum of atomic positions available for Ag/Si(111) depending on coverage, surface contamination and surface phase preparation path. Although the HCT model seems to be the currently favored structure for the full 1 ML coverage equilibrium surface, the Ag/Si(111) system is extremely sensitive to metastable and kinetically induced effects rather than thermodynamically driven equilibrium effects. Surface Si adatoms must be incorporated as a vital component of
the structure. For example, a Ag-$\sqrt{3}$ structure formed at 0.25 ML on a 7x7 surface has different atomistic details than a $\sqrt{3}$ structure formed by deposition to high coverage and then thermally desorbed back to 0.25 ML. The former treatment accommodates Ag into a modified DAS structure, the latter modifies the DAS structure, especially the Si adatoms prior to taking their place as the sole gratification for surface dangling bonds. The end point is the same, the $\sqrt{3}$ structure without careful spot profile analysis is the same but the specific atomic arrangements of Si and Ag look different to different probe techniques. In short, there are many paths to the same surface projected Ag-($\sqrt{3}x\sqrt{3}$)R30° structure.

This Ag/Si(111) system is complex and subtle, yet in it’s complexity lies the potential for great utility. It is time to put that tremendous potential to use in practical applications.