

MILLISECOND CRYSTALLIZATION KINETICS OF $\text{InGaO}_3(\text{ZnO})_m$

A Thesis

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ABSTRACT

As display technologies continue to advance, new materials are required for the thin film transistors that control each pixel. While silicon has been the dominant active channel material, oxide semiconductors such as InGaZnO (IGZO) are increasingly being used due to their superior performance. However, IGZO is a ternary system with compositional dependent properties. Along one pseudobinary, the $\text{InGaO}_3(\text{ZnO})_m$ alloys display natural superlattices that have previously only been grown with high temperature ($> 1,000^\circ\text{C}$), long-duration anneals.

In this work, we study the formation of these natural superlattice structures using co-sputtering of IGZO and ZnO, and laser spike annealing (LSA). Compositions from pure $\text{In}_2\text{Ga}_2\text{ZnO}_7$ to pure ZnO were explored with peak anneal temperatures from 600°C to 1400°C and dwell times from $150\ \mu\text{s}$ to 10 ms. The kinetics of crystallization were studied using micro-wide-angle X-ray scattering with a $\sim 20\ \mu\text{m}$ FWHM beam. Using the lateral gradient LSA method, structural changes as a function of the peak annealing temperature and dwell time were analyzed, and the onset of crystallization was determined. Our results indicate that as-deposited Zn-rich films form nanocrystallites with compositionally disordered structures similar to *wurtzite*. This structure is unstable and transforms to a superlattice after annealing. Activation enthalpies for crystallization were determined to range from 1.5 to 4 eV with increasing Zn content. The increase in activation enthalpy with higher Zn content indicates that Zn acts as a barrier to the growth of the superlattice. We propose two potential models to explain the increased activation enthalpy and formation of the superlattice. The

first is based on the diffusion of Zn out of the superlattice structure and into a surrounding Zn-rich amorphous IGZO region. The second is the spinoidal-like decomposition of the as-deposited compositionally disordered structure where the In atoms form coherent layers to achieve the superlattice structure.

BIOGRAPHICAL SKETCH

Kate Roach graduated with her B.S. in Materials Science and Engineering from Cornell University in 2015. During her time as an undergraduate, she became involved with Professor Michael Thompson's group in 2013 on the IGZO project. Her undergraduate work focused on the impact of post-deposition annealing environments on the electrical characteristics of IGZO films. Kate has also been heavily involved with the rowing team during her time at Cornell, and likes to think of rowing as her second major.

"Strength does not come from a physical capacity. It comes from an indomitable will." -Mahatma Gandhi

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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 Introduction

Display technology has progressed significantly since the decline of cathode ray tubes (CRTs) that once dominated the market. CRTs have been replaced today with plasma, liquid crystal displays (LCDs), and more recently organic light-emitting diode (OLED) displays. While silicon has traditionally been used as the active semiconductor in these displays, the push to active-matrix OLEDs (AMOLEDs) and flexible substrates requires higher performing materials with large area uniformity. This has led to the development of oxide semiconductors such as indium gallium zinc oxide (IGZO) for use as the active material in thin film transistors (TFTs).

IGZO is a ternary system of In_2O_3 - Ga_2O_3 - ZnO . Currently, amorphous IGZO (a-IGZO) is the leading amorphous oxide semiconductor (AOS) in commercial applications [1]. Performance is strongly dependent on composition with mobilities exceeding $50 \text{ cm}^2/\text{Vs}$ for In-rich alloys [2, 3]. Even higher mobilities of $> 70 \text{ cm}^2/\text{Vs}$ can be achieved with novel processing such as laser spike annealing (LSA) [4]. However, instabilities under positive gate bias stress and negative gate bias illumination stress remain critical issues, with extensive efforts being taken to identify underlying mechanisms and determine practical solutions [5, 6]. Recent work has suggested an alternative IGZO morphology, known as c-axis aligned crystalline (CAAC), has the potential to address some of these challenges. The conditions for forming CAAC IGZO are not well-understood, with crystallization normally occurring during deposition on substrates held at

temperatures near 300°C or above. Recent studies suggest that this crystallization behavior is a sensitive function of the composition. In particular, reduced Zn concentrations result in an increase of the crystallization temperature [7].

In this thesis, I explore the role of composition on the crystallization behavior of IGZO using co-sputter deposition and LSA. A lateral gradient spatial profile method was coupled with micro-wide-angle X-ray scattering (μ -WAXS) to probe the behavior with varying temperature in steps on the order of 10°C. The behavior from ambient conditions to peak temperatures near 1,400°C was explored to determine structural changes and crystallization kinetics.

1.2 Current Technology

Hydrogenated amorphous silicon (a-Si:H) has dominated the TFT market due to low deposition temperatures ($< 350^\circ\text{C}$) and large scale processability. However, a-Si:H is limited by low mobilities ($< 1 \text{ cm}^2/\text{Vs}$), instability under illumination [8], and gate bias stress [9]. The low mobilities seen in a-Si:H devices originate from the strained sp^3 bonds that dominate the carrier pathway, leading to a high density of deep and localized states below the conduction band minimum, causing carrier trapping. Polycrystalline silicon (poly-Si) has also been investigated for TFT applications, with many advantages over a-Si:H including carrier mobilities above $100 \text{ cm}^2/\text{Vs}$ and improved stability. However, grain boundaries lead to inhomogeneities in device turn-on voltage (V_{on}) [10]. In addition, the high processing temperatures ($\sim 650^\circ\text{C}$) required to form the crystalline morphology make poly-Si TFTs less favorable for commercial applications [11].

1.3 Oxide Semiconductors

In the 1950's, oxide semiconductors such as ZnO were studied as active layers in semiconductor devices, intended to replace traditional semiconductors such as Si [12]. The results of advances in oxide material growth and deposition, as well as an understanding of intrinsic properties, proved that oxide semiconductors could compete with traditional semiconductors [13]. ZnO was predicted to produce good TFTs because of its high single crystal Hall mobility ($> 200 \text{ cm}^2/\text{Vs}$) and the ability to readily form thin films on unheated substrates. TFTs using ZnO as the semiconductor material demonstrated field-effect mobilities up to $40 \text{ cm}^2/\text{Vs}$ [14]. Unfortunately, ZnO TFTs suffer from the same grain boundary effects as poly-Si, and the amorphous phase is difficult to achieve. Another downside to the use of ZnO is the high density of mobile electrons (usually $\gg 10^{18} \text{ cm}^{-3}$) in the undoped state. This makes the control of carrier concentration difficult, which is critical in semiconductors, and leads to unstable TFTs as the channel conductance and V_{on} cannot be controlled.

One way to control the carrier concentration is by controlling the number of oxygen vacancies. Oxygen vacancies generate two free electrons that are available for conduction [15]. There are two types of oxygen vacancies that can form: low and high-coordination. A low-coordination vacancy acts as a shallow donor state while a high-coordination vacancy leaves behind a large empty space that disrupts metal cation bonding networks and yields deep trap states and donor states. Films with a high concentration of oxygen vacancies exhibit semi-metallic behavior due to their high carrier concentration. However, when the donor states are ionized to their 2^+ state, they act as charge scattering sites that decrease the mobility of the film.

Indium, gallium, zinc and tin are all good transparent conducting oxides due to their wide bandgaps and unoccupied s orbitals that act as the electron path [16]. While amorphous indium zinc oxide (a-IZO) is another well studied material, the incorporation of gallium, which forms a stronger bond with oxygen, is important in obtaining stable materials and controlling the carrier concentration. This is true only to a certain extent, as the addition of too much gallium causes the electron mobility to deteriorate [13]. Mixing gallium with the already proven successes of zinc and indium allows for more stable devices to be produced. The success of this mixture of elements was demonstrated when the first a-IGZO TFT was fabricated by the Hosono group in 2004, having much improved performance compared to a-Si:H [16].

Currently, a-IGZO is the only demonstrated material to balance high mobility with large area uniformity [17], solving the problem of low mobility in a-Si:H as well as the nonuniformity issues in poly-Si TFTs. The differences in mobility are due to differences in electronic structure between the two materials. Silicon has a conduction band minimum composed of anti-bonding and bonding hybridized sp^3 orbitals. The spatial directivity of the hybridized sp^3 orbitals causes strained bonds which leads to carrier trapping and deteriorated conduction pathways. In comparison, the conduction band minimum of post-transition-metal (e.g. In and Ga) oxide semiconductors is composed of metal ns orbitals (where n is the principal quantum number) as shown in Figure 1.1. These orbitals are spherical and can directly overlap even with distorted metal-oxygen-metal bonds in the amorphous structure. This allows amorphous oxide semiconductors to exhibit mobilities comparable to those observed in the crystalline phase ($10\text{-}50\text{ cm}^2/\text{Vs}$), making IGZO ideal for TFT use [1, 18].

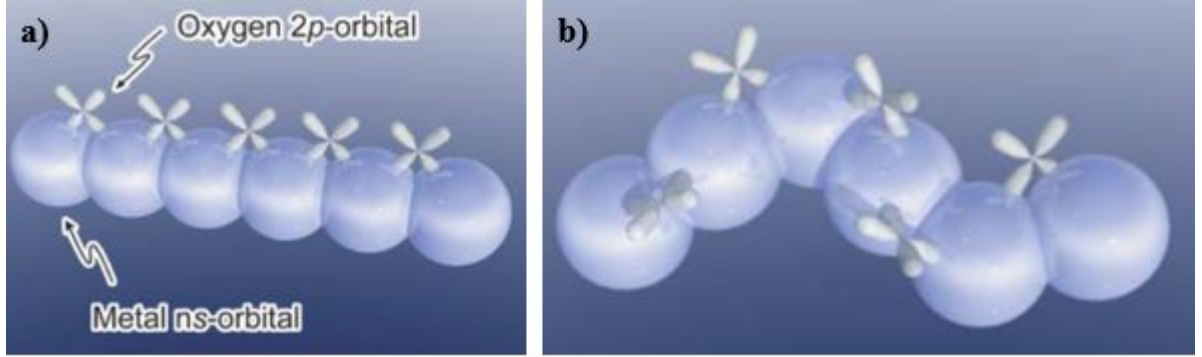


Figure 1.1: Carrier transport paths as proposed by Kamiya et al. [16] for post-transition-metal oxide semiconductors for a) crystalline and b) amorphous structures.

1.4 c-axis Aligned Crystalline (CAAC) IGZO

While a-IGZO is the current state of the art AOS for commercial applications, instabilities under positive gate bias stress and negative gate bias illumination stress remain critical issues [5, 6]. Recent work has suggested an alternative IGZO morphology with the potential to address some of these challenges: c-axis aligned crystalline (CAAC) IGZO [19, 20]. Initial reports suggested that CAAC IGZO TFTs were reliable, exhibited low off-state leakage currents, and had saturation mobilities exceeding $20 \text{ cm}^2/\text{Vs}$ [21]. It is suggested that CAAC may be a viable path to producing even more stable TFTs [22].

The structure of CAAC lies closer to crystalline than amorphous. However, CAAC appears to lack real grain boundaries with hexagonal arrangement of the a-b planes and continuous transition of alignment between domains. Work by Lynch et al. [19] showed CAAC to be composed of wavy sheets of c-axis aligned planes with lateral extensions on the order of 10's of nm. While the formation of this structure is not well understood, theories include the sputtering of 'pel-

lets' along cleavage planes of the polycrystalline IGZO target or a nucleation mechanism similar to that proposed for ZnO [19, 22]. Temperature both during and after growth has been found to have a large impact on CAAC formation, with post-deposition annealing shown to increase the amount of alignment [22]. During growth, optimal alignment of CAAC occurred near 300°C with a 1:1:1 In:Ga:Zn ratio target (InGaZnO_4). However, higher temperatures are necessary for films with less Zn (2:2:1 cation ratio or $\text{In}_2\text{Ga}_2\text{ZnO}_7$) [7]. This observed composition dependence was a motivating factor behind the current work.

1.5 Characteristics of ZnO and $\text{InGaO}_3(\text{ZnO})_m$

1.5.1 ZnO

Under ambient conditions, ZnO prefers the *wurtzite* crystal structure. The other two phases it can form, *rocksalt* and *zincblende*, are only seen at high pressures or during growth on a cubic substrate, respectively [23]. *Wurtzite* has a hexagonal unit cell with two lattice parameters, a and c , with an ideal ratio of $c/a = 1.633$. For ZnO, the c/a ratio is 1.602, slightly lower than ideal due to differences in electronegativity and structural defects [24].

Fabrication of TFTs using ZnO is typically accomplished using RF magnetron sputtering from ZnO targets [25]. Even deposited at room temperature, films are typically polycrystalline with preferential c-axis alignment normal to the film [26]. The mechanism for growth of textured ZnO on an amorphous substrate involves an initially disordered layer (~ 5 nm) followed by the nucleation of crystallites and, if substrate temperature is high enough to induce

coalescence, ordered growth [27, 28]. An amorphous ZnO morphology can be obtained through the use of cryogenically cooled substrates near 77 K during deposition for pulsed laser deposition, or below 325 K for reactive sputtering from a metallic Zn target [29, 30].

1.5.2 $\text{InGaO}_3(\text{ZnO})_m$

Studies on the structure of IGZO materials first began in 1985 by Kimizuka and colleagues [31–33]. Homologous oxides $\text{RMO}_3(\text{ZnO})_m$ ($R = \text{Sc, In}$; $M = \text{Al, Ga, Fe}$) are layered structures composed of alternating RO_2 layers and $m \pm 1$ (M/Zn)-O blocks, where m is the number of ZnO components [33]. $\text{InGaO}_3(\text{ZnO})_m$ has a $\text{Yb}_2\text{Fe}_3\text{O}_7$ -type structure and is isostructural with $\text{InFeO}_3(\text{ZnO})_m$. Both $\text{InFeO}_3(\text{ZnO})_m$ and $\text{InGaO}_3(\text{ZnO})_m$ have been shown to alternate between the $R\bar{3}m$ symmetry when m is odd and the $P6_3/mmc$ symmetry when m is even due to alternating inversion boundaries [34]. Structural details from these single-crystal studies often report a mixture of $m \pm 1$ phases. For InGaZnO_4 , the structure can also be considered to consist of edge sharing Zn/Ga- O_5 trigonal bipyramids sandwiched by monolayer edge-sharing InO_6 octahedra [31]. An example of this structure can be seen in Figure 1.2. With increasing values of m , there exist $m + 1$ layers of Zn/Ga between In layers. Recently, Narendranath et al. [35] investigated the coordination geometries of Zn and Ga inside the bulk of these layered structures. Their results indicate a stratification of an outer Zn layer with a random mixing of Ga and Zn inner layer where Zn shifts more from pentacoordinated to tetraordinated with greater values of m .

These superlattice structures can be identified based on their X-ray diffrac-

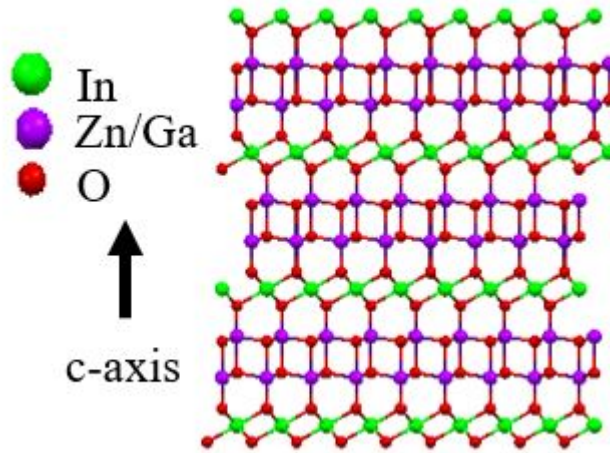


Figure 1.2: Ball and stick model of InGaZnO₄ ($m = 1$).

tion patterns. Figure 1.3 shows powder diffraction patterns for Phases I to VI and ZnO where Phase I corresponds to $m = 1$ (InGaZnO₄), Phase II corresponds to $m = 2$ (InGaZn₂O₅), etc. With increasing m values, a greater number of lower angle periodic peaks, which are indicative of the layered structure, appear. The number of lower angle periodic peaks that appear corresponds to $m + 1$. Additionally, the strongest peak for Phases I through VI is seen to shift to larger 2θ values with increasing m .

Temperature plays a large role during both the growth of these layered structures as well as during post-deposition annealing. Crystallization and growth mechanisms were studied by Nomura et al. [36] using reactive solid-phase epitaxy and furnace annealing up to 1,400°C. They showed single-crystal films formed when growth occurred from a ZnO epitaxial seed layer that acted as a template for further aligned growth. Without the ZnO layer, even samples heated at 1,400°C were polycrystalline. Lateral growth proceeded three orders of magnitude faster than out of plane growth, indicating that diffusion proceeds more quickly within the Ga/Zn layers than across the InO₂ layers. This same

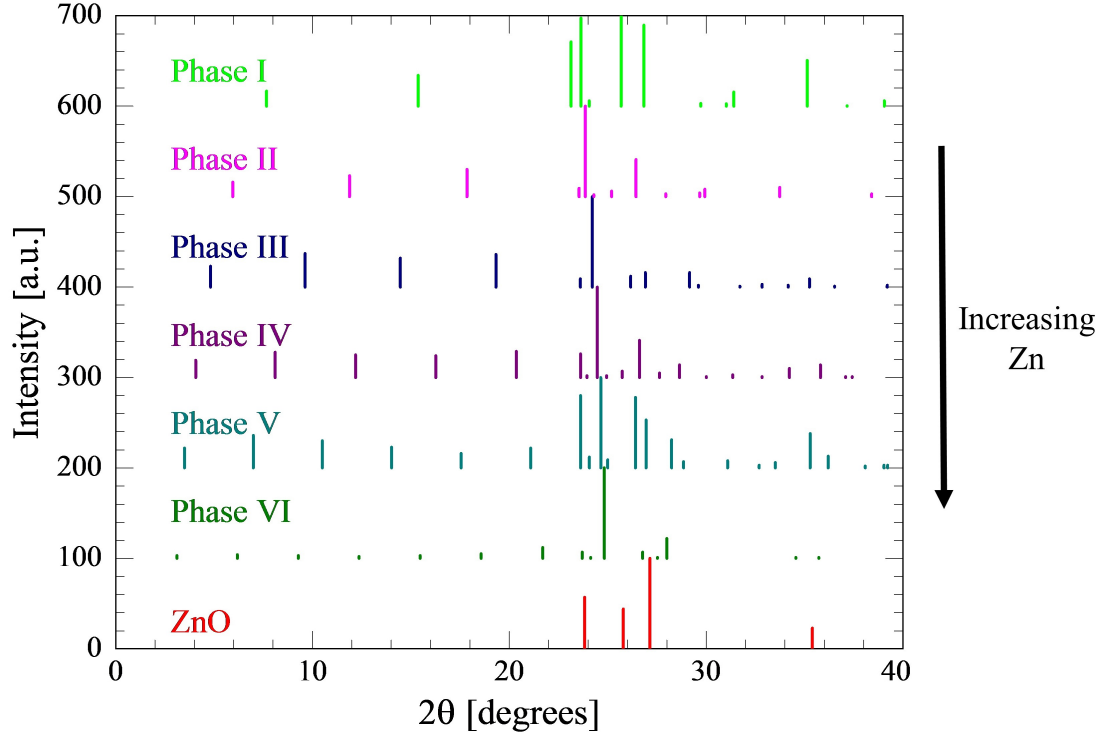


Figure 1.3: Powder diffraction patterns for Phases I through VI and ZnO using an X-ray wavelength of 1.162 Å

growth technique was used to fabricate a single crystal $\text{InGaZn}_5\text{O}_8$ TFT with a field-effect mobility of $80 \text{ cm}^2/\text{Vs}$ [37].

Other studies using ZnO buffer layers to change the composition of the resulting films have been performed. Seo et al. [38, 39] reported the growth of $\text{InGaO}_3(\text{ZnO})_m$ structures using various thicknesses of ZnO buffer layers below and above the deposited IGZO film, and annealing at $1,000^\circ\text{C}$ for multiple hours. However, with buffer layer thicknesses above 100 nm, the excess ZnO disrupted the formation of the natural superlattice structure.

1.6 Annealing Methods

Annealing of IGZO can be done to produce structural changes as well as improve device performance through the reduction of trap states near the conduction band minimum [40]. Furnace annealing in air is a common method for studying the crystallization behavior of IGZO. Suko et al. [41] studied the crystallization of a-IGZO to InGaZnO₄ from 300°C to 1,000°C in increments of 100°C and found that polycrystalline films began forming at 700°C. This is in good agreement with Cho et al. [42] who report a crystallization temperature of 630°C. Using high resolution transmission electron microscopy, Suko et al. also observed that crystallization began at the film surface, likely due to the greater mobility of those atoms as opposed to those in the bulk. They predicted the preferred c-axis orientation of the crystallites was due to the low surface energy of (111) in *bixbyte*-type In₂O₃, which corresponds to the $\langle 001 \rangle$ direction of the IGZO structure.

Lasers have also been used to anneal IGZO and study crystallization. Nakata et al. [43] report the existence of two sharp peaks at 2θ values 31° and 36° during X-ray diffraction that represent the crystallization of IGZO using an excimer laser with nanosecond pulses. The peak at 36° is somewhat disputed, and other excimer laser annealing studies have suggested that it is due to the formation of Zn₂SiO₄ at the substrate interface or the existence of a spinel structure [44, 45]. Further, it has been suggested that the crystallization depends on whether or not films are initially aligned, as the 36° peak was not seen after crystallization of CAAC [45]. The benefits of using laser annealing for fabricating devices include the production of fewer oxygen vacancies due to the short time scales, localized heating, and minimal damage to the substrate.

CHAPTER 2

EXPERIMENTAL

2.1 Sputter Deposition

Sputtering is a common physical vapor deposition technique that has been widely adopted for the commercial deposition of IGZO to deposit uniform, large area films. The process involves ejecting material from a target onto a substrate in a high vacuum environment by bombardment with energetic ions such as Ar^+ . Ejected target atoms are subsequently deposited on the substrate or chamber wall. As ejected material coalesces on the substrate, layers of atoms are formed to produce thin films. Changing deposition conditions, including substrate temperature and sputtering gas, can be used to fabricate thin films with specific properties. Additionally, radio frequency (RF) and direct current (DC) power supplies can be used. For oxides such as IGZO, RF sputtering with a frequency of 13.56 MHz has become a common method of deposition in order to overcome charge buildup in the oxide target that can occur using DC sputtering. The use of a magnetron allows a more efficient deposition process by confining the charged plasma particles close to the surface of the sputter target. In addition, multiple targets can be bombarded in unison (co-sputtering) to create composition gradients across the substrate if the substrate is not rotated.

In this study, substrates of single crystal highly doped (100) Si wafers (0.01-0.02 $\Omega\text{-cm}$) were thermally oxidized in dry $\text{O}_2 + 3\% \text{ HCl}$ to form a ~ 100 nm oxide. IGZO films were deposited with powers ranging from 0-180 W for 30 minutes using 13.56 MHz RF magnetron sputtering without any intentional heating using two separately controlled targets. 2-inch sintered polycrystalline

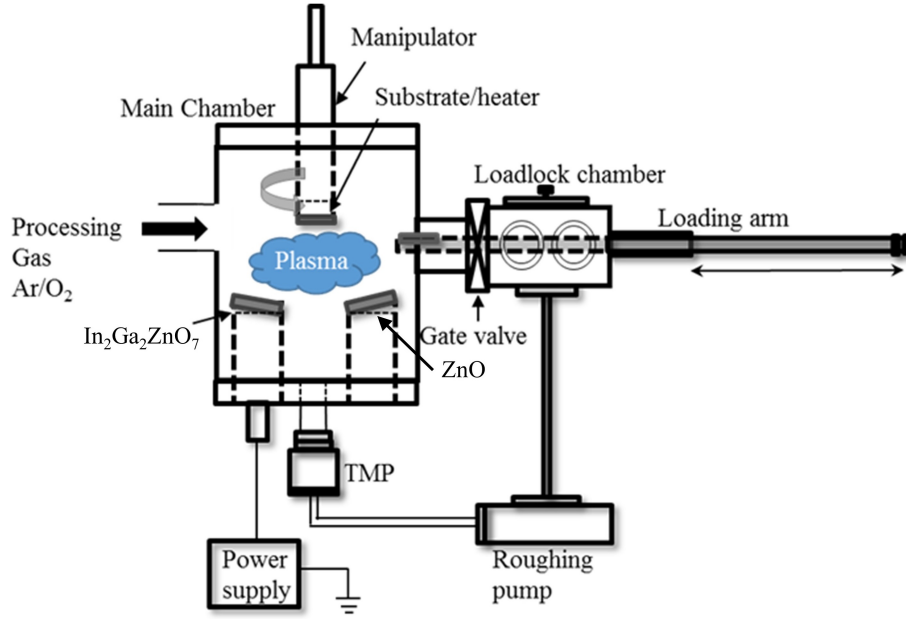


Figure 2.1: Major components of the sputter system.

targets of $\text{In}_2\text{Ga}_2\text{ZnO}_7$ and ZnO were used in a dedicated vacuum system with a 10^{-8} Torr base pressure, as shown in Figure 2.1. The $\text{In}_2\text{Ga}_2\text{ZnO}_7$ target was purchased from AJA International, Inc. (purity = 99.99%) and the ZnO target was purchased from Kurt J. Lesker Company (purity = 99.999%). Prior to deposition, the substrates and chamber were cleaned with an O_2 plasma for 5 minutes at 15 mTorr formed by powering the sample holder with 40 W RF. To ensure uniform thickness and more homogeneous film composition, substrates were rotated during deposition at 20 RPM, unless a thickness gradient was desired. Sputtering pressure and Ar/O_2 ratio remained constant for all samples at 5 mTorr and 9/1 with a total flow rate of 10 sccm. RF power of the ZnO target and $\text{In}_2\text{Ga}_2\text{ZnO}_7$ target was varied independently between 0 and 180 W during co-sputtering to achieve compositions between $\text{In}_2\text{Ga}_2\text{ZnO}_7$ and pure ZnO . Details specific to each sample can be found in Table 2.1. Targets were pre-sputtered for 5 minutes prior to opening the shutter to remove contamination

Sample	ZnO Power [W]	IGZO Power [W]	Time [min]	Thickness [nm]	In/Ga ratio	m
1	180	0	30	140	0	∞
2	180	120	30	224	0.92	5.96
3	180	180	15	40-220	1.06	3.94
4	120	180	30	214	1	2.63
5	60	180	30	154	1.11	1.36
6	180 (2 min)	180 (28 min)	30	122	1.09	0.71
7	0	180	30	121	1.08	0.45

Table 2.1: Deposition parameters and properties for all samples listed in order of decreasing m values.

from the surface of the target.

The composition and thickness of sputtered films can be controlled using the power supplied to each target. Figure 2.2 shows the changes in deposition rate with power for both the $\text{In}_2\text{Ga}_2\text{ZnO}_7$ and ZnO target, as well as the compositions in terms of m that can be achieved by varying the ratio of the power supplied to both targets, where m indicates the Zn content of the films.

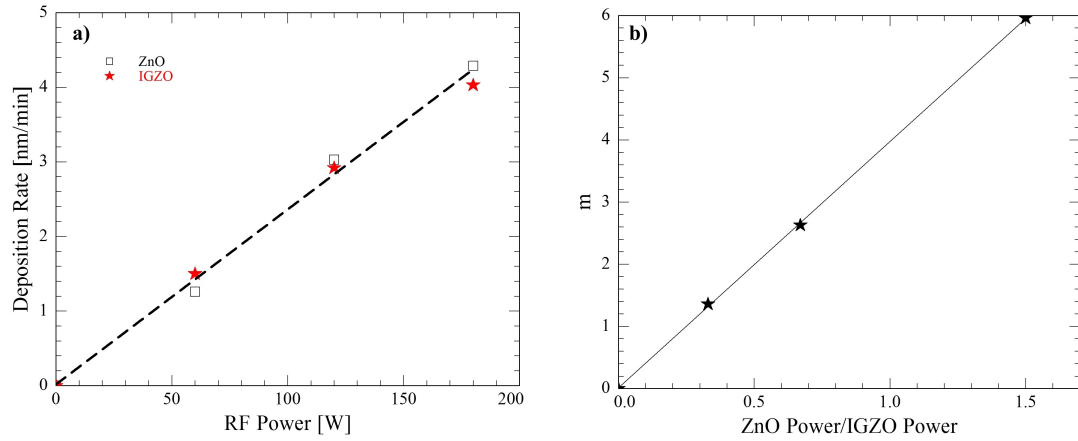


Figure 2.2: a) Deposition rate vs. RF power for ZnO and IGZO targets. b) Composition value m vs. the ratio of power [W] to the ZnO and IGZO targets.

2.2 Film Thickness

Film thickness measurements were performed using both profilometry and optical reflectivity techniques. For uniform samples, thicknesses were determined using profilometry on lithographically patterned surfaces. Microposit S1813 photoresist was used to pattern features with $100\text{ }\mu\text{m}$ wide lines spaced $100\text{ }\mu\text{m}$ apart. After development, a solution of 5% volume HCl was used to etch the IGZO and ZnO films. Depending on the Zn content of the film, etch times ranged from 10 seconds to three minutes, with less time needed for Zn-rich films. After etching, the photoresist was removed using acetone and isopropyl alcohol. Trench heights were measured using a Tencor P-10 profilometer. Five measurements were made at two different places on the sample, with the average of these ten measurements being reported as the film thickness.

For sample 3 ($m = 3.94$), the substrate was not rotated during deposition resulting in a thickness gradient across the film. To measure the minimum and maximum thickness values, ellipsometry was used to model the refractive index and extinction coefficient as a function of wavelength for IGZO. These values were then used with a Filmetrics F40 optical measurement system to determine the film thicknesses.

2.3 Compositional Analysis

During sputtering, the resulting composition of the thin film may not be the same as the composition of the target due to factors including varying elemental sputter yields and substrate temperature. To determine the composition of

the deposited films, inductively coupled plasma optical emission spectroscopy (ICP-OES) was used. This method involves measuring pure In, Ga, and Zn (at milligram precision) standards dissolved in dilute HCl, HNO₃, and deionized water. Four standards were made for each element to cover an order of magnitude concentration range. These standards were then run through an inductively coupled plasma to produce excited atoms that emit characteristic electromagnetic radiation. The intensity of the emission was measured using an array of charge coupled devices (CCDs), which was used to create calibration curves as shown in Figure 2.3. From the calibration curves, measured intensities from the samples were assigned a concentration with < 1% error.

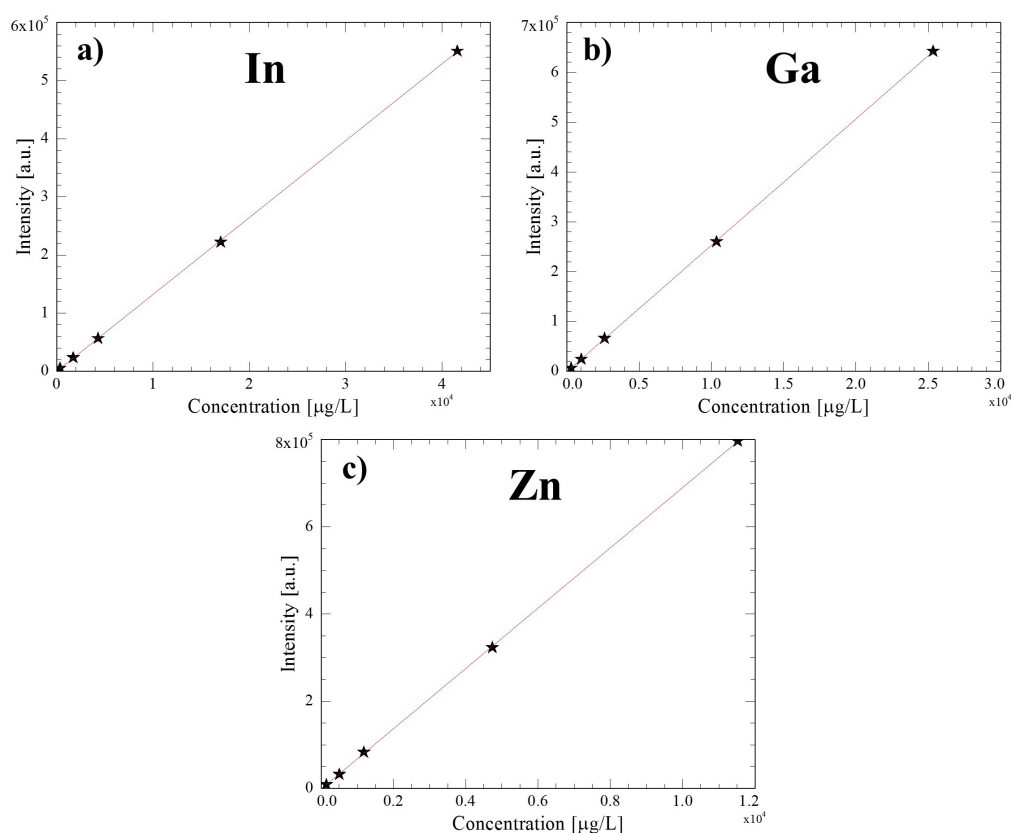


Figure 2.3: Calibration curves showing intensity vs. concentration for a) In, b) Ga, and c) Zn.

ICP-OES was used to quantitatively determine concentrations for key sam-

ples. For routine samples, another method for analyzing thin film composition was used: energy dispersive X-ray spectroscopy (EDS). This technique is based on bombarding the sample with electrons in order to produce and measure characteristic X-rays. There are two types of X-rays, characteristic and Brehmsstrahlung, that are produced due to inelastic scattering of the electron beam with the sample atoms. The first occurs when the high energy incident electron knocks out a core shell electron of an atom, creating a hole that is subsequently filled by an electron from an outer shell to produce a characteristic X-ray. The second occurs from the deceleration of incident electrons by the nuclei present in the sample to produce a background signal. By subtracting the Brehmsstrahlung background, elemental ratios in the sample can be determined to within $\pm 5\%$. This is demonstrated in Figure 2.4.

The background-subtracted spectrum was then integrated over the regions of interest. For In, the characteristic X-ray emission line of $L_{\alpha 1}$ (3.29 keV) was used, while $K_{\alpha 1}$ and $K_{\beta 1}$ were used for Zn (8.64 and 9.57 keV) and Ga (9.25 and 10.26 keV). The ionization cross-section and fluorescence yield must also be taken into account for each element to determine the elemental yield

$$Y(t) = N\Delta t\sigma(t)\omega e^{\frac{-\mu t}{\cos(\theta)}} I(t)\epsilon \frac{d\Omega}{4\pi} \quad (2.1)$$

where $Y(t)$ is the yield at a specific depth, N is the atomic density, Δt is the thickness of the layer under investigation, $\sigma(t)$ is the ionization cross-section at the specific depth, μ is the X-ray absorption coefficient, ω is the fluorescence yield, θ is the detector angle, ϵ is the detector efficiency, $d\Omega$ is the solid angle, and $I(t)$ is the e-beam intensity at a specific depth. There are a number of approximations that can be used to simplify this equation. Because the samples are thin films, the thickness dependence can be ignored. For a given measurement, Δt , ϵ , and $d\Omega$ are approximately constant. Additionally, $e^{\frac{-\mu t}{\cos(\theta)}} \approx 1$. This allows the

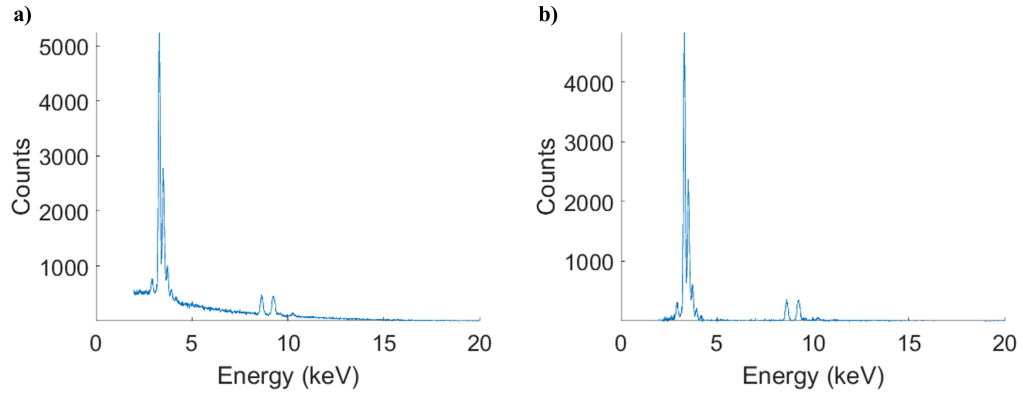


Figure 2.4: EDS spectrum of the regions of interest a) before and b) after background subtraction

equation for elemental ratios to be simplified to

$$\frac{N_i}{N_j} \approx \frac{\left[\frac{Y}{\sigma\omega} \right]_i}{\left[\frac{Y}{\sigma\omega} \right]_j} \quad (2.2)$$

Ionization cross-sections were determined based on the following equation:

$$\sigma = aq \frac{\log\left(\frac{E}{P}\right)}{EP} (1 - be^{-c\frac{E}{P}-1}) \quad (2.3)$$

where a , b , and c are parameters determined by the shell (e.g. K-shell), q is the number of electrons, E is the impact energy of the electrons, and P is the absorption edge of interest. The fluorescence yields (ω) used were determined by Krause [46].

ICP-OES is highly accurate, but is not time-efficient and requires destroying the sample. EDS is not as accurate, but is time-efficient and non-destructive. For these reasons, ICP-OES and EDS were both done initially on the same samples in order to calibrate the less-accurate EDS results with the more accurate ICP-OES results. The calibration data and resulting equations can be found in Figure 2.5. This allowed the measurement of all subsequent samples to be done efficiently and accurately using only EDS.

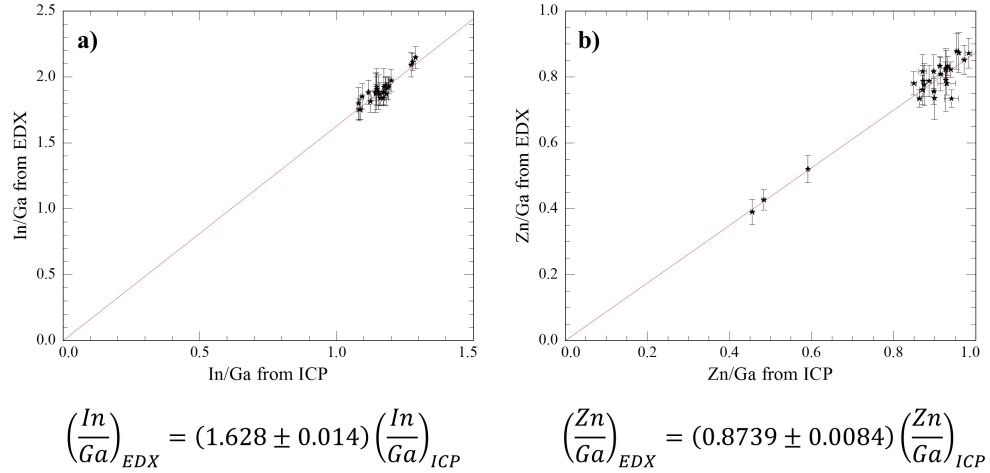


Figure 2.5: Calibration curves for the elemental ratios of a) In/Ga and b) Zn/Ga calculated using EDS and ICP-OES. Equations below graphs were used for the calibration of all subsequent EDS measurements

2.4 Laser Spike Annealing

Laser spike annealing (LSA) was originally developed for dopant activation in complementary metal-oxide semiconductor (CMOS) technology [47, 48]. In this work, we use it as a method to study a wide range of annealing temperatures and durations on the crystallization kinetics of $InGaO_3(ZnO)_m$. LSA was achieved using a line-focused continuous wave CO_2 laser ($\lambda=10.6 \mu m$, $90 \mu m$ by $500 \mu m$ full width at half maximum [FWHM] focus) scanned over the sample, as shown in Figure 2.6a. A characteristic annealing time, the dwell, is defined as the laser FWHM in the scan direction divided by the scan velocity. Thin film platinum thermistor measurements were used to determine the spatial profiles at various peak temperatures and dwell times, an example of which is shown in Figure 2.6c. These data were fit to a sum of Gaussian profiles to convert from spatial position to peak anneal temperature. An example of the temporal profiles for a shorter ($250 \mu s$) and longer ($10 ms$) dwell are shown in Figure 2.6b. For

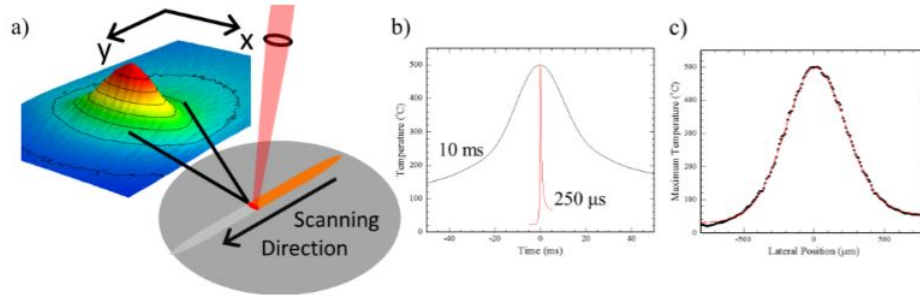


Figure 2.6: a) Schematic of LSA geometry with measured temperature profile in the heated zone. b) Time-temperature profiles of long (10 ms) and short (250 μ s) anneal durations to a peak center temperature of 500°C. c) x-direction spatial profile of 250 μ s LSA.

the current study, peak temperatures ranging from 600°C to 1,400°C and dwell times from 150 μ s to 10 ms were used.

2.5 Micro-Wide-Angle X-Ray Diffraction (μ -WAXS)

Micro-wide-angle X-ray diffraction (μ -WAXS) was performed at the Cornell High Energy Synchrotron Source (CHESS). Similar to powder diffraction, μ -WAXS is used to determine the short range order of the samples. At CHESS, the X-ray beam was focused to a spot only $\sim 20 \mu$ m FWHM using capillary X-ray optics [49], allowing the structure of the LSA annealed film to be spatially probed across the $\sim 500 \mu$ m Gaussian profile. The resulting scattering is characteristic of the sample composition and atomic arrangement, with X-rays scattered when the Bragg condition is satisfied:

$$n\lambda = 2d_{hkl} \sin(\theta_B) \quad (2.4)$$

where n represents an integer value, λ is the X-ray wavelength, d_{hkl} is the interplanar spacing, and θ_B is the Bragg angle. Scattered X-rays were recorded using

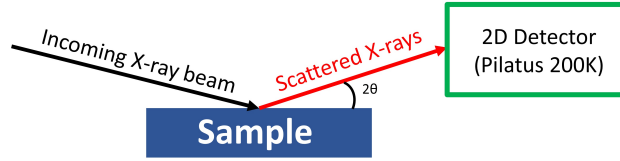


Figure 2.7: Schematic of the set-up used for μ -WAXS. The sample was moved on the axis coming out of the page to profile across the annealing gradient.

a Pilatus 200k area detector producing a 2D pattern of the relative intensities. Figure 2.7 demonstrates the set-up that was used.

There are a number of parameters that impact the recorded intensities including the sample-to-detector distance (SDD) and pixel size of the detector. The SDD and pixel size are related to 2θ by:

$$2\theta = \tan^{-1}\left(\frac{xp}{SDD}\right) \quad (2.5)$$

where 2θ corresponds to the scattering angle, x is the peak position in pixels, and p is the size of the detector pixels. The SDD was determined using calibration films of gold and cerium (IV) oxide. Precise rotational alignment ($< 0.5^\circ$) was maintained with regard to the LSA scan lines to ensure measurements along equivalently annealed areas. A step-size of $10 \mu\text{m}$ was used across the temperature gradient.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Overview

This chapter describes the analysis and interpretation of the data obtained using μ -WAXS. First, data from the area detector were radially integrated using the Nika software package to give intensity vs. 2θ diffraction patterns [50]. The International Centre for Diffraction Data WebPDF-4+ 2015 Powder Diffraction File (PDF) database was then used to identify possible phases. Over the full range of conditions, observed phases include PDF 00-036-1451 ZnO (186), PDF 00-019-1479 Zn₂SiO₄, PDF 04-007-5728 ZnGaInO₄ (166), PDF 00-040-0252 InGaZn₂O₅ (194), PDF 00-040-0253 InGaZn₃O₆ (166), PDF 00-040-0254 InGaZn₄O₇ (194), and PDF 00-040-0256 InGaZn₆O₉. The equilibrium structures of InGaZnO₄, InGaZn₂O₅, InGaZn₃O₆, etc. will hereafter be referred to as Phase I, II, III, etc., and the ZnO and Zn₂SiO₂ phases will simply be referred to as such. Table 3.1 lists the samples along with the phases observed under different LSA conditions. Throughout the rest of this chapter, the analysis leading to this table will be shown as well as proposed models describing why these phases formed.

In the following sections, scattering due to air and the amorphous SiO₂ peak were subtracted to show only peaks from the IGZO films. Figure 3.1 shows an example of data from a ZnO sample before and after background subtraction. The SiO₂ peak was modeled as a Gaussian function and the scattering due to air was modeled as linear. To track changes due to LSA regions, a characteristic peak from each phase was chosen that had no overlap with other observed phases in the sample and modeled as a Lorentzian function. This peak was then

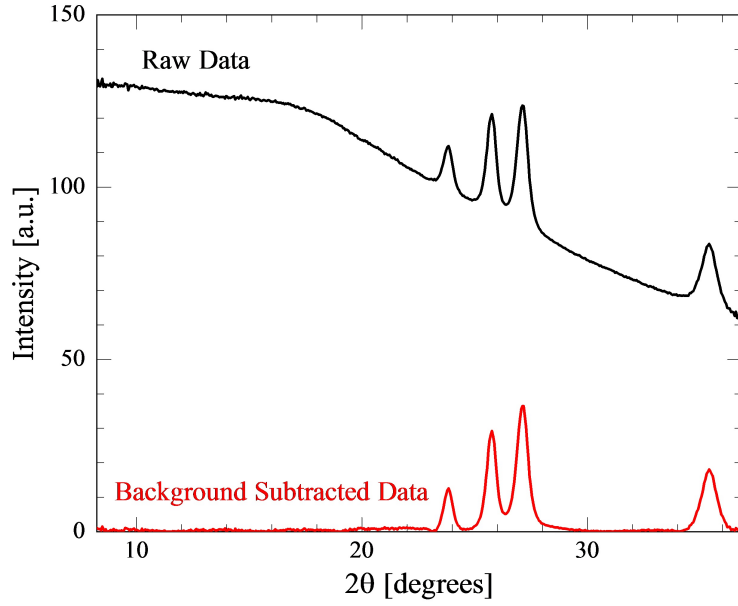


Figure 3.1: Example intensity vs. 2θ plots of raw data and background subtracted data for ZnO.

tracked through all of the LSA scans on a sample to determine kinetic behaviors. The (1 0 16) peak was used for Phase VI, the (1 0 12) peak for Phase IV, the (0 0 4) peak for Phase III, the (0 0 6) peak for Phase II, and the (0 0 6) peak for Phase I.

Grain sizes and lattice constants were estimated by fitting diffraction peaks with Lorentzian functions. The minimum grain size was then determined by the Scherrer equation as

$$t = \frac{K\lambda}{B\cos(\theta)} \quad (3.1)$$

where t is the diameter of the crystal particle, K is the shape factor estimated here as 0.9, B is the FWHM of the peak in radians, λ is the X-ray wavelength, and θ is the Bragg angle [51]. The lattice parameters a and c were determined by:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \quad (3.2)$$

where d_{hkl} is the interplanar spacing for miller indices h , k and l . While this

equation specifically describes a hexagonal crystal system, a rhombohedral lattice can be expressed using a and c as a non-primitive hexagonal lattice with three points per cell [52].

The following sections are reported in terms of measured m values (Zn concentration) and corresponding sample number in parentheses.

Peak Temp.	Dwell Time	Sample						
		1	2	3	4	5	6	7
As-deposited	n.a.	z	cd	cd	cd	a	a	a
600°C	10 ms	z	cd	n.a.	cd	a	a	a
	150 μ s	z	cd	n.a.	cd	a	a	a
800°C	10 ms	z	cd	n.a.	cd	a	a	a
	150 μ s	z	cd	n.a.	cd	a	a	a
1,000°C	10 ms	z	cd	n.a.	cd	I	I	I
	150 μ s	z	cd	n.a.	cd	a	a	a
1,200°C	10x10 ms	n.a.	?	n.a.	d	I	I	?
	10 ms	z+zs	cd+II+III	cd+II	I	I	I	I
	5 ms	n.a.	cd+II+III	n.a.	I	I	I	I
	2 ms	z+zs	cd+II	n.a.	cd	I	I	I
	1 ms	z+zs	cd+II	n.a.	cd	I	I	I
	750 μ s	z	cd+II	n.a.	cd	I	I	I
	500 μ s	z	cd	n.a.	cd	a	I	I
	250 μ s	z	cd	n.a.	cd	a	I	I
	150 μ s	z	cd	n.a.	cd	a	I	I
1,400°C	10 ms	z+zs	d	n.a.	d	d	?	d
	150 μ s	z	cd	n.a.	cd	I	I	I

Table 3.1: List of phases observed within each LSA scan. d refers to damaged, a is a-IGZO, n.a. indicates the peak temperature and dwell time were not used, cd indicates a compositionally disordered structure, z refers to ZnO, zs refers to zinc silicate, and ? indicates a phase that was not identified.

3.2 $m = \infty$ (1)

As-deposited, ZnO ($m = \infty$) samples displayed textured nanocrystallites corresponding to the *wurtzite* phase. The texturing observed using the area detector and corresponding intensity vs. 2θ plot can be seen in Figure 3.2. The slight shift of peaks to larger 2θ values suggests that the film is under compressive stress. This is in agreement with the film stress measurement using a Tencor FleXus-2320 that showed a compressive stress of ~ 50 MPa. Additionally, other reports of RF sputtered ZnO films have demonstrated compressive stress as-deposited as well [25]. The lattice parameters a and c were found to be 3.24 ± 0.01 Å and 5.19 ± 0.02 Å. These values are in the same range as those reported in literature of $a = 3.25$ Å and $c = 5.207$ Å [53].

Differences in intensity for the various peaks compared to the expected powder diffraction peaks are likely due to the preferential alignment of ZnO during sputtering [26]. The azimuthal angle can be measured from the area detector images to determine the orientation of grains. The texturing of the (002) plane corresponds to a 90° azimuthal angle, indicating c-axis alignment. The (101) plane displays an azimuthal angle peak near 150° . This is unexpected as the (101) plane geometry would suggest alignment near 120° and it is unclear why this appears. Using the four peaks shown in Figure 3.2, the estimated grain size as-deposited was 11 ± 2 nm.

After anneals to peak temperatures of $1,200^\circ\text{C}$ and above with dwell times of 1 ms or greater, the ZnO phase and a zinc silicate phase were observed. This is a result of the interaction between the SiO_2 layer and the ZnO thin film. Figure 3.3 shows the ZnO and zinc silicate phases forming at a peak temperature of

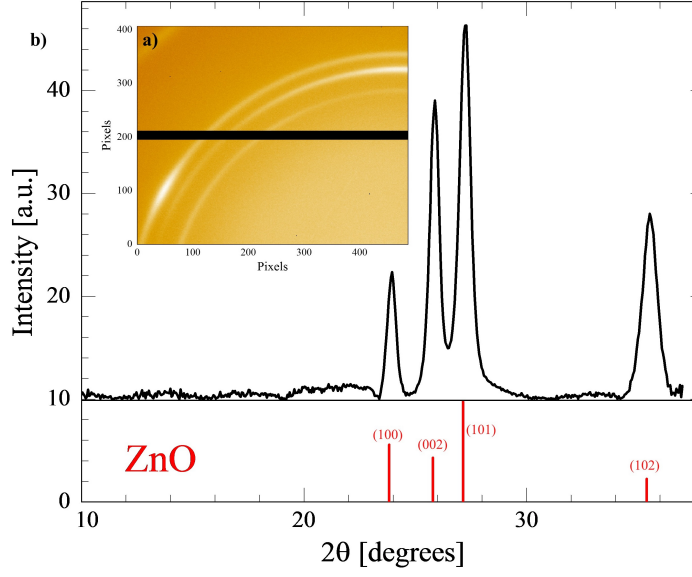


Figure 3.2: a) Area detector pixel image of sample 1 ($m = \infty$) as-deposited. b) Corresponding radial integration of intensity vs. 2θ with expected peaks for ZnO shown below.

1,400°C and a 10 ms dwell. The ZnO phase exhibits more compressive stress in the c-axis as the (100) peak is in the same position while the (002) peak is shifted to a larger 2θ value. Additionally, the zinc silicate phase is likely a slightly different stoichiometry given the shift of peaks from the PDF data of Zn_2SiO_4 . The appearance of the zinc silicate phase depends largely on dwell time. It is not seen at 1,400°C for 150 μs , but is observed at 1,400°C for 10 ms. This suggests that diffusion of Zn into the SiO_2 layer is required to form the silicate. With shorter anneal durations, this cannot occur. After annealing, grain size of the ZnO phase increased slightly to 14 ± 1 nm.

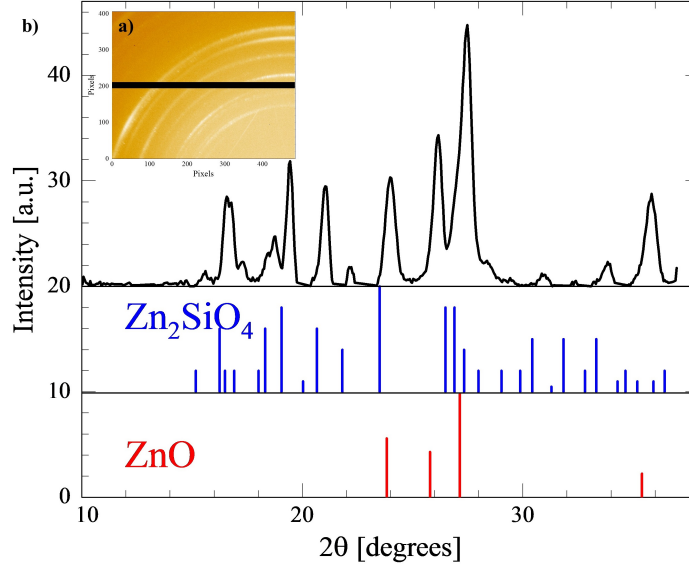


Figure 3.3: a) Area detector pixel image for sample 1 ($m = \infty$) after 1,400°C 10 ms LSA. b) Corresponding radial integration of intensity vs. 2θ with expected peaks for ZnO and Zn_2SiO_4 shown below.

3.3 $m = 0.45$ (7)

Without any intentional substrate heating during deposition, the film sputtered from the $\text{In}_2\text{Ga}_2\text{ZnO}_7$ target was amorphous as-deposited. This is in agreement with previous work that has found higher temperatures during deposition are required to achieve alignment [7, 19]. Figure 3.4 shows the area detector image as well as the corresponding background-subtracted radial integration. The peak position was found to be $24.7 \pm 0.1^\circ$ using a Gaussian function (shown overlaid in Figure 3.4) at a wavelength of $1.162 \text{ \AA}$. This corresponds to a 2θ value of $33.6 \pm 0.1^\circ$ for scattering with the more common $\text{Cu K}\alpha$ X-ray source, which is in good agreement with previous reports [7]. The slight asymmetry of the amorphous peak is believed to be an artifact of the background subtraction and dead pixel space between plates of the detector; this asymmetry has not been previously observed using other X-ray diffraction setups.

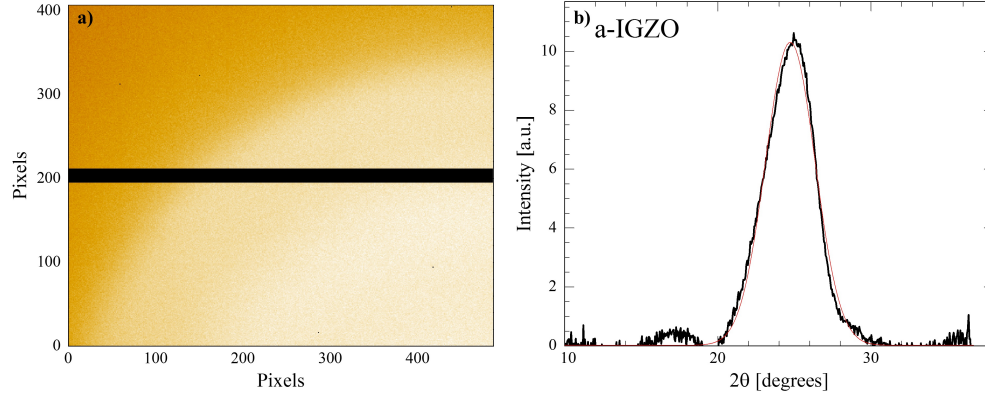


Figure 3.4: a) Area detector pixel image of sample 7 ($m = 0.45$) as-deposited. b) Corresponding radial integration of intensity vs. 2θ with a-IGZO peak fit with a Gaussian function overlaid.

After LSA, formation of peaks corresponding to Phase I were seen, and the transformation from amorphous to crystalline is shown in Figure 3.5. The crystalline rings observed in μ -WAXS in Figure 3.5 are not textured (in contrast to the ZnO film) and represent randomly-oriented polycrystalline grains. The crystalline peaks were observed during LSA for peak annealing temperatures of 1,000°C for 10 ms, and 1,200°C for all dwell times. The greater temperatures required in this work versus previously reported values for crystallization (600°C range) is almost certainly due to the shorter time scales of LSA versus furnace annealing [54]. For anneals with a peak center temperature of 1,200°C, the crystallization region was wider for long dwells compared to short dwells. This indicates that the threshold temperature for crystallization decreases with dwell and confirms that the phase transformation is kinetically driven.

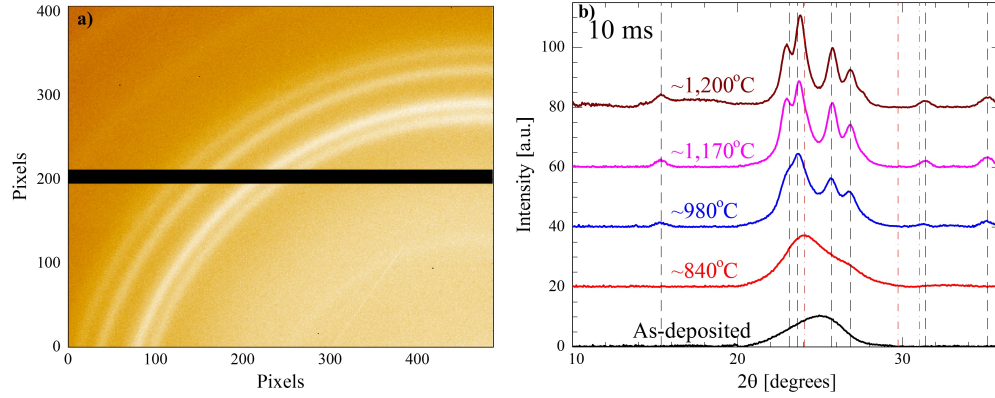


Figure 3.5: a) Area detector pixel image of sample 7 ($m = 0.45$) after 1,200°C 10 ms LSA. b) Corresponding radial integration of intensity vs. 2θ with expected peaks for Phase I overlaid. Red lines indicate intensities $< 10\%$ of maximum.

3.4 $m = 5.96 (2)$

Similar to the pure ZnO film, this Zn-rich sample formed highly-textured nanocrystallites as-deposited with grain sizes of 8.1 ± 0.1 nm. Figure 3.6 shows the area detector pixel image, the background-subtracted radial integration, and expected Phase VI and ZnO peaks. The area detector image looks very similar to the one seen in Figure 3.2, indicating preferential alignment during sputtering. In the 2θ scan, four strong peaks were observed. Comparing these to expected spectra for ZnO and Phase VI (the closest expected crystal phase), we tentatively assign these peaks to the Phase VI structure as (1 0 1), (0 0 16), (1 0 8) and (1 0 16) planes. However, these peaks are also very similar to the ZnO peaks for the (1 0 0), (0 0 2), (1 0 1) and (1 0 2) planes, which are expected at only slightly larger 2θ values. This is not totally surprising since Phase VI is just a layered structure similar to ZnO, but with a repeat distance in the c-axis 8-times larger than ZnO. Indeed, the lattice constant c for Phase VI of 43.26 Å is almost 8x larger than the ZnO value of 5.207 Å. The high intensity of the peak at 35° (1 0 16) is consistent

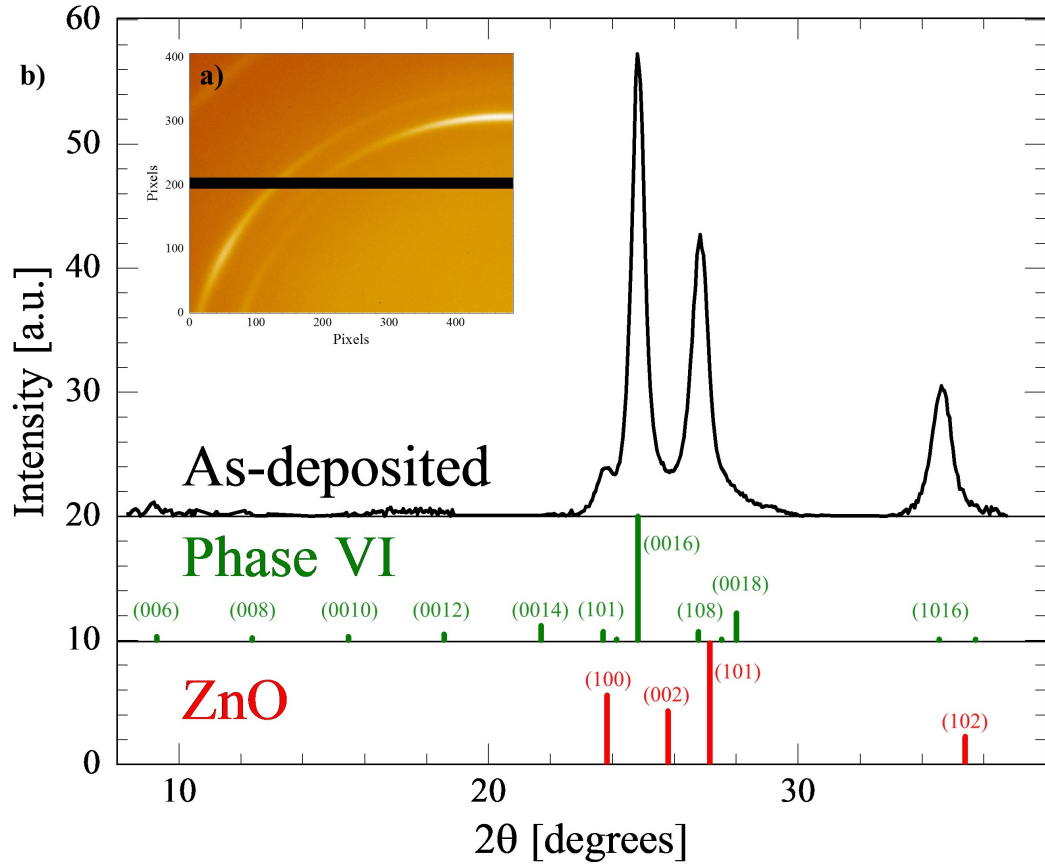


Figure 3.6: a) Area detector pixel image of sample 2 ($m = 5.96$) as-deposited. b) Corresponding radial integration of intensity vs. 2θ with expected peaks for Phase VI and ZnO shown below.

with the strong c-axis texturing.

While the peaks that do appear correspond to the peak positions for Phase VI, which would be expected based on the composition, the lack of lower angle periodic peaks (e.g. (0010), (0012), and (0014)) suggests that the fully ordered superlattice is not formed. Instead, the as-deposited structure likely resembles a compositionally disordered structure similar to *wurtzite*. This occurs because there is not enough mobility to develop the long range order of the layered structure during room temperature deposition. Thus, In atoms are not able to form coherent layers to sandwich the Zn and Ga, and instead are randomly

interspersed throughout the bulk while still retaining the local structure. In essence, the structure is homologous to ZnO with chemical substitution shifting the lattice constant. In subsequent discussion, this structure is just referred to as the as-deposited structure.

After LSA at peak temperatures above 1,200°C, the as-deposited structure transformed into Phase II and, at the highest temperatures, Phase III. Figure 3.7 shows the diffraction pattern after an anneal at 1,200°C for 10 ms. The appearance of the lower angle periodic peaks indicates development of superlattice structure, but not to the full Phase VI extent. As discussed in section 3.1, the intensity of specific (non-overlapping) peaks can be used to track the development of each phase. The intensity of the characteristic peaks for the as-deposited phase, Phase II, and Phase III are shown in Figure 3.8 as a function of the annealing temperature. The amplitude of the as-deposited structure (reflected in the peak at $2\theta = 35^\circ$) increases initially with temperature indicating increased crystallinity and grain growth. Above 1,000°C for the 10 ms anneal, the amplitude plummets sharply. The temperature of this decrease increases with decreasing anneal duration, reaching 1,150°C for the 500 μ s anneal. As the as-deposited amplitude decreases, peaks corresponding to Phase II begin to form. For the 5 and 10 ms anneals at temperatures near 1,200°C, the Phase II amplitude also begins to decrease with the appearance of Phase III. Phase III was only considered to exist when the Lorentzian fit returned values within the expected limits; only 2θ values between 9.5° and 9.8° were accepted.

The phase development was strongly dependent on the dwell time. For all dwells, the as-deposited structure decreased as the anneal temperature approached 1,200°C. Phase II was not immediately observed, but began to form at

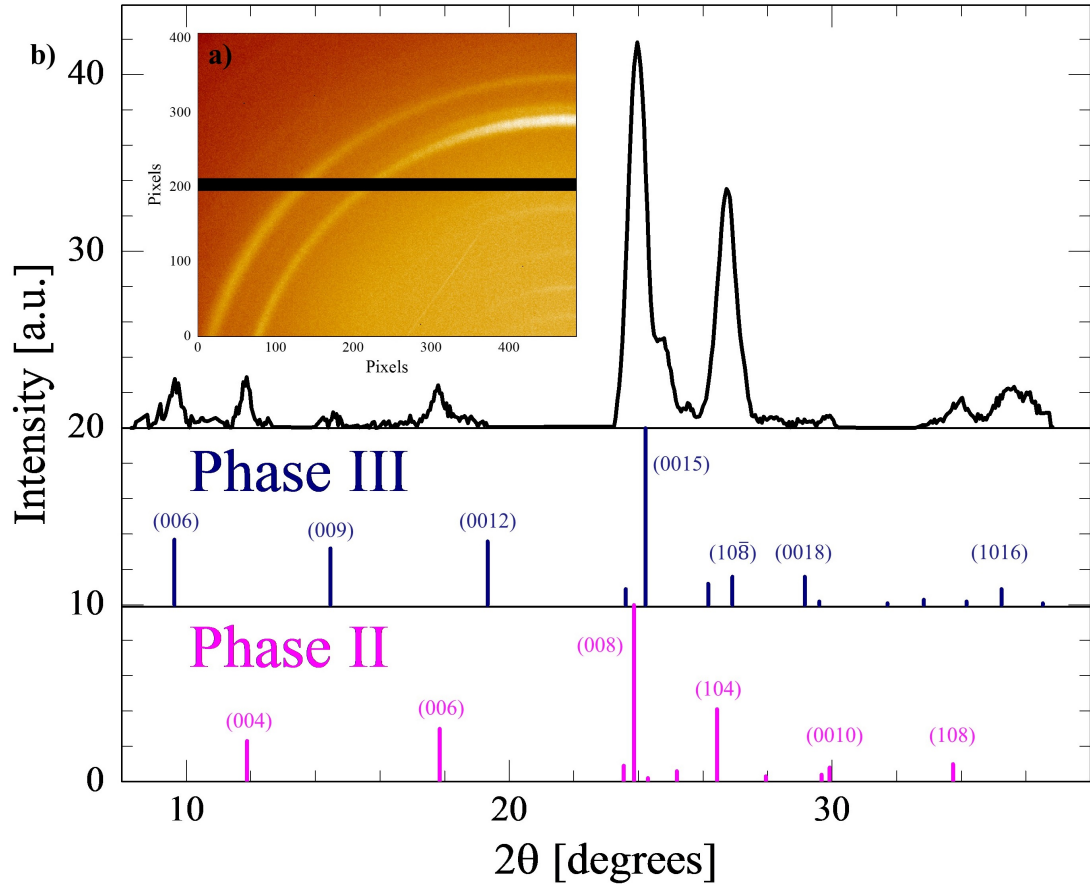


Figure 3.7: a) Area detector pixel image of sample 2 after 1,200°C 10 ms LSA. b) Corresponding radial integration of intensity vs. 2θ with expected peaks of Phases II and III shown below.

approximately 50-75°C higher temperatures. For dwells below 750 μs , no Phase II was observed to the highest anneal temperature of 1,200°C. Similarly, Phase III was only observed after the longest anneals (5 and 10 ms) at the higher temperatures (1,200°C). Both of these phases formed at the expense of the as-deposited structure. The observation that Phase III began to form at the highest temperatures and longest times suggests that, with sufficient time and temperature, the equilibrium Phase VI structure may ultimately form.

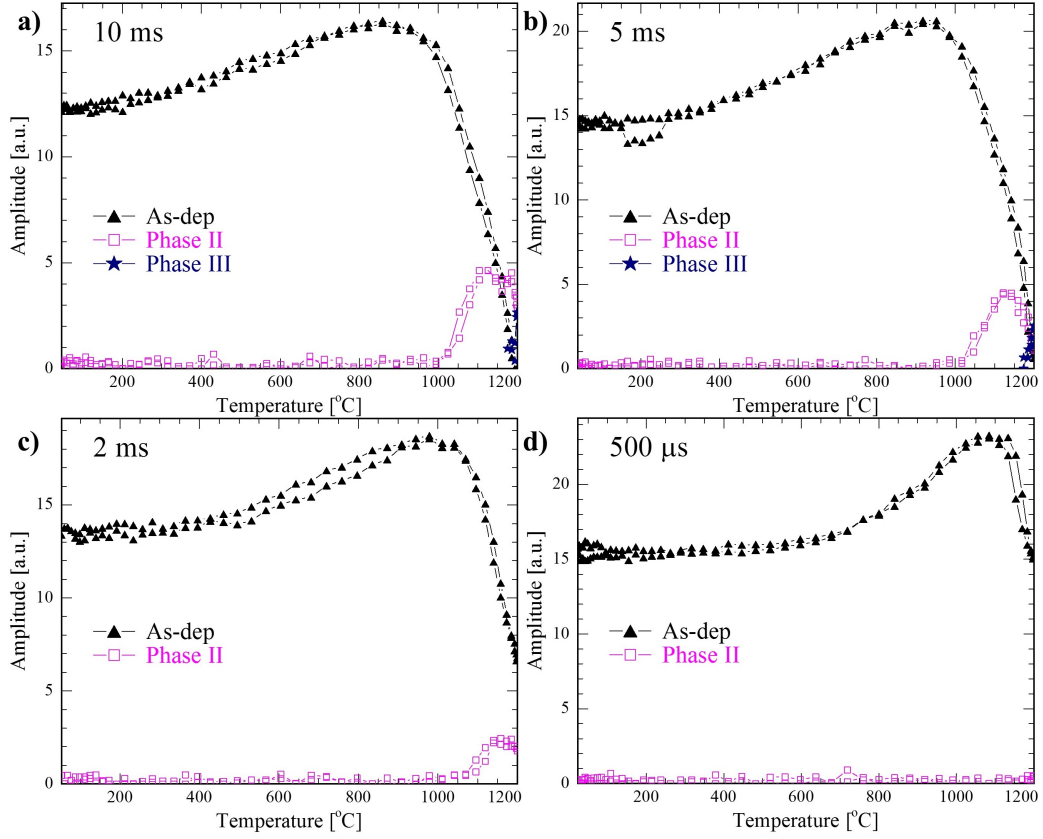


Figure 3.8: Amplitude vs. temperature for a peak center temperature of 1,200°C at a) 10 ms, b) 5 ms, c) 2 ms, and d) 500 μ s.

3.5 $m = 3.94$ (3)

For this sample, the substrate was not rotated during deposition to create a thickness gradient across the sample ranging from ~ 100 -220 nm. Over this range of thicknesses, the composition remained within 1% (atomic fraction). LSA using a short (250 μ s) and long (10 ms) dwell time at 1,200°C peak center temperature was alternated across the sample to determine if the film thickness impacted the crystallization kinetics. For this sample, μ -WAXS was performed using higher energy X-rays ($\lambda = 0.6326$ Å) with a Pilatus 300k area detector. Additionally, data is reported in terms of intensity vs. Q , where Q is related to 2θ

by

$$Q = \frac{4\pi \sin(\frac{2\theta}{2})}{\lambda} \quad (3.3)$$

where λ is the X-ray wavelength and Q has units of $\text{\AA}^{-1}$.

As-deposited, textured nanocrystallites of size ~ 6 nm were observed with diffraction peaks corresponding to some of the peaks expected for Phase IV, which would be expected based on the composition. However, as in the previous sample, no periodic lower angle peaks were observed, indicating that the full superlattice did not form. Figure 3.9 shows the area detector image, diffraction peaks, and expected peaks for Phase IV. We tentatively assign the observed as-deposited peaks to the Phase IV planes of (00 12), (1 0 6), (1 0 12) and (1 0 18), which corresponds to a layered repeat unit of 6 compared to ZnO. This is in agreement with the lattice constant c of 32.906 $\text{\AA}$ for Phase IV, which is $\sim 6\times$ larger than 5.207 $\text{\AA}$ for ZnO.

After a 250 μs LSA to 1,200°C, no structural transformations were observed. For 10 ms dwells, however, peaks corresponding to Phase II were observed. Figure 3.10 shows the diffraction pattern after a 10 ms LSA along with expected peaks for Phase II. With this high temperature anneal, the low angle diffraction peaks are clearly observed.

The transformation from the as-deposited structure to Phase II was tracked by fitting the characteristic peaks. Figure 3.11 shows the changes in amplitude for the as-deposited phase and Phase II as a function of temperature. For the 250 μs anneal, only the as-deposited structure is seen and exhibits an increased amplitude at higher temperature, likely again due to grain growth or increasing alignment. For the 10 ms anneal, the as-deposited structure exhibits a slight increase with temperature initially before beginning to decrease above 850°C.

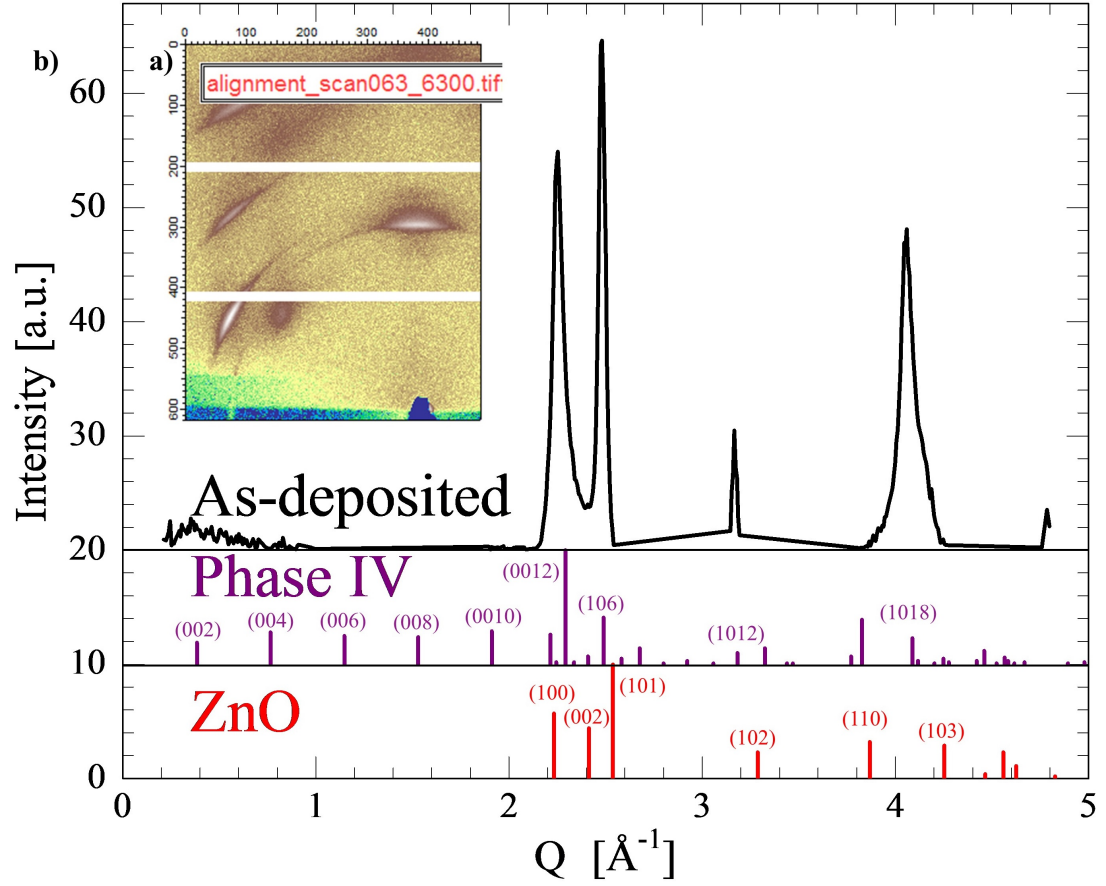


Figure 3.9: a) Area detector pixel image of sample 3 as-deposited. b) Corresponding radial integration of intensity vs. 2θ with expected peaks for Phase IV shown below.

The Phase II structure begins to develop only at temperatures above 1,100°C for the 10 ms dwell.

Across the thickness gradient, only the silicon background was observed to change; the crystallization behavior did not. This indicates that film thickness does not play a role in the crystallization kinetics of these superlattice structures, with bulk nucleation and growth dominating the kinetics.

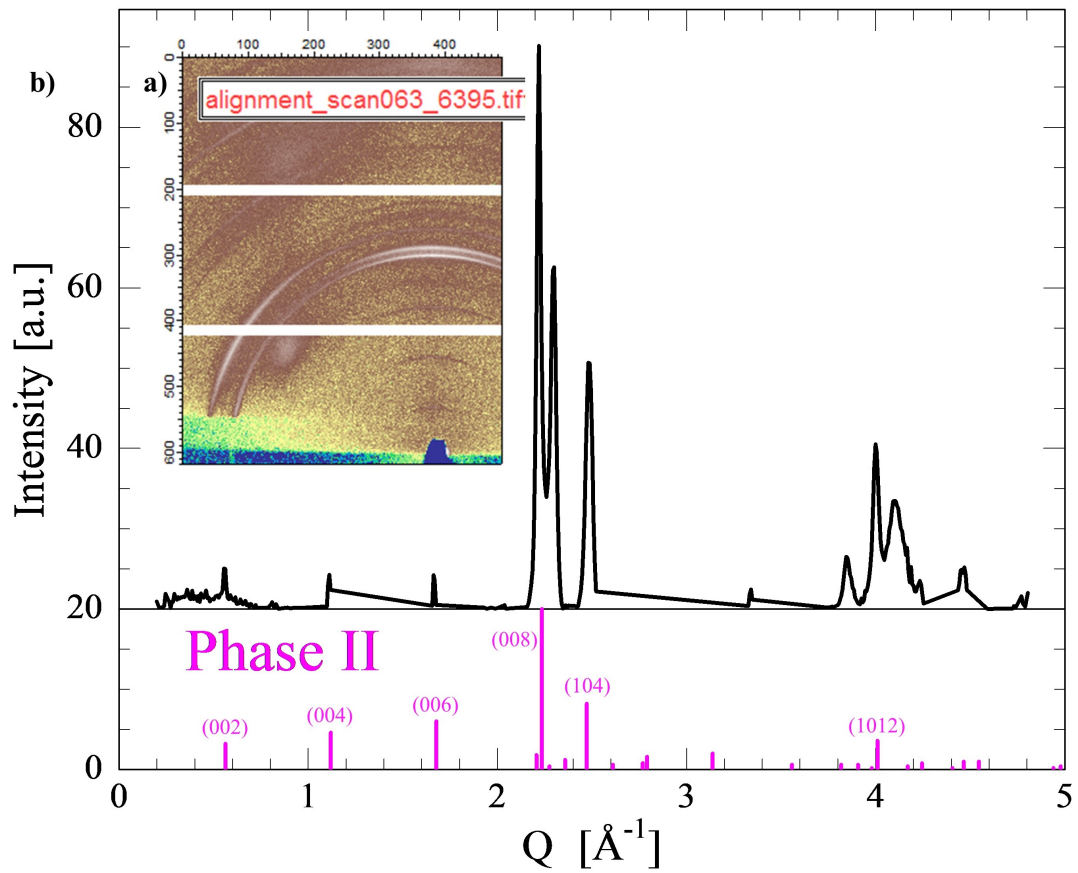


Figure 3.10: a) Area detector pixel image of sample 3 after 1,200 °C 10 ms LSA. b) Corresponding radial integration of intensity vs. 2θ with expected peaks for Phase II shown below.

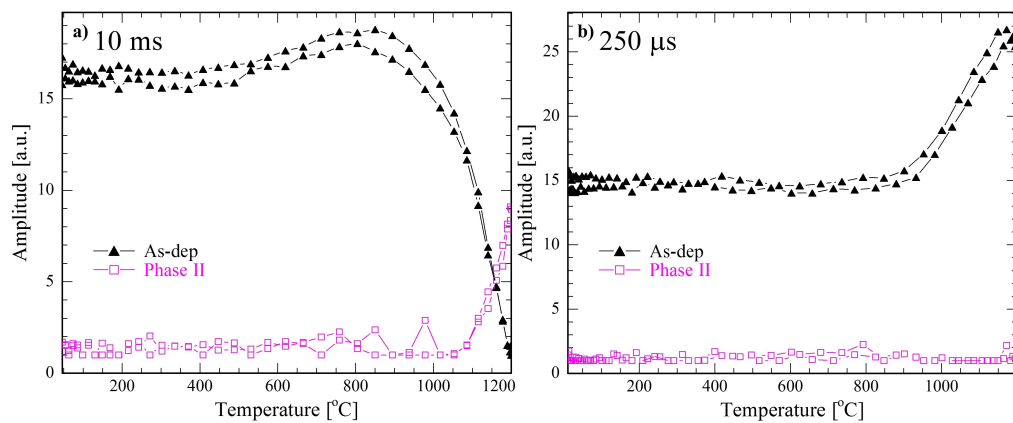


Figure 3.11: Amplitude as a function of temperature of the as-deposited and Phase II peaks after a 1,200 °C a) 10 ms, and b) 250 μs LSA.

3.6 $m = 2.63$ (4)

As with other Zn-rich samples, as-deposited $m = 2.63$ exhibited textured nanocrystallites with grain sizes of 6.1 ± 0.1 nm. Figure 3.12 shows the area detector image, diffraction peaks, and expected peaks for Phase II. The three primary peaks in Figure 3.12 match well to the Phase II structure and are tentatively assigned as the (008), (104), and (108) planes. From the area scan, strong c-axis texture of the (008) peak is observed while texture near an azimuthal angle of 150° is observed for the (104) peak. As with previous Zn-rich samples, the deposited structure more closely resembles a distorted *wurtzite* structure than superlattice as the periodic lower-angle peaks are not seen. This structure is more distorted than sample 2 ($m = 5.96$) as the composition is further from pure ZnO. Additionally, the peaks of Phase II correspond to a unit cell $\sim 4\times$ the size of ZnO, with c equal to 5.207 Å for ZnO and 22.52 Å for Phase II.

After LSA to a peak temperature of $1,200^\circ\text{C}$ for dwell times of 5 ms or more, some of the as-deposited structure transformed to Phase I, as seen in Figure 3.13. Only a portion of the as-deposited structure has transformed to Phase I, resulting in overlapping peaks. For example, the peak at 23.8° is an overlap of the as-deposited (008) and the Phase I (101) planes. Phase I forms with comparable texturing as seen in Figure 3.13, where the two smallest rings correspond to the (006) and (009) planes, and show c-axis alignment. The (101) peak from Phase I forms the polycrystal-like ring on the as-deposited textured peak. Similarly, the (104) textured peak from the as-deposited structure splits into three peaks after annealing: more polycrystalline (104) and (015) from Phase I, with remnants of the textured as-deposited (104) in the center.

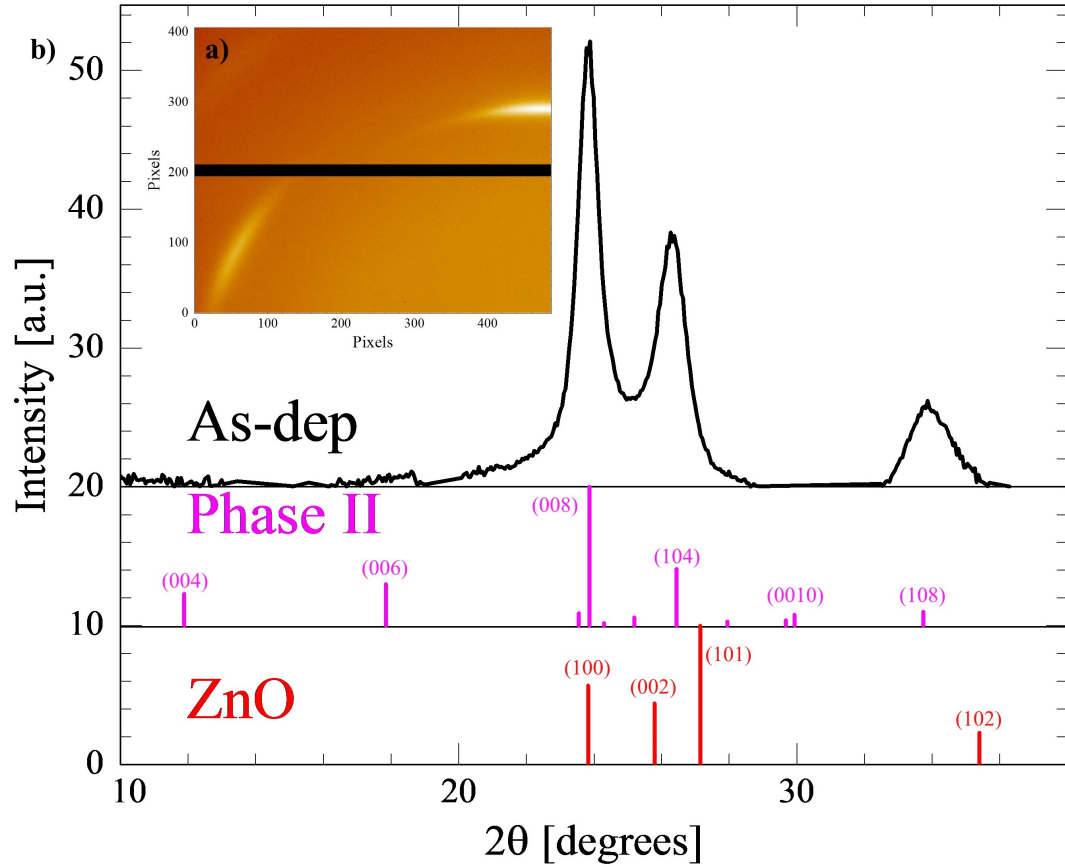


Figure 3.12: a) Area detector pixel image of sample 4 ($m = 2.63$) as-deposited. b) Corresponding radial integration of intensity vs. 2θ with expected peaks for Phase II and ZnO shown below.

Figure 3.14 shows the phase transformation from the as-deposited structure to Phase I as a function of annealing temperature. Similar to sample 2 ($m = 5.96$), at dwell times of 5 ms or greater, the as-deposited Zn-rich phase exhibited an increase in crystallinity at lower temperatures before decreasing rapidly. Although the data is noisy, the temperature at which this decrease occurs does appear to increase with decreasing anneal duration. As the as-deposited structure amplitude decreases, the Phase I amplitude exhibits a rapid increase for anneal durations greater than 2 ms.

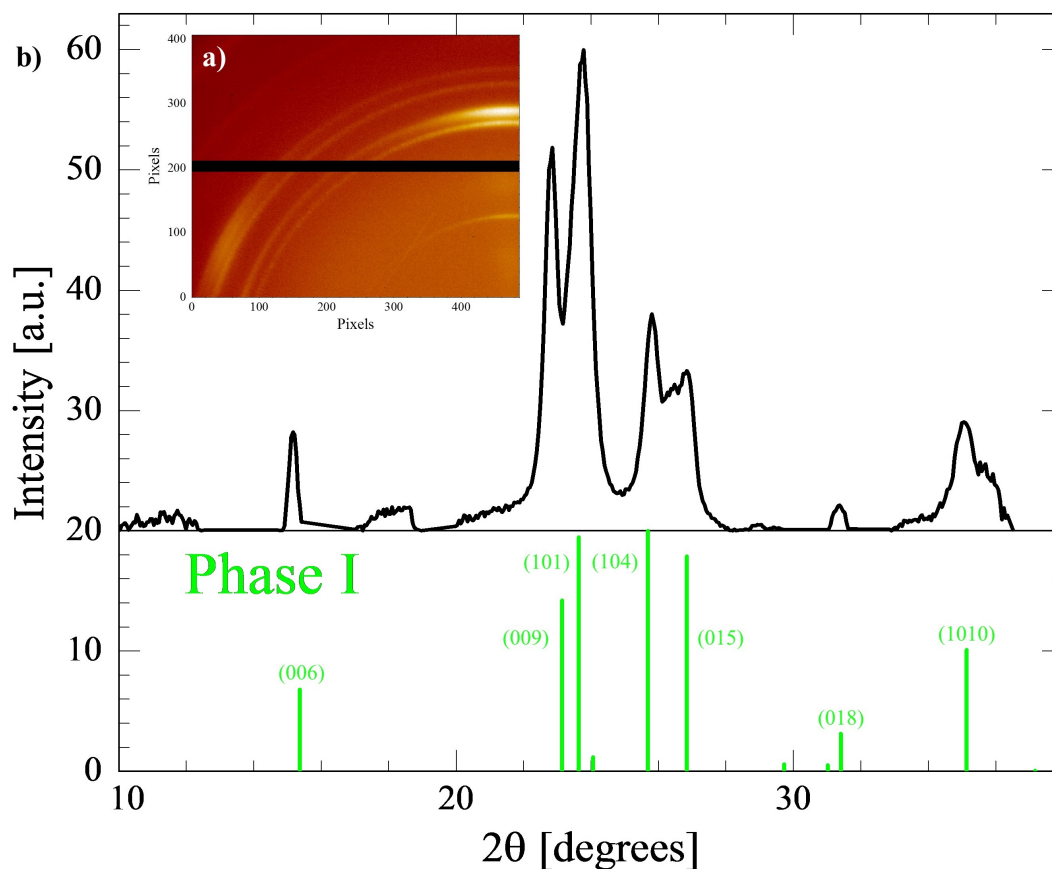


Figure 3.13: a) Area detector pixel image of sample 4 ($m = 2.63$) after 1,200°C 10 ms LSA. b) Corresponding radial integration of intensity vs. 2θ with expected peaks for Phase I shown below.

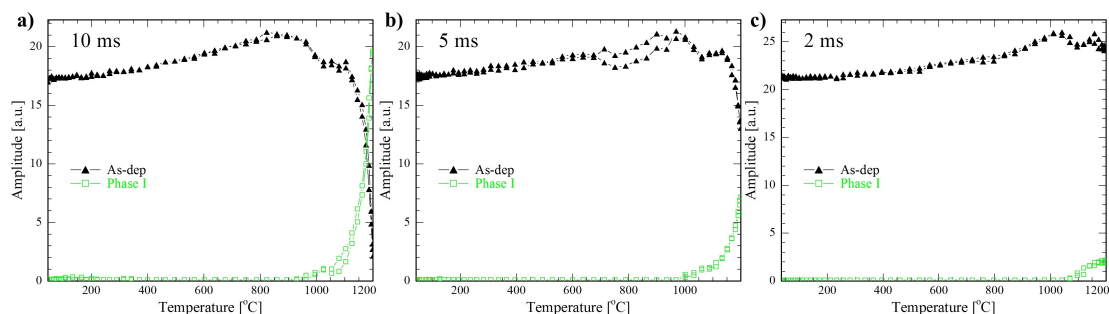


Figure 3.14: Amplitude vs. anneal temperature with a peak center temperature of 1,200°C at anneal times of a) 10 ms, b) 5 ms, and c) 2 ms.

3.7 $m = 1.36$ (5)

Moving further from pure ZnO, this sample as-deposited exhibited only an amorphous IGZO peak. As with sample 7 ($m = 0.45$), after LSA Phase I was formed. Crystallization was observed at a peak temperature of 1,000°C with dwell times of 10 ms, but not for 150 μ s. After LSA to a peak temperature of 1,200°C, Phase I only formed at dwell times of 750 μ s or greater, while shorter times remained amorphous. While both sample 5 ($m = 1.36$) and sample 7 ($m = 0.45$) formed Phase I peaks, sample 5 required longer dwell times to crystallize, indicating that the increased Zn content inhibits formation of Phase I at shorter dwell times.

3.8 $m = 0.71$ (6)

The m value for this sample is somewhat misleading as this represents the ~10 nm ZnO buffer layer below the sputtered $\text{In}_2\text{Ga}_2\text{ZnO}_7$ film ($m = 0.45$). The thin ZnO interlayer was expected to crystallize textured during deposition and act as a seed layer for subsequent textured growth of the $\text{In}_2\text{Ga}_2\text{ZnO}_7$. While this sample initially appeared to only contain the a-IGZO peak as-deposited, sector analysis (Figure 3.15) of the μ -WAXS image revealed significant texturing near 2θ of 26° in the normal direction, corresponding to the (002) peak of ZnO. This is clear evidence that the buffer layer had indeed crystallized. After LSA, peaks corresponding to Phase I were seen with crystallization occurring from LSA scans at 1,000°C for 10 ms, but not 150 μ s, and for all dwells at 1,200°C. This indicates a similar behavior to sample 7 ($m = 0.45$).

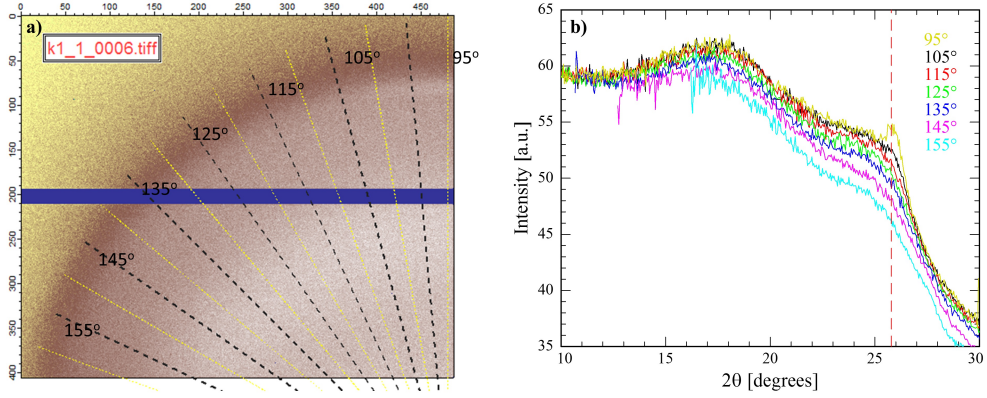


Figure 3.15: a) Area detector pixel image of sample 6 ($m = 0.71$) as-deposited with sectors shown. b) Corresponding radial integration of intensity vs. 2θ for each sector. Expected position of (002) peak of ZnO is overlaid as the dashed line in red.

3.9 Crystallization Kinetics

Phase I was selected for analysis of crystallization kinetics because it appeared in 4 different samples (4, 5, 6, and 7). To determine the crystallization temperature, the Lorentzian amplitude was plotted as a function of the peak annealing temperature for each dwell time (from laser scans to a center temperature of 1,200°C). Figure 3.16 shows how the crystallization temperature was determined for sample 7 ($m = 0.45$) for 10 ms and 250 μ s dwells. A sharp increase in the amplitude marks the onset of crystallization. These data were fit with either parabolic or linear functions depending on the dwell time to estimate the volume fraction crystallized. The crystallization temperature was determined to be at the intersection of the sharp increase and the unannealed baseline.

The crystallization temperature as a function of composition and dwell time is shown in Figure 3.17. With increasing Zn fraction (m), the crystallization temperature increases for all dwells. This relationship was unexpected as the as-

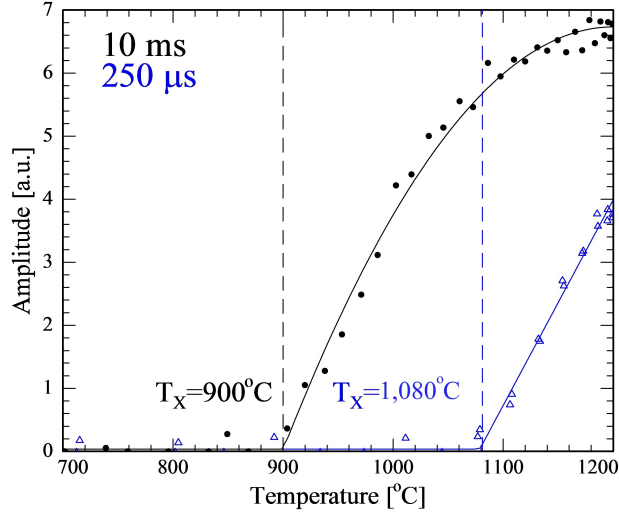


Figure 3.16: Peak amplitude vs. temperature for dwell times of 10 ms and 250 μ s at a peak center temperature of 1,200°C for sample 7 ($m = 0.45$).

deposited films exhibit the opposite behavior, with increasing m values leading to more crystalline structures. Additionally, it had previously been predicted that increasing Zn content would lead to a decrease in crystallization temperature [7]. The increasing crystallization temperature with m implies that the excess Zn acts as a barrier to the growth of ordered structures in these films.

To estimate an activation enthalpy for this process, inverse dwell time (a kinetic rate) was plotted against inverse crystallization temperature for each composition (Figure 3.18). With increasing Zn fraction (m), the apparent activation enthalpy increases from ~ 1.5 eV to 4 eV. This implies that the kinetic barriers to forming Phase I increase with Zn content. The behavior of the ZnO buffer layer used for sample 6 ($m = 0.71$), which was expected to act as a template for crystallization, did not dramatically shift the kinetics. However, the additional Zn in the buffer layer increased the activation enthalpy to 2.6 ± 0.2 eV from the 1.5 ± 0.2 eV observed for the pure $\text{In}_2\text{Ga}_2\text{ZnO}_7$ films. This implies that the buffer

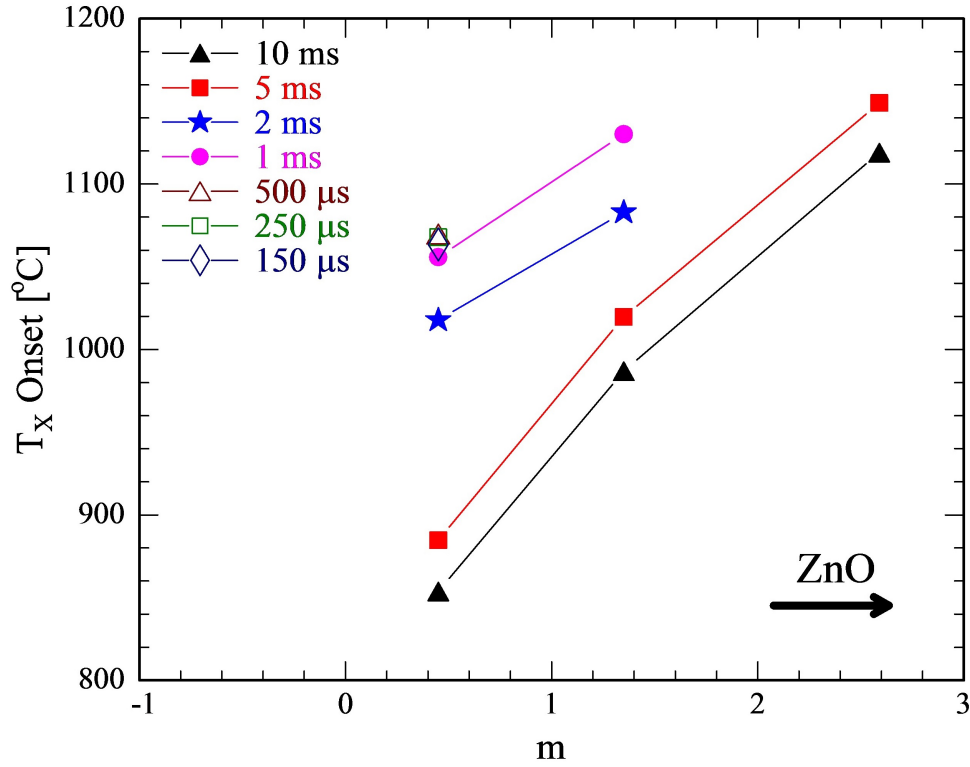


Figure 3.17: Onset of crystallization temperature vs. m at various dwell times and a peak center temperature of 1,200°C.

layer does not act as a seed layer but, similar to the other Zn-rich films, acts as a barrier to the growth of Phase I. A similar behavior was seen with buffer layers greater than 100 nm in furnace annealing studies at 1,000°C [38].

For $\text{In}_2\text{Ga}_2\text{ZnO}_7$ films, the crystallization temperature for all dwells below 1 ms was essentially a constant at ~1,060°C. This is reflected in the vertical rise for the $m = 0.45$ data in Figure 3.18. This behavior suggest a liquid-like kinetic regime. This is unexpected and requires further study as the melting points for the constituent oxides of ZnO, In_2O_3 and Ga_2O_3 are all much higher at 1,974°C, 1,912°C, and 1,807°C respectively [55].

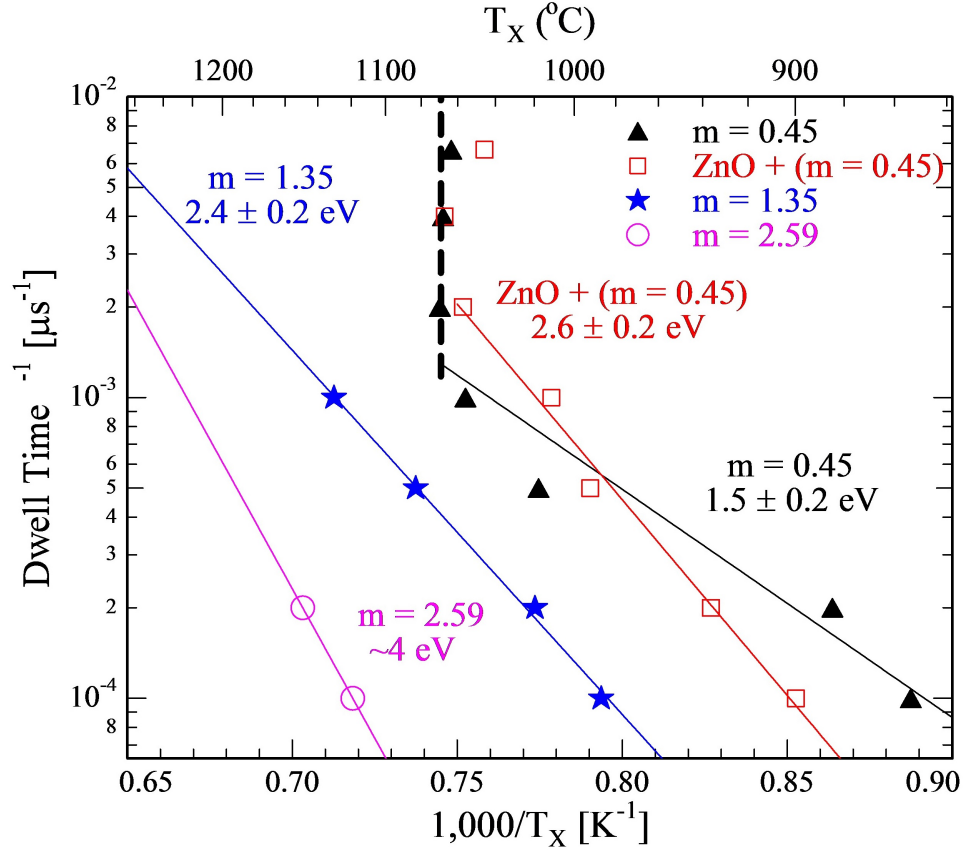


Figure 3.18: Inverse dwell time vs. inverse crystallization temperature with overlay activation enthalpies.

3.10 Discussion

To explain both the appearance of phases with lower Zn content in higher Zn content films and the increasing activation enthalpy with m , we propose two models.

- In Model A, the as-deposited structure is a compositionally disordered structure similar to *wurtzite* as has been argued in the previous sections. To explain the increased enthalpy with m and formation of the superlattice structure after annealing, we propose the diffusion of Zn out of the as-

deposited structure to form regions of superlattice structure surrounded by an amorphous Zn-rich amorphous IGZO region. This outward diffusion would occur initially to generate the low m phases. At high temperatures and for long enough times, Zn would diffuse back into the superlattice structure to generate higher m phases until the equilibrium structure determined by the film composition was reached. This diffusion would occur faster in the plane of the Zn/Ga layers rather than through the In layers, as predicted by Nomura et al. [36]. Within this model, the activation enthalpy would represent the diffusivity of Zn in the films. With increasing m values, more Zn would need to diffuse out of the lattice, potentially resulting in an increased activation enthalpy. As no other diffraction peaks besides the superlattice structure are seen, the excess Zn would have to diffuse into a surrounding Zn-rich amorphous IGZO region. Figure 3.19 shows a schematic of this model.

- For Model B, we again consider the as-deposited structure compositionally disordered and similar to *wurtzite*. Figure 3.20 shows this *wurtzite* structure with In and Ga randomly dispersed in the lattice. In this model, mobile In atoms within this structure begin to diffuse to form the superlattice. With increasing temperature, the In atoms form coherent layers within the as-deposited structure in a spinoidal-like decomposition. As the temperature increases further, the coherent In layers, which initially started close together, begin to diffuse further apart. While the first superlattice that forms would be Phase I or Phase II, with increasing temperature, this would begin to transform into Phase III. This continues until the equilibrium structure is formed. In Figure 3.20, sample 2 ($m = 5.96$) is used as an example, with the ultimate predicted equilibrium structure shown

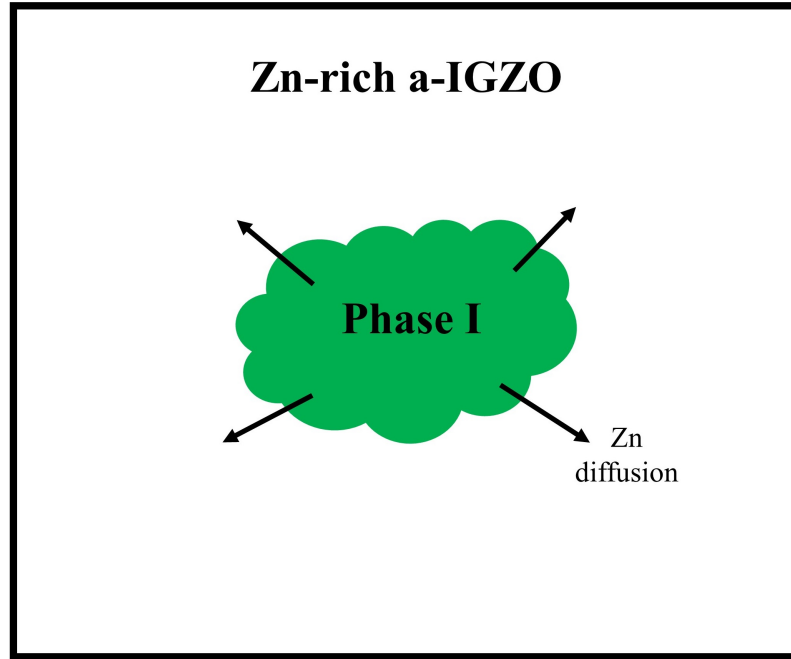


Figure 3.19: Schematic of Model A showing the diffusion of Zn out of the superlattice structure.

in the last step as Phase VI. For films with more Zn and less In, more energy is required to form coherent In layers, which leads to an increase in activation enthalpy with increasing m .

Texturing after LSA appears to be determined by the as-deposited structure. For Zn-rich samples which displayed c-axis alignment as-deposited, the c-axis alignment was also observed in the superlattice structure after LSA. The samples that were amorphous as-deposited did not exhibit any texturing of the superlattice structure after LSA, instead showing uniform polycrystallinity. Figure 3.21 shows the area detector image from Zn-rich sample 4 ($m = 2.63$) and less Zn-rich sample 7 ($m = 0.45$) after LSA. The Zn-rich sample shows clear c-axis texturing of the first two rings, which are the (006) and (009) planes respectively. The less Zn-rich sample displays more uniform rings for both, indicating almost no

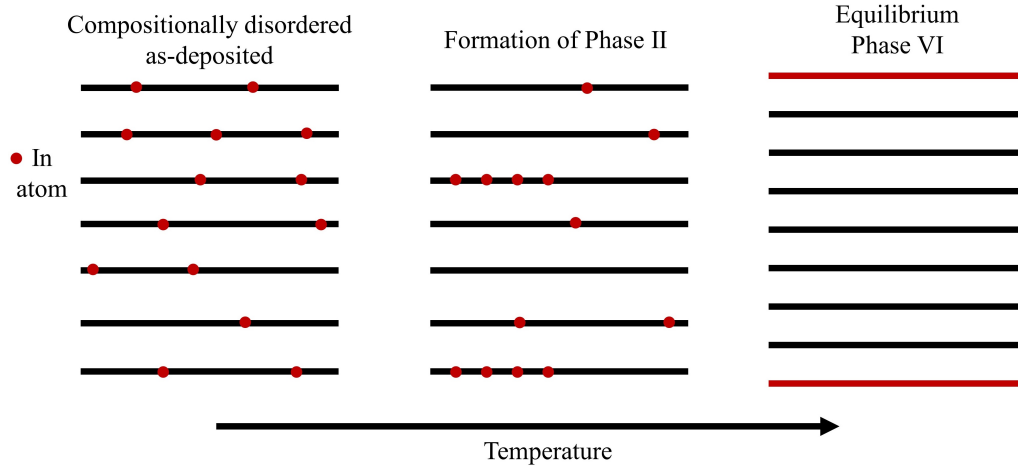


Figure 3.20: Schematic of Model B showing the spinoidal-like decomposition of the superlattice structure for sample 2 ($m = 5.96$).

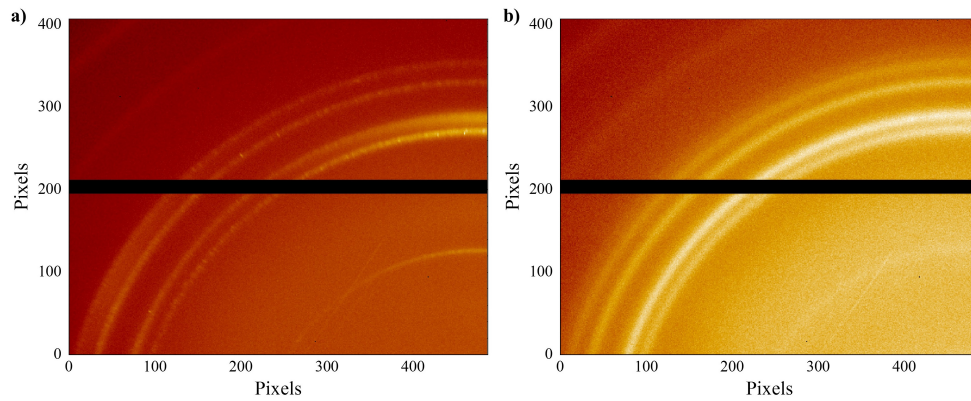


Figure 3.21: Area detector pixel images for a) Zn-rich sample 4 ($m = 2.63$) and b) less Zn-rich sample 7 ($m = 0.45$) showing the increased c-axis alignment of the Zn-rich sample.

c-axis alignment.

3.11 TEM Imaging

Transmission electron microscopy (TEM) analysis was performed on the Zn-rich sample 2 ($m=5.96$). If nucleation and growth dominated the structural devel-

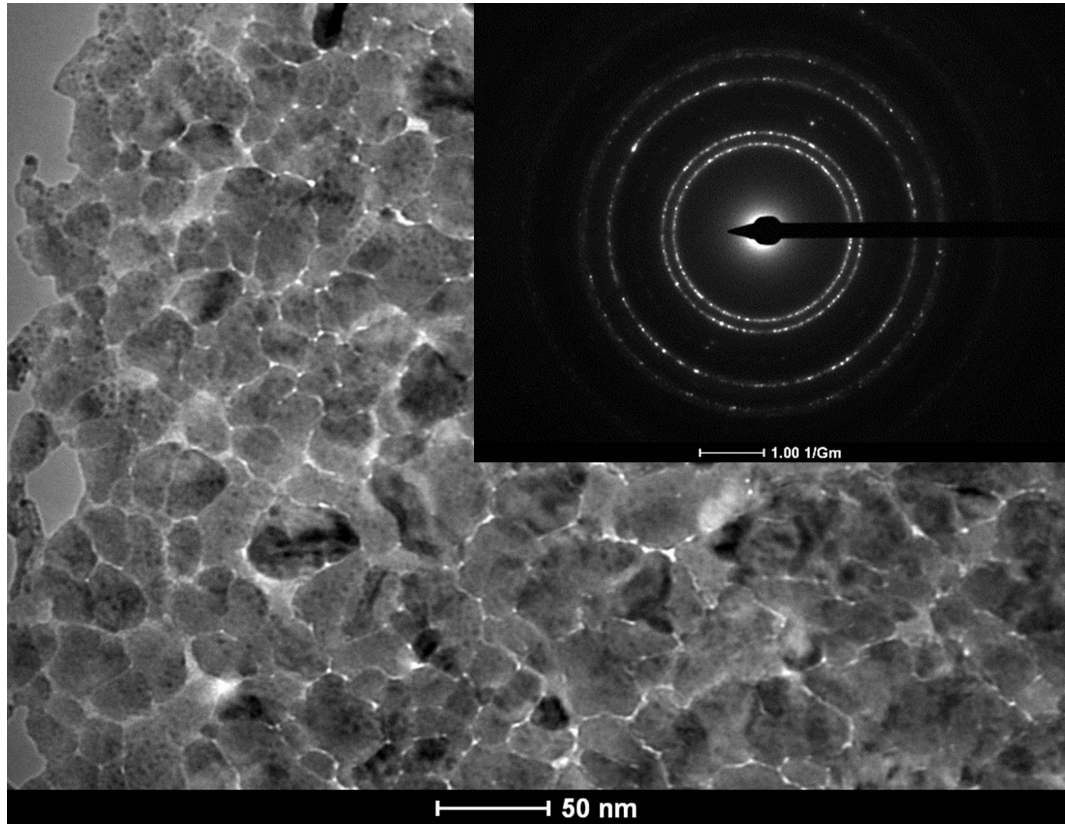


Figure 3.22: Bright field TEM image of sample 2 ($m = 5.96$) at a lower temperature using an accelerating voltage of 120 keV. Diffraction pattern included in corner using a $40\ \mu\text{m}$ aperture and camera length of 1.35 m.

opment (Model A), TEM should show crystalline grains surrounded by amorphous (or maybe different) phase regions. Plan-view samples were prepared by mechanical polishing on a wedge. Temperatures along the wedge can only be estimated and are difficult to quantify, so only relative temperatures are reported.

Figure 3.22 shows a bright field TEM image of the polycrystalline structure at a lower temperature anneal, indicating a columnar grain structure similar to ZnO with randomly oriented grains on the order of $\sim 20\ \text{nm}$. The diffraction pattern displays rings confirming the presence of randomly oriented crystal-

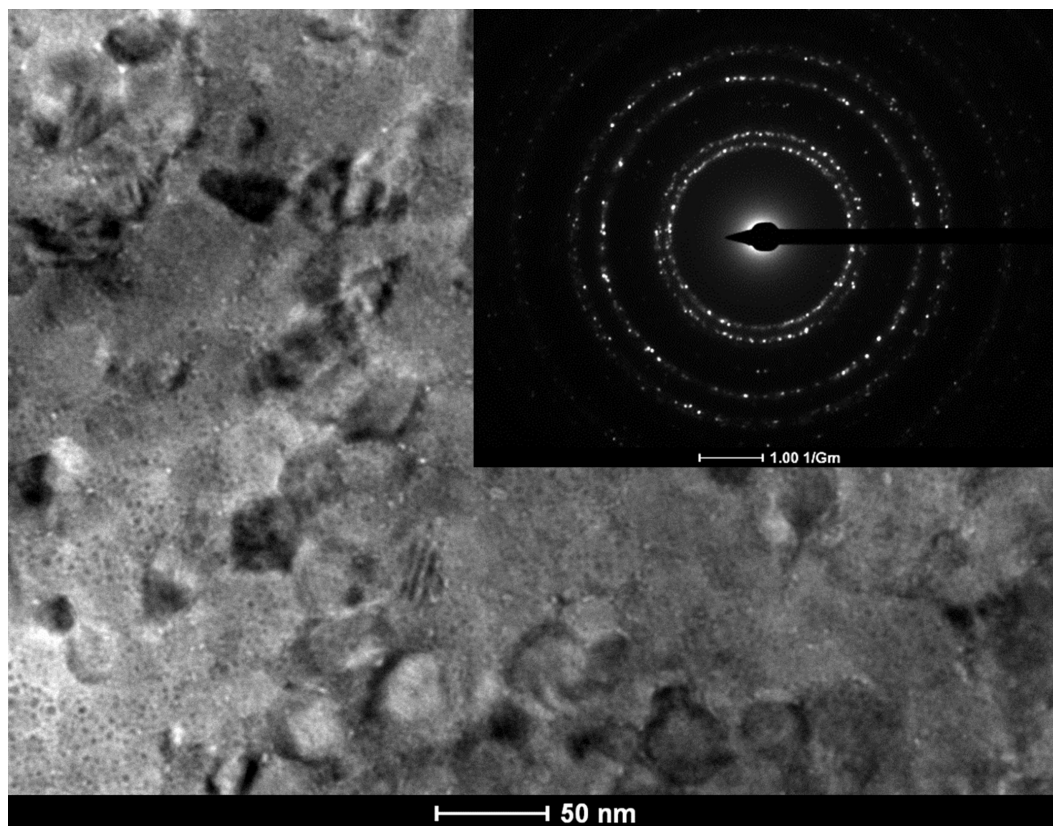


Figure 3.23: Bright field TEM image of sample 2 ($m = 5.96$) at a higher temperature. Corresponding diffraction pattern shown in corner.

lites. Moving into a higher temperature region, a similar grain pattern was seen (Figure 3.23). Some grain growth appears to have occurred as the boundaries between grains are no longer as clearly defined. The diffraction pattern from this region shows slightly broader diffraction rings that are in essentially the same position as in the low temperature region. Grains observed in TEM are larger than the size predicted using XRD, which is consistent with the Scherrer equation predicting only a minimum grain size. These TEM images unfortunately do not clearly rule out or support either model, and further high resolution TEM work is necessary.

The TEM diffraction patterns were converted to d-spacing to compare with

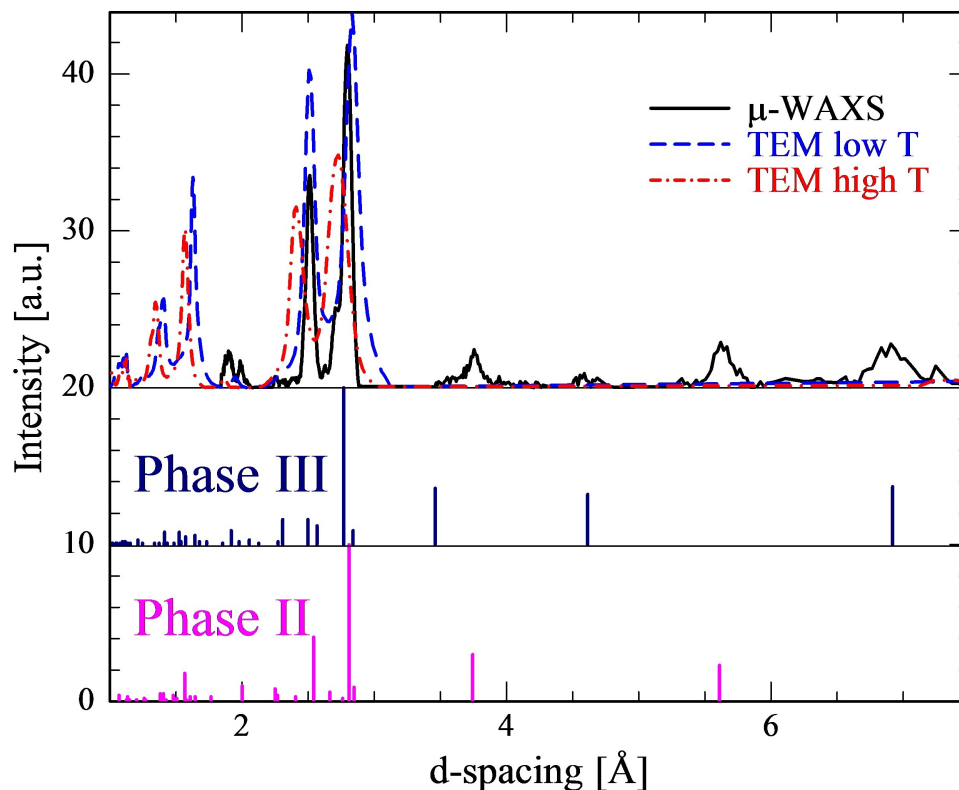


Figure 3.24: Intensity as a function of d-spacing comparing results from TEM and μ -WAXS. Expected peaks for Phases II and III shown below.

the μ -WAXS results. Figure 3.24 shows the intensity vs. d-spacing plot for both the TEM and μ -WAXS results, along with expected peaks for Phases II and III. The location of the major peaks from TEM align well with both the μ -WAXS results and predicted peaks for Phases II and III.

Samples also exhibited a "blister"-like morphology within the LSA regions at very high temperatures. These were first observed using a scanning electron microscope (SEM) during compositional analysis. Figure 3.25 shows two SEM images of sample 2 ($m = 5.96$) after annealing at 1,200°C for a longer and shorter duration. To determine the cause of the blisters, TEM analysis was performed. Figure 3.26 shows a bright field TEM image with the diffraction and

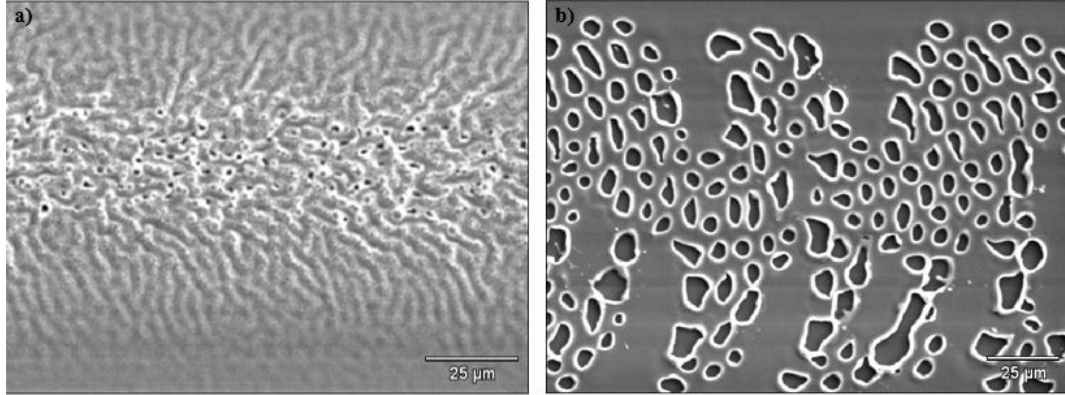


Figure 3.25: SEM images of sample 2 ($m = 5.96$) after LSA at 1,200°C for a) 5 ms and b) 750 μ s. Images taken using an accelerating voltage of 20 kV.

compositional analysis. The diffraction pattern in this region indicates a single crystal structure. Corresponding EDS chemical analysis reveals the structure to be composed mostly of silicon, indicating that the IGZO film and SiO₂ delaminated, leaving only the underlying single crystal Si substrate. We believe this is due to the rapid expansion of Ar during LSA that was trapped in the film during deposition. Similar effects have been seen in other films where blisters became larger with thicker films and shorter annealing times. The wavy pattern in Figure 3.25a is thought to be from the migration of Ar towards the hottest region where they expanded and burst, delaminating the film. With shorter duration anneals, the rapid heating caused more extensive blistering at lower temperatures. Blistering has been observed in other sputtered thin films after annealing due to Ar entrapment, and one solution would be to use elevated substrate temperatures during deposition [56].

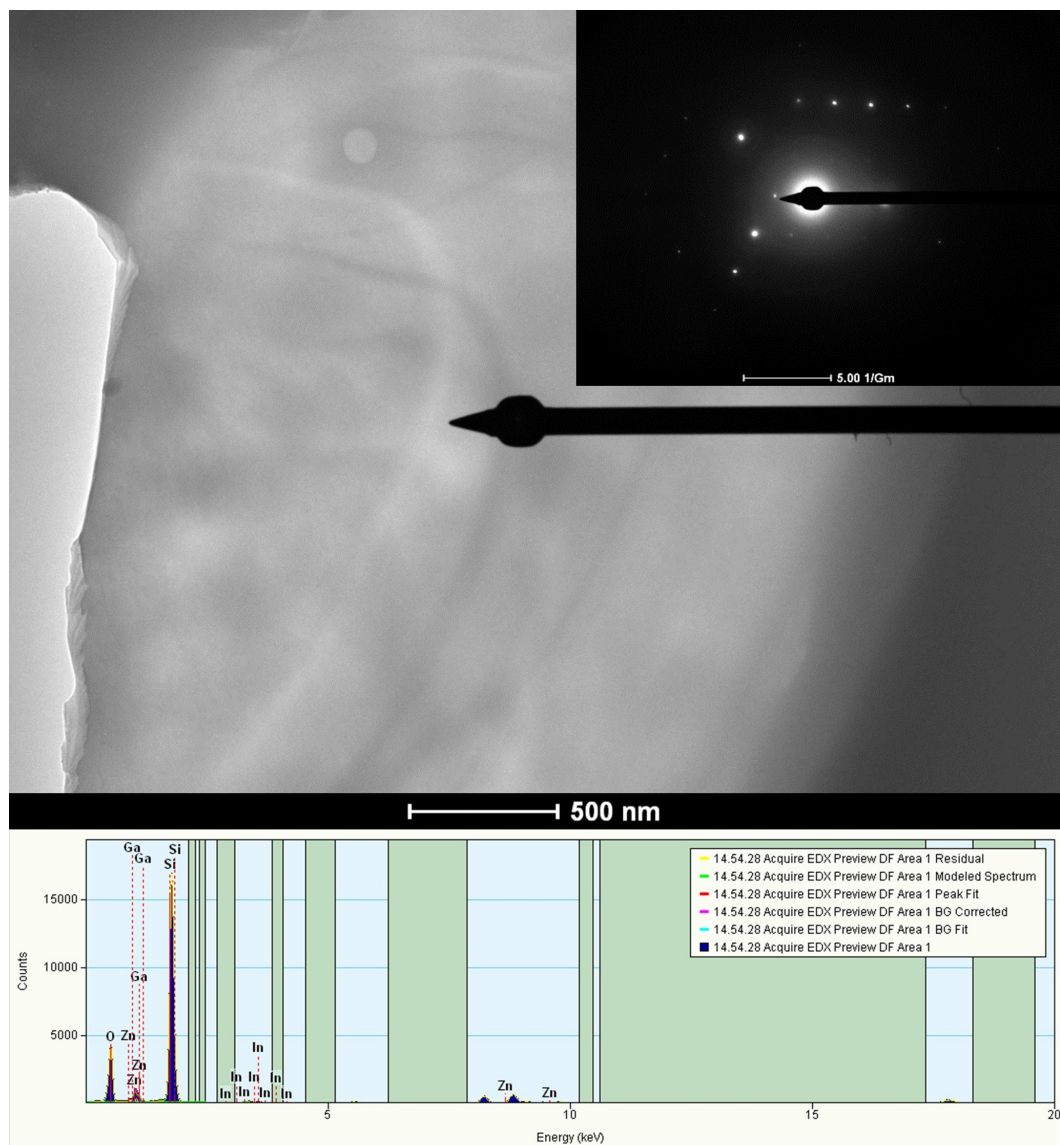


Figure 3.26: Bright field TEM image of a blister region showing where the diffraction pattern was observed, the corresponding diffraction pattern, and the EDS compositional analysis. EDS shows almost no In, Ga, or Zn suggesting delamination and IGZO film loss.

CHAPTER 4

CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

In this work, we studied the formation of superlattice structures as a function of Zn content in $\text{InGaO}_3(\text{ZnO})_m$ films. Zn-rich films as-deposited exhibited compositionally disordered structures similar to *wurtzite* that became more disordered with compositions further from pure ZnO (decreasing m). Using LSA with peak temperatures over $1,000^\circ\text{C}$ and longer dwell times (> 1 ms), superlattice structures formed at the expense of the as-deposited structures, suggesting a nucleation and growth mechanism. The superlattice structures were confirmed by matching the μ -WAXS data with known powder diffraction files. At lower temperatures and shorter dwell times, only grain growth and increased crystallinity were observed with no structural changes. Crystallization temperature changed as a function of dwell time, suggesting that the structural changes were kinetically limited. Additionally, increasing Zn content led to an increase in crystallization temperature. Calculated activation enthalpies based on the crystallization temperatures indicate that increasing Zn content inhibits the formation of superlattice structures.

We propose two models to explain the formation of the superlattice structures. For both models, the initial structure is compositionally disordered and similar to *wurtzite* with chemical substitutions that shift the lattice constant. The first model proposes the superlattice structure is formed through the diffusion of Zn out of the as-deposited structure and into amorphous regions that surround the superlattice region. In the second model, In atoms form coherent lay-

ers within the as-deposited structure. While they begin close together, the layers expand until the equilibrium structure is formed given high enough temperatures and long enough times. While TEM analysis was performed to confirm the formation of the superlattice structure, additional work is needed to distinguish between the two models.

Additionally, a liquid-like region of increased kinetic behavior was observed near $\sim 1,060^{\circ}\text{C}$ for films deposited from only the $\text{In}_2\text{Ga}_2\text{ZnO}_7$ target. This was unexpected as the melting points of all constituent oxides are much greater.

4.2 Future Work

The fundamental mechanisms leading to the development of these structures remains uncertain. Two models have been proposed in the current work, however it is not currently possible to distinguish between the two. As proposed previously, further high resolution TEM work would likely shed more light on the proposed mechanisms. In addition, other questions remain on the formation of these layered structures.

One proposed study is the role of "stacking faults" and how these might impact the structures that are formed. Stacking faults refer to a non-ideal arrangement of Zn/Ga and In layers within the structure. For example, in InGaZnO_4 ($m = 1$), the equilibrium structure should have two Zn/Ga layers between In planes. A stacking fault could then be 3 Zn/Ga layers sandwiched between the In layers. Similarly, for $\text{InGaZn}_{3.5}\text{O}_{6.5}$, how would alternating layers of 4 Zn/Ga layers and 5 Zn/Ga layers compare in free energy to an equivalent bulk 4 Zn/Ga block and 5 Zn/Ga block? Computational studies are likely required

to elucidate these subtleties. Additionally, the origin of the liquid-like region seen for the $m = 0.45$ film is still unclear, and further LSA studies using shorter dwell times may illuminate what is occurring.

Because these are complicated layered structures, there also remains some question of how various stacking of the InO_2 layers would alter the diffraction of X-rays. This is not included in the current work, but is instead left to inspire future work. The Hendricks-Teller model describes the impact of 1D disorder on the structure factor of layered materials [57]. To apply this to the $\text{InGaO}_3(\text{ZnO})_m$ system, the In can be thought of as layer 1, and the Zn/Ga can be thought of as layer 2. In an ideal InGaZnO_4 crystal, the stacking sequence is such that an In layer is always followed by a Zn/Ga layer, and a Zn/Ga layer is alternately followed by a Zn/Ga layer or an In layer. For an ideal structure then, layer 1 has a 100% chance of being followed by layer 1, and layer 2 has a 50% chance of being followed by layer 1 or layer 2. By calculating the structure factor and predicted diffraction intensity using the software program DIFFaX, these probabilities can be used to generate a thin film structure. This method was used to demonstrate several different probabilities for the In and Zn layering system and determine if stacking faults in the Phase I system could produce diffraction peaks corresponding to those seen in Phase II. Figure 4.1 shows the calculated diffracted intensity vs. 2θ plots for these structures as well as the Phase II peaks in red. The clear conclusion from these graphs is that stacking faults in Phase I cannot produce diffraction peaks seen in Phase II.

While all of the reported studies were performed with room temperature deposition, the author believes studies of heating during deposition would also be useful. Though strong c-axis alignment was not seen in the low Zn con-

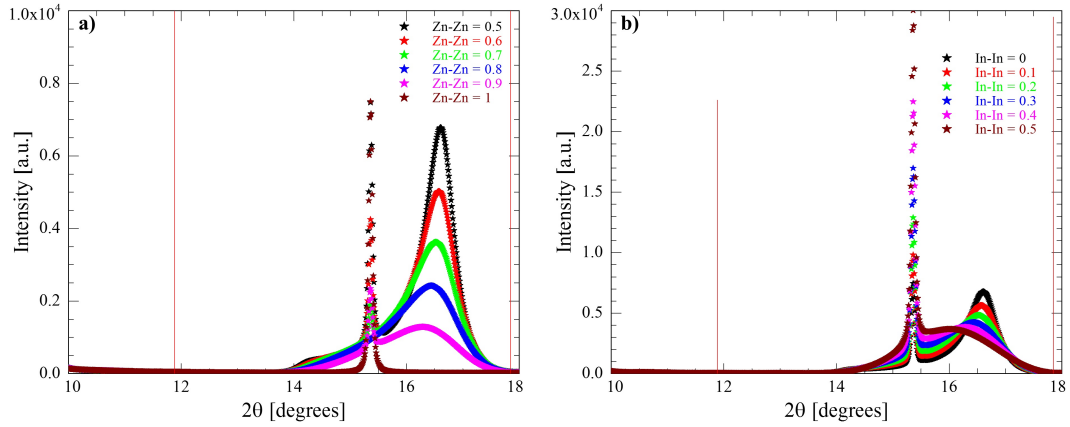


Figure 4.1: Calculated diffraction pattern for Phase I with stacking faults in the a) Zn-Zn probability and b) In-In probability. Zn-Zn indicates the probability of a Zn layer being followed by a Zn layer, similarly for In-In. Overlay lines in red correspond to an expected peak for Phase II. The conclusion here is that there is no way to form the Phase II peak through stacking faults of Phase I.

tent films, literature suggests that crystallization kinetics may be different when starting with an already aligned substrate. Additionally, heated deposition might allow the deposited ZnO buffer layer to epitaxially grow and act as a template for subsequent aligned growth of the IGZO.

As these materials are recommended for TFT devices, the fabrication of TFTs using co-sputtering and LSA would provide the next steps to determine electrical characteristics of these structures. For fabrication, area-scans of LSA would be more beneficial to create these structures over a larger area than is possible using single-scans.

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