

INVESTIGATIONS INTO $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ STRUCTURES GROWN ON C-PLANE
SAPPHIRE USING PULSED LASER DEPOSITION

by

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT	xii
 CHAPTER	
1. INTRODUCTION	1
2. LITERATURE REVIEW	5
2.1 Crystal Structure of β -Ga ₂ O ₃	5
2.2 Material Properties of β -Ga ₂ O ₃	9
2.3 Crystal Structure of In ₂ O ₃	11
2.4 Material Properties of In ₂ O ₃	12
2.5 Bandgap Engineering by Forming Gallium Oxide Alloys	12
3. GROWTH AND CHARACTERIZATION TECHNIQUES	15
3.1 Deposition Technique	15
3.1.1 Pulsed Laser Deposition (PLD)	15
3.1.2 Target Preparation	17
3.2 Characterization	18
3.2.1 X-ray Diffraction (XRD)	18
3.2.2 Ellipsometry	20
3.2.3 UV-Vis Spectroscopy	22
3.2.4 Atomic Force Microscopy (AFM)	23
3.3.5 X-ray Photoelectron Spectroscopy (XPS)	25
4. RESULT AND DISCUSSION	28
4.1 Experimental	28
4.2 Impact of Growth Parameters	28

4.3 Phase Transition from Metastable κ -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ to β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$	47
4.4 β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ / β - Ga_2O_3 Superlattice.....	60
5. CONCLUSION AND FUTURE WORK	62
REFERENCES	64

LIST OF TABLES

Table	Page
2.1. Lattice parameters for all Ga_2O_3 polymorphs	5
2.2. Comparison of β - Ga_2O_3 with other leading semiconductor materials.....	10
4.1 Bandgap reduction of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for $x = 0\%$ to 10%	36
4.2. Materials properties of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ at a fixed pressure of 1×10^{-3} torr and variable substrate temperatures.....	38
4.3. Materials properties of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ at a fixed temperature of 720°C and variable oxygen inflow into the main chamber	39

LIST OF FIGURES

Figure	Page
1.1. Applications of WBG for power electronics	3
2.1. Interconversion of Ga ₂ O ₃ polymorphs and their hydrates	6
2.2. (a) crystal structure of β- Ga ₂ O ₃ showing O and Ga sites. (b) Ga (1) is the tetrahedral and Ga (2) is the octahedral site are the two-fold Ga sites, and (c) O (1) and O (3) are the two tri-coordination sites and O (2) is the four coordination site	7
2.3. 2θ-χ relationship of the orthorhombic and hexagonal structures of Ga ₂ O ₃	9
2.4. (Color online) Unit cell of the In ₂ O ₃ bixbyite structure. Large (red) balls oxygen, small (dark) balls In-b and In-d (bright)	11
3.1. Schematic diagram of PLD system.....	16
3.2. Schematic diagram demonstrating Bragg's law	19
3.3. Configuration of ellipsometry	21
3.4. UV-Vis spectroscopy	22
3.5. Schematic of atomic force microscopy	24
3.6. Force-distance curve for Atomic Force Microscopes	25
3.7. Processes that result from X-ray bombardment of a surface include (a) emission of a photoelectron, (b) x-ray fluorescence, and (c) emission of an Auger electron.....	26
4.1. (a) XRD measurement of (In _{0.02} Ga _{0.98}) ₂ O ₃ grown at different substrate temperatures and (b) corresponding FWHM measurement of (-402) plane.....	30
4.2. (a) XRD measurement of (In _{0.02} Ga _{0.98}) ₂ O ₃ grown at different oxygen inflow and (b) corresponding FWHM measurement of (-402) plane	30
4.3. (a) XRD measurement of (In _{0.05} Ga _{0.95}) ₂ O ₃ grown at different substrate temperatures and (b) corresponding FWHM measurement of (-402) plane.....	31

4.4. (a) XRD measurement of $(\text{In}_{0.05}\text{Ga}_{0.95})_2\text{O}_3$ grown at different oxygen inflow and (b) corresponding FWHM measurement of (-402) plane	32
4.5. (a) XRD measurement of $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ grown at different substrate temperature and (b) corresponding FWHM measurement of (-402) plane	33
4.6. (a) XRD measurement of $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ grown at different oxygen inflow and (b) corresponding FWHM measurement of (-402) plane	33
4.7. (a) XRD measurement of optimized $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ grown with different In concentration and (b) corresponding FWHM measurement of (-402)	34
4.8. Tauc plot for IGO thin films (inset optical transmittance plot)	36
4.9. Literature data vs current work showing bandgap engineering using In as alloy in $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films for different polymorphs. Monoclinic (m), hexagonal (h), cubic (c), and rhombohedral (rh) crystal polymorphs are indicated by upward triangles, circles, squares, and diamond shape markers, respectively. The yellow stars represent current work	37
4.10. Impact of substrate temperature on thickness of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x=2\%$ (b) $x=5\%$, and (c) $x=10\%$	39
4.11. Impact of oxygen partial pressure on thickness of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x=2\%$ (b) $x=5\%$, and (c) $x=10\%$	41
4.12. Survey spectrum of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.08$, and (d) $x = 0.1$ respectively	42
4.13. High resolution $\text{Ga}3d_{5/2}$ XPS spectra of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.08$, and (d) $x = 0.1$ respectively	43
4.14. High resolution In 3d core level XPS spectra of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.08$, and (d) $x = 0.1$ respectively	44
4.15 High resolution O 1s core level XPS spectra of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.08$, and (d) $x = 0.1$ respectively	45
4.16. X-ray photoelectron spectroscopy (XPS) spectra of O1s of $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ for (a) $P_{\text{O}_2} = 5 \times 10^{-2}$ torr, (b) $P_{\text{O}_2} = 1 \times 10^{-2}$ torr, (c) $P_{\text{O}_2} = 1 \times 10^{-3}$ torr, (d) $P_{\text{O}_2} = 1 \times 10^{-4}$ torr, and (e) $P_{\text{O}_2} = 1 \times 10^{-5}$ torr	46

4.17. (a) Monoclinic β -galia structure and its nearest-neighbor configuration of Ga(1)O ₄ tetrahedron, Ga(2)O ₆ octahedron lattice sites. O(1) and O(2) are threefold coordinated, and o(3) is fourfold coordinated oxygen lattice sites. (b) Bixbyite cubic lattice structure with 8b and 24d Wyckoff position. The oxygen positions are in the corner positions of the cube. (c) Orthorhombic Ga ₂ O ₃ lattice structure with an ab plane on an oxygen layer is shown with a dashed line [112]. (d) Hexagonal InGaO II crystal structure (In in purple, Ga in green). Ga is fivefold, and In is sixfold coordinated [100]	49
4.18. X-ray 2 θ - ω diffraction diagram for 8% (In _x Ga _{1-x}) ₂ O ₃ (a) varying substrate temperature, (b) varying oxygen partial pressure of the chamber	50
4.19. Epitaxial relationship of (In _x Ga _{1-x}) ₂ O ₃ with the c-sapphire substrate (a) XRD phi scan of (-401) plane of (In _{0.10} Ga _{0.90}) ₂ O ₃ , and (b) phi scan of (104) plane of the sapphire substrate.....	51
4.20. (a) XRD 2 θ - ω scan of (In _x Ga _{1-x}) ₂ O ₃ with x=15% grown on c-plane sapphire, (b) rocking curve of the {004} diffraction peak, and (c) phi scan of {122} plane proving the presence of κ -(In _x Ga _{1-x}) ₂ O ₃	53
4.21. (a) Impact of laser power and fluence on (In _x Ga _{1-x}) ₂ O ₃ (x=10%), (b) zoomed in on (-402) and (004) diffraction peaks	54
4.22. (a) Impact of substrate temperature on (In _x Ga _{1-x}) ₂ O ₃ (x=10%) grown with high laser power (550mJ), (b) zoomed in on (-402) and (004) diffraction peaks.	55
4.23. (a) Impact of substrate temperature on (In _x Ga _{1-x}) ₂ O ₃ (x=10%) grown with low laser power (300mJ), (b) zoomed in on (-402) and (004) diffraction peaks	56
4.24. (a) Impact of oxygen partial pressure on (In _x Ga _{1-x}) ₂ O ₃ (x=10%) grown with high laser power (550mJ), (b) zoomed in on (-402) and (004) diffraction peaks.....	57
4.25. AFM analysis of (a) β -(In _x Ga _{1-x}) ₂ O ₃ and (b) κ -(In _x Ga _{1-x}) ₂ O ₃ for x =10%.	58
4.26. Impact of PLD growth parameters (laser power, substrate temperature, and oxygen partial pressure) on the growth of different polymorphs of (In _x Ga _{1-x}) ₂ O ₃ grown on c-plane sapphire	59
4.27. Diagram of the β -(In _x Ga _{1-x}) ₂ O ₃ / β - Ga ₂ O ₃ superlattice grown on c-sapphire using PLD	60

4.28. XRD 2θ - ω scans of β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ / β - Ga_2O_3 superlattice with $x = 2\%$, 5% , and 10%	61
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ABSTRACT

Alloys of Ga_2O_3 with In_2O_3 , ternary $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ were grown for $x \leq 15\%$ as a function of growth parameters such as substrate temperature (T_s), oxygen partial pressure (P_{O_2}), and laser power using Pulsed Laser Deposition (PLD) technique. The structural property of the as-grown layers was studied based on the growth parameters employing X-ray diffraction (XRD) analysis. Besides the monoclinic phase reflections of Ga_2O_3 and cubic bixbyite phase reflections of In_2O_3 , an extra peak was observed for indium concentration, $x \geq 8\%$ at specific growth conditions. The indium incorporation was reflected in a band gap reduction between 4.98 and 4.64 eV, as determined using UV-Vis analysis. Ellipsometry study showed a slight thickness variation due to evaporation of volatile Ga_2O and In_2O suboxides. X-ray photoelectron spectroscopy (XPS) analyses indicated that the $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ alloy contains a mixture of Ga and In cation valence states and oxygen vacancies that were reduced when the oxygen partial pressure during deposition was increased. During the analysis of the XRD spectra of the $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ alloy, the observation of an extra peak led to the investigation of metastable polymorphs of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$. This polymorph, κ -($\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ was confirmed through X-ray diffraction phi-scan of the $\{122\}$ reflection representing the orthorhombic phase. The spontaneous polarization of κ -($\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ makes it a promising candidate for 2DEG HEMT and ferroelectric devices. Detailed investigation of the impact of growth conditions in the κ -phase indicated that the appearance of this phase is due to specific growth conditions and does not depend on the nucleation process. The impact of PLD

growth parameters such as laser power, substrate temperature, and oxygen partial pressure was investigated using XRD to establish a phase diagram for the κ -phase and β -phase of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$.

1. INTRODUCTION

Since the invention of modern semiconductor technology, silicon (Si) has been widely used because of its abundant availability and comparatively better surface properties [1]. Due to the massive evolution of Si-based device processes, top competitors in the industry can now pack over 15 billion transistors in a single chip [2]. However, because of the increase in transistor density due to scaling according to Moore's law, Si-based transistors have reached its limit in planar device technology [3]. Additionally, Si is an indirect bandgap material, making it inefficient for optoelectronics devices such as LED and laser because of its low intrinsic quantum efficiency and photon creation capability [4], [5]. Moreover, with scaling, Si becomes comparatively inefficient for high-power devices because of its low breakdown voltage [6], [7]. So, although Si is still the best in the industry for manufacturing logic-based chips, wide bandgap semiconductors with better scaling capability and high breakdown voltages are currently getting researchers' attention to develop ultraviolet optoelectronics and high power devices [8], [9]. In addition, certain heterostructures can form two-dimensional electron gas (2DEG) in the channel region of field-effect transistor (FET) devices that can be utilized for high electron mobility transistors (HEMT).

High power devices require semiconducting materials with high electrical breakdown and thermal conductivity. Researchers are investigating wide-bandgap binary and ternary compounds and their alloys to achieve such properties. Breakdown voltage is proportional to the exponential power of the bandgap, which can be expressed as $E_c = \alpha(E_g)^n$, where E_c is the breakdown voltage, E_g is the bandgap, α is the ionization rate of holes and electrons and n is in the range of 2-2.5 [10]–[12]. Thus, implementing wide

bandgap semiconductors can offer magnitudes of higher breakdown voltages with comparatively thin layers, leading to better device scalability.

Traditionally, wide bandgap semiconductor alloys such as silicon carbide (SiC) and gallium nitride (GaN) demonstrated better performance than Si for high-power devices in terms of thermal efficiency, voltages, and frequency [13], [14]. However, due to a lack of high crystal quality substrates, which leads to dislocation and grain boundaries in the device structure, the full potential of these alloys is yet to be reached. Moreover, GaN and SiC substrates have very complex physical vapor growth techniques and adopting them in today's industry is very difficult and expensive. Gallium oxide (Ga_2O_3) has recently attracted researchers' attention for its ultra-wide bandgap and predicted high electrical breakdown voltage. Among the five different crystal structures of Ga_2O_3 (α , β , γ , δ and ϵ), β - Ga_2O_3 is the most thermally and chemically stable phase. Recent innovations allowed for high-quality single crystal β - Ga_2O_3 substrates manufactured by melt-growth methods such as the Czochralski method, vertical Bridgman method, floating zone, and edge defined film-fed growth techniques can be easily integrated into industries [15]–[18]. Figure 1 illustrates the applications of wide bandgap semiconductors (WBG) in the power electronics area.

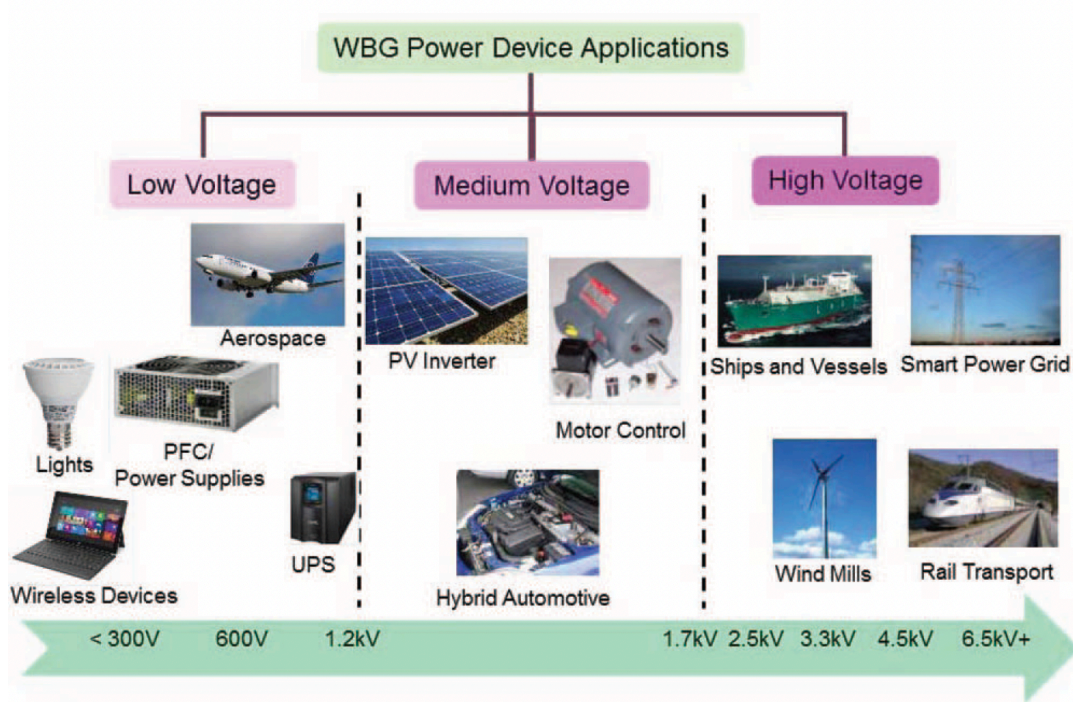


Figure 1.1: Applications of WBG for power electronics [16].

Besides power electronics, the large bandgap ($\sim 4.9\text{eV}$) of Ga_2O_3 makes it useful for optical and sensing technology. Ga_2O_3 is optically transparent at all wavelengths above 250 nm, which makes it a potential transparent conducting oxide for solar cells and optical sensors. Also, by varying the doping concentration and creating heterostructures, the conductivity of Ga_2O_3 can be changed from an insulator to a conductor [19], [20]. The alloys of Ga_2O_3 mixed with In and Al are reported to have bandgaps in the range of 3.5~8.6 eV, which is very useful for designing UV detectors [21]–[23]. Understanding the impact of the growth parameters and stability of these heterostructures is of paramount importance for the next generation of wide bandgap device technology.

Among the 5 polymorphs, $\beta\text{-Ga}_2\text{O}_3$ is the most stable and has had the most research interest. But the other polymorphs, most importantly, the $\epsilon\text{-Ga}_2\text{O}_3$ and the $\kappa\text{-Ga}_2\text{O}_3$, are receiving more attention due to having ferroelectric properties. Researchers

assigned ϵ -Ga₂O₃ to a Sn doped gallium oxide which exhibits neither α nor β phase of Ga₂O₃ [24]. Further investigation showed that the X-ray diffraction peaks belong to the space group Pna2₁, which is orthorhombic. This crystal structure resembles that of the κ -Al₂O₃ phase, and thus they denoted this phase as κ -Ga₂O₃ [25]. Stabilization of κ -Ga₂O₃ can help researchers realize high-performance HEMT devices due to its predicted high 2DEG density in heterostructures. However, research on κ -Ga₂O₃ is still in its infancy.

This thesis aims to study (In_xGa_{1-x})₂O₃ structures grown on c-plane sapphire using pulsed laser deposition. For this study, a low concentration of In ($x \leq 15\%$) will be incorporated for the (In_xGa_{1-x})₂O₃ thin films, and the impact of growth parameters such as substrate temperature and oxygen pressure will be investigated. Crystalline structure and quality will be investigated using x-ray diffraction (XRD), surface properties will be investigated using x-ray photoelectron spectroscopy (XPS) analysis, and optical properties will be examined using UV-spectroscopy and ellipsometry. The band-gap engineering property by alloying In with Ga₂O₃ will be determined and compared with contemporary results. For the second part of the thesis, the impact of laser power, oxygen partial pressure, and substrate temperature will be investigated for (In_xGa_{1-x})₂O₃ for $x = 8\%$, 10% , and 15% . κ -(In_xGa_{1-x})₂O₃ and ϵ -(In_xGa_{1-x})₂O₃ polymorphs and their behavior under different growth environments will be investigated using X-ray diffraction analysis. Finally, a superlattice of β -Ga₂O₃ / β -(In_xGa_{1-x})₂O₃ will be grown for $x = 2\%$, 5% , and 10% .

2. LITERATURE REVIEW

2.1 Crystal Structure of β -Ga₂O₃

Gallium oxide (Ga₂O₃) has five phases: α , β , γ , δ and ε . The composition, reciprocal space group, and lattice parameters of the phases of gallium oxide are given in table 2.1 [26]. Among these polymorphs, β -Ga₂O₃ is the most stable crystalline phase. This stable formation persists under different temperatures, whereas all other polymorphs are metastable and convert to β -Ga₂O₃ at high temperatures. The crystal structure of β -Ga₂O₃ is monoclinic and belongs to the space group C2/m [27]–[29].

Table 2.1: Lattice parameters for all Ga₂O₃ polymorphs

Phase	Composition (at % O)	Space Group	Lattice Parameters (nm, deg)
α -Ga ₂ O ₃	60	$R\bar{3}c$	a = 0.49791 c = 1.3437
β -Ga ₂ O ₃	60	$C2/m$	a = 1.2214 b = 0.30371 c = 0.57981 $\beta = 103.83^\circ$
γ -Ga ₂ O ₃	60	$Fd\bar{3}m$	a = 0.822
δ -Ga ₂ O ₃	60	$Ia\bar{3}$	a = 1.0
ε -Ga ₂ O ₃	60	$Pna2_1$	a = 0.5120 b = 0.8792 c = 0.9410
Ga ₂ O	33.3		

The crystal structure of Ga₂O₃ is quite similar to the crystal structure of Al₂O₃ because of the similarity between their ions Al and Ga. The metastable phase α -Ga₂O₃ resembles the corundum structure of the stable Al₂O₃. β -Ga₂O₃ possesses the highest formation energy and all other phases follow $\beta > \varepsilon > \alpha > \delta > \gamma$ order in terms of their formation energy [30]. Figure 2.1 illustrates the interconversion of Ga₂O₃ polymorphs and their hydrates [31].

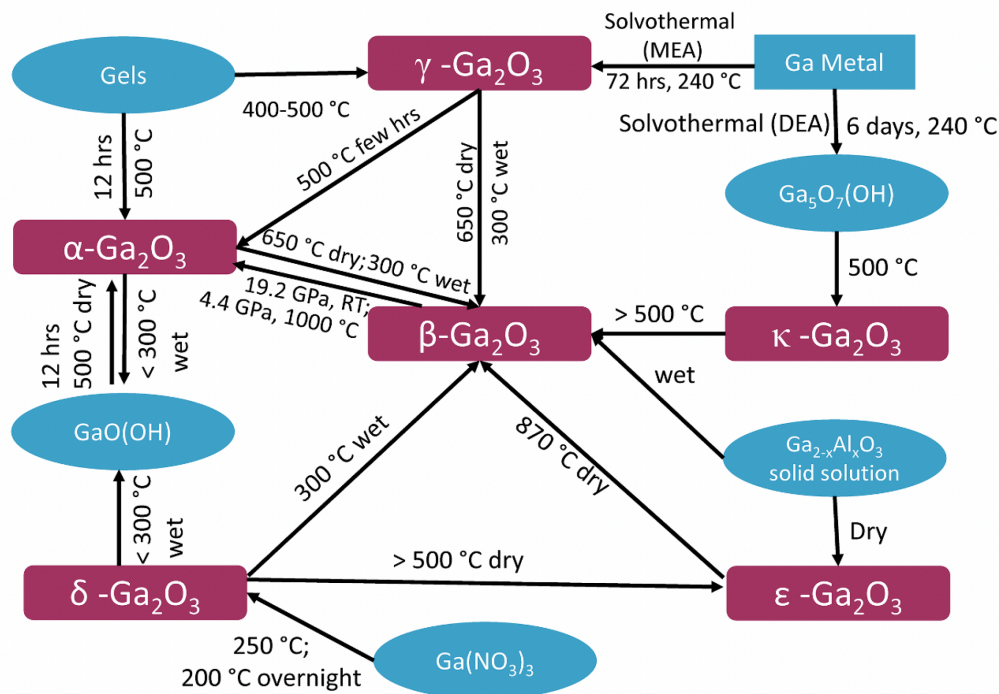


Figure 2.1: Interconversion of Ga_2O_3 polymorphs and their hydrates [31].

Roy *et al.* [28] used crystalline Gallia gel prepared from an aqueous solution and the hydration process created the $\alpha\text{-Ga}_2\text{O}_3$. Additional hydration in lower temperatures created GaO(OH) that transformed into $\delta\text{-Ga}_2\text{O}_3$. $\gamma\text{-Ga}_2\text{O}_3$ was formed in specific aging conditions and the stable $\beta\text{-Ga}_2\text{O}_3$ was found when any other polymorphs or its hydrates are annealed in the air above 1000°C or hydrothermally treated at a specific temperature and environment. They also showed that $\delta\text{-Ga}_2\text{O}_3$ could be heated over 500°C to achieve $\epsilon\text{-Ga}_2\text{O}_3$. Playford *et al.* [32] also synthesized Ga_2O_3 polymorphs using a similar solvothermal process to Roy *et al.* but refined. They discovered a new metastable polymorph exhibiting an orthorhombic crystal structure referred to as $\kappa\text{-Ga}_2\text{O}_3$ by thermal treatment of $\text{Ga}_5\text{O}_7(\text{OH})$ (process flow included in figure 2.1).

The crystal structure of monoclinic β - Ga_2O_3 is shown in the following figure 2.2. The angle $\alpha = \gamma = 90^\circ$ and $\beta = 103.8^\circ$, which is the angle between lattice parameters a and c .

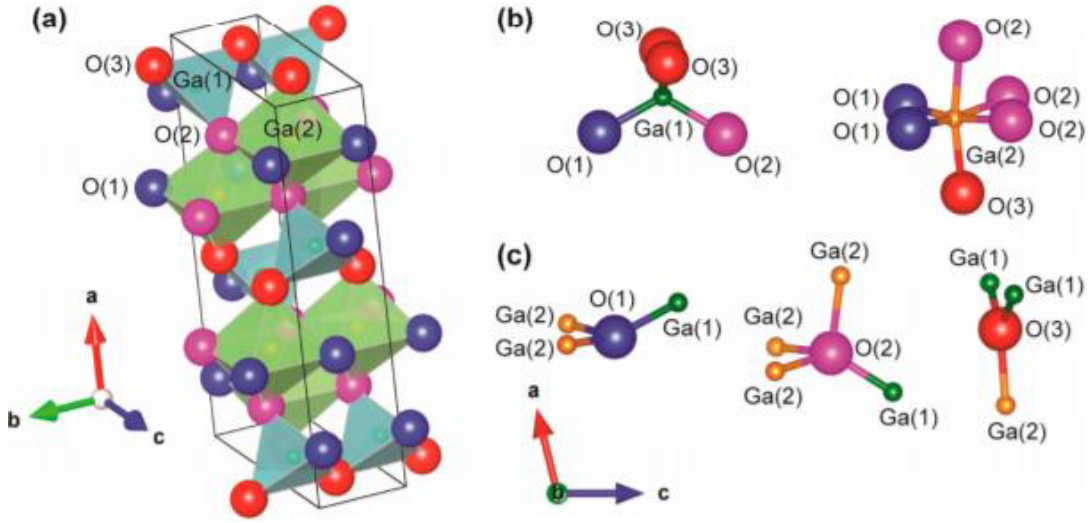


Figure 2.2: (a) Crystal structure of β - Ga_2O_3 showing O and Ga sites. (b) Ga (1) is the tetrahedral and Ga (2) is the octahedral site are the two-fold Ga sites, and (c) O (1) and O (3) are the two tri-coordination sites and O (2) is the four coordination site [33].

The unit cell of β - Ga_2O_3 comprises of 8 Ga and 11 O atoms. The Ga and O sites are inequivalent. The two inequivalent Ga sites are the tetrahedral Ga (1) site with four oxygen atoms surrounding it and the octahedral Ga (2) site with six oxygen atoms surrounding it. The available three oxygen sites are also nonequivalent, with O (1) and O (3) being tri-coordinated and O (2) being four-coordinated [33], [34]. Its monoclinic structure allows it to have a large electrical breakdown potential for bandgap engineering and phase transformation via alloying with other elements broadens beta gallium oxides potential even more for the next generation of electrical and optical devices.

Besides the most stable β - Ga_2O_3 , the thermodynamically transient phases require more attention due to their potential applicability. The ϵ - $(\text{InGa})_2\text{O}_3$ and κ - $(\text{InGa})_2\text{O}_3$ can

induce polarization differences by creating heterointerfaces with Ga_2O_3 or $(\text{AlGa})_2\text{O}_3$, which can be used to form a 2D electron gas with potentially high carrier density. The κ - Ga_2O_3 is ferroelectric and possesses spontaneous polarization which is larger than in GaN. According to DFT calculations the κ -($\text{AlGa})_2\text{O}_3/\kappa$ - Ga_2O_3 heterostructures are expected to have a very high 2D electron gas density [35]–[37].

The ε phase in Ga_2O_3 exhibits a 4H (ABAC sequence) stacking of oxygen atoms along the c axis with octahedra and tetrahedra Ga Sites forming two types of polyhedral parallel to (001). This structure resembles the κ - Al_2O_3 and Fornari *et al.* concluded that both κ and ε - Ga_2O_3 could be seen according to the size of the ordered domains and resolution of the characterization tool [38]. Due to κ - Ga_2O_3 having very small orthorhombic domains, electron diffraction tools are necessary to detect its presence. In addition, the orthorhombic structure can be distinguished from the hexagonal structure by performing a phi-scan in X-ray diffraction for the $\{122\}$ reflection of the orthorhombic lattice [39]. Figure 2.3 illustrates the XRD angle relation of orthorhombic and hexagonal structure of Ga_2O_3 . The 2θ - χ relationship between the hexagonal crystal reflexes and the orthorhombic crystal reflexes is given here. We can see from the figure that they have many diffraction reflexes common with each other, which makes the structures harder to distinguish from each other. But, there are some particular reflection planes unique to the orthorhombic structures, which will be used to distinguish the crystal structures of $(\text{InGa})_2\text{O}_3$ in later chapters.

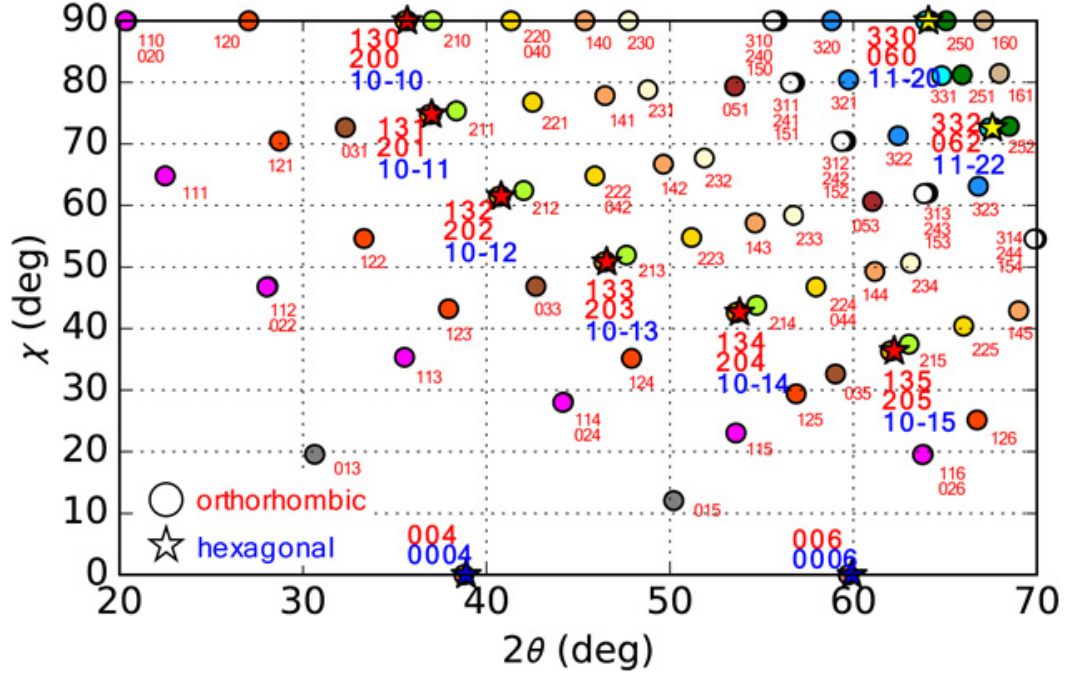


Figure 2.3: 2θ - χ relationship of the orthorhombic and hexagonal structures of Ga_2O_3 [39]

Boschi *et al.* [40] reported the first stabilized ε - Ga_2O_3 using low-temperature MOCVD and ALD. Fornari *et al.* also reported similar stability in ε - Ga_2O_3 using MOCVD and showed that very high-temperature annealing (1000°C) transforms it to β - Ga_2O_3 [38]. On the other hand, κ - Ga_2O_3 has been grown using different deposition techniques such as MOCVD, mist CVD, MBE, and PLD. Gottschalch *et al.* [41] reported for the first time that κ - Ga_2O_3 could be grown on a- and r-plane Al_2O_3 . Shimazoe *et al.* [42] reported heteroepitaxial growth of κ - Ga_2O_3 thin films on LiNbO_3 and LiTaO_3 substrates with Fe_2O_3 buffer layers. PLD and MBE require Sn or In to stabilize the kappa phase in Ga_2O_3 [43], [44]. Nishinaka *et al.* [39] reported ε - Ga_2O_3 substrates for the growth of single-crystalline κ - Ga_2O_3 thin films.

2.2 Material Properties of β - Ga_2O_3

The most stable polymorph of gallium oxide is β - Ga_2O_3 with a reported bandgap of 4.5-4.9 eV [45], [46]. Although pure Ga_2O_3 is an insulator, it is reported that it can

show significant n-type conductivity with the assumption that it occurs due to the oxygen vacancies in the thin film [10]. Bayraktaroglu disputed the premise by proposing that shallow donor impurities and monoatomic hydrogen atoms are responsible for the n-type conductivity [47]. Si, Sn, and Ge can be used as dopants to make an n-type gallium oxide with up to 10^{19} cm^{-3} electron density. On the other hand, p-type doping is difficult because of the high bandgap, shallow acceptor level compared to the host valence band, defects like anion vacancies, and cation interstitials [48]. The thermal conductivity of β -Ga₂O₃ depends strongly on its crystal orientation. It is highest in the [010] direction and the lowest along the [100] direction [49]. Table 2.2 compares β -Ga₂O₃ with other leading semiconductor materials used commercially in logic and power devices [50].

Table 2.2: Comparison of β -Ga₂O₃ with other leading semiconductor materials

Property	Si	GaAs	4H-SiC	GaN	Diamond	β -Ga ₂ O ₃
Bandgap, E_g (eV)	1.1	1.4	3.3	3.4	5.5	~4.9
Electron mobility, μ ($\text{cm}^2\text{V}^{-1}\text{S}^{-1}$)	1400	8000	1000	1200	2000	300
Breakdown field, E_b (MVcm^{-1})	0.3	0.4	2.5	3.3	10	8
Relative dielectric constant, ϵ	11.8	12.9	9.7	9.0	5.5	10
Baliga's FOM, $\epsilon\mu E_b^3$	1	15	340	870	24664	3444

As we can see from the table, because of the high bandgap the electron mobility is low. Still, the breakdown voltage is over two times higher than that of GaN, which is currently being used for producing state-of-the-art power electronics devices. Baliga's figure of merit, a metric widely used to express the sustainability of a material as a power

device, is almost three times that of GaN. Thus, successful and inexpensive integration of β -Ga₂O₃ in power semiconductor devices will significantly improve their performance.

2.3 Crystal Structure of In₂O₃

Indium oxide has six different polymorphs; among them, the cubic bixbyite is the most stable form at room temperature. The cubic unit cell has a total of 80 atoms with 48 oxygen and 32 indium atoms arranged with a lattice parameter of 10.117 Å [51]. There are two different symmetric In sites referred to as In-b and In-d. In-b sites contain 8 atoms and can be found to be more abundant than In-d sites, which include 24 atoms. This structure can be organized into three different layers, as shown in figure 2.4: a layer containing In-d atoms (referred to as D-layer), an oxygen layer (referred to as O-layer), and a mixed layer containing both In-b and In-d atoms (referred to as M-layer) [52]. Due to this alternating layered structure of indium oxide along the (001) direction, this material possesses a net dipole moment perpendicular to the surface. The In-b and In-d atoms occupy 8b and 24d Wyckoff positions, respectively, whereas oxygen atoms occupy the 48e Wyckoff position [53].

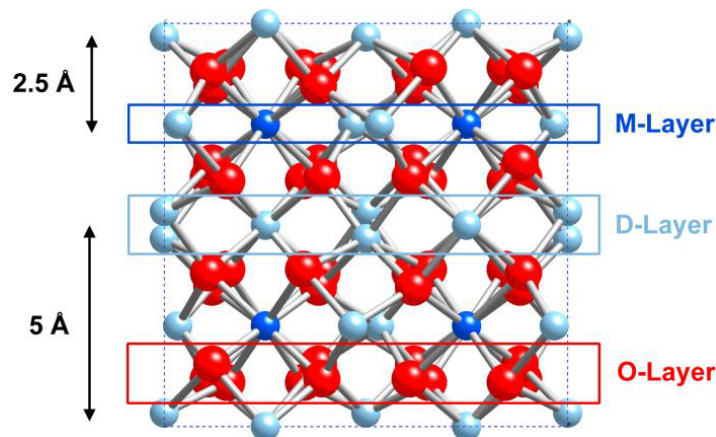


Figure 2.4: (Color online) Unit cell of the In₂O₃ bixbyite structure. Large (red) balls oxygen, small (dark) balls In-b and In-d (bright [53]).

2.4 Material Properties of In_2O_3

The optically determined bandgap of In_2O_3 is 3.75 eV [54], but some researchers also argued it to be around 2.9 eV [55]. In_2O_3 can be expressed as an n-type semiconductor for having conductive carriers arising from intrinsic donor defects [56]. Agoston *et al* also reported indium oxide to be an excellent conductor even without impurity doping due to its high carrier concentration, but only if grown in an oxygen-deficient environment [57]. Carrier concentration is reported to be between 10^{17} to 10^{20} cm^{-3} , and increasing the oxygen pressure during growth results in a reduction of the carrier concentration [58]. The most used conductive indium oxide is one that is doped with 9% tin oxide forming indium tin oxide (ITO), which exhibits resistivity of only 7.7×10^{-5} ohm-cm [59].

2.5 Bandgap Engineering by Forming Gallium Oxide Alloys

Heterostructure electronic and optical devices are born from the concept of bandgap engineering. When two or more binary materials having different bandgaps are used as device epitaxy, it will show a range of bandgap based on the concentration of the specific material on it. By forming alloys with In, Al, Gd, Fe, etc., Ga_2O_3 can provide a wide range of bandgap tunability (from 2.5eV to 8.6 eV) and functionalities, which opens a myriad of next-generation device applicability. This wide range of bandgap can cover almost the entire UV spectrum (144-354 nm) making it a very viable candidate for UV optoelectronic devices.

In this work, the alloys of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ will be investigated. Indium belongs to the same column III element group of Ga and their oxide forms a similar electronic structure [21],[60],[61]. $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ is a viable candidate for transparent conducting

oxide because indium reduces the resistivity of the layer while still maintaining a low optical absorption coefficient. As discussed above, In_2O_3 has a stable bixbyite cubic structure, whereas $\beta\text{-Ga}_2\text{O}_3$ has a stable monoclinic structure. Previous research on this alloy showed that with low In concentration, the $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ retained a monoclinic phase, while for increasing In concentration the alloy exhibited a mixed-phase containing both cubic and monoclinic phases. Finally, $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ alloys with high In concentration has a single crystalline cubic structure [62]–[64]. The incorporation of indium leads to an increase in lattice parameters a, b, and c. On the contrary the monoclinic phase decreases with increased In incorporation. Edwards *et al.* [65] investigated In-doped $\beta\text{-Ga}_2\text{O}_3$ and showed that In^{3+} ions occupy the octahedral sites up to the 40% In_2O_3 composition in GaInO_3 . This claim was validated by Vasylytsiv *et al.* [66] using X-ray diffraction analysis and Pasquevich *et al.* [67] using perturbed angular correlation, which is a method of nuclear solid-state physics with which magnetic and electric fields in crystal structures can be measured. Zhang *et al.* [60] grew $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ using PLD and showed that an increase in the In concentration changes the alloy crystalline structure. $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ with $x < 16\%$ exhibited single-crystalline monoclinic phase, and $x > 83\%$ showed single-crystalline cubic phase in XRD study. The In concentration in-between these values exhibited a combination of both cubic and monoclinic phases. Additionally, a bandgap tunability of 1.3 eV (3.8 eV to 5.1 eV) was reported, with the bandgap increasing with increasing Ga concentration in the alloy as expected. On the other hand, Binet *et al.* [68] found $\beta\text{-Ga}_2\text{O}_3$ phases up to $x < 40\%$ and showed improvement of epitaxy by annealing at 1400 °C in vacuum. Oshima *et al.* [69] used sapphire (0001) substrates on MBE to grow $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ on top of a $\beta\text{-Ga}_2\text{O}_3$

buffer layer. They showed that at higher substrate temperatures (over 700 °C), there was a phase transformation from single-crystalline monoclinic to poly-crystalline phases, but lower substrate temperature (under 600 °C) can be used to suppress this separation [69].

Besides these two stable phases, Hassa *et al.* [70] reported an orthorhombic κ -phase $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films stabilized with Sn for In content up to 35%. The In concentration allows bandgap engineering between 4.3eV and 4.9eV. Similarly, Nishinaka *et al.* [71] were able to form epitaxial ε - $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ films with In composition of $x=0.2$ without any phase separation.

3. GROWTH AND CHARACTERIZATION TECHNIQUES

3.1 Deposition Technique

3.1.1 Pulsed Laser Deposition (PLD)

PLD, for researchers, is one of the most promising growth technologies for obtaining high quality epitaxial growth of oxide alloy thin films because of its stoichiometric transfer of composition from the target. It is a physical vapor deposition (PVD) technique where the deposition is carried out in a vacuum chamber containing a heating system, gas inlets to control and vary deposition parameters for a wide range of thin film materials. Researchers at Bell Labs first used a PLD system to deposit superconducting materials at a very high temperature [72]. The schematic diagram of the PLD system is shown in figure 3.1.

The PLD system in Dr. Droopad's lab utilizes a Coherent excimer laser source (KrF) with a wavelength of 248nm. The excimer laser is a separate unit and through a variety of lenses and mirrors the laser beam is directed to focus on the target materials at an approximate angle of 45°. The laser beam can be controlled to provide a certain amount of power and pulses, and these high-power laser pulses ablate the target material to create a plasma cloud or a plume. This plume enables the stoichiometric transfer of target material into the substrate. The most important part of the PLD system is the laser, and excimer lasers such as KrF (248 nm wavelength) and XeCl (308 nm wavelength) are usually used because most target materials require high energy densities greater than 1 J/cm² to properly create a plume from the target [73].

The substrate and the target can be introduced using a load lock chamber and a transfer arm. Both the load lock chamber and the main chamber usually remain under

vacuum using a combination of turbomolecular pump and rough vacuum pumps. However, the pressure during thin film deposition can be controlled by introducing oxygen flow and changing the turbo pump speed. The inflow of gas is controlled by mass flow controllers (MFC).

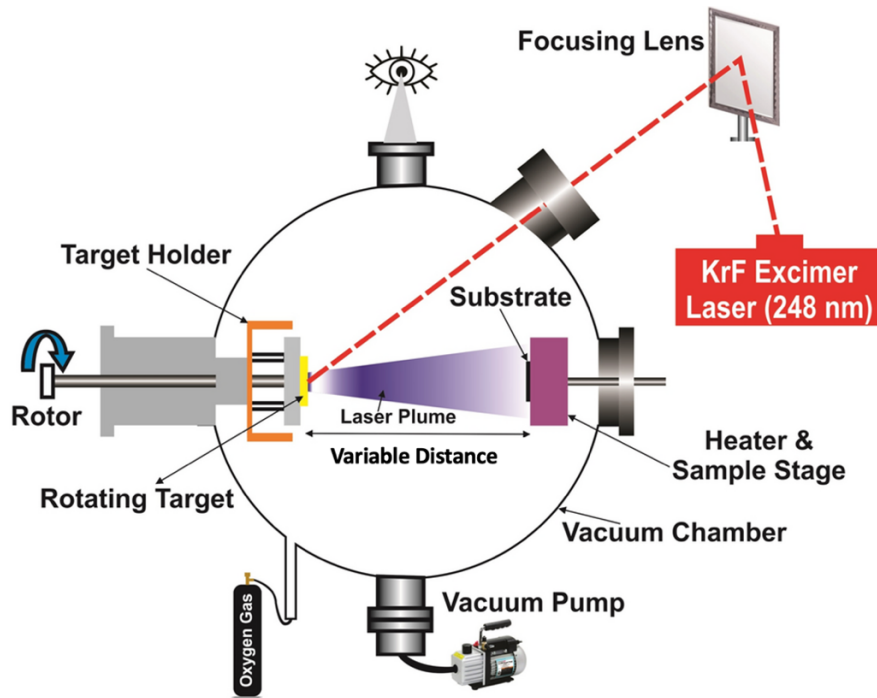


Figure 3.1: Schematic diagram of PLD system [74]

The target holder contains a total of six target disks and their position can be changed during or before growth using stepper motor controllers and the target itself rotates 360° to maintain stoichiometric growth and craterless ablation of the target disks. The sample stage contains a heater that achieve temperatures of up to 1000°C and can rotate 360° . The substrate holder can accommodate different shapes and sizes (max substrate size is 2 inches in diameter). To ensure uniform heating and deposition, the substrate is usually rotated during growth. The target and substrate distance can be varied using the sample stage, and optimal distance can be achieved experimentally.

Even though PLD is a relatively simple deposition technique compared to other physical vapor deposition techniques, it provides magnitudes of advantages. The stoichiometric transfer of target material under specific chamber conditions requires fewer control parameters but offers high-quality films. MFC controlled background gases and a wide range of temperature variability provide a high degree of freedom that can help to provide a better understanding of the growth process for optimizing growth recipes. In addition, the target materials can be programmed to change during the deposition process, which makes the growth of complex heterostructure thin films much more effortless. PLD not only allows researchers to investigate the influence of the compositional change of the thin films by changing substrate temperature and oxygen partial pressure but also helps to optimize morphology by changing laser repetition rate and power [75]. The reaction of the laser with the material depends on the target material. The absorption coefficient, specific heat, latent heat, reflectance, etc., impacts the ablation performance of a particular target interacting with the laser pulses.

3.1.2 Target Preparation

For the PLD deposition system, target preparation is an important because the deposition material comes from the ablation of a target. The targets are prepared using a ceramic sintering method. The first step is to measure high purity oxide powder or for alloys, measuring several oxide powders by taking their atomic weight percentage into account to produce the desired target with a certain mole fraction. The powders are mixed in a ball milling machine for 30-40 minutes. The next step is to put the powder in a circular-shaped mold of a specific diameter and press the content in that crucible for 24 hours at 300°C with 15000 lb./in² pressure creating a solid ceramic disk. Finally, the disk

is sintered in a furnace at 1000°C for 12-20 hours in a high-temperature furnace with flowing Ar gas.

3.2 Characterization

3.2.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is used to perform one of the most fundamental structural characterizations of thin films. It is a non-destructive method to determine the crystalline structure of a deposited film utilizing constructive interference. Waves interacting in the atomic plane of a material will create constructive and destructive interference with the arranged atoms, which is unique for a certain crystalline structure and can provide information on structural properties such as crystalline phases, defects, unit cell dimensions, lattice parameters, etc. [76]. The constructive interference, which occurs in certain special directions of a crystal structure, can be expressed using Bragg's law, $n\lambda = 2d\sin\theta$ [77]. Here, n is an integer defining the diffraction order, λ is the wavelength of the X-rays, θ is the incident angle, and d is the lattice spacing between diffracting planes. Figure 3.2 explains Bragg's law in a crystal plane [22].

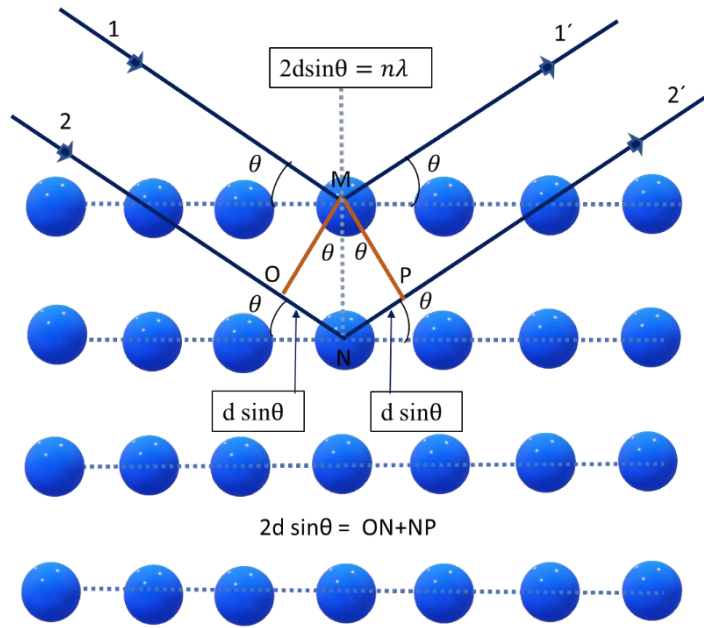


Figure 3.2: Schematic diagram demonstrating Bragg's law [22].

The source X-ray is generated in a cathode ray tube and is filtered to produce monochromatic radiation. The radiation is then collimated to concentrate and directed towards the sample through some limiters. The diffracted X-rays from the sample are detected, processed, and counted. It is possible to attain all possible diffraction directions of a lattice by sweeping the sample surface in a range of 2θ angles. A crystal will exhibit its characteristic diffraction pattern if its inter-planar spacing is free from any strain. A strained crystal lattice plane contains tensile strain (elongations) and compressive strain (contractions), which can change the inter-planar spacing of the $\{hkl\}$ lattice planes, causing a peak shift in the diffraction pattern. Thus, observing peak shift and quantitatively measuring inter-planar spacing can determine strain within the crystal structure. An orthogonal coordinate system is used to analyze inter-planar spacing and strain quantitatively.

In this study, a Rigaku SmartLab XRD machine is used to determine the impact of different parameters on the grown $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films and heterostructures. The Rigaku SmartLab XRD machine utilizes a $\text{Cu K}\alpha$ source ($\lambda = 1.540562 \text{ \AA}$), a goniometer stage where the sample is mounted, and Hybrid Photon Counting detectors (HPC). The system typically operates at 40 kV and 44 mA, and it can perform numerous diffraction techniques.

3.2.2 Ellipsometry

Ellipsometry is a fast and accurate technique primarily used for determining the thickness of the grown thin film layer(s). It can also provide knowledge of the optical constants of the thin films. An ellipsometer's main components include a light source, a polarizer, an analyzer, and a detector. Unpolarized light from the light source is sent through a polarizer which is basically an optical filter that only allows light with a specific electric field orientation to pass through. The polarizer converts light with parallel (p) and perpendicular (s) components, and the sample surface interacts with the polarized light. The reflected light goes through the analyzer, and finally, the detector detects any change in amplitude and phase compared to the input polarized light [78]. Figure 3.3 illustrates the basic ellipsometry configuration.

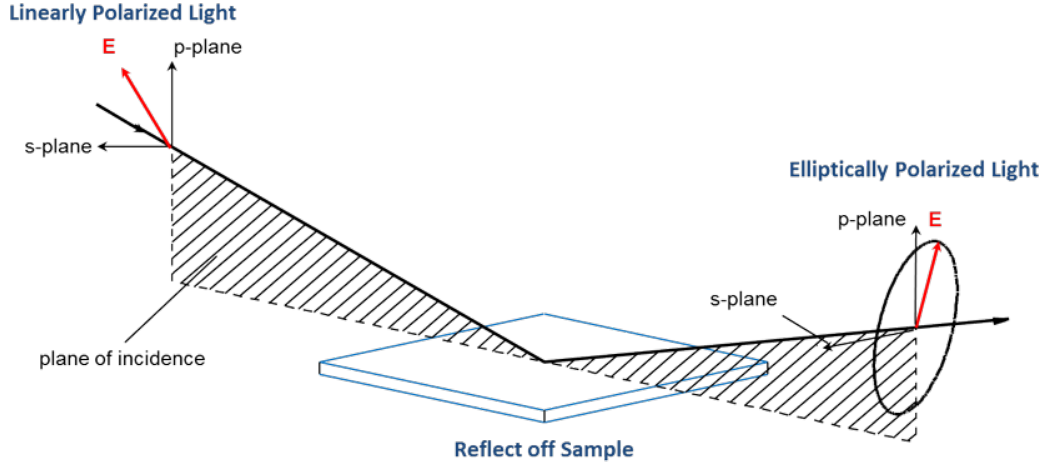


Figure 3.3: Configuration of ellipsometry [79]

The differential changes of both p and s components of the polarized light are measured in terms of ψ and Δ , where ψ is the relative amplitude change and Δ is the relative phase change of the reflected light [80]. The measurement can be expressed in terms of the complex reflectance ratio ρ as shown in equation (1)

$$\rho = \frac{R_p}{R_s} = \tan(\psi) e^{i\Delta} \quad (1)$$

$$\text{Where, } \tan(\psi) = \frac{\left(\frac{E_p}{E_s}\right)_{\text{Reflected}}}{\left(\frac{E_p}{E_s}\right)_{\text{Incident}}} \quad \text{and } \Delta = \Delta_p - \Delta_s$$

R_p and R_s are the complex Fresnel coefficient and Δ is measured from the phase difference between the p and s direction of the complex R_p and R_s . E_p and E_s are the electric field of p and s polarized light, respectively. The ψ and Δ values are mapped in the ellipsometer and various algorithms are used to fit the experimental data to determine the thickness and optical constants. The fit estimation provides a Root Mean Squared Error (RMSE), and the best estimate is where RMSE is the minimum [81].

In this study, an M-2000 Woollam ellipsometer is used to investigate sample thickness, roughness, and optical properties. Measurements are carried out at three

incident angles of 55°, 65°, and 75° degrees for a spectral range between 200nm to 800nm.

3.2.3 UV-Vis Spectroscopy

UV-Vis (ultraviolet-visible) spectroscopy can measure the transmittance or absorption of a layer at ultraviolet-visible wavelengths. Typically, spectrophotometers direct light through a sample and a reference to photodetectors. The transmitted light is recorded and processed by comparing it to the reference, which is usually the substrate to provide absorbance of light for the sample within the UV-Vis electromagnetic range. Typically, a plot of wavelength vs. absorbance or transmittance is seen as the output. Using this characterization tool, we can see how much light is absorbed and transmitted at each wavelength. The basic working principle of UV-Vis spectroscopy can be illustrated using figure 3.4 [82].

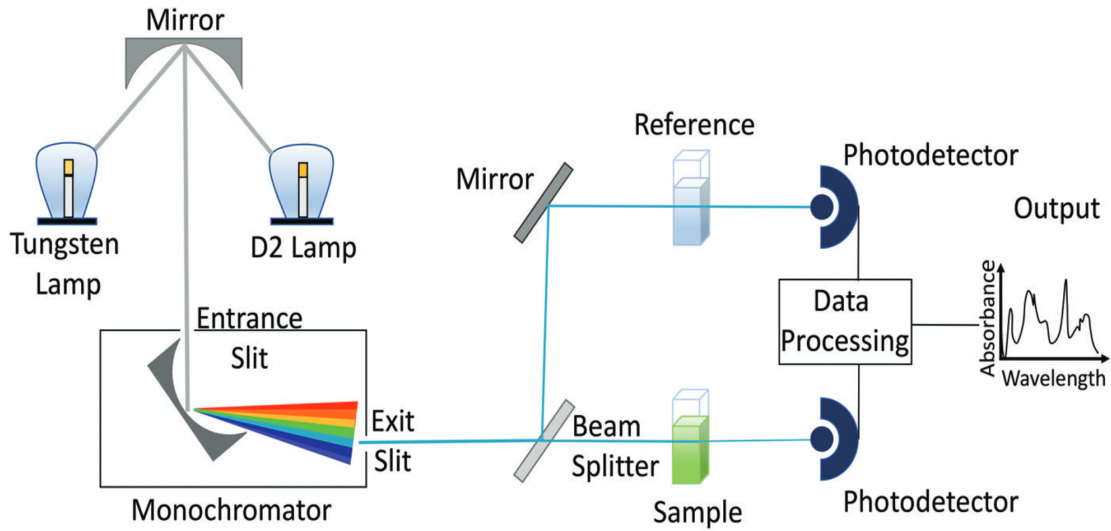


Figure 3.4: UV-Vis spectroscopy [82]

In this work, using the transmitted data collected from each sample, the direct bandgap can be determined using the power-law denoted by the following equation [83].

$$(\alpha h\nu)^2 = B(h\nu - E_g) \quad (2)$$

Here, α is the absorption coefficient, which is the absorption rate per nanometer wavelength, B is the absorption edge width parameter, and E_g is the bandgap for direct bandgap materials. E_g can be calculated by plotting $(\alpha h\nu)^2$ vs $h\nu$ (known as Tauc plot) and extending the linear portion of the curve. The intersection of this extended linear region with the x-axis represents the bandgap of the sample material. This work utilized the UV-2600 Shimadzu optical spectroscopy system for such measurements.

3.2.4 Atomic Force Microscopy (AFM)

Atomic Force Microscope (AFM) is a prevalent technique that provides high-resolution surface morphology for any sample [84]. It is a scanning probe microscopy technique that utilizes a fine tip to probe the sample surface. The resolution of the surface depends upon the dimensions and sharpness of the tip. The sharp tip rasters over the surface and utilizes a feedback loop to optimize parameters required to image the morphology of a surface. AFM does not require the sample to be conductive because it uses atomic forces from tip-sample interaction to map the surface. AFM can be utilized to measure any measurable atomic force using this tip-sample interaction – van der Waals, electrical, magnetic, thermal, etc. The schematics of an AFM system are shown in figure 3.5 [85].

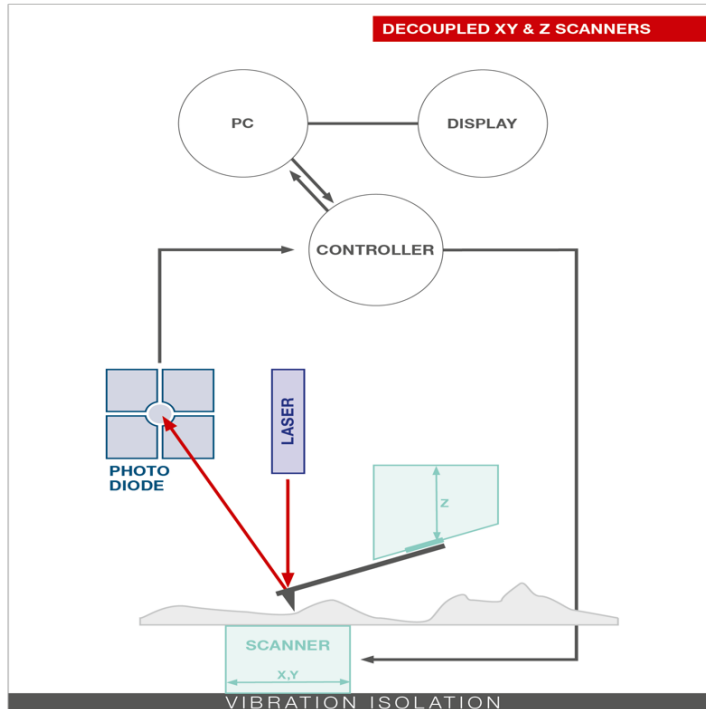


Figure 3.5: Schematic of atomic force microscopy [85]

A laser beam reflection from the AFM lever gets deflected due to atomic forces and the deflection is measured by the segmented position-sensitive detectors. If the stiffness of the cantilever is known, Hooke's law, $F = -kz$, is used to determine the force exerted by the AFM tip. Here, z is the measure of the lever bending and k is the stiffness of the lever. Attractive or repulsive forces can be measured based on the distance between tip and sample. Attractive force deflects AFM cantilever towards the surface when tip and sample surface are closer. During contact, repulsive force deflects cantilever away [86]. The force-distance interaction between the AFM tip and the sample surface is shown in figure 3.6 [87].

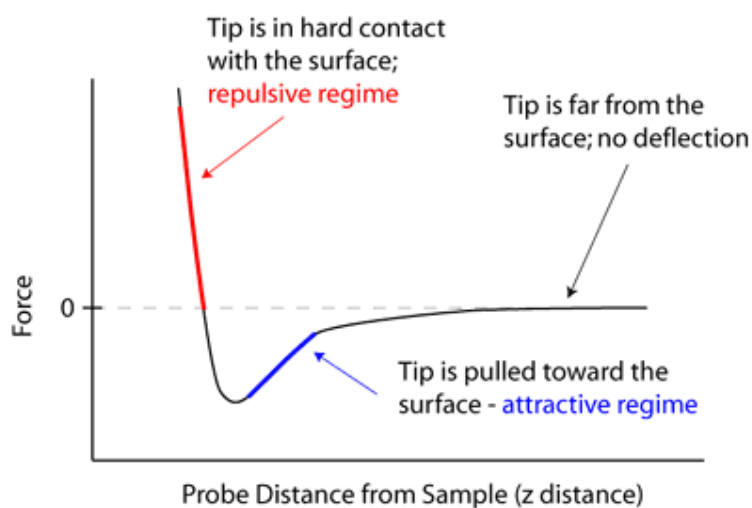


Figure 3.6: Force-distance curve for Atomic Force Microscopes [87]

As AFM technologies are evolving, many new modes and techniques of measurements are being introduced besides the basic contact mode. One of the most popular ones among them is the tapping mode, where intermittent contact interaction between the tip and sample is measured. The cantilever oscillates with its resonance frequency very near the surface (between 20nm to 100nm), and the interaction provides the surface morphology of the sample without any contact. In this research, tapping mode was used to determine the surface morphology of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ samples using a Bruker Dimension Icon AFM.

3.3.5 X-ray Photoelectron Spectroscopy (XPS)

To analyze the chemical nature of the surface in a thin film X-ray Photoelectron Spectroscopy (XPS) is one of the most popular techniques. The analysis is performed using x-rays in an ultrahigh vacuum environment. Chemical composition, bonding structures, and offsets can be investigated using XPS. When a monochromatic x-ray beam is incident on the sample surface, some core shell electrons are ejected from the

sample atoms due to the photoelectric effect. The detector measures the kinetic energy of the core electrons, which depends on the binding energy of those emitted electrons. As core levels of every element are unique, the kinetic energy can be used to determine the element. X-ray sources are usually soft x-rays such as Al K α (1486.6 eV) [88]. The kinetic energy emitted can be expressed as:

$$K.E. = h\nu - (B.E. - \phi) \quad (3)$$

Here, K.E. and B.E. are the kinetic energy of the electron and binding energy in the shell, respectively, $h\nu$ is the x-ray energy, and ϕ is the work function of the spectrometer. Removing the core electron from the atom causes an excited ionized state in the atom. By releasing energy, the atom tries to achieve a relaxation state. X-ray fluorescence or Auger electron emission occurs in a competing manner. XPS can also be used to detect Auger electrons for qualitative analysis [89].

The detection of electrons can provide an accurate description of the atomic species on the surface of the material. Figure 3.7 below illustrates the processes that happen in XPS when an X-ray is incident on a sample surface.

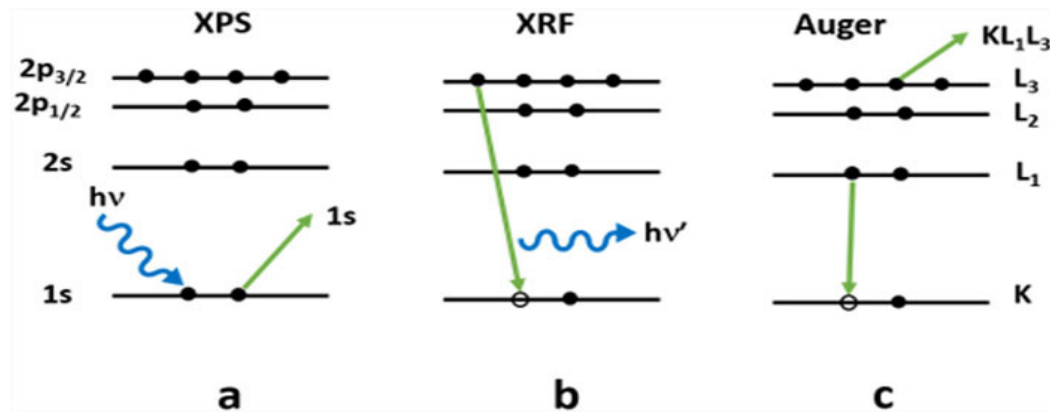


Figure 3.7: Processes that result from X-ray bombardment of a surface include (a) emission of a photoelectron, (b) x-ray fluorescence, and (c) emission of an Auger electron [89].

In this work, XPS measurement was carried out in the NEXSA XPS of our Shared Research Operation center and the analysis was performed using the Advantage analysis package. It utilizes a monochromatic Al K α X-ray source with an energy of 1486.6eV operating at 15kV and 14mA. A Shirley background was used during the analysis to fit the data and peak deconvolution was performed by using gaussian line shapes that identify components that contain chemical interaction of properties of the elements on the surface. Flood gun was always on during probing with XPS in order to neutralize charge of insulators or semiconductors. A three level depth profiling on the as-grown samples were performed each time in the XPS in order to remove surface contaminations.

4. RESULT AND DISCUSSION

4.1 Experimental

The first step of deposition is to prepare a target containing the correct percentage of In with β -Ga₂O₃ powder. High purity gallium oxide powder (99.999%) with indium content with molar ratio of In/(In+Ga) equating 0.02, 0.05, 0.08, 0.1, and 0.15 are mixed to create (In_xGa_{1-x})₂O₃ targets. In the PLD chamber, the (In_xGa_{1-x})₂O₃ thin films are grown on (0001) oriented c-plane sapphire stoichiometrically, so the ratio of In and Ga in the film should not change. The sapphire substrate was cleaned with acetone and isopropanol in an ultrasonic bath and then rinsed in deionized water. The ablation of the target onto the substrate was carried out using the krypton fluoride (KrF) laser with a 248nm wavelength. The pulse repetition rate was fixed at 5Hz, and a total of 5000 pulses was used to deposit on the substrate with 300 mJ beam power. To investigate the influence of substrate temperature and partial oxygen pressure on the (In_xGa_{1-x})₂O₃ thin films, the temperature was initially varied from 400°C to 720°C. Later, the temperature was fixed, and oxygen pressure in the chamber was varied from 5x10⁻² to 1x10⁻⁵ to investigate the impact of oxygen pressure. The target and the substrate were rotated for uniform film distribution, and the distance between them was fixed at 5cm. Finally, β -Ga₂O₃ / (In_xGa_{1-x})₂O₃ heterostructure was deposited on c-plane sapphire, and optimization of the growth parameters was performed for low In concentration in order to achieve crystalline monoclinic structure.

4.2 Impact of Growth Parameters

The high-resolution XRD 2 θ - ω scans for different In concentrations in the (In_xGa_{1-x})₂O₃ (IGO) thin films were taken in order to determine the impact of substrate

temperature and oxygen partial pressure on the crystal quality. Figure 4.1 shows the XRD 2θ - ω spectra for $x = 2\%$ IGO thin films grown at different substrate temperatures (300°C - 720°C) while keeping the oxygen partial pressure fixed at 1.1×10^{-3} torr. The x-ray spectra show the formation of (-201) oriented single-phase β -(In_{0.02}Ga_{0.98})₂O₃ thin films grown at temperatures above 500 °C. The film exhibits amorphous crystallinity below this temperature due to not having the proper nucleation energy. The diffraction peaks fall within the {-201} family of planes for β -Ga₂O₃, and the reflection planes (-201), (-402), (-603), and (-804) correspond to the 2θ angles around 18.81°, 38.65°, 58.57°, and 82.97° respectively. The c-sapphire substrate reflection planes are indicated with (0001), (0006), and (0009) at the diffraction angles of 20.52°, 41.56°, and 64.49° respectively.

Crystallinity increases with increasing temperature as the lowest full width half maxima (FWHM) of 0.2726 degrees was obtained at a growth temperature of 720 °C. The degraded crystallinity at low growth temperature can be attributed to having insufficient energy for the ad-atoms to migrate and nucleate on the surface. Hwang *et al.* [90] also reported an amorphous phase at low substrate temperature but increased crystallinity was obtained after annealing. Figure 4.2 exhibits β -(In_{0.02}Ga_{0.98})₂O₃ thin films with varying oxygen pressure during PLD deposition at a fixed substrate temperature of 720 °C. The grown film exhibits amorphous behavior at deficient oxygen (chamber pressure below 10^{-4} torr). Even though PLD deposition is stoichiometric, the oxygen atmosphere during growth can significantly impact the crystallinity of the grown thin film. Park *et al.* [91] also reported crystallization characteristics of IGO thin films with varying oxygen pressure. Their research showed that increasing oxygen pressure increases the crystallinity to a certain extent. In addition, Kaleemulla *et al.* [92] showed that

crystallinity of In_2O_3 films increased with higher oxygen partial pressure. These results obtained for the $\beta\text{-(In}_{0.02}\text{Ga}_{0.98})_2\text{O}_3$ suggest that the crystallinity of IGO thin films depends on oxygen partial pressure and follows the trend of In_2O_3 .

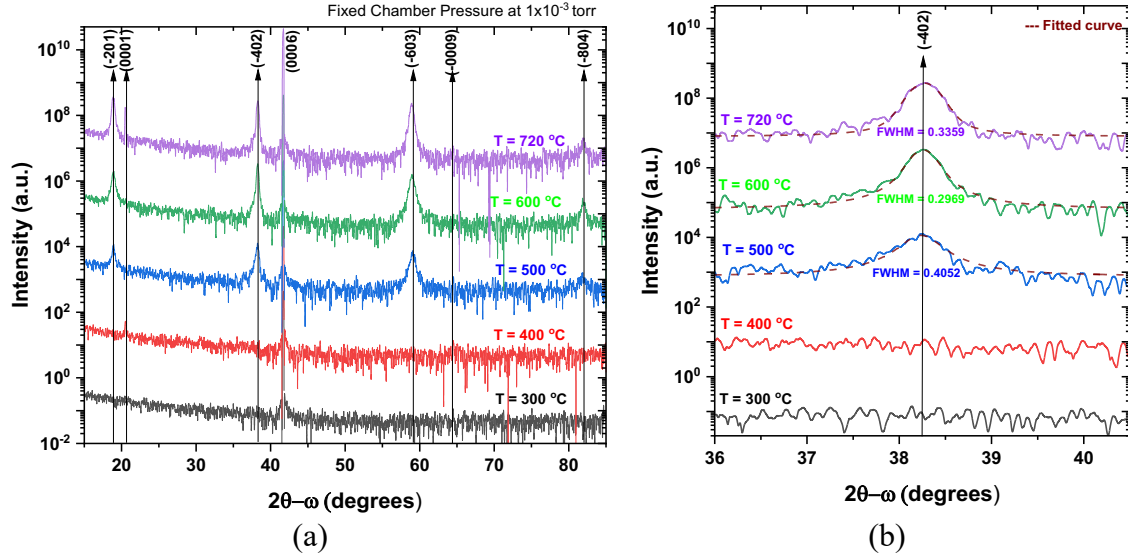


Figure 4.1: (a) XRD measurement of $(\text{In}_{0.02}\text{Ga}_{0.98})_2\text{O}_3$ grown at different substrate temperatures and (b) corresponding FWHM measurement of (-402) plane.

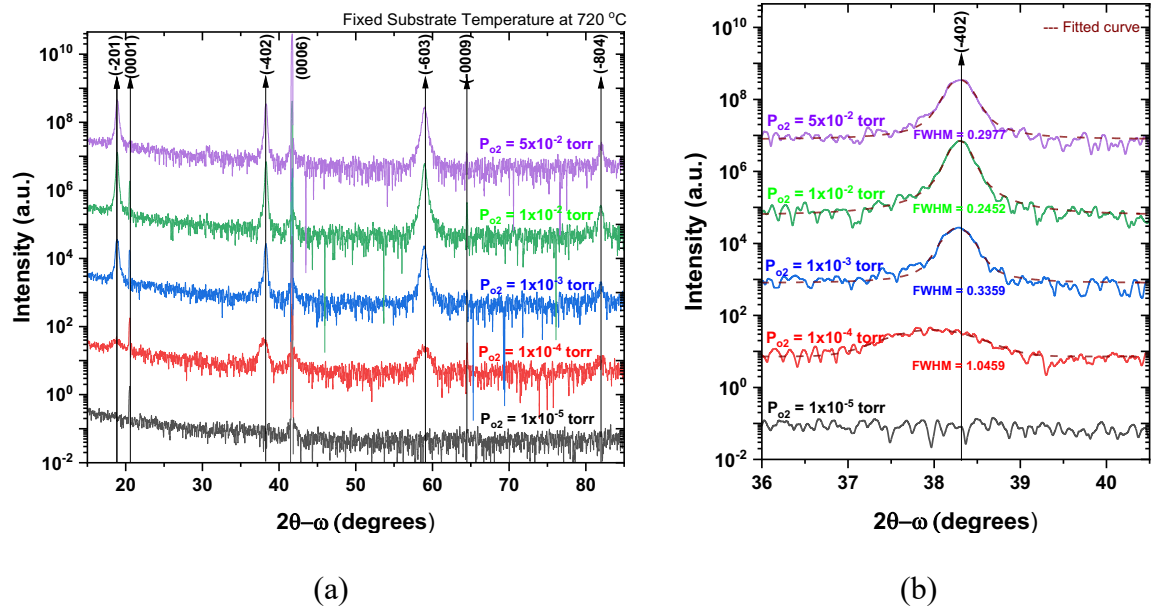


Figure 4.2: (a) XRD measurement of $(\text{In}_{0.02}\text{Ga}_{0.98})_2\text{O}_3$ grown at different oxygen inflow and (b) corresponding FWHM measurement of (-402) plane.

A similar analysis was performed for $x = 5\%$ $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films grown with varying temperatures and partial oxygen pressures, with the results shown in figure 4.3 and figure 4.4, respectively. In figure 4.3 we can observe a similar impact of temperature on crystallinity. Below 400°C , the grown films were amorphous. Between 500°C and 600°C , we can observe a polycrystalline phase of $(\text{In}_{0.05}\text{Ga}_{0.95})_2\text{O}_3$ thin films with both cubic and monoclinic phases present. The monoclinic β -(InGa) $_2\text{O}_3$ phase diffraction angles are almost identical to figure 4.1, whereas the peak due to the cubic (222) plane is visible at the diffraction angle of 30.69° . The crystal quality of the grown IGO films improves as the temperature increases, which is evident from the FWHM values. From figure 4.4, we also find the impact of oxygen partial pressures on the $(\text{In}_{0.05}\text{Ga}_{0.95})_2\text{O}_3$ thin films. Higher oxygen seems to cause polycrystallinity for the same substrate temperature compared to lower oxygen inflow in the PLD chamber. The cubic phase emerging at higher P_{O_2} requires further investigation.

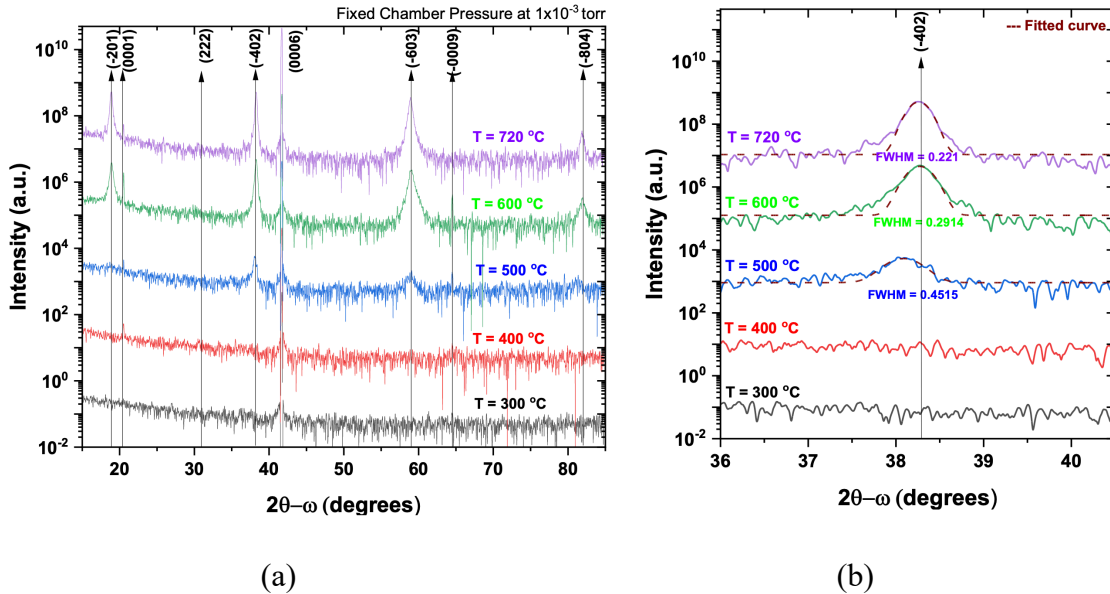


Figure 4.3: (a) XRD measurement of $(\text{In}_{0.05}\text{Ga}_{0.95})_2\text{O}_3$ grown at different substrate temperatures and (b) corresponding FWHM measurement of (-402) plane.

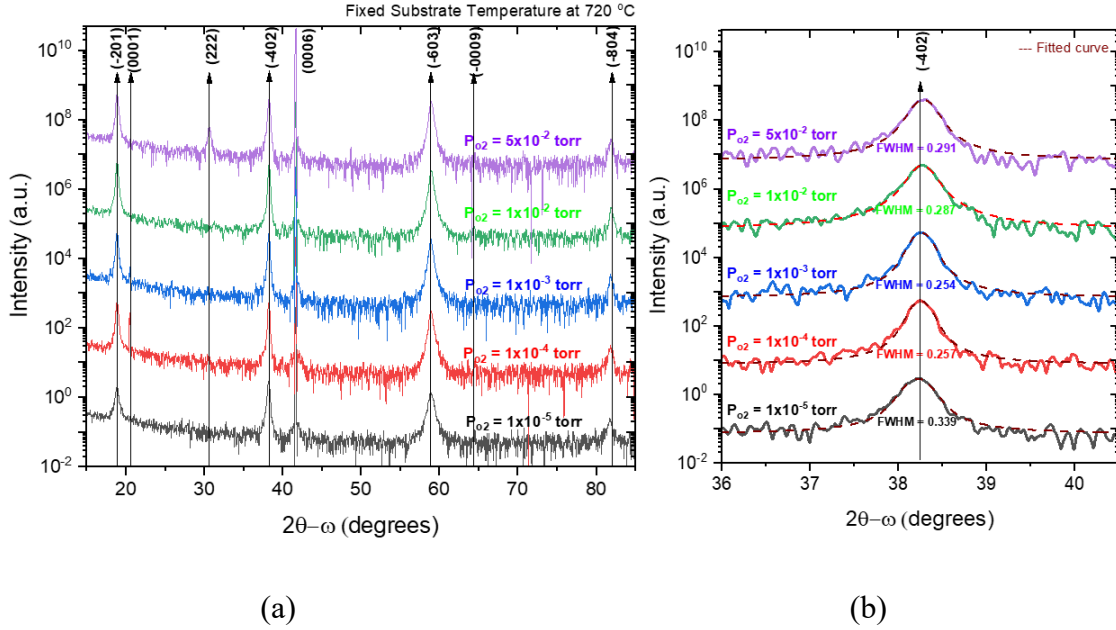


Figure 4.4: (a) XRD measurement of $(\text{In}_{0.05}\text{Ga}_{0.95})_2\text{O}_3$ grown at different oxygen inflow and (b) corresponding FWHM measurement of (-402) plane

The impact of substrate temperature for $x = 10\%$ $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films are shown in figure 4.5 and we can see similar results with varying temperatures with a fixed oxygen partial pressure in the chamber of 1×10^{-3} torr. The impact of temperature increase is identical to the previous studies, but at 500°C and 600°C , a different phase can be identified from the visible shoulder peak in figure 4.5 (b). The additional peak is identified either as the hexagonal ϵ -phase or the orthorhombic κ -phase. This opens up an interesting study on $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films and their different polymorphs, which will be investigated in detail in the next chapter.

Figure 4.6 illustrates the impact of different oxygen partial pressure during the growth of $x = 10\%$ $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films. Oxygen partial pressure seems to have less effect on the crystallinity but analogous to the results above. The single crystal IGO films seem to transform into polycrystalline thin films at a much higher oxygen pressure.

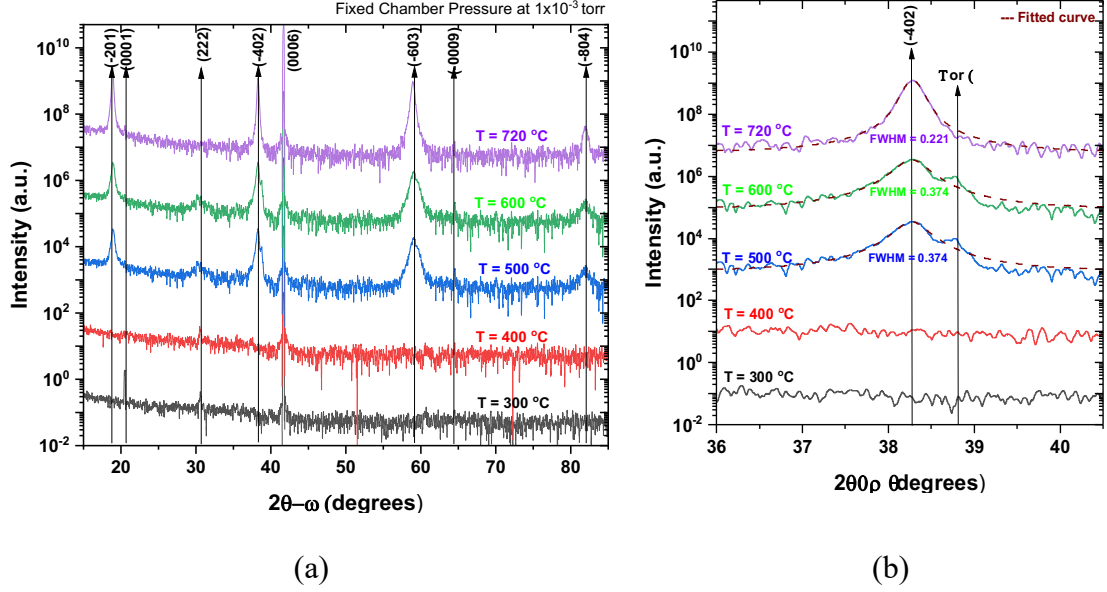


Figure 4.5: (a) XRD measurement of $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ grown at different substrate temperature and (b) corresponding FWHM measurement of (-402) plane

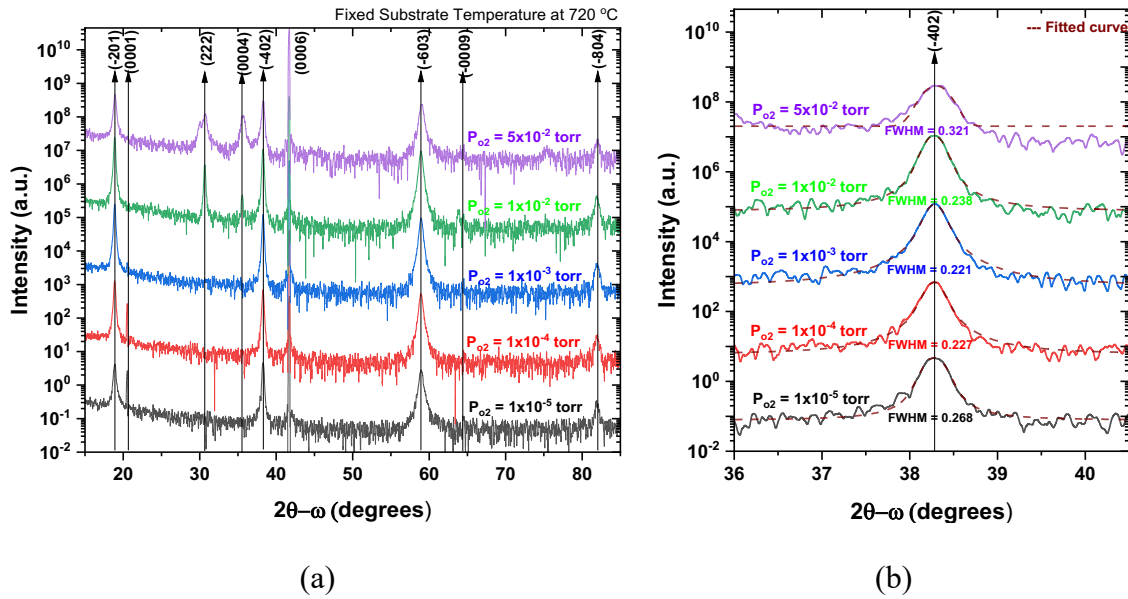


Figure 4.6: (a) XRD measurement of $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ grown at different oxygen inflow and (b) corresponding FWHM measurement of (-402) plane

Finally, a comparison of optimized $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films for $x=2\%$, 5% , and 10% is shown in figure 4.7.

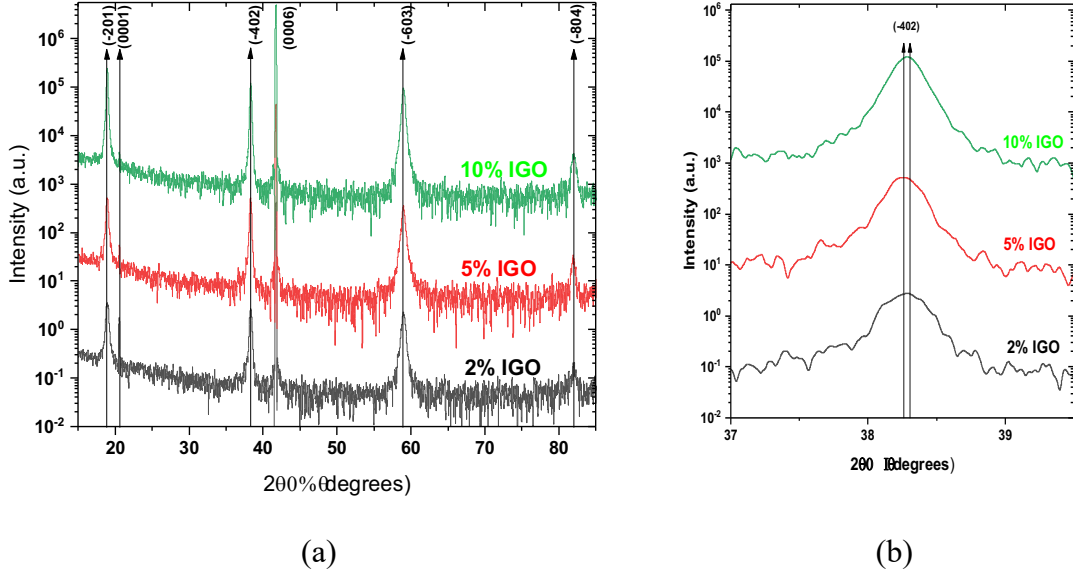


Figure 4.7: (a) XRD measurement of optimized $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ grown with different In concentration and (b) corresponding FWHM measurement of (-402) plane

Figure 4.7 shows that with a chamber pressure of 1×10^{-3} torr and substrate temperature of 720°C , all the IGO films with In concentration up to 10% exhibit similar crystallinity. Figure 4.7(b) shows that even at such low In concentration, the 2-theta angles appear to be increasing, suggesting an expansion of lattice constants caused by the inclusion of In into Ga ion lattice sites. In^{3+} ions have a radii of $0.94 \text{ \AA}$ and Ga^{3+} ions have a radii of $0.62 \text{ \AA}$. This increased radius size can be responsible for this change in the 2-theta angles because lattice constants expand by the inclusion of In ions into Ga ion lattice sites [93].

It is essential to determine the optical properties of a transparent thin film in order to realize its applicability for optical devices such as photodetectors. Transmission characteristics of the $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ films with $x=2\%$ to $x=10\%$ were measured using a Shimadzu UV-2600 spectroscopy. The inset of figure 4.8 illustrates the transmittance of the IGO thin films. A slight red shift in optical absorption edge can be seen around the 250 nm range of the spectra, which indicates that incorporating In in Ga_2O_3 causes a

reduction in the bandgap. The optical bandgap can be determined by transforming the transmittance data into a Tauc plot. Tauc plot involves a power law of the absorption spectra. As β -Ga₂O₃ is a direct bandgap material [94], [95], [96], the power law of absorption spectra for IGO can be written as

$$(\alpha h\nu)^2 = B(h\nu - E_g) \quad (4)$$

Here, α is the absorption coefficient, $h\nu$ is the incident photon energy, B is the absorption edge width parameter, and E_g is the band gap. From the transmittance data acquired from UV-Vis, the absorption coefficient α can be measured from the following equation

$$\alpha = \left(\frac{1}{t}\right) \ln \frac{T}{(1-R)^2} \quad (5)$$

Here, t is the film thickness, R is the reflectance, and T is the transmittance. A plot of $(\alpha h\nu)^2$ vs $h\nu$ (shown in figure 4.8) can be used to find the E_g of the IGO films by fitting the linear region on the x-axis and extrapolating to x-axis. The figure shows that the direct band gap decreases with increasing In concentration in the IGO films. In their theoretical study on IGO, Cheng *et al.* [97] attribute bandgap energy reduction to the formation of defects in the crystal or the presence of unoccupied electronic states below the conduction band. The bandgap of (In_xGa_{1-x})₂O₃ with $x = 2\%$, 5% , 8% , and 10% calculated from the Tauc plot are 4.91 eV, 4.82eV, 4.73 eV and 4.64 eV respectively. Table 4.1 summarizes the bandgap reduction for increasing In concentration. The bandgap reduction is in agreement with previous research works on IGO thin films [98], [99]. Holger von Wenckstern compiled the dependence of band gap or absorption edge energy on alloy composition of various polymorphs of (In_xGa_{1-x})₂O₃ [100]. A comparison

plot of our work with the compiled research data on $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ is illustrated in figure 4.9.

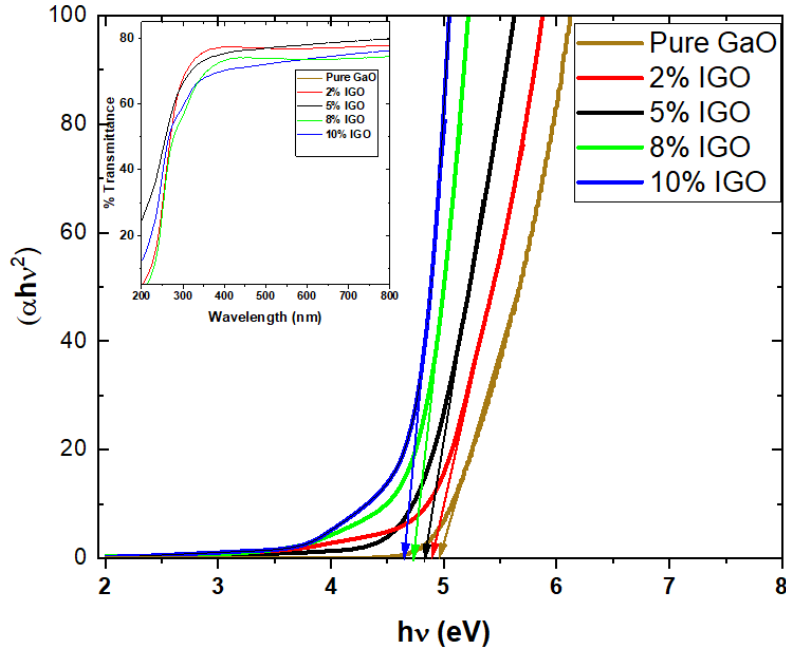


Figure 4.8: Tauc plot for IGO thin films (inset optical transmittance plot)

Table 4.1: Bandgap reduction of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for $x = 0\%$ to 10%

In content (x)	Bandgap (E_g)
0%	4.98 eV
2%	4.91 eV
5%	4.82 eV
8%	4.73 eV
10%	4.64 eV

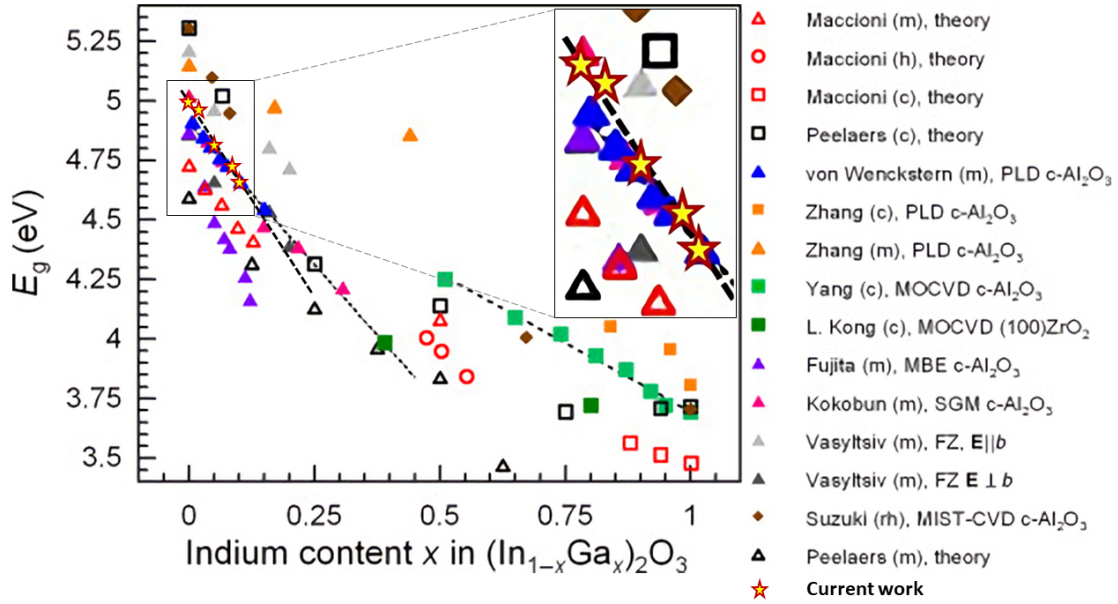


Figure 4.9: Literature data vs current work showing bandgap engineering using In as alloy in $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films for different polymorphs. Monoclinic (m), hexagonal (h), cubic (c), and rhombohedral (rh) crystal polymorphs are indicated by upward triangles, circles, squares, and diamond shape markers, respectively. The yellow stars represent current work.

Spectroscopic ellipsometry was used to further investigate the properties such as surface roughness of the as-grown $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$. The measurement was carried out at room temperature for wavelengths ranging from 200 nm to 1000 nm and three incident angles of 65°, 75°, and 85°. The ψ and Δ values for the entire interval of wavelengths were used to investigate the optical and physical properties. A substrate and as-grown film stack with roughness were used as the model for the analysis, and the model was fitted for ψ and Δ values for the entire wavelength interval with minimum mean square error (MSE). Table 4.2 and Table 4.3 shows the extracted data from ellipsometry showing the thickness and roughness of the as-grown thin films along with their refractive index for different substrate temperature (fixed chamber pressure at 1×10^{-3} torr) and different oxygen partial pressure (fixed substrate temperature at 720°C respectively).

Table 4.2: Materials properties of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ at a fixed pressure of 1×10^{-3} torr and variable substrate temperatures

In concentration in $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$	Substrate Temperature	Thickness (nm)	Refractive index at 632 nm	RMS roughness (nm)
2%	300 °C	65.73	1.87	4.08
	400 °C	50.31	1.88	3.89
	500 °C	42.88	1.91	2.12
	600 °C	40.65	1.85	2.52
	720 °C	35.35	1.79	1.93
5%	300 °C	52.76	1.92	4.28
	400 °C	62.53	1.81	4.91
	500 °C	45.24	1.92	3.81
	600 °C	39.00	1.83	2.84
	720 °C	36.94	1.81	1.64
10%	300 °C	65.27	1.92	4.50
	400 °C	62.71	1.87	3.52
	500 °C	51.24	1.97	2.05
	600 °C	38.60	1.92	4.86
	720 °C	33.79	1.89	2.05

From table 4.2, we can see that the deposition temperature has a significant impact on the growth of the IGO thin films. The thickness of the grown films seems to be decreasing with increasing temperatures, and the roughness is also reducing in a similar trend. This can be attributed to the growth quality and crystallization of the thin film. The crystal quality gradually improves when IGO is deposited with a higher substrate temperature (shown in the XRD study from figures 4.1 to 7.7). Improved crystal quality results in a denser structure of IGO film, resulting in lower thickness and improved roughness. Another reason for lower thickness with increasing temperatures can be attributed to evaporation of volatile Ga_2O species from the substrate surface [101], [94]. On the contrary, at lower substrate temperatures, the film becomes amorphous and less evaporation of Ga_2O occurs at a lower temperature. This leads to higher thickness and an

increase in the surface roughness in the as-grown IGO films. Yuan *et al.* [102] also reported similar phenomena in their study on aluminum gallium oxide thin films grown by pulsed laser deposition system. Figure 4.10 illustrates the impact of temperature on thickness and roughness for different In concentrations.

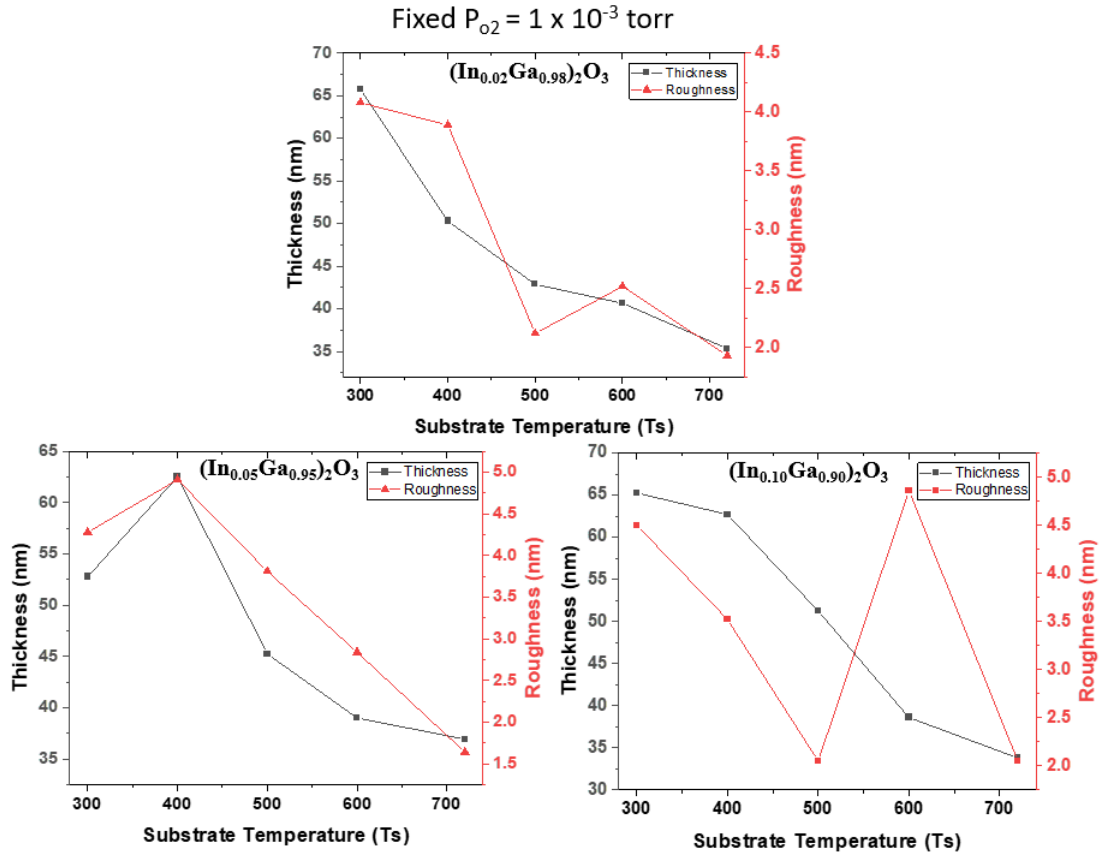


Figure 4.10: Impact of substrate temperature on thickness of $(In_xGa_{1-x})_2O_3$ for (a) $x=2\%$ (b) $x=5\%$, and (c) $x=10\%$

Table 4.3: Materials properties of $(In_xGa_{1-x})_2O_3$ at a fixed temperature of 720°C and variable oxygen inflow into the main chamber

In concentration in $(In_xGa_{1-x})_2O_3$	Chamber Pressure	Thickness (nm)	Refractive index at 632 nm	RMS roughness (nm)
2%	5×10^{-2} torr	42.74	1.97	1.14
	1×10^{-2} torr	38.58	1.89	2.56.
	1×10^{-3} torr	35.35	1.79	1.93

	1×10^{-4} torr	56.38	1.86	3.88
	1×10^{-5} torr	56.76	1.92	5.57
5%	5×10^{-2} torr	37.82	1.85	4.88
	1×10^{-2} torr	34.08	1.93	3.67
	1×10^{-3} torr	36.94	1.81	1.64
	1×10^{-4} torr	33.45	1.86	2.51
	1×10^{-5} torr	35.28	1.81	3.67
10%	5×10^{-2} torr	43.22	1.97	3.92
	1×10^{-2} torr	39.75	1.93	3.29
	1×10^{-3} torr	33.79	1.89	3.05
	1×10^{-4} torr	34.03	1.84	2.85
	1×10^{-5} torr	38.09	1.88	4.10

Similar to temperatures, the chamber pressure variance caused by different oxygen partial pressure during growth also impacts the thickness and roughness of the grown thin films (table 4.3). At higher oxygen partial pressure, increased scattering of ablated species by the molecules of oxygen gas can suppress volatile GaO suboxide evaporation, and the re-sputtering effect can diminish the growth thickness [43]. Figure 4.11 summarizes the impact of oxygen partial pressure on $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for different In concentrations.

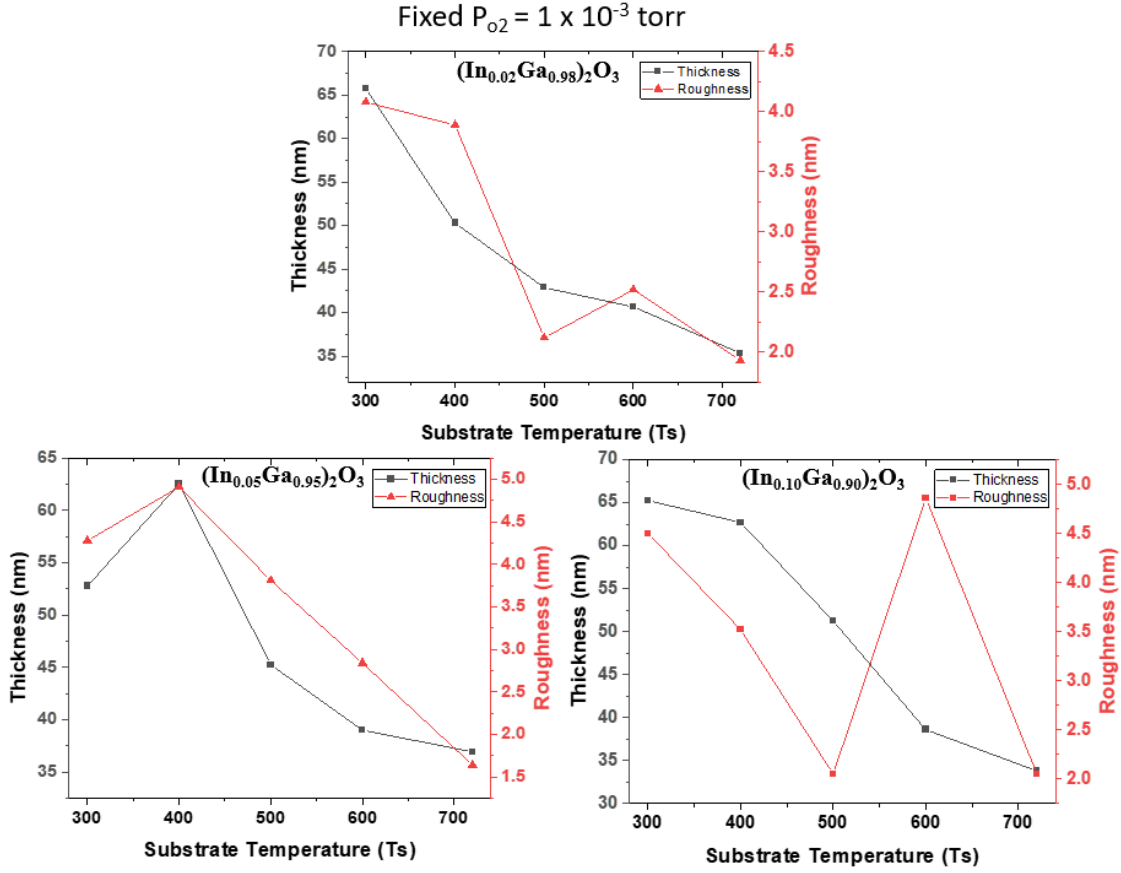


Figure 4.11: Impact of oxygen partial pressure on thickness of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x=2\%$ (b) $x=5\%$, and (c) $x=10\%$

The refractive index (n) extracted from the model is listed in both tables for 632 nm wavelength. As chamber pressure increases, the refractive index seems to be increasing also for all IGO thin films, but it is always within the range of 1.8 to 2. This result is in good agreement with the results reported on other oxide thin films like ZnO and TiO_2 [103], [104]. The increase in refractive index can be related to the change in crystalline structure (from amorphous to polycrystalline to single crystal) and increase in the grain size and/or the density of the layers.

Finally, the surface characteristics of the as-grown thin films were investigated using X-ray photoelectron spectroscopy to explore the surface composition and chemical

states of the $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films. The survey spectra of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for In composition of 2%, 5%, 8%, and 10% are shown in figure 4.12. The carbon peak at 184.8eV was used as a reference peak to correct every spectrum to mitigate charging effects. The scan shows gallium peaks, indium peaks, oxygen peaks, and a carbon peak. There are no other impurities visible from the spectrums. The In 3d region is chosen along with Ga 3d and O 1s in order to determine the oxidation states of the indium and gallium in the thin film.

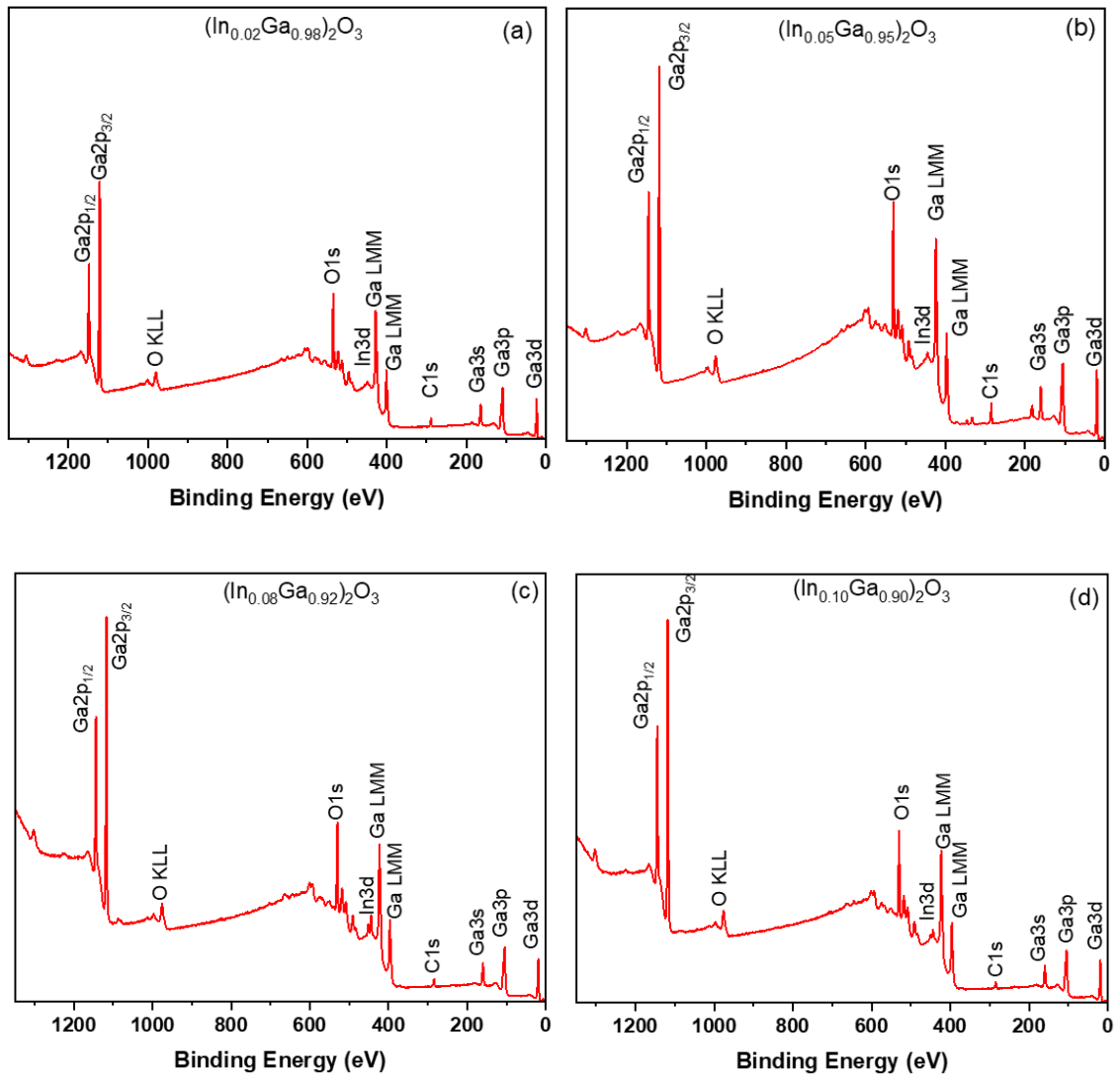


Figure 4.12: Survey spectrum of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.08$, and (d) $x = 0.1$ respectively.

Figure 4.13 shows the high-resolution XPS scan of Ga 3d peaks for all In concentrations. The peak located around 20.5 eV is assigned to the fully oxidized Ga^{3+} state. There is a slight shift to the lower binding energy with the increase of In concentration. This occurs because the incorporation of In causes the Ga-O bond to change. Huang *et al.* [105] also observed this phenomenon in their research.

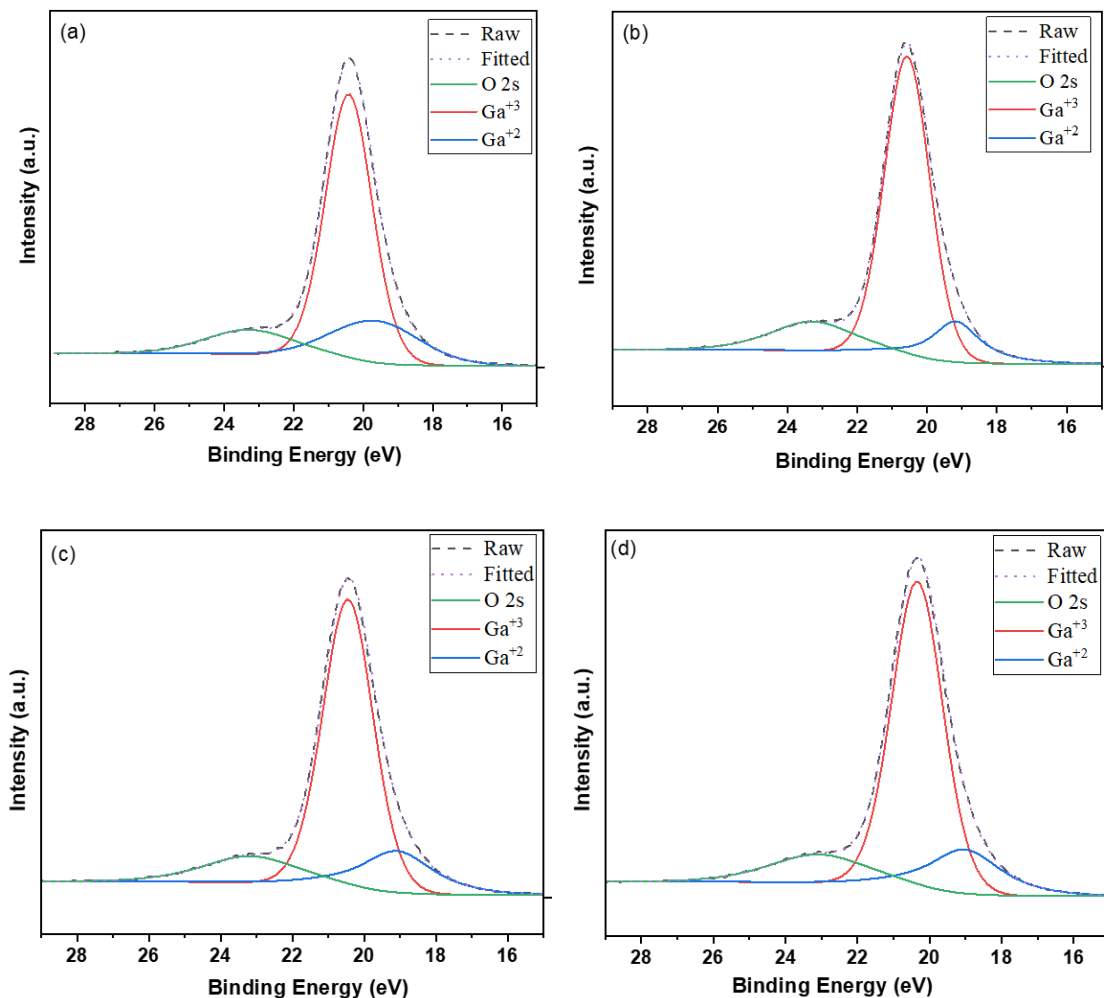


Figure 4.13: High resolution $\text{Ga}3d_{5/2}$ XPS spectra of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.08$, and (d) $x = 0.1$ respectively.

Figure 4.14 shows the In 3d region to determine the oxidation state of indium. The peak is deconvoluted into two regions: In $3d_{3/2}$ at 452 eV and In $3d_{5/2}$ at 455 eV.

With the increase of indium concentration, the relative intensity of the peaks seems to be increasing as expected. There is no significant shift in In core levels with the increase of In concentration.

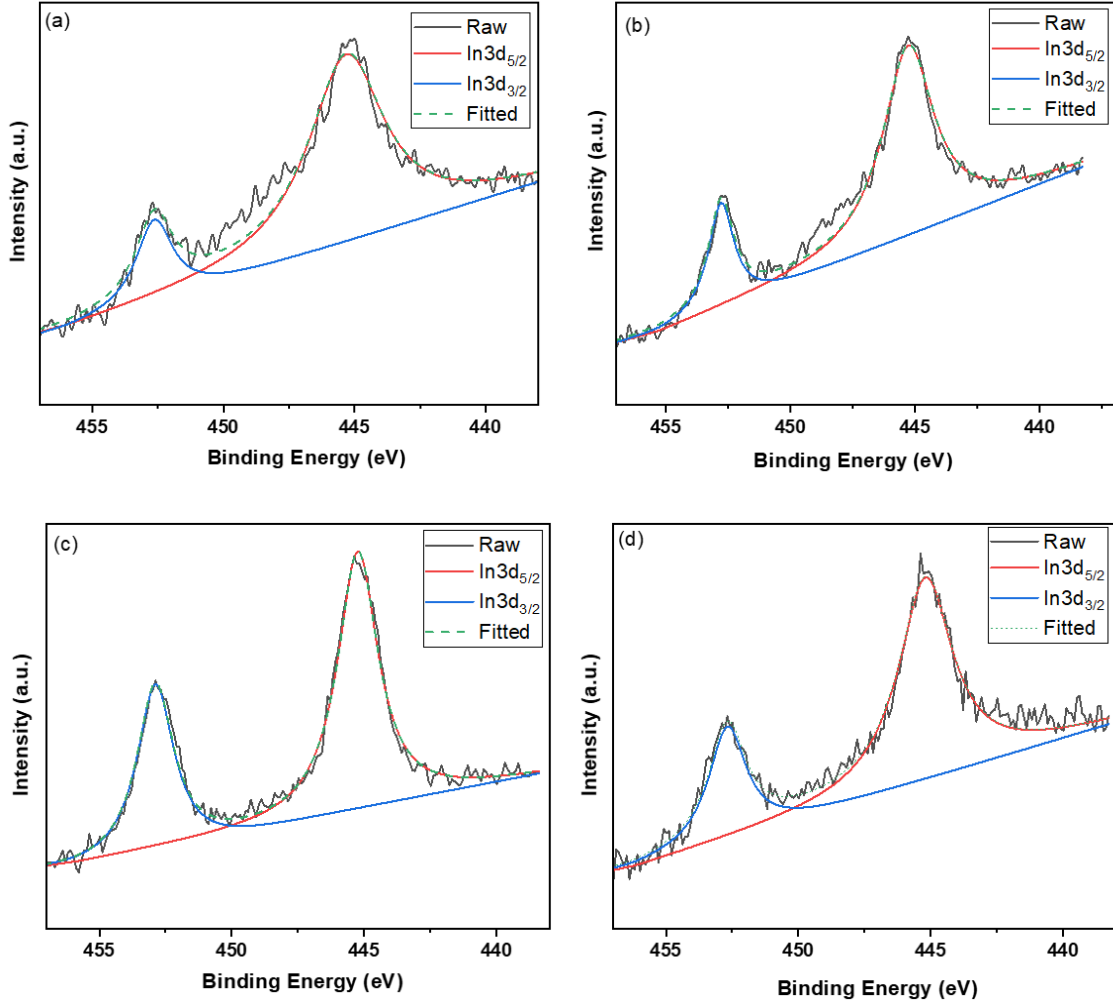


Figure 4.14: High resolution In 3d core level XPS spectra of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.08$, and (d) $x = 0.1$ respectively.

O1s peak for $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films with $x = 2\%$, 5% , 8% , and 10% is presented in figure 4.15. The O1s peak was deconvoluted into three peaks through a mixed Gaussian and Lorentzian fitting procedure. The peak with lowest binding energy, centered around 539.9 eV belongs to indium cation and denoted as O_I. The highest peak

belongs to the oxygen bonded gallium is centered around 531.1 eV and denoted as O_{II}. Finally, the peak with the highest binding energy, centered around 532.9 eV, belongs to adsorbed O₂ or oxygen vacancies of the thin film. The loosely bounded oxides or hydroxides are not considered because the sample was cleaned with ion sputtering. This fitted peak is denoted as O_{III}.

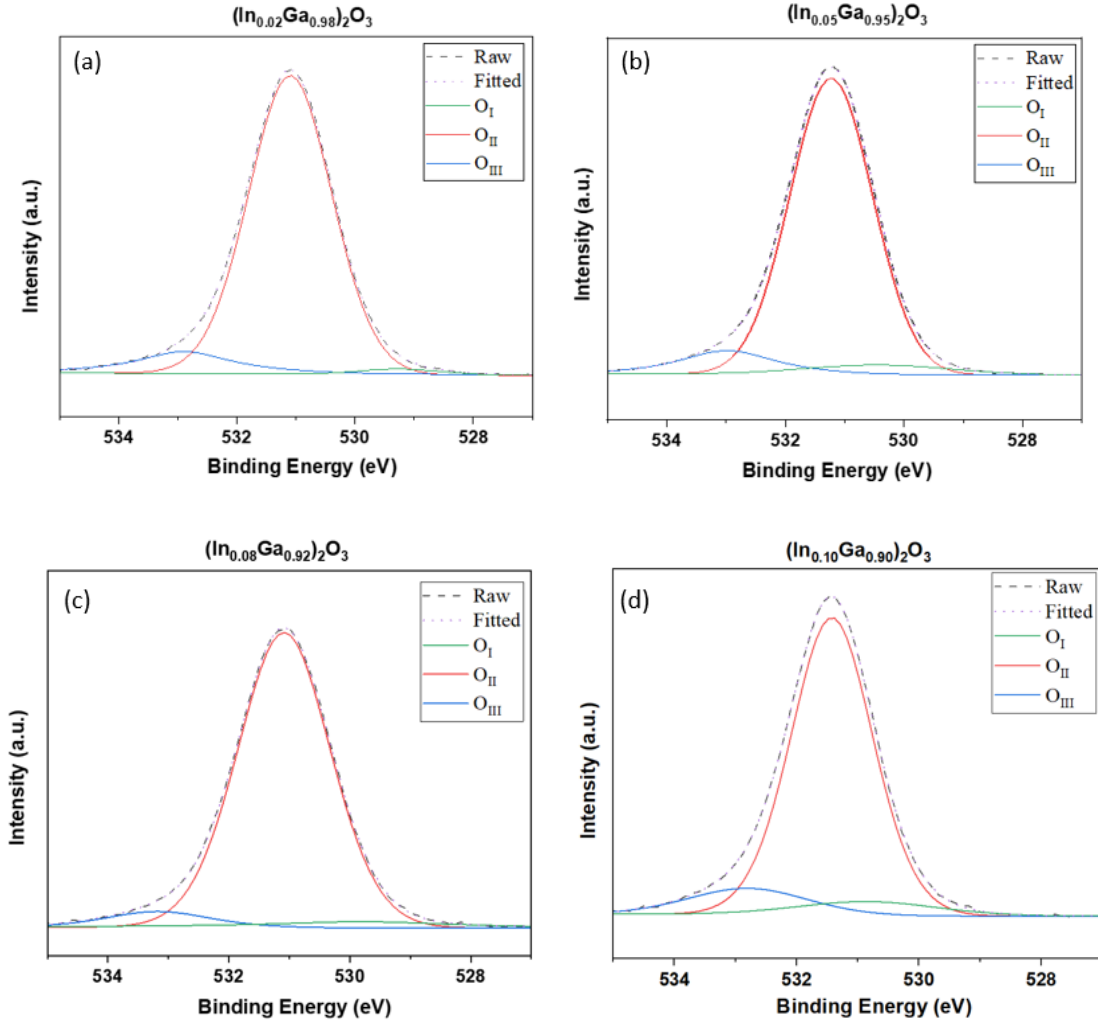


Figure 4.15: High resolution O 1s core level XPS spectra of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.08$, and (d) $x = 0.1$ respectively.

The impact of partial oxygen pressure on the $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films will be investigated for $x = 10\%$. The growth conditions, such as temperature, laser power, pulse

repetition, and pulse number will be kept constant at 720°C, 300mJ, 5Hz, and 5000 pulses, respectively. The chamber pressure was varied from 5×10^{-2} torr to 1×10^{-5} torr by varying oxygen inflow into the chamber. Figure 4.16 (a) – (e) illustrates the deconvolution of O1s spectra of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for different oxygen inflow into the chamber.

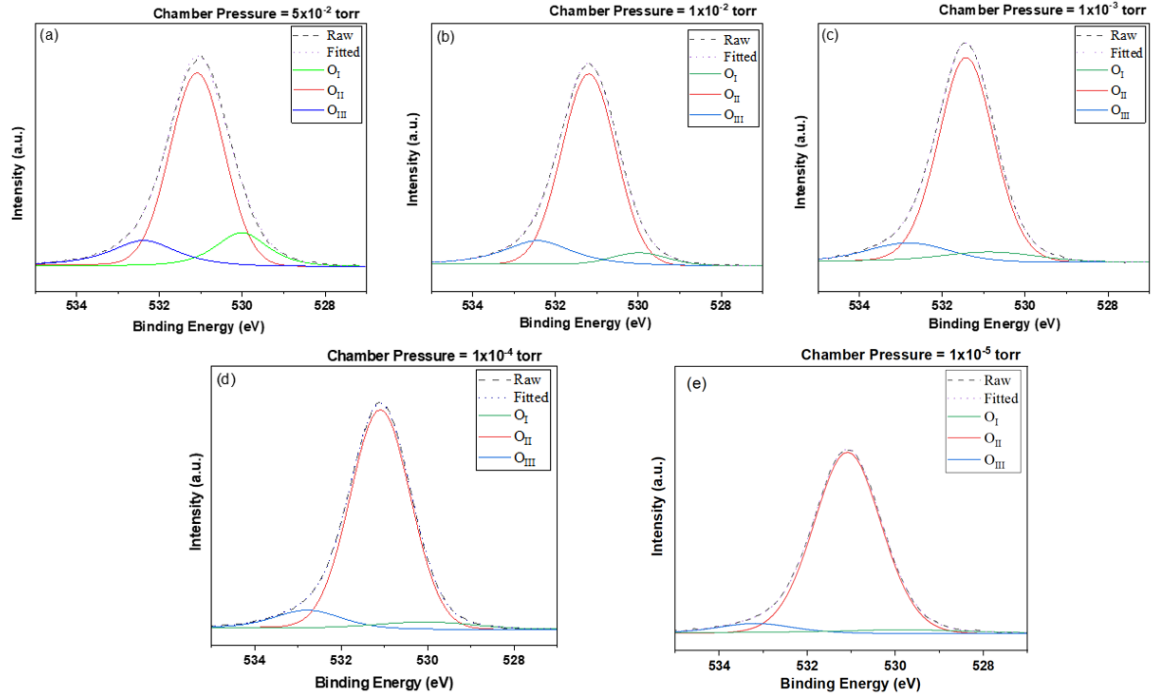


Figure 4.16: X-ray photoelectron spectroscopy (XPS) spectra of O1s of $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ for (a) $P_{\text{O}_2} = 5 \times 10^{-2}$ torr, (b) $P_{\text{O}_2} = 1 \times 10^{-2}$ torr, (c) $P_{\text{O}_2} = 1 \times 10^{-3}$ torr, (d) $P_{\text{O}_2} = 1 \times 10^{-4}$ torr, and (e) $P_{\text{O}_2} = 1 \times 10^{-5}$ torr.

The highest peak centered around (531.2 ± 0.12) eV is attributed to oxygen bonded to gallium. The O_I peak is centered around (530.1 ± 0.43) eV and the O_III peak is around (532.7 ± 0.19) eV is denoted as O_III . O_I and O_III are ascribed to the indium cation and absorbed O_2 , or $-\text{CO}_3$ or oxygen vacancies respectively [106]–[108], [23]. With the increased oxygen inflow in the chamber, we can see the proportional areas of the sub-peaks are being affected. This proves that partial oxygen pressure alters the O1s bonding

states. As oxygen vacancy state (O_{II}) in an oxide thin film is a matter of great importance, researchers used O_{II}/O_{total} to quantitatively determine the level of oxygen vacancy-related defects [97], [108], [109]. Here, O_{total} is the sum of O_I , O_{II} , and O_{III} . With the increase of oxygen inflow during growth, the O_{II}/O_{total} is declining. The excess oxygen in the chamber fills up the vacancies in the $(In_xGa_{1-x})_2O_3$ crystal lattice.

4.3 Phase Transition from Metastable κ -($In_xGa_{1-x})_2O_3$ to β -($In_xGa_{1-x})_2O_3$

In the previous chapter for $(In_xGa_{1-x})_2O_3$ with $x = 10\%$, the XRD study shows a clear indication of a second phase besides the β -($In_xGa_{1-x})_2O_3$ for a specific growth condition. In this chapter, this phase will be investigated with indium concentrations of 8%, 10%, and 15%. Usually, the ϵ -phase and the κ -phase are reported besides the β -phase for $(In_xGa_{1-x})_2O_3$, and the ϵ -phase and the κ -phase are typically separated from the β -phase using a small amount of Sn into the target material. The Sn in gallium oxide alloys promotes higher amounts of Ga to move into the octahedral position avoiding excess formation of suboxides [39], [41], [43], [70]. Throughout this chapter, a detailed investigation of the impact of deposition conditions on the crystal phases are carried out to determine the growth conditions and stability criteria of the ϵ -phase or the κ -phase in $(In_xGa_{1-x})_2O_3$.

Recalling figure 4.5, it is evident that higher substrate temperatures are required to grow stable single phase β -($In_xGa_{1-x})_2O_3$. The insufficient energy and mobility of surface adatoms at lower temperatures can be attributed to this phenomenon. However, at lower temperatures, either the ϵ -phase or the κ -phase peak was clearly visible along with the expected cubic phase. So, it is imperative that the crystalline and epitaxial relationship between different phases of the $(In_xGa_{1-x})_2O_3$ and the sapphire substrate is determined.

The monoclinic β -gallia structure has the space group $C2/m$ with two cation sites: fourfold Ga(1) and sixfold Ga(2). The oxygen atoms occupy O(1) and O(2) sites, which are threefold coordinated, and the O(3) bonds to four cations [23]. On the other hand, the cubic bixbyite structure belongs to space group $I\bar{3}a$ with two different sixfold coordinated cation sites, 8 are at the (b)-site and 24 are at the (d)-site. The surrounding oxygen around the cation are located at the corner of the cube [53]. In the ε -Ga₂O₃, the gallium atoms occupy three sites with octahedral/tetrahedral ratio of 2.2:1, and the crystal structure belongs to the hexagonal $P6_3mc$ space group. Maccioni *et al.* [36] theoretically showed that the ε -phase is the second most stable phase of gallium oxides following the β -phase. Lastly, the κ -phase of gallium oxide is just a special rearrangement of the Ga ions in the hexagonal ε -Ga₂O₃, where the edge-sharing octahedral and corner-sharing tetrahedral form zig-zag ribbons [110]. The crystal structure of these polymorphs is shown in figure 4.17.

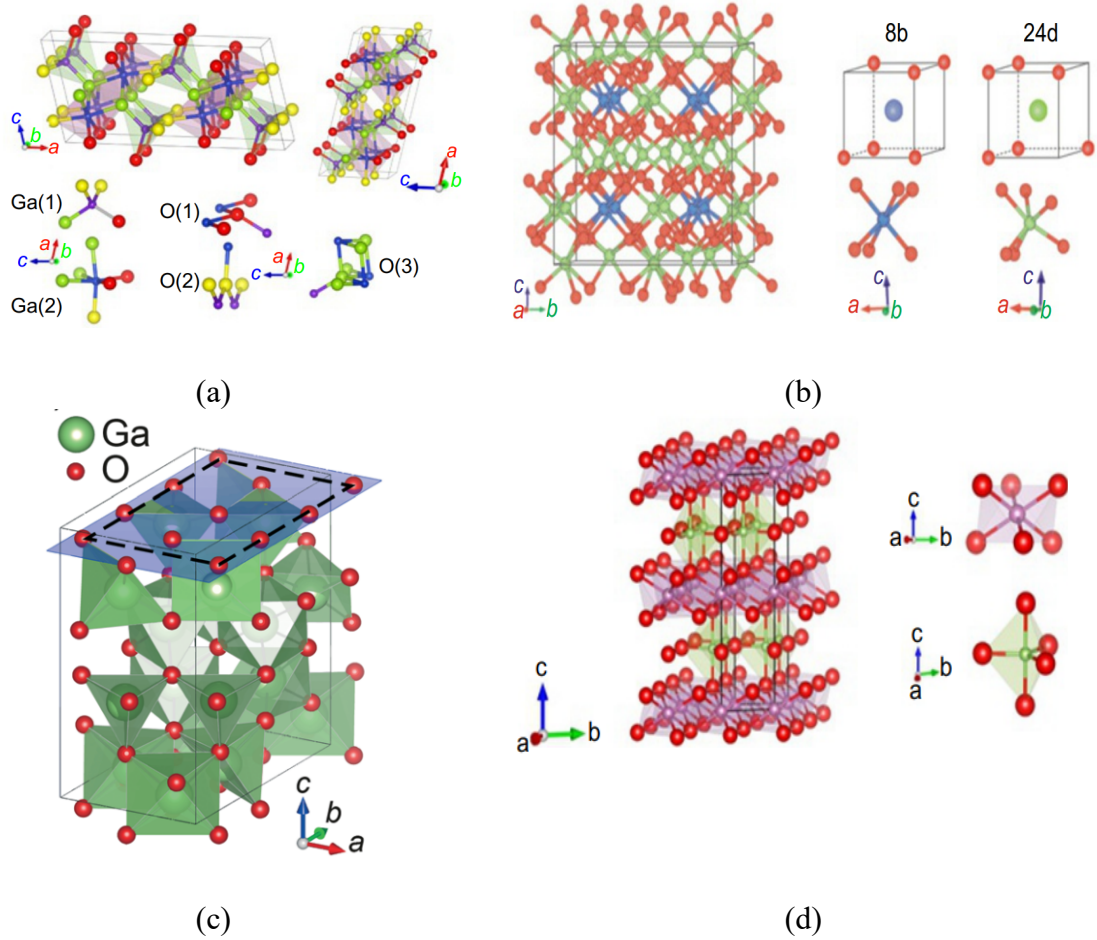


Figure 4.17: (a) Monoclinic β -galia structure and its nearest-neighbor configuration of the Ga(1)O₄ tetrahedron, the Ga(2)O₆ octahedron lattice sites. O(1) and O(2) are threefold coordinated and o(3) is fourfold coordinated oxygen lattice sites. (b) Bixbyite cubic lattice structure with 8b and 24d Wyckoff position. The oxygen positions are in the corner positions of the cube. (c) Orthorhombic Ga₂O₃ lattice structure with and ab plane on an oxygen layer is shown with dashed line [111]. (d) Hexagonal InGaO II crystal structure (In in purple, Ga in green). Ga is fivefold and In is sixfold coordinated [100].

Figure 4.18 shows the diffraction pattern of (In_xGa_{1-x})₂O₃ with x = 8% for different substrate temperatures and pressure. The laser power was constant, similar to the previous experiments.

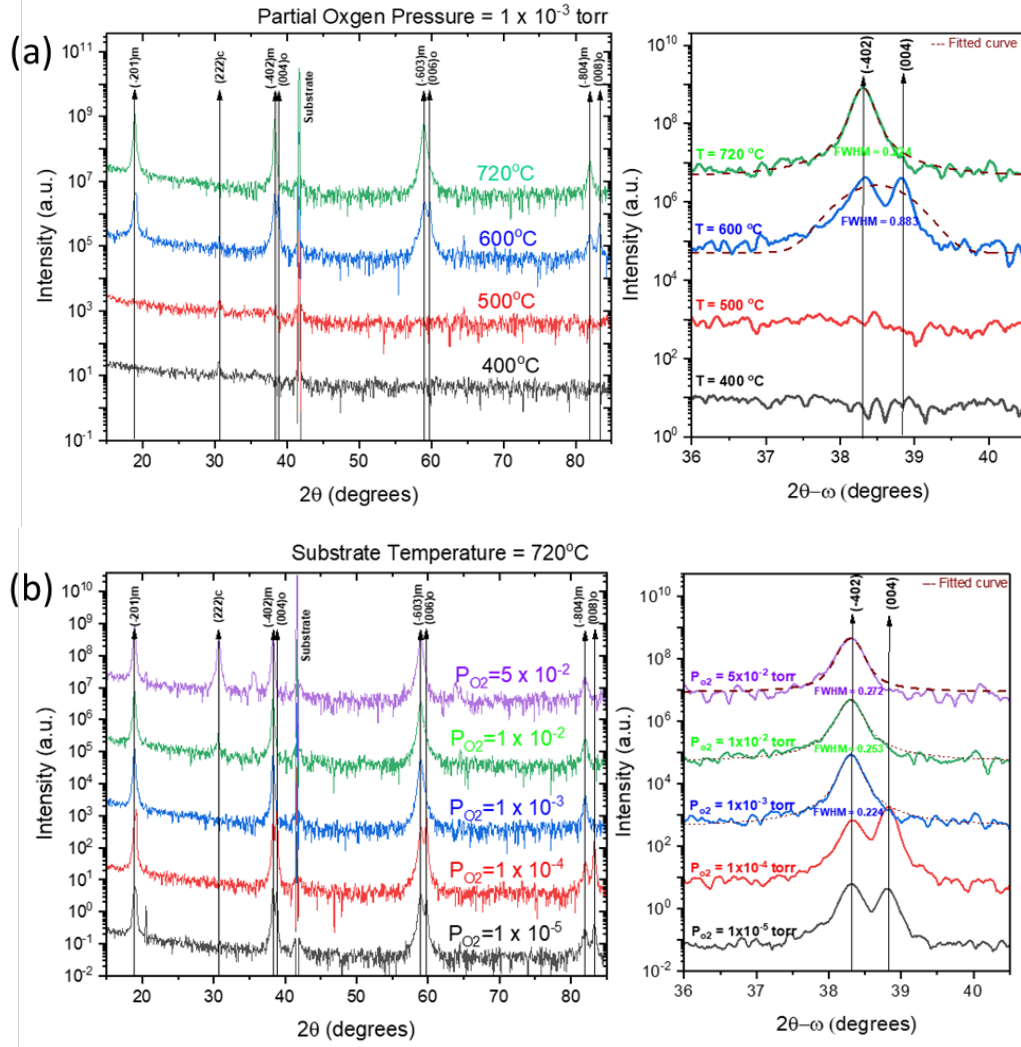


Figure 4.18: X-ray 2θ - ω diffraction diagram for 8% $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ (a) varying substrate temperature, (b) varying oxygen partial pressure of the chamber

From the figure, $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ with $x = 8\%$ exhibits a transient phase of Ga_2O_3 , and it is not the bixbyite cubic phase. Indium concentrations of less than 8% did not show any transient phase during XRD analysis. This phase can be attributed to both the ϵ -phase and the κ -phase; thus, further investigation is required to differentiate between them.

At first, an in-plane XRD phi scan will be performed for the $\{-401\}$ diffraction of the β -phase and the $\{104\}$ diffraction of the c-plane sapphire substrate. This analysis will be performed for the IGO sample with an indium concentration of 10% grown at high

temperature and 1×10^{-3} torr oxygen partial pressure so that only pure β -phase can be examined. The analysis shown in figure 4.19(a) shows six peaks 60° apart from each other, indicating sixfold in-plane rotational symmetry, which resembles pure β -Ga₂O₃ crystal structure [23]. As the c-plane sapphire (figure 4.19(b)) exhibits three peaks 120° apart, it proves that β -(In_xGa_{1-x})₂O₃ has two-fold in-plane rotational symmetry with the substrate's threefold rotational symmetry. Hence, the twofold (In_xGa_{1-x})₂O₃ thin film is epitaxially grown on three different axes of sapphire, resulting in a sixfold symmetry [112].

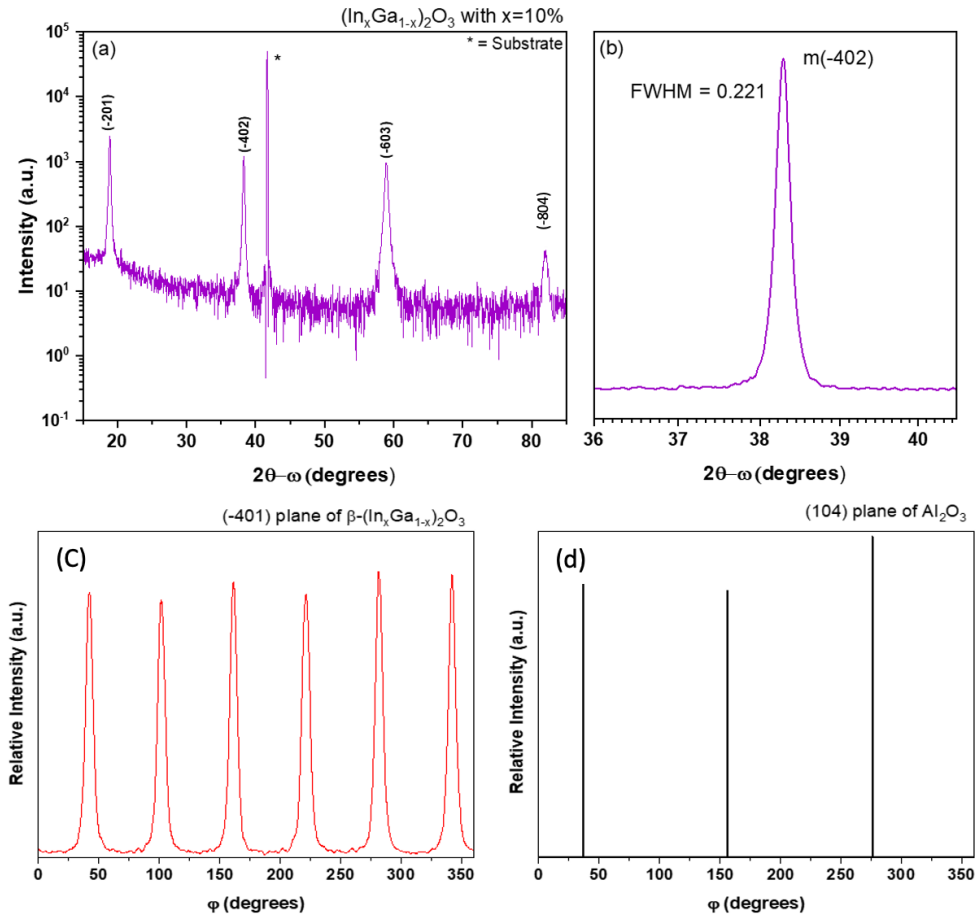


Figure 4.19: Epitaxial relationship of β -(In_xGa_{1-x})₂O₃ with c-sapphire substrate (a) XRD 2θ - ω scan of β -(In_xGa_{1-x})₂O₃ with $x=10\%$ (b) FWHM of (-402) reflex (c) ϕ scan of (-401) plane of (In_{0.10}Ga_{0.90})₂O₃, and (d) ϕ scan of (104) plane of sapphire substrate

As discussed in chapter 2.1, Kracht *et al.* reported a technique to distinguish between the almost similar hexagonal ϵ -phase and orthorhombic κ -phase. From figure 2.4 we can see that the orthorhombic and hexagonal phases share many strong diffraction planes with each other, but at lower angles, there are some comparatively strong diffraction planes that only belong to the orthorhombic crystal structure of Ga_2O_3 . XRD phi-scan of $\{122\}$ reflex of the orthorhombic lattice will not exhibit any diffraction peaks for the ϵ -phase but will show symmetric peaks for the κ -phase. The XRD 2θ - ω scan and phi scan for $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ for $x=15\%$ is shown in figure 4.20. This particular thin film was grown at a substrate temperature of 650°C , oxygen partial pressure of 1×10^{-3} torr, and with a high laser power of 550 mJ. The repetition rate was fixed at 5Hz, and 5000 pulses yielded a total thickness of approximately 120nm. Figure 4.20(a) shows reflections belonging to the (002), (004), (006), and (008) lattice planes of the orthorhombic crystal planes at angular positions of 19.15° , 38.84° , 49.82° , and 83.30° respectively. The film shows dominant orthorhombic crystallinity, but the peaks at approximately 28.8° and 82.6° can be indexed as the reflections corresponding to (222) bixbyite cubic lattice plane and (-804) monoclinic plane, respectively. The FWHM value illustrated in figure 4.20(b) is for the (004) reflection of the orthorhombic plane. We observed 12 peaks for the $\{122\}$ reflex (figure 4.20(c)), which confirms the presence of κ -($\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$. As 12 peaks were observed, it indicates the presence of three rotational domains of the orthorhombic structure.

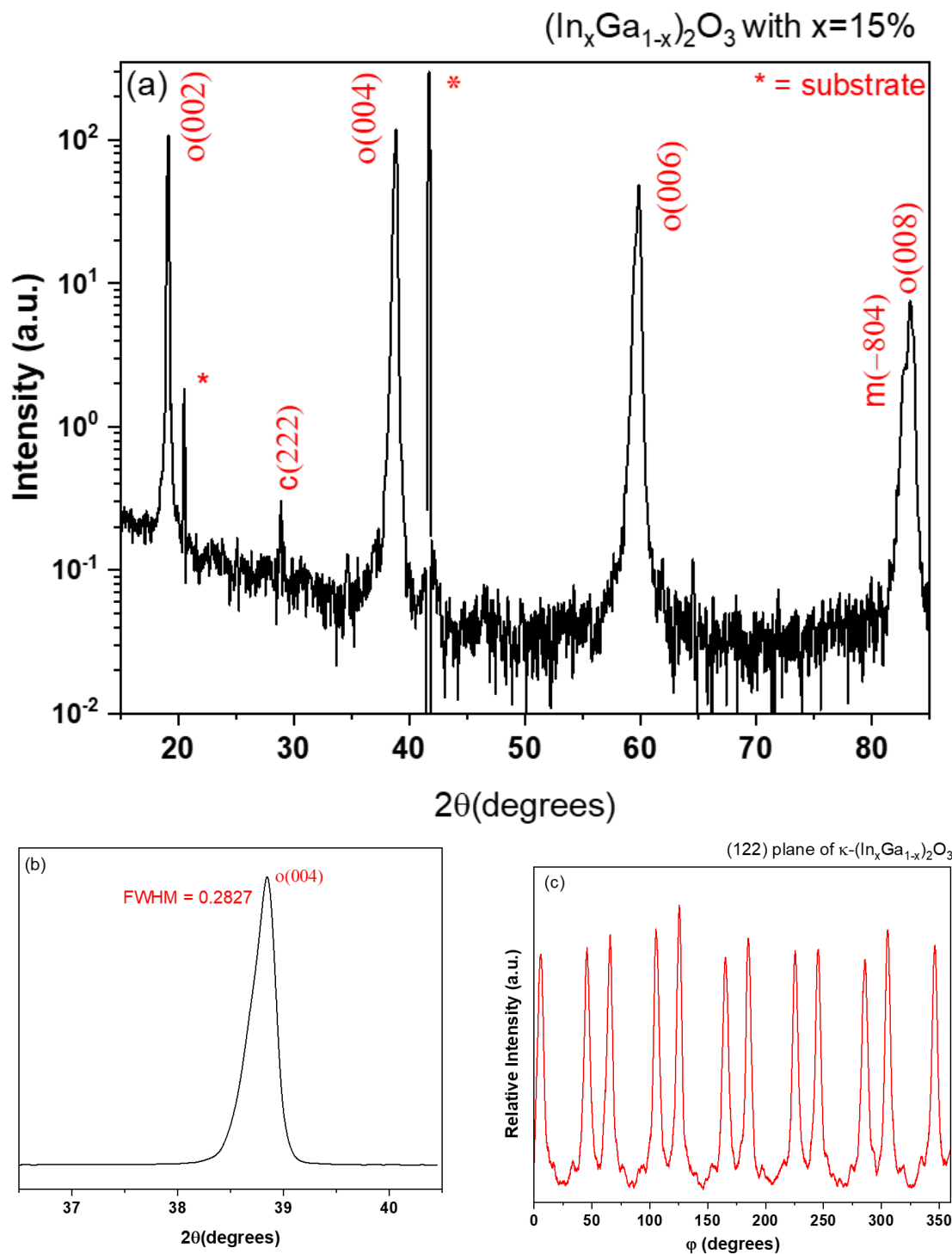


Figure 4.20: (a) XRD 2θ - ω scan of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ with $x=15\%$ grown on c-plane sapphire, (b) rocking curve of the {004} diffraction peak, and (c) ϕ scan of {122} plane proving presence of κ - $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$.

This successful determination of the κ -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ phase allows us to study the impact of PLD growth parameters on this metastable polymorph. At first, the impact of laser power is investigated with ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ ($x=10\%$). Figure 4.21 shows an X-ray diffraction analysis of three different samples grown with changing laser power from 300 mJ to 550 mJ. The substrate temperature was kept fixed at 720°C and oxygen partial pressure was fixed at 1×10^{-3} torr.

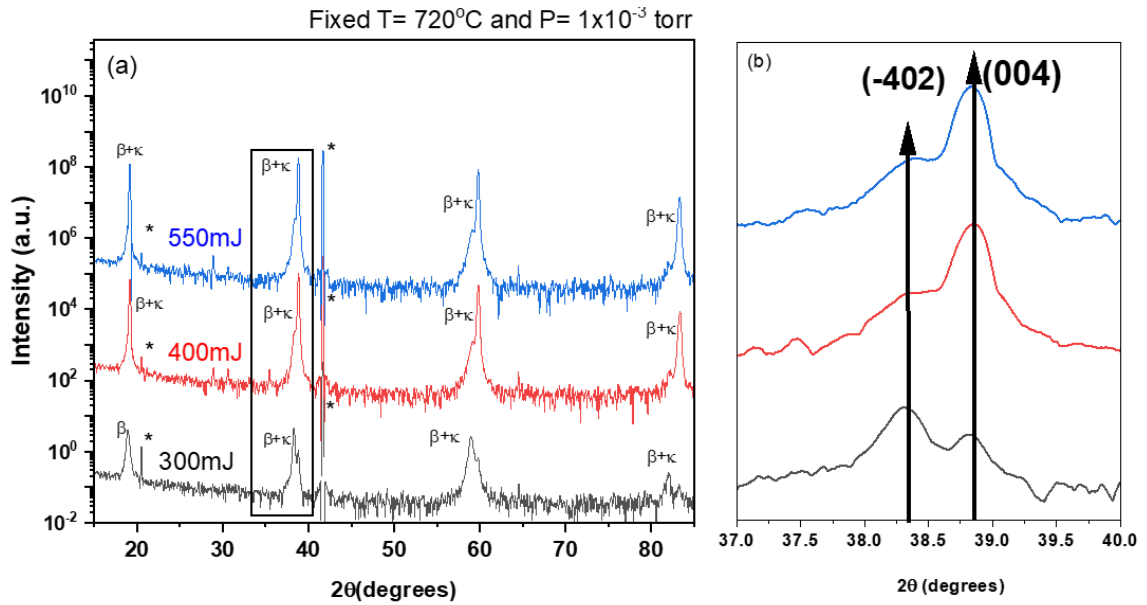


Figure 4.21: (a) Impact of laser power and fluence on ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ ($x=10\%$), (b) zoomed in on (-402) and (004) diffraction peaks.

From the plot, we can see that the κ -phase is more prominent at higher laser power compared to the contrary. For 10% indium concentration, the mix phase of κ and β can be clearly distinguished. The peaks corresponding to approximately 18.8°, 38.2°, 58.8°, and 82.4° are the monoclinic β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ reflections of the (-201), (-402), (-603), and (-804) planes respectively. On the other hand, the orthorhombic κ -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ planes (002), (004), (006), and (008) reflections are more predominantly at the diffraction angles of 19.16°, 18.86°, 59.83°, and 83.36° respectively. Figure 4.20 (b) illustrates the

phase separation for (-402) and (004) planes of the 2 polymorphs of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$. The dominant ferroelectric κ -phase for the higher laser power can be attributed to lower fluence during the growth of the thin film in PLD.

Next, the laser power and oxygen partial pressure were fixed at 550 mJ and 1×10^{-3} torr respectively for the $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ alloy. The substrate temperature was varied from 600°C to 800°C. Figure 4.22 illustrates the impact of substrate temperature on the phase transformation in $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ using X-ray diffraction analysis.

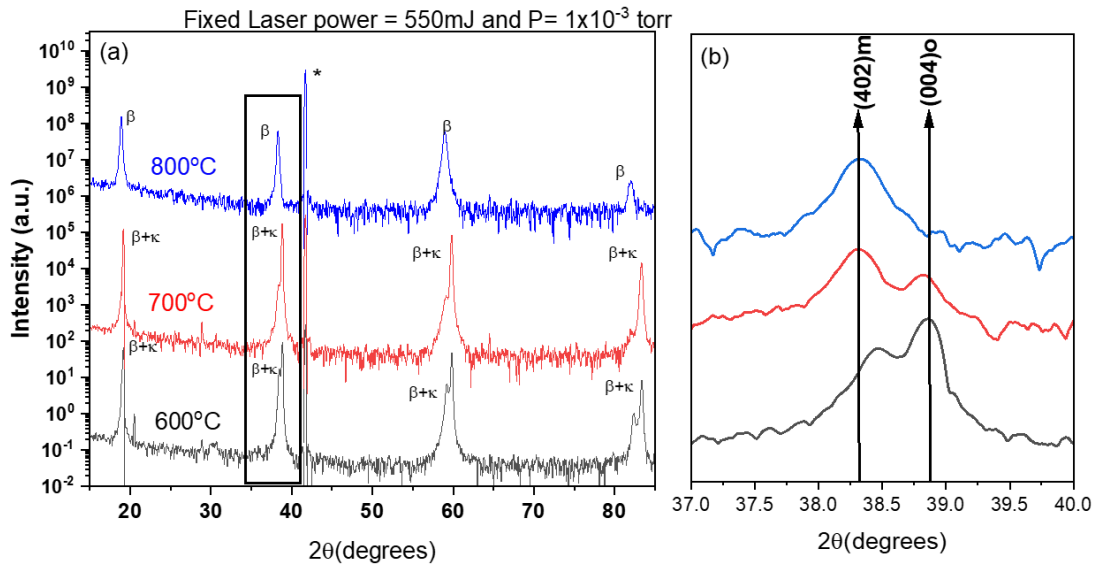


Figure 4.22: (a) Impact of substrate temperature on $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ ($x=10\%$) grown with high laser power (550mJ), (b) zoomed in on (-402) and (004) diffraction peaks.

The 2θ - ω spectra of $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ grown at 600°C exhibit a dominant κ -phase compared to the β -phase in the thin film. As the substrate temperature increases, the diffraction peaks of a more stable β -phase begin to emerge. At 800°C, the diffraction peaks due to the κ -phase disappear and the $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ thin film XRD exhibits all the diffraction peaks of a single crystalline monoclinic structure as seen in figure 4.22(a). Figure 4.22(b) is the blown-up version of the diffraction angles between 37° and 40° . This figure illustrates the polycrystalline $(\text{In}_{0.10}\text{Ga}_{0.90})_2\text{O}_3$ collapsing into a single crystalline β -

($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$. Playford *et al.* [32] explained this behavior in their study on the polymorphs of gallium oxide using the idealized views of the crystalline structure implementing the “diagrammatic elevation representation of wells”. He predicted that careful thermal studies with different heating rates would make all other polymorphs collapse into the stable β - Ga_2O_3 .

Similar characteristics of IGO thin films can be seen for films grown at lower laser power, maintaining all other parameters the same as before. The XRD 2θ - ω scan of ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ with $x=10\%$ grown on c-plane sapphire with laser power of 350 mJ and $P_{\text{O}_2} = 1 \times 10^{-3}$ torr is shown in figure 4.23.

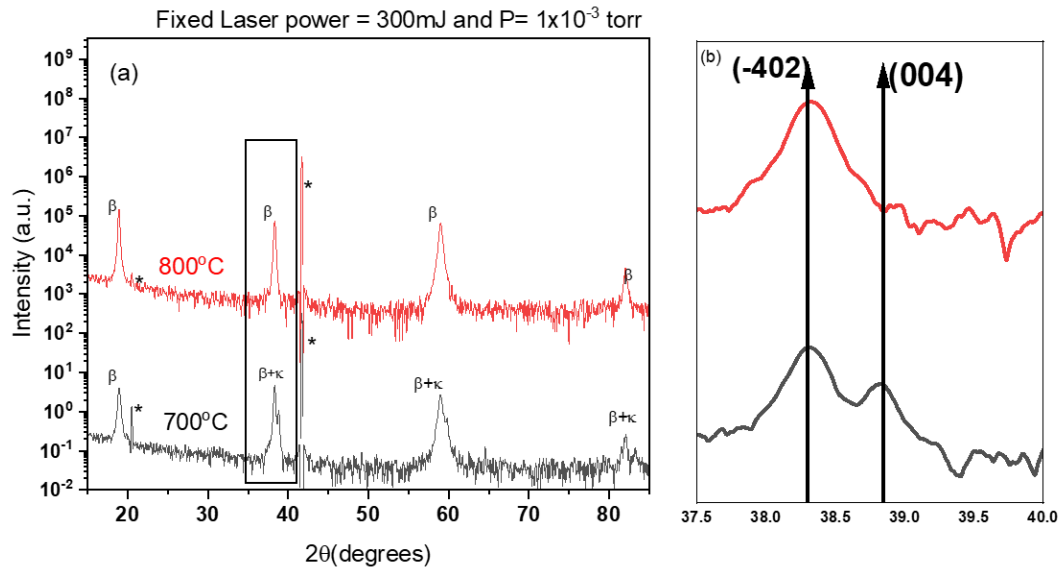


Figure 4.23: (a) Impact of substrate temperature on ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ ($x=10\%$) grown with low laser power (300mJ), (b) zoomed in on (-402) and (004) diffraction peaks.

Figure 4.22(b) shows that at lower laser power the monoclinic phase diffraction peaks are more visible than the orthorhombic κ -phases and as the temperature reaches 800°C, the XRD data only shows diffraction peaks of a single crystal β -gallia structure.

Finally, the phase transformation of the ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ was investigated by varying the oxygen partial pressure. Figure 4.24 shows the XRD diffraction study of

($\text{In}_{0.10}\text{Ga}_{0.90}$) $_2\text{O}_3$ thin films grown at 720°C and a high laser power of 550mJ by varying oxygen inflow into the PLD chamber. Three samples were investigated with different oxygen inflow to achieve oxygen partial pressure of 1×10^{-4} torr, 1×10^{-3} torr, and 5×10^{-2} torr.

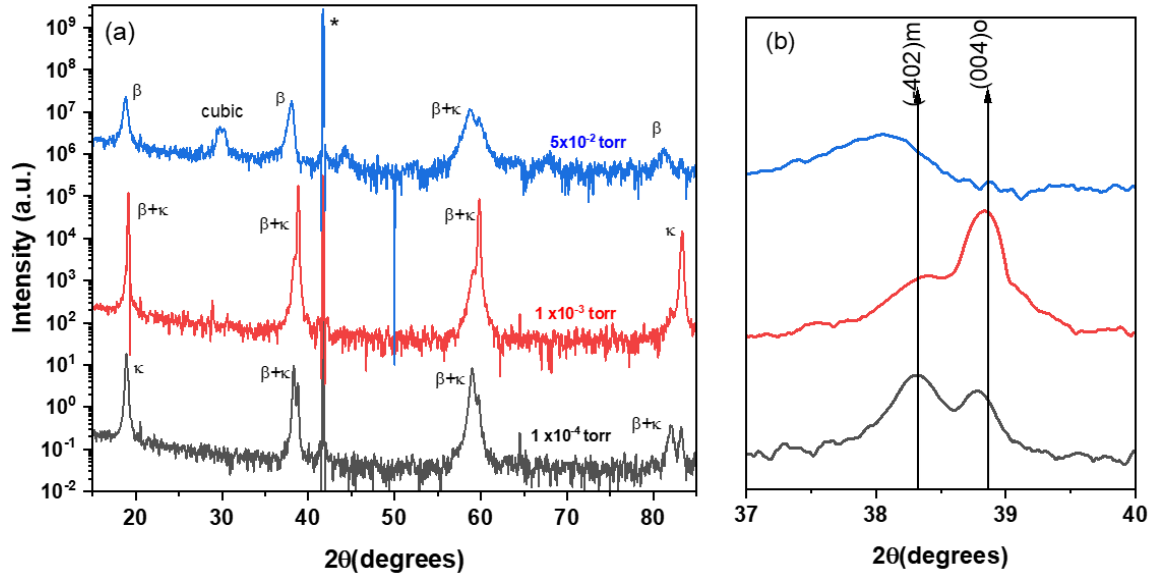


Figure 4.24: (a) Impact of oxygen partial pressure on ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ ($x=10\%$) grown with high laser power (550mJ), (b) zoomed in on (-402) and (004) diffraction peaks.

The XRD analysis shows high-quality ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ thin films in the orthorhombic κ -phase in oxygen partial pressure of 1×10^{-3} torr. Increasing the oxygen inflow diminishes the orthorhombic phase, and a polycrystalline thin film with cubic, monoclinic, and orthorhombic phases can be seen for the ($\text{In}_{0.10}\text{Ga}_{0.90}$) $_2\text{O}_3$ thin film grown at 5×10^{-2} torr oxygen pressure. At 1×10^{-4} oxygen partial pressure, the diffraction due to $\{-201\}$ reflection is dominant. Further investigation is required to assess the impact of chamber pressure on the polymorphs of ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$. To find out whether the κ -phase is for the nucleation in the as-grown thin films or the specific growth conditions, a 10 nm single-crystalline β -($\text{In}_{0.10}\text{Ga}_{0.90}$) $_2\text{O}_3$ was grown as the nucleation layer before growing

($\text{In}_{0.10}\text{Ga}_{0.90}$) $_2\text{O}_3$ high laser power and low substrate temperature. As the diffraction peaks due to the kappa phase reappear, we can conclude that the metastable phases originate due to PLD growth conditions, not nucleation.

The diffraction peak intensity and FWHM values indicate that the β -phase is much less intense and much broader than those of the film in the κ -phase. Kneiß *et al.* [43], in their study of tin-assisted κ - Ga_2O_3 grown using PLD, also found that the κ -phase possesses comparatively much better crystal quality than the β - Ga_2O_3 . They attributed this phenomenon to the reduced c-lattice constant of the κ -phase thin films. AFM analysis was performed for β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ and κ -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ for an indium concentration of 10%. The RMS roughness for β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ was roughly 6 nm whereas the roughness for κ -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ was much less (approximately 1.5 nm). We can also visibly observe the smaller grains and less pronounced grain boundaries for κ -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ in figure 4.25 (b) compared to the β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ shown in figure 4.25 (a).

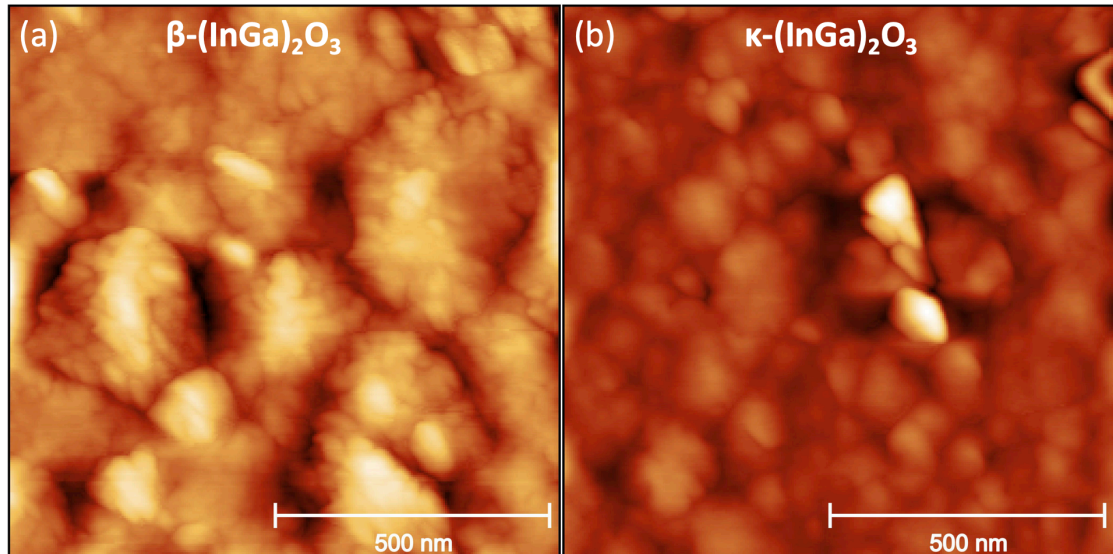


Figure 4.25: AFM analysis of (a) β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ and (b) κ -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ for $x = 10\%$.

Figure 4.26 summarizes the impact of laser power, oxygen partial pressure, and substrate temperature on the $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films creating a phase map between the β -phase and the κ -phase for In concentration above 8%.

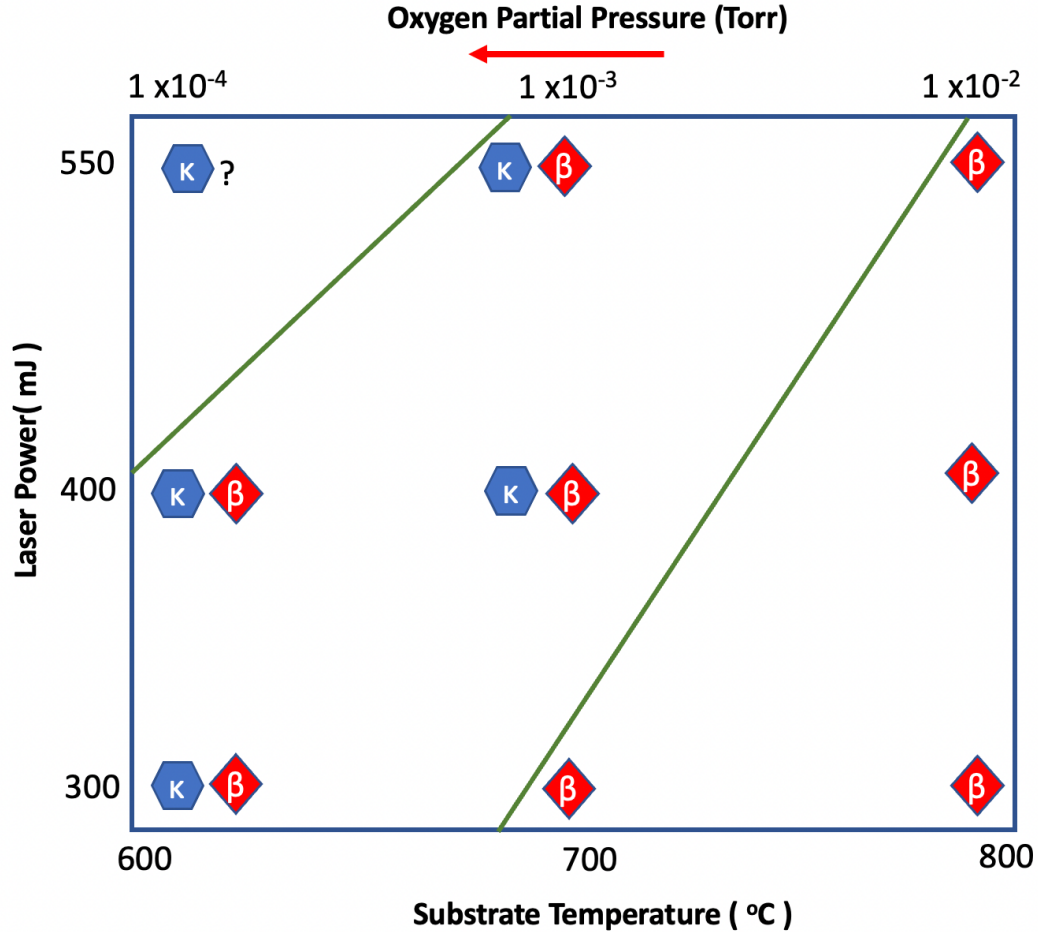


Figure 4.26: Impact of PLD growth parameters (laser power, substrate temperature, and oxygen partial pressure) on the growth of different polymorphs of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ grown on c-plane sapphire.

The relation between the polymorphs of Ga_2O_3 alloying with indium is an exciting research prospect. The presence of the ferroelectric κ -phase beside the most stable monoclinic and cubic phases indicates the possible applicability of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ in memory devices, along with its vast applications in power and optoelectronic devices.

4.4 β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ / β - Ga_2O_3 Superlattice

Additionally, β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ / β - Ga_2O_3 superlattice heterostructures are fabricated on c-plane sapphire using the exact parameters that were discussed before for the β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$. Single crystalline β - Ga_2O_3 are grown at a substrate temperature of 600°C, an oxygen partial pressure of 1×10^{-2} torr, and in 300 mJ of laser power. Five β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ / β - Ga_2O_3 stacks were grown with each layer grown with 1000 pulses ($\sim 10\text{nm}$ thickness) in a 5Hz repetition period (shown in figure 4.27). The superlattice structures were grown for In concentrations of 2%, 5%, and 10%. Figure 4.28 shows the two theta-omega XRD scans of the superlattice structures.



Figure 4.27: Diagram of the β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ / β - Ga_2O_3 superlattice grown on c-sapphire using PLD.

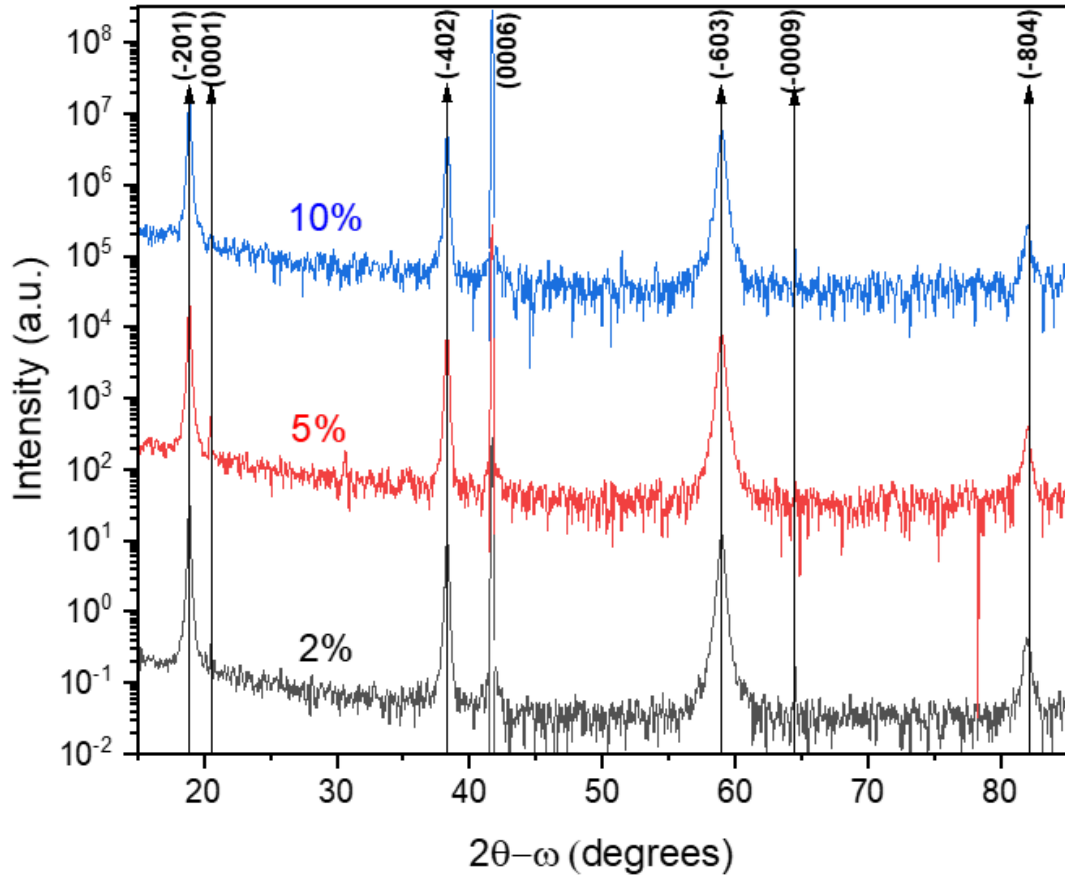


Figure 4.28: XRD 2θ-ω scans of β-(In_xGa_{1-x})₂O₃/β-Ga₂O₃ superlattice with x = 2%, 5%, and 10%.

Usually in XRD 2θ-ω plots, the peak shift or separation between the Ga₂O₃ and the alloy proves the formation of the heterostructure. But as we can see from the XRD spectra, there is no such visible phase shift. In addition, homoepitaxial Pendellösung fringes in HRXRD also determine superlattice heterostructure, where from the fringes, the thickness of the layers could be approximated [113]–[115]. A detailed study using SEM and TEM analysis is required to investigate and optimize superlattice structures of β-(In_xGa_{1-x})₂O₃/β-Ga₂O₃. Superlattice structure with some lattice mismatch opens up the possibility of quantum well applications as well as HEMT structures, where 2D electron gas (2DEG) can appear in the heterointerfaces. Additionally, these structures can be used for high-performance UV optoelectronics devices.

5. CONCLUSION AND FUTURE WORK

Indium gallium oxide alloy is one of the most promising candidates for the next generation of power devices because of its bandgap tunable properties in the wide bandgap region. Structural and compositional understanding of alloys like indium gallium oxide is thus important. This research demonstrates the growth conditions of single-crystalline β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ alloys with $x \leq 10\%$ on c-plane sapphire using pulsed laser deposition. The bandgap tunability was investigated using UV-Vis analysis, and it exhibits a linear bandgap reduction from 4.98eV to 4.64eV with the increase of In concentration. Epitaxial relationship and crystalline quality of ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ thin films and sapphire (0001) were investigated using X-ray diffraction analysis. The presence of the κ -phase was detected and later confirmed by distinguishing it from the ϵ - phase using XRD phi-scan of the {122} reflection of the orthorhombic phase. The {122} reflection was chosen because it is unique to orthorhombic crystal structure and does not belong to the hexagonal structure. Detailed phase relation of β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ and κ -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ was mapped out through a set of experimentation by varying the PLD growth parameters such as laser power, substrate temperature, and oxygen partial pressure. The ferroelectric orthorhombic phase of the ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ alloy heterostructures exhibit huge potential in the applications of high-performance memory and power devices. Finally, superlattices with five layers of β -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ / β - Ga_2O_3 on c-plane sapphire were grown using PLD. Further investigation is required to properly characterize superlattice structures for investigating the presence of quantum wells.

Future work includes further investigation into the polymorphs of ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$, especially the orthorhombic phase. TEM analysis can accurately illustrate the alloy

crystal structure. The coexistence of ferroelectric and semiconductor properties of this alloy is worthy of further studies, aiming in particular at developing novel device applications. Single domain κ -($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ heterostructures can allow large 2DEG concentration paving the way for ultra-high performance HEMT devices.

An understanding of the detailed defect structure of the ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ is the first step to growing homogeneous layers of different polymorphs. Further investigation of the growth mechanism of these metastable phases is of much importance.

Finally, electronic devices fabricated with superlattice structures of ($\text{In}_x\text{Ga}_{1-x}$) $_2\text{O}_3$ should be investigated to demonstrate the potential of this bandgap tunable alloy.

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