Titanium Incorporated Gallium Oxide (ga-Ti-O): Structure Property Relationship And Performance Evaluation For Extreme Environment Applications

Sandeep Manandhar

University of Texas at El Paso, sandeepmanandhar@gmail.com

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TITANIUM INCORPORATED GALLIUM OXIDE (GA-TI-O): STRUCTURE PROPERTY RELATIONSHIP AND PERFORMANCE EVALUATION FOR EXTREME ENVIRONMENT APPLICATIONS

SANDEEP MANANDHAR
Doctoral Program in Mechanical Engineering

APPROVED:

__________________________
Ramana V. Chintalapalle, Ph.D., Chair

__________________________
Calvin M. Stewart, Ph.D.

__________________________
David Roberson, Ph.D.

__________________________
Deidra Hodges, Ph.D.

__________________________
Charles Ambler, Ph.D.
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Sandeep Manandhar

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Dedicated to my parents
TITANIUM INCORPORATED GALLIUM OXIDE (GA-TI-O): STRUCTURE
PROPERTY RELATIONSHIP AND PERFORMANCE EVALUATION FOR
EXTREME ENVIRONMENT APPLICATIONS

by

Sandeep Manandhar, M.S.

DISSertation

Presented to the Faculty of the Graduate School of
The University of Texas at El Paso
in Partial Fulfillment
of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

Department of Mechanical Engineering
THE UNIVERSITY OF TEXAS AT EL PASO
December 2018
Acknowledgments

I would like to thank my mentor, Dr. Ramana Chintalapalle, for his guidance, financial support, and his overall help throughout my academic years, especially during this doctoral research. He pushed me toward becoming a better scholar, researcher, and person. I am very thankful for all his lessons and support that allowed me to complete this research.

I would like to thank Dr. Calvin M. Stewart (Mechanical Engineering), Dr. Deidra Hodges (Electrical and Computer Engineering), and Dr. David Roberson (Materials Science and Engineering), who agreed to be part of my doctoral committee and were willing to spend their valuable time to evaluate my dissertation research. Also, I am highly indebted to all of them for the feedback given from time to time.

I would like to thank my past and present team members at UTEP: Dr. Gustavo Martinez, Dr. Ernesto Rubio, Mr. Anil K Battu, Mr. Cristian Orozco, Ms. Marlyn Torres, Mr. Vishal Zade, and all others who have helped me in this endeavor and became part of a family. I would like to dedicate this to my parents (Mr. Gopal P Manandhar and Mrs. Beena Manandhar) and my wife (Mrs. Ritu Shrestha) who always pushed me to accomplish my goals and for their continual support. I would like to thank my family (Mr. Gaurav Manandhar, Mrs. Tenisha Pradhan, Ms. Aviana Manandhar, Mr. Ashish Manandhar, and Mrs. Karuna Manandhar) for always supporting my goals.

I wish to express my sincere thanks to the Department of Energy (DoE) and National Science Foundation (NSF) for the financial support through research grants. Part of the research presented in this dissertation was supported by the DoE; however, the views and opinions expressed by the author(s) herein do not necessarily state or reflect those of the United States government or funding agency thereof.
The existing power generation systems, which utilize fossil fuels, are in dire need of efficient, reliable chemical sensors that can operate safely at higher temperatures. These sensors control the combustion environment and the emissions during combustion. Several sensing materials such as SnO\textsubscript{2}, ZnO, TiO\textsubscript{2}, WO\textsubscript{3}, and Ga\textsubscript{2}O\textsubscript{3} exhibit high sensitivity to certain type of chemical molecules and in a certain range of temperatures. Among these candidate materials, β-Ga\textsubscript{2}O\textsubscript{3} is stable at very high temperatures and has shown functionality for oxygen sensing at higher temperatures (>700°C). However, the response time and sensitivity must be significantly improved in order to derive their full potential and utilize them in practical applications. In this work, we focus on the fabrication, characterization and performance evaluation of titanium (Ti) doped gallium oxide (Ga\textsubscript{2}O\textsubscript{3}) thin films (referred to GTO) for application in oxygen sensors. An in-depth study was performed on GTO sensors to improve response time and sensitivity of β-Ga\textsubscript{2}O\textsubscript{3}. The real environment condition for sensor (>700°C) application were simulated to understand the effect of temperature on the crystal structure, mechanical properties, electronic properties and oxidation states of Ti doped β-Ga\textsubscript{2}O\textsubscript{3}. Additionally, for utilizing Ti doped β-Ga\textsubscript{2}O\textsubscript{3} films in practical oxygen sensor applications, attempts were also made to predict the thermodynamic stability and performance of a model, doped Ga\textsubscript{2}O\textsubscript{3} system under extreme environments. A detailed thermal study to understand the effect of extreme environment on titanium (Ti) doped β-Ga\textsubscript{2}O\textsubscript{3} is performed. The real environment condition for sensor (>700°C) application was simulated to understand the effect of temperature on the crystal structure, mechanical properties, electronic properties and oxidation states of Ti doped β-Ga\textsubscript{2}O\textsubscript{3}. In the entire work, a wide variety of analytical techniques were employed to derive conclusions on the structure, morphology, chemical states, optical properties, thermo-chemical and thermo-mechanical stability of
nanostructured Ti-doped Ga$_2$O$_3$. The results are presented and discussed in this thesis along with structure-property relationships and implications for sensor technology.
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Chapter 1: Introduction

In recent years there has been a great deal of research efforts directed toward the development of small dimensional chemical sensing devices for practical applications ranging from toxic gas detection to manufacturing process monitoring (Eranna et al. 2004). Today’s increased demand for world energy production heavily relies on fossil fuel. As shown in Figure 1.1, International Energy Agency also predicts massive increase in fossil fuel utilization for energy production (IEA 2017). The energy production from fossil fuel requires a complex process to control efficient combustion, which also requires sensitive oxygen detectors. The combustion of fossil fuel has many environmental and health concerns due to hazardous emissions like NO\textsubscript{x}, CO, CO\textsubscript{2}, SO\textsubscript{2} etc. These emissions can be controlled or even reduced by implementing sensors for efficient combustion by maintaining O\textsubscript{2} in the combustion environment (Spirig et al. 2007). Also, in many industries, gases have become increasingly prevalent and important as raw materials which makes it very important to develop highly sensitive gas detectors. Such gas sensors should allow continuous monitoring of the concentration of particular gases in the environment in a quantitative and selective way (Mandelis and Christofides 1993). Due to the need to detect each one of these gases accurately, energy science and engineering researchers have opted for using arrays of gas sensors to improve the performance of the energy systems.
In the case of natural gas combustion, the CO emission due to efficient combustion is reduced to tens of ppm, and the detection of oxygen plays a very important role; however, when the excess of natural gas is introduced, the amount of CO emission rises, and its detection becomes important (Fleischer 2008). Nevertheless, the detection of these gases at combustion environment require robust and reliable systems capable of withstanding extreme environments. According to the U.S. Department of energy, novel technologies based on coal-firing and combustion turbines work on thermal loads in the range of 1000 °C to 1600 °C (Romanosky and Maley 2013). Also, automotive emissions can be drastically reduced by placing the monitoring gas sensor closer to the exhaust manifold where temperatures are capable of reach 1000 °C (Docquier and Candel 2002).

Recently, researchers are pushing efforts aimed at: (a) increasing of gas sensitivity and improvement of their selectivity, (b) reduction of electric power, and (c) decreasing of response and recovery times (Korotchenkov, Dmitriev, and Brynzari 1999). In the majority of cases, the researchers try to resolve the problems using miniaturization of gas sensors by using thin films, semiconductor, MOS and membrane technology (Eranna et al. 2004). However, many research efforts have not yet reached commercial viability because of problems associated with the sensor technologies applied to gas-sensing micro-systems. The problems of inaccuracies and inherent characteristics of the sensors themselves have made it difficult to produce fast, reliable, and low-maintenance sensing systems comparable to other micro-sensor technologies that have grown into widespread use commercially (Wilson and DeWeerth 1997). With the increasing demand for better gas sensors of higher sensitivity and greater selectivity, there is huge push to find more suitable materials with the required surface and bulk properties for use in gas sensors. Detection and quantification of gaseous species in the air as contaminants (polluting gases) at low cost is becoming important. Among the gaseous species to be observed are oxygen (O$_2$), nitrous oxide (NO), nitrogen dioxide (NO$_2$), carbon monoxide (CO), carbon dioxide (CO$_2$), hydrogen sulfide
(H₂S), sulfur dioxide (SO₂), ozone (O₃), ammonia (NH₃), and organic gases such as methane (CH₄), propane (C₃H₈), liquid petroleum gas (LPG), and many others (Eranna et al. 2004).

The semiconductor/metal oxide materials exhibit attractive properties to be used as a gas sensor. To utilize metal oxide as a gas sensor, the chemical sensitivity of their surfaces plays a crucial role. Metal-oxide based n-type semiconductors are the most commonly used sensing materials, and many of these sensor devices use the surface-driven property for gas detection applications. A metal oxide gas sensor can detect a change in the gas atmosphere due to a change in the electrical resistance. Due to this, a polycrystalline metal oxide thin films exhibit better performance than those of single crystals or large grain films (Rantala, Lantto, and Rantala 1998). The potential energy barriers between grain boundaries play an important role in the electrical conductivity of the polycrystalline material. A chemical sensor consists of two functions: the receptor function, which recognizes a chemical substance at the surfaces of the semiconducting particles, and the transducer function, which transduces the chemical signal on the semiconductor surface through the microstructure of the sensing semiconductor material into the electric output signal (Eranna et al. 2004). The change in resistance across the sensing element is recorded as the signal. The temperature of the sensor is one of the most important parameters. Firstly, adsorption and desorption are temperature dependent processes. Thus the dynamic properties of the sensors (response and recovery times) depend environment temperature. The surface coverage, co-adsorption, chemical decomposition, or other reactions are also temperature dependent, resulting in different static characteristics at different temperature (Mizsei 1995). On the other hand, temperature also has a huge effect on the physical properties of the sensor material (like charge-carrier concentration, Debye length, and work function). For example, at a higher temperature, the charge-carrier concentration (and the conductivity) increases and the Debye length decreases. This is one possible reason for the decreasing sensitivity of sensors at higher temperatures. At low temperature, most gas-sensor materials (metal oxides) are insulators rather than semiconductors (Mizsei 1995).
Chapter 2: Motivation and Significance of the Proposed Project

Sensors based on metal oxide semiconductors are most promising for power generation systems due to their low cost paired with low power consumption and small dimensions. Also, they provide on-line operation, high compatibility with microelectronic processing, and ease of integration into nanotechnology and portable device technology. Therefore, in recent years, extensive studies have been directed towards the fundamental understanding, research, and development of oxygen sensors based on metal oxides. However, even though there exists a very high demand for advanced oxygen sensors for combustion, the existing technologies suffer from poor response and recovery times and long-term stability. The recent approaches to improve the response time, selectivity and prevent sulfur poisoning have not met with the desired success.

Further research and development are needed to realize oxygen sensors that combine rapid response time, selectivity and long-term stability. This is the impetus for the proposed project to investigate the intrinsic and metal-doped Ga$_2$O$_3$ to design oxygen sensors that combine a rapid response, enhanced “3S” criteria, reliability, and robustness at extreme environments for application in power generation systems.

2.1 Research Objectives

The hypothesis that constitutes the pillar behind this dissertation work is: “the refractory metal doping into gallium oxide can improve the 3S criteria combined with rapid response and robustness for utilization in oxygen sensing at extreme environments for power generation systems.” The challenging goal of this work is, therefore, to create a fundamental understanding of the intrinsic and metal-doped gallium oxide sensors for detecting oxygen in power generation systems. The following are the specific research tasks and objectives.

2.1.1 Fabrication of Ga$_2$O$_3$ Thin Films for High-Temperature Oxygen Sensors

The first objective of this work is to fabricate high-quality intrinsic and metal-doped Ga$_2$O$_3$ thin films by RF magnetron sputtering. The goal is to improve the sensor response. The use of the
sputtering technique is justified by the repeatability of the process, the easiness of the integration with mass production systems and the non-equilibrium state that allow us to combine different materials without the necessity to follow Hume-Rothery rules for alloying (Wasa, Kitabatake, and Adachi 2004).

2.1.2 Optimization of Deposition Conditions

The deposition conditions will be tuned in order to achieve the best structural, electrical, electronic, and morphological conditions to enhance sensor performance. The effect of processing conditions, such as substrate temperature, sputtering pressure, and partial pressure of reactive gases, on the crystal structure, grain size, band gap, resistivity, and other related parameters will be studied in detail. The goal is to optimize the conditions to produce samples with high structural quality.

2.1.3 Establish a Structure-Property Correlation

To derive a structure-property relationship, which is helpful to provide a deeper understanding of the Ga$_2$O$_3$ films for sensor application, the effect of deposition parameters on the structure and property will be compared. Specific attention will be directed towards metal doping approach, due to the importance of improving sensor performance. with a special focus on response time, which is determined by the chemical reaction kinetics between the material surface and the oxygen molecules, and by consequence, by the diffusion process and surface reactions (Carpenter, Mathur, and Kolmakov 2012). For that reason, understanding of the defect chemistry of doped Ga-oxide is essential.

2.1.4. Evaluate Ga$_2$O$_3$ Based Thin Films for Oxygen Sensing at High Temperatures

Evaluating the sensor performance is critical to utilize the materials developed in sensor technology. Therefore, Ga$_2$O$_3$ based films will exposed to test gas(es) under a temperature of 700 °C or higher and evaluate their capabilities to detect oxygen under those conditions. In this case, samples produced under optimum conditions will be introduced into a vacuum chamber and test their variation in electrical conductivity when oxygen is introduced. Sensitivity, time response,
and selectivity will be determined. Furthermore, the evaluation of $\text{Ga}_2\text{O}_3$ based sensors detection range was evaluated, varying the partial pressure of oxygen introduced, in order to see the range of detection at the already mentioned temperatures.

### 2.1.5 Thermal Stability of $\text{Ga}_2\text{O}_3$ Based Thin Films

High-temperature oxygen sensors need to tolerate a minimum of 17,000 h of operation (Korotcenkov 2007); for that reason, the exposure and analysis of the properties before, during and after exposure is essential. Intrinsic and metal-doped $\text{Ga}_2\text{O}_3$ films will be introduced into a high-temperature furnace and expose to a temperature higher than 700 °C for several periods of time. Then, their structural, electrical, and sensor performance will be evaluated. A structure-property analysis will be made on the thermally treated samples, similar to as-deposited Ga-oxide films, in order to derive conclusions and validate their chemical and structural stability at higher temperatures.
Chapter 3: Literature Review

3.1. Gallium Oxide

Gallium oxide (Ga$_2$O$_3$) belongs to the family of transparent oxide semiconductors (TOS), which includes oxides of In, Zn, Sn, Cd, Cu, Mg metals (Medvedeva and Hettiarachchi 2010). Ga$_2$O$_3$ has been known for decades as its history dates back to 1875 when Lecoq de Boisbaudran (de Boisbaudran 1875) described newly discovered element gallium and its compounds. The early literature shows some basic research on the topic of Ga$_2$O$_3$. Later with the development of the new application of Ga$_2$O$_3$ was investigated for microwave and optical properties, as a material for phosphor and electroluminescent device, as a gas sensor, as UV detectors, as transparent conductive coatings, etc. (Kim and Kim 2014, Guo et al. 2014, Guo, Verma, et al. 2015). In recent days, there has been significant interest in gallium oxide related research as the potential of Ga$_2$O$_3$ has emerged as the future of wide bandgap semiconductor based electronics. While there are some wide bandgap semiconductor materials systems, including the high Al-content AlGaN alloys, BN, SiC, diamond, ZnSe, ZnS, and ZnMgO, that are potentially suitable for such applications but many of them come with limitations. To mention briefly, such limitations are: the persistent photoconductivity in AlGaN, the indirect gap of SiC, the environmental sensitivity of ZnO-based materials and the cost, lack of availability of high-quality films/substrates and lack of doping technology for some of the other materials (Reimer 2004). Thus, due to these limitations, the turning point was towards Ga$_2$O$_3$ expecting that it can overcome many of those limitations in device technology development.

3.2. Crystal Structure

There are five different possible crystal structures for Ga$_2$O$_3$. These polymorphs are designated as $\alpha$, $\beta$, $\gamma$, $\delta$, and $\varepsilon$ (Roy, Hill, and Osborn 1952, Yoshioka et al. 2007a). These polymorphs are different in their crystal space group and coordination number of Ga ions. All these phases can be synthesized by heating GaO(OH) in the air between 450 and 550 $^\circ$C as shown
in the figure below. However, only Ga$_2$O$_3$ can be obtained by baking any other polymorph of Ga$_2$O$_3$ in the air at a high temperature.

![Diagram of transformation relationship among various forms of Gallium Oxide](image)

Figure 3.1: Transformation relationship among various forms of Gallium Oxide (Recreated from (Roy, Hill, and Osborn 1952))

### 3.2.1 α- Ga$_2$O$_3$

The α-Ga$_2$O$_3$ has the same crystal structure of Al$_2$O$_3$ since Ga, and Al ion is similar and in the same group in the periodic table (Group IIIA) (Levin and Brandon 1998). It has a rhombohedral structure which is analogous to corundum structure (Chikoidze et al. 2016). The space group for this structure is $R\bar{3}c$ where experimentally calculated lattice parameters are $a=4.98$ Å and $c=13.43$ Å (Marezio and Remeika 1967). From the viewpoint of fabricating corundum-structured alloys for band gap engineering, α phase Ga$_2$O$_3$ is very appealing. The stabilization of the α-phase, which
crystallizes in the corundum structure (Figure 3.2), can be obtained by heteroepitaxy of thin films on Al₂O₃ (Daisuke and Shizuo 2008). In the corundum structure, the distance between Ga³⁺ ions are considerably shorter than in the monoclinic β-phase (Geller 1960). The oxygen ions are approximately hexagonal close packed and gallium ions occupy two-thirds of the octahedral sites. The band structure of α-Ga₂O₃ with rhombohedral (R̅3c space group) symmetry has been calculated by He et al. (He et al. 2006). It was shown that in comparison to β-type, α-Ga₂O₃ might have a higher band gap, refractive index, and reflectance but a lower effective mass of electrons. Since it has the highest band gap among all the Ga₂O₃ polymorphs, such large band gap draws the most attention to this polymorph for heterojunction of two crystals for photocatalytic applications (Ju et al. 2014). The key technology for the growth of is ultrasonic mist chemical vapor deposition (USCVD), which is a simple, safe, cost-effective and environmentally friendly growth method (Daisuke and Shizuo 2008, Chikoidze et al. 2016).

![Crystal structure of α-Ga₂O₃](image)

Figure 3.2: Crystal structure of α- Ga₂O₃ (Chikoidze et al. 2016)

### 3.2.2 β- Ga₂O₃

β- Ga₂O₃ is the most common and well-studied polymorph of gallium oxide. It has the base centered structure (Figure 3.3) and belongs to C2/m space group where experimentally calculated lattice parameters are: \(a=12.23\ \text{Å}, \ b=3.04\ \text{Å}, \ c=5.80\ \text{Å}\) and \(β=103.7^\circ\) (Geller 1960, Åhman,
Svensson, and Albertsson 1996). $\beta$-Ga$_2$O$_3$ has Ga ions coordinated in both tetrahedral and octahedral sites unlike the case with $\alpha$-Ga$_2$O$_3$ where Ga ions are only coordinated in an octahedral geometry. The coordination of Ga ions in the lattice has a significant impact on physical and electrical properties. $\beta$-Ga$_2$O$_3$ is the only polymorph of gallium oxide which is stable until its melting point while all other polymorphs are metastable and transform into $\beta$-Ga$_2$O$_3$ at temperatures above 750-900 °C (Lee, Akaiwa, and Fujita 2013). So, this polymorph can be obtained by baking any other polymorph of Ga$_2$O$_3$ in the air at a high temperature.

Figure 3.3: Crystal structure of $\beta$-Ga$_2$O$_3$

Due to crystalline anisotropy $\beta$-Ga$_2$O$_3$ is a poor thermal conductor. The thermal conductivity in $\beta$-Ga$_2$O$_3$ is very different along different crystal directions. The thermal conductivity is the highest along the [010] direction and lowest along the [100] direction at all temperatures used in the measurements (Shimamura et al. 2008). Thermal conductivity measured by laser flash methods is 13 W/mK along the [100] direction and 21 W/mK along the [010] direction (Villora et al. 2008, Galazka et al. 2014). $\beta$-Ga$_2$O$_3$ remains transparent well into the ultraviolet (UV) part of the spectrum, allowing its use as a transparent conducting oxide in this region (Kuramata et al. 2016, Galazka et al. 2017). These deep-UV photodetectors need to have a
cut-off wavelength of 280 nm for solar blindness. With a direct band gap of ~4.9 eV, $\beta$-Ga$_2$O$_3$ has a very high theoretical breakdown electric field (~8 MV/cm) (Higashiwaki et al. 2016, Armstrong et al. 2016, Kim et al. 2016), making it of interest for high power electronics (Ahn et al. 2016, Fujita 2015).

### 3.2.3 $\gamma$-Ga$_2$O$_3$

The research in $\gamma$-Ga$_2$O$_3$ almost nonexistent, so much less is known about $\gamma$-Ga$_2$O$_3$ because of its poor crystalline nature. However, it is widely accepted as it has the defect cubic spinel-type structure (MgAl$_2$O$_4$ type or simply AB$_2$O$_4$) with $Fd\bar{3}m$ space group (Zinkevich et al. 2004). The lattice parameters for this cubic structure is $a=8.23$ Å (Zinkevich et al. 2004). First principles calculations were made on primitive cells containing 6 tetrahedral cationic sites, 12 octahedral cationic sites, and 24 oxygen sites by introducing Ga-ion defects and found that 14 inequivalent configurations are possible (Yoshioka et al. 2007a). No clear preference of defect location (tetrahedral or octahedral sites) could be established (Yoshioka et al. 2007a).

![Figure 3.4: Crystal Structure of $\gamma$-Ga$_2$O$_3$ (Represented by MgAl$_2$O$_4$ structure (Tabaza, Swart, and Kroon 2014))](image)

### 3.2.4 $\delta$-Ga$_2$O$_3$

The $\delta$-Ga$_2$O$_3$ was first synthesized and described in 1952 by Roy et al. (Roy, Hill, and Osborn 1952). From the early studies of Roy et al. $\delta$-Ga$_2$O$_3$ is known as a body-centered cubic
crystal with $Ia\overline{3}$ space group (Roy, Hill, and Osborn 1952). The lattice parameter of this structure is $a = 10.0$ Å (Roy, Hill, and Osborn 1952), but more recently this value was updated as 9.402 Å (Yoshioka et al. 2007a). The crystal structure is analogous to bixbyite crystals such as In$_2$O$_3$ and Mn$_2$O$_3$ (Stepanov et al. 2016b).

Figure 3.4: Crystal Structure of δ- Ga$_2$O$_3$ (Represented by In$_2$O$_3$ structure (Wang, Tan, and Liu 2014))

### 3.2.5 ε-Ga$_2$O$_3$

The ε-Ga$_2$O$_3$ crystal structure is still not well understood. Roy et al. reported that a new phase of Ga$_2$O$_3$ could be obtained by heating δ-Ga$_2$O$_3$ above 500°C, which they designated as ε-Ga$_2$O$_3$ (Roy, Hill, and Osborn 1952). Also, ε-Al$_2$O$_3$ crystal structure is believed to be deposited when Sn-doped, highly conductive Ga$_2$O$_3$ films deposited by pulsed laser deposition (PLD) at temperatures above 475°C which had crystal structures similar to ε-Al$_2$O$_3$, and therefore suspected to be ε- Ga$_2$O$_3$ (Orita et al. 2002). If that is the case, the crystal structure of ε-Ga$_2$O$_3$ would be orthorhombic with $Pn\alpha_2\overline{1}$ space group. In 2007, Yoshioka et al. have calculated the lattice parameter for ε-Ga$_2$O$_3$ which has $a=5.12$ Å, $b=8.79$ Å, and $c=9.41$ Å (Yoshioka et al. 2007b).
3.3 GALLIUM OXIDE GROWTH AND DEPOSITION

Bulk crystals of Ga₂O₃ are synthesized by employing melt growth techniques. Whereas, a variety of techniques can synthesize gallium oxide crystals, films and nanostructures, including sputtering (Battu et al. 2017, Kumar et al. 2013, Manandhar and Ramana 2017b, Rubio et al. 2016, Chang et al. 2014) Battu et al. 2017), sol-gel (Minami 2003, Moos et al. 2011), laser ablation (Martin et al. 2009, Matsuzaki et al. 2006), chemical vapor deposition (Oshima et al. 2015, Dang et al. 2015, Kawaharamura, Dang, and Furuta 2012) and etc. Various methods can be employed to deposit the polycrystalline and single crystalline films of Ga₂O₃ on various substrates.

3.3.1 Melt growth

Melt growth is the most common and viable technology to produce single crystals of various materials. Melt growth method for Ga₂O₃ is the best method of for crystal growth regarding growth rate, scalability, and crystal quality(Stepanov et al. 2016b). Gallium oxide does melt congruently at about 1820 °C in an oxidizing environment, but it decomposes into volatile lower
oxides when heated under oxygen deficient atmosphere (Stepanov et al. 2016b). There are various methods for growing \( \text{Ga}_2\text{O}_3 \) using melt growth like

- Verneuil Method
- Floating Zone (FZ) Method (Ohira et al. 2008, Ueda et al. 1997)
- Czochralski (CZ) Method
- Edge-defined Film-fed Growth (EFG) Method
- Vertical Bridgman Method

### 3.3.2 Deposition

There are numbers of articles concerning the growth of gallium oxide thin films have been published so far. Fleischer and coworkers (Fleischer, Höllbauer, and Meixner 1994, Fleischer, Hanrieder, and Meixner 1990, Kumar et al. 2013) have produced stoichiometric \( \text{Ga}_2\text{O}_3 \) thin films with a high-frequency sputtering process using an ultrapure \( \text{Ga}_2\text{O}_3 \) ceramics target. Macri et al. (Macri et al. 1993) also used the same target when they studied the growth of films by reactive radio-frequency magnetron sputtering. Homogeneous \( \text{Ga}_2\text{O}_3 \) films have been deposited by electron-beam evaporation using a single-crystal high-purity \( \text{Gd}_3\text{Ga}_5\text{O}_{12} \) source (Passlack, Schubert, et al. 1995) which, however, introduces a few percents of gadolinium into the films, especially on the surface region (Passlack, Hong, et al. 1995). A spray pyrolysis process was used to grow stable \( \beta \)- \( \text{Ga}_2\text{O}_3 \) and \( \alpha \)- \( \text{Ga}_2\text{O}_3 \): \( \text{Co} \) (Kim and Kim 1987) thin films on glass substrates. Hariu et al. (Hariu et al. 1977) deposited gallium oxide by reactive vapor evaporation of gallium in an oxygen atmosphere. The use of chemical methods [chemical vapor deposition (CVD) and atomic layer epitaxy (ALE)] in the growth of gallium oxide thin films has also been reported (Lee et al. 2014, Shan et al. 2005, Valet and Hoffman 2001).

### 3.4 Metal-doped Gallium Oxide Thin Film

Doping in electronic oxides is always complicated by self-compensation, solubility, and defects issues (Nakai et al. 2015). There is also an asymmetry in that one conductivity (usually n-...
type) is favored over the other (Nakai et al. 2015). In Ga$_2$O$_3$, it is often observed that annealing in oxygen reduces the free electron density, while annealing in nitrogen or hydrogen leads to an increase in n-type conductivity (Kuramata et al. 2016, Galazka et al. 2014). N-type doping of β-Ga$_2$O$_3$ in both bulk crystals and epitaxial films have shown to produce controllable carrier concentrations from $10^{16}$ to $10^{19}$ cm$^{-3}$, with an upper limit near $10^{20}$ cm$^{-3}$. In MBE, the common dopants have been Sn and Ge (Ahmadi et al. 2017), while Si and Sn are the most common dopants in MOCVD (Stepanov et al. 2016a, Higashiwaki et al. 2016). In RF sputtering the dopants are W, Mo, and Ti and other various metals (Rubio et al. 2016, Rubio and Ramana 2013a, Battu et al. 2017, Manandhar and Ramana 2017a). Ion implantation using Si has also been used to enhance the conductivity of n-type layers for Ohmic contact formation in Ga$_2$O$_3$ (Sasaki et al. 2013, Higashiwaki et al. 2012). The choice of dopants appears to be merely a function of the availability of those dopants on the particular growth systems used and not due to the superiority of one n-type dopant over another.

3.5 APPLICATION OF β-GALLIUM OXIDE

3.5.1 Gas sensors using β-Ga$_2$O$_3$

Ga$_2$O$_3$-based gas sensors have been investigated in the literature. Oxygen sensors utilize the fact that the conductivity of β-Ga$_2$O$_3$ n-type polycrystalline films which is inversely proportional to the oxygen partial pressure in the surrounding ambient. At high temperatures β-Ga$_2$O$_3$ has an oxygen deficiency in the crystal lattice. This oxygen deficiency is in dynamic equilibrium process with surrounding atmosphere oxygen. The variations in the conductivity in the sensor are due to change in ionized oxygen vacancies concentration. Therefore, an increase in the concentration of reducing gases or a reduction in the proportion of oxygen in the environment in which the sensor is placed leads to an increasing number of conducting electrons and, hence, an increasing conductivity (Fleischer et al. 1997, Romanov et al. 2016). The linearity between the
sensor conductivity and the oxygen content is held for partial pressures above $10^{-10}$ Pa. For lower partial pressures conductivity decreases abruptly by several orders of magnitude. Fleischer and co-workers (Fleischer et al. 1997, Romanov et al. 2016) suggested that $\beta$-Ga$_2$O$_3$ undergoes a phase transition at very low oxygen pressures. However, they have not succeeded in identifying the new phase. At temperatures around 600 °C, the oxygen sensitivity of polycrystalline Ga$_2$O$_3$ diminishes significantly, and the films can instead be used to detect reducing gases such as hydrogen. As found by Fleischer and co-workers (Fleischer, Giber, and Meixner 1992), in the temperature range of 400-600 °C the conductance of these films depends reversibly on the partial pressure of hydrogen in the ambient atmosphere. The authors had concluded, that the H$_2$-induced changes in the electrical conductance of $\beta$-Ga$_2$O$_3$ result from reversible chemisorption of hydrogen on the whole surface grains of polycrystalline Ga$_2$O$_3$ with subsequent electron transfer from the adsorbed hydrogen to Ga$_2$O$_3$ (Romanov et al. 2016).

It should be noted that Ga$_2$O$_3$ sensor does respond towards reducing components like ethanol or propane which cannot be neglected while measuring the oxygen response even at high temperature of 800 °C (Moos et al. 2011). Additional catalytic or filter layers can suppress the cross-sensitivity to reducing components. For example, Ga$_2$O$_3$ sensors covered with nickel oxide have no response to methane at high temperatures (Romanov et al. 2016). Dense silicon dioxide coating decreases sensor response to all reducing gases except hydrogen.

Gas sensors based on polycrystalline Ga$_2$O$_3$ films are efficient only at elevated temperatures. At low temperatures, oxygen vacancies become frozen within the material. Although gas sensing can occur at these lower temperatures, it is limited to interactions at oxygen defect sites at the material surface. To overcome this limitation, it is desirable to dramatically increase the available surface area for sensor/analyte interaction. This can be accomplished through the use of nanomaterials. Arnold et al. (Arnold et al. 2009) demonstrated gas sensors based on Ga$_2$O$_3$ nanowires. The sensors had a rapid, reversible response at room temperature to acetone and methanol and a more limited response to some hydrocarbons such as toluene (Arnold et al. 2009).
Chapter 4: Materials and Methods

4.1 Materials

**Sputtering Targets:** Target materials for RF-sputter deposition were obtained from Plasmaterials and Kurt J. Lesker. The targets (99.99%) that were procured for this project are: (1) Ga$_2$O$_3$ and (2) Ti; nevertheless, a 99.95% Ti target was also employed to determine the modification caused to the chemical properties and sensor under different Ti concentration in Ga$_2$O$_3$ matrix. These targets were primarily used to test the key idea of the project. The dimensions of the target are the 2-inch diameter and 0.125-inch thickness. The targets are shown in Figure 4.1. For the case of Ga$_2$O$_3$, a 0.125-inch thick Cu backing plate is required to protect the target.

![Sputtering Targets](image)

**Figure 4.1: Sputtering Targets**

**Substrates:** Three different types of substrates were employed.

1. Quartz Glass: to evaluate optical characteristics of Ga$_2$O$_3$ based films;
2. Silicon (Si (100)): to facilitate characterization of film’s chemistry, thickness and perform the spectroscopic ellipsometric study; and
3. Quartz Glass (Figure 4.2) with integrated with Pt interdigital electrodes (200 nm thick with a distance of 10um between electrodes): to evaluate the sensor performance

![Image of actual electrode on quartz]

Figure 4.2: Actual electrode on quartz

4.2 Substrates Cleaning

Quartz glass and silicon wafers were employed for depositing the Ga$_2$O$_3$ based thin films. The quartz and silicon substrates were purchased from Chemglass Life Sciences and University Wafer Inc respectively. The dimensions of the quartz substrates were 1mm thick and 25x25 mm with both sides polished. These substrates were then cut into pieces using a glass cutter in order to obtain smaller size substrates with an average surface area of 1 cm$^2$. The small pieces cut from the wafer are used as the substrates on which the films will be deposited. The quartz substrates were cleaned by a bath of 99.9% ethanol for 15 minutes, in order to remove oxides and impurities on the surface of the substrate. P-type, Si (100) was employed; these wafers were cleaned with standard RCA cleaning procedure to remove organic, inorganic and metal particulate contaminants. The following steps were performed:

- SC1- Removal of insoluble organic contaminants using 5:1:1 H$_2$O/H$_2$O$_2$/NH$_4$OH mixture.
• SC2- Removal of ionic and heavy metal atomic components using a solution of 5:1:1 H₂O/H₂O₂/HCl solution
• Removal of native oxide by buffered oxide etches solution (HF/H₂O; 1:100).

The SC1 solution was prepared by heating 50 ml of Deionized water (DI) water to a temperature of 100 °C and then adding every 10 ml of NH₄OH and H₂O₂ to the DI water. The SC2 solution was prepared by 10 ml each of H₂O₂ and HCl to 50ml of water. The silicon substrates were soaked for 10 min in each solution and followed by 5 min of DI water rinse after each soak. Finally, the silicon substrates were treated with BOE to remove any native oxide on it (Louisville, n.d.).

4.3 **Radio Frequency (RF) Sputtering Deposition System**

RF Sputtering deposition is a process for depositing thin films where the energetic wave is running through an inert gas in a vacuum chamber. This energetic wave ionizes the inert gas. This causes the target material (Ga₂O₃ and Ti) or cathode to be bombarded with these high energy ions to sputter off atoms as fine spray covering the substrate. RF sputtering employs magnets behind the negative cathode to trap electrons. The negative cathode trap electrons over the negatively charged target material, so they are not free to bombard the substrate which allows faster deposition rates (Koenig and Maissel 1970).

In our system, the RF sputtering deposition system consists of a pair of electrodes, the two cathodes (Ga₂O₃ and Ti) that are located at the target side, and the anode where the substrate is placed. A target is made up of the material that will be used for thin film deposition onto substrates. The pair of electrodes is located inside the low-pressure vacuum chamber; the design of the vacuum chamber can change depending on the needs. The chamber is filled with the inert sputtering gas such as Argon (Ar). The gas plasma is struck using an RF power source, causing the gas to become ionized. The positively charged gas ions become attracted to the negatively biased target surface, which accelerates towards the surface of the target causing ion bombardment.
This causes atoms of the target material to break off from the target in vapor form. This vapor then condenses on all surfaces including on the substrate. Secondary electrons are also emitted from the target surface as a result of the ion bombardment. These electrons do not contribute significantly to sustaining the ejected atoms onto the substrate surface and are likely to cause unwanted heating, however if a magnetic field is applied parallel to the target surface, the secondary electrons circle the magnetic field lines and stay near the target ultimately increasing ionization efficiency (Jones and Clare 2012, Nalwa 2002).

After the samples were properly cleaned, they were introduced inside the vacuum chamber of the RF sputtering machine. The sputtering machine used is the Excel instruments Model DCSS-12. The samples were clipped on the sample holder that is 8 cm away from the plasma gun. The chamber was initially pumped down to a base pressure of ~0.21 mPa; however, the sputtering pressure was at ~0.5 Pa. The Ti and Ga₂O₃ targets was placed in a 8 cm sputtering gun. The sputtering gun was chilled by water with the help of Polyscience recirculation chiller. An initial sputtering power of 20 W was applied to the target via the sputtering gun while introducing high purity argon (Ar) into the vacuum chamber to ignite the plasma. Once plasma was ignited, the power was increased to 100 W at the Ga₂O₃ gun and to the respective variable power for Ti gun to deposit the films. The flow of the Ar was controlled using MKS mass flow meter with the values from 10-40 sccm (standard cubic centimeter per minute). Before each deposition, the both targets were pre-sputtered for 20 minutes using argon keeping the shutter above the substrate to prevent deposition on the substrate. The depositions were performed at 500 °C where the substrates were heated using the sample holder which contains an integrated hot plate, and the temperature was registered using a K-type thermocouple located within the sample holder/heater. Different composition of samples were deposited using this technique by varying target sputtering power in Ti target as table 1 presents the list of samples.
Table 3.1: List of samples and conditions of deposition

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Target Sputtering Power (W)</th>
<th>Temperature (°C)</th>
<th>Ar: O₂ Flow (sscm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTO-0</td>
<td>100</td>
<td>0</td>
<td>500</td>
</tr>
<tr>
<td>GTO-20</td>
<td>100</td>
<td>20</td>
<td>500</td>
</tr>
<tr>
<td>GTO-40</td>
<td>100</td>
<td>40</td>
<td>500</td>
</tr>
<tr>
<td>GTO-60</td>
<td>100</td>
<td>60</td>
<td>500</td>
</tr>
<tr>
<td>GTO-80</td>
<td>100</td>
<td>80</td>
<td>500</td>
</tr>
<tr>
<td>GTO-100</td>
<td>100</td>
<td>100</td>
<td>500</td>
</tr>
</tbody>
</table>

4.4 Analytical Tools

The analytical tools employed to characterize the physical and chemical properties of Ti-doped Ga₂O₃ films are Rutherford Backscattering Spectrometry (RBS), X-ray Photoelectron Spectroscopy (XPS), Spectroscopic Ellipsometer, Grazing Incidence X-ray Diffraction (GIXRD), UV-Vis Spectroscopy, Scanning Electron Microscopy (SEM), X-ray Absorption Near Edge Structure (XANES), Transmission Electron Microscopy (TEM) and Atom Probe Tomography (APT). These techniques allowed us to create the behavioral map needed to achieve this research goal and gather evidence of the effect of variation of Ti concentration on the properties and phenomena of Ga₂O₃ films.

4.4.1 Rutherford Backscattering Spectrometry (RBS)

The film composition was determined by Rutherford backscattering spectrometry (RBS) with 1.5 MeV He⁺ ions using ion accelerator (3 MeV NEC Tandem Ion Accelerator). The RBS system provides two stages of acceleration (negative ion acceleration from the source end to the terminal in the middle and positive ion acceleration from the middle to the high energy end.) The accelerated ions are then focused using magnetic quadrupole and y-axis electrostatic steerer. The helium gas was used as helium ion source which was a radio frequency (RF (alphatross) plasmas
which accelerated helium ions to the end stations. The analysis was performed using helium beam energy of 1500 KeV in an incident angle $\alpha=0^\circ$, the exit angle $\beta=20^\circ$, scattering angle of $\theta=160^\circ$ and detector resolution of 20 KeV. The backscattered helium ions were collected at the scattering angle of $160^\circ$ using a surface barrier detector. The schematic of the setup is depicted in Figure 4.3.

![Figure 4.3: RBS schematic diagram](image)

The RBS spectra were then theoretically fitted using SIMNRA simulation software (Mayer 1997, Mayer 1999). The fitting of the experimental curve with a simulated curve using SIMNRA code for a fixed set of experimental parameters: (1) incident He+ ion energy, (2) integrated charge, (3) energy resolution of the detector and (4) scattering geometry which yields the stoichiometry and thickness of the films. This software utilizes experimental parameters such as incident angle, scattering angle, incident ion energy, the solid angle of the detector, total charge deposited by incident beam and Rutherford backscattering cross section to calculate theoretical spectrum. The composition and film thickness are systematically varied to fit the experimental spectra best.

### 4.4.2 X-Ray Photoelectron Spectroscopy (XPS)

XPS was employed to evaluate surface chemistry and film stoichiometry. The XPS is a technique that uses x-ray inelastic scattering phenomena to quantify the chemical data. The high energy x-ray interacts with the surface atoms of the sample, causing the electron emission which is called the photoelectric effect. The emitted electron will have kinetic energy measured by
\[ KE = h\nu - BE - \Phi \]  

where KE is the kinetic energy of the electrons, \( h \) is Planck’s constant, \( \nu \) is frequency, \( BE \); binding energy and \( \Phi \) is the spectrometer work function (Alford, Feldman, and Mayer 2007). If the photon energy is less than work function, then no electron is emitted from the orbital. These emitted electrons carry a kinetic energy equal to the difference between a photon and binding energy. Since each element has unique sets of core level, kinetic energy can be sued to determine the concentration of elements in surface. Also the, variations in elemental binding energy or chemical shift is to determine the chemical state of the material. (Vemuri et al. 2010)

The XPS was performed using Kratos Axis Ultra DLD spectrometer using high-performance Al K\( \alpha \) monochromatic X-ray source (1486.6 eV) and a high-resolution hemispherical analyzer. The X-ray source for XPS was operated at 150 W, and emitted photoelectrons were collected normal to the sample surface. Data was acquired in a \( 700 \times 300 \ mu m^2 \) area with a pass energy of 20 eV, which produced a full width at half-maximum of 0.59 eV for the Ag 3d\(_{5/2}\) core level of a reference Ag surface. Charge neutralization was achieved with low-energy electrons (<2 eV). XPS data were analyzed by CasaXPS software using Gaussian/Lorentzian (GL(30)) line shape and Shirley background correction. The sample surfaces were cleaned using ultraviolet ozone cleaner for 5 min before loading in XPS chamber, but despite this treatment, samples were contaminated by carbon impurities due to exposure in air. Carbon contaminations can be easily removed by ion sputtering and high-temperature annealing\(^3\), but such treatments could significantly change the surface chemistry and crystallinity. The binding energy of carbon (C 1s) at 284.8eV was used as the charge reference. Survey scans were typically carried out at pass energies of 80 or 160 eV, while high-resolution scans were performed using pass energy of 20 eV. For the concentration of various elements present, i.e., Ga, Ti, and O, the error of estimation is \( \pm 0.01 \) at. %.
4.4.3 Spectroscopic Ellipsometry

The optical properties and surface/interface characteristics were probed by spectroscopic ellipsometry (SE). The ellipsometric angles $\Psi$ and $\Delta$ from 200 nm to 1600 nm wavelength were determined at 300 K in the air on a J. A. Woollam vertical variable-angle spectroscopic ellipsometer with computer controlled Berek wave plate compensator (J.A. Woollam Co, Lincoln, NE). The selected angles of incidence between 60°, 65°, and 70°. The ellipsometry data analysis for all samples was performed using commercially available WVASE32 software (Woollam 2005).

Optical constants of the Ti-doped Ga$_2$O$_3$ films were primarily probed by SE. It measures the relative changes in the amplitude and phase of the linearly polarized monochromatic light. The monochromatic incident light is then obliquely reflected from the surface of the sample. The experimental parameters obtained by ellipsometry are the angles $\Psi$ (azimuth) and $\Delta$ (phase change). These are related to the microstructure and optical properties, defined by (Jellison 1996, Fujiwara 2007, Ramana et al. 2008, Mudavakkat et al. 2012)

$$\rho = \frac{R_p}{R_s} = \tan \Psi \exp(i\Delta)$$

where $R_p$ and $R_s$ are the complex reflection coefficients of the light polarized parallel and perpendicular to the plane of incidence, respectively. The spectral dependencies of ellipsometric parameters $\Psi$ (azimuth) and $\Delta$ (phase change) can be best fitted with appropriate models. This model will help extract film thickness and the optical constants, i.e., the refractive index (n) and extinction coefficient (k) (Jellison 1996, Fujiwara 2007). In this case, the Levenberg-Marquardt regression algorithm was used for minimizing the mean-squared error (MSE): (Jellison 1996)

$$\text{MSE} = \frac{1}{2N-M}\sum_{i=1}^{n} \left[ \left( \frac{\psi_{exp} - \psi_{calc}}{\sigma_{\psi_i}} \right)^2 + \left( \frac{\Delta_{exp} - \Delta_{calc}}{\sigma_{\Delta_i}} \right)^2 \right]$$

(3)
where $\Psi_{\text{exp}}$, $\Psi_{\text{calc}}$, and $\Delta_{\text{exp}}$, $\Delta_{\text{calc}}$ are the measured (experimental) and calculated ellipsometry functions, $N$ is the number of measured $\Psi$, $\Delta$ pairs, $M$ is the number of fitted parameters in the optical model, and $\sigma$ are standard deviations of the experimental data points.

Extracting meaningful physical information from ellipsometry requires the construction of an optical model of the sample. The optical model generally accounts several different layers with distinct optical dispersions. Interfaces between these layers are optical boundaries at which light is refracted and reflected per the Fresnel relations. We constructed the stack model used to simulate the spectra purpose of determining the optical constants of Ti-doped Ga$_2$O$_3$ films where the model contains, from the top, Ti-doped Ga$_2$O$_3$ film, SiO$_2$ interface, and Si substrate. The surface and interface roughness were also considered to fit the experimental data accurately. The Cauchy dispersion model was used since the films are transparent in the visible region. The Cauchy equation can be expressed as a refractive index $n$ as a function of wavelength $\lambda$:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$ (4)

where $A$, $B$, and $C$ are the Cauchy coefficients and specific to the material. The $A$ is the constant that dominates $n(\lambda)$ for long wavelengths, and the $B$ controls the curvature of $n(\lambda)$ in the middle of the visible spectrum, and $C$ influences the $n(\lambda)$ to the greater extent in shorter wavelength. Also, the principle behind Cauchy’s model is also used for the dispersion function $k(\lambda)$:

$$k(\lambda) = d + \frac{e}{\lambda^2} + \frac{f}{\lambda^4}$$ (5)

where $d$, $e$, and $f$ are constants for a specific material (Mudavakkat et al. 2012, Vargas, Murphy, and Ramana 2014a, Tan et al. 2010). The determination of the optical constants, $n$, and $k$, as well as thickness verification, are enabled by the model.
4.4.4 Grazing Incidence X-Ray Diffraction (GIXRD)

GIXRD is a technique of performing X-ray diffraction for thin films where there is not much material for a good single. The X-ray source is stationed at grazing incidence to pass x-ray through much of the material. It uses the same principles of traditional XRD where a monochromatic x-ray is emitted and directed towards the material where atoms cause the x-ray to diffract. The scattered x-ray will undergo constructive or destructive interferences based on the crystal structure. The diffracted X-ray is collected by the detector at various angles which should satisfy Bragg’s law (shown below) to identify the phase, unit cells.

\[ n\lambda = 2d\sin\theta \]  

(6)

where \( n \) is the integer, \( \lambda \) is the x-ray wavelength, \( d \) is the interplanar distance and \( \theta \) is the Bragg’s angle. Figure 4.4 shows the graphic representation of X-ray and crystalline material interaction.

![Schematic diagram of X-ray and crystalline material interaction](image.png)

Figure 4.4: Schematic diagram of X-ray and crystalline material interaction

The measurements on Ga\(_2\)O\(_3\) films grown on Si were performed using a Bruker D8 Advance X-ray diffractometer. All of the measurements were made ex-situ as a function of Ti content in Ga\(_2\)O\(_3\) thin films. GIXRD patterns for Ti-doped Ga\(_2\)O\(_3\) films were recorded using Cu K\(\alpha\) radiation (\(\lambda=1.54056\ \text{Å}\)) at room temperature. The GIXRD patterns were recorded with the X-
ray beam fixed at a grazing incidence of 1°. The scanning was performed in a 2θ range of 10–67° using the “detector scan” mode, where the detector was independently moved in the plane of incidence to collect the diffraction pattern. The step size and the scan speed were 0.01° (2θ) and 2°/min, respectively. For these set of conditions, the X-ray beam passes sufficiently long distances through the coating to provide the observed diffraction patterns. The data were acquired and analyzed using EVA software in order to compare the XRD peaks and check for the crystal structure and lattice parameters. The XRD measurements were performed systematically after every step of the characterization procedure, i.e., deposition, heat treatment, and long-term stability test.

4.4.5 UV-Vis Spectroscopy

The optical properties of Ga$_2$O$_3$ films were evaluated using spectrophotometry measurements employing a Cary 5000 UV–vis–NIR double-beam spectrophotometer. The transmittance and reflectivity of the film were recorded. Films grown on optical grade quartz substrate were employed for optical property measurements. The quartz substrates employed to extend the transparency range down to ~190 nm and determined the absorption edge extending into the ultraviolet (UV) region, which is more than sufficient to determine the band gap shift in deficient or stoichiometric or metal incorporated Ga$_2$O$_3$ films. The measurements were done in the range of 175-3300 nm wavelength using deuterium emitter for UV region and a halogen lamp for visible region. The transmittance and reflectance values allow calculating the band gap of the films. The measurements were made using the film grown on quartz under a sampling beam while keeping the bare quartz substrate under the reference beam.

The absorption coefficient ($\alpha$) is determined using the thickness ($t$) of the film and value of the transmittance spectra ($T$) using the following formula

$$\alpha = -\frac{\ln T}{t}$$  \hspace{1cm} (7)
Then we can calculate the photon energy (hν) by using the wavelength (λ) in the next equation:

\[ h\nu = \frac{1240}{\lambda} \]  

(8)

The band gap value is calculating by using the following equation (Orita et al. 2000b, Rebien et al. 2002, Sinha, Adhikary, and Chaudhuri 2005)

\[(a h\nu) = B (h\nu-E_g)^{1/2}\]  

(9)

where \(h\nu\) is the energy of the incident photon, \(a\) is the absorption coefficient, \(B\) is the absorption edge width parameter, and \(E_g\) is the band gap. The optical absorption coefficient, \(a\), of the films is evaluated using the standard relationship, taking the film thickness into account.

4.4.6 Scanning Electron Microscopy (SEM)

Scanning electron microscope is a technique that employs a very focused beam of electron to reveal the features on the samples. The high energy electrons are emitted from an electron gun, which are focused towards the specimen to scan the surface. The image is created by a rastering process where the beam illuminate one point at the time (Microscopy 2013). The samples were mounted on top of a small circular stage of 1-inch diameter with double sided carbon tape to avoid any charging and assist in electron flow easier. The SEM provided detailed images at various magnifications of the samples, with the intention of providing a better image of the grain size, as well as the morphology of the thin films. The electron incident current and voltage was varied depending on the samples to obtain the best resolution image. After the image is saved, it is was analyzed using Image J software (Abràmoff, Magalhães, and Ram 2004), which allows you to measure the grain size of the films. SEM was performed using a Hitachi S-4800 electron microscope. SEM was performed on samples grown on Si wafers. The samples were pasted on the SEM stub using silver paint and coated with 10nm of carbon to avoid charging during imaging.

4.4.7 X-ray Absorption Near Edge Structure (XANES)

X-rays are ionizing electromagnetic radiation which has sufficient energy to excite a core electron of an atom to an empty below the ionization threshold called an excitonic state which is
above the ionization threshold. As shown below in figure 4.5, different core electrons have distinct binding energies; consequently, if one plots the X-ray absorbance of a specific element as a function of energy (Weng, Waldo, and Penner-Hahn 2005). The XANES experiments were carried out at beamline 6.3.1 of Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). Beamline 6.3.1 utilizes a variable line space (VLS) monochromator on a bend magnet source to provide photons with energies from 100 to 2200 eV into a multi-purpose end-station that is like the end-station on Beamline 6.3.2(Underwood and Gullikson 1998). Reference Ti L-edge, Mg K-edge, and O K-edge spectra were also collected from TiO$_2$ and MgO standards for calibration for different gratings used. Spectra were collected at room temperature in the total electron yield (TEY) mode with the signal obtained from the sample drain current. No substantial charging problems were detected. Ga L-edge, O K-edge, and Ti L-edge were collected for all samples.

Figure 4.5: Schematic of X-ray absorption spectrum
4.4.8 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a technique that employs a very high energy focused beam of electron from tungsten filament. The whole optical system of the microscope is enclosed in high vacuum. High vacuum must be maintained in the column so that the collision of electrons with air molecules and hence the scattering of electrons are avoided. The magnetic coils are placed in the columns to focus the electron beam on the sample. These magnetic coils placed at specific intervals in the column acts as an electromagnetic condenser lens system for the TEM. The samples from FIB lift out process and thinned out placed in the vacuum on the path of the electron beam. The electron beams pass through the specimen and scattered by the crystalline structures. The beam of electron that has been partially transmitted through the very thin part of the samples will carry insight about the structure of the sample. The spatial variation in this information is then magnified by a series of magnetic lenses until it is recorded by hitting a fluorescent screen, photographic plate, or light sensitive sensor like CCD (charge-coupled device) camera. The image detected by the CCD may be displayed in real time on a monitor or computer. TEM was done using 200kV electron beam source at FEI Tecnai F20 TEM.

4.4.9 Atom Probe Tomography (APT)

APT samples were prepared using the FEI Quanta dual beam FIB. The APT specimen preparation method by site-specific FIB lift-out and annular milling. (Thompson et al. 2007) A CAMECA LEAP 4000XHR system equipped with pulsed UV laser (355 nm wavelength) was employed perform APT experiments. The laser pulse energy of 40pJ at the 100kHz frequency with specimen temperature of 40 K was used for experiments. The APT results were reconstructed and analyzed using Interactive Visualization and Analysis Software (IVAS) 3.6.8 using standard reconstruction procedure. (Larson et al. 2013)

4.5 Thermal Stability

The long thermal stability of Ti-doped Ga$_2$O$_3$ films was studied to observe the changes in material chemistry when exposed to the extreme environment. Since the gas sensor was tested at
700 °C, the thermal studies were also done at 700 °C. The films were introduced to CM Rapid Temperature Furnace at 700 °C for 4 hours in the air. The heating rate was kept constant at 10 °C/minute. The films were then analyzed for structural and composition variation and compared to observe any significant changes in the material properties and chemistry.

4.6 HIGH-TEMPERATURE OXYGEN SENSOR PERFORMANCE

The oxygen sensing characteristics of the materials were evaluated using the quartz glass substrate with interdigital electrodes deposited on the surface, and the films deposited on top of electrodes. The electrodes were attached to two wires using high temperature silver paste (Ted Pella) and cured it for two hours. The sensor performance was evaluated at a temperature of 700 °C; the electrical measurements were recorded using Keithley 6514 electrometer, and the input current (10nA) was supplied via a Keithley 220 Programmable Current Source. Since the principle behind the sensor is change in resistivity at different partial pressure, Ohm’s Law was employed as follows

\[ V = IR \] (10)

where V is voltage, I is input current, and R is the resistance of the film. But resistivity was calculated using:

\[ \rho = \frac{R A}{l} \] (11)

where \( \rho \) is the resistivity, A is the cross-sectional area of electrodes, and l is the distance between interdigital electrodes. Also conductivity can be calculated using equation below

\[ \sigma = \frac{1}{\rho} \] (12)

So to control different partial pressure two gas tanks were employed for this investigation, a 99.99% Ar as the baseline gas, and a 99.99% O₂ as the analyte gas; both gasses were controlled using an MKS mass flow controller to achieve different partial pressures of oxygen. All the sensor performance responses were recorded as a function of Ti sputtering power and Ti concentration and feature such sensitivity and time response are presented. The films were evaluated regarding initial sensitivity and response time. They were tested under the different partial pressure of oxygen
(8, 12, 23, 31 and 40 Pa of pO$_2$) in cyclic periods of pure Ar flow for a constant time followed by Ar/O$_2$ flow for the same period. The schematic of the testing is shown below in Figure 4.6.

Figure 4.6: Schematic for oxygen sensing setup
Chapter 5: Synthesis and Structural Characterization

Gallium oxide (Ga$_2$O$_3$) has received the attention of the scientific and research community in recent years. Ga$_2$O$_3$ has found a wide range of applications in various fields, viz., electronics and photonics (Tomm et al. 2001, Ramachandran, Dendooven, Botterman, Sree, et al. 2014), gas sensing (Baban, Toyoda, and Ogita 2005a, Bartic et al. 2007b), deep ultraviolet (UV) photodetectors (Orita et al. 2000b, Zhang, Ou, Tang, Sivan, Yao, Latham, Khoshmanesh, Mitchell, O'Mullane, and Kalantar-zadeh 2014), and spintronics (Hayashi et al. 2006, Guo, Wu, et al. 2015). Excellent, deep transparency in the UV region of the electromagnetic spectrum coupled with a wide band gap ($E_g$~5 eV) makes Ga$_2$O$_3$ a perfect candidate for transparent electrodes in UV-based photovoltaics (Zhang et al. 2011), optoelectronics (Guo, Wu, et al. 2015), (Zhang et al. 2011, Xu et al. 2015b, López et al. 2013, Rubio and Ramana 2013b) and luminescent displays (López et al. 2013).

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Innovative approaches to tailor the functionality and/or promising future applications in emerging technologies are driving the current significant interest in single-phase Ga$_2$O$_3$ as well as Ga$_2$O$_3$-based multi-component architectures or hybrid materials with nanostructured morphologies (Ramachandran, Dendooven, Botterman, Pulinthanathu Sree, et al. 2014, Bartic et al. 2007a, López et al. 2013, Rubio and Ramana 2013b, Patil et al. 2015a, Shimura and Yoshida 2012, Oleksak, Stickle, and Herman 2015, An et al. 2016, Feng et al. 2014, Kumar et al. 2013). For instance, the enhanced performance of Ga$_2$O$_3$-graphene oxide hybrid nanomaterials suggests the possibility to design new electrode materials for lithium ion batteries (Patil et al. 2015b). Similarly, excellent luminescence has been demonstrated in Sn- or Cr-doped Ga$_2$O$_3$ nanowires, which may have applications in luminescent display devices (López et al. 2013). Solution-processed Ga$_2$O$_3$ dielectrics and In$_2$O$_3$/Ga$_2$O$_3$ hybrid structures in thin-film transistors with the desired mobilities and negligible hysteresis are expected to open new possibilities for the development of low-cost and large-area green electronics (Oleksak, Stickle, and Herman 2015, Xu et al. 2015a). Enhanced photocatalytic activity reported for metal-incorporated Ga$_2$O$_3$ or metal/Ga$_2$O$_3$ hybrid materials can offer ways to improve the efficiency in energy-harvesting devices (Shimura and Yoshida 2012, Zhang, Ou, Tang, Sivan, Yao, Latham, Khoshmanesh, Mitchell, O'Mullane, and Kalantar-zadeh 2014). Doping metal ions, such as Ni, Zn, and Pb, into Ga$_2$O$_3$ has been reported to enhance the photocatalytic activity (Shimura and Yoshida 2012, Zhang, Ou, Tang, Sivan, Yao, Latham, Khoshmanesh, Mitchell, O'Mullane, and Kalantar-zadeh 2014, Wang et al. 2013, Sakata et al. 2008, Zhang et al. 2015). However, while evolving new functionalities and emerging applications involving Ga$_2$O$_3$ nanomaterials or hybrid structures are promising, control over the surface/interface chemistry, phase, and composition is the key to tailor the materials’ performance to meet the requirements of a given application or to search for a new technological application. The interplay between the nano/micro-structure, composition, and optical/electronic properties of Ga$_2$O$_3$-based materials is thus quite important, especially for optical, optoelectronic, electrical, and photo-catalytic-based energy-related applications.
Intrinsic $\beta$-Ga$_2$O$_3$ is a wide-band gap insulating oxide, but it can be changed to an n-type semiconductor by selective doping. However, while the mechanism of n-type conduction in $\beta$-Ga$_2$O$_3$ appears to be mostly by the generation of electrons from oxygen vacancy ionization, the overall electrical conductivity of the resulting materials after doping is still under debate (Yamaga et al. 2003, Varley et al. 2010). Doping with carefully chosen metal ions can significantly alter the properties $\beta$-Ga$_2$O$_3$, making it suitable for technological applications. From an optical properties point of view, doping of $\beta$-Ga$_2$O$_3$ with Sn, Cr, Cu, or W has been reported to induce changes in the optical absorption and band gap (López et al. 2013, Rubio and Ramana 2013b, Zhang et al. 2011). In the present work, we report on the direct, functional relationship between the structural and optical properties of titanium (Ti)-incorporated Ga$_2$O$_3$, where tailor-made materials for optical and photo-catalytic applications are readily possible. While reports existing in this direction are meager, Ti incorporation into Ga$_2$O$_3$ for the design and development of novel functional materials is interesting for the following reasons. Similar to Ga$_2$O$_3$, TiO$_2$ finds application in solar cells\(^{24}\), photo-catalysis (Dakhel 2013, Nazeeruddin, Baranoff, and Grätzel 2011, van de Krol, Liang, and Schoonman 2008), and integrated sensors (Gong et al. 2010, Wang et al. 2014). Therefore, materials designed by doping Ti into Ga$_2$O$_3$ are expected to offer unique properties and phenomena useful for photo-catalytic applications. Furthermore, the very limited efforts on the Ti-Ga-O solid solution system report that Ti ions can be incorporated into Ga$_2$O$_3$ to a large amount (~10.4%) without affecting the crystal structure, which is quite controversial from fundamental perspective of solid state materials and the rule of mixtures to derive solid solutions (Dakhel 2013). As such, an attempt is made in this work to understand the Ti-induced structural effects in Ga$_2$O$_3$ nanocrystalline films and their implications on the properties and performance. Interestingly, contrary to other metal ions, we demonstrate a Ti-induced red-shift in $E_g$ and tuning of the index of refraction of Ga$_2$O$_3$. 

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\(^{24}\) Note: This citation is not properly formatted. It should be formatted as a full reference within the text. For example, (Dakhel 2013).
5.1. CRYSTAL STRUCTURE (GIXRD)

X-ray diffraction patterns of GTO films are shown in Fig. 5.1 as a function of applied sputtering power to the Ti target. For comparison, the XRD curve of pure intrinsic Ga2O3 nc-films is also included. The GIXRD pattern of intrinsic Ga2O3 corresponds to the monoclinic β-phase (space group C2/m) with peaks (-201), (400), (002) (111), (510), and (-204) corresponding to 2θ values of 18.95, 30.05, 31.74, 35.17, 48.59, and 64.17, respectively (Geller 1960), according of JCPDS (00-043-1012). Note that β-Ga2O3 is also found as a layered structure in hydrated phases (Kalantar-zadeh et al. 2016), Battu et al. 2018). The evolution of these peaks shows an interesting trend as a function of Ti incorporation into Ga2O3 nc-films. The first characteristic feature that can be noted is the dominance of the (400) peak at 2θ=30.05° for intrinsic Ga2O3 nc-films. The intensity of this peak is seen to increase with Ti incorporation up to 1.5 at%. Coupled with the (400) peak, there is a corresponding slight increase in intensity for the (111) peak. However, changes in the (111) peak are minor compared with the (400) peak. Further increasing the sputtering power to the Ti target beyond 60 W, i.e., Ti content higher than 1.5 at%, seems to introduce structural changes in Ga2O3, as is evident from the GIXRD patterns. Clearly, Ti incorporation causes the (111) peak to grow in intensity while suppressing the intensity of the (400) peak. Finally, the (400) and (111) peaks become broader and merge for samples deposited with the highest, equal sputtering powers (100 W) to Ga2O3 and Ti targets. This observation indicates the size reduction as well as a secondary phase formation, i.e., TiO2 in the matrix of Ga2O3. In other words, instead of single-phase β-Ga2O3, higher Ti content (beyond 1.5 at%) induces the formation of Ga2O3-TiO2 mixed or composite oxide films. The grain size calculated using XRD data was found to be ~12 nm for intrinsic Ga2O3 films, while Ti incorporation slightly decreased the grain size to ~9 nm.
Figure 5.1: GIXRD pattern of GTO nc-films produced under variable Ti sputtering power. Structural evolution as a function of Ti content is evident.
5.2. Rutherford Backscattering Spectrometry (RBS)

The Rutherford backscattering (RBS) spectra of GTO films are shown in Fig. 5.2. The backscattered ions observed were due to various elements, and the positions are indicated by arrows for the experimental spectrum. The scattering from Ga, the heaviest among the elements present either in the film or substrate, occurs at higher backscattered energy (~1140 keV) as shown in RBS curves for intrinsic and GTO films (Fig. 5.2). The RBS data of GTO films i.e., without any sputtering power to Ti target, shows that there is no backscattered ions due to Ti. The evolution of Ti peak (~1030 keV) is clearly seen in the RBS spectra as the sputtering power to the Ti-target is increased. The measured height and width of the Ti or Ga peaks are related to the concentration and thickness distribution of Ti or Ga atoms in the oxide film and the parameters serve as a calibration check for composition and thickness since known Rutherford scattering cross section and experimental parameters can be used to calculate this height and width. As indicated in Fig. 6.1, the step edge and peaks due to ion backscattering from Si (substrate) and O atoms (film) are observed at ~810 and 270 keV, respectively. The composition and thickness of the films were determined by simulating the experimental spectrum for the set of experimental conditions. The procedure utilized to derive the chemical composition of the grown films is represented for all the samples (Fig. 5.2). The experimental curve (circles) along with the simulation curve (lines) calculated using SIMNRA code are as shown in Fig. 5.2. The simulated curve was calculated using SIMNRA code for the fixed set of experimental parameters: (1) incident He$^+$ ion energy, (2) integrated charge, (3) energy resolution of the detector, and (4) scattering geometry. It can be seen in Fig. 1 that the simulated curves (solid line) calculated using the experimental parameters are in good agreement with the experimental RBS spectra. This observation indicates that film composition is reasonably simulate the spectra and, hence, provides the estimation of film composition. For intrinsic Ga$_2$O$_3$ films i.e., without any Ti, the RBS data indicate that the stoichiometry of the samples is correspondent or close to the concentration of Ga:40 at% and O:60 at% leading to O/Ga ratio of 1.5, which are expected theoretically. These results are in good agreement with our previous reports on intrinsic Ga$_2$O$_3$ films, where a deposition temperature of
300 °C or higher is needed to obtain nearly stoichiometric Ga$_2$O$_3$ films. (Kumar et al. 2013) The Ti content estimated from RBS data is shown in Fig. 5.3. For clarity purposes, the evolution of Ti peak with sputtering power is presented in the inset of Fig. 5.3. Increasing Ti-content from 0 to ~5 at% is evident with increasing sputtering power from 0 to 100 W.

![RBS data of Ga-Ti-O films deposited with variable Ti-content](image)

Figure 5.2: RBS data of Ga-Ti-O films deposited with variable Ti-content. The data shown are for: (a) intrinsic Ga$_2$O$_3$; (b) GTO-60; (c) GTO-80; and (d) GTO-100. Data shown include experimental curves (circles) and SIMRA simulated curves (lines). The backscattered ions due to Ga, Ti, Si, and O and their respective energy positions are as indicated. A reasonable agreement between the experimental and simulated RBS curves can be seen.
Figure 5.3: The Ti concentration with sputtering power. It is evident that the Ti-content increases from 0 to ~5 at% with increasing sputtering power from 0 to 100 W.

5.3. X-ray Photoelectron Spectroscopy (XPS)

The surface concentration of dopants (Ti) and chemical valence states of elements present is desired for Ga-Ti-O films since many of the practical applications are driven by surface reactive processes. The XPS measurements also allowed us to determine the atomic percentage of Ti as well as the chemical valence states of the constituent ions present in the GTO samples. The XPS survey spectra of representative GTO films are collected before collecting high resolution scan of each elements. The XPS survey spectra show Ga, Ti and O are the main constituents of the deposited films. To determine the chemical states of the metal ions, present in the films, detailed analysis of the core level spectra of the main constituents was performed. The high-resolution
scans of Ga 3d, Ti 2p, and O 1s were recorded and analyzed to obtain their chemical states and the interaction between respective metal ions and oxygen. XPS spectra for Ga 3d and O 1s in intrinsic Ga$_2$O$_3$ nanostructures obtained with the same procedure as Ti-doped Ga$_2$O$_3$. The core-level XPS spectra of the Ga 3d region are shown in Fig. 5.4a. The data shown are for samples with a variable Ti-content. The Ga 3d peak for GTO-0 is located at a binding energy (BE) of $\sim$20.5 eV which agrees to the literature (Ghosh et al. 2007). The National Institute of Standards and Technology (NIST) database also gives the value of 20.4 ± 0.5 eV for Ga 3d$_{5/2}$ in Ga$_2$O$_3$ (Naumkin et al. 2012).

The high-resolution core-level XPS spectra of O 1s from different GTO samples are presented in Fig. 5.4b. The data shown are as a function of variable Ti-sputtering power. The peak position for pure Ga$_2$O$_3$ is located at BE $\sim$530.8 eV, which is consistent with values reported in the literature (Hollinger, Skheyta-Kabbani, and Gendry 1994, Syed et al. 2017). This BE is usually assigned to oxide (i.e., Ga-O-Ga bonds) which corresponds to the position of O 1s for Ga$_2$O$_3$ when gallium is present in its highest chemical valence state (Ga$^{3+}$)(Ramana et al. 2014, Trinchi et al. 2004, Ou et al. 2012). The shoulder of O 1s peak at higher energy is usually associated with oxygen bonded to carbon (labeled as CO$_2$). A slight shift in O 1s peak is observed with increasing Ti content in GTO film due to increasing amount of titanium bonded to oxygen. The peak at 530.3 eV of BE relates to Ti$_2$O$_3$ (Bharti et al. 2016, Xu et al. 2008, Hussain et al. 2016). Thus, Ti occupies gallium sites in gallium oxide structure. O 1s core characteristics of both Ga$_2$O$_3$ and Ti$_2$O$_3$ appear in XPS spectra, as both elements can participate in bonding in the same charge.

The high-resolution core-level spectra of Ti 2p are presented in Fig. 5.4c. Ti 2p$_{3/2}$ spectral fitting parameter from NIST database (Naumkin et al. 2012) and numerous literature assign binding energy of 458.6 eV and 457.13 eV to Ti$^{4+}$ (TiO$_2$) and Ti$^{3+}$(Ti$_2$O$_3$) (González-Elipe et al. 1989, Massaro et al. 2002, Tao, Luttrel, and Batzill 2011). Ti$^{4+}$ do not have unpaired d electrons and does not exhibit multiplet splitting, but Ti$^{3+}$ have unpaired d electrons and theoretically exhibit multiplet structure which may not be well resolved as found in XPS literature (Gupta and Sen 1975). As shown in XANES results, Ti 2p peak shows steady increase in TiO$_2$ phase with addition of Ti by increasing sputtering power while Ti$_2$O$_3$ peak stays consistent after GTO60. Also the
atomic concentration of titanium was calculated from the XPS spectral intensity of Ti 2p (Fig. 5.4c), and steady increase in Ti concentration up to 5 at%, which matches the bulk concentration calculated using Rutherford backscattering spectroscopy (RBS) (Manandhar and Ramana 2017a).

Figure 5.4: High-resolution XPS data of Ga, O, and Ti core level peaks in GTO films deposited with variable Ti-concentration. a, Ga 3d high-resolution XPS spectra. b, O 1s high-resolution XPS spectra. c, Ti 2p core-level XPS spectra.

5.4. SURFACE MORPHOLOGY – ATOMIC FORCE MICROSCOPY (AFM)

The AFM data of GTO films are shown in Fig. 5.5. The topographic images along with the corresponding 3D surface images are shown. For GTO-0 films i.e., without Ti, nano-particulate morphology the film surfaces, where the conically shaped grains are distributed uniformly all over the film surface, is evident. The root-mean-square surface roughness value noted for intrinsic Ga₂O₃ films was ~1 nm. The AFM results of intrinsic Ga₂O₃ films are in excellent agreement with those reported in the literature (Leedy et al. 2017, Ramana et al. 2014). The remarkable effect of
Ti incorporation on the surface morphology of Ga$_2$O$_3$ films is evident in the AFM data of samples deposited with increasing sputtering power of Ti from 40 to 100 W.
Figure 5.5: AFM surface morphology for GTO films. Topographical 2D images (left column) and the corresponding 3D surface images (right column) are shown. All the images are obtained at 500 nm x 500 nm.

However, one important observation made is, while the effect is not pronounced in the beginning, the effect of Ti is reflected in terms of size reduction and making film surfaces smoother as evident in the AFM data. The effect is more visible for GTO-100 samples, which are deposited with the highest sputtering power to the Ti target. Thus, the Ti content in Ga2O3 films retains the well resolved uniform morphology and densely packed grains and grain boundaries until 1 at%, at which point changes become significant. Such changes in surface morphology was also evident in W-doped Ga2O3 films. In addition, Ti incorporation induced disordering and surface amorphization was reported in Ti-doped WO3 films (Ramana et al. 2013, Kalidindi, Manciu, and Ramana 2011).

5.5. TRANSMISSION ELECTRON MICROSCOPY (TEM)

The TEM data of intrinsic Ga2O3 (GTO-0) films are presented in Figure 5.6. TEM image of a thin cross-section lamellae from GTO-0 film is shown in Fig. 5.6a, where crosssection of the Ga2O3 film sample highlights the apparent interfaces between the Si substrate, the Ga2O3 film, and the C/Pt protective layers. It is evident that the microstructure the Ga2O3 films is uniform. The interface microstructure characterizes the dense, columnar structure vertically while some degree of surface roughness (the waviness) exists along the horizontal direction. The later may be due to disorder on the surface of the film while the observed interface structure is a characteristic feature of samples made by sputter-deposition and thermodynamic conditions employed for sample fabrication. The selected area electron diffraction (SAED) patterns of GTO samples are shown in Fig. 5.6b. It is evident that the SAED pattern exhibits a ring made up of bright spots that indicate that the films were composed of randomly oriented nano-crystalline Ga2O3 (Egerton 2005). The pattern was successfully indexed with ICDD PDF4+ database software and they match with the
simulated diffraction patterns of Ga$_2$O$_3$. Thus, together with GIXRD analyses, the SAED analyses confirm the formation of nanocrystalline Ga$_2$O$_3$ films.

![TEM image of intrinsic Ga$_2$O$_3$ films](image1)

![SAED pattern of Ga$_2$O$_3$ films](image2)

Figure 5.6: TEM data of intrinsic Ga$_2$O$_3$ films. (a) TEM image of a thin cross-section lamellae from GTO-0 film; (b) SAED pattern of Ga$_2$O$_3$ films. The presence of rings made up of bright spots indicate that the films were composed of randomly oriented nanocrystalline Ga$_2$O$_3$.

The TEM data of Ti doped Ga$_2$O$_3$ films are shown in Fig. 5.7. TEM images of a thin cross-section lamellae from GTO films are shown along with their respective SAED patterns. The cross-section lamella from all the GTO films exhibit the interface microstructure similar to intrinsic Ga$_2$O$_3$ films. This observation indicates that the Ti incorporation retain the characteristic columnar growth and dense interface microstructure of the Ga$_2$O$_3$ films. However, the effect of Ti doping is visible in SAED patterns, which could not be successfully indexed to single phase Ga$_2$O$_3$ films as discussed for GTO-0 films. Instead, formation of Ga$_2$O$_3$-TiO$_2$ composite occurs with increasing Ti content. While the changes not significant or visible in electron diffraction for GTO-40, the SAED patterns indexed with a high confidence to Ga$_2$O$_3$-TiO$_2$ composite for the samples GTO-60 to GTO-100. The TEM results corroborate with the XPS data, where the formation of Ga$_2$O$_3$-TiO$_2$
composite films with a presence of increasing Ti$^{4+}$ ions with increasing sputtering power to the Ti target was evident.

Figure 5.7: TEM data of GTO films. The TEM images of a thin cross-section lamellae from GTO films as a function of increasing Ti content are shown (top panel). The corresponding SAED patterns of GTO films are also presented (bottom panel). Emergence of complex ring pattern, compared to intrinsic Ga$_2$O$_3$, is evident in Ti-doped Ga$_2$O$_3$.

5.6. SURFACE AND INTERFACE CHEMISTRY

To probe the chemical changes and better understand the dopant Ti chemistry in β-Ga$_2$O$_3$ and identify the TiO$_2$ phase which was inconclusive in TEM, X-ray Absorption Near Edge Structure (XANES) was employed. In XANES, the fine structure observed above the edge, so-called white line, reflects the local site symmetry around the X-ray absorbing atom, the analysis of this region is for the fingerprint of the elements. It is well known that β-Ga$_2$O$_3$ has a spinel structure, containing Ga atoms in both tetrahedral and octahedral sites(Geller 1960, Shimizu et al. 1996). The Ga L-edge spectra shown in Fig. 5.8a is due to excitation of electrons in the 2p$_{3/2}$ orbital
of Ga, leading to sharp increase in absorption of Ga-containing materials at 1116.4 eV (Calvin 2013). However, the edge for Ga in Ga$_2$O$_3$ is shifted to 1120 eV due to valence dependency which causes edges to shift (Agarwal and Verma 1970). Therefore, the first peak labeled A (or edge) in Ga L edge spectrum is assigned to Ga atoms in octahedral sites while subsequent peak labeled B is assigned to Ga in tetrahedral sites (Shimizu et al. 1996). As the Ti concentration is steadily increased the signature peak of tetrahedral Ga atoms is diminished, which is presumably due to the replacement of Ga atoms in tetrahedral sites by Ti atoms.

In Fig. 5.8b, O K-edge spectra of GTO samples is shown along with the TiO$_2$ standard. The O K-edge spectra for TiO$_2$ standard matches signature features of anatase (Wu et al. 1997) which confirms the TiO$_2$ phase. In anatase (TiO$_2$ standard), first two peaks at low energy (I and II) is due to dipole transitions to band states of t$_{2g}$-e$_g$ symmetry separated by the “ligand-field splitting” of O 2p states hybridized with the Ti 3d states localized at the Ti sites (De Groot et al. 1989). The next two peaks (III and IV) in TiO$_2$ standard is due to transitions to oxygen 2p hybridized with Ti 4p states of respective local symmetry b$_3$ and e in their octahedral environment (Wu et al. 1997). The O K-edge XANES spectrum of the Ga$_2$O$_3$ (GTO-0) nanostructure sample is quite different from that of the TiO$_2$ standard. For the GTO-0 sample, XANES spectrum exhibits two main peaks at ~535 eV and ~542 eV (A and B, respectively), similar to that of the β-Ga$_2$O$_3$ (Tourtin et al. 1998). Also from the crystal structure, it can be deduced that oxygen also resides in both octahedral and tetrahedral sites. Here, the difference of the O K-edge XANES spectra shown in Fig. 5.8b between the two samples (TiO$_2$ standard and GTO-0) is the pre-edge feature due to Ti doping after GTO-60. This pre-edge (~530eV) arise from the existence of an energy state in the band gap. In Fig. 5.8c, Ti L-edge XANES spectra of GTO samples are shown, but there was no titanium detected by XANES below for GTO-20. For anatase (TiO$_2$) standard and all GTO samples, two sets of peaks are observed which are separated by ~6
eV. This splitting is due to core-hole spin-orbit splitting of the 2p levels (Van Der Laan 1990, De Groot et al. 1989). It is believed that the structure of these two sets of peaks is from splitting of the d-derived final states into $t_{2g}$- and $e_g$-like levels (Ruus et al. 1997, Crocombette and Jollet 1994). This two set of the peak is also seen in GTO samples where titanium is above the detection limit in XANES. This XANES study basically suggests Ti doping in β-Ga$_2$O$_3$ substitutes at tetrahedral position but at higher concentration Ti phase separates in TiO$_2$ (anatase) as shown in illustration in Fig 5.8d.

Figure 5.8: XANES spectra of Ga L edge, O K-edge, and Ti L-edge GTO films deposited with variable Ti-concentration. a, Ga L-edge. b, O K-edge. c, Ti L-edge. d, Illustration of Ti doping in Ga$_2$O$_3$ matrix.
Chapter 6: Optical Properties

6.1. SPECTROPHOTOMETRY

The spectral transmission characteristics of GTO films were shown in Fig. 5.1. It is evident that the GTO films in general show high transparency throughout the entire spectral range; however, the sharp decrease in transmission towards the UV and/or near-UV region corresponds to incident radiation being absorbed across $E_g$. A further analysis of the optical spectra is performed to better understand the effect of Ti incorporation on the optical properties and to derive a quantitative structure-chemical composition-optical property relationship. For $\beta$-Ga$_2$O$_3$ with a direct band gap (Orita et al. 2000b, Rebien et al. 2002, Sinha, Adhikary, and Chaudhuri 2005) the absorption follows a power law of the form:

$$ (\alpha h\nu) = B (h\nu-E_g)^{1/2} $$

(13)

where $h\nu$ is the energy of the incident photon, $\alpha$ is the absorption coefficient, $B$ is the absorption edge width parameter, and $E_g$ is the band gap. The optical absorption coefficient, $\alpha$, of the films is evaluated using the standard relationship, taking the film thickness into account. The absorption is noted to be higher in GTO films compared with Ga$_2$O$_3$ nc-films without Ti incorporation. The absorption data and the plots obtained for Ga$_2$O$_3$ and GTO nc-films are shown in Fig. 6.2. $(\alpha h\nu)^2$ vs. $h\nu$ data fits to linear plots in the high absorption region, suggesting direct allowed band transitions across $E_g$. Regression analysis and extrapolating the linear region of the plot to $h\nu=0$ provide the $E_g$ value, as indicated with an arrow. The $E_g$ value for intrinsic Ga$_2$O$_3$ (without Ti incorporation) is $5.40 \pm 0.03$ eV. The $E_g$ values were found to decrease with increasing sputtering power to the Ti target, i.e., Ti content in the films.
Figure 6.1: Spectral transmittance characteristic of GTO films. The shift of the absorption edge with increasing sputtering power to the Ti metal target is evident.

The variation of $E_g$ with Ti target sputtering power is shown in Fig. 6.3, which can be used to explain the effect of Ti incorporation on the band gap. To correlate the changes to Ti content, Ti at\% determined from RBS is linked (top X-axis) to the sputtering power. The $E_g$ value decreases continuously with progressive incorporation of Ti in the films. For the highest sputtering power to the Ti target of 100 W, $E_g$ decreases significantly, to 4.47 (±0.02) eV. The shift in the band gap is $\Delta E_g$=0.9 eV, which is a quite substantial red shift in the band gap of Ga$_2$O$_3$ with Ti incorporation.
Figure 6.2: $(\alpha h\nu)^2$ vs. $h\nu$ plots for Ga$_2$O$_3$ and Ti-incorporated Ga$_2$O$_3$ films. Extrapolating the linear region of the plot to $h\nu=0$ provides the band gap value, as indicated with an arrow.
Figure 6.3: Variation in band gap and refractive index as a function of Ti sputtering power. The linked top X-axis shows the Ti at% determined from RBS. A direct correlation between $E_g$ and $n$ with applied sputtering power (i.e., Ti content) can be seen.

The effect of Ti incorporation and the physics and chemistry of the electronic structure changes leading to a substantial red shift in the band gap can be understood as follows. We first consider the crystallographic data of Ga and Ti oxides separately, and we then consider the Ti incorporation-induced changes in the crystal structure of Ga$_2$O$_3$. Most important to note is the fact that both Ga$_2$O$_3$ and TiO$_2$ exhibit polymorphism. While Ti oxide exhibits rutile or anatase phases routinely, the monoclinic structure is thermodynamically favorable for Ga$_2$O$_3$ (Kumar et al. 2013, Yamaga et al. 2003). If the ionic size and other structural parameters are compatible or comparable, a solid solution without any structure change can be expected for Ti incorporation into a Ga$_2$O$_3$ lattice, i.e., Ti atoms can occupy the lattice positions of Ga inside the β-phase structure of Ga$_2$O$_3$. This indeed is clearly seen in XRD data (Fig. 1), where there is no evidence of a secondary phase or no distortion of the peaks of the parent β-Ga$_2$O$_3$ for Ti concentrations ≤1.5 at%. Therefore, for the set of conditions employed in this work, combined crystal structure and chemical analyses indicate that Ti-incorporated Ga$_2$O$_3$ films accommodate Ti atoms without any structural distortion up to 1.5 at%, at which point the onset of Ti incorporation-induced changes result in texturing and/or secondary phase formation, as seen in the XRD results. The reason for the Ti-Ga$_2$O$_3$ single phase system could be the comparable ionic radii of Ga$^{3+}$ and Ti$^{4+}$ ions, which are 0.062 nm and 0.069 nm, respectively (Shannon 1976). Therefore, Ti ions can occupy the Ga$_2$O$_3$ structure without any perturbation only up to a certain limit. Exceeding this limit might result in Ti occupying interstitial positions, leading to changes in crystallography. Depending on the dopant concentration, such changes might be reflected in crystalline-to-amorphous transformation and/or changes in the texturing of GTO films.

The effect of Ti incorporation into Ga$_2$O$_3$ on the optical properties can then be understood as follows. The band gap value measured in this work for Ga$_2$O$_3$ films without any Ti incorporation (5.4 eV) is in reasonable agreement with that reported for β-Ga$_2$O$_3$ in the literature (Kumar et al. 2013, Rubio and Ramana 2013b). Titanium incorporation effectively reduces $E_g$, leading to a
substantial red shift, as noted in Fig. 6.3. For initial Ti incorporation, where the Ti content is ≤1.5 at%, Ti ions incorporated will form donor levels within the band gap of Ga$_2$O$_3$. This is due to the substitutional nature of Ti in Ga$_2$O$_3$, as evidenced by the crystal structure studies. Increasing the sputtering power to the Ti target from 0 to 100 W increases the effective concentration of Ti incorporated into Ga$_2$O$_3$. However, the progressive increase in Ti content results in the formation of a Ga$_2$O$_3$-TiO$_2$ mixed oxide, which causes a further reduction in the band gap. The substantial shift can be fully attributed to the Ti incorporation-induced changes. The evidence for this comes from structural analyses of the films, where no perturbation to the parent crystal structure is seen for Ti concentrations from 0 to 5 at. %, although formation of a Ga$_2$O$_3$-TiO$_2$ composite seems to occur at higher Ti contents. As shown in Fig. 5.4, the band gap of Ti oxide (TiO$_2$) is ~3.2 eV (Kumar et al. 2013). The measured $E_g$ is not even close to this value, which is an indication of the composite film being predominantly Ga$_2$O$_3$ in the matrix, while the presence of TiO$_2$ may be only as a minor component. In addition, as the band gap of the sample decreases with Ti doping, a change in the corresponding refractive index ($n$) values was also observed in ellipsometry measurements (not shown). The refractive index was calculated at 632.8 nm for all the samples. The $n$ values increased steadily from 1.90 to 1.98 with increasing Ti content from 0 to 5 at%. Furthermore, incorporation of Ti in Ga$_2$O$_3$ should create an oxygen vacancy, rather than Ga vacancy, as stated in the literature (Dakhel 2013). We believe that there may be further options available to further tune the structure and optical properties of Ti-Ga$_2$O$_3$ materials, which could be useful for improved sensor and TCO applications.
6.2. Spectroscopic Ellipsometry

Having understood the spectral transmittance and band gap, we now turn our attention to the optical constants of GTO films. Optical constants of the Ti-doped Ga$_2$O$_3$ films were primarily probed by spectroscopic ellipsometry (SE), which measures the relative changes in the amplitude and phase of the linearly polarized monochromatic incident light upon oblique reflection from the sample surface. The experimental parameters obtained by SE are the angles $\Psi$ (azimuth) and $\Delta$ (phase change), which relation to the microstructure and optical properties, defined by (Jellison 1996, Fujiwara 2007, Ramana et al. 2008, Mudavakkat et al. 2012):

$$\rho = \frac{R_p}{R_s} = \tan \Psi \exp(i\Delta)$$

where $R_p$ and $R_s$ are the complex reflection coefficients of the light polarized parallel and perpendicular to the plane of incidence, respectively. The spectral dependencies of ellipsometric parameters $\Psi$ (azimuth) and $\Delta$ (phase change) can be fitted within appropriate models to extract the GTO film thickness and optical constants, i.e., the refractive index ($n$) and extinction coefficient ($k$), based on the best fit between experimental and simulated spectra (Jellison 1996, Fujiwara 2007). In the present case, the Levenberg-Marquardt regression algorithm was used for minimizing the mean-squared error (MSE) (Jellison 1996):

$$\text{MSE} = \frac{1}{2N-M} \sum_{i=1}^{n} \left\{ \left( \frac{\Psi_{\text{exp}} - \Psi_{\text{calc}}}{\sigma_{\Psi_i}^{\text{exp}}} \right)^2 + \left( \frac{\Delta_{\text{exp}} - \Delta_{\text{calc}}}{\sigma_{\Delta_i}^{\text{exp}}} \right)^2 \right\}$$

where $\Psi_{\text{exp}}$, $\Psi_{\text{calc}}$, and $\Delta_{\text{exp}}$, $\Delta_{\text{calc}}$ are the measured (experimental) and calculated ellipsometry functions, $N$ is the number of measured $\Psi$, $\Delta$ pairs, $M$ is the number of fitted parameters in the optical model, and $\sigma$ are standard deviations of the experimental data points. Extracting meaningful physical information from ellipsometry requires the construction of an optical model of the sample which generally accounts several distinct layers with individual optical dispersions. Interfaces between these layers are optical boundaries at which light is refracted and reflected per the Fresnel relations. The stack model used to simulate the spectra purpose of determining the optical constants.
of Ti-doped Ga$_2$O$_3$ films is schematically shown in Fig. 6.9. The model contains, from the top, Ti-doped Ga$_2$O$_3$ film, SiO$_2$ interface, and Si substrate. The surface and interface roughness were also considered to accurately fit the experimental data.

The Cauchy dispersion model was used since the GTO films are transparent in the respective wavelength region and also for other reason that it was successful to fit the data and explain the optical properties of intrinsic Ga$_2$O$_3$ films (Ramana et al. 2014). Also, this model was able to account for the optical properties of other wide band gap oxides such as La$_2$O$_3$ (Ramana et al. 2011), Y$_2$O$_3$ (Mudavakkat et al. 2012), and HfO$_2$ (Vargas, Murphy, and Ramana 2014b, Vargas, Murphy, and Ramana 2014a). The Cauchy equation for refractive index $n$ as function of wavelength $\lambda$ can be expressed as:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$  \hspace{1cm} (16)

where A, B, and C are the Cauchy coefficients and specific to the material. A is the constant that dominates $n(\lambda)$ for long wavelengths, B controls the curvature of $n(\lambda)$ in the middle of the visible spectrum, and C influences the n(\lambda) to the greater extent at shorter wavelengths.\(^{49}\) Also, the principle behind Cauchy’s model can also be used for the dispersion function $k(\lambda)$:
\[ k(\lambda) = d + \frac{e}{\lambda^2} + \frac{f}{\lambda^4} \]

(17)

where \(d\), \(e\) and \(f\) are constants specific to the material. (Mudavakkat et al. 2012, Vargas, Murphy, and Ramana 2014a, Tan et al. 2010) Thus, the Cauchy model and fitting of the recorded experimental data allow for the optical constants (\(n\) and \(k\)) determination as well as thickness verification. The spectral dependencies of the ellipsometric parameters, \(\Psi\) and \(\Delta\), determined for GTO films are shown in Fig. 6.10. The spectral dependencies of ellipsometric parameters \(\Psi\) (azimuth) and \(\Delta\) (phase change) are fitted with appropriate models to extract film thickness and the optical constants, i.e., the refractive index (\(n\)) and extinction coefficient (\(k\)), based on the best fit between experimental and simulated spectra. (Jellison 1996, Fujiwara 2007) The curves obtained for Ti-doped Ga\(_2\)O\(_3\) films indicate (Fig. 6.10) a reasonable agreement between the experimental and simulation data for the entire range of Ti-concentration.
The microstructure information, specifically, film thickness, roughness and interfacial oxide thickness of GTO films, was also obtained from SE analysis. The film thickness variation as a function of Ti sputtering power and/or Ti concentration is presented in Fig. 6.11. It is evident that the film thickness is steadily increasing with Ti sputtering power. Most important is that the interfacial oxide (SiO2) thickness is limited to 2–3 nm. Figure 11 also, shows the variation of surface roughness of the Ti-doped Ga2O3 films determined from SE analysis.
Figure 6.6: Thickness and roughness of Ti doped Ga\(_2\)O\(_3\) films grown at various sputtering power

The dispersion profiles of the index of refraction (\(n\)) determined from SE data for Ti-doped Ga\(_2\)O\(_3\) films are shown in Fig. 6.12a. The ‘\(n\)’ dispersion profiles indicate a sharp increase at shorter wavelengths corresponding to fundamental absorption of energy across the band gap. The ‘structure and Ti-content’ dependence is evident in the dispersion curves (Fig. 6.12a), where a progressive increase of \(n\) value with increasing Ti content (Fig. 6.12b) is evident in GTO films. The spectral dependence of the extinction coefficient (\(k\)) determined from SE data for Ti-doped Ga\(_2\)O\(_3\) films is shown in the insert of Fig. 6.12a. It is evident that the extinction coefficient values are low and very close to zero in most parts of the spectrum (insert, Fig. 6.12a) which indicates very low optical losses due to absorption. The onset or sharp increase in \(k\) at high photon energy or short wavelength is due to the fundamental absorption across the band gap. An understanding of the structural quality of Ti-doped Ga\(_2\)O\(_3\) films can also be derived from the dispersion profiles of \(k(\lambda)\). Specifically, the curves (Fig. 6.12a) indicate that the \(k\) value of the Ti-doped Ga\(_2\)O\(_3\) films is almost zero in the visible and near-infrared spectral regions, while for photon energies toward
the ultraviolet region, the extinction coefficient increases sharply. The $k(\lambda)$ behavior is obviously related to the optical quality of the films. Strong absorption with no weak shoulders or tailing behavior for the Ti-doped Ga$_2$O$_3$ films can be attributed to the high quality of the grown layers with a very high transparency, which is also confirmed by the spectrophotometry analysis of films. The strong absorption across the band gap is reflected in rapid increase in $k$ values. The band gap values determined from spectroscopic ellipsometry are compared with that of spectrophotometry analyses as presented in Fig. 6.8. The trend of band gap variation with Ti content agrees in both the measurements.
Figure 6.7: a, Refractive index (n) dispersion profiles of GTO samples; b, Variation of ‘n’ values of GTO samples at different two wavelength. Ti-induced increase in n values is evident.

6.3. Model and Structure-Property Relationship

A simple model can be formulated to account for the observed functional dependence of optical constants on Ti-content in GTO films. Note that, for thin films and nanomaterials, the optical constants are sensitive to the microstructure and chemistry.(Jellison 1996, Keswani et al. 2017, Kosacki, Petrovsky, and Anderson 1999, Krishnamoorthy et al. 2017, Kumar et al. 2013)

The optical parameters are influenced by various factors such as surface/interface structure, crystal quality, packing density, lattice parameters, and defect structure.(Jellison 1996, Keswani et al. 2017, Kosacki, Petrovsky, and Anderson 1999, Krishnamoorthy et al. 2017, Kumar et al. 2013, Mudavakkat et al. 2012, Ramana et al. 2011, Rubio and Ramana 2013a, Vargas, Murphy, and Ramana 2014a, Vemuri, Engelhard, and Ramana 2012) Thus, the Ti incorporation induced changes in the n-values and their dispersion profiles can be explained by considering the nanometric structure and chemistry of the GTO films. The good optical quality of the intrinsic Ga₂O₃ films (without any Ti) can be attributed to their nanocrystalline structure and chemical stoichiometry, as indicated by the structural and chemical characterization. Usually, the low-packing density and/or stoichiometric defects can result in relatively low-values of optical constants compared to the bulk of the crystalline materials.(Vargas, Murphy, and Ramana 2014a, Vemuri, Engelhard, and Ramana 2012, Mudavakkat et al. 2012) For instance, the optical constants of wide band gap HfO₂ and Y₂O₃ films were strongly influenced by their structural quality(Mudavakkat et al. 2012, Vargas, Murphy, and Ramana 2014a); amorphous HfO₂ and Y₂O₃ films were found to exhibit low values of n and k which are explained on the basis of the structural disorder and low packing density in the amorphous matrix.(Vargas, Murphy, and Ramana 2014a, Mudavakkat et al. 2012) Thus, the good optical quality in terms of n-values reasonably close the those reported for Ga₂O₃ bulk and very low k values with extremely low absorption loses is attributed to the improved structural order when the films are deposited at 500 °C. Thus, in nc-Ga₂O₃ films, the nanostructure is characterized by dense, randomly oriented nanocrystals. This
leads to enhancement in packing density, which results in enhanced density of absorption and index of refraction. The additional evidence for the proposed mechanism comes from our earlier reports on the optical properties of nanocrystalline Y_2O_3 (Mudavakkat et al. 2012) and HfO_2 (Vargas, Murphy, and Ramana 2014a) films and other reports existing in the literature (Ramana et al. 2011, Kosacki, Petrovsky, and Anderson 1999, Vemuri, Engelhard, and Ramana 2012). Furthermore, such behavior was also noticed in nanocrystalline ZnO (Malandrino et al. 2008) and CeO_2 (Toro et al. 2004). Thus, the increased n values in GTO films as a function of increasing Ti content can be attributed to the chemical changes. As to chemical composition changes, the refraction variation mechanisms seems to be dominant in Ti-doped Ga_2O_3. It is known that Ti^{4+} ion has a very high refraction and, respectively, the substitution of “TiO_2” for “Ga_2O_3” could increase the refractive index. The examples of such analysis of several doped crystals could be found elsewhere (Atuchin et al. 1995, Atuchin et al. 1989, Korotkov and Atuchin 2008). Perhaps, the dominance of Ti induced chemical effects are more pronounced than structural effects to induce enhancement in n values. Based on the results reported in the literature on the optical quality of CeO_2 (Toro et al. 2004), HfO_2 (Vargas, Murphy, and Ramana 2014a) and Y_2O_3 (Mudavakkat et al. 2012) films, one would expect to see a decrease in the n-values with progressive Ti content in GTO films. This is due to the fact that the structural characterization employing XRD and SEM analyses indicate that Ti-incorporation induces structural changes, where nanocrystalline GTO films eventually becomes amorphous at higher Ti content. However, the observed trend i.e., n-value increase with Ti, is primarily due to the chemical change where the formation of Ga_2O_3-TiO_2 composite formation is evident. The index of refraction of TiO_2 is higher compared to that of Ga_2O_3. Therefore, increasing sputtering power to the Ti target results in higher Ti content, which is responsible for Ga_2O_3-TiO_2 composite formation and hence the overall enhancement in n values. Furthermore, such Ti-incorporation facilitated Ga_2O_3-TiO_2 composite formation may also be affecting the physical density of the films which in turn contribute to the n-enhancement. In order to validate this hypothesis we considered further analysis of the GTO optical data to determine the relative density of the films.
It is well known that the refractive index is closely related to the physical properties and density of the films. (Vargas, Murphy, and Ramana 2014a, Vemuri, Engelhard, and Ramana 2012, Atuchin et al. 1995) Thus, the observed increase in refractive index of GTO films with addition of Ti can be attributed to increasing packing density of the films. In order to further confirm and validate this hypothesis, the relative density of the GTO films is calculated using Lorentz-Lorenz relationship. The Lorentz-Lorenz (Kaiser 2003) equation is:

\[ p = \frac{\rho_f}{\rho_b} = \frac{(n_f^2-1)(n_b^2+2)}{(n_f^2+2)(n_b^2-1)} \] (18)

where \( p \) is the packing density, \( \rho_f \) is the density of the thin film, \( \rho_b \) is the density of the bulk material, \( n_f \) is mean refractive index of the film and \( n_b \) is the refractive index of the bulk material. The bulk refractive index (\( n_b \)) of \( \beta \)-\( Ga_2O_3 \) is 1.9201 (Stepanov et al. 2016b, Bhaumik et al. 2011) and the refractive index of the film measured at 550 nm is employed in Lorentz-Lorenz equation to calculate relative density of the film. The calculated relative density of GTO films is presented in Figure 6.13. It can be noted that the physical density of GTO film increases with Ti content increase. Thus, the results and analysis of SE data confirm the density increase in Ti incorporated GTO films and accounts for the observed enhancement in \( n \)-values.
Figure 6.8: Relative density of the GTO films. It is evident that the increasing Ti content improves the physical density of the GTO films.
Chapter 7: Sensor Performance

The temperature dependent electrical data, which serves the baseline characteristics for sensor applications, of GTO samples are shown in Fig. 7.1. It is generally accepted that barrier formation between grains is responsible for the sensor conductivity and that these barriers have a Schottky-type nature (Schipani, Aldao, and Ponce 2012). Therefore, as a first step, determination of activation energy is quite important for utilization of GTO for sensor applications. The temperature-dependent electrical data (Fig. 7.1a; Arrhenius plots) of GTO samples were analyzed to obtain the activation energy of the films using the relation:

\[ R = R_\infty e^{\left(\frac{E_A}{kT}\right)} \]  

(19)

where \( R_\infty \) is the resistance at infinite temperature, \( E_A \) is the activation energy, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( R \) is the resistance. The \( E_A \) values determined are presented in Fig. 7.1b, where the effect of Ti content on the \( E_A \) values is shown. It can be seen that the \( E_A \) continuously decrease with increasing Ti in Ga\(_2\)O\(_3\). This observation is imperative since the \( E_A \) reduction is expected to contribute the enhanced sensitivity. The \( E_A \) value for intrinsic Ga\(_2\)O\(_3\) films was 1.02 eV, which reduces to a final value of 0.62 eV when the Ti concentration is \(~5\) at%. Significant reduction in EA is an indication that thermal energy required for oxygen detection becomes smaller by the incorporation of Ti-ions into Ga\(_2\)O\(_3\).
Figure 7.1: a, Electrical data of GTO films. Arrhenius plots are shown for samples with variable Ti content. b, Activation energy of GTO films. Continuous decrease in EA values with Ti incorporation into Ga$_2$O$_3$ can be noted.
The oxygen sensor response data of GTO films are shown in Fig. 7.2. The performance characteristics were evaluated at 700 °C in terms of initial sensitivity and response time. The data shown are obtained in the experiments conducted under different pO\(_2\) (8-40 Pa) in cyclic periods of pure Ar flow for a constant time followed by Ar/O\(_2\) flow for the same time period. The repeatability and stability of the sensors was evaluated (Fig. 7.2) at 700 °C for several hours as a function of pO\(_2\). All of the GTO films demonstrated the stability and repeatability for the extended duration of the tests (≥100 h). No discontinuity or breakdown was observed over the range of pO\(_2\) examined. Intrinsic Ga\(_2\)O\(_3\) response also presented changes in the resistance value under Ar exposure, corresponding the polarization effects caused by the ionic conductivity of the films, and the constant increment on the base resistance is attributed to the grain boundary capacitance of the films (Fleischer et al. 1995). As shown Fig. 7.2, it can be observed that GTO-0, GTO-20, and GTO-40 responded by the increase in resistance when oxygen is introduced. This response of pure Ga\(_2\)O\(_3\) has been previously observed in the literature (Baban, Toyoda, and Ogita 2005b). However, the changes in response behavior becomes evident when the Ti content becomes appreciable. For Ti a concentration of ≥1.5 at%, the sensor response to oxygen flips and resistance now decreases after oxygen is introduced and vice-versa. This remarkable behavior observed for GTO films under pO\(_2\) is totally different and has not been achieved or reported earlier for intrinsic Ga\(_2\)O\(_3\). Also, the changes are rapid; the response behavior in GTO films is rather instantaneous and occur rapidly upon oxygen release into the argon stream. However, when the oxygen was cut off, the reversal to original resistance takes bit of a longer time. This phenomenon confirms that out-diffusion of oxygen is relatively slow. To ensure reproducibility, interval between successive measurements is set to ~10 min.
The response time GTO sensors are determined, using the standard procedures, from the sensor characteristics at various pO$_2$ (Fig. 7.2). The response time for intrinsic Ga$_2$O$_3$ (GTO-0) is 80±10 s, whereas for the films deposited with 5 at% of Ti-doped Ga$_2$O$_3$ exhibits a rapid response time of only 4±1 s. This is a remarkable result and demonstrates the effect of Ti into Ga$_2$O$_3$ to promote oxygen sensor performance. The sensor response data is presented in Fig. 7.3a, where the results indicate that increasing Ti content in Ga$_2$O$_3$ decreases the response time i.e., improves the sensor performance. The results indicate that the 5 at% Ti doped Ga$_2$O$_3$ is nearly ~20 times faster as compared to intrinsic Ga$_2$O$_3$. Note that the response time can be influenced by the surface reactions rate or/and the diffusion rate. When pO$_2$ is increased, the oxygen molecules adsorbed at the surface split and occupy the vacancies near the surface. A diffusion process of oxygen inside the film, across the grain boundaries, will reestablish equilibrium with the gas phase (Baban, Toyoda, and Ogita 2005b).
The materials that respond to change in pO$_2$ in the upper-temperature range (700 °C and above) are reflecting the equilibria between the atmosphere and their bulk stoichiometry. In general, the relationship between oxygen partial pressure and the electrical conductivity of the mixed valence oxide sensor may be represented (Moseley 1992) by:

$$\sigma = A \ast \exp \left[-\frac{E_A}{kT}pO_2^{1/m}\right]$$  \hspace{1cm} (20)

where $E_A$ represents the activation energy of the sensing film, $k$ is the Boltzmann constant, $A$ is a constant, $T$ is the absolute temperature, pO$_2$ is the partial pressure of oxygen, and $m$ is a parameter determined by the carriers ($n$ or $p$ type) and defects in the oxide (Moseley 1992, Ramamoorthy, Dutta, and Akbar 2003). The value of $|m|$ is the sensitivity of the sensor; higher the $|m|$ value, higher the sensitivity and vice versa (Ramamoorthy, Dutta, and Akbar 2003). The electrical data at various pO$_2$ were used to calculate the m-values, which are presented in Fig 7.3b. In intrinsic Ga$_2$O$_3$ films (GTO-0), the m-value is -0.8, which is quite higher than theoretical value (at 1000 °C) of -4 as presented in the literature (Frank et al. 1998, Baban, Toyoda, and Ogita 2005b). However, the Ti doping in Ga$_2$O$_3$ shows the reduction of m value up to -6.92 for GTO-100, i.e., Ti concentration of 5 at%. From eq. 2, it is clear that the lower value of m value corresponds to a higher sensitivity of sensor in terms of its response to changes in pO$_2$. Also, lower value of $E_A$ corresponds to lower sensitivity to the temperature fluctuations. The value of m for pure Ga$_2$O$_3$ (GTO-0) and highest Ti concentration of 5 at% (GTO-100) are -0.8 and -6.92, respectively, where lower m value of GTO-100 demonstrates a better oxygen sensitivity. Similarly, GTO-100 samples with lowest $E_A$ (0.62 eV) implies precise measurements of pO$_2$ when employed for oxygen sensing.
Figure 7.3: Oxygen sensor performance of characteristic values of GTO films. (a) Response time. (b) m value determined from functional electrical characteristics of GTO.

The quality and atomic scale defects and clustering were further examined by atom probe tomography (APT) of the sample with highest Ti concentration, i.e., 5 at% (GTO-100). Specifically, APT allows us to verify dopant clustering (if any) at the highest concentration. The APT specimens were lifted out using focused ion beam (FIB) using Omni Probe and mounted on the micro-post for annular milling. The APT reconstructions of GTO-100 specimen are shown in Fig 7.4 with Ga atoms in red and Ti in blue. The APT reconstruction shows a 37.78 x 35.98 x
119.1 nm³ volume. From the APT reconstruction, Ti is evenly distributed through the entire film thickness and no noticeable cluster formation of Ti atoms even for the highest Ti concentration. Thus, the XANES and APT data accounts for the structural and chemical quality of the GTO films.

Figure 7.4: APT reconstruction of GTO-100 samples. a, Sample tip as prepared after FIB annular milling. b, All-atomic view of APT reconstruction showing Ga in red and Ti in blue. c, Atomic view of only Ga atoms. d, Atomic view of only Ti atoms
Chapter 8: Thermal Stability

8.1. Surface Morphology

The SEM shows some degree of grain growth due to annealing process. The figure 8.1 and 8.2 show the difference between as prepared and annealed GTO grain growth.

![Figure 8.1: SEM as prepared](image-url)
Recently, we have demonstrated the change in optical properties and crystallinity by doping Ti in $\beta$-Ga$_2$O$_3$ (Manandhar and Ramana 2017a). Grazing incidence x-ray diffraction (GIXRD) of the as prepared GTO thin films showed that the films were becoming amorphous with addition of Ti. Similarly, when annealed at 700 °C for 4 hours the crystallinity did not change much. The figure 8.3 shows the clear difference in GIXRD.
Figure 8.3: a, XRD of GTO samples as prepared; b, XRD of GTO samples annealed

The spectral transmission characteristics of GTO as prepared and annealed films are shown in Figure 8.4. It is evident that the GTO films, in general, show high transparency throughout the entire spectral range; however, the sharp decrease in transmission towards the UV and/or near-UV region corresponds to incident radiation being absorbed across $E_g$. Further analysis of the optical spectra is performed to better understand the effect of Ti incorporation on the optical properties and to derive a quantitative structure-chemical composition-optical property relationship. For $\beta$-Ga$_2$O$_3$ with a direct band gap (Orita et al. 2000a, Rebien et al. 2002, Sinha, Adhikary, and Chaudhuri 2005) the absorption follows a power law of the form:

\[
(\alpha h\nu) = B (h\nu-E_g)^{1/2}
\]

(21)
where $h\nu$ is the energy of the incident photon, $\alpha$ is the absorption coefficient, $B$ is the absorption edge width parameter, and $E_g$ is the band gap. The optical absorption coefficient, $\alpha$, of the films is evaluated using the standard relationship, taking the film thickness into account. In as prepared and annealed GTO samples, the absorption is noted to be higher in GTO films compared with Ga$_2$O$_3$ nc-films without Ti incorporation. The absorption data and the plots obtained for Ga$_2$O$_3$ and GTO nc-films are shown in inset of Figure 8.4 ($\alpha h\nu$)$^2$ vs. $h\nu$ data fits to linear plots in the high absorption region, suggesting direct allowed band transitions across $E_g$. Regression analysis and extrapolating the linear region of the plot to $h\nu=0$ provide the $E_g$ value.

Figure 8.4: Transmission spectra (a) as prepared and (b) annealed

The $E_g$ value for intrinsic as prepared and annealed Ga$_2$O$_3$ (without Ti incorporation) is 5.40 ($\pm$0.03) eV and 5.09 ($\pm$0.1) eV respectively. eV. The calculated $E_g$ values were found to decrease with increasing sputtering power to the Ti target, i.e., Ti content in the films in both as prepared and annealed GTO samples. The variation of $E_g$ with Ti target sputtering power is shown in Figure 8.5, which can be used to explain the effect of Ti incorporation on the band gap. To correlate the changes to Ti content, Ti at% determined from XPS is linked (top X-axis) to the sputtering power. The $E_g$ value decreases continuously with progressive incorporation of Ti in the
films. For the highest sputtering power to the Ti target of 100 W, $E_g$ decreases significantly, to 4.47 (±0.02) eV for as prepared samples. But for Ti target of 100 W annealed samples the $E_g$ decreases to 3.5 eV. The shift in the band gap for GTO-100 from as prepared to annealed samples is $\Delta E_g=0.93$ eV which is a quite substantial red shift in the band gap due to annealing.

![Figure 8.5: Band gap as prepared vs annealed](image)

The microstructure information, specifically, film thickness and interfacial oxide thickness of both as prepared and annealed Ti-doped Ga$_2$O$_3$ films were also determined from SE analysis. The variation of film thickness as a function Ti sputtering power and Ti concentration is shown in Figure 8.6. It is evident that the film thickness is steadily increasing with Ti sputtering power. Most important is that the interfacial oxide (SiO$_2$) is limited to 2–3 nm at the interface. But when same samples were annealed, the thickness has been reduced which may be relate to densification of the films.
The spectral dependence of the extinction coefficient (k) determined from SE data for Ti-doped Ga$_2$O$_3$ films is shown in Figure 8.7a. It is evident that the extinction coefficient values are low and very close to zero in most parts of the spectrum (Fig. 8.4a) which indicates very low optical losses due to absorption. The onset or sharp increase in k at high photon energy or short wavelength is due to the fundamental absorption across the band gap. An understanding of the structural quality of Ti-doped Ga$_2$O$_3$ films can also be derived from the dispersion profiles of k(λ). Specifically, the curves (Fig. 8.7a) indicate that the k value of the Ti-doped Ga$_2$O$_3$ films is almost zero in the visible and near-infrared spectral regions, while for photon energies toward the ultraviolet region, the extinction coefficient increases sharply. The k(λ) behavior is obviously related to the optical quality of the films. Strong absorption with no weak shoulders or tailing behavior for the Ti-doped Ga$_2$O$_3$ films can be attributed to the high quality of the grown layers with a very high transparency, which is also confirmed by the spectrophotometry analysis of films.
shown in previous work (Manandhar and Ramana 2017b). The dispersion profiles of the index of refraction (n) determined from SE data for Ti-doped Ga$_2$O$_3$ films are shown in Figure 8.7b. The results indicate a similar behavior as noted in k curves. The "n" dispersion curves also indicate a sharp increase in higher photon energy or shorter wavelength corresponding to fundamental absorption of energy across the band gap. However, the effect of growth condition is evident in the dispersion curves (Fig.9b.), where there is an increase in “n” values with increasing titanium concentration. This increase in refractive is indicates close packing of the crystal with addition of Ti.
The surface concentration of dopants (Ti) and its oxidation state is required to understand thermal stability of thin films. The XPS measurements also allowed us to determine the atomic percentage of Ti as well as the chemical valence states of the constituent ions present in the surface of as prepared and annealed GTO samples. The XPS survey spectra of representative GTO films are collected before collecting high-resolution scan of each element. The XPS survey spectra show Ga, Ti and O are the main constituents of the deposited films. The presence of C 1s is evident in the survey spectra; the carbon peak in the XPS spectra is due to adventitious carbon from exposure to air following fabrication, before being placed in the XPS system. Therefore, the spectra were calibrated to the C 1s peak at a binding energy (BE) of 284.6 eV (Miller, Biesinger, and McIntyre 2002). To determine the chemical states of the metal ions, present in the films, a detailed analysis of the core level spectra of the main constituents was performed. The high-resolution scans of Ga 3d, Ti 2p, and O 1s were recorded and analyzed to obtain their chemical states and the interaction between respective metal ions and oxygen for both as prepared and annealed GTO samples. XPS spectra for Ga 3d and O 1s in intrinsic Ga$_2$O$_3$ nanostructures obtained with the same procedure as Ti-doped Ga$_2$O$_3$. The core-level XPS spectra of the Ga 3d region are shown for both as prepared and annealed samples in Fig. 8.8a. The data shown are for samples with a variable Ti-content. The Ga 3d peak for GTO-0 is located at a binding energy (BE) of $\sim$20.5 eV which agrees to the literature (Ghosh et al. 2007). The National Institute of Standards and Technology (NIST) database also gives the value of 20.4 ± 0.5 eV for Ga 3d$_{5/2}$ in Ga$_2$O$_3$ (Naumkin et al. 2012).

The high-resolution core-level XPS spectra of O 1s from different samples are presented in Fig. 8.8b. The data shown are as a function of variable Ti-sputtering power. The peak position for pure Ga$_2$O$_3$ is located at BE $\sim$ 530.8 eV, which is consistent with values reported in the literature (Hollinger, Skheyta-Kabbani, and Gendry 1994, Syed et al. 2017). This BE is usually assigned to oxide (i.e., Ga-O-Ga bonds) which corresponds to the position of O 1s for Ga$_2$O$_3$ when
gallium is present in its highest chemical valence state (Ga$^{3+}$) (Ramana et al. 2014, Trinchi et al. 2004, Ou et al. 2012). The shoulder of O 1s peak at higher energy is usually associated with oxygen bonded to carbon (labeled as CO$_2$). A slight shift in O 1s peak is observed with increasing Ti content in GTO film due to the increasing amount of titanium bonded to oxygen. The peak at 530.3 eV of BE relates to Ti$_2$O$_3$(Bharti et al. 2016, Xu et al. 2008, Hussain et al. 2016). Thus, Ti occupies gallium sites in gallium oxide structure. O 1s core characteristics of both Ga$_2$O$_3$ and Ti$_2$O$_3$ appear in XPS spectra, as both elements can participate in bonding in the same charge.

The high-resolution core-level spectra of Ti 2p are presented in Fig. 8.8c. Ti 2p$_{3/2}$ spectral fitting parameter from NIST database (Naumkin et al. 2012) and numerous literature assign binding energy of 458.6 eV and 457.13 eV to Ti$^{4+}$ (TiO$_2$) and Ti$^{3+}$ (Ti$_2$O$_3$)(González-Elipe et al. 1989, Massaro et al. 2002, Tao, Luttrell, and Batzill 2011). Ti$^{4+}$ do not have unpaired d electrons and does not exhibit multiplet splitting, but Ti$^{3+}$ have unpaired d electrons and theoretically exhibit multiplet structure which may not be well resolved as found in XPS literature (Gupta and Sen 1975). As shown in XANES results, Ti 2p peak shows a steady increase in TiO$_2$ phase with the addition of Ti by increasing sputtering power while Ti$_2$O$_3$ peak stays consistent after GTO60. Also, the atomic concentration of titanium was calculated from the XPS spectral intensity of Ti 2p for both as prepared and annealed GTO samples (shown in Fig. 1c). The steady increase in Ti concentration up to 5 at% which matches the bulk concentration calculated using Rutherford backscattering spectroscopy (RBS)(Manandhar and Ramana 2017a) for as prepared GTO samples. Also, the Ti concentration is almost the same for the annealed samples. The increase in Ti concentration is observed as a function of Ti sputtering power comparing as prepared and annealed GTO sample is shown below in Fig. 8.9.
Figure 8.8: XPS as prepared vs annealed
Figure 8.9: Ti concentration as prepared vs annealed

To probe the chemical changes and better understand the dopant (Ti) position in β-Ga₂O₃ crystal lattice and identify the TiO₂ phase which was inconclusive in TEM, X-ray Absorption Near Edge Structure (XANES) was employed. In XANES, the fine structure observed above the edge, so-called white line, reflects the local site symmetry around the X-ray absorbing atom, the analysis of this region is for the fingerprint of the elements. It is well known that β-phase of Ga₂O₃ has a spinel structure, containing Ga atoms in both tetrahedral and octahedral sites (Geller 1960, Shimizu et al. 1996), whereas the α-phase of Ga₂O₃ has a corundum structure, containing only Ga atoms in octahedral sites(Shimizu et al. 1996, Marezo and Remeika 1967). The Ga L-edge spectra shown in Fig. 8.10a is due to excitation of electrons in the 2p₃/₂ orbital of Ga, leading to a sharp increase in absorption of Ga-containing materials at 1116.4 eV(Calvin 2013). However, the edge for Ga in Ga₂O₃ is shifted to 1120 eV due to valence dependency which causes edges to shift(Agarwal and Verma 1970). So the first peak labeled A (or edge) in Ga L-edge spectrum is assigned to Ga atoms in octahedral sites while subsequent peak labeled B is assigned to Ga in tetrahedral sites(Shimizu
et al. 1996). As the titanium concentration is steadily increased the signature peak of tetrahedral Ga atoms is diminished, which is presumably due to the replacement of Ga atoms in tetrahedral sites by Ti atoms.

In Fig. 8.10b, O K-edge spectra of GTO samples is shown with the TiO$_2$ standard. The O K-edge spectra for TiO$_2$ standard matches the signature features of anatase (Wu et al. 1997) which confirms the TiO$_2$ phase. In anatase (TiO$_2$ standard), first two peaks at low energy (labeled I and II) is due to dipole transitions to band states of t$_{2g}$-e$_g$ symmetry separated by the “ligand-field splitting” of O 2p states hybridized with the Ti 3d states localized at the Ti sites (De Groot et al. 1989). The next two peaks (labeled III and IV) in TiO$_2$ standard is due to transitions to oxygen 2p hybridized with Ti 4p states of respective local symmetry b$_3$ and e in their octahedral environment (Wu et al. 1997). The O K-edge XANES spectrum of the Ga$_2$O$_3$ (GTO-0) nanostructure sample is quite different from that of the TiO$_2$ standard. For the GTO-0 sample, its Total Electron Yield (TEY) XANES spectrum exhibits two main peaks at ~535 eV and ~542 eV (labeled A and B respectively), similar to that of the β-Ga$_2$O$_3$ (Tourin et al. 1998). Also from the crystal structure, it can be deduced that oxygen also resides in both octahedral and tetrahedral sites. Here, the difference of the O K-edge TEY-XANES spectra shown in Fig. 5b between the above two samples (TiO$_2$ standard and GTO-0) is the pre-edge feature due to Ti doping after GTO-60. This pre-edge (~530eV) arise from the existence of an energy state in the band gap. In Fig. 5c, Ti L-edge XANES spectra of GTO samples are shown, but there was no titanium detected by XANES below for GTO-20. For anatase (TiO$_2$) standard and all GTO samples, two sets of peaks are observed which are separated by ~6 eV. This splitting is due to core-hole spin-orbit splitting of the 2p levels (Van Der Laan 1990, De Groot et al. 1989). It is believed that the structure of these two sets of peaks is from splitting of the d-derived final states into t$_{2g}$- and e$_g$-like levels (Ruus et al. 1997, Crocombette and Jollet 1994). This two set of the peak is also seen in GTO samples where titanium is above the detection limit in XANES. This XANES study suggests Ti doping in β-Ga$_2$O$_3$ substitutes at the tetrahedral position but at higher concentration, Ti phase separates in TiO$_2$ (anatase) as shown in the illustration in Fig 8.10d.
Annealing of doped samples usually creates clusters of dopants. So, the quality and atomic scale defects and clustering were further examined by atom probe tomography (APT) of the sample with highest Ti concentration, i.e., 5 at% (GTO-100) as prepared at annealed. Specifically, highest concentration samples would show most clustering effect if it occurs. Since the sample were deposited at 500 °C the diffusion when prepared, Ti might lead to clustering of Ti which defeats the idea of doping β-Ga2O3 structure if they remain in different phase. The APT specimens were lifted out using focused ion beam (FIB) using Omni Probe and mounted on the micro-post for
annular milling. The APT reconstructions of GTO-100 as prepared specimen are shown in Fig 8.11 with Ga atoms in black and TiO$_2$ in green. From the APT reconstruction, TiO$_2$ is evenly distributed through the thickness of the film and no noticeable cluster formation of Ti atoms even for the highest Ti concentrations in gallium oxide for both as prepared and annealed GTO-100 samples.
Figure 8.11: APT as prepared vs annealed
Chapter 9: Summary and Conclusions

The different studies performed in this research allowed us to understand the overall behavior of Ti-doping into Ga$_2$O$_3$ sputter deposited films. The evaluation of the optical-structural-chemical properties of the films revealed that the Ti-content and chemistry would have a profound influence on the electronic behavior and sensor response of the Ti-doped Ga$_2$O$_3$ films. Increasing sputtering power to the Ti target increases Ti-doping content in the films; therefore, tailoring the composition is possible by the careful choice of processing conditions. Regarding the optical properties of the films, the transmittance spectra showed that the Ti-incorporation reduces the transparency of the films, and at the same time, the band gap values of the films decrease with increasing Ti-content.

Furthermore, the index of refraction of the films increased with increasing Ti-atomic content. The surface morphology and the crystal structure of the films change from monoclinic to amorphous whenever Ti is doped into the film. The chemical state analysis of the films suggested the only Ga$^{3+}$ was present in the films, whereas for Ti-doped samples, Ti$^{4+}$ was the dominant oxidation state, but the presence of sub-3+ oxide was encountered. The thermal stability of the Ga-Ti-O films indicated the three main phenomena occurred during annealing at 700 °C. These were no significant Ti-diffusion or loss of Ti concentration. The surface morphology of the films, evaluated using SEM, indicate a transition towards mesoporous films. The valence states of the films, analyzed using XPS, showed that no significant change in Ga and Ti ions.

Similarly, the thermal stability of the films studied by analyzing the surface morphology and chemistry of three films after exposing them to 4 hours at 700 °C indicate no significant changes. The evaluation of the oxygen sensor capabilities demonstrated that the time response of the films in the sensor could be improved by tuning the Ti-content in the films. The ideal Ti-sputtering power for enhancing the time response while sustaining stability is within the range of 60W-100W. For the cases where Ti-doping occurred below that range the response time was unacceptable. The already mentioned improvement in the time response of the Ga$_2$O$_3$ based
sensors is attributed to the increasing Knudsen diffusion coefficient. The sensors were evaluated using integrated interdigital electrodes, where a predefined distance of 100 micrometers is used as separation between electrodes and the films is deposited on top of these electrodes. The optimum range of Ti-doping is when the films are deposited between 60W and 100W of sputtering power under the deposition conditions that this work followed. The activation energy of the films was also studied, and the behavioral trend acted similarly to the band gap values of the films, where the energy reduced with increasing Ti-incorporation.
Chapter 10: Future Work

The following work is recommended for the continuation of this research:

- Investigation of the electrical properties via Hall Effect method to determine the change in carrier mobility, carrier concentration, and the type of conductivity that Ti-doped films. This experiment will not only benefit the on-going investigation of high-temperature oxygen sensors, but also will provide information relatively crucial for an application such as transparent conductive oxides, and high-power electronics.

- Manufacturing Ga-doped TiO$_2$ sensor for in-situ testing. This will reverse the charge imbalance and will allow the study of Ga in TiO$_2$ structure.

- Continuation of different refractive metal doping. This work investigated the effect of Ti-doping in the oxygen sensor characteristics of Ga$_2$O$_3$. Nevertheless, the doping of material with different oxidation state may help to improve the sensing process of the film, while keeping the stability that Ga$_2$O$_3$ offers. Refractive metals such as Hf and Mo are among the metallic ions that may be considered for improvement of the oxygen sensors performance.
References


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Vita

Sandeep Manandhar was born July 28, 1985, in Nepal. In May 2009 Mr. Manandhar received a Bachelor of Science in Materials Science and Engineering from the University of North Texas (UNT). Immediately after that, he enrolled in the graduate program for Materials Science and Engineering at UNT and received a Master of Science in Materials Science and Engineering in May 2011. Mr. Manandhar then worked as Post Masters Research Associate for two years in Pacific Northwest National Laboratory. Mr. Manandhar started his Ph.D. in the University of Washington in 2014 and then transferred to the University of Texas at El Paso in 2016 in Department of Mechanical Engineering. He did two summers of Ph.D. Research Intern at Pacific Northwest National Laboratory in summer of 2016 and 2017. He has several first author and co-author publications in various innovative scientific journals.

Permanent address: 7303 Spring Cypress Rd # 1222
Spring, TX 77379

This dissertation was typed by Sandeep Manandhar.