STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF WET-CHEMICAL DEPOSITED β-GALLIUM OXIDE NANOSTRUCTURED FILMS

Ph.D. Thesis

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DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE JULY 2022

STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF WET-CHEMICAL DEPOSITED β-GALLIUM OXIDE NANOSTRUCTURED FILMS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by SIDDHARTHA SUMAN (Roll No. 1701105010)



DEPARTMENT OF METALLURGY ENGINEERING

AND MATERIALS SCIENCE

INDIAN INSTITUTE OF TECHNOLOGY INDORE JULY 2022

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled STRUCTRAL, OPTICAL AND ELECTRICAL PROPERTIES OF WET-CHEMICAL DEPOSITED β-GALLIUM OXIDE NANOSTRUCTURED FILMS in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF **METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian** Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July, 2017 to May, 2022 under the supervision of Dr. Ajay Kumar Kushwaha (supervisor), Department of Metallurgy Engineering and Materials Science, IIT Indore and Dr. Mrigendra Dubey (co-supervisor) Department of Metallurgy Engineering and Materials Science, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

> Signature of the student with date 2022 (SIDDHARTHA SUMAN)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

30.09.2022

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Siddhartha Suman

I Dedicate this thesis to

MY WORLD 'MAA'

"Sarita Kumari"

MY PILLAR 'PAPA'

"Shree Manoj Kumar Singh"

MY STRENGTH 'DI'

"Astha Singh"

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LIST OF PUBLICATIONS

A. Peer-reviewed Journals:

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3. <u>Siddhartha Suman</u>,and Ajay K Kushwaha*, "Low Temperature Aqueous Route Deposited Gallium Oxide Nanostructured Film for Memristor Application". Journal of Solid-State Chemistry 313, 123293 (2022).

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- <u>Siddhartha Suman</u>, N. Mukurala, Lokanath Mohapatra, and Ajay K Kushwaha "Single step wet chemical deposition of cesium doped β-Ga₂O₃ nanostructured films for memristor application". Memories- Materials, Devices, Circuits and Systems 100015 (2022). DOI - https://doi.org/10.1016/j.memori.200.100015
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- 7. Abhinav Maurya, <u>Siddhartha Suman</u>, Aditya Bhardwaj, Lokanath Mohapatra, Ajay K. Kushwaha "Surface dependent electrodeposition of Ni-Co alloy for efficient hydrogen evolution reaction" Electrocatalysis 1-10 (2022).
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- 9. Nagaraju Mukurala, <u>Siddhartha Suman</u>, A. Bhardwaj, K. Mokurala, Sung Hun Jin and Ajay K. Kushwaha, "*Cu₂FeSnS₄ decorated Ni-TiO₂ nanorods heterostructured photoanode for enhancing water splitting performance*" Applied Surface Science, 551, 149377 (2021).
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B. Book Chapter

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- 2. Ajay K. Kushwaha*, H. Kalita, <u>Siddhartha Suman</u>, A. Bhardwaj and R. Ghosh, "Two Dimensional (2D) Thermoelectric Materials". Book: Thermoelectricity and Advanced Thermoelectric Materials, Elsevier 2020.
- 3. Ajay K. Kushwaha*, Nagaraju Mukurala, Krishnaiah Mukurala and <u>Siddhartha Suman</u>, *"Recent Advancements in Electrodes and Electrolytes of Dye Sensitized Solar Cells"* Book: Photosynthetic Protein based photovoltaics, CRC Press Taylor & Francis Group - 2018.
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- 3. <u>Siddhartha Suman</u>, Nagaraju Mukurala, Nitin Chaudhary and Ajay K. Kushwaha*, *"Electrochemical detection of chromium ions (Cr*⁺⁶⁾ *in drinking water by means of hydrothermally grown Bi-TiO₂ nanorods"*. International Conference on Advanced Functional Materials and Devices (ICAFMD- 2019), NIT Warangal.
- 4. Nagaraju Mukurala, <u>Siddhartha Suman</u> and Ajay K. Kushwaha*, "Impact of reaction time and temperature on structural and optical properties of Cu₂FeSnS₄ particles grown via solution approach" International Conference on Advanced Functional Materials and Devices (ICAFMD- 2019), NIT Warangal.

ABSTRACT

Wide bandgap metal oxides offer high resistance to the charge flow, thus have interesting feature of charge storage that eventually can be considered for memory-based applications. Among different wide bandgap metal oxides, gallium oxide (Ga₂O₃) has suitable properties for memory devices. However, high quality Ga_2O_3 films are necessary for utilizing the potential of this material in memory and other electronic devices. The wet-chemical deposited Ga₂O₃ films mostly suffer from quality issues, therefore dedicated efforts to develop high quality Ga_2O_3 films using wet-chemical approach are required. Hence, this thesis work focuses on the development of effective protocols for wet-chemical deposition of Ga₂O₃ nanostructured films and improve the quality of the films. Primarily, the gallium oxide (Ga₂O₃) nanostructures are synthesized using hydrothermal technique. The rice-like nanostructures are obtained in gallium chloride and gallium nitrate precursors, whereas nano-cuboids are formed in the case of gallium acetylacetonate. The as-synthesized nano-cuboids are in the metastable phase " α " and converts to a stable " β " phase after annealing at higher temperature (~850°C). Post synthesis, thermal annealing also results in the creation of nano pores on the surface of these nano-cuboids. Pore size increases with an increase in annealing temperature till 950°C. Further increase in annealing temperature reduces the size of pores and a smoother surface appears. The annealing induced surface restructuring offers significant alteration on nano-cuboid properties that could be beneficial for surface-related applications.

To improve the adhesiveness and other surface properties of the film, direct deposition of precursor solution on substrate using spin coating method is investigated. The spin coated Ga₂O₃ films mostly suffer from surface cracks which hinders its practical application. Hence, removal of surface cracks of the film becomes the next objective of the thesis project, and it is achieved by adding secondary solvent (water) and heat treatment under oxygen environment. The assynthesized film (without water and oxygen) shows cracks all over the surface. De-Ionized (DI) water and oxygen atmosphere act as efficient medium that alter surface energy of thin films when heat treatment is performed. The developed protocols demonstrate crack-free films with suitable electronics properties that can be utilized for various electronics and optoelectronics application. The control over

the grain size of the film is another challenge, hence direct growth of gallium oxide (Ga_2O_3) nanostructured on substrate via chemical bath deposition is further studied. The uniformity, density and crystallite size of the film vary when the pH of precursor solution changes from pH 6 to pH 9. The as-deposited nanostructured film is in hydroxide phase which further converts to a mixed phase (' α ' and ' β '), when heat treated at 600°C. The densely packed Ga₂O₃ nanostructured film is achieved at pH 8, which also shows better electrical conductivity and stable current density. The memristive measurement for densely packed nanostructured film results in R_{OFF}/R_{ON} ratio in order of 10², whereas the V_{set} and V_{reset} values are observed to be 2.7V and -3.1V, respectively.

Further, to tailor the electrical properties of the Ga₂O₃ nanostructured films, doping of Ga₂O₃ nanostructures with different concentration of Cesium (Cs) is studied. The concentration of Cesium (with respect to concentration of gallium) precursors significantly alters the structural, morphological, and electrical properties. Diamond shaped morphology remains intact for lower doping concentration of Cs (1 to 7.5% of Cs molarity with respect to Ga molarity in precursor solution) whereas, when doping concentration is increased (10 to 100% of Cs with respect to Ga molarity in precursor solution) the morphology drastically changed to flower and clustered particles. The electrical conductivity of doped Ga₂O₃ nanostructured films enhanced significantly with incorporation of the cesium. The higher resistance is measured in memristor device when the doping concentration is lesser. As an outcome to this, a resistance ratio (Roff/Ron) of memristor is obtained only 10¹ but doping improved the switching speed of the memory device. Thus, an appropriate doping concentration can be useful to optimize the device performance in term of resistance ratio and switching speed. In summary, wet chemical approach is demonstrated to prepare high quality β -Ga₂O₃ nanostructured films with provision to have significant control over structural, morphological, optical and electrical properties to make them suitable for electronic device applications.

Keywords: Wide bandgap, Gallium Oxide, Nanostructured Films, Wet Chemical Route, Memristors

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ABBREVIATIONS

α	Alpha
β	Beta
γ	Gamma
δ	Delta
Ag/AgCl	Silver/silver chloride
ALD	Atomic layer deposition
CV	Cyclic Voltametry
Cs	Cesium
CVD	Chemical vapor deposition
DI	Deionized water
eV	Electron volt
FTO	Fluorine doped Tin Oxide
FE-SEM	Field emission scanning electron microscopy
FWHM	Full width half maximum
Ga ₂ O ₃	Gallium oxide
Ga ₂ O ₃ IPA	Gallium oxide Isopropyl alcohol
Ga ₂ O ₃ IPA HCl	Gallium oxide Isopropyl alcohol Hydrochloric acid
Ga ₂ O ₃ IPA HCl JCPDF	Gallium oxide Isopropyl alcohol Hydrochloric acid Joint committee powder diffraction data file
Ga ₂ O ₃ IPA HCl JCPDF MOCVD	Gallium oxide Isopropyl alcohol Hydrochloric acid Joint committee powder diffraction data file Metal organic chemical vapor deposition
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Ga ₂ O ₃ IPA HCl JCPDF MOCVD M-S NH ₃ PLD	Gallium oxide Isopropyl alcohol Hydrochloric acid Joint committee powder diffraction data file Metal organic chemical vapor deposition Mott-Schottky Ammonia Pulsed laser deposition
Ga ₂ O ₃ IPA HCl JCPDF MOCVD M-S NH ₃ PLD PEALD	Gallium oxide Isopropyl alcohol Hydrochloric acid Joint committee powder diffraction data file Metal organic chemical vapor deposition Mott-Schottky Ammonia Pulsed laser deposition
Ga ₂ O ₃ IPA HCl JCPDF MOCVD M-S NH ₃ PLD PEALD RF	Gallium oxide Isopropyl alcohol Hydrochloric acid Joint committee powder diffraction data file Metal organic chemical vapor deposition Mott-Schottky Ammonia Pulsed laser deposition Pulsed enhanced atomic layer deposition Radio frequency
Ga ₂ O ₃ IPA HCl JCPDF MOCVD M-S NH ₃ PLD PEALD RF SMU	Gallium oxide Isopropyl alcohol Hydrochloric acid Joint committee powder diffraction data file Metal organic chemical vapor deposition Mott-Schottky Ammonia Pulsed laser deposition Pulsed enhanced atomic layer deposition Radio frequency Source Meter Unit
Ga ₂ O ₃ IPA HCI JCPDF MOCVD M-S NH ₃ PLD PEALD RF SMU UV	Gallium oxide Isopropyl alcohol Hydrochloric acid Joint committee powder diffraction data file Metal organic chemical vapor deposition Mott-Schottky Ammonia Pulsed laser deposition Pulsed enhanced atomic layer deposition Radio frequency Source Meter Unit
Ga ₂ O ₃ IPA HCI JCPDF MOCVD M-S NH ₃ PLD PEALD RF SMU UV XRD	Gallium oxide Isopropyl alcohol Hydrochloric acid Joint committee powder diffraction data file Metal organic chemical vapor deposition Mott-Schottky Ammonia Pulsed laser deposition Pulsed enhanced atomic layer deposition Radio frequency Source Meter Unit Ultraviolet -visible spectroscopy X-Ray Diffraction

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Chapter 1: Introduction and Literature Review

This Chapter provides introductory information of gallium oxide (Ga₂O₃) and its different phases and crystal structures. The structural and electrical properties of ' β ' phase Ga₂O₃ is discussed. Various synthesis and deposition technique of Ga₂O₃ nanostructures and films are reviewed. Recent advancement in wet-chemical approach for deposition of Ga₂O₃ nanostructured film are presented. Further, the motivation, scope and objectives of the thesis are defined. At the end of the chapter, the outline of thesis is given.

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1.1. Introduction

Transition-metal oxide nanostructures (MONSs) have offered significant advancement in magnetic, electrical, and optical applications[1],[2],[3]. In metal oxides, the s sub shell of metallic ions (+ve ions) are filled by electrons but d sub shells are partially filled [4]. These properties enrich them with variety of diverse features, including reactive electronic transitions [5], high dielectric constants [6], large bandgaps [7][8], strong electrical characteristics [9][10] etc. Further development of nanostructures has accelerated the utility of transition metal oxides and resulting in a range of changes in both physical and chemical related characteristics. The connection between the bond length and energy bandgap (Figure 1.1) for several compound semiconductors have shown promising characteristics for practical use. Metal oxide semiconductors having wide bandgap, such as SnO₂ [11][12][13], NiO [14], Cu₂O [15], corundum Ga₂O₃ (α-Ga₂O₃) [16], and α -In₂O₃ [17], has drawn attention related to functionalities toward future of various device applications. Majority usage of wide band gap semiconductor specially gallium oxide is in the field of high voltage and high-power applications. These applications comprise of transport, industries, power transmission etc. However, a new and emergent field of consumer electronics or the application which require low power are also trending now. At present Silicon (Si) is widely accepted and used for electronics and optoelectronic devices. Introduction of other metal oxide semiconductors such as gallium oxide further extend the range of devices and application parameters. The Ga₂O₃ have been incorporated into electronic applications due to its facile synthesis technique, stability in harsh environment, availability of single crystal substrate etc. The Ga₂O₃ further requires more investigation to develop potential properties for selective applications and it is ongoing.

Gallium oxide (Ga₂O₃) occurs naturally in five polymorphs and phases [18]. The subsequent phases, however, must take place under specific circumstances, and the ' α ' and ' β ' are most stable phase. Readily available β -phase is very common, having monoclinic crystal structure with the space group (C2/m), making it an excellent candidate for electronics applications[19]. As a result, a range of methods/techniques for deposition of β -Ga₂O₃ thin films have been developed [20],[21]. Nanostructured thin films are further allowed to use the

potential of nanoscale materials and its unique properties. As a result, several nanostructures of β -Ga₂O₃ were created, including nanoparticles, nanorods[22], prism[24], and spindle structure [25]. The β -Ga₂O₃ cluster nanotubes[23], nanowires were synthesized using gallium arsenide (GaAs) and gold (Au) as a precursor in a VLS method, [26]. Heat treatment in hydrothermal growth was also used to obtain the morphology of nanorods and the quadrilateral prism of GaO(OH) [27]. Similarly, hydrothermal methods have been used to create gallium oxide nanostructures such as nanobelt, nanoribbons, nanowire and nanosheets etc. [28][29]. Nanostructured films behave differently than their bulk materials with same chemical compositions. Depending on the material and deposition process, these films have features that seem columnar, polycrystalline, amorphous, under when observed at molecular level [30],[31],[32]. Synthesis of Ga₂O₃ nanostructures and deposition of films are currently attracting a lot of interest[33],[34],[14], with objective to effective control over structural, optical and electrical properties.



Figure 1.1: Relationship between bond length and energy bandgap for several compound semiconductors used in practical applications. [Reprinted from S.Fujita et al., J. Appl. Phys. 54 (2015) 030101, copyright from IOP Science]

Metal oxide films has also shown excellent potential for data storage, particularly as resistive memory devices which are commonly known as memristors. Memristor (a combination of "memory" and "resistor") technology is regarded as an emerging technology for making high speed storage devices. Current Voltage (I-V) profile of memristor shows hysteresis loop, which allows it to change the conductance states regularly. Storage of data in memory device (memristor) is caused due to materials phenomena like phase change, migration of ions and spin etc., these material properties are basically present as an active layer of the memristive devices. The properties of materials have direct impact on switching time, retention time, resistance ratio and ultra-high-density memory etc, considering this aspect of materials for memristor devices, gallium oxide (Ga₂O₃) has shown his strong candidature among different metal oxides. Ga_2O_3 nanostructured films were used as an active insulating layer of memristors device, were mixed ion conduction were reported for causing memristive behavior, similarly thin film of gallium oxide were incorporated in a memristor to use the device as an artificial synapse [35],[36],[37],[38]. Electronic features like as electron flow, channel creation, surface resistance, and skin resistance are affected by the film quality [39]. Therefore, it is necessary to develop high quality films of Ga_2O_3 with tuning of bandgap, mobility and doping etc. to control the memristor behavior and performance.

1.2. Crystal Structure of Gallium Oxide

Gallium oxide (Ga₂O₃), was traced way back in 1875 by Lecoq de Boisbaudran. [40]. Following his breakthrough, gallium became a popular element, with several gallium-based compounds finding use in a variety of applications. Interest in this material peaked in the 1950s and 1960s, but it faded until the 1990s, when its semiconducting qualities were finally established. Gallium oxide was first thoroughly investigated in 1952 [18], when the polymorphism of Ga₂O₃ was discovered during an investigation of Gallia gel (Al₂O₃- Ga₂O₃-H₂O system) using X-ray and electron diffraction methods. Gallium oxide can exist in a variety of polymorphs as shown in figure 1.2, which are denoted as ' α ' ' β ' ' γ ' ' δ ' ' ϵ ' [41][44]. A transient κ - Ga₂O₃ polymorph has also been discovered [42]. Polymorphs of Ga₂O₃ differ in their crystal space group as well as to the amount of Ga ions coordinated. Under certain circumstances, all these gallium oxide phases may be synthesized. Alpha-gallium oxide (α -Ga₂O₃), falling to space group R3c is rhombohedral in nature, similar to (α -Al₂O) that is corundum in nature [43]. α -Ga₂O₃ polymorph can be synthesized by heating gallium oxyhydroxide (GaO(OH)) in air between 450°C and 550°C.



Figure 1.2: Polymorphs of gallium oxide (Ga_2O_3) ; (a) Alpha-gallium oxide $(\alpha$ -Ga₂O₃), (b) Betagallium oxide $(\beta$ -Ga₂O₃), (c) Gamma-gallium oxide $(\gamma$ -Ga₂O₃) and (d) Epsilon-gallium oxide ε -Ga₂O₃. [Reprinted from J. Zhang et al., Appl. Phys. Lett. 8 (2018) 242102, copyright from APL Materials]

	α	β	γ	δ	3	к
Crystal structure	Corundum	Monoclinic	Cubic defectiv e	Cubic	Pseudo hexagonal	Orthorhomb ic
Space group	R3m	C2/m	Fd3m	Ia3	P63mc	Pna2 ₁
Lattice parameter	a = b = 4.98– 5.04, $c =$ 13.43– 13.62	a = 12.12-12.34, b =3.03and 3.04, $c = 5.80-5.87$	<i>a</i> = 8.24– 8.30	<i>a</i> = 9.4–10	<i>a</i> = 2.90, <i>c</i> = 9.25	a = 5.05, b = 8.69, c = 9.27
Effective mass (m _e *)	0.276 <i>m</i> 0	0.342 <i>m</i> 0	-	-	0.24 <i>m</i> 0	-
Density (gcm ⁻³)	6.48	5.94	5.76– 5.93	4.98– 5.18	5.88-6.06	-
Bandgap (eV)	5.2 and 5.3	4.5–4.9	4.5–5.0	-	4.5-5.0	4.6–4.9
Electron mobility(cm ² Vs ⁻ ¹)	24	200	1.6	-	-	-

Table 1.1: Comparison of different phases of gallium oxide.

Beta-gallium oxide (β -Ga₂O₃) belongs to the space group C2/m and is monoclinic. The ' β ' phase Ga₂O₃ can be synthesized or formed by providing heat treatment to other polymorph of Ga₂O₃ in air at high temperatures [45]. The third form, gamma-gallium oxide (γ -Ga₂O₃), is accepted to have a faulty cubic spinel type structure same as MgAl₂O₄ structure belonging to Fd3m space group [46]. A study by Playford et al. demonstrates, original notion of α -Ga₂O₃ being just a nanocrystalline version of β -Ga₂O₃ and not as separate polymorph [5]. In case of β -Ga₂O₃, Roy et al. detected powder X-ray diffraction (XRD) pattern that was unique when compared to other available polymorphs, still they were unable to determine the polymorph's structure [45]. Roy et al. in their work reported, synthesis of delta-gallium oxide (δ -Ga₂O₃) and kappa-gallium oxide (κ -Ga₂O₃)respectively, in the year 1952 [46]. They hypothesized that the Ga₂O₃ form had a C-type rare-earth structure which is similar to Mn₂O₃ and In₂O₃.

1.3. Structural, optical, and electrical properties of β-Ga₂O₃

Initially the lattice parament of beta phase ' β ' of Ga₂O₃ were published by Kohn et al., and Geller et al. where they reported computational study about structure and found out that it belongs to C2/m group. Tests for pyroelectricity and negative piezo reinforced the conclusion that the crystal's most likely space group was C2/m [47][48]. Chase and Walton observed that crystal's structural symmetry looked to be weaker than that of the r2/m point group. Optical and morphological examinations further corroborated the attribution of lower symmetry. They proposed crystal cell of β -Ga₂O₃ has a pseudo symmetrical triclinic structures and belong to P1 space group. However, the finding has been called into doubt, by other researchers in the subject [49]. As Geller pointed out, there had been countless earlier studies on crystals β -Ga₂O₃ that had revealed no departure from the monoclinic structure [50]. As a result, any divergence from the more symmetric structure must be very tiny. Ahman et al. reported the most current and precise investigation of the β -Ga₂O₃ crystal structure [51]. Despite the fact that, few results deviate slightly from published data of Konh and Geller, the accuracy of reported study was nearly ten time more than earlier publications. Study over the diffraction patterns proved the presence of C-centered monoclinic cell belonging to C2/m space group. Figure 1.2(b) depicts a β -Ga₂O₃ unit cell, which can be described crystallographically as two inequivalent Ga locations, one with tetrahedral geometry Ga (I) and second with octahedral shape Ga(I) and (II) respectively. The oxygen (O₂) ions were organized in disordered cubic closed-packed array, that are labeled as O(I), O(II), and O(III) in three distinct crystallographic positions [51]. Other two O_2 atoms are trigonally coordinated, while one is tetrahedrally coordinated. Most studied polymorph of Ga_2O_3 is the beta (β) polymorph. Apart from ' β ' phase rest of the polymorphs are metastable in nature and generally

convert when heat treated at temperatures over 750-900°C, whereas β -Ga₂O₃ is the only stable polymorph across wide temperature range till melting point of Ga₂O₃. Figure 1.3 depicts the relationships between the available phases of Ga₂O₃ and how the metastable phases gets converted to the most stable phase of β -Ga₂O₃. Because of the thermal stability of β -Ga₂O₃, methods like vapor phase epitaxy and crystallization from a melt ingot can be used to manufacture bulk single crystals and epitaxial films. Because of its availability and exceptional qualities, β -Ga₂O₃ has piqued the interest of researchers more than other polymorphs of Ga₂O₃. Even though β -Ga₂O₃ is extensively described in comparison to other polymorphs of Ga₂O₃, still some differences are present in the published data on material characteristics.



Figure 1.3: Transformation of phases of gallium oxide. [Reprinted from R. Roy et al., J. Am. Chem. Soc. 74 (1952) 719-722, copyright from American Chemical Society]

There have been numerous theoretical studies on electronic structure of β -Ga₂O₃. Computational technique like density functional theory (DFT) offer a good qualitative representation of the electrical structure and estimated band gap values [52]. Since, DFT is based on ground-state theory, the exchange-correlation

potential between excited electrons is overestimated. Using hybrid density functional theory, more accurate findings were reported. Hybrid functional theories provides accurate findings for energetics and structure, as well as bandgaps that are considerably more in accordance with the experiment [53]. Mostly various analysis demonstrated similar type of conclusions: conduction-band minimum in β -Ga₂O₃ is a point while valence band is flat. However, due to valence bands inadequate dispersion, its precise placement has little effect on the amplitude of the bandgap. According to H. He et al., valence band maximum for β-Ga₂O₃ is almost degenerate at the Mk-points, with the energy being at 0.03eV. Figure 1.4 shows the high symmetry which led to more degeneracy and its electronic band structure to be an indirect bandgap of 5.03eV [43]. M. Janowitz et al. conducted an experimental study on the β -Ga₂O₃ electrical structure [54]. The researchers used angle-resolved photoemission (ARPES) to determine basic difference and band structure along the high symmetry axes. Comprehensive analysis of ARPES bands along significant high-symmetry lines revealed practically complete agreement with the hypothesis. The effective masses of Ga₂O₃ also agreed well with the theory.



Figure 1.4: Band structure of β -Ga₂O₃. [Reprinted from H. He et al., Phys rev. B 74 (2006) 195123, copyright from American Physical Society]

Pure stoichiometric β -Ga₂O₃ is colorless and mostly transparent for UV-C region in light spectrum due to its broad bandgap. The coloration of the crystals, on the other hand, might be induced by contaminants. Galazka et al. discovered a high link between conductivity and optical characteristics [55]. Insulating β -Ga₂O₃

crystals were either colorless or had a mild yellowish coloration produced by slight absorption in the visible blue range. The theoretical refractive index of Ga_2O_3 was predicted from first principle study and experimentally determined for bulk single crystals and thin films. For Ga₂O₃ single crystals formed using the floating zone approach, Bhaumik et al. assessed temperature-dependent refractive index along the [010] crystallographic direction and the direction perpendicular to the (100)plane. They also calculated the Sellmeier equation coefficient for wavelengths ranging from 0.4 to 1.55um at temperatures ranging from 30 to 175°C. It was determined that the refractive index increases linearly with temperature, with the refractive index's thermal coefficient being roughly $10-5^{\circ}$ C. Ga₂O₃ may emit up to three distinct bands of light, including green (2.4 eV), blue (2.8-3.0 eV) and UV (3.2-3.6 eV). The sample preparation technique and impurities have little effect on UV band emission. Given that 4.8 eV is bandgap of Ga_2O_3 , it is exceedingly improbable that ultra violet luminescence is caused by band edge recombination. Instead, the UV band is generated by the recombination of self-trapped holes and free electrons. In Ga_2O_3 crystals, there is a link between the intensity of the blue band and resistivity [34], suggesting that oxygen vacancies, which are also engaged in the blue emission process and are assumed to be responsible for n-type conductivity.

1.4. Deposition of β-Ga₂O₃ films

The surface properties of the films and stability both plays a crucial role in performance of the devices. The surface properties and topography of the film depends upon the way the film is deposited, whereas the stability is subjected to the material properties. Gallium oxide (Ga₂O₃) films were deposited using distinctive route like chemical and physical deposition techniques. For understanding mechanism of deposition some of relevant work is discussed here. Laser pulses are used in pulsed laser deposition (PLD) to ablate material from target. In pulsed laser deposition (PLD), laser shots are generally used to ablate material from a target. On hitting the target with laser pulse, a plasma plume forms that is generally directed in the direction of substrate. Yu et al. used a krF excimer laser to deposit Ga₂O₃ epitaxial films on (0001) c plane sapphire substrate at 200mT of oxygen partial pressure. They came to the conclusion that amorphous films could be formed at temperatures up to 400°C. Gaining enough thermal energy

by atoms to migrate to the surface when the (substrate) temperature escalates from 400° C to 850° C, resulting in creation of (201) oriented films [56]. Figure 1.5 shows the work of Ou et al., where they reported improved crystalline quality of Ga₂O₃ film deposited at substrate temperature of 850° C. Films showed sudden absorption edge at a deep UV region (around 250 nm), when substrate temperatures ranged from 550° C to 1000° C, they also observe that as the temperature increased the bandgap also varied form 4.56 eV to 4.87 eV [57]. The conductivity of thin films was investigated by Stefan et al. for Ga₂O₃ film of (201) orientation on sapphire with a SiO₂ concentration of 1%. Films produced at 650°C substrate temperature as well as at an oxygen pressure of $6x10^{3}$ mbar had a conductivity of 0.2 Scm⁻¹ [58].



Figure 1.5: Ga_2O_3 thin films deposited via pulsed laser deposition technique: (a) XRD pattern of Ga_2O_3 films grown at different temperatures, (b) XPS spectra showing Ga_2P_3 core level of Ga_2O_3 films, (c) optical coefficient versus photon energy of Ga_2O_3 films and (d) conductivity measurement of Ga_2O_3 thin films with an effect of substrate temperature. [Reprinted from S. L. Ou et al., Mat. Chem. Phys. 133 (2012) 700-705, copyright from Elsevier BV]

In PLD, generally there is no use of catalyst in the deposition procedure therefore there in minimal contamination of the product. PLD involves small substrate deposition thus large-scale synthesis is a challenging task. ALD (atomic layer deposition) is a similar technique for regulating thickness of film up to single atomic layer while retaining uniform nature of films [59]. Shan et al. performed synthesis of Ga_2O_3 thin film via plasma enhanced atomic layer deposition (PEALD) for studying structural and optical properties of obtained thin film. Silicon (100) and sapphire (001) were the substrate on which the films were deposited. The structural study showed (Figure 1.6) amorphous nature of asdeposited and annealed films (at low temp.), bus as they annealed to higher temperature (700°C) films showed a monoclinic structure of (400) orientation confirming the beta phase formation. Film roughness is found out to be 4Å which is considered to be smooth as compared to other ways [60]. ALD grown films shows minimal dispersion and with that the refractive index were smaller for thin film at lower temperature as compared to the films annealed at higher temperature [61].



Figure 1.6: Ga_2O_3 thin films grown over silicon and sapphire substrate using plasma enhanced atomic layer deposition (PEALD); (a) SEM micrograph of as-deposited Ga_2O_3 thin film patterned over SiO₂/Si substrate, (b) XRD pattern of as-deposited and annealed Ga_2O_3 films at different temperature, (c) leakage current characteristics and (d) bandgap of Ga_2O_3 films. [Reprinted from F. K. Shan et al., J. Appl. Phys. 98 (2005) 023504, copyright from Applied Physics Letters]

When considering the condition for relatively large area deposition, chemical vapor deposition (CVD) technique is considered. Different phases of Ga_2O_3 can be grown using CVD techniques. Among CVD technique, metalorganic vapor phase epitaxy (MOCVD) deposition of (Ga_2O_3) thin films on different substrates has been reported to achieve diverse epitaxial orientations [62]. Sun et

al. fine-tuned flow rate of hydrochloric acid (HCl) in MOCVD reactor to precisely regulate the phases of Ga₂O₃, then fabricated solar-blind photodetectors with good performance based on different phases of Ga₂O₃ [63]. Using trimethylgallium (TMGa) as gallium precursor Kim et al. deposited Ga₂O₃ thin films on sapphire substrates by using same technique, where they reported changes occurred to the films at deposition temperature (750°C–1050°C) [64][65]. Chen et al. worked on development of pristine ' β ' and ' ϵ ' phases of Ga₂O₃, this was achieved by controlling the pressure at constant temperature of 500°C [66]. S. Lee et al. demonstrated the growth of homoepitaxial single crystal of β -Ga₂O₃ via mist chemical vapour deposition method (Figure 1.7). It was observed that for optimum growth of films was at 700° - 800°C, doping of tin (Sn) were also incorporated to the study and they found out doping caused variation in the conductivity as well as the carrier concentration also varied from 10¹⁸ cm⁻³ to 10²⁰ cm⁻³ [67].



Figure 1.7: MIST-CVD grown Ga₂O₃ thin films (a) XRD patterns of unintentionally doped Ga₂O₃, (b) optical transmission curve of doped Ga₂O₃ films, (c) Cross-sectional schematic image of β -Ga₂O₃ Schottky diode and (d) I–V characteristics between ohmic contacts on n-type doped β -Ga₂O₃ substrates. [Reprinted from S.D. Lee et al., Appl. Phys. Lett. 55 (2016) 1202B8, copyright from The Japan Society of Applied Physics]

In sputtering deposition process, positively charged ions eject atoms from the target material. Jianjun et al. discovered alteration of in various properties like (electrical and optical) on varying thickness of Ga₂O₃ films over indium tin oxide (ITO) substrate [68]. Chengyang et al. demonstrated small sheet resistance of 225.5 ohm⁻² by alternating layers of Ga₂O₃ (i.e. (25 nm)/ITO (11 nm)), it has lowest transmittance ~62.9% for two periods of 72 nm thick at 300 nm thick film [69]. The above-described methods are among the best suited methods for deposition of Ga₂O₃ thin film. However, limitations like good step coverage, thickness of a films, dependency over the thickness leading to structures containing voids cannot be avoided while the deposition process. Using deposition procedure that can create higher step coverage as possible is one efficient strategy to prevent such issues. Recently, synthesis of nanostructured films by soft-chemistry pathways at low temperatures has piqued the interest of many researchers due to evident benefits such as economies, energy efficiency, and environmental friendliness.

1.5. Wet chemical deposition of β-Ga₂O₃ nanostructured films

Wet chemical deposition offers easy and effective pathways to prepare nanocrystals of gallium oxide. Synthesis of Ga₂O₃ nanostructures based thin films is also been investigated for its usage in multipurpose application, Sato and Nakamura reported synthesis of Ga₂O₃ nanostructures by precipitating gallium oxy hydroxide (GaOOH) in a solution, which was resultant of mixing gallium chloride (GaCl₃) and various alkalis reagents (NH₄OH, NaOH, NaHCO₃, Na₂CO₃, KOH) [70]. In other report, Hamada et al. synthesized monodispersed GaOOH particles using sulphate reagent with diameters of 100 nm by hydrolysis at high temperatures [71]. Avivi et al. followed sonochemical process to create cylindrical (scroll-like) stacked GaOOH crystals using little quantity of metallic gallium (Ga). Forcing Ga³⁺ ions to hydrolyze in water in presence of urea, Tas et al. reported synthesis of GaOOH single crystals with quadrilateral prisms and spindle-like morphology, after calcination spindles nanostructures lost their morphology, whereas quadrilateral prisms remains as it is even after calcination [72]. Different phases of Ga_2O_3 (i.e. ' α ' and ' β ') nanotubes was reported via using an alumina membrane and immersing it in a solution of amorphous Ga₂O₃.H₂O which was followed by drying and heating of the alumina membrane at 500°C [73]. Patra et al. used a microwave oven to synthesize submicrometer-sized rods of GaOOH via refluxing an aqueous solution of gallium nitrate $(Ga(NO_3)_3)$ and ammonium hydroxide (NH₄OH) [22]. Ristic et al. investigated use of sol-gel technique synthesizing

gallium oxyhydroxide and gallium oxide via hydrolysis of gallium chloride (GaCl₃) and gallium isopropoxide in aqueous solution of tetramethylammonium hydroxide [74]. Zhang et al. described green hydrothermal technique for the synthesis of GaOOH nanorods at 200°C by using Ga₂O₃ and water as starting materials without the need of a surfactant. Non-hydrothermal synthesized (Ga₂O₃/GaOOH) nanostructures are frequently threadlike or belt-like, with significantly longer lengths and smaller widths than those manufactured using hydrothermal procedures. The shape of nanostructures (Ga₂O₃ or GaOOH) fabricated using hydrothermal technique is often rod shaped or spindle shaped crystal, having width of 100 nm resulting to a modest surface area to volume ratio, as shown in figure 1.8 [75].



Figure 1.8: Hydrothermally synthesized Ga₂O₃ nanostructures;(a) XRD pattern of as synthesized powder, (b) TG-DSC curve of the nanostructures and (c),(d) TEM image of the nanostructures. [Reprinted from Y.C. Zhang et al., Mater. Lett. 61 (2007) 1497-1499, copyright from Elsevier B.V.]

For annealing temperatures above 550 °C, the spin-coating Ga_2O_3 passivation films are changed from amorphous to crystalline as reported by Y. Xiang et al. [76] as shown in figure 1.9.



Figure 1.9: Spin coated Ga₂O₃ film on silicon substrate; (a) SEM and HRTEM of deposited Ga₂O₃ films and (b) XRD pattern of Ga₂O₃ films. [Reprinted from Y. Xiang et al., J. Alloys Compd. 699 (2018) 1192-1198, copyright from Elsevier B.V.]



Figure 1.10: Ga₂O₃ film deposited via sol-gel synthesis method; (a) X-ray diffraction patterns of Ga₂O₃ films at different temperatures, (b) absorption coefficient of Ga₂O₃ films prepared at different temperatures and (c) photoconductive measurement of Ga₂O₃ films deposited at different temperatures. [Reprinted from Y.Kokubun et al., Appl. Phys. Lett. 90 (2007) 031912, copyright from Applied Physics Letters]

As illustrated in figure 1.10, Y. Kokubun et al. employed the sol-gel process to manufacture Ga₂O₃ thin films by heat treating at 600°C, to use in a solar blind UV photodetector [77]. H. Shen et al. described how to produce polycrystalline
Ga₂O₃ films for solar blind photodetector applications using the sol-gel technique, they demonstrated a response time in sec (0.10) and a decay speed of 0.10 sec, suggesting response devices for solar blind photo detectors to be relatively fast [78]. Photoconductive detectors using planar geometry were prepared via sol-gel technique using indium doped gallium oxide films and growing them on sapphire substrates for UV light detection. [79].

In wet chemical approach, large-scale manufacturing with rationally controlled synthesis is possible, even other attributes like surface effects and quantum size effects, the form and size of nanostructures can have a significant impact on the characteristics of materials at the nanoscale. This exciting research provide realistic approaches for the synthesis of nanocrystals with customizable shape and size, considerably more rational control over nanocrystals is still required, particularly the ability to design and optimize nanostructures as per requirement. Similarly, cost-effective mass manufacture of nanocrystals is necessary to meet future demand for nanoscale applications from an industrial viewpoint. Unfortunately, while many new synthetic techniques are capable of manufacturing high-quality nanocrystals with strong monodispersity, they can only create sub-gram amounts of samples in the lab.

1.6. Optical and electrical properties of β-Ga₂O₃ nanostructured films

Optical behavior for the nanostructures can be seen from two perspectives. Firstly, how they are found naturally and secondly to be made up of aggregates of crystallites of varying size and orientation, as well as varying degrees of defects. Bandgap of Ga₂O₃ films depend on various parameter. Higher Bandgap (Eg) values for Ga₂O₃ films is attributed to the amorphous structure. When compared to other transparent wider bandgap oxides materials, these two variables add disorder, resulting in a somewhat greater bandgap obtained for films fabricated in ambient atmosphere and temperature [43]. Figure 1.11(a) shows the bandgap for Ga₂O₃ deposited via E beam evaporation using high purity single crystal of Gd₃Ga₅O₁₂ as a target material, bandgap to be 4.4eV was reported by M. Passlack et al. [2]. When the Ts changed from 25–800°C bandgap varied from 4.66 to 5.17eV, due to structural disordered induced in the crystalline structure of the films grown at lower temperatures, which may be caused due to excess oxygen to support this behaviour. In general, Ga_2O_3 films (amorphous and nanocrystalline) exhibit great transparency in the visible spectrum domain. Ga_2O_3 films formed at 25°C have an band gap value of 5.17 (0.02) eV, which drops to 4.96 (0.03) at 800°C [80][81].

To understand the electrical properties of Ga₂O₃, the role of defects should be understood. A close link between variation in O₂ partial pressure with electrical conductivity throughout β -Ga₂O₃ processing (growth characteristics, synthesis parameter, annealing) led to the hypothesis that O₂ vacancies were entirely liable to give Ga₂O₃ semiconducting characteristic. When formed at low partial pressures of oxygen, undoped β -Ga₂O₃ is an insulator, but when synthesized at higher partial pressures of oxygen, it changes to an n-type semiconductor. Because of the donorlike doping phenomenon, Cojocaru et al. explored the electrical characteristics of β -Ga₂O₃ and determined that due to lattice oxygen deficit in non-stoichiometric β -Ga₂O₃ films the conductivity varied at high-temperature [83].



Figure 1.11: (a) The band gap of this Ga_2O_3 film prepared at 4.4 eV, which is the same as the band gap of bulk Ga_2O_3 . [Reprinted from M. Passlack et al., J. Appl. Phys. 77 (1995) 686, copyright from Journal of Applied Physics] and (b) transmittance behavior of Ga_2O_3 films as an effect of temperature. [Reprinted from S.S. Kumar et al., J. Phys. Chem. C 117 (2013) 4194-4200, copyright from American Chemical Society].

Harwig et al. reported β -Ga₂O₃ film exhibits both electronic and ionic conductivity ranging from room temperature to higher temperature (27-627°C) which disrupt AC/DC conductivity [83]. At high temperatures, non-stoichiometric (β -Ga₂O₃) nanostructures is entirely follow n-type semiconductor materials

characteristics. For a long time, electrical conductivity of intrinsic n-type β-Ga₂O₃ has been ascribed to oxygen (O₂) vacancies, as with other metal oxides. Ueda et al. synthesized β -Ga₂O₃ single crystals and studied the relation between electrical conductivity with respect to oxygen flow rate under controlled circumstances [84]. Nitrogen (N₂) doped β -Ga₂O₃ synthesized in pure oxygen (O₂) environment was found to be a non conducting (insulator), but crystals produced in a pressure ratio of 0.4: 0.6 combination of N₂ and O₂ gases displayed the highest electrical conductivity. In contrast, intentional doping is a familiar strategy for improving electrical characteristics of semiconductors. Numerous studies show that intentionally doping β -Ga₂O₃ with silicon (Si), tin (Sn), zinc (Zn), and other elements enhances conductivity and free-carrier concentration. Villora et al. demonstrated that on purposeful doping with Si, electrical conductivity of β -Ga₂O₃ increases by three orders of magnitude due to free charge carrier $(10^{16}-10^{18} \text{ cm}^{-3})$ that might match to the effective Si impurity [85]. As a result, purposeful donor doping not only improves Ga₂O₃ electrical characteristics, it has the potential to increase the performance and sensitivity of Ga₂O₃ based gas sensors.

1.7. β-Ga₂O₃ nanostructured films toward resistive memory devices

One of the primary methods for storing information as data is the storage of charge, as in dynamic random access memory (DRAM), flash memory and static random access memory (SRAM) [86]. Information (data) generally get stored when there is change in the atomic configurations or alignment of ferromagnetic metal layers in a new class of memory devices [87]. Because of the resistance change, these devices are known as resistive memory devices. Because of their connection to the circuit theoretic idea of memiristive systems, they are sometimes referred to as memiristive devices as shown in figure 1.12 [88].

A memristor has two switching state: high resistance state (HRS), it's a condition when the active layer offers more resistance to the flow of charge and low resistance state (LRS) when the active layer offers negligible resistance to charge as shown in figure 1.13. Metal oxide is commonly utilized as the insulating layer in memristors with metal contacts as the top and bottom electrodes. The

reduction of an oxide material creates a metallic conduction route in the direction of the anode.



Figure 1.12: Schematic of memristor: top contact (Metal)/insulator/bottom contact (metal) [MIM] structure, where acting insulating layer is Ga_2O_3 in our case. [Reprinted from B. Mohammad et al., Nanotechnology Rev. 5 (2016) 311-329, copyright from DE GRUYTER]

The mechanism of memristor can be understood from figure 1.13. On applying a potential or any external stimulus to the device the charge starts to migrate from top metal contact as shown in figure 1.13(A). Once the charge starts migrating, at a certain potential a channel is created between the top contact and bottom contact as shown in figure 1.13 (B). As a result, the device gets transacted from high resistance state towards low resistance state, and system's SET process is initiated. Once the channel is form, increase in voltage increases the channel width between the two contacts as shown in figure 1.13 (C). This state remains for a specific period of time known as retention time. Once the external stimuli or potential is removed the channel between the contacts break and some of the charge remains close to the bottom contact as shown in figure 1.13 (D). The oxidation of the insulating layer materials border on the anode causes the device to reverse switch from low resistance to high resistance. This procedure is known as the RESET procedure [90]. Basically, when the external stimuli is removed even at that stage the information of data is stored in the form of charge in the insulating layer. This phenomenon is basically the fundamental principle of memristor device.



Figure 1.13: Schematics of resistive switching: (A) beginning with the formation of conductive channel, (B,C)followed by set process (electroforming conductive filaments) (On state, HRS to LRS transition), and (D) finally reset process (rupture of filament) (Off state, LRS to HRS transition). [Reprinted from B. Mohammad et al., Nanotechnology Rev. 5 (2016) 311-329, copyright from DE GRUYTER]

Properties like wide bandgap, high saturated electron velocity, moderate thermal conductivity, fair electron density, relatively high mobility etc., let Ga₂O₃ to be taken into consideration for memory devices. These electrical properties are indirectly linked to the structural presences of the Ga₂O₃ nanostructured films. From last two decade, reversible bipolar resistance switching characteristics for Ga₂O₃ thin films have been produced and investigated [91]. Gao et al. investigated the effect of top electrode materials on the bipolar resistive switching behaviour of Ga₂O₃ films and found the role oxygen vacancies migration near the electrode area is important in the resistive switching process [91]. The modification of the Schottky barrier at the Pt/GaOx interface caused by oxygen vacancy migration has been postulated to showcase switching mechanism in Pt/GaOx/ITO based device, whereas switching in Ti/GaOx/ITO device has been attributed to the redox reaction taking place between Ti and GaOx interface as shown in Figure 1.14.

Resistance switching properties with an oxygen migration mechanism have been discovered in a range of oxide materials [92] [93]. Ga₂O₃, a binary metal oxide with a large band gap of 4.9 eV, is regarded as suitable candidate for memory device, due to its inherent high resistance and extraordinarily sensitive oxygen conductivity (e.g.- RRAM) [94][95]. Discovery of unipolar resistance switching in Ga₂O₃ films is always looked due to its existing material library, but it would also provide information that could help researchers better understand the resistance mechanism [96]. By directly witnessing reversible enrichment and depletion of oxygen ions at the blocking electrodes in response to bias polarity, Aoki et al. proved the significance of oxygen ion mobility to create bipolar memristive activity in Ga₂O₃ films [36]. GaOx homogeneous resistive switching, on the other hand, happens progressively across the bias period of sub milliseconds to seconds. The time dependency, as shown in figure 1.15, enables for the reversible modification of the I-V hysteretic loop.



Figure 1.14: (a) I-V curves for Pt/GaOx/Pt device , with an inset showing the ln(I)-V1/2 plot for the HRS in the under positive bias, (b) I-V properties of Ti/GaOx/ITO device at room temp. with inset showing curves in a double Napierian logarithmic plot. [Reprinted from X.Gao et al., Appl. Phys. Lett 97 (2010) 193501, copyright from Applied Physics Letters]

The fabrication of the device can be still simplified with the available methodologies like wet chemical route. Ga₂O₃ can be easily modified as per the desired conditions using the wet chemical route. Deposition of Ga₂O₃ thin film can be persuaded with several other procedures apart from the above reviewed work. Doping of the Ga₂O₃ nanostructures can be simpler and more cost effective by using wet chemical route as a result faster switching time, longer retention ratio of data can be managed. Thus, wet chemical route for deposition of Ga₂O₃ nanostructures could be interesting and potential method for future prospects of its applications. Figure 1.15 explains the schematic representation of transition between HRS and LRS due to flux of oxygen vacancies (C_v) and conductivity (σ), initially these two are separated with a certain value which can be seen from figure 1.15(4). Eventually after the potential is removed the gap between the two goes to the initial state which can be seen at figure 1.15(5).



Figure 1.15: Under electrochemical potentials, GaO_x resistive switching is studied based on oxygen vacancy donor drift diffusion. [Reprinted from Y. Aoki et al., Nat. Comm. 5 (2014) 3473, copyright from NATURE]

1.8. Scope and objectives of thesis work

The metal oxide semiconductor materials have demonstrated a strong presence in a variety of applications such as photodetector, gas sensing, electronics device etc. Traditional semiconductors like ZnO, TiO₂ are mostly investigated for fabrication of resistive memory devices. Since wide band gap offers more resistance to the flow of charge, thus an interesting nature of charge storage can be explored which eventually can be considered for memory-based application. However, wide bandgap metal oxide i.e., Ga₂O₃ has received limited interest in the field of resistive memory devices. Mostly physical vapor deposition method is deployed to deposit the Ga₂O₃ films. These methods result in good quality films, but the large-scale manufacturing and large area deposition is the direction where the above-mentioned techniques are still progressing. Therefore, wet chemical techniques are also gaining attention due to possibility of large area deposition and large-scale manufacturing. This thesis work also focused on the wet-chemical approach for development of Ga₂O₃ nanostructured films and improvement of films qualities/properties. The specific objectives of the thesis project are as follows:

- Synthesis of Ga₂O₃ nanostructures using wet-chemical approach for film deposition.
- Deposition of Ga₂O₃ nanostructures film using spin coating process and fabrication of high-quality film by removal of the surface cracks of the films.
- Direct deposition of nanostructured Ga₂O₃ films on conducting substrate using single step aqueous route and controlling the density of the nanostructures to achieve film.
- Deposition of doped Ga₂O₃ nanostructured films to control the applied electrical properties.
- Investigation of the electrical properties of Ga₂O₃ nanostructures films and study applicability of these films for resistive memory devices.

1.9. Thesis outline

The thesis is organized into six chapters. Chapter-1 gives a brief introduction of gallium oxide (Ga_2O_3) that comprises of different physical properties. Brief description of '\beta' phase of Ga2O3 is discussed based on its structural and electrical properties. Various fabrication technique for synthesizing Ga₂O₃ films is reviewed in this chapter. The chapter also present recent literature review on the Ga₂O₃ nanostructured film prepared using wet-chemical approach and their properties. The chapter 2 discuss about wet chemical approach to synthesize Ga₂O₃ nano-cuboids. The study demonstrates the influence of annealing on the surface. Pore size increases as the annealing temperature rises to 950°C. However, annealing at a higher temperature (1000°C) reduces the size of the nanopores, resulting in a smooth surface of the nano-cuboid. On a time, scale basis, surface restructuring of the nanostructure is known to correlate to distinct processes of chemisorption induced restructuring and metal-oxide interfaces. Furthermore, the oxidative situation induces lattice atom diffusion, resulting in significant and minor surface oxide layers, surface remodeling, and lattice rearrangement. The influence of temperature on Ga₂O₃ might be very important in understanding the material's stability. Understanding the surface characteristics and restructuring

behaviors of Ga₂O₃ nanostructures at high temperatures will allow us to develop and choose the best materials for dependable power electronic devices. Chapter 3 investigate different methodology of wet chemical based approach for depositing Ga₂O₃ films via spin coating method. Crack-free Ga₂O₃ films were synthesized in a variety of circumstances, including those without secondary solvent, with secondary solvent, secondary solvent with heat treatment in open air, and oxygenrich settings. Use of deionized (DI) water in the mixing of gallium precursor and organic solvent, followed by thermal treatment of the produced film under oxygenrich conditions., satisfactorily cures surface fractures in Ga₂O₃ films. The presence of oxygen during film production is attributable to a considerable increase in the intensity of the (XRD) peak for crack-free films and a spectral (Raman) shift of 1 cm⁻¹. The average roughness of crack-free film, as measured by AFM, is around 0.48 nm. Current-Voltage measurement reveals a greater current density (A.cm⁻³) value in crack-free films, which increases further with higher-temperature annealing. This crack-free Ga₂O₃ film may be used to create efficient electronics devices. In chapter 4, To make Ga₂O₃ films, a single step beaker chemical approach is employed to deposit GaO(OH) based nanostructured film at a lower temperature before annealing. The deposition carried out at 60°C in a beaker and hotplate with single precursors, making it a realistic and simple technique for wide area deposition of Ga₂O₃ films. Controlling the precursor pH, for example, results in larger crystallites and denser Ga₂O₃ nanostructures. A pH of 8 is optimal for the formation of a dense and compact Ga₂O₃ nanostructures layer. When films were annealed at 600°C, the structural investigation indicated the existence of " α and β " phases. Gallium oxide nanostructures have a diamond-like shape and maximal UV absorption due to their broad bandgap characteristics. The charge carrier density (ND) of the gallium oxide nanostructure sheet is 10^{17} cm⁻³. After testing for memristive behavior and annealing at 600°C, the resistance ratio (R_{OFF}: R_{ON}) is 10^2 , with reset and set voltages of -3.1V and 2.7V respectively. The novel method is simple and looks to be favorable for large-scale gallium oxide film deposition, which might lead to a wide range of electronics and optoelectronic applications. Chapter 5 discusses cesium doped gallium oxide nanostructures, synthesized using single step aqueous technique. Cs doping concentrations in precursor solution of Ga₂O₃ is varied from 1- 100% (Cs molarity with respect to Ga molarity in precursor solution) maintaining same pH value of 8. Doping altered the structural, morphological, electrical, and memristive properties of nanostructured films. The structural presence of Cs ions was determined by X-ray diffraction (XRD) and shifting of the structural plane (401) verifies the doping of cesium ions into the proximity of Ga₂O₃. When 50% and 100% Cs molarity with respect to Ga molarity is taken in precursor solution, it results to form dicesium oxide (Cs₂O). The lower amount of doping concentration slightly changes the film conductivity but when high amount of dopant is introduced significantly high increase in conductivity is measured as compared to pristine Ga₂O₃ nanostructures. The memristive behavior of the nanostructured films is also tested, which showed lower doping concertation is favorable for memristive behavior Resistance ratio of 10^1 was observed which is one order lower as compared to pristine Ga₂O₃ nanostructured films.

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Chapter 2: Wet-chemical synthesis of β-gallium oxide nano-cuboids and surface restructuring by thermal annealing

Gallium Oxide (Ga₂O₃) nanostructures are synthesized using a hydrothermal approach and the effect of different gallium precursors on the morphology of gallium nanostructures is studied. The rice-like nanostructures are obtained in gallium chloride and gallium nitrate precursors, whereas nano-cuboids are formed in the case of gallium acetylacetonate. The size of the edge defined nano-cuboid is in the range of $0.6\mu m \times 0.3\mu m \times 0.2\mu m$. The as-synthesized nano-cuboids are in the metastable phase " α " and converts to a stable " β " phase after annealed at a higher temperature (~ 850°C). Post synthesis thermal annealing also results in the creation of nanopores on the surface of these nano-cuboids. Pores size increases with an increase in annealing temperature till 950°C, further increase in annealing temperature reduces the size of pores and a smoother surface appeared. The annealing induced surface restructuring offers significant alteration on nano-cuboid properties that could be beneficial for surface-related applications.

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2.1. Introduction

The wide bandgap materials have shown excellent potential for optoelectronics, microwave, electroluminescent devices, transparent coatings, energy devices and power electronics applications [1]. Gallium oxide (Ga₂O₃) is a wide-bandgap semiconductor, hence transparent for visible light and suitable for high voltage- high power electronic devices [2]. Further, the high intrinsic carrier mobility of 10^{17} – 10^{19} cm³, higher critical breakdown field 8 MV/cm, Baliga figure of merit of more than 3000 switching frequency, excellent power density and heat dissipation factor make gallium oxide a potential candidate [3-8]. In nature, gallium oxide can be found in different polymorphs stated as α , β , γ , δ and ε phases [9]. However, the occurrence of all the above phases are required some specific conditions and $\alpha,\,\gamma,\,\delta,$ and ϵ phases are metastable in nature. The $\beta\text{-phase}$ is more abundant and has a monoclinic crystal structure with C2/m space group and it has been proposed as a suitable candidate for power electronic devices [10]. Typical fabrication of a power electronic device includes the deposition of gallium oxide thin films. Therefore, the β -phase gallium oxide thin films have been fabricated by a variety of methods/ techniques [11]-[12]. In which, the nanostructure-based thin films offer the utilization of distinguished properties of nanoscale materials as compared to bulk film. Consequently, different nanostructures such as nanoparticle, nanorods[13], nanotubes [14], quadrilateral prism [15] and scroll-like spindle structure [16] of β -Ga₂O₃, were synthesized. The synthesis of β -Ga₂O₃ clusters nanowires was reported using GaAs precursor and Au as reactive sites in VLS process [17]. Further, the morphology of nanorods and quadrilateral prism of the GaO(OH) were obtained through the heat treatment in hydrothermal growth [18]. Similarly, the controlled growth of gallium oxide nanostructures like nanoribbons, nanosheets, nanowire and nanobelt [19][20] have also been synthesized via hydrothermal method. Recently, GaO(OH) nanostructures were prepared via hydrothermal route using Ga_2O_3 and NaN_3 as a precursor [21],[22]. Control on the shape and size of Ga₂O₃ nanostructure has been reported by tuning the synthesis parameters like temperature, growth time, precursor concentration etc. in the hydrothermal process [23], Sn doped Ga₂O₃ nanostructures was grown using hydrothermally to study the photocatalytic properties and different concentration of Sn doping were studied, it was evident from the result that doped

nanostructures have good response towards photocatalytic activity as compared to pristine Ga_2O_3 [24]. Although hydrothermal synthesis is extensively used in synthesis of gallium oxide nanostructures but the effect of different precursors on size and shape of nanostructures was least explored. Therefore, in present work three different precursors of gallium are considered for the hydrothermal synthesis of gallium nanostructures. In which, the use of gallium acetylacetonate as a gallium precursor results in nano-cuboids morphology. Since the Ga_2O_3 nano-cuboids structures are least investigated, hence created further interest on this unique structure.

Hydrothermally synthesized Ga₂O₃ usually has GaO(OH) at the surface and hydroxide converts into oxide after thermal annealing [25]. Annealing at an optimal temperature becomes vital role for the nanostructure to improve surface smoothness, which is due to the reduction in structural defects and improvement in the crystallinity of the nanoclusters [25]. A large number of dangling bonds and local atomic defects exist at the surface of the nanoclusters; therefore, the surface tends to have instability at the surface and offer a better platform for surface-based applications [26]. In this study, an interesting observation is recorded when hydrothermally synthesized nano-cuboids are thermally annealed, the surface becomes rough, and nanopores have appeared. An increase in the annealing temperature up to 950°C results in increases in the size of pores. Further increase in the annealing temperature (1000° C) reduces the size of the nanopores and results as a smooth surface of nano-cuboid. The restructuring of the nano-cuboid surface is related to surface oxidation, surface defect manipulation and atomic rearrangement. It is known that surface restructuring of the nanostructure is in corresponding to different phenomena of chemisorption induced restructuring and interfaces of metal-oxide on the time scale basis [27]. Further, the oxidative condition causes the lattice atom diffusion, which leads to major and minor surface oxide layers to accompany by surface restructuring and lattice rearrangement. The effect of temperature on the Ga_2O_3 might be very crucial to understand the stability of the material. The understanding of surface properties and restructuring behaviors of Ga₂O₃ nanostructures at high temperatures will enable to design and select the best materials for reliable power electronic devices.

2.2. Experimental Section

2.2.1. Synthesis of β-Ga₂O₃ nano-cuboids

Gallium oxide nanostructures were synthesized using three different precursors of gallium i.e. gallium acetylacetonate (GO-Ga), gallium chloride (GO-Cl), gallium nitrate (GO-Ni) via hydrothermal technique. In a typical procedure, 0.1M concentration of gallium precursor was dissolved in DI water by continuously stirring the solution at 500 rpm at room temperature. Once a homogeneous colorless solution was observed, ammonium hydroxide was added dropwise to achieve a pH of 10, due to which the solution color turns to milky white. In case of gallium acetylacetonate after the precursor was mixed in water initially the pH of the solution was acidic in nature (pH 3), however addition of ammonium hydroxide (NH₄OH) dropwise in the solution the final pH of 10 was achieved.



Figure 2.1: Schematic diagram of the synthesis of gallium oxide nanostructures via the hydrothermal route. As- synthesized sample has a brownish color, and after annealing, it turns to a whitish color.

Gallium chloride being slightly more acidic from acetylacetonate the initial pH of solution after adding water was in between (pH 2 - pH 3) but on adding the NH₄OH, the pH was converted to basic in nature (pH 10). It was noted that the count for drops of NH₄OH were more in case of chloride as compared to acetylacetonate. Gallium nitrate as a precursor had an initial pH of 3 after adding NH₄OH dropwise

the pH was brought to a value of (pH-10). The above solution in a beaker was transferred to a preheated hot plate operating at 65° C for 5 hours under continuously stirring. The obtained solution is transferred to teflon liner in an autoclave and heated at 140° C for 10 h. Once, the autoclave was cooled down to room temperature, the solution in the liner was washed and dried distinctively for 6000 rpm for 7 min and repeated about 3 to 4 times. The collected precipitate was dried in a vacuum oven at 70°C for 6 hours. Figure 2.1 represents the entire synthesis process. A similar procedure was followed in the case of gallium nitrate as well as gallium chloride. The effect of annealing temperature on nanostructures and phase change was studied by thermal annealing of grown gallium oxide samples at various temperatures (600°C, 800°C, 850°C, 950°C, 1000°C).

2.2.2. Structural and morphological characterization of β-Ga₂O₃ nano-cuboids

The prepared samples were characterized using various techniques. XRD spectra of the synthesized sample were recorded using Bruker D-8 advance X-ray diffractometer instrument with Cu as an exciting source of X-ray with a wavelength of 1.54 Å, at room temperature. Morphology study was conducted by scanning electron microscope (JEOL make model number: JSM-7610F Plus) at a working distance of 4.5mm and operating voltage of 5 KV. Raman spectra of the synthesized sample was analyzed using a Horiba instrument ranging from 100 nm to 800 nm by 532 nm laser source.

2.3. Results and Discussion

2.3.1. Crystalline and morphological properties of β-Ga₂O₃ nanocuboids

Morphological characterization of grown nanostructures illustrates a variation in morphologies when different gallium precursors are used in hydrothermal synthesis. In the case of gallium acetylacetonate as a precursor, cuboid like shape is obtained with an average size of $0.6\mu m \times 0.3\mu m \times 0.2\mu m$, as shown in (Figure 2.2a). The growth of nano-cuboid has occurred when gallium acetylacetonate (GO-GA) is dissolved in water and it hydrolyzes into primary GaO(OH) compound. Due to the acidic nature of the precursor on adding the

neutralizer i.e ammonium hydroxide immediate supersaturation with respect to GaO(OH) solubility occurs. The colloidal solution of GaO(OH) nuclei are generated in the saturation; finally, the formation of cuboid like structure is obtained. Whereas gallium chloride precursor results in rice like morphology with an average size of 1.5μ m in length and 0.5μ m in width (Figure 2.2b). A similar kind of morphology is also obtained in the case of gallium nitrate, whose average size of 1.3μ m in length and 0.5μ m in width (Figure 2.2c). The synthesized Ga₂O₃ nanostructure are smaller in size as compared with commercially purchased Ga₂O₃ powder (Afla-Aesar: Product No.- 032102.14) shown in (Figure 2.2d). The role of gallium in its precursor plays a vital role regarding the formation of different nanostructures of gallium oxide. This can be attributed to the interaction of gallium ions during the reactions.



Figure 2.2: Morphology of Ga_2O_3 nanostructures synthesized using different precursors of gallium. (a) Gallium Accetylacetonate (GO-GA), (b) Gallium chloride (GO-Cl), (c) Gallium nitrate (GO-Ni) and (d) Commercially purchased Ga_2O_3 powder.

. The release rate of gallium ions from the source precursor is main cause of the different nanostructures. Apart from the release of ions the nanostructures are also affected by the kind of counter anions used. As the concentration of gallium ions in chloride and nitrate is distinct from acetylacetonate thus after reacting with hydroxide ions of water and ammonium hydroxide, nuclei are created in an impulsive manner due to which there is very less control on the proportional growth. Whereas in case of acetylacetonate the release rate is different when compared to other precursor thus the release rate is different, and the formation of nanostructure takes place in proportional manner giving a cuboid like shape as a final product.



Figure 2.3: (A) XRD pattern of Ga₂O₃ nanostructures synthesized using gallium acetylacetonate; (i) As grown sample, (ii) anneal at 800°C (GA-800), (iii) at 850°C (GA-850), (iv) at 950°C (GA-850), (v) at 1000°C (GA-850). (B) XRD pattern of Ga₂O₃ nanostructures synthesized using different precursors of gallium and annealed at 1000°C; (i) Gallium Accetylacetonate (GO-GA), (ii) Gallium chloride (GO-Cl), (iii) Gallium nitrate (GO-Ni) and (iv) Commercially purchased Gallium oxide powder.

The crystalline properties of nano-cuboids are investigated as shown in XRD patterns in (Figure 2.3). The as-synthesized powder is in the GaO(OH) phase, which generally found in the orthorhombic structure. Annealed of these samples at a higher temperature, first converts the GaO(OH) phase to α -Ga₂O₃, then β -Ga₂O₃ phase. X-ray diffraction pattern demonstrates that annealing below 850°C results in α -Ga₂O₃. The presence of peaks at 24.3° (012), 33.7° (104), 35.8° (113), 41.2° (012), 50.1° (024), 54.9° (116), 63.2° (018), 64.6° (214), 73.6° (1110), 76.3° (220), 78.9° (306) is in agreement of ICSD pattern- 27431 of α -Ga₂O₃.

Whereas annealing temperature at 850°C results in β -Ga₂O₃ phase, as shown in Figure 2.3A (iii). The monoclinic phase of β -Ga₂O₃ consist of C2/m symmetry, Ga atom has tetrahedral and octahedral like coordination in the lattice, with GaO₆ octahedra and GaO₄ as tetrahedral [2]. Further crystalline properties of other samples (synthesized using different precursors) are investigated after annealing at 1000°C. The XRD pattern shown in Figure 2.3B, confirms the formation of β -Ga₂O₃ phase nanostructures despite having three different precursors of gallium. Diffraction pattern of commercial β -Ga₂O₃ powder shows intense peaks due to large size crystallites as compared to synthesized samples

2.3.2. Analysis of surface restructuring of β-Ga₂O₃ nano-cuboids

During the structural analysis of β -Ga₂O₃ nano cuboids, the samples are undergone for thermal annealing at various temperatures ranges from 600°C to 1000°C. The annealed samples are also analyzed using HRSEM, in which the surface of nano-cuboid has shown significant transformation and restructuring when annealed at various temperatures (Figure 4). Since as-synthesized samples have GaO(OH) phase, which gets converted into α -Ga₂O₃ to β -Ga₂O₃ after thermal annealing during this noticeable change in the surface of nano cuboids has occurred. The as-synthesized samples have a smooth surface, but annealing at elevated temperature causes surface transformation due to GaO(OH) to Ga₂O₃ conversion. The annealing at 600°C shows pore formation at the surface of the nano-cuboid. Further annealing at a higher temperature, the size of the pores increases up to an annealing temperature of 950°C. It is observed that pore filling or annihilation has happened at 1000°C and the surface of the cuboid appears smoother, which can be ascribed due to recrystallization and restructuring at surface of gallium oxide nano-cuboid. Annealing supports the pore formation by eliminating the hydroxide particles present in that phase. Annealing at the higher temperature, signifies the increase of grain density, reduction in defects and improves the crystalline quality of the Ga₂O₃ samples. Effect of annealing on surface plays a vital role as it creates pores to an optimum temperature, but on further annealing, the reconstruction of the surface takes place as shown in Figure 2.4.



Figure 2.4: Surface morphology of Ga_2O_3 nano-cuboids after annealing at various temperature and schematic of surface. (a, b & c) as synthesized; (d, e & f) annealed at 600°C; (g, h & i) annealed at 850°C; (j, k & l) annealed at 950°C and (m, n & o) annealed at 1000°C.

The change in crystalline properties with respect to variation in annealing temperature from 850°C, 950°C and 1000°C are presented in Figure 2.3(A). An increase in annealing temperature and corresponding decreases the value of FWHM, which is due to the surface restructuring of the samples [28]. The FWHM values for plane (111) changes from 0.39 to 0.52 when samples are annealed at 850°C and 1000°C, respectively. Since the crystal size is similar (nanostructures), such change in FWHM is related to the relative change in the surface properties of the samples. Similar observations are reported by M. Vashista et al., which signifies structural disorder and fatigue in the nanostructure as one of the reasons for having wider FWHM [29]

Further, the crystallinity of β -Ga₂O₃ is investigated using Raman analysis, as shown in Figure 2.5. Raman active modes are classified under three main groups according to their wave number corresponding to 142.2, 143.3, 166, 197 cm⁻¹ under lower frequency modes which occur due to the tetrahedral to octahedral chains transitions. Similar frequency modes are also observed by dohy et.al. Where they consider these vibrations are also caused due to the vibration and transition of tetrahedra chains [30]. The peaks at 343.1, 346.2, 413.2, 472.5, 477.1 cm⁻¹ are indicating the partial presence of Ga_2O_6 octahedra stretching in all the samples [31][32]. It has been reported that the shift obtained at 650.3, 654.07, 764.8, 766.2 cm⁻¹ is due to the bending and expanding of the bonds between the gallium and oxygen (Ga-O) atoms while forming gallium oxide [32]. The pattern obtained for samples annealed at 800° C is slightly shifted toward higher wavenumbers as compare to the samples, which is annealed at 850°C. This might be due to conversion from α -Ga₂O₃ phase to β -Ga₂O₃ phase. It has been reported via Raman analysis that annealing at higher than 800°C confirms the monoclinic structure of β phase gallium oxide [31][33]. In our study, a shift of 0.8 cm⁻¹, 1.6 cm⁻¹ and 0.8 cm⁻¹ are observed at lower, mid and higher frequency modes, respectively, when the annealing temperature is changed from 800°C to 850°C as shown in table 2.

Sifting (cm ⁻¹)	α -Ga ₂ O ₃	β -Ga ₂ O ₃
Low Freq. mode	197.139	197.943
Mid Freq. mode	343.7	344.7
High Freq. mode	650.3	651.1

Table 2: Raman vibration of α and β -Ga₂O₃.

Within the of β phase gallium oxide, there is a slight shift in peak position and intensity of the Raman spectra of samples annealed at 850°C and 1000°C. The peak position is shifted from 197.94 cm⁻¹, to 197.74 cm⁻¹ when the annealed at 850°C and 1000°C, respectively. There is also variation in the peak intensity from 0.92 (a.u.) to 0.95 (a.u.). When the size of the pores is varied, the interacted phonons have their wave vector out of the Brillouin zone, which eventually shifts the peak to lower frequency [34]. Hence, such a change in Raman spectra of β phase gallium oxide attributes toward the surface restructuring of the nanostructures because the spectra depend on the phonon coherence length [34]. The change in surface properties of the nano-cuboid surface is related to surface oxidation, surface defect manipulation and atomic rearrangement. Further, the oxidative condition may induce the lattice atom diffusion and leads to major and minor surface oxide layers to accompany by surface restructuring and lattice rearrangement.



Figure 2.5: Raman spectra of gallium oxide nanostructures annealed at various temperature, (i) at 800°C (GA-800), (ii) at 850°C (GA-850), (iii) at 950°C (GA-950) and (iv) at 1000°C (GA-1000).

2.4. Mechanism of pore formation and surface restructuring

Formation of pore in gallium oxide nanostructure as shown in (Figure 2.6), can be defined by two main causes firstly elution of gallium and oxygen at the defect site. Defects such as point defect, non-stoichiometry defects etc. These defects are mainly caused due to the synthesis technique involved while forming these nanostructures. While annealing is carried out it is possible that the defect site will cater towards the bulk while elution will occur at the surface. This will result in change in the ratio of morphology and stoichiometry of the material. At higher temperature annealing volume fraction of the porosity increases due to which the vacancy pair get evolved with larger diameter of pores. Due to the change in the ratio between the two, there will be a considerable change in the structural properties of the Ga₂O₃ nanostructures. Secondly, an important factor is decomposition of volatile gas and decimation of non-reacted materials. As we anneal the samples, we found that the molecules of volatile gas and non-reacted materials starts migrating towards the surface due to changes in surface energy. In this case it might be possible to have a decreasing surface energy therefore the molecule is moving towards it. Since the annealing temperature is getting closure to the meting point of gallium oxide, phenomenon like conditioning of gallium atom on the surface is also taking place, which result in healing of pores on the surface. At higher temperature the oxygen atom present in the lattice of Ga₂O₃ as well as the oxygen atom present in the surrounding atmosphere are controlled via dynamic equilibrium. Thermal energy becomes the external stimulus for causing the change in the structure surface [35][36]. As a result, when the value of oxygen in the surrounding of Ga₂O₃ powder gets ionized. Oxygen forms the bond with gallium to pursue with the restructuring of the surface, similar behavior was studied by Aaron Puzder et. el. where it was seen oxygen atom were attracting the Cd atom on the surface [37]. This phenomenon is observed at higher temperature when considered for the material to be stable, thus at 1000°C we observe an identical diffraction pattern obtained for all the " β " phase at below this temperature, the material tend to become passive for the environment and gallium atom tend to make a stable healed surface structure. First principle study for terminated surface

by Somesh Kr. Et.al. gives an idea for the reason for surface restructuring of nano cuboids [38].



Figure 2.6: Schematic diagram of pore formation. (a) desorption of gallium and oxygen from the defect site, (b) oxygen vacancies and gallium vacancies react together to form pores, (c) healing of pores with defect free gallium oxide.

2.5. Summary

 Ga_2O_3 nanostructures have been synthesized via the hydrothermal method without the inclusion of any surfactant or additive. Cuboid like shape was achieved using gallium acetylacetonate as a gallium precursor. The change in the morphology of nanostructures was found when different precursors were used for synthesis. Annealing of Ga_2O_3 nanostructures has resulted in a change in the crystalline phase and surface morphologies. Annealing at higher temperatures (>600 °C) has created pores on the surfaces of cuboid structure till a temperature of 950°C, on further annealing the surface was intended to restructuring as well as smoother surface appears in case of 1000°C. Raman active modes of annealed sample depicted the occurrence of both the α -Ga₂O₃ and β -Ga₂O₃ at different temperatures. Shifting of peaks in Raman spectra were subjected to the phase change from α -Ga₂O₃ to β -Ga₂O₃. The surface restructuring was induced by annealing of the samples, which were evident from the change in peak intensity and shifting of the peaks of Raman spectra in an ordered manner. The surface controlled gallium oxide nanostructures (via annealing) can be an excellent material for various surface-related applications and power electronics devices, gas sensors, catalytic and coatings, etc.

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Chapter 3: Surface cracks healing in wetchemical deposited βgallium oxide films and their electrical properties

In this chapter, solution based low temperature gallium oxide (Ga₂O₃) films with high quality is present need for large area deposition, cracks and other parameters resist the use of these films in applications. Good quality crack free films of Ga₂O₃ have been developed. Deposition of Ga₂O₃ thin films by spin coating method and investigation of removal of surface cracks by adding secondary solvent (water) under oxygen environment has been performed. The as-synthesized film (without water and oxygen) shows cracks all over the surface. Deionized (DI) water and oxygen atmosphere act as efficient medium that alter surface energy of thin films while undergoing heat treatment. Increase in surface roughness is observed (from 0.28 nm to 0.98 nm) with increase in annealing temperature. Improvement in the crystalline feature results into augmented current density value. The developed crack-free films can be utilized for various electronics and optoelectronics application.

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3.1. Introduction

Fabrication of thin films on arbitrary substrate is challenging and solutionbased approaches have shown promising potential with regard to film deposition. Due to quick and easy approach to grow uniformly thick films from few nanometer to few micrometers with some key advantages like large area processing, thickness of the film can be controlled via optimizing the viscosity and other parameters, compact disk production is one of the premier example of large area film deposition. Recently, gallium oxide (Ga₂O₃) have been utilized for various optoelectronics application using solution-based approach. Y. Kokubun et al. prepared Ga₂O₃ by sol-gel technique to demonstrate the use in solar blind UV photodetector [1]. Planar geometry photoconductive detectors were explored by preparing indium doped gallium oxide by sol-gel method, the films were grown on sapphire substrate for sensing the UV rays [2]. H. Shen et al. reported polycrystalline films of Ga₂O₃ prepared via sol-gel technique for solar blind photodetector. Fabricated films showed fast response of 0.10 sec and decay speed of 0.10 sec thus proposing for fast response devices solar blind photo detectors [3]. However, the quality of the film grown using the solution approach is not up to standard, as can be obtained by chemical vapor deposition (CVD)[4], pulsed laser deposition (PLD)[5], and atomic layer deposition (ALD)[6], plasma-enhanced atomic layer deposition (PEALD) [7] etc.[8]¹[9]¹[10] Solution based approach has shown another possibility for large area-deposition in the economical process. Due to quality issue, the solution deposited films are not primarily used in electronics and optoelectronics applications. Further, surface irregularities such as cracks on the solution deposited films are one of the major concerns. Cracks on the films have an adverse effect on the electronics properties such as flow of electrons, channel formation, surface resistance and skin resistance, which are essential to optimize device performance. These factors are strongly related to the surface structure of the thin films [11]. Cracks on the thin films are majorly caused during heat treatment and evaporation of the colloidal suspension from materials. A study on fracture tendency in sol gel derived silica, and organo silica-based coatings were carried out by Kappert et al. and they observed the formation of cracks reduces by increasing the film thickness [12]. The control on the cracking behavior of the film by using secondary solvent was proposed by Jin et al. [13]. The introduction of secondary fluid during film deposition increased the particle network between the solvents [14]. It has been seen that with the high modulus of the particles, the solvent tends to exhibit cracking during the process. The crack formation is attributed to the shape of the particle and the network formed when they are heated [15]. It has been proposed to have crack-free films, by using particles that allow for relaxation during heat treatment [16]. Study based on coatings involves solvent with a colloidal precursor, which allows slow evaporation of the solvent that avoids the crack formation when subjected to heating. The formation of cracks can be related to the lower rate of oxy gen invasion weather [17]. The solvent not having solid binding force can be removed easily [18]. However, aspect like heating conditions play a key role for making crack-free films. If the two conditions are processed in a controlled manner, the crack-free film can be prepared. Herein, these two conditions (solvent and heating environment) are optimized to develop crack-free thin film of Ga₂O₃.

In this work, we have analyzed synthesis of crack-free Ga₂O₃ thin film under different scenario such as without secondary solvent, with secondary solvent, secondary solvent with heat treatment in open air and oxygen rich atmosphere. Addition of deionized (DI) water during the mixing of gallium precursor and organic solvent, followed by heat treatment of the deposited film in oxygen rich conditions, successfully heals the surface cracks of the Ga₂O₃ films. The lattice rearrangements and surface phenomena are depicted from X-ray diffraction (XRD) and Raman based analysis. A significant intensity increment in the XRD peak for the crack-free films and Raman shift of 1 cm⁻¹ is attributed to the presence of oxygen during the formation of films. The average roughness of the crack-free film is approximate 0.48 nm evaluated using AFM. Current-Voltage measurement demonstrates better current density value in crack-free films, which further improves with annealing at higher temperature. Such solution grown crackfree Ga₂O₃ thin film can be utilized to design efficient electronics devices.

3.2. Experimental section

3.2.1. Preparation of spin coating solution and deposition of β-Ga₂O₃ film

The coating solution was prepared with two different approaches (Figure 3.1): first, using DI water as a secondary solvent and secondly, without DI water while preparing the solution. In the process, gallium nitrate hydrate $(Ga(NO_3)_3.9H_2O)$ (0.1M) was dissolved in the mixture of 2-methoxyethanol (5ml) and monoethaloamine (0.02g) at room temperature for 30 min, which was then transferred to a pre-heated hot plate at 60°C for 1hr under continuous stirring. The solution turned from transparent to milky white, ensuring the formation of gallium oxyhydroxide (GaOOH). Similarly, for crack-free thin film formation, 0.5 ml of water was added to the above solution precursor, and the color of the solution turned from transparent to milky white with less viscosity in nature. The solution was subjected to spin coating on pre-cleaned quartz substrates. Initially, the spin coating was done at 1000 r.p.m for 10 sec to properly coat the substrate which was further rotated at 3000 r.p.m for 20 sec to remove excess solvent (for uniform thickness across the substrate.)

After depositing thin films, the drying process was divided into two segments; in the first case, the drying process consisted of an oxygen environment in a closed chamber, whereas in the second case, the drying was done in an open environment. Thin films were dried for at 450° C for 20 min. Five cycles of spin coating and drying were involved in attaining smoother films. Thin films were further subjected to annealing at different temperatures after the completion of the fifth cycle. To study the electrical behavior of the fabricated films two equidistant dots of conductive silver paste were placed on the Ga₂O₃ thin film deposited over the quartz substrate, the tips of micro positioner were placed over the silver dots. Potential was applied to the conductive dots using a source meter instrument.



Figure 3.1: Systematic diagram for the formation of gallium oxide thin film using spin coating technique.

3.2.2. Structural, optical and electrical characterization of β-Ga₂O₃ films

The prepared films were characterized using (Bruker D-8 advance) X-ray diffractometer instrument with Cu K_{α} as an exciting source of X-ray with a wavelength of 1.54 Å, at room temperature. The morphology study was conducted by scanning electron microscope (make: JEOL model number: JSM-7610F Plus) at a working distance of 4.5mm and operating voltage of 5 KV. Raman spectra of the synthesized thin films were analyzed using a Horiba instrument ranging from 100 nm to 800 nm by a 532 nm laser source. Surface roughness was calculated using atomic force microscopy AFM (Park System NX10). I-V characteristics were measured using a source meter instrument (Keithley - 2604B).

3.3. Results and Discussion

3.3.1. Role of DI water and oxygen environment on removal of surface cracks of the solution processed β-Ga₂O₃ thin films

The addition of deionized (DI) water and the effect of the oxygen environment during the film's heat treatment is shown in figure 3.2. On heating of the film, island like structures were observed on the surface of the film when it was deposited in absence of both water and oxygen environment, as shown in figure 3.2(a). The addition of water and heating in open air shows lesser cracks on the surface of thin film as shown in figure 3.2(b). Similarly, cracks were still visible when deposition was carried out in oxygen environment but without water (figure 3.2(c)). Figure 3.2(d) depicts crack-free film deposition in presence of both water and oxygen environment.

XRD patterns of Ga₂O₃ films heated at 800°C confirms the formation of gallium oxide. The presence of (104), (2-10), and (300) peaks indicate the presence of α -Ga₂O₃, as given in figure 3.3 [19]. The film deposited in both cases - without water and with water accompanied by annealing in air - exhibit similar crystalline pattern. Similarly, no change in the crystalline pattern is observed when the film is deposited without water and annealed in oxygen rich atmosphere. Thus, only the addition of water or heat treatment in oxygen alone has no significant impact on the structural property of the film. However, water as a secondary solvent and heat treatment in the oxygen-rich atmosphere together, reduces the stress between the films and shows a shift in the XRD peak of α -Ga₂O₃.



Figure 3.2: Scanning electron microscopic images of Ga_2O_3 thin films after heat treatment at 800° C, (a) film deposited without using water and heated in air atmosphere, (b) deposited using water and heated in open air atmosphere, (c) deposited without using water and heated in oxygen rich atmosphere, and (d) deposited using water and heated in oxygen rich atmosphere.



Figure 3.3: XRD pattern of Ga_2O_3 thin films after heat treated at 800°C, (a) film deposited without using water and heat treat in air atmosphere, (b) deposited using water and heat treated in air atmosphere, (c) deposited without using water and heat treat in oxygen rich atmosphere, (d) deposited using water and heat treat in rich oxygen atmosphere. Shifting of the plane (104), (2-10), and (300) can be seen from the zoomed image present in the right panel of the figure.

Comparison of Raman spectral lines of films with cracks and crack-free films, show notable variations (figure 3.4). Slight shift in the spectral lines is observed. The dominant peak observed for cracked and crack-free thin films (203.8 cm^{-1} and 202.5 cm^{-1} respectively), is fundamental attribute of the Ga₂O₃. The change of the Raman spectrum in crack-free films might imply different oxygen vacancy distribution. Oxygen deficiencies will affect the surface when there is a change in the partial pressure of the oxygen during heat treatment.[20] Typically, the remained stress of the materials must be completely released by formation of cracks and breaking. However, in this case the stress is not completely released despite the cracks formed. The stress which is developed during growth is also dependent on the relative kinetic of the various process that contribute to the stress generation, due to the constraint of the substrate the grain boundary diffusion has a small influence on relaxing the stresses in the thin films. Thus, the stresses in the grain boundary are relaxed but the stresses in the interior of the grain remain high.[21] Since, Ga₂O₃ films are deposited on the substrate thus the stress has remained after formation of cracks.



Figure 3.4: Comparison between the Raman pattern of Ga_2O_3 thin films with cracks and without cracks after annealing at 800°C. The blue shift of (approx. 1.3 cm⁻¹) in the case of crack-free film compared to crack films is shown in the inset.

As observed in SEM images, cracks connect multiple domains of the film and make island-like patterns on the top of the surface. The molecules of Ga and O form an interparticulate system as an after effect of DI water addition. DI water as a secondary solvent helps to reduce the saturation level, improving bond strength between the molecules in the solution. The cracks are caused due to the yield stress as a function of saturation of the organic solvent. When the solution is heated without oxygen, the saturated solvent molecules dries up very quickly, leaving behind empty spaces or voids. It gets further channelized and results in the formation of cracks on the surface. The oxygen deficiencies persists on the surface when annealed in the air.[20] However, when annealing is performed in oxygen, despite the oxygen atoms taking time to diffuse in Ga₂O₃, the concentration of oxygen vacancies reduces at the surface of the film.[22][23] Oxygen environment endows the thin film with effective relaxation during heat treatment. On the contrary, when the film is heated in the absence of oxygen, it does not have enough oxygen atoms to diffuse into the film. As a result of which the film is less relaxed which eventually causes stress between the atoms and becomes significant cause of crack formation.

Figure 3.5 demonstrate the mechanism behind crack-free films when water is added to precursor solution and heated in oxygen rich condition. The absence of water (during sol formation) induces greater viscosity. Nevertheless, in the wateradded precursor solution, an interparticulate system between the molecules is formed, resulting in lesser viscosity.



Figure 3.5: Formation of crack-free Ga₂O₃ films by addition of secondary solvent and annealing in oxygen rich condition.

On being subjected to heat treatment, the film's evaporation is rapid due to the absence of water in the mixture of organic solvent as their boiling point becomes low, whereas water-based solution tends to have a higher evaporating temperature, thus eliminating the rapid heating phenomena. The absence of an oxygen atmosphere causes the molecules to gain the desired energy quickly and evaporate at a random pace. Leaving behind island like structure over the substrate. However, heating in oxygen rich condition suppresses the energy required for the molecules to evaporate at a fast pace. Therefore, the films experience less stress over the surface. As a result, the film is in a relaxed state. This relaxation helps the molecules to adhere and thus rendering crack-free thin films as a product.

3.4. Effect of annealing temperature on morphological, crystallinity properties of β-Ga₂O₃ films

The surface morphology for both the cracked and crack-free films annealed at different temperatures ranging from 700°C to 1000°C are shown in figure 3.6. Annealing at higher temperatures have no bearing on cracks in cracked films. The cracks were randomly distributed throughout the surface of the film as shown in figure 3.6 (a), (b), (c) and (d), whereas crack-free films had a uniform surface throughout the thin film. However, an increase in the annealing temperature leads to increase grain size, in case of crack-free films, as depicted in the inset of figure 3.6 (e), (f), (g), and (h).

The surface texture of cracked free Ga_2O_3 thin film is further investigated using atomic force microscopy. Distinctive topographic images of crack-free film are observed when films are annealed at different temperature, as shown in Figure 3.7. The root mean square surface roughness of films varies between, 0.28 nm, 0.33 nm, 0.36 nm, and 0.97 nm for the films annealed at 700°C, 800°C, 900°C, and 1000°C, respectively. The change in the roughness indicates the significant variation in the crystallinity of the film. It is visible that the grain size of the film significantly increased with increase in the annealing temperature. The average grain size is found to be nearly 30.1 nm, 33.7 nm, 36.8 nm and 45.6 nm for the crack-free thin films annealed at 700°C, 800°C, 900°C, 1000°C, respectively.



Figure 3.6: High resolution SEM image of Ga_2O_3 thin films annealed at different temperatures in oxygen rich atmosphere. The film deposited without the addition of water (a) annealed at 700°C, (b) annealed at 800°C, (c) annealed at 900°C, and (d) annealed at 1000°C. The film deposited with water (e) annealed at 700°C (f) annealed at 800°C (g) annealed at 900°C and (h) annealed at 1000°C. Inset shown is at a scale bar of 100 nm.



Figure 3.7: Atomic force microscopic images of crack-free Ga_2O_3 thin films annealed at different temperature in the presence of oxygen rich atmosphere (a) annealed at 700°C (b) annealed at 800°C, (c) annealed at 900°C, and (d) annealed at 1000°C.

XRD 30.16°, 30.41°, 34.9°, 64.3°, The peaks at 31.26°, 35.36° , 37.4° , 48.49° , 64.75° , 64.78° are well matched with ICSD-27431 of α -Ga₂O₃ and ICSD-34243 for β -Ga₂O₃. The as-synthesized thin film did not show any evidence of available phases of Ga₂O₃, figure 3.8(a) shows the lowest category of crystallinity among the other annealed thin films. Similarly, thin film annealed at 600°C also, have no evident planes present as shown in figure 3.8(b); it is attributed to the disorderly arranged atoms. Spectra observed at 700°C shown in figure 3.8(c) can be assumed to possess planes for the ' α ' phase of Ga₂O₃. In the obtained spectra for 700°C corresponding planes were merged; thus, a single broad hump can be seen, possibly due to amorphous halo phenomena [24]. On further annealing, at 800°C, the peaks tend to have a mixed phase of both ' α 'and ' β ', which is difficult to notice as the peaks of ' α ' have a greater impact as seen from figure 3.8(d). The β phase is evident at 900°C, the planes have changed with a minute variation in the two theta angles.[25] The XRD spectra for 900°C and 1000°C, as shown in

figure 3.8(e) and (f), have a clear and sharper nature compared to the lower annealing temperatures [26].

The XRD patterns of the crack-free film demonstrate improvement in crystallinity with increase in annealing temperature. Full width at half maximum (FWHM) value of the most intense peak for crack-free thin film is 0.972, 0.775 and 0.687 at 800°C, 900°C and 1000°C, respectively. The full width at half maximum (FWHM) of the most intense peak decreases with increase in annealing temperature. Correspondingly, the crystallite size evaluated for crack-free thin films annealed at 800°C, 900°C and 1000°C were found to be 10.5 nm, 13.2 nm and 13.3 nm respectively. Improved crystallinity with increase in temperature is evident in the spectra observed from zoomed graph shown in figure 3.8(g).



Figure 3.8: XRD pattern of crack-free Ga_2O_3 films annealed at different temperature in oxygen rich atmosphere (a) as synthesized, (b) annealed at 600°C, (c) annealed at 700°C, (d) annealed at 800°C, (e) annealed at 900°C, (f) annealed at 1000°C and (g) effect of annealing temperature on the crystalline nature can be seen from the zoomed spectra.

Structural properties of crack-free Ga₂O₃ thin films are further examined by Raman spectral analysis as shown in figure 3.9. The Raman spectrum of the crackfree films show peaks demonstrating the presence of three main groups, i.e. lower frequency modes, mid frequency modes and higher frequency modes. These spectral features signify the ' α ' and ' β ' phase formation of Ga₂O₃ [27][28]. Spectral line present near 200 cm⁻¹ for all annealed thin films at different temperatures show a significant intensity growth.



Figure 3.9: Raman spectra of Ga_2O_3 films (a) annealed at 700°C, (b) annealed at 800°C, (c) annealed at 900°C, (d) annealed at 1000°C and (e) effect of annealing temperature on the dominant mode can be seen from the zoomed spectra.

The change in the intensity can be ascribed to the restructuring of the surface resulting from the heat treatment on the thin films. Zoomed spectral lines in figure 3.9(e) shows a blue shift in Raman lines, these shifts are ascribed to the movement of Ga and O atoms simultaneously. It causes the change in bond length between the atoms, due to which Raman interacting phonons eventually have their wave vector out of the Brillouin zone, as a result shifting of the peak is observed [29]. The study by Katiyar's et al. demonstrates the phenomena of these interactions where the nearest Ga and O atom show stronger interactions than the long-range atoms of G and O. As the temperature is increased, the strength of interaction between the two atoms is increased [30]. This increasing strength phenomena toggle towards the blue shift of the peaks as the annealing temperature is increased.

Further, such a condition may induce surface defect manipulation and lead to surface restructuring with help of lattice atom diffusion. Conclusively, the variation depicted in spectral lines are significant indicators of the heat treatment offered to the thin films.

3.5. Optical Properties of crack free annealed β-Ga₂O₃ films

The optical properties of the crack free Ga_2O_3 nanostructured films were explored using UV-Visible spectra. The spectra were obtained for the films annealed at 600°C, 700°C, 800°C, 900°C and 1000°C respectively. The maximum absorption was observed in short UV range (figure 3.10a), which justifies the wide bandgap nature of Ga_2O_3 . Humps observed in absorbance curve may be attributed to the surface defects and the presences of residual compounds on the surface of the films. The bandgap (figure 3.10b) calculated for the crack free films annealed at 600°C, 700°C, 800°C, 900°C and 1000°C was ranging from 4.3eV to 4.7eV. The band gap obtained is also well versed with the typical band gap of Ga_2O_3 .



Figure 3.10: UV-Visible spectra of spin coated Ga_2O_3 nanostructured film (a) absorption spectra of films annealed at 600°C, 700°C, 800°C, 900°C, 1000°C and (b) figure depicts the Tauc plot of Ga_2O_3 film annealed at different temperatures.

3.6. Electrical Properties of β-Ga₂O₃ films

To study the impact of different annealing temperatures on the electrical properties of cracked and crack-free films, the current voltage (I-V) measurements were performed at room temperature. On testing the films annealed at different temperature improvement in the current density value for both kind of films can be seen. However, the crack-free films show a relatively higher value of current density than the cracked films.

Nanostructured films showed current density value of 10⁻¹¹ A/cm² when annealed at 700°C for cracked film shown with blue color curve in the figure 3.11(a). Whereas, when the films annealed at 800°C (green color curve) 900°C (red color curve) and 1000°C (black color curve) were tested individually there was subsequent increase in the current density (by one order) to 10^{-10} A/cm² for all the three sample. Figure 3.11(b) depicts current density value for crack-free films. In the case of crack-free films, a visible increase in the current density is observed when the nanostructured films were annealed at 700°C (blue color curve) to higher temperature of 1000°C (black color curve). Improvement of current density can be attributed to the better crystalline properties and defect free nature of the nanostructured films which is caused due to annealing. Therefore, at a read voltage of -4.5V we observe 1.04x10⁻⁹ A/cm² for crack-free films annealed at 1000°C, which is better as compared to the current density of films annealed 700°C corresponding to value of 6.4×10^{-9} A/cm² at -4.5V. Since the grain size increased with increase in annealing temperature, it reduced the effective grain boundaries which in turn reduced the overall grain barrier loss.



Figure 3.11: Current-Voltage characteristics of Ga_2O_3 thin film annealed at different temperature 700°C, 800°C, 900°C and 1000°C. (a) cracked film (b) crack-free Ga_2O_3 thin film.

3.7. Summary

The crack formation is a major obstacle for thin film deposition using solution-based approach, which is countered using water as a secondary solvent. It has been observed that addition of water lowers the viscosity of depositing solution and annealing in oxygen rich conditions become an efficient medium to relax the surface energy. Improved crystallinity of the films is observed in correlation with increase in annealing temperature. Current density value of the thin films increases with improvement in crystallinity of the thin films, which were achieved at the higher annealing temperature. The proposed approach demonstrates the fulfilment of the essential requirement of smooth and uniform thin film formation. Consequently, it can be utilized for deposition of large-area films for various electronic and optoelectronic applications.

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Chapter 4: Structural, optical and electrical properties of densely packed β-Ga₂O₃ nanostructured films deposited via pHcontrolled crystal growth

Gallium Oxide (Ga₂O₃) nanostructured film is deposited via a single step aqueous method by controlling the pH value of precursor solution. The uniformity, density and crystallite size vary when the pH of precursor solution changes from pH 6 to pH 9. The as-deposited nanostructured film is present in hydroxide crystalline phase which gets converted to a mixed phase (' α ' and ' β ') when heat treated at 600°C. The densely packed Ga₂O₃ nanostructured film (at pH 8) shows better electrical conductivity and stable current density of 10⁻⁸ A/cm². The memristive measurement for densely packed nanostructured film results in R_{OFF}/R_{ON} ratio in order of 10², whereas the V_{set} and V_{reset} values are observed to be 2.7V and -3.1V respectively. This single step process is suitable for deposition of good quality, large crystallite, densely packed nanostructured Ga₂O₃ films that can be utilized in various electronic and optoelectronic applications.

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4.1. Introduction

Gallium oxide (Ga₂O₃) is an emerging inorganic material that has shown its utility in various applications such as conventionally considered catalytic and gas sensing properties, UV sensors, electronics devices etc. [1],[2],[3],[4],[5]. Subsequently in the past few years, Ga₂O₃ has enthralled researchers as an emerging semiconductor material for various solid-state electronic devices [6]. Ga₂O₃ has been proposed to be a good competitor to traditional semiconducting materials like Si, SiC, GaN in power electronics [7],[8]. Kura et al. fabricated chromium doped Ga₂O₃ films using co-sputtering technique for resistive memory devices where they studied the role of varying gallium to oxide ratio. Ga_{0.82}Cr_{0.18}O₁₂ based film was found to be the best performing switching device [9]. R.V. Tominov et al. reported memristors with a high resistance state (HRS) at +4V and a low resistance state (LRS) at -6V for gallium oxide nanostructures films fabricated via local anodic oxidation [10]. Bipolar resistive switching was reported by M.N. Almadhoun et al., using the junction between gallium oxide and p-type silicon and resistance ratio of 10^8 with retention time of 10^5 s were observed. The nanoscale layer of gallium oxide supported the gallium filament formation and dissolution, resulting in reversible switching [11]. Nanostructures of Ga₂O₃ (nanowires, nanorods, nanobelts and nanosheets) are presently gaining momentum with respect to nanoscale applications targeting evolution of better electronics and optoelectronics devices [12]. A. Paraye et al. observed increased pH and sulphur concentration resulted in a decrease in thickness when CZTS was electrodeposited on gold substrate in a single step with glycine as the complexing agent [13]. The effect of the pH of sol on the morphological and optical properties of CuO thin films prepared by the sol-gel dip coating process, showing significant improvement in the surface morphology and average grain size of films by using different pH solutions were reported by S.S. Niavol et al. Investigations with respect to synthesis and characterization of Ga₂O₃ nanostructures are making headway rapidly [14], [15]. Alteration of synthesis parameters (for deposition of nanostructured films) lead to significant control over properties of Ga₂O₃ films. Ga₂O₃ is polymorphic in nature and mostly available in ' α ', ' β ', ' γ ' and ' δ ' phases. The tetrahedral ' α ' phase and monoclinic ' β ' phase are most stable phases and are being synthesized using various approaches [16],[17]. The physical vapor

deposition or vacuum based techniques have rendered very high quality of Ga_2O_3 films. These methods require high-end equipment that led to higher cost of film deposition, which may not be very suitable for several low-cost applications. Therefore, the solution-based approaches are desirable as they can be used for deposition of large area films at lower cost, with minimum usage of high-end equipment's.

Y. Kokubun et al. used sol-gel method to prepare Ga₂O₃ film for ultraviolet photo detector. They prepared the precursor solution at 60°C and performed spin coating to form the film, followed by drying at 90°C and annealing at 300°C [18]. Spraying of aqueous solution of gallium nitrate carried out at 300°C by Hao et al. demonstrated good quality of Ga₂O₃ films [19]. T. Miyata et al. sprayed the mixture of gallium chloride and ethanol over a hot substrate (700°C -800°C) for deposition of poly crystalline β -phase gallium oxide film [20]. T. Kawaharamura et al. used the mist of gallium acetylacetonate and hydrochloric acid to deposit α-Ga₂O₃ at 400°C [21]. A soft chemistry route without using surfactant was demonstrated to produce different morphology of gallium oxide with controlled particles size [22]. Tas et al. synthesized gallium hydroxide by adding urea to an aqueous solution of gallium nitrate at 90°C, and Ga₂O₃ was achieved after annealing at 600°C [23]. Nanorods of gallium oxide hydrate was grown by J. Zhang et al. using hydrothermal process by mixing gallium oxide with hydrochloric acid in DI water and heating the solution at 180°C for 24 hours. Aspect ratio of the nanorods were controlled by adding different amount of diethylene glycol [24]. Reddy et al. synthesized Ga₂O₃ nanorods via hydrothermal method, by using ammonium hydroxide as a pH balancer at 95°C [25]. Synthesis of GaOOH nanorods via laser ablation followed by solution phases was studied by Huang et al. [26]. A study on growth of vertical array of α -GaOOH was carried by H. Lian et al. by building a continuous flow reactor and the reaction was carried at 95°C [27]. R Gopal et al. reported cubic phase of Ga₂O₃ by using salicydeneimin modified precursor of gallium isopropoxide via sol gel synthesis method [28]. M. Yu et al. studied new approach for producing high-performance solar blind photodetectors and using solgel process successfully produced the α/β phase polycrystalline Ga₂O₃ thin film. The photodetector displayed high detectivity and fast reaction time post optimization of the annealing environment [29]. Li Yuan et al. investigated

structural, morphological and electrical properties for solution processed Ga_2O_3 thin film and studied the role of amorphous Ga_2O_3 thin film in fabricating TFTs [30]. In most of the solution-based approach, the deposition was mostly performed at elevated temperature and was followed by multiple steps including annealing. The role of solution pH was investigated mainly to establish different morphologies and to tune various properties of metal oxide nanostructures. However, the impact of pH control in solution process growth of nanostructures in development of densely packed films, is yet to be explored.

Herein, a single step beaker chemistry approach is demonstrated to deposit the GaO(OH) nanostructured film at lower temperature followed by annealing to achieve Ga₂O₃ films. The deposition is carried out at 60°C with single precursors in a beaker and hotplate, that makes it simple and feasible for large area deposition of Ga₂O₃ films. Notably, control over precursor pH leads to formation of large crystallites and denser Ga₂O₃ nanostructures. An optimum value of pH-8 leads to relatively denser and compact Ga₂O₃ nanostructured film when compared to other pH values. Structural analysis of thin films reveals the presence of ' α ' and ' β ' phases, after they are annealed at 600°C. The gallium oxide nanostructures have diamond like morphology, with maximum absorption in the UV range pertaining to wide bandgap properties. The charge carrier density (N_D) for the Ga₂O₃ nanostructured film is in the range of 10¹⁷cm⁻³. Memristive properties of the deposited films are investigated for deposited nanostructured film and a resistance ratio (R_{OFF} : R_{ON}) of 10², with set and reset voltages at 2.7V and -3.1V, respectively were observed for films annealed at 600°C. The developed procedure is simple and is potentially beneficial for large scale deposition of Ga₂O₃ films that can be used for electronics and memory-based device applications.

4.2. Growth of Ga₂O₃ nanostructures in single step process

4.2.1. pH-controlled growth/enlargement in β-Ga₂O₃ nanostucture toward films formation

A single step beaker chemistry was performed at 60°C to deposit gallium hydroxide films on fluorine doped tin oxide (FTO) substrates. Prior to deposition reaction, the FTO substrate were cut into size of 2cm×1cm followed by cleaning of the substrate to eliminate the native unwanted particles and remove carbon

particles present on the surface. The cleaning process involved sonicating FTO substrates in soap solution, DI water, acetone and ethanol, respectively for 15 min each; after cleaning the substrates were blow-dried. Cleaned substrates were partially covered with the teflon tape with a hanging support. The schematic in figure 4.1 depicts the way substrates were suspended in gallium chloride (GaCl₃) solution. The precursor solution was prepared dissolving 0.1M GaCl₃ in 20ml DI water under constant stirring at room temperature. The solution was stirred for 15 min till it turned transparent. The beaker with solution was kept at preheated hot plate at 60°C. Ammonia solution was added drop wise to the above heated solution, to attain pH values of 6, 7, 8, 9 and 10 from initial pH value of 2.1. The solution turned milky white once the pH reached 6.



Figure 4.1: Gallium oxide film deposition process via aqueous solution route by simple beaker chemistry.

On subsequent addition of ammonia, the solution became relatively viscous. The cleaned FTO substrate was then hung inside the beaker to submerge substrate into the solution. After 10 hours the FTO substrates were taken out and allowed to naturally cool down to room temperature. Eventually substrates were cleaned by sonicating in DI water. The cleaned substrates were dried at 70°C for an hour. Lastly, all the thin film substrates were annealed at 600°C for the duration of 30 mins.

4.2.2. β-Ga₂O₃ films characterization

The deposited Ga_2O_3 films were characterized using Bruker D-8 advance X-ray diffractometer instrument with Cu as source of X-ray with a wavelength of 1.54 Å, at room temperature. Glancing angle XRD (GIXRD) was operated with

step size of 0.04° and omega for maximum intensity was 1.5° for the thin films. Morphological properties were analyzed by scanning electron microscope (JEOL make model number: JSM-7610F Plus). UV-Visible spectroscopy measurement was done by using UV-Vis instrument (Simadzu-2600). The Mott Schottky analyses were performed using an electrochemical system (Auto-Lab, PG start 204A). Three electrodes set up were used, Ga₂O₃ on FTO substrate as an anode electrode, Pt wire as cathode and Ag/AgCl electrode as reference electrode. The electrode was dipped into liquid electrolyte containing buffer solution of potassium hydroxide (KOH), 0.1M in concentration. The pH of the electrolyte was fixed at 12. I-V characteristics were measured using a source meter unit (Keithley 2604B).

4.3. Results and Discussion

4.3.1. Effect of pH value of the precursor's solution on morphological, structural and of β-Ga₂O₃ nanostructured films

In the nucleation stage, film growth begins with the nucleation of crystallites, followed by formation of grains, which coalesce to cover the entire substrate surface and exhibit a dense structure. The overall growth mechanism with schematic of Ga_2O_3 nanostructured film formation is discussed in the (figure 4.2). Figure 4.2 depicts the mechanism for the deposition of Ga_2O_3 nanostructured film. Firstly, the reaction between the ammonia solution and water results into formation of NH⁴⁺ and OH⁻ ions. The OH⁻ present in the solution reacts with the gallium ions, as an equation in figure 4.2. These phenomena occur due to the thermal hydrolysis of metal ions in aqueous solution due to applied temperature. Due to increase in ionic product of water, which occurs due to change in the concentration of hydroxyl ions and hydrogen ions as a result the interaction generally changes coordination number of gallium, by utilizing the vacant p orbitals for accepting the lone pairs to form Ga-O bonds. These structural units reach a state which inherit and super saturate to precipitated crystals. The agglomeration of particles proceeds in the aqueous solution to nucleate and crystal growth of gallium (III) oxide take place.

Secondly, gallium and oxygen atoms from $Ga(OH)_3$ gets disengage into gallium oxy hydroxide and water due to the molecular interaction taking place at particular temperature above than room temperature as shown in the equation present in figure 4.2. As the initial concentration of the solution is highly acidic, Ga-OH subgroups gather H from the solution which turns Ga–OH₂⁺ subgroups (protonated groups) that connects easily with OH⁻ groups from other available GaO₆ octahedra. Furthermore, gallium and oxygen ions get kinematically activated at 60°C in this case. The growth on FTO surface can be understood by the relation between surface energy of the substrate (E_S) and the nucleus (E_n) and the interfacial energy (E_{in}) between the two parameters. When $E_{in} = E_S + E_n$ the critical energy barrier of heterogeneous nucleation (ΔGc^*) becomes equal to (ΔGc) homogeneous nucleation. The relation between the two nucleation is given by $\Delta Gc^* = f(\Theta)\Delta Gc$, as a result occurrence of homogeneous nucleation take place without the influence of the FTO substrate. Finally, the transition to Ga₂O₃ takes place which is due to the annealing on the as deposited film. The removal of hydroxide atoms takes place after required temperature is reached. Once, the substrate is removed, the nanostructure film can be seen on the substrate holding a whitish layer confirming the growth. The saturated precursor is precipitated out in bottom of the flask.

Figure 4.3(a)-(j) depicts the surface topography of the Ga_2O_3 nanostructured films deposited at different pH (6, 7, 8, 9 and 10) of precursor solution. Formation of diamond like structure can be seen in all the nanostructures grown with different pH. As the pH of precursor solution increases to a value of pH 8, both the size of Ga_2O_3 nanostructure and the density, increases. Further increase in the pH value to 9 and 10, does not result in optimum deposition of nanostructures.

Ga₂O₃ nanostructure grown at pH 6 exhibit dimensions of approx. (210 nm \times 110 nm) which increases to approx. (530 nm \times 300 nm) for pH 8. On comparing nanostructures growth at pH 8 with pH 7, pH 9 and pH 10, 1.5 times crystal enlargement is observed. The uniformity of Ga₂O₃ nanostructure at pH 8 is better in comparison to the nanostructure at other pH values. The average area of the Ga₂O₃ nanostructures at pH 8 as shown in (Figure 4.4).



Figure 4.2: Systematic methodology for the formation of gallium oxide nanostructured film on FTO substrate.



Figure 4.3: Scanning electron micrograph of aqueous route deposited diamond shaped nanostructured films: (a & b) deposited at pH 6, (c & d) deposited at pH 7, (e & f) deposited at pH 8, (g & h) deposited at pH 9 and (i & j) deposited at pH 10.



Figure 4.4: Variation of average size of the particle corresponding to the SEM micrograph obtained at different pH values (a) at pH 6, (b) at pH 7, (c) at pH 8, (d) at pH 9, (e) at pH 10. Corresponding size of the particle (f) at pH 6, (g) at pH 7, (h) at pH 8, (i) at pH 9 and (j) at pH 10.

Thus, it is inferred that Ga_2O_3 nanostructure density varies as a function of pH value. The pH of the precursor solution affects the rate of the reaction and nucleation. When ammonia is added to the solution it results in formation of NH⁴⁺ and OH⁻ ions as ammonia gets hydrolyzed. Thus, giving rise to OH⁻ ions concentration in the solution. Thus, a specific morphology is obtained at a set amount of OH⁻ ion concentration. When the pH is increased the OH⁻ ions concentration also increases that gives rise to the anisotropic growth direction, as a result change in morphology take place. On further increasing the pH, the growth rate gets increased due to increase of the OH⁻ concentration that changes the reaction rate which also results in new morphology. On increasing the concentration of OH⁻ ions as compared to Ga³⁺ ions concentration, reaction rate changes due to which precipitation rate is changed in the solution [31]. Secondly, the dissolution of precipitation occurs due to the interaction between Ga³⁺ ions and OH⁻ ions. At lower pH the large amount of Ga³⁺ is formed giving rise to formation of seed layer and therefore results in a specific morphology [32].



Figure 4.5: Scanning electron micrograph of Ga_2O_3 nanostructured films (deposited at pH 8); (a) diamond like morphology of Ga_2O_3 nanostructure in as-deposited film, (b) annealed Ga_2O_3 nanostructured film, (c) cross section image of as-deposited film, (d) cross section image of annealed Ga_2O_3 nanostructured film.

The surface of Ga_2O_3 nanostructure become smooth when thermally annealed at 600°C (Figure 4.5). The surface smoothening is caused due to thermal decomposition of molecules present at the surface, which might be a function of the rate of change of temperature with time [33]. Thermal annealing is also beneficial in removing structural and surface defects from the crystals [34],[35]. The measured thickness of nanostructured film is approx. 630nm, (Figure 4.5(c) and 4.5(d)). The EDAX analysis reveals the Ga:O atomic percentage ratio to be 31.6%: 68.4% for as-deposited films and 39.5%:60.5% for annealed films, as shown in figure 4.6. The concentration of gallium increases with respect to oxygen after annealing because thermal decomposition of the gallium oxyhydroxide occurs at higher temperature and removes surface hydroxyl groups [22].



Figure 4.6: EDS spectrum of nanostructured films fabricated at pH 8; (a) as deposited films and (b) annealed at 600°C

Structural study for the grown nanostructured films at different pH are done using XRD analysis, as shown in Figure 4.7. The diffraction peak (401) at 36.03° confirms the presence of monoclinic phase (β) of Ga₂O₃ which is known to be the most stable phase of Ga₂O₃. The XRD pattern of the FTO substrate is also evident for all the nanostructured films deposited at various pH values. Ga₂O₃ nanostructured films deposited at pH 8 and pH 9, have the intense (401) XRD peak.

However, Ga_2O_3 nanostructured films deposited at pH 10 shows decrease in intensity of the (401) peak. An intense peak of (401) indicates better orientation and dense Ga_2O_3 nanostructure growth with improved crystallinity. Further, full width at half maximum (FWHM) value of (401) plane is calculated to be 0.27, 0.25, 0.22, 0.22 and 0.24 for Ga_2O_3 nanostructured films deposited at pH 6, pH 7, pH 8, pH 9 and pH 10, respectively. The full width at half maximum (FWHM) of the plane (401) decreases with increase in the pH value from 6 to 9. Crystallite size increases from 30.9nm at pH 6, through 33.5nm (pH 7), 37.9nm (pH 8) to 38.0nm at pH 9 but decrease to 34.7nm for pH 10 as shown in table 3.



Figure 4.7: XRD pattern of Ga_2O_3 nanostructured films grown at different pH (thermally annealed at 600°C); (a) FTO substrate, (b) at pH 6, (c) at pH 7 (d) at pH 8,(e) at pH 9, (f) at pH 10 and (g) in-large XRD pattern for (401) peak.

Table 3: Effect of pH on crystallite size of nanostructures.	
pH Value	Crystallite Size
рН б	30.9 nm
pH 7	33.5 nm
pH 8	37.9 nm
pH 9	38.0 nm
pH 10	34.7 nm

Table 3: Effect of pH on crystallite size of nanostructures.

The effect of annealing on the structural properties of dense Ga₂O₃ nanostructured film is further investigated using glancing angle X-ray diffraction (GIXRD) patterns (Figure 4.8). The as-deposited film has diffraction peaks of (210), (111), (211), (311), (410), (511), (020), (610) and (121) at 2 theta value of 35.29° , 37.25° , 40.5° , 45.7° , 48.07° , 60.1° , 62.44° , 65.32° and 66.91° , respectively which indicate formation of gallium oxyhydroxide phase. When films are annealed at 500°C and 600°C, the XRD pattern get changed and diffraction peaks of (401), (012), (024), (511), (214) and (71-1) appears at 36.03° , 41.35° , 50.19° , 54.73° , 63.48° and 64.94° which corresponds to ' α ' and ' β ' phase of Ga₂O₃. The reflections of the annealed sample were indexed according to the β -Ga₂O₃ ICSD structure 34243 (JCPDS PDF no. 01-076-0573, monoclinic phase)[36] and reflection pattern

of α -Ga₂O₃ was according to JCPDS PDF no. 00-006-0503. Presence of ' β ' phase can be confirmed by the appearance of (401) and (71-1) planes in both films annealed at 500°C and 600°C. Due to FTO substrate, further increase in annealing temperature is not possible, which may offer a pure ' β ' phase [37].



Figure 4.8: XRD pattern of Ga_2O_3 nanostructured films (a) FTO substrate, (b) as-deposited film, (c) film annealed at 500°C and (d) film annealed at 600°C.

4.3.2. Optical Properties of β-Ga₂O₃ nanostructured films

Figure 4.9(a) shows the UV-Vis absorption spectra of the Ga_2O_3 nanostructured films. The Ga_2O_3 film exhibit maximum absorption intensity around 235nm (UV-C) in deep UV region for both as-deposited and annealed films. Since the absorption is negligible in visible range therefore the Ga_2O_3 is transparent in nature which does not reflect any color from the visible range. The optical bandgaps for the films were calculated from the UV-Vis data using power law for direct bandgap semiconductors [38],[39]. The optical absorption coefficients were estimated. The bandgap is calculated to be 4.14eV for as-deposited films, 4.20eV and 4.24eV for film annealed at 500°C and 600°C, respectively (Figure 4.9(b)).



Figure 4.9: UV-Visible spectra of solution processed Ga_2O_3 nanostructured film (a) absorption spectra of as-deposited films and films annealed at 500°C and 600°C and (b) figure depicts the tauc plot of Ga_2O_3 film.

4.3.3. Electrical properties of β-Ga₂O₃ nanostructured films

The electrolyte/electrode interface is examined to calculate the charge carrier density and the flat band potential of Ga_2O_3 films. The measurement is performed at frequency of 1kHz, the slope and intercept are independent of the frequency. Based on the linear part of the C⁻² (V_B) the flat band potential V_{FB}, donor concentration and the width of the depletion region W are determined. The capacitance value depends on the flat band in the following equation

$$C_{sc} = \left(\frac{2}{e\varepsilon\varepsilon_0.N_D.S^2}\right) \cdot \left(V_B - V_{Fb} - \frac{KT}{e}\right)$$

where *e* is the electron charge, N_D denotes the charge density, ε is the dielectric constant of the semiconductor, ε_0 is the vacuum permittivity, *T* is the absolute temperature, *k* is the Boltzman constant, and *S* is the surface area of the electrode. Simplifying the above equation, the Charge density (N_D) can be derived to:

$$N_D = \left(\frac{2}{e\varepsilon\varepsilon_0}\right) \cdot \left(\frac{d\left(\frac{1}{C^2}\right)}{dV}\right)^{-1}$$

The Mott-Schottky plot of Ga_2O_3 film is shown in Figure 4.10(a-e). The charge carrier density of the Ga_2O_3 film deposited at pH 6, pH 7, pH 8, pH 9 and pH 10 are 4.7×10^{17} , 4.1×10^{17} , 3.3×10^{17} , 3.7×10^{17} and 4.1×10^{17} cm⁻³, respectively. The flat band potential for these films deposited at different pH is found to be in

the range of -0.90V to -0.99V. It has been reported that the carrier concentration of epitaxial layer Ga_2O_3 is in the range of 10^{15} to 10^{17} cm⁻³ [40]. Films produced via aqueous route also have charge carrier density in similar range, hence these films can be considered suitable for the electronic device applications. The cyclic voltammetry measurements of Ga_2O_3 nanostructure as working electrode shows the reduction peak at -0.96V as mentioned in Figure 4.11.



Figure 4.10: Mott-Schottky plots for gallium oxide (Ga_2O_3) nanostructured film deposited at different pH; (a) obtained at pH 6, (b) obtained at pH 7, (c) obtained at pH 8, (d) obtained at pH 9 and (e) obtained at pH 10.

The Ga_2O_3 nanostructured films grown at different pH are further investigated by performing current voltage measurements (Figure 4.12 a). The Ga_2O_3 nanostructured films deposited at pH 6, 7 and 10 show general current characteristics while Ga_2O_3 nanostructured films deposited at pH 8 and pH 9 show a gradual and slow change in current value. This observation indicates that the charge passing through the relatively dense films (for pH 8 and pH 9) encounter more resistance. Whereas, for Ga₂O₃ nanostructured films at pH 6, pH 7 and pH 10 the movement of charge is partially supported by FTO substrate and leading to high conductivity. Hence, the densely packed nanostructured films show better characteristic of a Ga₂O₃ nanostructured film and relatively suitable structure for various applications like optoelectronic devices, memory devices etc.



Figure 4.11: Cyclic voltammetry measurement of Ga_2O_3 nanostructured film deposited on FTO substrate at different pH (a) at pH 6, (b) at pH 7, (c) at pH 8, (d) at pH 9, (e) at pH 10 and (f) Comparison of all the pH based substrate at an scan rate of 100 mV/sec.

4.3.4. Memristive properties of β-Ga₂O₃ nanostructured films

The basic structure of the device is given in inset of Figure 4.12(b) where a top contact of silver is deposited on the nanostructure film of Ga₂O₃, whereas a bottom contact is of FTO/Ag made on surface of substrate, replicating a metal insulator metal (MIM) structure. Herein silver is the metal contacts, and gallium oxide is the sandwiched insulator. The Ga₂O₃ based memristive device is subjected
to a potential window of -4V to +4V. A high resistance state (HRS) is maintained till the applied voltage reaches 2.7V (V_{set}). Further increase in voltage leads to sudden jump in current attaining SET stage. When the applied voltage is reversed, the current stays the same, maintaining a low resistance state (LRS). The low resistance state continues for some time. On applying negative bias, similar phenomenon is observed. At -3.1V (V_{RESET}) the reset is triggered, and the device attains RESET stage. Further change in voltage conditions the device to enter high resistance state (HRS) again. The resistance ratio (R_{OFF}: R_{ON}) is in the order of 10² which proposes that the information can be stored with significant difference and can be recalled after some time duration.



Figure 4.12: (a) Current-Voltage characteristics of the different pH-based films and (b) memristive behavior of the densely packed Ga_2O_3 nanostructured film representing, individual cycles for memristive behavior (i.e. 50th Cycle, 100th Cycle, 150th Cycle, 200th Cycle and 250th Cycle).

Figure 4.13(b) shows typical characteristic curve of memristors. For better visualization of the memristive cycle individual cycles are shown in Figure 4.13(b-f). The device was tested for 250 cycles as shown in Figure 4.13(a). Some recent work reported for gallium oxide based memristors have resistance ratio from 2 to 20 (at 0.7V) for co-sputtered gallium oxide and chromium based devices [9]. In other work Ga₂O₃ nanostructures were incorporated as the resistive material for memristor in which +4V and -6V were the potentials where HRS and LRS were triggered respectively, resistance ratio was evaluated to 5 for the device [10]. Device based on bipolar resistive switching mechanism reported a resistance ratio of 10^8 for gallium oxide and p-type silicon based device, the HRS and LRS were trigger at +2.5V and -2V, respectively [11]. The result shows that the nanostructure



of Ga₂O₃ films can be casted for memory devices and can be utilized for neuromorphic applications.

Figure 4.13: (a) all together 250 cycles for the device fabricated with pH 8 thin film. Individual cycles for the device fabricated with pH 8 thin film (b)50th Cycle, (c) 100th Cycle, (d) 150th Cycle, (e) 200th Cycle and (f) 250th Cycle.

The overall mechanism of storing charge can be understood from Figure 4.15. At 0 volt the device is in reset state or initial state where no interaction between ions is taking place. When voltage is increased, the ions start to move through the semiconductor as shown in step 2. However, this potential is not enough to make a proper channel for the flow of charges thus the device is in high resistance state. Once the potential is increased, the channel formation takes place and a sudden change in current value at a potential is achieved in step 3. In step 4, the channel becomes prominent because of large value of current due to full migration of Ag^+ ions into the semiconductor, making a direct path from top to bottom contacts.



Figure 4.14: Mechanism for the Ga_2O_3 nanostructured film grown on FTO substrate showing memristive behavior.

On applying the negative potential or even after removal of potential, the current value remains same. Top contact undergoes oxidation at surface, resulting in changes in chemical state of the deposited metal, which might affect the charge trapping of metal contact. Charge carrier trapping occurs due to the movement of charges from delocalized states to localized state of Ga_2O_3 , and trapped states can be in the crystal lattice of Ga_2O_3 intrinsic to the possible ligand on the nanocrystal interface or within the whole environment. This phenomenon is illustrated as the memristive behavior of the device. In the step 5, the channel tends to decrease, and the migrated ions tend to reduce the channel length of the device. This is followed by step 6 where the channel is broken; the migrated ions return to the top contact leaving behind some ions near the bottom contact which will help the device for faster switching by making the filament formation fast in the next cycle. As there is no flow of electrons taking place in the device, it tends to get back to high resistance state or reset state.

4.4. Summary

Densely packed Ga₂O₃ nanostructured films were synthesized using single step low temperature chemical growth process. Variation in the topography of nanostructured film was a result of different pH value. Annealing of the film caused phase change leading to a stable phase of Ga₂O₃. Ga₂O₃ nanostructured films deposited at pH 8 were relatively denser as compared to pH 6, pH 7, pH 9 and pH 10. The UV-Vis spectroscopy showed effective absorption in the short UV range making Ga₂O₃ nanostructured thin films a suitable candidate for solar blind photodetector and UV sensors. The Ga₂O₃ nanostructured film have charge carrier concentration in the range 10¹⁷ cm⁻³ signifying their utility for high-power based electronics devices. I-V characteristics curve showed a uniform current density value for pH 8 and pH 9 as compared to pH 6, pH 7 and pH 10. Memristor device was fabricated using Ga₂O₃ nanostructured film deposited at pH 8, with resistance ratio of 10^2 and set and reset voltages of 2.7V and -3.1V respectively. Low temperature based Ga₂O₃ film formation over FTO substrate was found to be aptly suitable method for various applications in the field of optoelectronics, electronics devices, sensors, coating etc.

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Chapter 5: Structural and electrical properties of cesium doped β-Ga₂O₃ nanostructured films

Cesium doped gallium oxide (Cs-Ga₂O₃) nanostructured films are deposited using wet-chemical approach. Effect of different concentration of Cs (1% to 100% molar concentration with respect to concentration of Ga precursor) on morphological, structural, optical and electrical properties of doped Ga₂O₃ nanostructured films are investigated. The morphology (diamond shaped nanostructures) remains intact for lower doping concentration of Cs (1 to 7.5% of Cs molarity with respect to Ga molarity in precursor solution) whereas when doping concentration is increased (10 to 100% of Cs with respect to Ga molarity in precursor solution) the morphology drastically changed to flower and clustered particles. The shift in diffraction pattern indicates the presence of Cs inside the Ga₂O₃ crystals. The high amount of Cs in precursors solution (half or equal molarity of Cs with respect to Ga molarity (50 to 100%)) in precursor solution results doping as well as formation of dicesium oxide. The doping of Cs is further confirmed by X-ray photoelectron spectroscopy. The electrical conductivity of doped Ga₂O₃ nanostructured films varies with variation in Cs ions concentration. The higher resistance is noticed in memristor device when the doping concentration is lesser. The RON/ROFF ratio is decreased after Cs doping and to be found only 10¹ orders but cs doping improved the switching speed of the memory device.

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5.1. Introduction

The development of memory devices with high speed, low power consumption, large capacity, long life time, and ease of operation based characteristics become necessity for rapidly developing digital world [1][2]. To achieve the best possible trade-off between cost and computation performance different ways are incorporated to ensure the proper balance between the these two [3][4]. Significant efforts have been made in the recent decade to produce resistive switching materials and technologies. Complete and in-depth understanding of the electrode/switching medium interface on a nanoscale is being developed to further combine computation via memristor with gradual manipulation of device conductance. Gallium oxide (Ga₂O₃) based electronic devices have been considered due to its wide bandgap, different available phases, stable nature and facile material processing etc. [5][6][7]. For memristor applications, charge carrier densities[8], mobility [9] and variable resistance are the key parameters of a materials and gallium oxide has shown his presence for the same [10][11][12][13]. However, issues like retention time, switching, filament formation are commonly notices in the memristive device [3][14]. These issues can be addressed by modifying conductance progressively by manipulating charge flow. Designing an efficient material or electrode architectures is undeniably one of the most effective ways to achieve this goal.

Doping is an option to control the density of charge carrier and tune the electrical properties of memory element of storage devices [15]. X.B. Yan et al. have shown repeatable bipolar resistive switching at a low threshold voltage and a low compliance current. As a result the resistive switching were dependent on electrochemical processes and Ag^+ ion transport[16]. The role of Pt dispersed in SiO₂ was investigated by B. J. Choi et al. and they found rapid (100 ps) switching with long state retention (no detectable relaxation after 6 months), and high durability (>3x10⁷ cycles) [17]. Kura et al. deposited chromium (Cr) doped Ga₂O₃ films via co-sputtering method for resistive memory devices and Ga_{0.82}Cr_{0.18}O₁₂ stoichiometric composition film was found to be the relatively better performing switching device [18]. Gallium oxide nanostructures produced through local anodic oxidation have a high resistance (HRS) at +4V and a low resistance state at -6V [19]. M.N. Almadhoun et al. developed bipolar resistive switching using the

junction of gallium oxide and p-type silicon, obtaining a resistance ratio of 10^8 and a retention period of 10⁵s [20]. Self-rectifying resistive switching behavior were explored by J.H. Park et al. via using a combination of different material i.e. GaO/NbO as an active layer to reduce the operating voltage. At Ti and GaO_x interface the carrier transport reduced the electric field and NbOx /Pt stack were responsible for rectifying behavior. As an outcome the on/off ratio was 20 with high selectivity of 10^4 and operating speed of 200-500ns [21]. J.J. Huang et al. proposed bipolar resistive switching in a Pt/GaO_x/TiN structure were they reported that when active layer were sputter deposited in presences of Ar and oxygen the resistance ratio was increased by 2.5 times [22]. The nanoscale layer of gallium oxide aided in the production and dissolution of gallium filaments, resulting in reversible switching. Memristors based on low-dimensional materials exhibit desirable performance and stability such as long retention and great endurance. Cesium ions doping with metal oxide nanostructure have good impact on the optical and electrical properties. The ions present enhances the current flow due to the presences if Cs^+ ions. In a study by P Srivastava et al. showed the influence of Cs doping on various materials properties (structural, morphological and electrical). They observed a decrement in bandgap for 2% doping and they also reported a significant enhancement of current value by 3 order of magnitude [23]. Therefore, presence of cesium ions on gallium oxide significantly alters the electronic and electrical properties which certainly affect the memristors behavior.

In this chapter, single step aqueous method is used to deposit cesium doped gallium oxide nanostructures films at low temperature. Cs molarity with respect to Ga molarity in precursor solutionis varied from 1% to 100% molar concentration while retaining the same parameters of reactions (pH, temperature, drying time and annealing temperature). The presence of Cs ions is indicated by an X-ray diffraction (XRD) pattern, and a shift in the plane (401) validates the doping of cesium ions in Ga₂O₃ crystals. Due to an increase in cesium doping concentration, diamond-shaped nanostructures get deformed at higher doping concentration of cesium. Cs doped nanostructured film also shows pinched hysteresis loop in memristive property measurement.

5.2. Experimental Section

5.2.1. Deposition of cesium doped β-Ga₂O₃ nanostructures film

The FTO substrate was sliced into $2 \text{cm} \times 1 \text{cm}$ pieces before the deposition procedure, which were subsequently cleaned to eliminate any naturally existing unwanted particles and avoid organic particles on the surface. Cleaning technique involves sonicating FTO substrates for 15 minutes in a sequential order starting with soap solution, DI water, acetone, ethanol, and blow drying at the end respectively. Teflon tape was used to partially coat clean substrates, and support was used to attach a hanging support. To make the precursor solution, an aqueous solution of gallium chloride was prepared at ambient temperature. The solution was then transferred to a 60°C hot plate, where ammonia was added to the solution drop by drop as the temperature rose. FTO substrate was suspended within the beaker and dipped into the stirring solution at pH 8. The FTO substrates were taken out after 10 hours and allowed to cool to room temperature before being sonicated in DI water for 1 minute. For 30 minutes, the substrate was annealed at 600°C. To prepared Cs-doped films, cesium chloride was used with variable amount keeping the gallium precursor concentration constant at 0.1M for all the cases. The concentration of cesium chloride was taken from 1% to 100% equal molar amount with respect the gallium precursor. Then similar deposition process was adopted as in case of undoped gallium oxide film for deposition of Cs doped gallium oxide films. To investigate the electrical and memristive properties of the nanostructured films, two probe system was adopted as shown in figure 5.1. Conductive silver paste was used to make the metallic contacts, one contact pad was made over the top surface of the nanostructures films (top contact), and second contact was made on the FTO substrate (bottom contact). The probe was placed on the respective pads using a micro positioner having gold coated tips, keithley source meter were used to record the I-V characteristic. For all the device measurement, the device size and contact size is similar. In this case 1cm×1cm area of the film was taken where 5mm² silver metal contact was drawn. The current density is calculated then plotted accordingly.

5.2.2. Deposition of β -Ga₂O₃ films with high amount of cesium

The deposition of nanostructured films was further carried away with same procedure how the doped nanostructured films were deposited. But In order to increase the cesium precursor, the amount of cesium precursor was increased with respect to doping. Cesium chloride at 25 Mol%, 50 Mol% and 100 Mol% was used, in equal molar amount with respect to gallium precursor. Similar deposition process was adopted as in case of undoped gallium oxide film for deposition of Cs doped gallium oxide films.



Figure 5.1:Schematic of Cs-Ga₂O₃ nanostructured thin film based memristors.

5.2.3. Structural and electrical characterization of cesium doped β-Ga₂O₃ nanostructured film and high amount of Cs incorporated Ga₂O₃ nanostructured films

A Bruker D-8 advance X-ray diffractometer system with copper (Cu) as the X-ray source (λ =1.54nm) was used to investigate the structural properties of deposited Cs-Ga₂O₃ nanostructured films. Scanning electron microscope was used to examine morphological characteristics (JEOL make model number: JSM-7610F Plus). UV-Visible spectroscopy measurement was done by using UV-Vis instrument (Simadzu-2600). XPS analysis were performed by SPECS surface nano analysis GmBH. I-V characteristics measurement was done by Keithley 2604B.

5.3. Results and discussion

5.3.1. Structural and morphological properties of cesium doped β-Ga₂O₃ nanostructured films



Figure 5.2: Topographic image of cesium doped gallium oxide (Cs-Ga₂O₃) 1 Mol% - 10 Mol% (Cs molarity with respect to Ga molarity in precursor solution);(a,b) undoped, (c,d) 1 Mol%, (e,f) 2.5 Mol%, (g,h) 5 Mol%, (i,j) 7.5 Mol% and (k,l) 10 Mol%.

Figure 5.2 depicts the surface topography of cesium doped gallium oxide (Cs-Ga₂O₃) nanostructured films synthesized using different concentrations of the cesium in precursor solution. Diamond shaped nanostructures are seen for the lower concentration of cesium, (1 Mol% to 7.5 Mol% Cs molarity with respect to Ga molarity in precursor solution). However, at 10 Mol% the morphology of the growing nanostructures changes (Figure 5.2(k,l)). On increasing the doping concentration to 25 Mol%, 50 Mol% and 100 Mol% morphology changes completely as shown in figure 5.10. The diamond like morphology vanishes, which can be ascribed to the formation of other compound i.e. dicesium oxide (Cs₂O) with Ga₂O₃. Nanostructures of Cs-Ga₂O₃ initializes with nucleation of crystallites which is followed by formation of grains, thus in minimal doping the Ga ions are present in majority giving more nucleation points to grow Ga₂O₃ nanorods. But as the concentration is increased cesium ions also plays a dominant role for the nucleation to occur. Resulting to this case the probability of formation of Cs₂O increases.



Figure 5.3: Cross-sectional image of cesium doped gallium oxide (Cs-Ga2O3) 1 Mol% - 10 Mol% (Cs molarity with respect to Ga molarity in precursor solution);(a) undoped,(b) 1 Mol%, (c) 2.5 Mol%, (d) 5 Mol%, (e) 7.5 Mol% and (f) 10 Mol%.

Thickness of the grown nanostructures is shown in figure 5.3. The average thickness of the undoped film is approximately 773nm whereas the thickness for 1 Mol%, 2.5 Mol%, 5 Mol%, 7.5 Mol% and 10 Mol% is approximately 888nm, 1.33microm, 1.61micron, 1.8micron and 1.81micron respectively. At 2.5 Mol% doping concentration the SEM image shows larger grain size as compared to other

sample this may be due to optimal growth parameter that is offered while during reaction, whereas at higher doping concentration i.e. 25 Mol%, 50 Mol%, 100 Mol% respectively, it is true that the SEM images have larger grain size than other sample, this can be due to the formation of dicesium oxide with change in morphology from rods to flower and aggregate particles.



Figure 5.4: XRD spectra for cesium doped gallium oxide (Cs-Ga₂O₃) nanostructured thin films on FTO substrate: 1 Mol%-10 Mol% (Cs molarity with respect to Ga molarity in precursor solution).

The XRD pattern is shown in figure 5.4 and is utilized to undertake structural investigations for the creation of Cs doped nanostructured thin films. The peak (401) at ~36° confirms the presence of monoclinic phase (β) of Ga₂O₃ (ICSD no. - 27431), most stable phase of among all the reported phases for Ga₂O₃. The FTO substrate's XRD pattern can be detected in all the nanostructured films made at different doping concentrations. The intensity of peak (401) is observed to be maximum in case of undoped sample as compared to the doped sample, this is attributed to the pristine presence of β -Ga₂O₃ phase. However, on doping it is observed that the intensity of plane (401) keeps on decreasing. Other attributes of doped nanostructures films is also studied where crystallite size is calculated for

the doped nanostructures and it was decreasing with increase in the doping concentration, 37.9nm, 37.3nm, 33.27nm, 31.26nm, 31.19nm and 31.00nm, for undoped, 1 Mol%, 2.5 Mol%, 5 Mol%, 7.5 Mol% and 10 Mol% nanostructured films, respectively.



Figure 5.5: Spectral comparison among the $Cs-Ga_2O_{3:}$ (a) 1 Mol% - 10 Mol% (Cs molarity with respect to Ga molarity in precursor solution)

Study over micro strain was also done on the doped film, and it seen that the strain increased when the doping was low i.e., 3.848×10^{-3} , 4.36×10^{-3} , 5.54×10^{-3} , 5.67×10^{-3} , 5.83×10^{-3} . Microstrain for the doped nanostructured is calculated using the following equation [20], where β is FWHM, θ is the angle /peak position in radians, D is crystallite size, λ is wavelength of X-ray source, K is shape factor and ϵ is induced strain.

$$\beta_{hkl}.Cos\theta_{hkl} = \frac{k.\lambda}{D} + 4.\varepsilon.Sin\theta_{hkl}$$

Due to doping the induced strain got affected by the substitution of Cs ions with Ga ions having higher ionic radius. The microstrain for 1 Mol%, 2.5 Mol%, 5

Mol% 7.5 Mol%, 10 Mol%, is calculated to be 3.8×10^{-3} , 4.3×10^{-3} , 5.5×10^{-3} , 5.6×10^{-3} and 5.8×10^{-3} respectively. The microstrain increased as the doping concentration increased. Change in microstrain in the doped nanostructures is mostly caused because of favorable interstitial incorporation at lower concentration (1 Mol% to 5 Mol%), whereas for relatively higher doping concentration (i.e. 7.5 Mol% - 10 Mol%) exchange and interstitial replacement take place [21]. The XRD pattern of nanostructured films is shifted as compared to undoped films (shown in figure 5.4). This behavior is attributed to the evident replacement of Ga ions with Cs ions when the doping concentration is less (i.e.1 Mol% to 10 Mol%) [22].

XPS measurement for chemical bonding states of Cs-Ga₂O₃ nanostructured films is studied in detail. The core level peaks from the Ga 3d, Ga 2p, and O1s states were exhibited in the standard XPS survey spectrum (Fig.5.5(a) with energies ranging from 0 to 1300eV. In Figure 5.5(a), the core levels of O KILL Auger, O1s, Ga LMM, Ga3d, Ga2p, and Eu 3d can be shown, which is calibrated by the C1s peak at 285.0 eV [24]. As shown in Figure 5.5(a), the Ga 3d spectra at ~20.5eV represent the Ga₂O₃ [25]. The Ga–O bonding with the oxygen vacancy site was represented in Figure 5.6(a) as a stem from Ga 2p. The peak at roughly 20.5eV was the Ga^{3+} signature. Ga 3d had an energy peak of roughly 22eV, which might be attributed to the presence of gallium in β -Ga₂O₃. The distinctive peaks of Ga–O matched to component 4 of O1s peak at 534.8eV. Figure 5.6(b) demonstrate main Cs peaks at 724.8 and 740 eV representing Cs 3d5/2 and Cs 3d3/2respectively, XPS lines identify Cs atoms that exist in the vicinity and indicates that Cs is present on the surfaces of the nanostructured films or at interfaces; the absence of peak shifts indicates the absence of numerous Cs sites [26][27]. The existence of Ga_2O_3 was confirmed by the position of the Ga3d binding energy peaks in Figure 5.6(c) shows Ga 2p1/2 and Ga 2p3/2 peaks are centered at 1145.4eV and 1118.5eV (D = 26.9eV), respectively, which is consistent with previous reports [28][29]. Figure 5.6(d) shows the binding energies of four kinds of oxygen signals (O1, O2, O3, O4): 531.1eV, 532.8eV, 533.5eV, and 534.8eV, respectively. In addition, the component 1 of O1s peak at around 531.1eV was attributed to lattice oxygen, which was combined with an activation energy barrier (E_a) of 1.05eV to release O_2 and leave oxygen vacancies, whereas the component 2 and component 3 of O1s peak at 532.8eV and 533.5eV, respectively,

were attributed to H₂O, both of which were accompanied by the presence of oxygen vacancies [30][31][32].



Figure 5.6: XPS spectra for cesium doped gallium oxide (Cs-Ga₂O₃) nanostructured films; (a)-Scanning survey, (b)selective spectrum of cesium (Cs), (c) selective spectrum of gallium and (d) selective spectrum of oxygen.

5.3.2. Optical properties of cesium doped β-Ga₂O₃ nanostructured films

Figure 5.7(a) shows the UV-Vis absorbance spectrum of Cs doped Ga₂O₃ nanostructured films. It exhibits absorption in the UV-C region with a minimal absorption in visible range. Since Ga₂O₃ is transparent and does not reflect any color from the visible range. The bandgap decreases from 4.1eV to 3.9eV, from undoped to 10 Mol%. At lower doping concentration i.e. undoped, 1 Mol%, 2.5 Mol%, 5 Mol%, 7.5 Mol%, 10 Mol% and the bandgap values obtained are 4.1eV,4.06eV, 4.05eV, 4.03eV, 4.0eV and 3.9eV, respectively (Figure 5.7(b)). The decrease in the bandgap value can be ascribed to the presences of Cs ions in the vicinity of Ga₂O₃ nanostructures which changes the energy distribution of the allowed states to some extent. Doping generally creates allowed shallow states in the bandgap. And due to small ionization energies of shallow states after

incorporating to the Ga_2O_3 nanostructures the generated energy level becomes close to the conduction band edge as a result the corresponding bandgap decrease.



Figure 5.7: (a) UV-Vis Spectra of Cs doped Ga_2O_3 nanostructured films, (b) Bandgap for Cs doped Ga_2O_3 nanostructured films at different doping concentration (1 Mol%, 2.5 Mol%, 5 Mol%, 7.5 Mol% and 10 Mol%).

5.3.3. Electrical properties of cesium doped β-Ga₂O₃ nanostructured films

To examine the impact of doping at various doping concentrations on the electrical properties of nanostructured thin films (Figure 5.8), current-voltage (I-V) measurements were carried out at ambient temperature. Testing the nanostructured thin films at different doping concentrations of Cs reveals an increasing order of the current density value. The current value tends to be limited in the range of 10⁻⁸A.cm⁻² for undoped films. The current density is relatively small as compared to doped films because of the absences of Cs ions the flow of charge occurs in Ga₂O₃ which offers more resistance to the flow as a result this behavior is observed. Whereas, when the doping of cesium is increased chronologically it is observed that the current density value tends to increase. Initially when the doping concentrations is small i.e. for 1 Mol% and 2.5 Mol%, current density remains in the range of 10⁻⁷-10⁻⁸A.cm⁻². However, increasing the doping concentration current density increase drastically for 5 Mol%, 7.5 Mol% and 10 Mol% doped nanostructured films ranging from 10⁻⁵-10⁻⁶ A.cm⁻². The effect of morphology also affects the electrical properties, as an example nanowire shows more conductivity as compared to other morphologies like sheets or rods etc.[37], as studied by I.E. Stewart et al. where he increase of conductivity by 4000 times for nanowire as compared to nanoparticles[38]. Similarly grain boundaries and grains also plays an important role in case of electrical properties, as the grain size varies due to any factor, it reduces the effective grain boundaries which in turn reduced the overall grain barrier loss [39]. Thickness of films is also a vital parameters to be considered for affecting the electrical properties, it is generally noted that the conductivity of the films increases with increase in the thickness, as it caused due to variation in the passage of the electric current which is also dependent on the grain boundaries [39]. As stated for undoped nanostructured films, when doping is done the arability of ions supports the flow of charge as a result resistance offered to the flow of charge is reduced and hence the current density drastically changes. The current density value also varies as per the doping concentrations since the number of ions presence in the vicinity decides how the flow of charge may get influence.



Figure 5.8: I-V profile for cesium doped gallium oxide (Cs-Ga₂O₃) nanostructured films doped at various Cs molarity with respect to Ga molarity in precursor solution (1 Mol% to 10 Mol%).

5.3.4. Memristive properties of cesium doped β-Ga₂O₃ nanostructured films

The memristive properties of the Cs doped nanostructured films is depicted in figure 5.9. The characteristics of pinched hysteresis are observed for 1 Mol%, 2.5 Mol% and 5 Mol% of Cs molarity (with respect to Ga molarity concentration), confirming the memristive behaviour. Memristive behavior is investigated by measuring voltage-current sweep analysis (Figure 5.9(a-f)), at a potential window of -5 to +5 Volts. On applying voltage to top electrode (silver contact) from 0 to +5 V, current increased gradually and the device underwent transition from initial high resistance state (HRS) to a low resistance state (LRS), referred as a set process. The device remained in the LRS during the subsequent sweep from +5 to 0 V and after withdrawing the applied voltage, signifying a non-volatile resistive switching behavior of memristor. The device undergo transition from the LRS to HRS, when a negative bias is applied, defined as a reset process. Undoped nanostructured device showed a resistance ratio of 75 whereas for the doped nanostructured films at 1 Mol%, 2.5 Mol%, and 5 Mol% the resistance ratios was in order of 4.2, 3.79 and 3.68 which is smaller than the undoped nanostructured film. The resistance ration for 7.5 Mol% and 10 Mol% were negligible lesser than 10^1 order thus not accounted for further investigation. The switching speed for the doped nanostructured film appears to be faster as compared to the undoped nanostructured film due to difference in the resistance ratio. The noises present in the hysteresis curve for some of the nanostructured films can be due to non-uniform contact between the metal electrode and nanostructured active layer. This could be due to the non-homogeneous roughness of the nanostructured films. Irregular spike in the IV also arises due to the carbon resistance present at the testing electrodes as well as magnetic induction arising from nearby equipment's which perturbs the IV curve in small time frame. The presences of metal ions near the bottom electrode helps the filament formation to take place rapidly. These phenomena is not supported for the undoped nanostructured films since there is no extra metal ions present. Under minimal doping condition, the device response was able to show the nonvolatile behavior. At 1 Mol%, 2.5 Mol% and 5 Mol% doping concentration due to the lesser amount of cesium ions the overall effect was influenced by the resistance offered by the Ga₂O₃. However, on increasing the doping concentration the device demonstrated linear behavior which can be ascribe to the Cs ions present. For the devices fabricated at doping concentration more than 5 Mol% the pinched hysteresis was loop was still present, but negligible difference was observed between the set cycle and reset cycle. Several reports show that oxygen vacancies have significant role as defect for the resistive switching, these are present as extrinsic or intrinsic defect depending on weather they are caused by dopants or some different phenomena [40]. On varying the thin film deposition conditions, the intrinsic oxygen vacancies defects can be varied. Bas et al. observed that the memristive properties can be influenced at a critical oxygen content for TiO_{2-x} films [41]. Younis at al. reported loss in resistive switching for electrodeposited CeO₂ films at 300°C [42].



Figure 5.9: Memristive characteristics of cesium doped gallium oxide (Cs-Ga₂O₃) nanostructured films doped at various Cs molarity with respect to Ga molarity in precursor solution (a) Undoped, (b) 1 Mol%, (c) 2.5 Mol% and (d) 5 Mol% and (e) 7.5 Mol% and (f) 10 Mol% concentration.

Those investigations on intrinsic oxygen defect modulation lead to the conclusion that the quantity of oxygen vacancy defects accessible in the device's oxide influences the resistance ratio, as well as the forming and switching variability. As the condition is varied (doping concentration more than 5 Mol%) the conductivity of the film also get varied which influence the device performance in several way. The memristive characteristics for 10 Mol% Cs doped nanostructured film, there is no difference between the charging cycle and retention

cycle. Charge storage can be understood from the phenomena between oxygen vacancies and filament formation. The filament formed is when sufficient amount of vacancies are accumulated in the insulating region [43]. But on doping with cesium the vacancies inside the insulating layer can be diffused away through spontaneous diffusion which generally gets activated on applying voltage [44]. Oxygen vacancies concentration inside the insulating layer gradually reduces, corresponding to drift of device conductance. For increased doping concentration, the oxygen vacancies inside the insulating layer is reduced below a critical value, thus the filament is ruptured [43][45]. This condition can be ascribed to the extrinsic effect of the material. In some study, extrinsic oxygen doping defects were also reported to alter the resistive switching which can be caused as an effect of doping. Li et al. show that up to 2 atom% Cu doping increases electrical carrier mobility in nickel oxide (No) by a factor of three and may be utilized to lower the resistive switch's set voltage [46]. Furthermore, doping Ta₂O₅ with Si improves oxygen transport by forming oxygen vacancy transport channels, resulting in more controlled resistive switching [47]. For higher doping concentration greater than 10 Mol% the memristive behavior appears to be similar as obtained for 10 Mol% nanostructured films. K.J.Gan et al. reported flexible device having good memory window of $>10^5$ and set and reset voltage at 1.3V and -0.65V respectively [48]. S.Wang et al. reported a resistance ratio of 10^4 for a vertical sandwiched device having Vset and Vreset at +2V and -2V respectively [49]. Cs-Ga₂O₃ doped nanostructured showed a resistance ration of 10^1 which can be varied when the doping concentration is less than 10 Mol%. Despite this qualitative identification, it is unknown how the concentration and mobility of oxygen vacancies in the oxide influence the resistive switching behavior of memristive devices when under external bias. Therefore, at lower doping concentration the memristive effect is visible whereas higher doping concentration will not be a viable option for making memristors.

5.4. High amount of cesium incorporation in β-Ga₂O₃ nanostructured films

On increasing the concentration of cesium precursor with respect to gallium precursor. The percentage of cesium incorporated is more when compared to the doping category, Thus, on increasing the concentration way above 10 percent shall be considered as incorporation of material into the parent material. To observe the effect of large incorporation of cesium precursor to the gallium precursor, films were deposited at three different compositions i.e. 25 Mol%, 50Mol% and 100 Mol%.

5.4.1. Morphological and structural properties of high amount of cesium incorporated β-Ga₂O₃ nanostructured films

High amount of cesium incorporated Ga_2O_3 nanostructured films were deposited at molar percent of 25 Mol%, 50 Mol% and 100 Mol% with respect to gallium precursor, morphology changes completely when compared to doped nanostructured films (figure 5.2). Rice like morphology is observe for 25 Mol% films whereas for 50 Mol% and 100 Mol% flower like and clustered particles like morphology is observe as shown in figure 5.10. The diamond like morphology vanishes, which can be ascribed to the formation of other compound i.e. dicesium oxide (Cs₂O) with Ga₂O₃.

Nanostructures of Cs-Ga₂O₃ initializes with nucleation of crystallites which is followed by formation of grains, thus in minimal doping the Ga ions are present in majority giving more nucleation points to grow Ga₂O₃ nanorods. But as the concentration is increased cesium ions also plays a dominant role for the nucleation to occur. Resulting to this case the probability of formation of Cs₂O increases. As the cesiun ions are also present in plentiful amount therefore the probability of incorporation of cesium with gallium increases. Hence, the morphology of the end product is of different shape. Nanostructures at higher doping concentrations i.e., for 50 Mol% and 100 Mol% shows presences of dicesium oxide (ICSD no. -27919). Corresponding peaks of dicesium oxide were confirmed from the XRD pattern shown in figure 5.11. Peaks (104) at 30.5°, (113) at 43.9°, (021) at 49.3° and (1010) at 54.5° confirms the formation. Crystallite size is calculated for the heavily incorporated films and it was decreasing with increase in concentration, 31.00nm, 29.42nm and 28.79nm for 25 Mol%, 50 Mol% and 100 Mol% films respectively. Micro strain study showed that the strain decreased when the cesium concentration with respect to gallium concentration was increased, i.e., 5.96×10^{-3} , 5.51×10^{-3} and 5.17×10^{-3} for 25 Mol%, 50 Mol% and 100 Mol% respectively.



Figure 5.10: Topographic image of high amount of Cs incorporated Ga_2O_3 nanostructured:(Cs molarity with respect to Ga molarity in precursor solution) (a,b) 25 Mol%, (c,d) 50 Mol%, (e,f) 100 Mol%.



Figure 5.11: XRD pattern of high amount of Cs incorporated Ga₂O₃ nanostructured films on FTO substrate: 25 Mol%-100Mol% (Cs molarity with respect to Ga molarity in precursor solution).

The steep decrease of microstrain for 50 Mol% and 100 Mol% is caused due to higher doping concentrations and inclusion of increased cesium ions in the vicinity of Ga_2O_3 . Even on increasing the doping concentration to higher values i.e., 25 Mol%, 50 Mol% and 100 Mol%, formation of newer compound starts taking place. It can be stated that to some extent migration of small part of Cs₂O particle may get unified into Ga₂O₃ lattice [23].

5.4.2. Optical, electrical and memristive properties of high amount of cesium incorporated β-Ga₂O₃ nanostructured films

The optical study for the heavily incorporated cesium into the gallium oxide is done using the UV visible spectra as shown in figure 5.12. The absorbance spectra show major absorption in the UV region for 25 Mol%, 50 Mol% and 100 Mol% respectively. The absorption curve shows the influence of the Ga₂O₃ to be more as compared to the influence caused by the Cs₂O. Therefore, on calculating the bandgap of the films, it was observed that the band gap reduced slightly on increasing the concentration of cesium with respect to gallium. For 25 Mol%, 50 Mol% and 100 Mol% the bandgaps were 3.98eV, 3.94eV and 3.89eV respectively.



Figure 5.12: (a) UV-vis spectra of high amount of Cs incorporated Ga₂O₃ nanostructured films, (b) Bandgap for heavy incorporation of Cs into Ga₂O₃ films at different concentrations (25 Mol%, 50 Mol% and 100 Mol%).

Current voltage measurements for heavily incorporated cesium into Ga_2O_3 films is shown in figure 5.13(a). I-V profile observed for the heavily incorporated films demonstrate the current density in range from 10^{-6} A.cm⁻² to 10^{-3} A.cm⁻². The current density value increases with increase in the concentration range from 25 Mol% to 100 Mol% respectively.

The drastic change in current density value can be attributed to the presences of Cs ions. As the concentration of cesium precursor is increased there is corresponding increase in the Cs ions present. This leads to the incorporation of Cs ions in majority thus giving higher conductivity. The availability of ions for the current value also increases, offering less resistance to the flow of charge.



Figure 5.13: I-V profile for high amount of Cs incorporated Ga₂O₃ nanostructured films at different Cs precursor concentrations with respect to gallium precursor (25 Mol%, 50 Mol% and 100 Mol%).

The memristive behaviour of heavily incorporated cesium into Ga₂O₃ films can be observed at figure 5.13. The memristor device fabricated from the heavily doped films were unable to showcase any better I-V profile desired for memristor device. The resistance ratio for 25 Mol%, 50 Mol% and 100 Mol% seems to be negligible as shown in figure 5.13((a), (b), (c)). The negligible resistance can be accounted for very less data retention. This behaviour is caused due to the presence of Cs metal ions, as in heavily incorporated Cs into Ga₂O₃ films the overall number of Cs ions thus they tend to reduce the resistance and increases the conductivity. Therefore, due to large flow of charge and negligible resistance the ratio becomes negligible. As the memristive properties is concerned doping with optimum concentration will help to achieve desired nature whereas on heavily incorporating cesium will lead to formation of dicesum oxide suppressing the basic nature of gallium oxide that is offering the desired resistance.

5.5. Summary

In summary, Cesium doped gallium oxide nanostructures were deposited at 60°C via single step aqueous route. 1 Mol% to 100 Mol% concentration of cesium with reference to gallium precursor concentration were varied while keeping the all the reaction parameters constant. The morphology of diamond-shaped nanostructures changed due to an increase in cesium doping concentration. A shift in the X-ray diffraction (XRD) plane (401) confirms incorporation of cesium ions. Presence of dicesium oxide is detected when the concentration of Cs reaches 50 Mol% and 100 Mol% of the Ga concentration. XPS analysis of the doped Ga₂O₃ nanostructure reveals presence of Cs ions. The bandgap of doped nanostructured films reduced as the doping concentration increased. Electrical study of nanostructured film showed approximate 10³ increase in current density when high amount of Cs is doped in Ga₂O₃ nanostructured film. Pinched hysteresis loop was observed for doped nanostructured films, the resistance ratios of 10¹ is observed for films deposited with lower doping concentration (1At %) and further increase in doping amount leads to reduction in the value of resistance ratios.

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Chapter 6: Summary and Conclusions

Thesis briefly presented an overview on development of nanomaterials for memory device memristor. Classification of memory devices, basic principle of memristor and development of active layer are discussed. Recent developments on active layer for memristor application were presented. In addition, introduction of different approaches for synthesizing active layer, and the basic principle involved in synthesis process are overviewed. Among various semiconducting materials, wide bandgap semiconducting materials are extensively reviewed to consider it utilization for memristors.

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6.1. Summary and Conclusions

The thesis briefly focused on development of high-quality β -Ga₂O₃ films via a wet chemical method that can be used in electrical and optoelectronic devices. The synthesis of gallium oxide (Ga₂O₃) nanostructures using solution-based approach with different methodologies is discussed. Recent development on wet chemical route and nanostructured films were presented. In addition, introduction of memristors and basic principle involved is overviewed.

In one of the studies, Ga₂O₃ nanostructures were synthesized via hydrothermal technique, while modifying numerous parameters like initial precursor and annealing temperature to observe the effect on nanostructures. Different initial precursor (gallium acetyl acetonate, gallium chloride and gallium nitrate) resulted in nano-cuboids and rice shaped morphologies. Cuboids shaped nanostructures were interesting outcome. Variation on the annealing temperature caused these nano-cuboids to undergo surface restructuring. The study shows effect of thermal annealing, on the surface. Increases in annealing temperature up to 950°C result in increased pore size. A higher annealing temperature (1000°C) lowers the size of the nanopores, resulting in a smooth surface of nano-cuboid. Surface oxidation, surface defect manipulation, and atomic rearrangement are all involved in the remodeling of the nano-cuboid surface. Furthermore, the oxidative situation induces lattice atom diffusion, resulting in significant and minor surface oxide layers, surface remodeling, and lattice rearrangement. The influence of temperature on Ga_2O_3 might be very important in understanding the material's stability. Understanding the surface properties and restructuring behaviors of Ga₂O₃ nanostructures at high temperatures can help us develop and select the best materials for reliable power electronic devices.

Deposition of Ga₂O₃ nanostructured thin films using spin coating technique is explored, were deposition over quartz substrates done, by using mixture of gallium nitrate and organic solvent. The synthesis of crack-free Ga₂O₃ films in several scenarios, including those without secondary solvent, with secondary solvent, secondary solvent with heat treatment in open air, and oxygen-rich environments. The addition of deionized (DI) water during the mixing of gallium precursor and organic solvent, followed by heat treatment of deposited film in oxygen-rich circumstances, satisfactorily cures surface fractures in Ga_2O_3 films. The presence of oxygen during film production is attributable to a considerable increase in the intensity of the XRD peak for crack-free films and a Raman shift of 1 cm⁻¹. The average roughness of the crack-free film, as measured by AFM, which is around 0.48 nm. Current-Voltage measurement reveals a greater current density value in crack-free films, which increases further with higher-temperature annealing. This solution-grown crack-free Ga_2O_3 film may be used to create efficient electronics devices.

To involve various attributes and characteristics of thin film. Direct deposition of Ga₂O₃ nanostructured films via single step aqueous route method is investigated. This methodology help us to reduce the steps involved in deposition process, a different wet chemical route is explored where direct nanostructure is grown onto the FTO substrate. Single step aqueous route is used to deposit the GaO(OH) nanostructured film at a lower temperature before annealing to produce Ga_2O_3 films. The deposition is carried out at $60^{\circ}C$ in a beaker and hotplate with single precursors, making it a realistic and simple technique for wide area deposition of Ga₂O₃ films. Controlling the pH of the precursor, guide us to produce bigger crystallites and denser Ga₂O₃ nanostructures. At pH 8 the production of a thick and compact layer of Ga₂O₃ nanostructures is reported. When films were annealed at 600°C, the structural investigation indicated the existence of " α and β " phases. Ga₂O₃ nanostructures have a diamond-like shape and maximal UV absorption due to their wide bandgap characteristics. The charge carrier density (N_D) of the Ga₂O₃ nanostructure film is reported to be 10^{17} cm⁻³. After testing for memristive behavior for Ga₂O₃ nanostructured film annealed at 600°C, resistance ratio (R_{OFF} : R_{ON}) is 10² is observed, with set and reset voltages of 2.7V and -3.1V, respectively. The unique process is straightforward and appears to be suitable for large-scale Ga₂O₃ film deposition, which might lead to a variety of electronics and optoelectronic applications.

In other work, slight modification with the aqueous route is carried out to vary the electrical behavior of the nanostructured films. To do so doping of Ga₂O₃ nanostructures is carried out using single step aqueous technique. Cesium doping id done to see the overall response over the memristive behaviour. Cs doping
concentrations in precursor solution of Ga₂O₃ is varied from 1-100% (Cs molarity with respect to Ga molarity in precursor solution) maintaining same pH value of 8. Doping altered the structural, morphological, electrical, and memristive properties of nanostructured films. The structural presence of Cs ions was determined by Xray diffraction (XRD) and shifting of the structural plane (401) verifies the doping of cesium ions into the proximity of Ga₂O₃. When 50% and 100% Cs molarity with respect to Ga molarity is taken in precursor solution, it results to form dicesium oxide (Cs₂O). The lower amount of doping concentration slightly changes the film current density but when high amount of dopant is introduced significantly high increase in current density is measured as compared to pristine Ga₂O₃ nanostructures. The memristive behavior of the nanostructured films is also tested, which showed lower doping concertation (i.e. 1 Mol% to 2.5 Mol%) is favorable for memristive behavior. Resistance ratio of 10^1 was observed which is one order lower as compared to pristine Ga₂O₃ nanostructured films. To conclude, controlling the surface of nanostructures, film cracks, crystal expansion and doping are some of the aspects that are extensively reviewed to consider for quality improvement of the films. The output of these experiments can be incorporated for future endeavors of device development at large scale.

6.2. Future Scope

 Ga_2O_3 nanostructures of various sizes and morphologies grown via solution-based techniques might be an intriguing topic to investigate for its impact on diverse applications. Furthermore, large-scale Ga_2O_3 production utilizing a solution-based technique is still difficult, and its deposition on various substrates is an uncharted area that must be addressed. Another area of interest is the solutionbased fabrication of heterostructure-based films employing Ga_2O_3 and TiO_2 nanorods, as well as extensive analysis for optoelectronics and power electronics. Furthermore, the fabrication of a stable and durable heterostructure is a difficulty that must be addressed. The use of these nanostructures-based films for sophisticated applications is another potential avenue that requires further exploration.
