Synthesis and characterization of Indium doped Aluminum Oxide and Anodic Aluminum oxide (Al_2O_3)

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STUDENT DECLARATION

I hereby declare that the data presented in this Dissertation report entitled, **"Synthesis and characterization of Indium doped Aluminum Oxide and Anodic Aluminum oxide** (Al_2O_3)" is based on the results of investigations carried out by me in the Physics Discipline at the School of Physical and Applied Sciences, Goa University under the Supervision of Dr. Rajeshkumar Shankar Hyam and the same has not been submitted elsewhere for the award of a degree by me. Further, I understand that Goa University or its authorities / School of Physical and Applied Sciences will be not be responsible for the correctness of observations / experimental or other findings given the dissertation.

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COMPLETION CERTIFICATE

This is to certify that the dissertation report **"Synthesis and characterization of Indium doped Aluminum Oxide and Anodic Aluminum oxide** (Al_2O_3)" is a bonafide work carried out by Mr. Prashanth Narayan Gowda under my supervision in partial fulfilment of the requirements for the award of the degree of M.Sc in Physics at the School of Physical and Applied Sciences, Goa University.

8/5/24

Signature and Name of Supervisor: Dr. Rajeshkumar Shankar Hyam

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School stamp

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Abstract

Aluminum oxide has been used in electronic devices for its wide variety of properties, it becomes necessary to control electrical conduction and charge transport in Al_2O_3.Various studies have used Aluminum Nitarte as the precursor for both doped & undoped Alumina nanopowder preparation.In this study we dope Indium atoms into the host lattice of Alumina by using hydrothermal method by preparing a solid suspension of commercially available Aluminum oxide powder by using Indium-acetylacetonate (In-acac) as the Indium precursor. Study its structural and electrical properties for possible applications in resistive switching devices by study of I-V characteristics of Indium doped Alumina powder. We also look into the thin film properties of Al_2O_3 by using anodization method of a thin Aluminum foil at room temperatures in oxalic acid at 40 volts, which are otherwise usually done at low temperatures. Study how nanostructures are formed with increasing time duration of Anodization from 2 to 8 hours and study its possible application as a charge storage device. The synthesised Indium doped Aluminium Oxide show increased electrical conduction with increasing doping concentration and lattice expansion. The Anodized samples show the successful formation of porous nanostructures.

Chapter 1

INTRODUCTION

1.1 Metal Oxide Nanostructures

Metal oxide devices and nanostructures have gained popularity over conventional semiconductors over the years since there is the need of sustainable materials which are abundant in earth's crust to harvest and store energy. Conventional materials for energy storage and production like silicon other semiconductors are depleting in nature, are inefficient and have limitations which are not sustainable in the long run. Semiconductor solar cells and photo-diodes made from silicon and other semiconductor materials Gallium ,etc; suffer from disadvantages of being single crystal structures. Silicon and others have reduced mobility in amorphous state due to directional dependent electron conduction ,which is not the case for most metal oxides.[18] This creates difficulty and complexity involved in their fabrication,limited efficiency and are expensive which demands for the search of cost effective non crystsalline or poly-crystalline materials with lower design complexity and easier fabrication methods. Some commonly used non metal and metal semiconductors include Graphene Oxide, Single Walled Carbon Nano Tubes (SWNTS), MoS_2 etc; but the large scale re-producability and production of these materials is difficult due to complexity in synthesis, high cost and reliability issues.

This is when unconventional materials like metal oxides semiconductors (MOS) or Metal Oxide Nanostructures are gaining attention in energy storage, photovoltaic applications, Solar cells, Transparent Thin Film transistors (TFT), Resistive Switching, Random Access Memory (RAM) devices, Transparent Conducting Oxide (TCO) like Indium oxide, Indium Tin Oxide (ITO), Fluorine Tin Oxide (FTO) are being used in Organic LED's, Flat Panel Displays, diodes, Gas Sensors, catalysis (Water Splitting/ Hydrogen production and Storage), etc; due to their ease of availability and abundance in earths crust, ease of synthesis and tunable band gap with addition of suitable dopants can greatly change their electronic, chemical and structural properties to meet the specific requirements. Most commonly used metal oxides are TiO_2, In_2O_3, Ga_2O_3 and SnO which have semiconducting properties when doped with certain metals. Insulating metal oxides like Aluminum Oxide which belongs to same group in periodic table and is similar to these oxides but is difficult dope due to high degree of charge localization. Combining these different metal oxides can lead to unique properties and device applications. Amorphous nature of of metal oxides dosen't inhibit their electron transport which is of great use. In order to make use of MO devices,its important to understand its band structure,physical,chemical and structural properties[12]. In MO, the Valence Band (VB) is made of occupied 2p

Oxygen anti-bonding states, and the Conduction Band (CB) is made up of of unoccupied *ns* metal bonding states. Additionally these materials show great resistance to corrosion, chemical attacks and surface degradation over time which improves their life span and durability. Metal oxides are insoluble in water which makes them a good candidate for outdoor solar applications in extreme conditions and whether. They have excellent thermal stability in addition to high melting points in excess of 1000 degree Celsius which means materials like alumina don't easily undergo a structural phase transition under high temperatures. Combining the properties of different oxides like Alumina and Indium oxide can lead to unique applications.

1.2 Aluminum Oxide Properties

Wide band gap Metal oxides like Aluminum oxide (**Alumina**) are transparent to visible region (400 to 700 nm) of sunlight which makes them useful as a passivisation layer for gate electrode in PV (Photo-Voltaic) cells and conducting transparent electronics like display technology and smart windows. Alumina are insoluble in water which makes them a good candidate for outdoor solar applications in extreme conditions and whether. They have excellent thermal stability in addition to high melting points in excess of 2000 degree Celsius which means Alumina's don't easily undergo a structural phase transition under high temperatures which keeps their physical and chemical properties intact. This property is useful in high and low temperature sensor applications. Alumina also finds applications as a charge transport layer in UV-Vis photo-detectors doped with semiconducting metals with high spectral selectivity. This eliminates the use of optical filters or monochromators to achieve responsivity to a specific wavelength. Their insulating behavior and large band gap (greater than $5eV$). Alumina also serves as a good charge encapsulation layer in such devices because of their large band gap which prohibits the premature recombination of optically generated electron hole pairs.

Aluminum oxide is a ceramic material. Ceramic materials are formed between a metallic and a non-metallic element which very hard, brittle, less-ductile, easily fracture. A very high enthalpy of formation, insulating materials with low electrical (about 10^{-8} S/m) and good thermal conductivity. Aluminum oxide is primarily ionic compound, the hardest known naturally occurring material after diamond,which makes it a good material for cutting use as an abrasive material. Its a polymorphic material that is it has different structural phases at different temperatures like α, γ, θ, or kappa (κ); depending on the source of the extraction i.e; Bayerite, Boehmite or Gibbsite). Out of these alpha α alumina is the most common naturally occurring phase which is also the most stable phase of alumina which forms at around 1000 degrees. Rest other phases like γ, θ, κ etc; are meta-stable phases which occur at 500 to 900 degree Celsius. The structure becomes more becomes more stable and has more close packing structure with increasing temperature. The η, γ and θ phases are called as transition aluminas [19] which are dehydrated variants of Aluminum hydroxide (spinel structure) and alpha (α) phase is anhydrous. The source of eta (η) alumina is Bayerite and Gamma (γ) Alumina is derived from Bohemite.

1.3 Aluminum Electrolytic capacitors

An electrolytic capacitor is a polar capacitor whose anode positive and the cathode is the negative terminal.Since the anode is has a grown oxide layer which limits the reverse voltage usage

Aluminum electrolyte capacitors consist of an anode made of oxidised Aluminum and a counter electrode of pure Aluminum which is called as cathode. A suitable electrolyte is filled between the two electrodes which can be either acidic or basic solution depending on the requirement. The actual construction involves two aluminum foils with a separator in between. These folis are then wound on an element and then the electrolyte solution is impregnated[17]. If only one aluminum foil has an oxide layer then its called an unipolar capacitor and if both anode and cathode have oxide layer then its called bipolar capacitor. Compared to other conventional capacitors The aluminum electrolytic capacitors have a higher capacitance per unit area. The methods of growing the oxide layer involve electrochemical methods like anodization in an acidic solution.In commercial construction of these capacitors, an aluminum foil is etched and then anodized in solution like boric acid to obtain anodic aluminum oxide whose depends on the magnitude of the applied AC or DC voltage. The operating voltage of these capacitor's depends on the thickness of the dielectric layer formed. The general reaction involved in formation oxide layer on the aluminum foil is given by:

$$2AL + 3H_2O \longrightarrow AL_2O_3 + 6H + +6e^-$$

(at anode)

$$6H^+ + 6e \longrightarrow 3H_2$$

(at cathode)

The capacitance can be increased by increasing the surface of the working electrode either by pre or post etching in phosphoric acid. This step makes the aluminum oxide surface rough thus increasing its surface area and its ability to store charge. The capacitance depends on the Surface area of the electrodes and is inversely proportional to the distance between the plates/electrodes, given by the general equation for parallel plate capacitor:

$$C = \frac{\epsilon_0 \epsilon_r S}{d}$$

where ϵ_0 is the permittivity of vacuum in (Farad-m^{-1})

ϵ = relative permittivity of the dielectric

S—is the surafce area of the electrodes

d—is the distance between the two eletrodes

[8]

Chapter 2

LITERATURE REVIEW

In this section we discuss the work done in past years with Aluminum oxide and Indium oxide and how it has evolved as a material, along with synthesis routes, device applications and how they affect the structure and electronic properties of both Alumina and Indium oxide. The charge transport mechanism, band gap, resistance and structural and optical properties,etc; which has led to several different applications.

2.1 Synthesis of Alumina Nanostructures:

Synthesis of metal oxides nanoparticles/ composites can be done using two approaches that is top down or bottom up. Most common methods of forming aluminum oxide and its nanoparticles involves solution based and physical methods. Precipitation, co precipitation, solvo-thermal, hydrothermal, sol gel etc, are solution based methods which involve low cost but are time consuming. Other expensive physical methods involving high vacuum techniques like Chemical Vapour Deposition (CVD), Atomic Layer Deposition (ALD), thermal evaporation, electron beam epitaxy, DC Magnetron Sputtering have been also used to deposit nanometer thin layer of pure aluminum metal on a glass/silicon or metal substrate which is then oxidised to get Aluminum oxide layer in an oxidising environment. These physical methods can offer great control over stoichiometry, and atomic level control during deposition.

Electrochemical methods like anodization are also used to grow nanometer to micrometer thick layer of Alumina on a thin aluminum substrate in an acidic or basic electrolyte. The nature of the synthesised material and its morphology (shape, size), structure depends heavily on the precursors used for preparation, the synthesis route (chemical or physical), the concentration of the reagents, pH, nature of solvent involved (water or alcohol), temperature, pressure etc; Which govern the final properties of the material. Aluminum oxides are also synthesised by thermal decomposition of Aluminum Hydroxides or Oxy-hydroxides. Aluminum Tri-Hydroxides ($ALOH_3$) are called Aluminum Oxyhydroxides ($ALOOH$). Industrial Aluminum oxide prepared from its naturally occurring ore Bauxite which is a mixture of iron and aluminum hydroxides. Hollow and spherical alumina nanoparticles were formed by Guangxin Xue et al.[15] by using hydrothermal method, using Aluminum nitrate as the precursor and glucose to control the morphology. Crystalline phases of alumina were observed only at calcination temperatures above 700 degree Celsius.

2.2 Synthesis of Anodic Aluminum Oxide:

Stepniowsk et.al [13] synthesised porous anodic aluminum oxide using two-step anodization at relatively high temperatures since well ordered PAAO are usually obtained at low temperatures, around 0 to 10 degree Celsius. The duration of anodization was much shorter (120 minutes and less) than the conventionally implemented 4 to 6 hours. The anodized samples at 40 degree Celsius showed lower ordering of the pores when the anodization time was 30 minutes. The order of the pore was improved by increasing the anodization time. By FE-SEM study they also concluded that the pore diameter increases linearly with anodizing potential and for a fixed potential the pore diameter increases with the anodization temperature.

S. Lee et al.[6] made hydrophobic Nanoporous anodized alumina which has some transparency on a glass substrate. The transparency of the anodized aluminum increased with increasing time of anodization, as the aluminum below the oxide layer is removed with increasing time which gave better transparency, as aluminum oxide is transparent in visible region. The transparency increased of doing pore widening.

2.3 Applications:

RS is a type physical phenomena where the resistance of a dielectric material changes when its subjected to the application of a external electric field. It is different from dielectric breakdown phenomena, which result in a permanent reduction in resistance and may cause damage to the sample such that switching back to the original state is not possible.

Zhu et al[19] fabricated resistive switching by anodization of aluminum in in 0.15 M/L Oxalic acid solution at 25 degree Celsius. The device showed both unipolar and bi-polar switching with high resistance to low resistance ratio of 10^4, no forming process was required.

S. Kim and Y. K. Choi[4] fabricated RS device by plasma oxidation of aluminum. From the I-V plot study, the device showed unipolar resistive switching with a high on to off ratio of 10^4. The device required a forming process to activate the device. The plasma oxidised alumina showed better endurance to switching cycles compared to conventionally synthesised aluminum oxide.

Seung Won et al[17], used sputtered Indium zinc oxide as the electrode for transparent and flexible electronics on based resistive switching device. The device showed excellent transparency in the visible region due wide band gaps of IZO and Alumina. The conduction mechanism was confirmed to be ohmic in nature from current voltage plot. The device showed good flexibility and endurance under bending.

Doping has been used to improve and modify the resistive switching devices and for other transparent electronics nano-scale devices where some conductivity is still required along with good optical transparency or reflectivity. This can also be done by introducing a solid conductive phase in insulating alumina such as indium tin oxide as done by T. Kusunose et al [5] by pressure-less sintering of Aluminum Oxide powder with ITO powder . The formed pellets showed good transparency along with electrical conductivity much higher than otherwise highly insulating Al_2O_3. The transparency and conductivity was dependent on the the concentration of ITO grain in Alumina.

Chapter 3

RESEARCH METHODOLOGY

3.1 Anodization of Aluminum

3.1.1 Introduction to Anodization

The reaction involved in Aluminum anodization at oxide/electrolyte interfaces:

$$Al_2O_3 + nH_2O_{(l)} \longrightarrow 2Al^{3+}_{(aq)} + (3-n-x)O^{2-}_{(ox)} + xOH^- + (2n-x)3H^+_{(aq)}$$

Anodizaion involves basic electrochemical setup of Anode and Cathode electrodes dipped in a conducting electrolytic solution which can be acid etc; of certain pH, concentration. The electrolyte solution can be of single species or a mixture of different species of anions and cations dissolved in distilled water.

The Anode is the Aluminum sheet of certain dimensions (length, breath in centimeters) and thickness usually in millimeters or even in micrometers. The Anode is commonly called as the working electrode or the active electrode, its called so because the main reaction mechanism of interest takes place at Anode. The second electrode is called the counter electrode since it does not take part in any chemical reaction and merely acts as an inert electrode.[9]. This electrode is made of inert metals like Platinum or sometimes even carbon material.

Anodization is basically carried out in different ways: depending on the magnitude of the anodizing voltage and the duration of the anodizing pulse [2]. Anodization can be carried out in different electrolytic solutions of varying concentration depending on the application of the AAO and the type of geometry of pores and arrangement (pore size, interpore distance, surface area). The most commonly used acidic solutions for Anodization of aluminum are [7]:

- Sulfuric acid (H_2SO_4)
- Oxalic Acid ($H_2C_2O_4$)
- Selenic acid (H_2SeO_4)
- Malonic acid ($HOOCCH_2COOH$)
- Tartaric acid ($HOOC(CHOH)_2COOH$
- Citric acid ($HOOCCH_2COH(COOH)CH_2COOH$)

The reason for doing two step anodization is to grow more ordered pores on templates of etched PAAO in phosphoric acid, which removes the disordered pores formed during 1^{st} step of anodization. The etching in Phosphoric acid and Chromic acid mixture leaves concave textures on Aluminum surface which acts as a template or a mask for further growth of ordered PAAO. These are mainly: 1) MA (Mild Anodization), 2) HA (Hard Anodization), 3) PA (Pulse Anodization),and HPA (Hybrid Pulse Anodization) [10]. The MA is also called low field method and the HA is called the High field, since MA anodization is low Electric field and the HA is High electric filed. The HA is carried out at 100 to 140 V with Phosphoric acid as electrolyte. The MA anodiztion is between 40 to 60 Volts usually performed (0.3 to 0.5 M) Oxalic acid solution. In this study we will focus on only Mild Anodization which is performed at relatively low values of Direct current Voltage between 40 to 60V (40 V in this study) under potentiostatic conditions. Anodization of Aluminum is usually carried out in low temperatures between 0 to 10 degree Celsius to avoid dissolution of oxide layer and to avoid excess heat due to joule heating which may cause burning of the oxide layer.

The amount of anions incorporated in to the AAO layer depends on the concentration of the acid electrolyte, which decides the final electrical, chemical and structural properties of the grown oxide layer. In case of Oxalic acid as the electrolyte the Oxalate ions $C_2O_4^{2-}$ move into the anodic oxide through the oxide/electrolyte interface since the anions are negatively charged and are drifted towards positively charged anode due to the electric field [3].

The parameters which mainly influences the pore dimensions and growth are the Current density (j), Anodization voltage (U), temperature (T), and type of electrolyte used (Strength of the acid), Time and the concentration of the electrolyte (Molarity). Under potentiostatic conditions the pore diameter D_p depends on the the Voltage of the anodization experiment(U):

$$D_p = k.U$$

Where the value of k in nm/V depends on the type of electrolyte /acid used. Larger pore size increases the surface area of the AAO and the porosity decides the refractive index of AAO.

3.1.2 Experimental Details:

Aluminum anodization was carried out in a 0.3 M Oxalic ($C_2H_2O_4$) acid solution for 2, 4, 6 and 8 hours respectively at room temperature.

Prior to that the pre-existing oxide layer on the Aluminum sheet was removed by electropolishing in a solution containing a mixture of (1:4 Solution of Perchloric acid ($HClO_4$) and Ethanol (C_2H_5OH)); i.e:- a 40 ml solution of 8 ml of Perchloric acid and 32 ml of Ethanol. This step also makes the Aluminum surface clean and removes surface scratches and unevenness.

The 1 by 4 cm^2 Aluminum sheets were cleaned with soap water and sonicated in Ethanol for 15 minutes before electropolishing them for 60 seconds at 20 Volts. 1st step anodization was done at 40 Volts in a 40 ml solution of 0.3 M Oxalic acid solution which was sonicated for 15 minutes initially. Platinum sheet was used as inert electrode or Cathode and the cut Aluminum sheet was used as anode or active electrode. A distance of 2cm was maintained between the electrodes. A high voltage DC power supply was used to carry out all the experiments under potentiostatic conditions (constant-voltage).

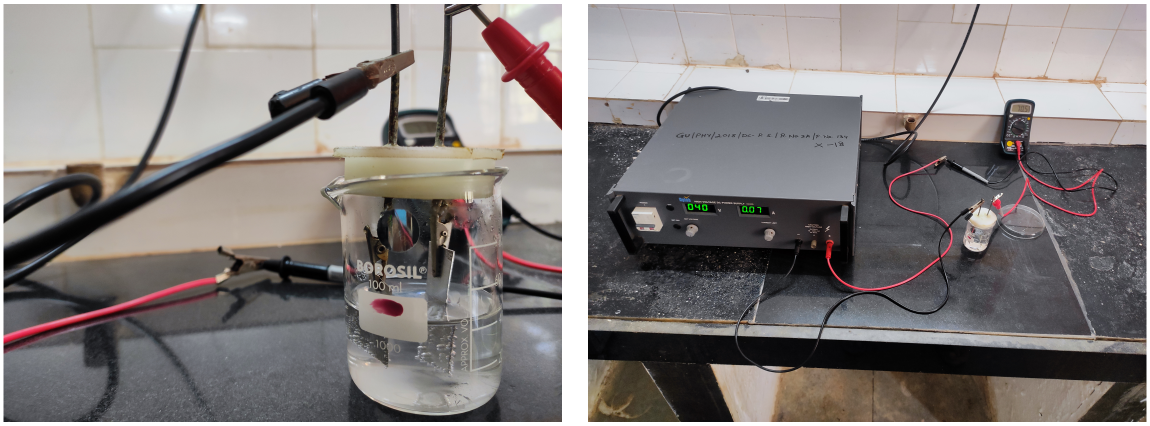

Figure 3.1: Electrode setup of Anodization of Aluminum (left) and Anodization process complete setup (right)

Figure: 3.1 shows oxygen bubbles evolving at Aluminum anode (right electrode) and hydrogen bubbles at Platinum electrode (left electrode).

3.2 Hydrothermal Synthesis:

3.2.1 Introduction Hydrothermal Method:

Hydrothermal synthesis involves formation of nanoparticles, composites, crystals, under high temperature and pressure environments in water, similar to how crystals are formed in the earths crust. Its a great method to control the morphology, particle size, shape, and also the way the structure grows by changing various parameters like temperature, concentration of precursors, pH, and time of reaction. Controlling these parameters can greatly change the physical and chemical properties of the final material. The different morphologies which can be obtained are nanorods, nanotubes, hollow spheres, plates, etc.

The advantages of hydrothermal synthesis involve low cost, less pollution (water as solvent), easy to use, reaction control on chemical level and good yield. Disadvantages involve long synthesis time, tedious process of purification and filtration to get final product. Based on the temperature range Hydrothermal synthesis can be sub critical (below 240 C) and supercritical (above 240 C). Under high temperature and pressure conditions the vapour pressure increases and the viscosity of water decreases which causes greater mobility of ions in the reaction chamber which accelerates the reaction kinetics involved. The pressure of the sealed autoclave chamber depends on the degree of fill of water and the reaction temperature. Usually the fill of the teflon beaker is 50% of its capacity which means a water vapour pressure of about 0.1 Gpa at 200 Celcius [16].

3.2.2 Experimental Details:

A solid suspension of Aluminum oxide powder with Indium acetyl acetonate was made in a 100 *ml* solution containing deionised water.

Commercially available calcinated Aluminum oxide powder (Thomas baker) was used as it is. Indium acetylacetonate (In-acac) (99.99% trace metal basis) was used from Sigma Aldrich as the Indium precursor. 1 gram of Alumina powder was taken along with 1mg, 5mg and 10mg In-acac precursor separately and were labelled as 0.1% ,0.5% and 1% respectively. The one with no In-acac addition was labelled as 0% (undoped).

The suspension was then sonicated in an ultrasonic bath for 15 to 20 minutes to evenly disperse the particles so that no agglomeration takes place during the hydrothermal process. The sonicated solution was then transferred to a 200 ml capacity teflon beaker which was then tightly sealed in the hydrothermal autoclave using nut and bolts inorder to maintain the desired pressure. The Autocalve was then placed in an oven at a temperature of 180 degree Celsius for 24 hours to heat. It was then cooled down for 24 hours more, naturally.

After cooling to room temperature the powder was washed with distilled water and filtered by allowing it to settle for few hours as the powder was insoluble. The obtained powder was then dried in an Oven at 80 degrees Celcius for 3 to 4 hours to obtain the Indium doped Aluminum Oxide Nanopowder. The powder samples were then grounded to finely using mortar-pastel for X-ray diffraction analysis.

Figure 3.2: Hydrothermal Autoclave image (left) & Teflon beaker fitted in autoclave (right)

3.3 Characterization Techniques

3.3.1 X-ray Diffraction method:

X ray diffraction is a technique that determine a materials composition or crystalline structure. For larger crystals such as macro molecules and inorganic compounds, it can be used to determine the structure of atoms within the sample. If the crystal size is too small, it can determine sample composition, crystallinity, and phase purity. This technique sends x ray beams through it. X ray beams are chosen because their wavelength is similar to the spacing between atoms in the sample, so the angle of diffraction will be affected by the spacing of the atoms in the molecule, as opposed to using much larger wavelengths, which would be unaltered by the spacing between atoms [1]. The x rays then pass through the sample, and bounce off of the atoms in the structure which changes their direction and of the of the beam at different angles, theta, from the original beam. This is called as the angle of diffraction. Some of these diffracted beams cancel each other out, but if the beams have similar wavelengths, then constructive interference occurs. Constructive interference is when the x ray beams that are whole number integers of the same wavelength add together to create a new beam with a higher amplitude. The greater amplitude of the wave translates into a greater signal for this specific angle of diffraction. The angle of diffraction can then be used to determine the difference between atomic planes using Bragg's law, $2dsin(\theta) = n\lambda$ where lambda is the wavelength added, theta is the angle of diffraction, and d is the distance between atomic planes. The distance between atomic planes can then be used to determine composition or crystalline structure.

X ray diffraction of nanoscale materials: When the crystallite size decreases from bulk to nanometer scale materials, there will be broadening of the x ray peaks. This is given by the scherrer formula

$$D = \frac{\kappa\lambda}{\beta cos\theta}$$

Where κ is the scherrer constant and its value lies between 0.8 to 0.9, λ is the wavelength of the x rays used (usually Copper $k\alpha$, at 1.54 angstrom). The average crystallite size may not always be equal to the particle size as particles can be made made of several crystallite phases making them poly crystalline rather than single crystal.

3.3.2 Raman Spectroscopy:

Raman scattering occurs because photons (particles of light) exchange part of their energy with molecular vibrations in the material.the Raman effect is observed with a Raman spectrometer.

The first step is to illuminate the sample with a single colour of light, using a laser. If you were to shine blue light onto a material, you might expect to just see blue light reflected from it. Most of the light that scatters is unchanged in energy (Rayleigh scattered).

Only around 1 part in 10 million of the scattered light is Raman scattered. With a Raman spectrometer, you can detect the Raman scattered light that has changed colour and shifted in frequency. It has changed frequency during the scattering process by interacting with molecular vibrations.

Raman spectroscopy measures the energy difference between vibrational modes by analysing the scattered light. Scattering occurs when a photon polarises the electron cloud of a molecule and raises it to a “virtual” energy state. Raman scattering occurs if the photons change energy during the scattering process. This is because the excited molecule has relaxed to a higher or lower vibrational state than it had originally.

Raman scattering is inelastic because photons change energy by interacting with molecular vibrational energy levels. Raman scattering is called ‘Stokes’ when the scattered light loses energy. Raman scattering is called ‘anti Stokes’ when the scattered light gains energy.

Stokes Raman scattering occurs when the molecule moves from the ground state to a virtual state, before dropping down to a higher energy vibrational state than it had originally. Anti Stokes Raman scattering occurs when the molecule starts in a vibrationally excited state, moves to a virtual state, before finally relaxing to its ground state. We rarely use anti Stokes Raman light as it is less intense than the Stokes. However, it does represent equivalent vibrational information of the molecule.

In contrast, Rayleigh scattering occurs when the molecule returns to its ground vibrational state. It releases a photon with the same energy as the incident photon. Therefore, Rayleigh scattered light has the same frequency and colour as the incident light. Rayleigh scattering is around 10^7 times more intense than Raman scattered light. Modern spectrometers use highly efficient filters to remove the Rayleigh scattered light. This makes it easy to detect Raman scattering.

Chapter 4

ANALYSIS AND CONCLUSION:

4.1 X-ray Diffraction Data:

Figure 4.1 shows the X-ray data of all the four samples ,that is Al_2O_3 doped with 0% , 0.1% , 0.5% and 1% of Indium.

Figure 4.1 shows the X-ray diffraction data of all samples and the undoped Aluminum Oxide (0%) can be fitted to Corundum phase of Aluminum Oxide which belongs to the hexagonal crystal system by Rietveld profile matching ($\chi^2 = 9.96$) using Full Prof software as shown in figure 4.2 . The data matches with PDF CARD NO:- **01-071-3646** and the JCPDS CARD NO:- **00-010-0173** with 80% score with some peaks of impurity which can be other polymorphic phases of Alumina or Impurity.

From the X ray diffraction pattern (Figure 4.3) it can be seen that there is shift in

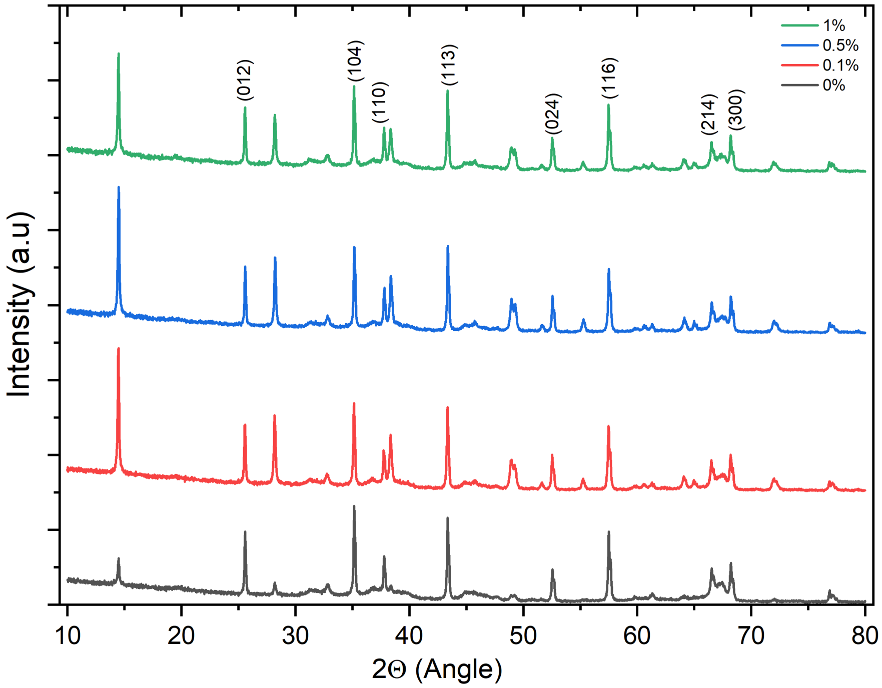

Figure 4.1: X Ray Diffraction data of Al_2O_3 doped with different concentration of Indium doping: 0%, 0.1%, 0.5% and 1%

the 2θ values of Aluminum oxide peak towards lower values. The shift delta between the undoped Alumina (0%) and Alumina doped with indium (0.1%) is maximum observed at 0.04 shift towards lower angles, for (012) peak as shown in the figure. The shift is observed all peaks with some planes getting more effected than others. This may due to the the incorporation of dopant atoms in to the host structure. The atoms can occupy either substitutional sites (replace host atom) or occupy interstitial sites. Since the ionic radii of Indium is bigger than the ionic radii of Aluminum, an increase in lattice constant is expected, which shifts the 2θ value towards lower

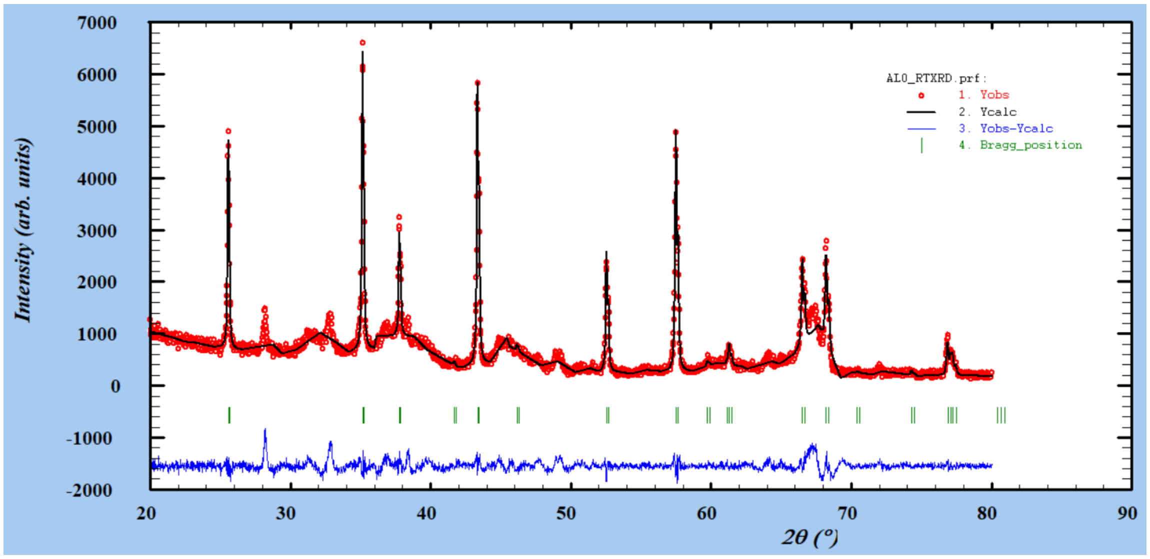

Figure 4.2: Rietveld Refinement of Undoped (0%) Al_2O_3 powder

values according to the braggs law:

$$d = \frac{n\lambda}{2 \cdot \sin\theta}$$

due to change in the d-spacing between the atomic planes due to the presence of dopant atom. The shift between 0% and 1% is 0.02 2θ . There appears are slight shift of 0.5% doped Alumina towards higher values but the peak 2θ value matches with undoped Alumina. But the magnitude of shift observed is low and can also be due to other factors like thermal stress but the samples were not subjected to any annealing or high temperature heat treatment. The less shift between 0% & 0.5% samples can be due to Indium atoms not being able to penetrate the host lattice as is is usually seen in some cases when dopant concentration increases.

Also the intensity of the peaks goes on decreasing with increased concentration of

Indium doping. This can be due to the change in the electron density at the surface of aluminum oxide crystals which changes the way X rays diffract from the atoms by their interaction with electron cloud of atoms. X rays are diffracted not due to atomic planes only but the electron distribution at surface plays the major role and the greater the number of such atoms in a plane, the greater the intensity of the diffracted x ray will be.

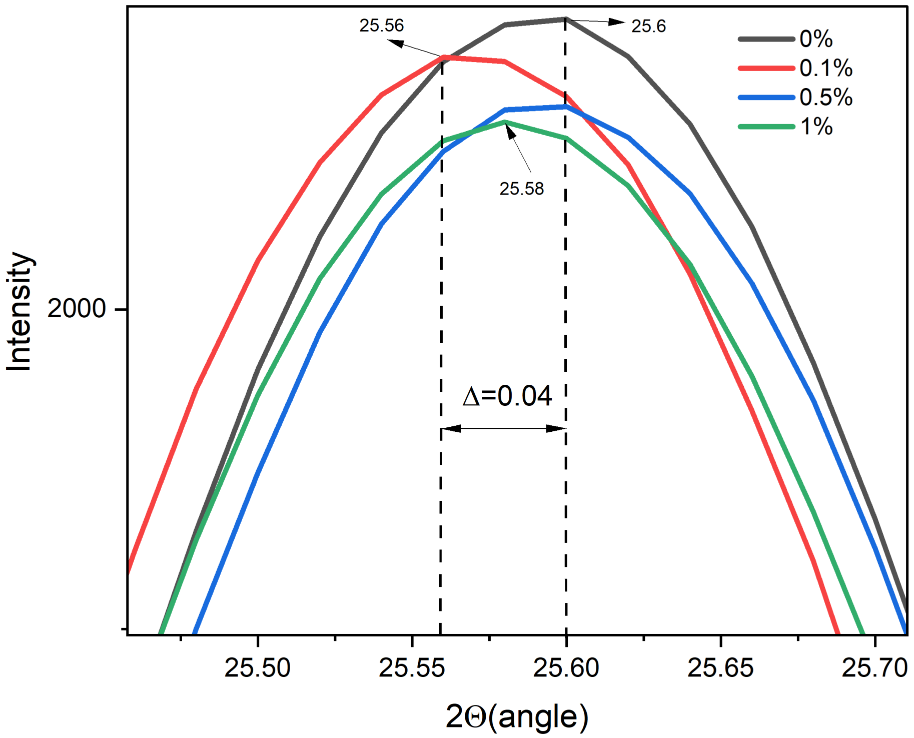

Figure 4.3: 2θ Shift in Aluminum oxide (012) peak with varying concentration of Indium doping

4.2 Raman Spectroscopy Data:

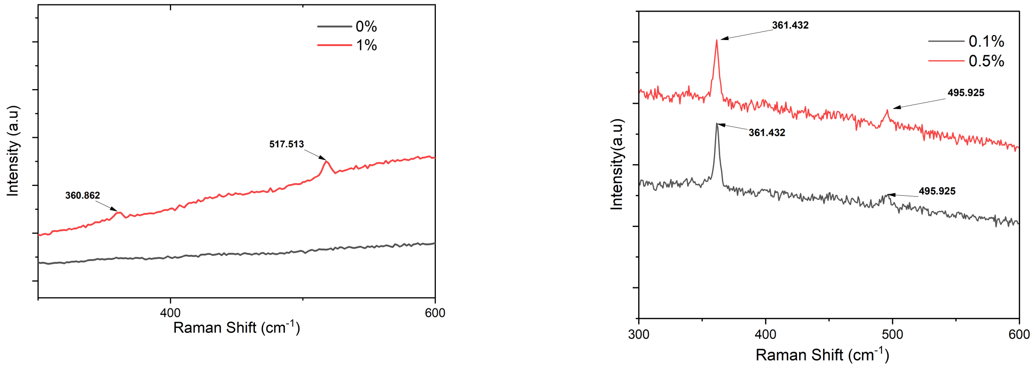

Figure 4.4: Raman shift of Al_2O_3 doped with 0% & 1% (left) and 0.1% & 0.5% Indium (right)

Raman spectra was obtained at laser excitation wavelength of 785 nm.The raman band at 360.862 cm^{-1} , 361.432 cm^{-1}, 495.925 cm^{-1} and 517.513 cm^{-1} can be assigned to cubic-Indium-oxide vibrational modes as seen from the literature [11]. The Raman band at 360.862 cm^{-1} is due $(In-O-In)$ stretching vibration . The band at 517.513 cm^{-1} corresponds to $(In-O)$ stretching vibrations. The bands at 495.925 cm^{-1} in 0.1% and 0.5% samples can be assigned to stretching vibration (InO_6) Octahedron. In 1% doped alumina the band at 495.925 cm^{-1} disappears and a new band at 517.513 cm^{-1} appears. It can be seen that there is a slight shift of the Indium-oxygen vibrational modes towards higher wave number ;i.e, from 360.862 cm^{-1} in 1% sample to 361.432 cm^{-1} in 0.1% & 0.5% samples. This can be due to the decrease in the bond length of $In-O$ which shifts the wavenumber towards higher value. The intensity of the Raman bands decreases with increasing concentration.

The decrease in the intensity of the Raman modes can be due to distortion in the geometry of crystals at higher concentrations of Indium doping due to the presence of Aluminum oxide particles. Which might prohibit proper crystal growth as the two have different crystal structures and stable phases with the stable phase of Indium oxide being cubic and of Alumina being Hexagonal.

4.3 Current-Voltage (I-V) data:

The I- V characteristics of the 0% , 0.5% & 1% samples are shown in Figure: 4.5 . The procedure was done by using the pellets of these samples and a keithly meter was used to measure the current response with the change in the applied voltage. It can be seen that with increased concentration from 0.1% to 1% there is an increase in the current window from 0.6 μA for 0.1%, 1.2 μA for 0.5% and 3 μA for 1% samples in the positive cycle of voltage scan. Similar effect is seen in the negative cycle of scan but with less current than positive cycle. The hysteresis observed in the samples increases with increases concentration of doping [14].

Hysteresis observed in the current-voltage curves of electronic devices is a phenomenon where the curve's shape is altered on the basis of the measurement speed. This effect is driven by internal processes that introduce a time delay in the response to an external stimulus, leading to measurements being dependent on the history of the past disturbances. The measurement is performed in a cycle of forward and reverse directions, to return to the starting point.

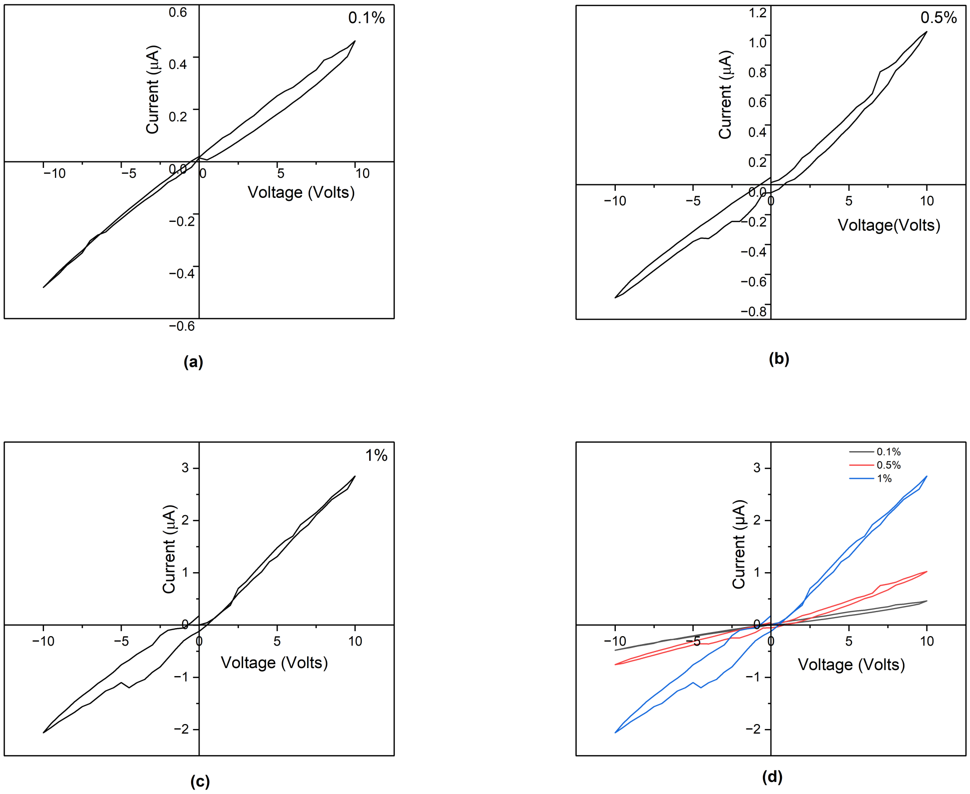

Figure 4.5: Current-Voltage behaviour of Al_2O_3 pellets when sweeping DC voltage from +10 to -10 V; (a)0.1% ,(b) 0.5% ,(c) 1% and (d)0.1% ,0.5% & 1%

4.4 Scanning Electron Microscopy Data:

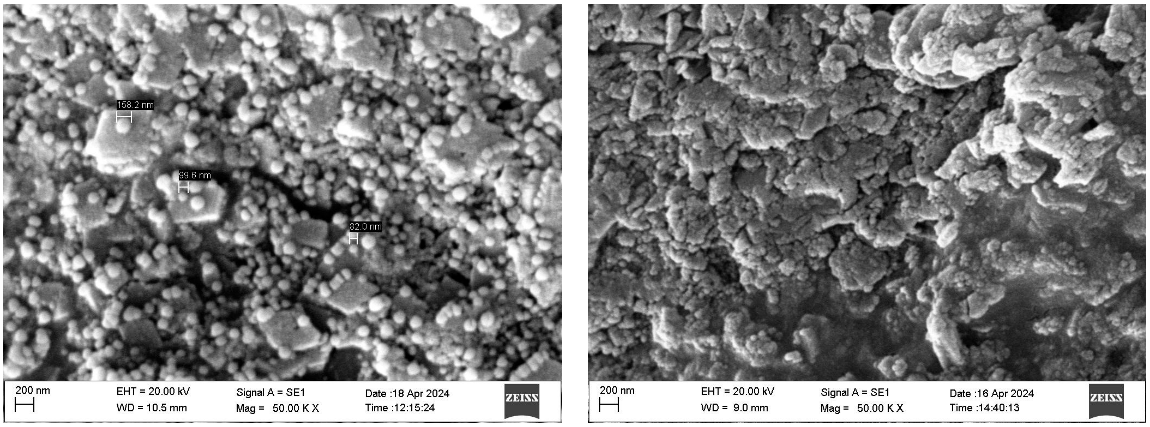

Figure 4.6: SEM images of Al_2O_3 powder 0% (left) and 1% (right)

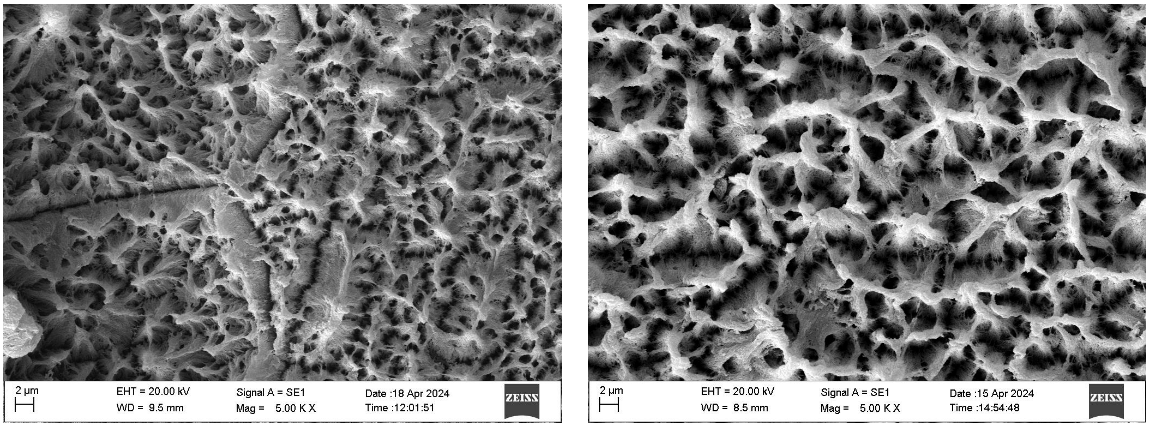

Figure 4.7: SEM images of Anodized Aluminum foil for 2 hours (left) and 8 hours (right)

The Scanning Electron Microscopy data of Al_2O_3 powder and Anodized Aluminum are shown in Fig. 4.6 and Fig. 4.7 respectively. For un-doped Al_2O_3 nanopowder the particle size varies from 150 nm to 80 nm as can be see from figure and show spherical particles size for undoped (0%) sample. Whereas for Al_2O_3 doped with 1% Indium, there seems to be a change in the texture of the samples with the surface being rough as compared to undoped sample. This can be due to reduced crystallinity or due to agglomeration of particles at surface which can also be related with decreased peak intensity in X-ray diffraction pattern of 1% sample .

4.5 Anodization experimental data:

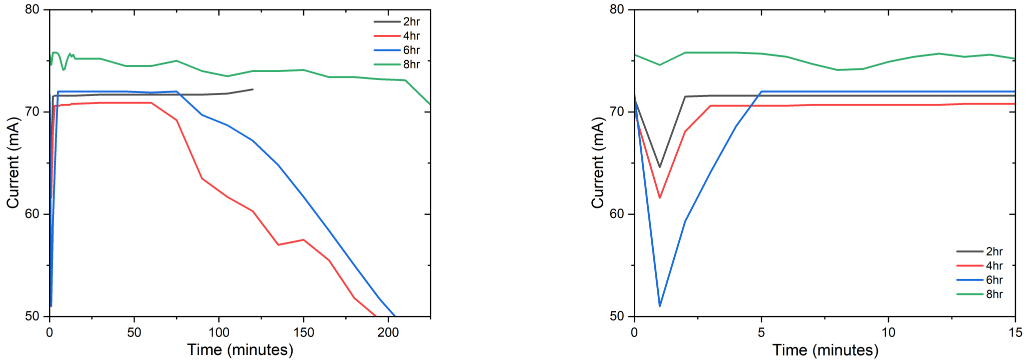

Figure 4.8: Current-Voltage (I-V) data of Anodized Aluminum (left) and enlarged view for first 15 minutes (right)

Figure show the anodization current-voltage behaviour of Anodic Aluminum oxide for different anodizing times increasing in order from 2,4,6 and 8 hours. The current behaviour is typical of what is observed in the literature with the current first decreasing in the first 20-30 seconds after turning of the potentiostat at 40 V. This is due to the formation of the dielectric layer which is insulating due to which the current falls off sharply as the bare aluminum reacts immediately with the ions in the electrolyte which protects it from further corrosion and damage. After which the current rises quickly and stabilizes due to the the balance between the oxidation and the dissolution of the aluminum oxide layer. With the formation of the dielectric layer the current starts to peak after few minute/ hours due to the electrolyte ions/ species reacting with the barrier and the aluminum ions within which starts to dissolve the layer of oxide which is of the reasons for the increase in current.

After few hours the current decreases almost linearly which shows that the oxide layer is growing thicker due to which the resistance of the anodic aluminum oxide keeps on increasing with time and the current gradually decreases.

4.6 Temperature Variation Of Capacitance:

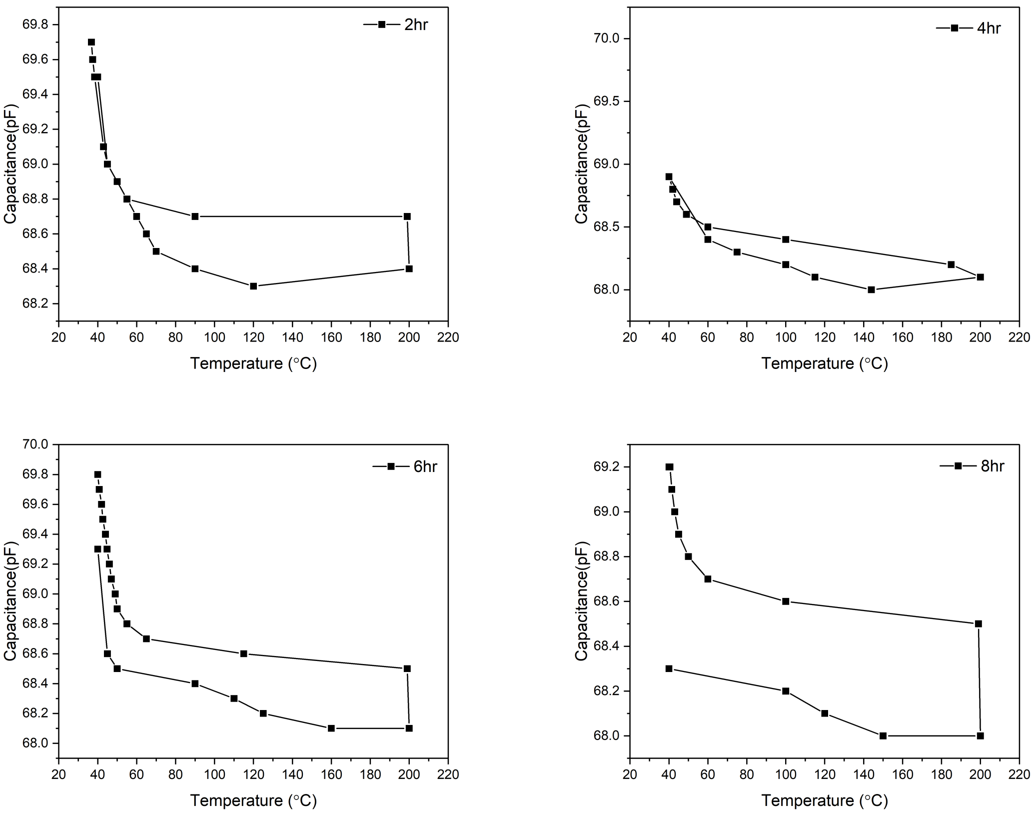

Figure 4.9: Temperature Variation of capacitance in Anodized samples for 2, 4, 6 & 8 hours

While the conductivity increases with temperature, this does not have a significant effect on capacitance. The permittivity of the dielectric in a capacitor decreases with temperature, which leads to a decrease in capacitance. The random movement of molecules at higher temperatures contributes to a decrease in capacitance. With increasing temperature heat provides kinetic energy to the electrons in a substance which excites the electrons.This increases the rate of flow of electrons.This means the electrons are more likely to break away from one end and would travel to the other end of capacitor.Which decreases the capacity of dielectric to resist the flow of electrons.

4.7 Conclusion:

The as synthesised Indium doped Al_2O_3 powder samples show different characteristics from the undoped Al_2O_3 as confirmed by the x-ray diffraction pattern , Raman spectroscopy analysis, Current-Voltage and SEM analysis. Sharp peaks with some broadening can be seen, with the new peaks appearing in the doped samples which can possibly be cubic -Indium oxide peaks . Some unkown peaks are present with some may be due to inherited impurity of the commercial Aluminum oxide powder or other minor phases of Al_2O_3 making the analysis difficult. The slight shift in the 2-theta values may be due to the incorporation of Indium atoms in the Alumina lattice, due strain caused by large ionic radii difference between indium and Aluminum atoms.

Discernible Raman bands can be observed for doped samples which confirms the formation of cubic Indium oxide. No Raman bands can be assigned to pure Al_2O_3 phase in both doped and undoped samples, the reason for which is not clear.Hence,doping cannot be confirmed from Raman spectra. From SEM analysis it can be concluded that the undoped sample have better crystallinity and uniformity than than the doped samples. And the particles in undoped sample look less agglomerated compared to doped sample (1%) with bigger particle size. The doped samples show agglomeration & surface texture. The I-V characteristics show hysteresis in the samples, showing possible application in memory devices.

The Indium doped Aluminum Oxide samples can have future applications in transparent display technology like wearable A.I glasses where photo-detection is needed with good transparency for monitoring the environment around the user. The anodized samples with porous Aluminum oxide can have applications in energy storage in both solid state and electrolytic capacitors due to high surface area and length provided by the nanostructures; also as templates for Electrode materials in Supercapacitor applications.

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