Synthesis of Zirconium Oxide Thin Films using Langmuir-Blodgett Technique

A

Thesis

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Of Degree of

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By

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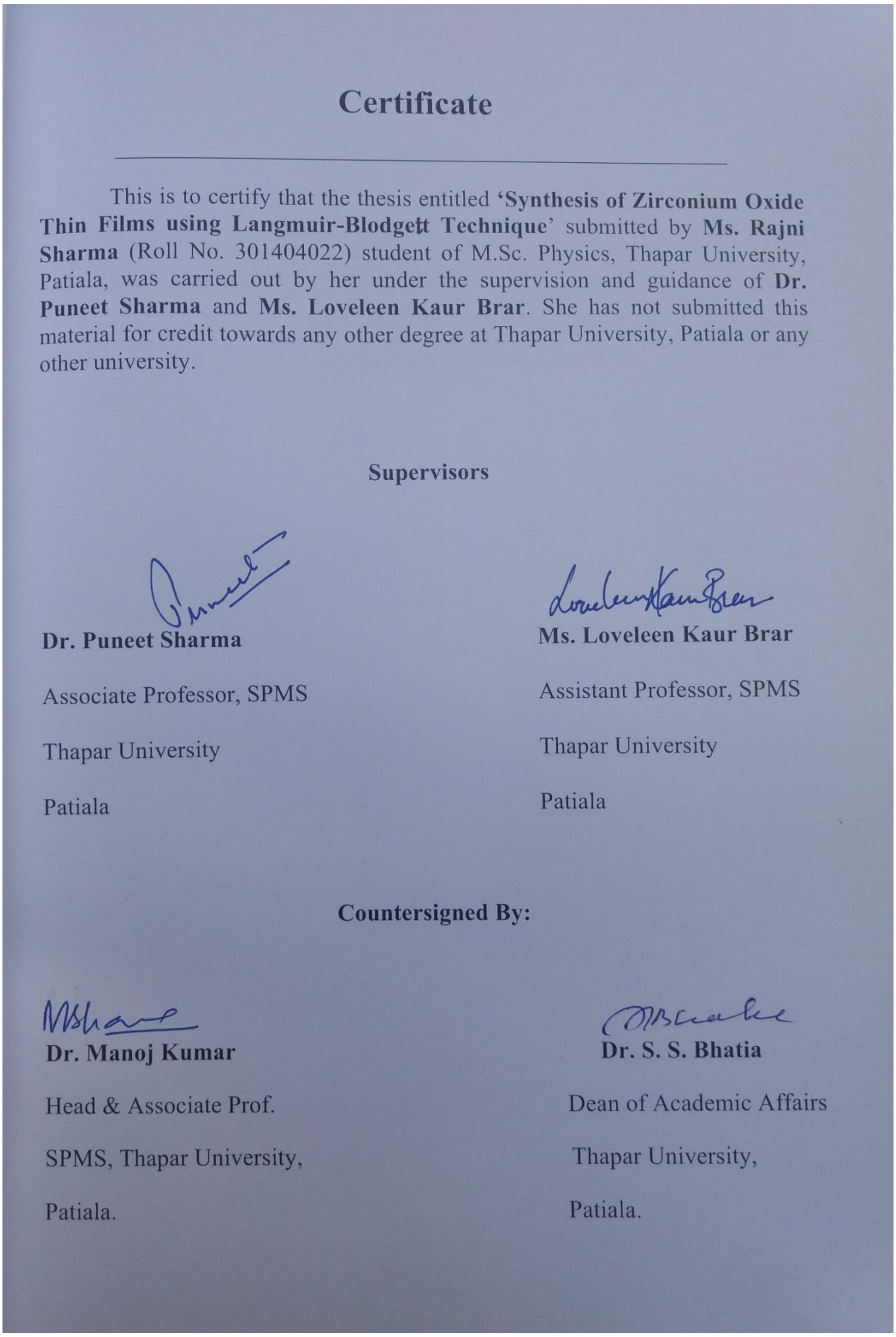

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This is to certify that the thesis entitled **'Synthesis of Zirconium Oxide Thin Films using Langmuir-Blodgett Technique'** submitted by **Ms. Rajni Sharma** (Roll No. 301404022) student of M.Sc. Physics, Thapar University, Patiala, was carried out by her under the supervision and guidance of **Dr. Puneet Sharma** and **Ms. Loveleen Kaur Brar**. She has not submitted this material for credit towards any other degree at Thapar University, Patiala or any other university.

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I hereby declare that thesis entitled **"Synthesis of Zirconium Oxide Thin Films using Langmuir-Blodgett Technique"** is the original work carried out by me under the supervision of **Miss. Loveleen Kaur Brar**. The matter embodied in this thesis has not been submitted anywhere else for the award of any degree.

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Dedicated to my

Family

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Rajni Sharma

Abstract

Zirconium Oxide thin films were prepared on glass substrate by Langmuir-Blodgett (LB) Deposition Technique. ZrO_2 thin film have very wide range of applications such as for photonics materials, antireflection material, resistive oxygen gas sensors, as a gate dielectric and high temperature fuel cells. We have used the deposition of metal stearate monolayers followed by their oxidation as a method for the synthesis of zirconium oxide thin films. The zirconyl stearate films have been studied and deposited for first time as to the best of our knowledge. These LB films deposited on hydrophilic substrate are z-type in nature. The composition of mixed Langmuir films of metal stearate and stearic acid is determined by its pH. The 200 layer deposition at 20 ^{0}C is followed by proper heating protocol to ensure complete removal of the stearic acid and/or any other carbon impurity. The resulting films of ~100nm thickness show pure monoclinic phase. The films have a band gap ~ 6.0eV with a strong PL emission peak is at 490nm and a weak peak is at 423nm. So the films formed by LB deposition methods are suitable for luminescent applications.

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CHAPTER 1

INTRODUCTION TO ZIRCONIUM OXIDE

1.1 Introduction:

Zirconium oxide (ZrO_2) is one of the most widely used ceramic oxide which finds use as an important optical and refractory material. The oxide of zirconium is one of the main components of glazed enamels. ZrO_2 has a high resistance to crack propagation. It shows corrosion inertness to temperatures higher than the melting point of alumina. It is electrically conductive above 600ºC and is used in manufacturing high temperature furnaces. Zirconium oxide also has a very high thermal expansion and high strength. Zirconium oxide is used in coatings due to high refractive index, large band gap and its excellent thermal stability. All these properties also led to many applications in laser mirrors and optical fibres [1]. From electrical point of view zirconium oxide is very interesting because it has very high dielectric constant. Zirconium oxide also used as a solid state electrolyte of solid oxide fuel cells. Due to its exceptional hardness zirconium oxide is used in artificial hip joints replacements. Also due to hardness and its mechanical properties it is widely used in dental crowns and bridges. It is an alternate to the mostly used SiO_2 gate dielectric in semiconductor technology. Zirconium oxide can exist in number of crystallographic and amorphous forms.

1.2 Structure of ZrO_2:

Zirconium oxide exists in three crystalline forms: monoclinic, tetragonal and cubic. In the monoclinic Zr^{4+} ion has surrounded by seven oxygen atoms means that it has seven fold coordination but in the tetragonal and cubic phases Zr^{4+} is surrounded by eight oxygen atoms. It changes from monoclinic to tetragonal at 1370^0C and from tetragonal to cubic at 2320^0C.The most naturally occurring form with monoclinic structure is baddeleyite. Cubic zirconia in nature is found as tazheranite.

Upon cooling the behaviour of zirconia destroys the mechanical properties and it makes zirconia unusable for structural application. Oxides which dissolve in zirconia slow down the crystal structure changes for e.g. MgO, and Y_2O_3. With the sufficient amounts added of these oxides the high temperature cubic structure can be maintained to RT(room temperature). These oxides are oxygen deficient compared with zirconia. The presence of these oxides distorts the shape of monoclinic and tetragonal and makes cubic form the most stable form down to the RT. During heating and cooling such cubic zirconia does not go through destructive phase transitions

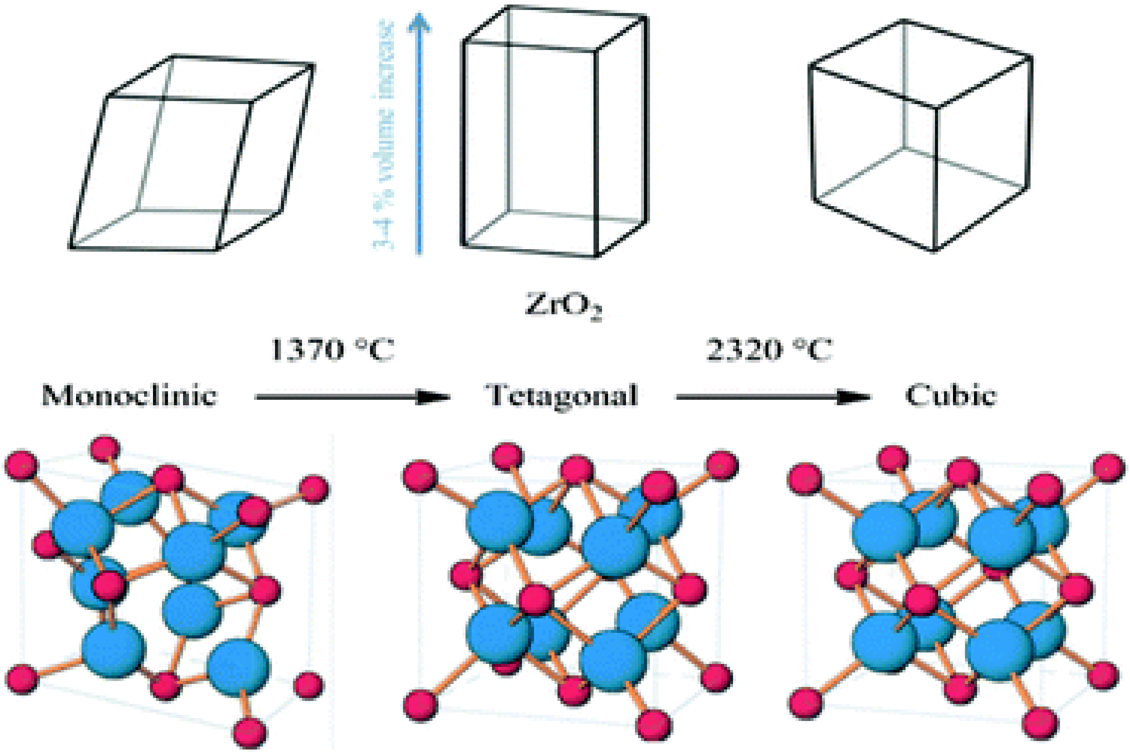


Figure1.1: Structure of zirconium oxide[2]

1.3 PROPERTIES OF ZrO_2:

Following are the most important properties of ZrO_2:

PROPERTY	**VALUE**
Chemical symbol	ZrO_2
Cation	Zr^{4+}
Molar mass	123.218 g/mol
Melting Point	2715°C
Boiling Point	4300°C
Electronic Configuration	$(Kr)5s^2 4d^2$
Band gap	5eV-7eV
Dielectric Constant	~ 25
Thermal Conductivity	$4.2 Wm^{-1}K^{-1}$

Density	5680kg/m^3
Refractive index	2.2
Hardness	18 GPa for monoclinic phase 14 to 11 GPa for amorphous
Lattice Parameter	~2.5A^0

1.4 Properties of thin films of ZrO_2:

Thin films of zirconium oxide are of interest because of their properties such as high dielectric constant and high refractive index [3]. The properties like homogeneity and transparency leads to many optical applications. The deposited films generally have high density, less optical scatter, great index stability, and small surface roughness. The properties of films are very much dependent upon the substrate interface structure; morphology which can control by growth conditions and the deposition processes. Also the zirconium oxide thin films are existing in monoclinic phase, tetragonal phase and cubic phase. But the film thickness, stress, grain size, impurities changes their phase. Dielectric properties and band gap of the films are strongly dependent up on the phase. Basically the properties of the films are dependent upon the behaviour of the substrate. The ZrO_2 films are also biocompatible.

1.5 Applications of thin films of ZrO_2:

Thin films of ZrO_2 have wide range of applications:

- Antireflection coating, achromatic beam splitters, color selective beam splitters.
- Laser mirrors
- Coating materials against oxidation, electronic devices, high refractive mirrors, decorative devices.
- Resistive oxygen gas sensors.
- High temperature fuel cells.
- As a gate dielectric material in semiconductor transistors.
- As hosts in planar waveguide materials for solid-state lasers.
- Photonics materials.

CHAPTER 2

LITERATURE SURVEY

2.1 Synthesis of ZrO_2 thin films:

N.L. Zhang et al 2002[4]. ZrO_2 thin films were deposited on Si by ultra high vacuum electron beam evaporation and they are thermally annealed in O_2 ambient at different temperatures. XPS reveals that zirconium is in the fully oxidized state Zr^{4+}. XRD results the films were amorphous. The surface morphology was studied with AFM. Microstructure remain unchanged when rapid thermal annealing upto 600°C. Further increase in annealing temperature thin films of ZrO_2 tend to be polycrystalline.

K.Kukli et al 2002[5]. Zirconium oxide thin films were prepared from ZrI_4 and H_2O_2-H_2O by atomic layer deposition method on Si substrates. The thickness of the film were varied from 3-30nm. By increasing the temperature range from 272^0C to 325^0C then cubic polymorph changes to tetragonal polymorph. The hysteresis for the capacitance voltage curves was narrowest for the films deposited at 325^0C. The thickness increase by increasing the temperature by approximately 0.7-1.0nm.

Choudhury et al 2003[6]. ZrO2 thin films deposited on Si(100), quartz and glass substrates by using cw CO_2 laser assisted evaporation. From XRD pattern structure of the films were studied and XRD pattern shows that the structure is tetragonal having lattice constants a= 0.5074nm and c= 0.572nm. The structure depends upon the deposition temperature of the substrate. Optical measurements shows that ZrO_2 thin films have a direct band gap and it depends upon the deposition temperature. From UV-Vis spectra band gap is 5.25eV. The dc conductivity shows the variation with temperature. This suggest that an activated process having single activation energy.

Ramana et al 2009[7]. Zirconium oxide thin films were deposited by sputter deposition technique on quartz substrates. The average crystallite size of thin films (L) ranging from 5 to 25nm. The optical properties were studied by optical transmission and reflectance measurements. The band gap value decrease with decrease in crystallite size. This relationship between crystallite size and band gap suggest that the applications can be achieved by controlling the crystallite size.

Juyun Park et al 2010[8]. By radio frequency magnetron sputtering ZrO2 thin films prepared on p type Si(100) with different plasma gas ratios. ZrO2 thin films were measured by AFM, XRD, XPS and Spectroscopic ellipsometry. In this paper we conclude that roughness and thickness of thin films are constant. XPS data showed that with increasing O_2 gas ratio oxidation state of zirconium sub oxides were changes to zirconia form.

P.Y.Kuei et al 2011[9]. The characterization of ZrO_2 thin films prepared by thermal oxidation of a deposited Zr metal layer on silicon oxide were determined. From XRD results thermal ZrO_2 films showed polycrystalline structure. With increased oxidation temperature, the decrease in leakage current density was observed. This high-k value and low leakage current density were attributed.

K.Joy et al 2011[10]. From sol gel dip coating technique highly transparent nanocrystalline ZrO2 thin films were prepared. Zirconia thin films annealed at 400^0C; their XRD spectra shows that tetragonal phase was formed with particle size 13.6nm. Photoluminescence spectra gives intense peaks at 391nm and at 300nm it shows broad band centred. The luminescence is dependent upon the defects present in the film which makes it suitable for making oxygen sensor.

L. P. Borilo et al 2012[11] Zirconia thin films with thicknesses of 40-120 nm on glass, single-crystal silicon, quartz, polycor, and sapphire substrates have been prepared from zirconium oxochloride and ethanol FFSs. The films prepared on glass or quartz are amorphous; those on silicon, polycor, or sapphire have a crystal structure. The resulting ZrO_2 films have refractive index of 1.86 – 2.08, are insulators, with high bandgap width of 5.0eV-5.2eV.

V.R. Chinchamalatpure et al 2012[12] The ZrO_2 thin films deposited on Si(100) were deposited by sol gel process and prepared by using spin coating technique. XRD of ZrO2 films shows the films crystallized at higher temperature and exists in two phases at 700°C temperature. The I-V characteristics of ZrO_2 thin films on Si shows decreased saturation current on increasing temperatures.

Khojier et al 2013[13]. By using direct current magnetron sputtering technique zirconium films were prepared on glass substrate and then annealed at different temperatures in oxygen constant flow. It is observed in XRD that crystallite size and nanostrain increase with annealing temperatures. AFM shows the granular structure. The annealed films were transparent at higher temperatures and at low temperatures they are grey, brown respectively. The variation of electrical resistance of sample with applied voltage was constant while it is increased with annealing temperatures. The crystallite size, nanostrain, and surface roughness increased with the annealing temperature.

N.Jeyakumaran et al 2014[14]. By sol gel dip coating method zirconium oxide thin films were deposited on glass substrates, using alcoholic solutions. After film coating, sol gel derived films were heated at 500ºC. XRD data exhibited that at 500ºC monoclinic and tetragonal phases have been formed of ZrO_2 films. From XRD the grain size was 2.25nm. Photoluminescence studies displayed a strong emission peak at 426nm and weak emission

peak at 488nm**.**

Abdulhussein K. Elttayef et al 2015 [15]. Nanostructure ZrO_2 thin films are deposited on glass substrate with different thickness 85nm and 100nm by R.f. Sputtering method. XRD pattern shows the formation of polycrystalline ZrO_2 films after annealing with particle size 13.17nm and 37.29 nm for thickness 85nm and 100nm. The average roughness were measured with AFM. The transmittance is found to increase as the film thickness decreases.

M.A.Mamun et al 2015 [16]. The nano mechanical and structural properties of Atomic Layer deposition(ALD) of ZrO_2 films of varying thickness deposited on p-type Si(100) substrate, ALD deposition cycles were obtained. The nano mechanical properties of the films were tested using nano indentation and the morphology was investigated by using AFM. By using field emission scanning microscopy structural and surface properties were explored. The nanoindentation results indicates that films becomes consistently softer as the number of ALD deposition cycles increase and the film grows thicker. Further annealing enhance the hardness and toughness of the films.

Alireza Hojabri et al 2016[17]. By using direct current magnetron sputtering technique zirconium oxide(ZrO_2) thin films were formed on quartz or silicon substrates. From X-ray Diffraction pattern it is determined that by increase in thermal time 60-240min. The structure of thin films changes from amorphous to crystalline. Also the AFM revealed that surface morphology and roughness depends upon annealing time. There is reduction of band gap with increase in annealing time.

2.2 Oxide thin films using Langmuir Blodgett Technique:

Zou Gang et 2002[18]. Yttiria stabilized zirconium oxide(YSZ) films are prepared using langmuir Blodgett films. These Zr containing complex ions mixed with arachidic acid and form continuous monolayer on pure water. From XRD and XPS show that the films are for single phase YSZ with fluorite cubic structure. Average size of the grains and morphology are affected by annealing temperature.

Kondalkar et al 2015[19]. Tungsten oxide thin films were deposited by thermal decomposition of 200 layers Langmuir Blodgett films containing WO3. The tungsten oxide thin films is made of closed packed granules that exhibits high crystallinity with interstitial voids. Tungsten oxide thin film deposited by LB technique show good coloration efficiency.

Sumit Sharma et al 2015[20]. Ultra thin films of nickel oxide (NiO) were prepared on Si substrate by using Langmuir Blodgett Technique. From XPS spectroscopy, XRD, AFM deposition and structure was evaluated. The samples were annealed at different temperatures in vaccum. Sheet resistance was determined as a function of annealing temperature.

2.3 MOTIVATION:

In last few years magnetron sputtering, sol gel techniques were used to deposited ZrO_2 thin films. But all these methods are expensive and they do not allow for the precise control on film thickness, porosity and morphology. But the Langmuir Blodgett technique allows to transfer the films on solid substrate with control on thickness of the order of monolayer and also the morphology and porosity of the final films can be controlled by the pH of the subphase. This can lead to the precise control of the films formed and hence their properties.

CHAPTER 3

Langmuir Blodgett Technique

3.1 Langmuir-Blodgett :

The two dimensional crystalline arrangement of molecules at the air water interface is called as Langmuir film. When multilayers or monolayer are transferred onto the solid substrate then it is called Langmuir Blodgett film.

There are some concepts of Surface Chemistry which are related to the LB technique are explained as following sections.

3.2 Surface Tension:

The molecules have degree of attraction in liquid. This attraction between the molecules depends upon the properties of the material. In the bulk, the interactions of the molecules are balanced by the attractions in all directions. The molecules are present at the air water interface has large attraction towards the liquid than towards the air or gas . The force applied on the surface molecule is known as surface tension.

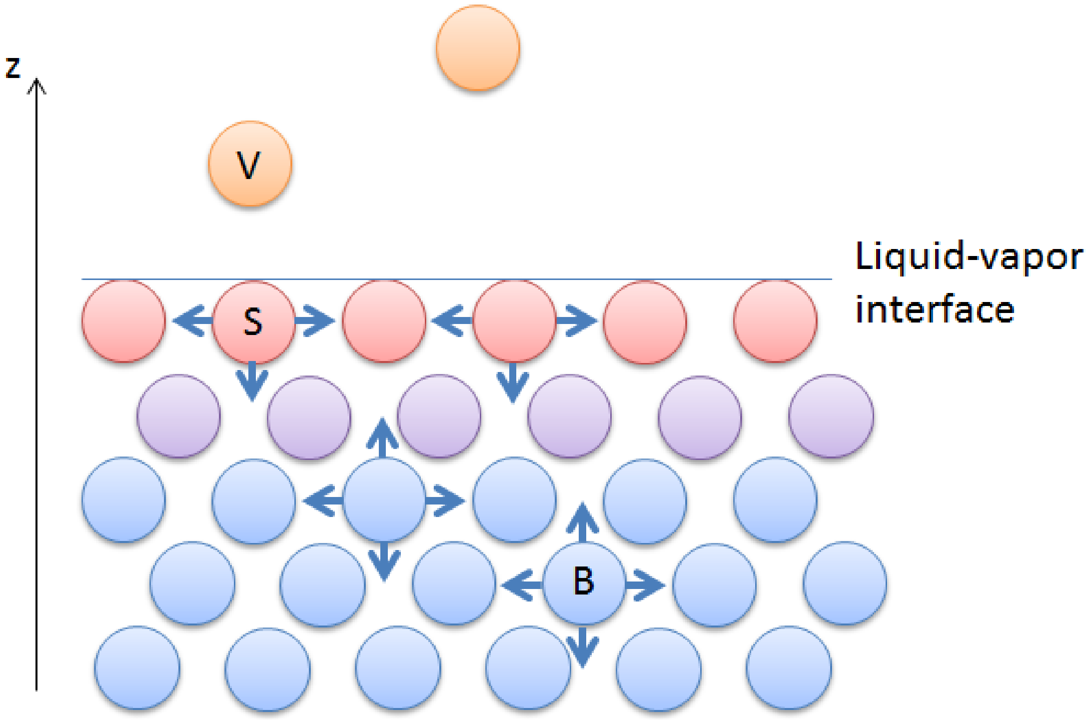


Figure3.1: Interaction of molecule at air water interface[21]

3.3 Langmuir Blodgett Technique:

The two dimensional arrangement of molecules at the air water interface is known as Langmuir Film. A method of producing mono and multi molecular films by transfer the Langmuir Films i.e. monolayer of amphiphillic compounds formed on the air water interface to the surface of the solid substrate. Basically Langmuir Blodgett(LB) is a technique to deposit films on the solid substrate. We can deposit thin films by various methods such as magnetron sputtering, sol gel method, spray pyrolysis method. But the Langmuir Blodgett Technique is the best technique because this technique is used to prepare monomolecular layer of amphiphillic molecules on the air water surface and then transfer it into solid substrate. Langmuir Blodgett is the best technique for preparing thin films because:

(i) The control on the monolayer thickness.
(ii) Deposition is homogeneous over large areas.
(iii) Multilayer structure are formed.
(iv) The crystal parameter and packing of the film can be controlled by changing various LB parameters.

And the most basic advantage for the LB technique is that it can be deposited on any type of solid substrate. First of all we discussed about the concept of monolayer[22].

3.4 Monolayer:

Monolayer is the layer of molecules, atom or ions; but the layer is single is called monolayer. But the Langmuir monolayer is one molecule thick layer of amphiphillic material or compound that contains both a hydrophilic(water loving part or polar) and hydrophobic(water hating or non polar) is called as Langmuir monolayer. This property of monolayer is very important because from this we can easily determine the special structures of the amphiphillic compounds. The hydrophilic part is called the "head" which is a polar molecule and the hydrophobic part is called the "tail" which is a non polar molecule.

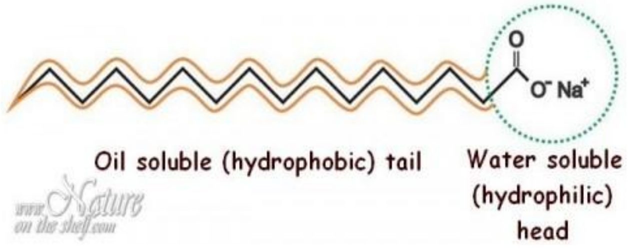


Figure 3.2 Typical amphiphillic molecule [23]

3.5 Monolayer Formation:

With constant compression mode of barriers Langmuir monolayer is formed at the interface of air and water. Firstly the molecules on the surface formed the monolayer. Because Langmuir monolayer is necessary which is multi or monolayer transferred from the liquid surface on to the solid substrate. There exists many amphiphillic surfactants which lower the surface tension of the water. Many of them are insoluble in water so that simply dissolving them in suitable solvent e.g. chloroform. With compression of barriers spread molecules form a stable monolayer on air water interface. This compressed monolayer is transferred onto a solid substrate.

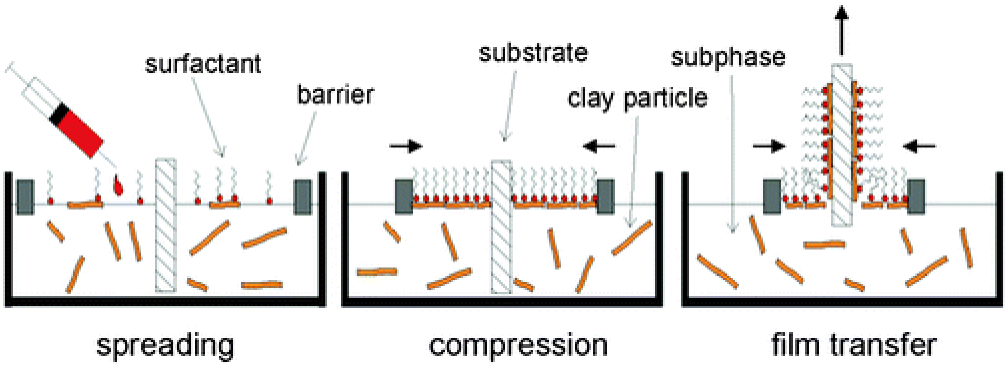


Figure3.3: Formation of monolayer[24]

3.6 Surface Pressure-Area Isotherms:

Surface pressure-area isotherms can be defined as a measurement at constant temperature of surface pressure, for the available area for each molecule. This is the most important indicator of the monolayer properties of the amphiphilic materials. There are number of regions are formed in the isotherms. These regions are also known as phases. This process is carried out at constant temperature so that it is called as Surface Pressure-Area Isotherms[24]. An isotherm is taken by reducing the area with barriers at constant rate and by varying the surface pressure. As the surface area is decreased from its initial value then surface pressure is increases gradually. The behavior of regions are determined by:

(a)Physical and chemical properties of the amphiphilic.

(b)Temperature and composition of subphase.

These are solids, liquids and gases. In the gaseous state the molecules are in random motion and they exert little force on each other. When the surface area of the monolayer is decreased then molecules will interact each other. The liquid phase is formed that is called the expanded monolayer phase. As the molecular area is further reduced then condensed phase appears.

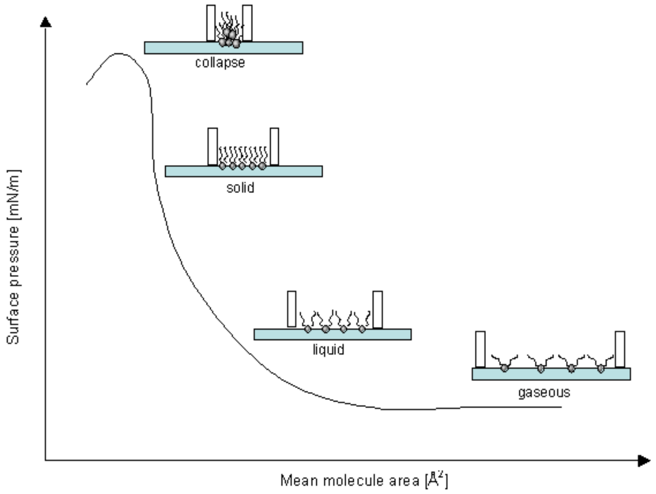


Figure3.4: Surface Pressure Area Isotherm [25]

In the condensed monolayer state the molecules are very close to each other and oriented towards the hydrocarbon chains pointing away from the water surface. The area per molecule in that state is similar to that of the cross-sectional area of hydrocarbon chain. The surface area is increase continuously with decreasing the surface pressure until the point is reached when there is no increase in surface area this point is referred as “collapse”. Collapse mainly depends upon the factors i.e. the rate at which the monolayer is compressed. Therefore the pressure should specify the exact conditions for collapse.

3.7 Langmuir Blodgett Film Deposition Technique:

Different parts of the experimental setup of the LB technique is discussed in this section. First of all we discussed about the pressure when condensed monolayer is formed and then we discussed about the dipping of substrate in the condensed monolayer phase for the film deposition.

Different Parts of the Setup:

(a)Trough:

The general objective of the Langmuir Blodgett trough is to study the properties of monolayers of amphiphillic molecules. LB trough helps us to prepare monolayer of amphiphillic molecules at the surface of liquid. Then the formed monolayer is compressed or expanded on the surface so that the modification of surface density and area per molecule. This process is done by spreading the subphase basically water on the trough and compress it with the barriers. The troughs are made up from PTFE(Polytetrafluroethylene) and is glued onto an aluminium base plate. The temperature is adjusted with the water bath circulator which is connected to the trough with special connectors.

Figure3.5: Schematic illustration of LB Trough[26]

(b)Substrate:

The substrate can be of two types; hydrophilic or hydrophobic. If the substrate is hydrophilic then first layer will be during up cycle. But if the substrate is hydrophobic then first layer deposited during the down cycle. The main conditions for substrate is that it should be clean and smooth.

(c) Barriers:

Barriers are made up of hydrophilic material so that the film does not escape out. The material for barrier is polyacetal which is not resistant to acids or chloroform; so that these are not used as cleaning agents.

(d) Barrier Driving System:

By using micro step driven stepping motor the barrier position is controlled. The motor moves the barrier holder by using a tooth belt. The holder is attached to a linear motion system which is already equipped with ball bearings.

(e) Surface Balance:

The surface pressure is determined by using the Wilhelmy plate. The wilhelmy plate is carefully sandblasted platinum plate or a clean paper plate which is put under the subphase. The force acting on the plate depends upon the surface pressure. This surface pressure can be measured by electro balance and this is called the surface balance.

3.8 Parameters affecting the LB film:

The parameters of the film deposition are: temperature, concentration, pH, nature of solvent, amphiphillic character of depositing molecules, transfer process, type and nature of the solid substrate.

3.9 Deposition:

When the surface pressure and temperature of monolayer is controlled then the film is in stable state. The monolayer is formed by poring the solvent with microsyringe on the solution. The compression is provided by the barriers from the sides of the trough. So that

Langmuir Blodgett films are formed by transferring these Langmuir monolayer on the solid substrate. In case of Langmuir Blodgett deposition the sample is moved vertically but in case of Langmuir Schaefer the sample is moved horizontally. By dipping solid substrate up and down by keeping constant surface pressure through the computer feedback system between surface balance and barrier moving system. The structure of hundred of layers are formed. These structures are called LB films.

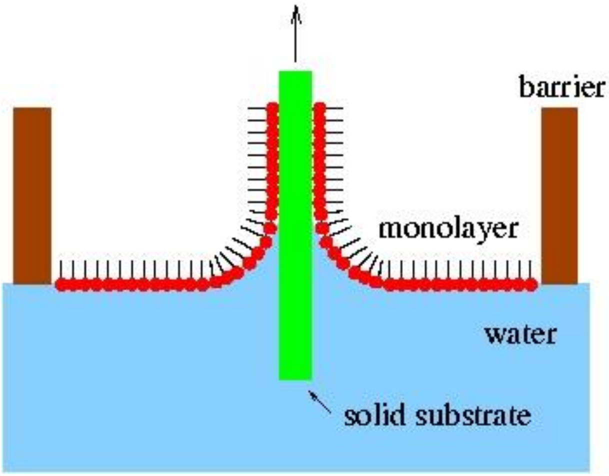


Figure3.6: Film transfer on solid substrate[27]

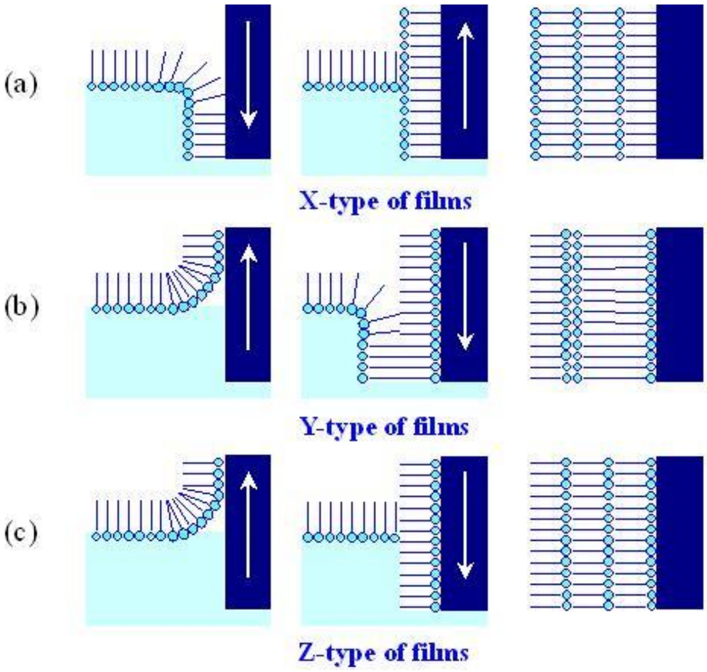


Figure3.7: different type of deposition[28]

The deposition is mainly depends upon the behavior of the substrate. If the substrate is hydrophilic then monolayer is deposited on each traversal. It is the arrangement of head to head and tail to tail pattern and deposition is Y type. There are instances in which the monolayer are deposited when the substrate is inside the subphase. This means that films are deposited downstroke only and these instances are called X type deposition.

Also there are some instances in which monolayer are deposited when the substrate is upwards the subphase and the films are deposited upstroke only and these are called as Z type deposition.

3.10 Transfer Ratio:

Transfer ratio is to determine the quality of the film deposition. Film transfer is measured by the measurement of deposition ratio. It is defined as the ratio of decrease in area occupied by monolayer at the water surface to the coated area of the solid substrate is called the transfer ratio and it is denoted by τ.

$$\tau = A_L / A_S$$

where A_L= decrease in area occupied by monolayer at the water surface

and A_S= coated area of the solid substrate.

For good deposition transfer ratio is taken as unity. Transfer ratio having range 0.95 to 1.05 is significantly very poor deposition.

3.11 Types of Langmuir Blodgett Deposition:-

There are three modes of deposition in Langmuir Blodgett deposition X type, Y type and Z type. From all of these three Y type deposition is very common. In Y type deposition substrate moves both up and down movements. In X type deposition substrate is oves only with up movements and in case of Z type deposition the films are deposited only with down movements of substrate.

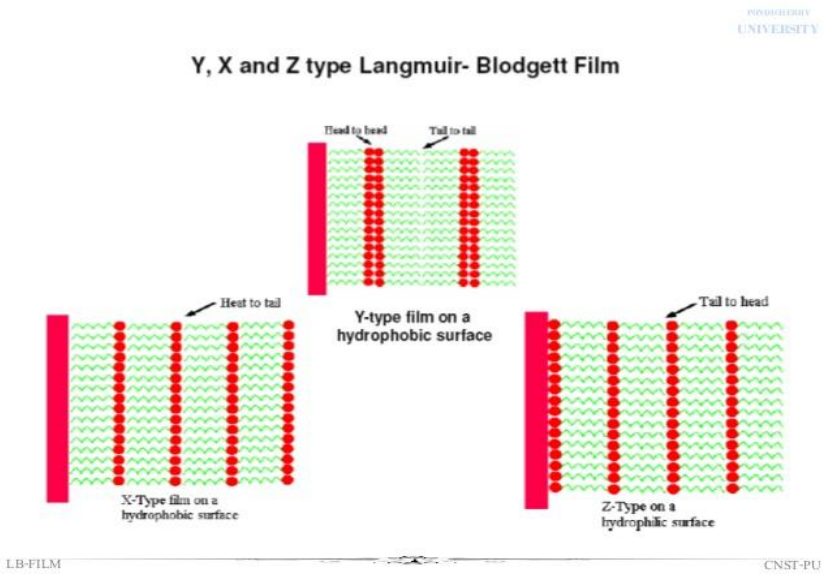


Figure3.8: Schematic of modes of Langmuir Blodgett Deposition[29]

CHAPTER 4

MATERIALS AND METHODS

This chapter gives the details about the materials and methods viz, synthesis and characterization methods used in the present work.

4.1 Materials:

The main chemicals and reagents used in this work are: Zirconyl Chloride Octahydrate ($Cl_2OZr.8H_2O$, Sigma Aldrich, 98%), Stearic acid ($C_{17}H_{35}COOH$, Sigma Aldrich, > 98.5%.), chloroform ($CHCl_3$, SDFCL, 99%) , ethanol (C_2H_5OH, Loba Chemie, 99.9%). All the chemicals were used as obtained without further purification. Deionized water used was obtained from Millipore Q3 system with resisitivity of 18.2 MΩ. Borosil glass slides cut in size of 2.3 X 2.3 cm were used as substrates.

4.2 Methods

4.2.1 Trough Cleaning:

The cleaning of trough is very necessary. Trough is cleaned with Ethanol (99% pure) and then followed by rinse with deionized water. The trough was cleaned before and after each experiment.

4.2.2 Cleaning of Substrates:

Borosil glass substrates used for film deposition were cleaned using piranha cleaning method. The glass slides were carefully cleaned in 3:7 (v/v) mixture of 30% H_2O_2 and 95% H_2SO_4 , (heated for one hour) followed by sonication in DI water for five minutes. Furthermore the glass slides are ultrasonicated with acetone, ethanol and with deionized water for five minutes each.

4.2.3 Preparation of subphase for isotherms and deposition:

The isotherms for the characterization of the langmuir films are taken on DI water and ziconyl chloride(ZrCl) solution subphase(0.1mM). The ZrCl is unstable above 23 ^{0}C so the subphase solution is always maintained at 20 ^{0}C. pH of the solution was modified using 0.1 M NaOH solution.

4.3 Preparation of langmuir films and LB film deposition:

The langmuir film characterization and the Langmuir Blodgett deposition work has been carried out on KSV NIMA Minitrough having surface area of 24300mm^2 and Teflon barriers.

Stearic acid dissolved in chloroform (0.66mg/ml) is used as the spreading solution for the formation of langmuir films. The 30 microlitres of the stearic acid solution in the form of small drops using(Hamilton microsyringe) is placed on the water/solution surface. Solvent evaporation time of 15 minutes is given in each experiment before starting the compression process with barriers.

All the isotherms are taken at subphase temperature of 20 ^{0}C with barrier speed 7mm/min.

The deposition of the LB films is done at 20mN/m. The films were allowed to stabilize at deposition pressure for 10 minutes before deposition. For the deposition the substrate dipping speed is maintained at 5mm/min for both up and down with a wait of 2 min for drying at the top.

4.3.1 Drying and stepped heating protocol:

The films formed were then dried in vaccum for 30 minutes in the vaccum desiccators.

- Heat at 120^{0}C for one hour for removal of any absorbed water molecules.
- Stepped heating in furnance with rate of 5^0/min.

STEP 1:

- Heat till 380^{0}C for removal and decomposition of stearic acid followed by:

STEP 2:

Sample Name	Temperature	Time
Zr500	500 ^{0}C	5 hrs.
Zr600	600 ^{0}C	5 hrs.

4.4 Characterization Techniques:

4.4.1.Surface Pressure-Area Isotherms:

π-A isotherms are the most basic characterization tools for Langmuir films. They have already been discussed in section 3.6.

4.4.2. X ray Diffraction(XRD):

X ray crystallography used to determine the crystal structure that means how the atoms are closely packed in the crystalline state. It is the most important characterization technique used in material science. By using this technique size, shape, average atomic spacing, orientation of single and poly crystal are determined. X ray diffraction provides most definitive structural information and inter atomic distance and bond angles. This analysis is based on the constructive interference of x rays. When the conditions satisfy Bragg's law which gives as

$$2d\sin\Theta = n\lambda$$

Where n = an integer

d = interplanar spacing

Θ = diffraction angle

λ = wavelength of x rays

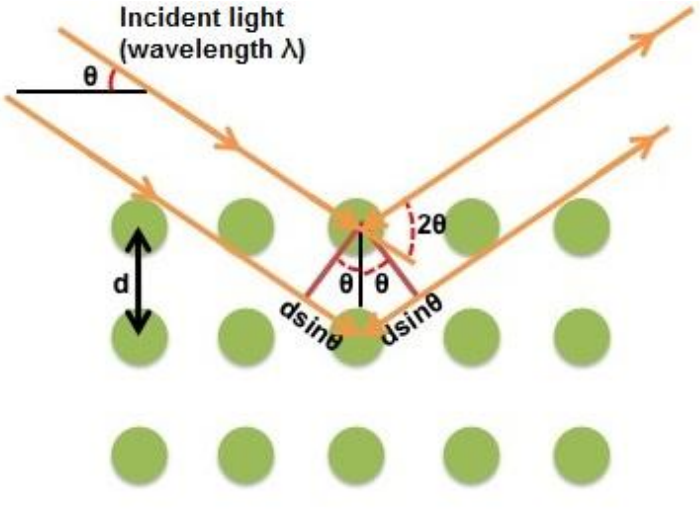


Figure4.2: Bragg's law reflection[30]

4.4.3.Field Emission Scanning Electron Microscopy(FESEM):

FESEM provides elemental and topographical information at higher magnification. It works with electrons not with light. From field emission source these electrons are emitted . When we compare it with Scanning Electron Microscopy(SEM) then FESEM produces more clearer, less distorted images with high resolution. Basically this technique applies to observe structures that may be as small as 1 nm. The main advantage of using FESEM is that there is no need of placing conducting coating on insulating materials. FESEM used in semiconductor device cross section analysis for gate widths, film thickness. It gives very high resolution and magnification. It gives detailed 3D imaging. To produce FESEM image, the electron beam is sweep across the area being inspect, producing many signals. These signals are then analyzed and translated into the images of the topography, then image is show.

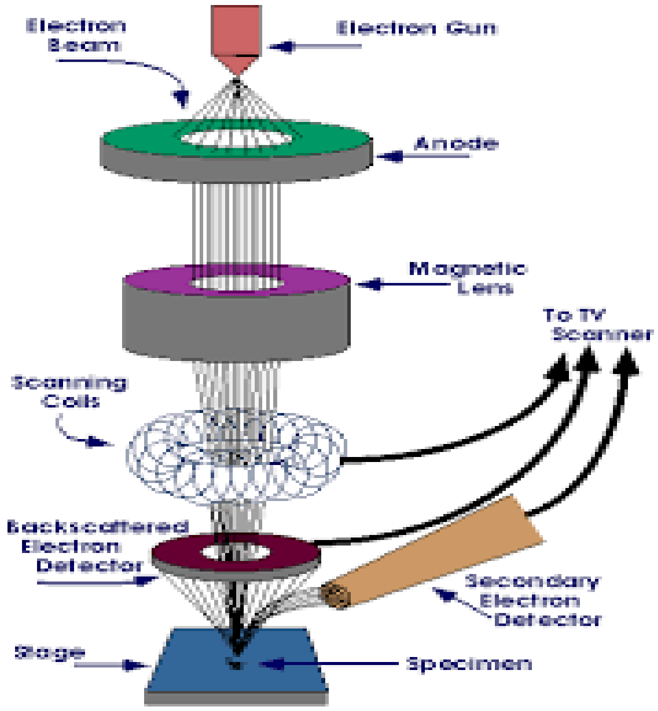


Figure4.3: Schematic of FESEM[31]

4.4.4.Fourier Transform Infrared Spectroscopy(FTIR):

This is very important characterization technique for determining the molecular structure and the functional group. It may be applied to the analysis of solids, liquids and gases. FTIR is based on the principles of molecular spectroscopy.

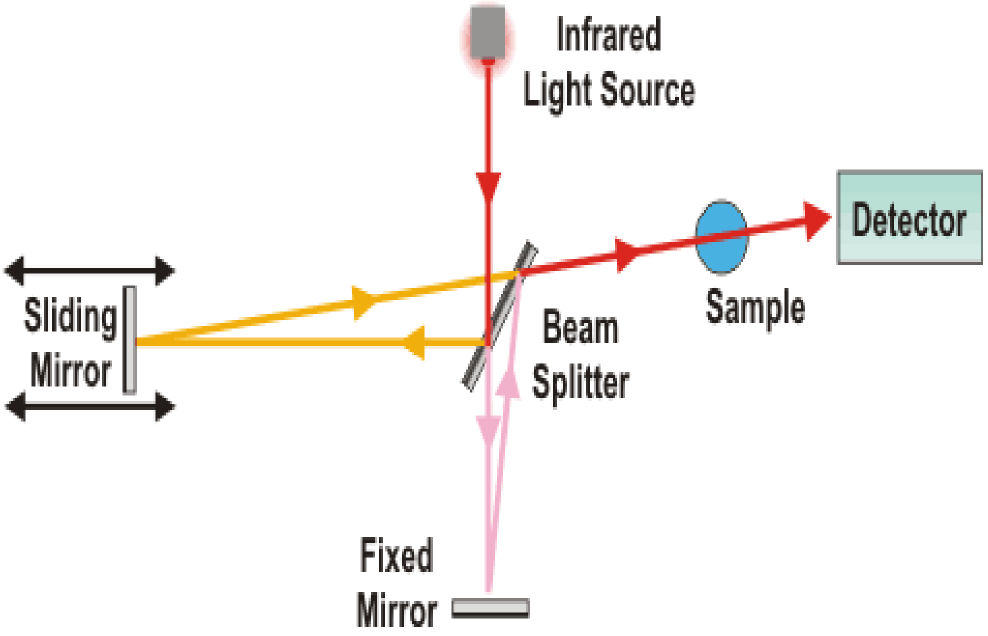


Figure4.4: Setup for FTIR[32]

The basic principle is that it absorb light at specific wavelength. In FTIR spectrometer small quantity of sample is required and it is scanned in 4500 to 500cm^{-1}.

4.4.5 UV-Visible Spectroscopy:

Uv visible is one of the most popular analytical technique because it is versatile and in this we are able to detect nearly every molecule. It is the technique that analyzes the compound in ultra violet and visible region of electromagnetic spectrum. When the light passes through the matter; many of processes are occurs such as reflection, transmission, scattering etc. But in the case of uv visible spectroscopy we only consider the absorbance to occur. When the light is passes through the sample then transmittance is measured. For determining the bandgap Tauc Plot was used. For direct bandgap $(\alpha h\nu)^{1/r}$ the value of r is 2 and for indirect bandgap r is ½. From the transmittance the absorbance can be easily measured i.e. A= -log(T). in this case sample is placed between the light source and the photodetector and the intensity of the sample is measured.

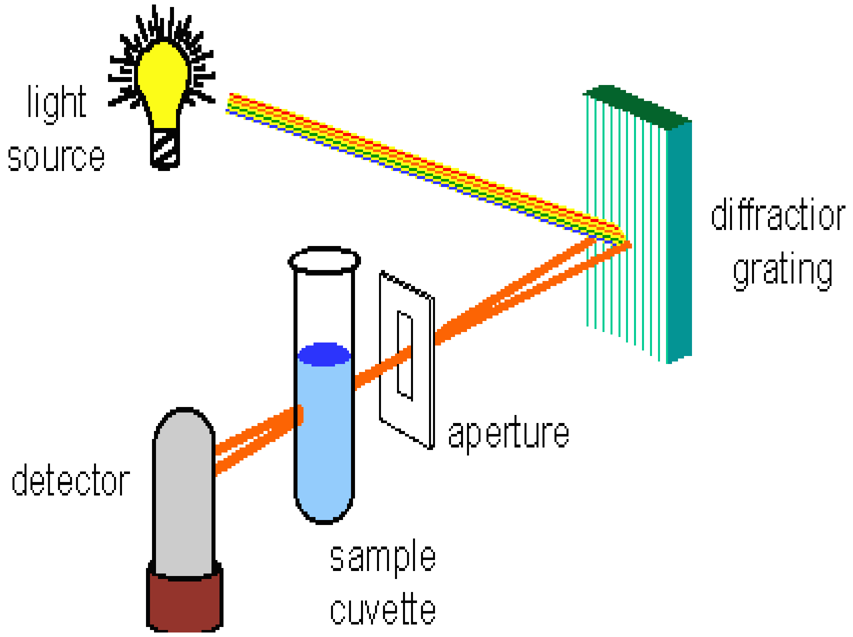


Figure4.5: Ultra violet Visible Spectroscopy[33]

4.4.6 PHOTOLUMINISCENCE:

Photoluminescence spectroscopy is a nondestructive method of inquiring the electronic structure of materials. This is suitable for the characterization of both natural and inert materials. The samples in this can be either in solid, liquid or gaseous forms. Light is directed onto a sample, where it is absorbed and there is a process called photo-excitation takes place. The photo-excitation causes the material to a higher electronic state, and will then release energy in the form of photons. The emission of light or luminescence through this process is photoluminescence (PL). From PL spectrum we can easily find band gap, impurity concentration and we an easily detect the defects present.

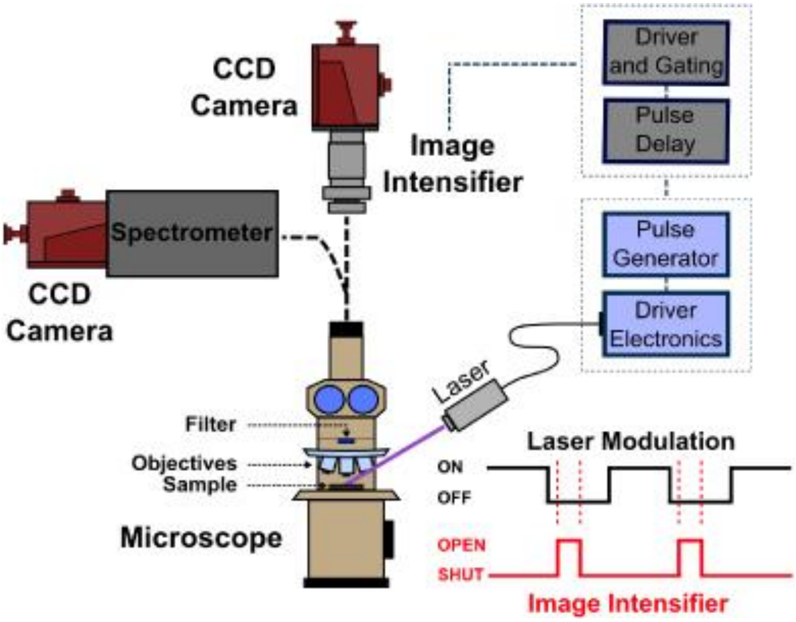


Figure4.6: Photoluminiscence Setup[34]

CHAPTER 5

RESULTS AND DISCUSSION

Overview

This chapter gives the various results that we have obtained in the present work. The results regarding surface pressure-area isotherms, XRD, FESEM, UV Vis, Photoluminescence, FTIR are discussed.

5.1 SURFACE PRESSURE(π) –AREA(A) ISOTHERMS:

Figure 5.1 shows the π-A isotherms for stearic acid(SA) on deionized(DI) water and zirconyl chloride solution for different pH values. All the isotherms are taken at 20 ^{0}C. For stearic acid on DI water surface π-A isotherms shows three distinct regions gas, liquid and solid. The transition pressure π_t between the liquid and the solid phase is 15.5mN/m and the mean molecular area (MmA) in solid phase is 27.5A^{02} . This experiment is in very good agreement with the literature [35]. This confirmed that the SA which we are using as obtained is of sufficient purity. For zirconyl chloride solution subphase the π-A isotherms also show three distinct regions. The transition pressure and mean molecular area between liquid and solid phase varies with the pH of the subphase. The data obtained is given in table 5.1.

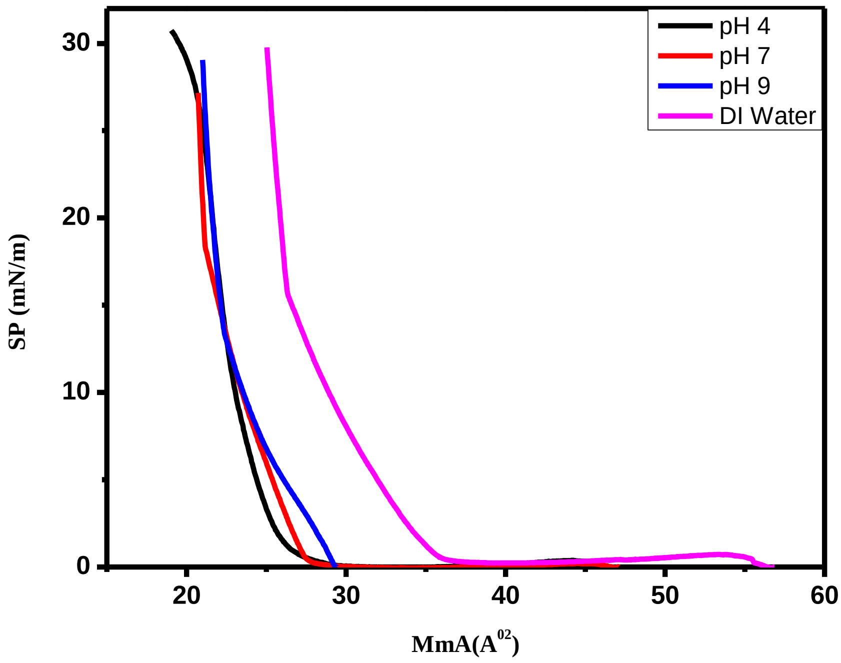


Figure 5.1: Surface Pressure area isotherm at different pH

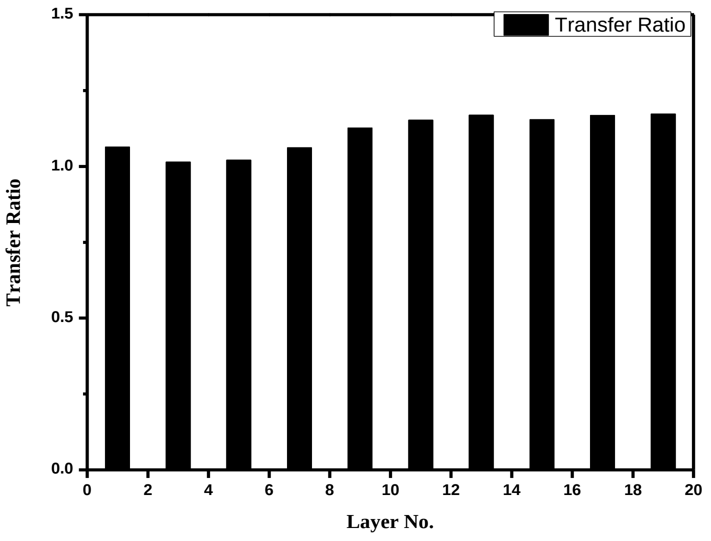
Table 5.1

pH	MmA for solid phase(A^{02})	Π_t liquid to solid phase(mN/m)
4	23.8	22.8
7	21.76	21.2
9	22.76	22.1
Deionized Water	27.5	15.5

For all the Langmuir films formed on the ziconyl chloride solution sub-phase the mean molecular area for the solid phase is less as compared to that for the stearic acid on DI water. This clearly indicates that the films formed in this case are that for the Ziconyl stearate. For all the pH values the liquid to solid transition happens at nearly same pressure which is so much larger as compared to that for SA. This indicates that the interaction involved are different for zirconyl chloride solution and DI water. MmA for all the films formed on the zirconyl chloride solution subphase is less as compared to that for film on DI water. This indicates that compression of film due to 2+ charge on zirconyl ion. We also observe that initially the area decrease with increase in pH but on further increase it decrease. We know from literature that as pH increases the more number of zirconyl ions will get incorporated into the film. We believe that the increase in MmA is due to the enhanced stearic repulsion between the more number of zirconyl ions in the film at pH 9.

5.1.1.Dipping:

Figure 5.2 shows the transfer ratios for the first 10 deposition cycles for the deposition of the ZS films on glass substrate. In the figure all the even numbers represent the down part of the dipping cycle when no deposition takes place. The image clearly shows that the ZS deposits with Z-Type configuration. Figure 5.2(b) shows the proposed structure of ZS films.



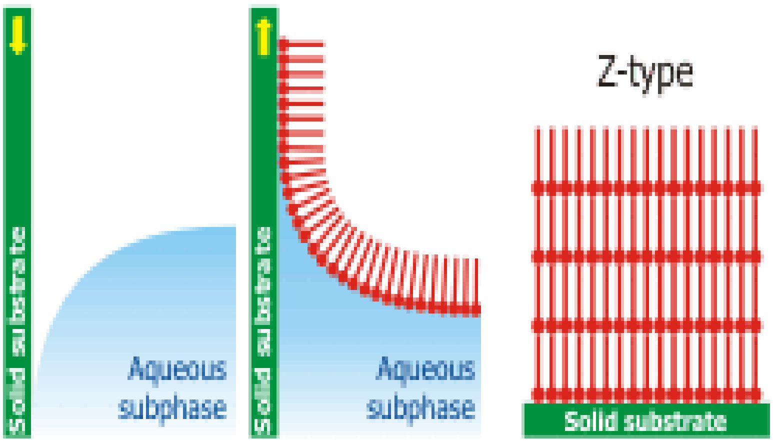


Figure 5.2(a) shows the transfer ratio for 10 cycles of ZS films and Figure 5.2(b) shows the proposed structure of ZS films

5.2 X ray Diffraction(XRD):

Figure 5.3 shows the XRD diffraction pattern of thin films obtained after heating at the final temperatures of 500 ^{0}C and 600 ^{0}C. For both the samples a peak at ~28.6 ^{0} is observed which is getting enhanced for the Zr600 sample. This peak corresponds to (-111) plane for monoclinic phase of ZrO_2 (ICDD-010741200). This confirms the formation of single phase ZrO_2 thin films after heat treatment for both the temperatures. The enhancement of peak for Zr600 sample indicates grain growth/enhanced crystallinity.

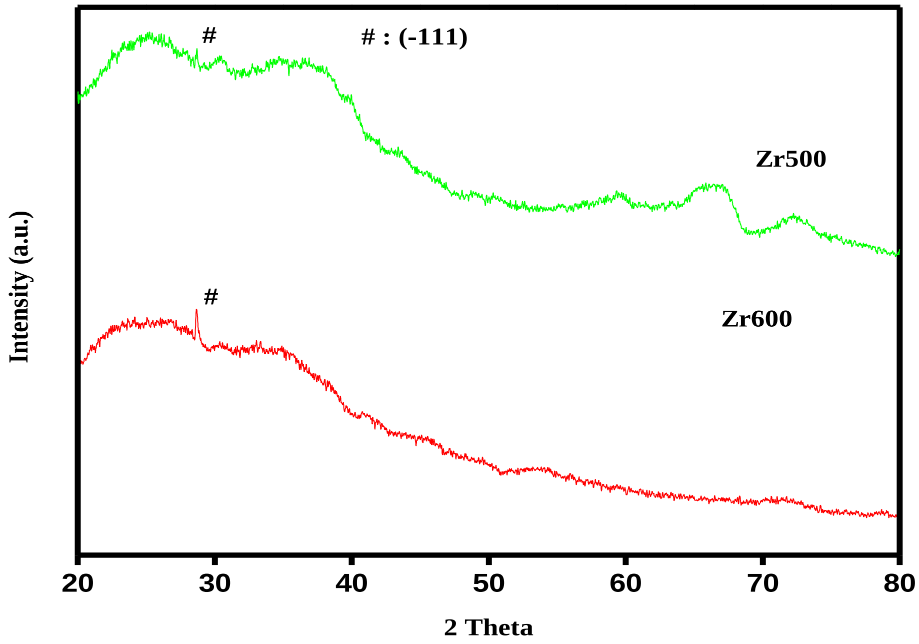


Figure5.3: XRD pattern of ZrO_2 thin films on glass substrate annealed at 500 ^{0}C and 600 ^{0}C

5.3 Field Emission Scanning Electron Microscopy (FE-SEM):

Figure 5.4 depicts the morphology of ZrO_2 thin films on glass substrate as obtained from the FE-SEM. Figure 5.5 (a) shows the cross-sectional image for the Zr600 sample. The film thickness is ~ 100nm. The FE-SEM images clearly show that the Zr500 film is rougher with wide distribution of grain sizes. The film formed at 600 ^{0}C is denser. The grain size analysis for it was carried out. Figure 5.5 (b) shows the grain size distribution obtained for ~300 grains. The graph shows that the grain sizes for the film follow log-normal distribution with mean around 16 nm.

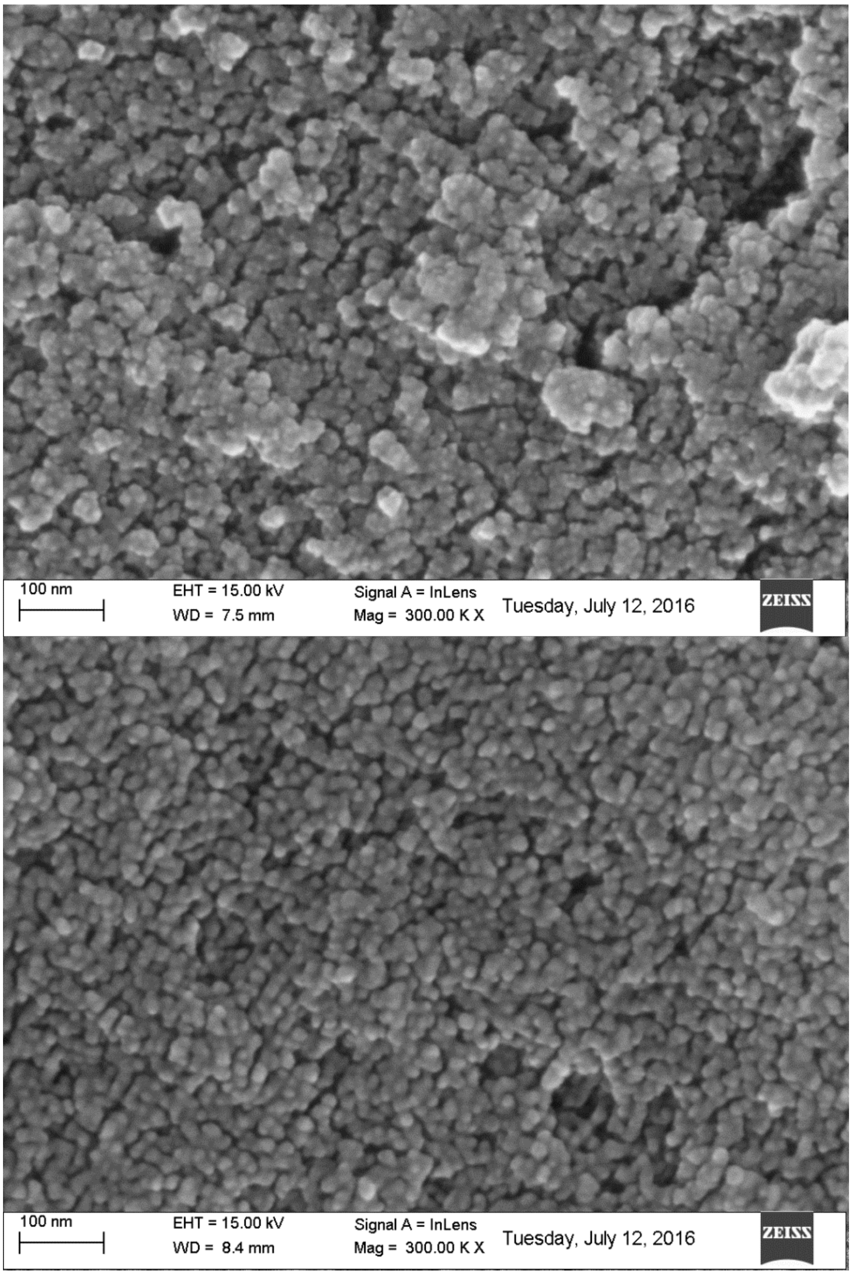


Figure5.4: FE-SEM images of the surface of the thin films of ZrO_2 deposited at (a)600 ^{0}C and (b) 500 ^{0}C

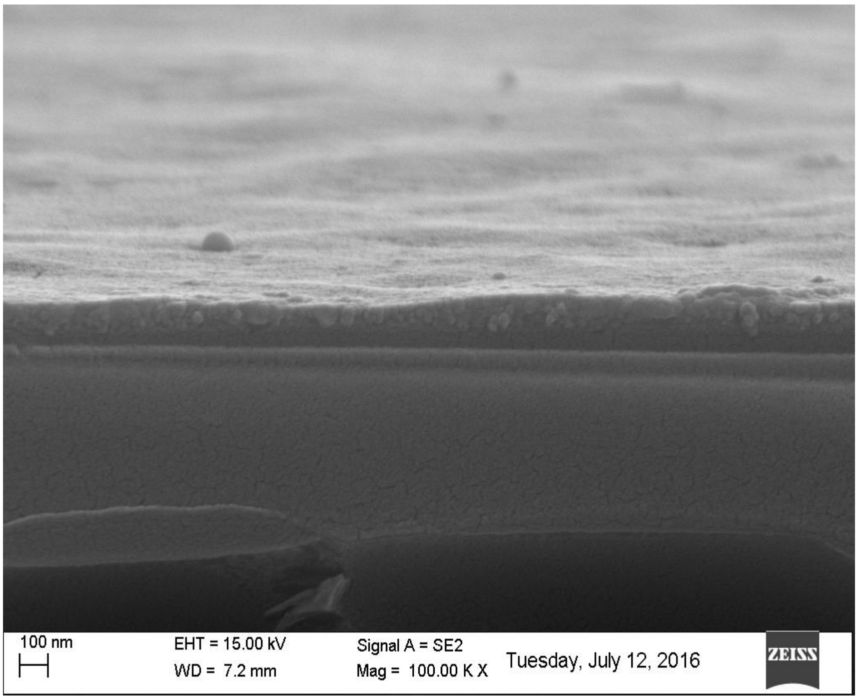


Figure 5.5(a): Cross sectional image Zr600 sample

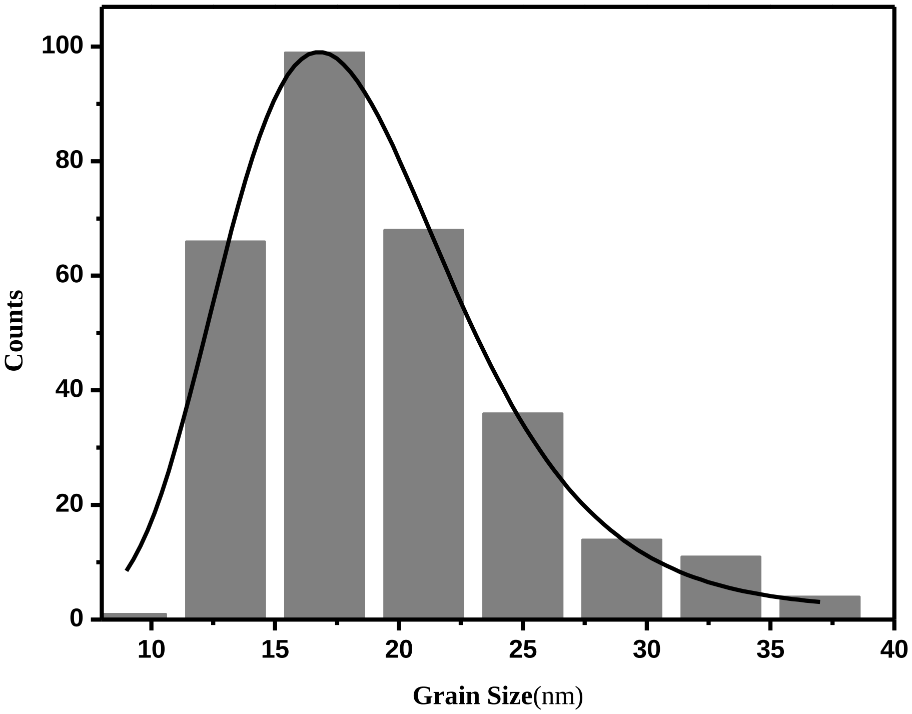


Figure 5.5(b): Grain Size Distribution for ~300 grains

5.4 OPTICAL PROPERTIES:

5.4.1. UV-Visible Spectroscopy:

Figure 5.6 shows the transmittance spectra of the deposited zirconium oxide thin films which was obtained from UV Visible spectroscopy. Zr600 sample shows higher transmittance which indicates that film is more crystalline as compared to Zr500 sample[36]. This supports the XRD data.

To determine the direct bandgap of the films we have plotted $(\alpha h\nu)^2$ as a function of energy (figure 5.8). At 500^0C the band gap is 5.9eV and at 600^0C the band gap becomes 6.0eV. Increase in the band gap observed in UV with temperature is due to the enhanced packing density and improved crystallinity.

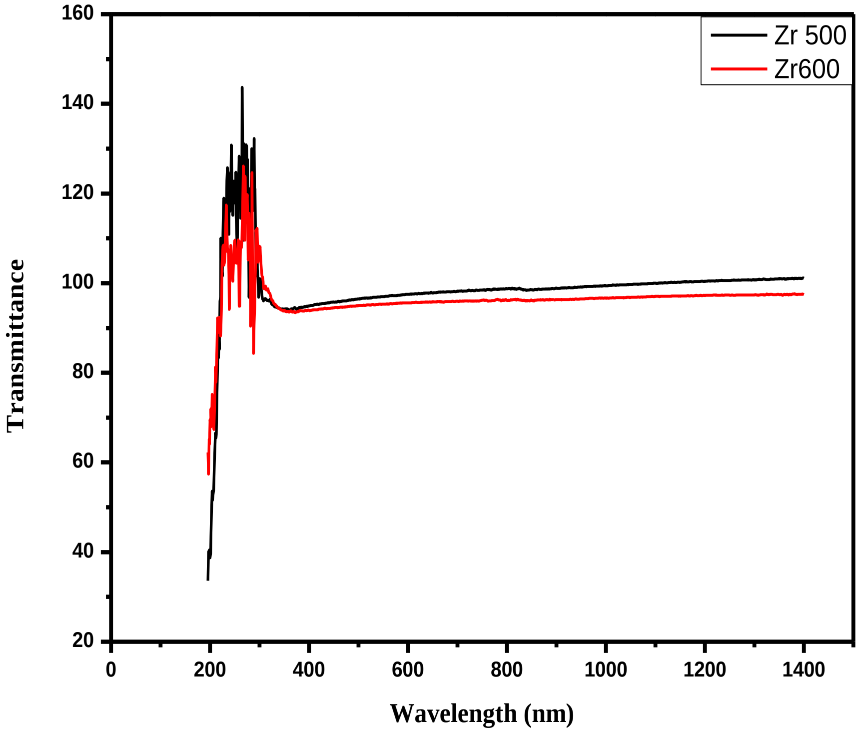


Figure 5.6: Transmittance spectra of thin films of ZrO_2 at 500 ^{0}C and 600 ^{0}C

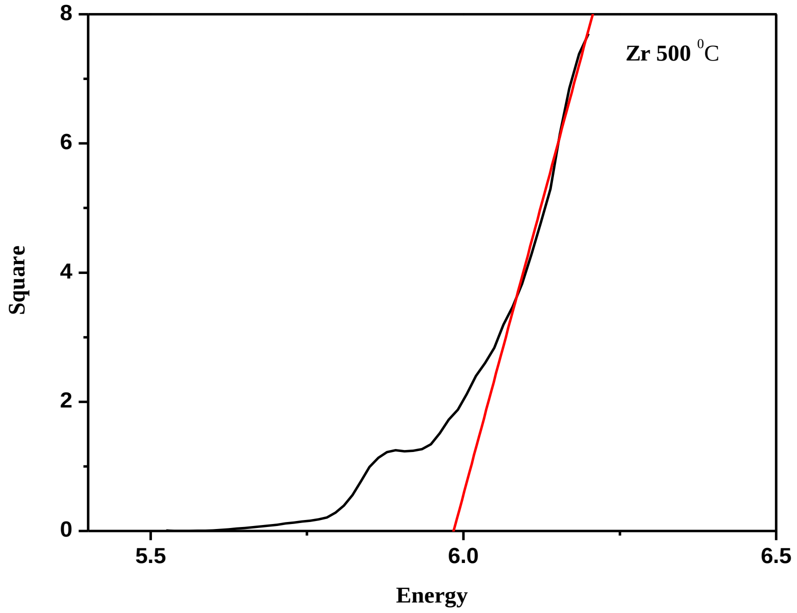


Figure 5.7(a): Bandgap of ZrO_2 thin films at 500^{0}C

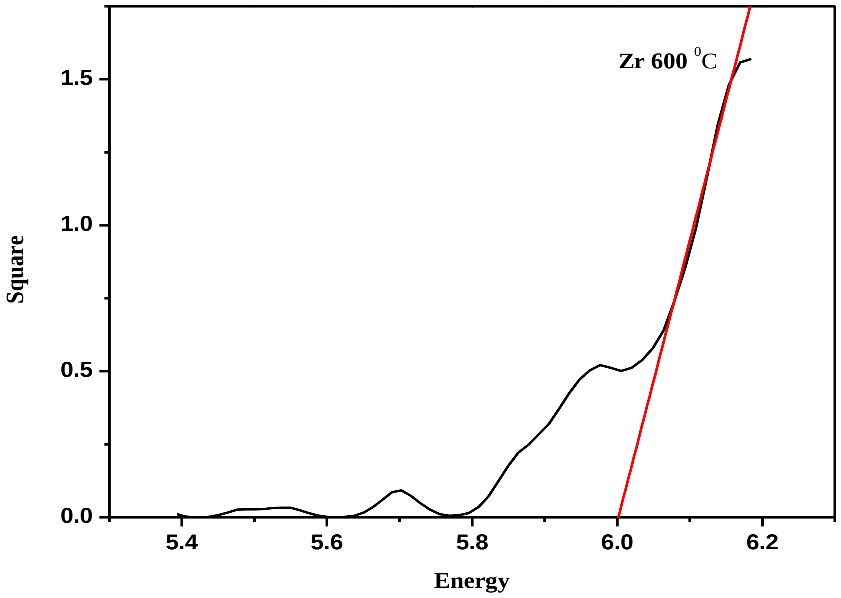


Figure 5.7(b) Bandgap of ZrO_2 thin films at 600^{0}C

5.5 Fourier Transform Infrared Spectroscopy(FTIR):

The chemical bonds present in the ZrO_2 films are characterized by transmission mode FTIR measurements in the range 500-4500cm^{-1}.. Figure 5.8 gives FTIR spectra. The main peaks observed are 752cm^{-1}, 1574cm^{-1}, 2314cm^{-1}. The peak at 2314cm^{-1} resulted from the absorbed water molecules. The peak at 752cm^{-1} is the characteristic of monoclinic ZrO_2. Peak at 1574cm^{-1} are due to stretching and bending of O-H bonds due to absorbed water molecules.

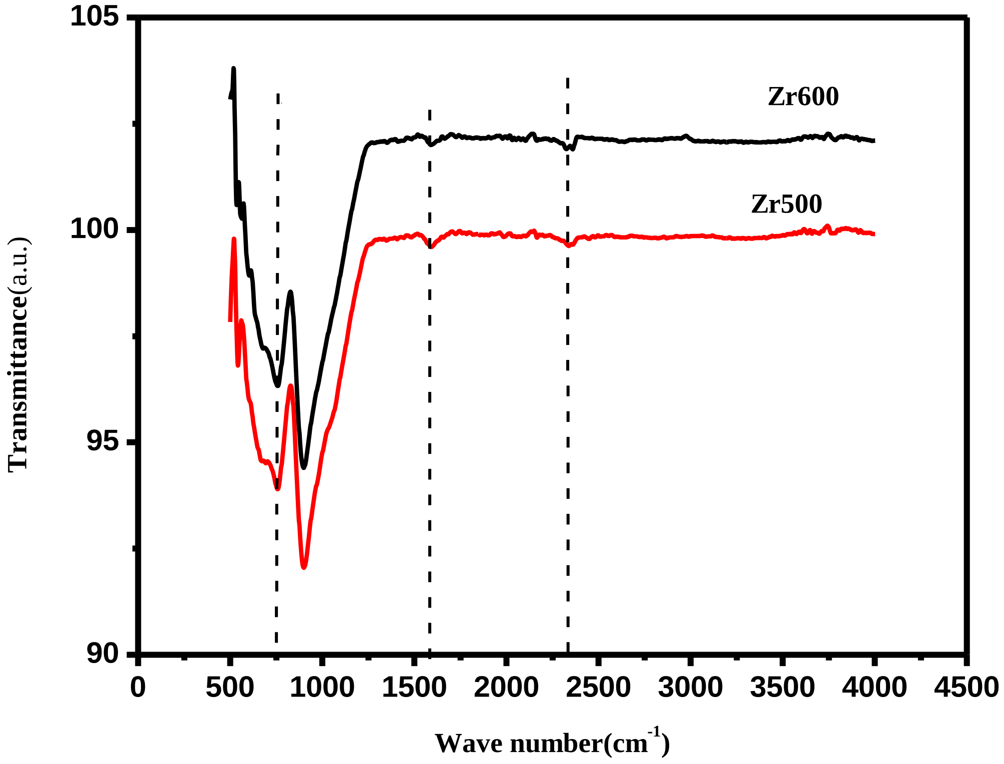


Figure 5.9: FTIR spectra of ZrO_2 thin films at different tempeartures

5.6 Photoluminescence(PL):

Figure 5.10 shows the emission spectra of ZrO_2 thin films at temperatures 500 ^{0}C and 600^{0}C. In our experiment the excitation wavelength is 190nm because the band gap is 6eV. The PL spectra of the films shows intense peak at 490nm. As the crystallinity increase then peak intensity is also increases. The weak peak at 423nm are because of the tetragonal phase but we find no signature of tetragonal phase in XRD pattern. Fluroscence in ZrO_2 is related to the recombination of electrons trapped by O_2 vacancies and holes created in the valence band[37]. For monoclinic ZrO_2; Zr^{4+} is surrounded by 7 oxygen ions and the peak observed at 490nm is attributed to the distortion to the surrounded oxygen ions[38].

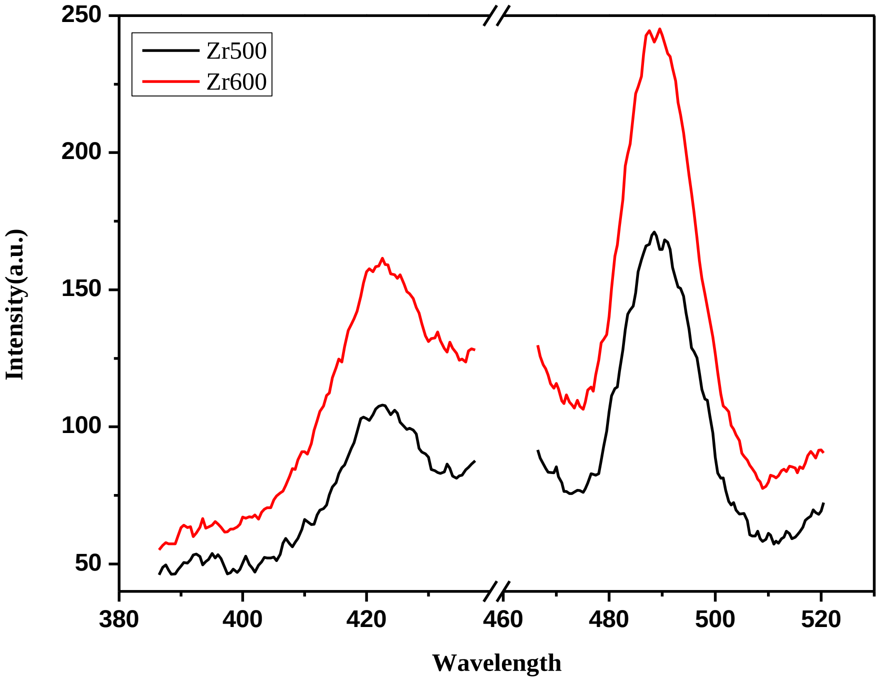


Figure 5.9 Photoluminescence spectra of ZrO_2 thin film

CHAPTER 6

Conclusions and Future Scope

6.1 Conclusions

ZrO_2 thin film have very wide range of applications such as for photonics materials, antireflection material, resistive oxygen gas sensors, as a gate dielectric and high temperature fuel cells. We have used the phenomenon of metal stearate monolayer for the synthesis of zirconium oxide thin films using zirconyl stearate LB films. The zirconyl stearate films have been studied and deposited for first time as to the best of our knowledge. The LB films deposited on hydrophilic substrate are z-type in nature. The composition of mixed Langmuir films of metal stearate and stearic acid is determined by its pH. For the present work the maximum incorporation of zirconyl ions occurs for pH 9. The 200 layer deposition at 20 ^{0}C is followed by proper heating protocol to ensure complete removal of the stearic acid and/or any other carbon impurity. The resulting films have a thickness of ~100nm and show pure monoclinic phase. An increase in the final heating temperature enhances the uniform grain growth as well as the density of the films. The films have a band gap ~ 6.0eV with a strong PL emission peak is at 490nm and a weak peak is at 423nm. So the films formed by LB deposition methods are suitable for luminescent applications.

6.2 Future Scope

The zirconyl stearate LB films show Z type deposition. Z-type deposition is a very rare and interesting phenomenon in LB film deposition. So this phenomenon needs to be studied further for complete understanding of the system especially behavior of the zirconyl ion in the monolayer. For ZrO_2 the value of band gap is 6eV so for further studies we should deposit the films onto Si and quartz substrate to get more precise information. The luminescent properties, roughness and porosity of the films need to be characterized as a function of pH of the sub phase and heating temperature.

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