Synthesis of Nickel Oxide thin films using Langmuir-Blodgett Technique

A
Thesis
Submitted for the Award
of the Degree of

Master of Science in Physics
By
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Certificate

This is to certify that the thesis entitled **"Synthesis of Nickel Oxide thin films using Langmuir-Blodgett Technique"** submitted by **Ms. Palvi** (Roll No. 301404018) 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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Declaration

I hereby declare that thesis entitled **"Synthesis of Nickel 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 for their

love and support

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Palvi

Abstract

Nickel oxide is an important material in regard with its applications. Ni_2O_3 form of nickel oxide is not as well studied as the NiO. Ni_2O_3 has important applications as buffer layer for organic photovoltaics and auto emission catalyst. We present here a novel method for the synthesis of transparent hexagonal Ni_2O_3 thin films using LB technique. The synthesis route involves the deposition of 200 layers of dense Nickel Stearate Langmuir layers followed by their decomposition and oxidation via stepped heating protocol.The characterization of the synthesized films shows that the Ni_2O_3 phase is enhanced at higher temperature with denser films and larger grain size. Increased grain size results in increased transmittance properties and reduced dielectric constant. FTIR is used to confirm the complete removal of carbonaceous content, which may lead to defects and decrease the quality of the films.

CONTENTS

CHAPTER 1

INTRODUCTION TO NICKEL OXIDE

1.1 Introduction:

Nickel Oxide (NiOx) is a conducting, electrochromic, thermoelectric material showing transparency having a band gap varying from 3.6 to 4.0eV **[1]**. NiOx is a rock salt type antiferromagnetic oxide semiconductor. Its thin films are generally p-type.

NiOx is one of the best material for the optical, electrical and gas sensor applications due to its electronic and catalytic properties. NiOx is an important material used in device applications such as dye-sensitized photocathodes, gas sensors, organic light-emitting diodes, magnetic materials and electrodes in alkaline batteries. It is also used as adhesive and coloring agent for enamels. NiOx is used in nanofibres, nanowires and also used for making electrical ceramics. NiCd rechargeable batteries are also made using NiOx. NiOx is also used as a catalyst and as anti-ferromagnetic layers. Recent applications include resistive switching memory and electrochromic smart windows.

Nickel Oxide has the following characteristics:

- electrochemically stable
- long life
- ease of manufacturing
- inexpensive starting materials
- ion storage material

1.2 Structure and Properties of Nickel Oxide:

Structure of Nickel Oxide:

Nickel (II) Oxide exhibits NaCl structure with Ni^{2+} ions occupying octahedral sites that are surrounded by $6O^{2-}$ ions at the FCC sites. The lattice parameter is 4.177 Å **[2]**.
NiOx is often non-stoichiometric in nature and due to this non-stoichiometry, change in colour is observed. The stoichiometric NiOx is green and the non-stoichiometric NiOx is

black. For the non-stoichiometric NiOx due to the restrictions of the NaCl structure the extra oxygen cannot be placed rather, Ni vacancies are created thus giving NiOx a p-type semiconductor character.

In bulk, Nickel (II) Oxide shows cubic (fcc) structure with a small rhombohedral distortion below the Neel temperature, T_N (~523 K). This distortion is because of the confinement of ferromagnetically ordered spins within the (111) plane **[3,4]**.

The stable crystal structure of nickel oxide at a high temperature is polymorph bunsenite. By cooling the crystal, the crystal structure converts to rhombohedral. It should be noted that these crystal structures form during thermodynamically stable transitions. Different fabrication techniques can produce non-stoichiometric structures at room temperature **[5]**.

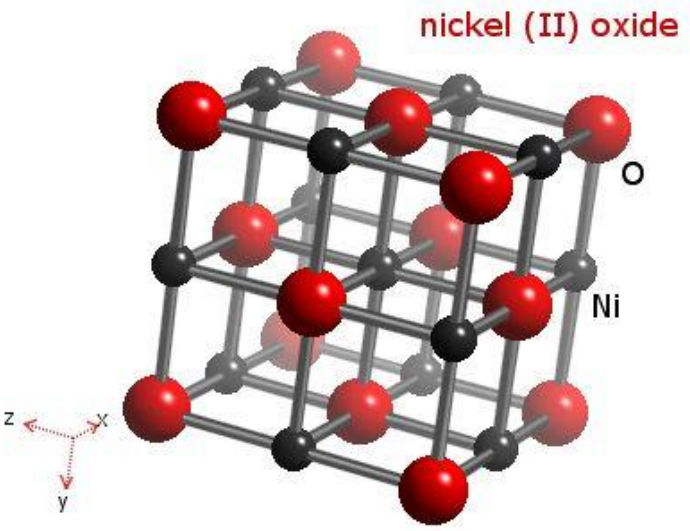

Figure 1.1: Simple cubic structure of Nickel (II) Oxide [6]

General Properties:

NiOx has a high value of specific capacitance, high chemical and thermal stability, easy availability and environment friendly nature. NiOx is used for different applications, such as solar thermal absorber, fuel cells, electrochromic display devices and gas sensors. NiOx is an insulator, however, due to the defects and Ni^{2+} vacancies, NiOx shows semi conductive properties i.e. during annealing in the air, its resistivity can be decreased by increasing the concentration of Ni^{2+} vacancies.

Table 1.1. Properties of Nickel Oxide

FORMULA	NICKEL OXIDE
Crystal Structure	Rock Salt (Octahedral)
Cation	Ni^{++}
Lattice Parameter (a)	4.177 Å
Coefficient of refraction	2.23
Binding Energy	530eV
Density	$6.67 g/cm^3$
Dielectric Constant	10
Electron Configuration	$[Ar] 3d^{10}$
Melting point	1957℃
Molar mass	74.6928 g/mol
Optical Density	0.915
Oxide ion polarizability	High
Refractive index (n_D)	2.18
Resistance	10^{-8} (ohm.m)

1.3. Properties of Nickel Oxide as Thin Films:

- **Electric Properties:** The electric properties of Nickel Oxide films are connected with their microstructures, composition and with the annealing atmosphere. Generally, resistivity of thin films increases with the thickness **[7].**
- **Magnetic Properties:** With the change in thickness saturation magnetization increases while coercivity deceases. At the room temperature, the M-H curves of thin films confirm ferromagnetic behavior **[8]**.
- **Optical Properties:** Nickel Oxide thin films have high degree of optical transmittance in the visible region **[7]**. The estimated band gap of the films is observed to be 3.6-4.0 eV. When the annealing temperature is increased, the band gap shifts towards lower energy. Also when the annealing temperature is increased, there is an increase in the transmittance.
- **Electrochromic Properties:** Electrochromic materials are those materials that exhibit a reversible colour change induced by an applied electric field or current. As the annealing temperature is changed the resistance and hence the colour of the film changes. Electrochromic effect is only observed in the films prepared at low temperatures. The electrochromic properties of the films are generally investigated as a function of film thickness **[9]**.
- **Structural Properties:** Structural investigations of the films show the polycrystalline structure with distribution of grains. Annealing under air leads to the production of large grains, which further leads to better crystalline structure, and also lowers the vacancies of oxygen **[10].**

1.4. Applications of Nickel Oxide as Thin Films:

The main applications of Nickel Oxide thin films are:

- Electrochromic coatings.
- Adhesive and coloring agents for enamels.
- Functional layer materials for gas sensors, such as H_2 sensor.
- As a catalyst for O_2 evaluation.

- Anti-ferromagnetic layers.
- Anode in oxygen fuel cell.
- Counter electrode in smart windows.

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CHAPTER 2

LITERATURE SURVEY

A literature review is presented to clarify the current state of the art in NiOx. NiOx thin films are generally deposited by techniques such as sputtering, pulsed laser deposition, spray pyrolysis (SP), sol-gel and atomic layer deposition.

2.1 Synthesis of Nickel Oxide thin films by various techniques:

P.S. Patil et al 2002 [1]: In this paper the SP technique was used to deposit NiOx thin films from the hydrated nickel chloride salt solution on glass substrate. It was observed that by increasing the volume of sprayed solution, the film thickness, band-gap and hence the resistivity of the film can be changed.

Y.M. Lu et al 2002 [2]: In this paper the thin films of NiOx thin films were synthesized by sputtering. Ni was used as a target and Si and glass were used as substrates. A mixture of oxygen and argon gases is used in the chamber. It emerged that the deposition rate is linear function of the power. With increased substrate temperature the film resistivity increases.

J.L. Garcia-Miquelet al 2003 [3]: Using sol-gel technique and with the help of nickel acetate complexes, NiOx thin films were successfully deposited on conductive glass substrates for large area electrochromic applications.

Jin-Young Park et al 2004 [4]: NiOx films for electrochemical and electrochromic applications are deposited using sol-gel. In this work, β-phase Ni $(OH)_2$ nanoparticles of ~7nm were synthesized. The synthesized particles were suspended in an absolute ethanol and ethylene glycol mixed solvent with acetyl acetone and glycerol as additives and thus sols were prepared. Spin coating was used to prepare coated films .The film was treated at different temperature. The film showed a porous structure and was good adherent to the substrate. When the coloration efficiency was 33.5 cm^2 /C, as transmittance modulation of 41.2%, and a response time of 1.0–2.5 s during the coloring/bleaching

process, this film showed electrochromic properties.

Romana Cerc Korošecet al 2006 [5]: NiOx thin films were prepared by sol-gel method using two precursors: nickel sulphate and nickel acetate. For electrochromic response, the grain size is deemed important. When nickel sulphate is used as a precursor, films prepared have good response at the complete decomposition whereas for nickel acetate films, it is obtained only at 25% decomposition. For both the films, the electrochromic properties were almost same.

B Sasi et al 2007 [6]: In this paper pulsed laser technique was use to prepare nanostructured NiOx thin films. Annealing process has large effect on the surface roughness and particle size. The presence of Ni_2O_3 in the as-deposited films was observed.

XIANG Rong et al 2010 [7]: In this paper, NiOx thin films on quartz-glass substrate are deposited by using RF magnetron sputtering method. The properties of NiOx thin film are greatly dependent on the sputtering voltage.

Vikas Patil et al 2011 [8]: In this paper sol gel spin coating method was used to deposit nanocrystalline NiOx thin films. All the films are cubic in phase. At the room temperature, the films show the semiconducting nature.After annealing the film, its electrical conductivity increased from 10^{-4} to 10^{-2} $(\Omega\ cm)^{-1}$. When the films were annealed from 400℃ - 700℃, there was decrease in the band gap.

Marek Guziewicz et al 2011 [9]: In this paper, NiOx films were fabricated by sputtering method using quartz and silicon as the substrates. It was verified that all the films formed (with or without annealing) were of p-type conductivity. The films settled at room temperature in the absence of oxygen have the value of transmittance approximately 50% in the visible range and resistivity about 65 □cm. In deposition gas mixture when the amount of oxygen is increased the value of conductivity increased, but the value of transmittance decreases below 6% and the resistivity was 0.125 □cm. When the temperature was elevated upto 500 ℃ the value of transmittance was above 60% and conductivity decreases. When annealing of Nickel Oxide films was done in Ar, it causes

resistivity to rise dramatically.

Safwat A. Mahmoud et al 2011 [10]: NiOx thin films on glass substrates are deposited using SP technique. The films formed are crystalline as well as non-crystalline depending on the substrate temperature. At low substrate temperature the films show amorphous structure and at higher substrate temperature a cubic structure is formed.

A.M. Soleimanpour et al 2012 [11]: NiOx thin films for hydrogen sensing properties were synthesized by using sol-gel method on glass and silicon substrates. It was found that the films formed by this method were polycrystalline and could be used for the fabrication of H_2 gas sensors.

S. Sriram et al 2013 [12]: NiOx thin films were deposited by spray pyrolysis technique using fresh and aged precursor solutions. From the structural, optical, electrical studies it is clear that the film prepared from the aged solution has more grain size, larger band gap and low resistivity as compared to the film prepared by fresh solution.

Ahmed J. Hassan 2014 [13]: NiOx thin films on glass substrate using spray pyrolysis technique were studied. Nickel nitrate salt solution was used to prepare the cubic phase films of thickness ~200 nm.

M. Jlassi et al 2014 [14]: NiOx thin films were deposited on glass by using the sol–gel method combined with spin coating. The optimum annealing temperature for preparation of NiOx films with p-type conductivity and high optical transparency is 600^0C. It was also found that a multilayer structure (of four layers) gives a good transmission of about 80%. The electrical resistivity was improved when NiOx layers were annealed at 600 ^{0}C in atmosphere of nitrogen. The value of resistivity is $900\times10^3\Omega$cm when the samples were treated under air and when treated under nitrogen then the value is about 40 Ω cm.

M. M. Gomaa et al 2015[15]: NiOx thin films were prepared on glass using chemical bath deposition and spray pyrolysis methods. The chemically deposited films were deposited as nickel hydroxide phase while all sprayed NiOx films have cubic structure. Sprayed and CBD-NiO films have different optical transmittance and band gap.

2.2 Synthesis of oxide thin films using LB technique:

Zou Gang et al 2002 [16]: By using Langmuir–Blodgett (LB) films, ultrathin Y_2O_3-stabilized ZrO_2 (YSZ) films have been prepared. Metal complexes were incorporated into Arachidic Acid to form multilayers. The films are single phase with fluorite cubic structure. It was also observed that the annealing temperature affects the grain size and morphology of the film.

Vijay V. Kondalkar et al 2015 [17]: In this paper thermal decomposition method was used to convert the multilayer LB film of octadecylamine-tungsten complex into pebbles like nanocrystalline WO_3 thin films. In Li^+ charge-balancing ion, the electrochromic performance was observed. Also the WO_3 thin film composed of closely and uniformly packed nanoparticle array shows high crystallinity with nanosized interstitial voids and shows good coloration efficiency, fast switching kinetics and have the potential for the fabrication of EC practical device.

Sumit Sharma et al 2015 [18]: Monolayers of NiOx on Si substrate were deposited using Langmuir-Blodgett technique. Samples were annealed at various temperatures in vacuum for 30 minutes each. Sheet resistance was measured and was found to be the function of annealing temperature.

2.3 Motivation:

In last few years, sputtering, spray-pyrolysis and sol-gel techniques have emerged as some of the main methods for the synthesis of NiOx thin films. All these methods are either expensive or do not allow for the precise control of the film thickness and hence the film properties. In these methods an adequate surface morphology with a large surface area is required.

Langmuir-Blodgett technique allows for the consolidation and transfer of films onto the substrates with monolayer precision and control. This can lead to precise control of film thickness as well as the porosity and hence the final properties of the films.

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CHAPTER-3

LANGMUIR BLODGETT TECHNIQUE

3.1.Introduction:

Langmuir Film: The 2-D arrangement with crystalline structure of molecules at the air-water interface is known as Langmuir film.

Langmuir-Blodgett Film: A Langmuir-Blodgett film is a set of monolayers with the thickness of one molecule deposited on a solid substrate. The LB film can consist of a monolayer or multilayers.

The LB technique is one of the techniques for preparing organized molecular assemblies. We can dream about the 'Molecular electronics' because of the LB technique. In Molecular electronics, organic molecules play an important role in the transmission and storage of data **[1]**.

In LB technique, a single layer of molecules is arranged on a liquid surface and then transferred onto a solid substrate to prepare a thin film. By repeating this same process number of times, multilayers can be prepared. When the layer of molecules is on the liquid surface, it is named as **Langmuir monolayer** and when transferred onto the solid substrate, it is named as **Langmuir–Blodgett film**.

3.2.What makes LB films appealing?

The deposition of the thin films is done by various techniques. Some of them are: sol gel, spin coating, sputtering, electro-deposition, absorption from solution etc. The LB technique is very good technique to form high quality thin films as it allows:

i. The accurate control on the thickness of monolayer.
ii. The homogeneous deposition of the monolayer on large areas.
iii. The control on the internal layer structure.
iv. To prepare multilayers with different layer composition **[2].**
v. To change the nature, deposition pressure and other parameters of the thin films.

The other appealing feature of the LB technique is that for depositing the monolayers of nanometer scale any kind of substrate can be used.

3.3. Basic concepts of Langmuir Blodgett Films:

Monolayer: A single layer of atoms, molecules or cells is termed as the Monolayer whereas a **Langmuir monolayer** is a layer of insoluble organic materials, which is spread onto an aqueous subphase having thickness of one-molecule. Basically Langmuir monolayers are amphiphilic materials which contain both hydrophobic and hydrophilic parts as shown in figure 3.1.

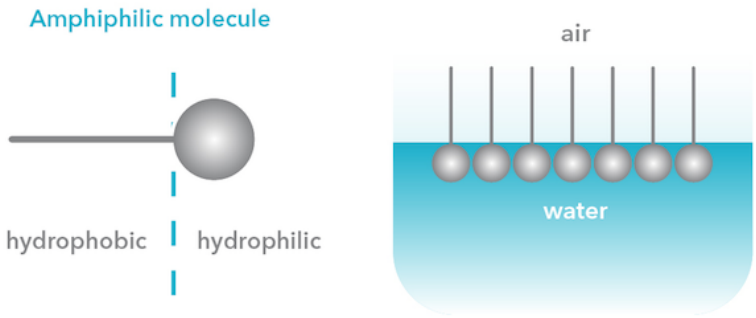

Figure 3.1: A schematic illustration showing the formation of monolayer by amphiphilic molecules [3]

The properties of these films are that they are highly organized and defect free of molecular dimension and these properties of such films mainly depend on the fabrication method. The more conventional method of LB film preparation is to dip the solid substrate vertically through the spread monolayer and this results in well-ordered monolayer on the substrate.

Monolayer Formation: Langmuir monolayer is prepared at the air-water interface with the compression of the barriers. The particles become more stable in this interface because the attractions between the particles result in the accumulation of particles. The LB deposition process is shown in the figure 3.2. In this process the solution is prepared by dissolving low concentration of amphiphilic molecules in volatile solvent such as

chloroform. Then very small (microlitres) amount of dilute solution is spread drop wise on the surface of water. Then the solvent will evaporate leaving a monolayer on air-water interface. Then at the end this compressed and well-arranged monolayer is transferred onto a solid substrate.

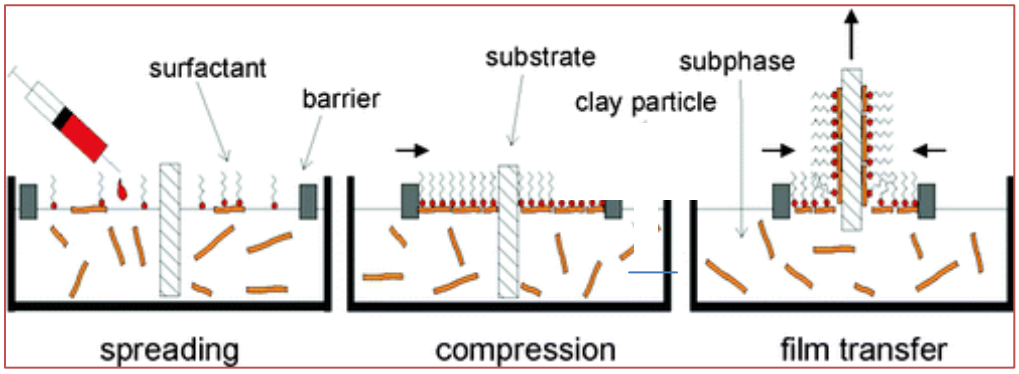

Figure 3.2: Schematic diagram of LB deposition process [4]

Surface Tension: The molecules in the liquid have attraction between each other, which depends upon the properties of the substance. The molecule at the interface as compared to the molecule towards the air will have larger attraction as shown in figure 3.3. The line of force acting on the surface molecule is the surface tension.

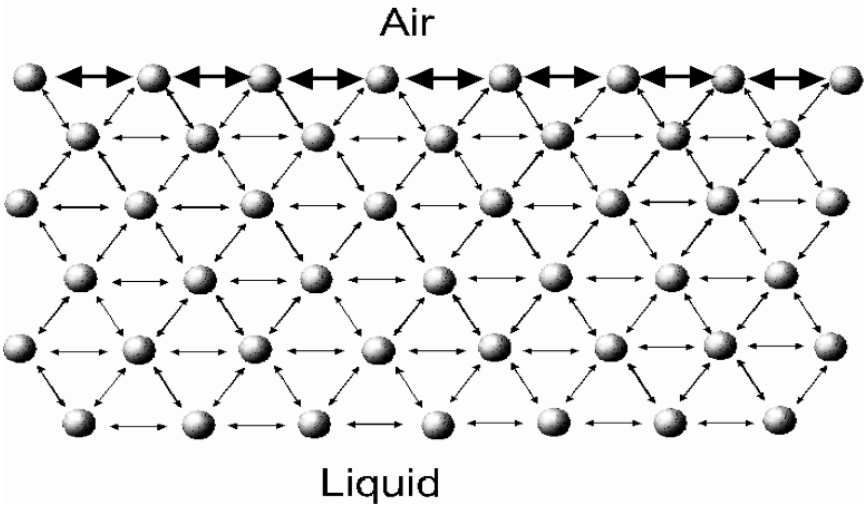

Figure 3.3: Schematic diagram of the molecular interaction at the air and water [5]

The units for the surface tension are dynes/cm or mN/m. Surface tension depends on the following:

(a) **Nature of the liquid**: Water has strong intermolecular interactions because of the presence of electronegative element and hence charge distribution is more and thus more is the interaction between the positive and negative charged dipoles, and thus high surface tension.

(b) **Dependence on temperature.** The surface tension is decreased with the increase in the temperature. Because of the reason that with an increase in the temperature, the interaction of polar molecules decreases due to the change of molecular dipoles, so lesser interaction and less surface tension.

(**c) Surfactants:** These are the molecules, which are amphiphilic in nature. The presence of surfactants will also lower the surface tension because of the reason that amphiphilic nature of surfactant make them to interact with water surface. So forces lying on surface of water are changed and surface tension is decreased.

Surface Pressure-Area Isotherms: We can obtain a lot of information from a surface pressure vs. surface area (π-A) isotherm. It is a graph that is drawn up between the surface pressure of the subphase, which is covered with the monolayer, and surface area per molecule that is spread on the subphase. This recording is performed at constant temperature; hence the name isotherm is given. The surface pressure is measured by the Wilhelmy plate and is determined by

$$\pi = \gamma_0 - \gamma$$

where γ is the surface tension of the monolayer-covered subphase and γ_0 is the surface tension of the pure liquid subphase .This relation implies that the surface pressure is mainly the reduction of the surface tension of the air-water interface by the presence of the monolayer-forming material.

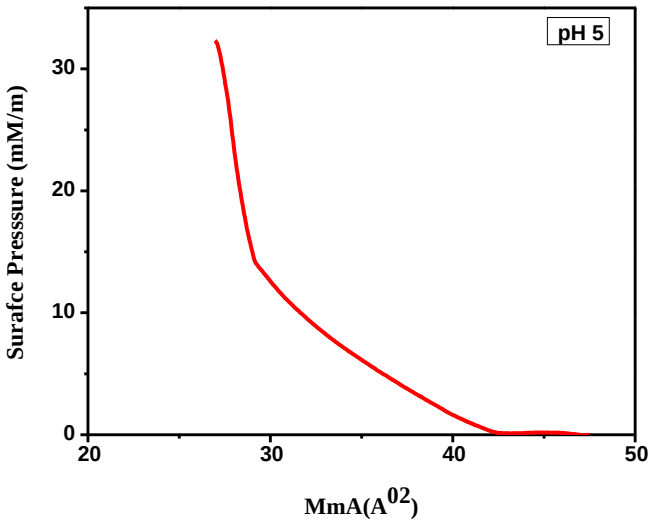

Figure 3.4: Schematic diagram of surface pressure area isotherm

Basically these isotherms gives the first hand information on the monolayer formation, molecular area, monolayer phases, collapse behaviour, compressibility, interaction of species in the subphase with the monolayer, monolayer stability, level of mixing in the mixed monolayers. This topic will be further discussed in the chapter characterization techniques.

3.4. Transfer of monomolecular layer onto solid substrate:

The LB method of deposition of ordered monomolecular films onto solid substrate is based on the transfer of Langmuir monolayers. In this case the Langmuir film formed at the air water interface can be transferred by two methods. These methods are:

1. Langmuir-Blodgett (LB) technique (Vertical Deposition)
2. Langmuir-Schaefer (LS) technique (Horizontal Deposition)

Langmuir-Blodgett Technique:

Langmuir and Blodgett introduce this technique. In this technique monolayer is vertically transferred off the water subphase and onto the solid substrate. The monolayer can be transferred both onto hydrophilic or hydrophobic solid substrate by the upward or downward motion of the substrate respectively.

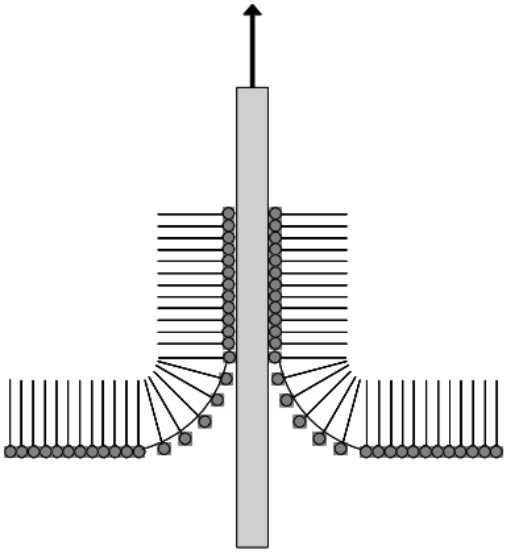

Figure 3.5 (a): Schematic diagram of Langmuir Blodgett Technique [6]

Langmuir-Schaefer Technique:

Langmuir and Schaefer introduce this technique. Using this technique, Langmuir monolayer is horizontally lifted up from air-water interface to air-solid interface by placing the substrate horizontally on the monolayer.

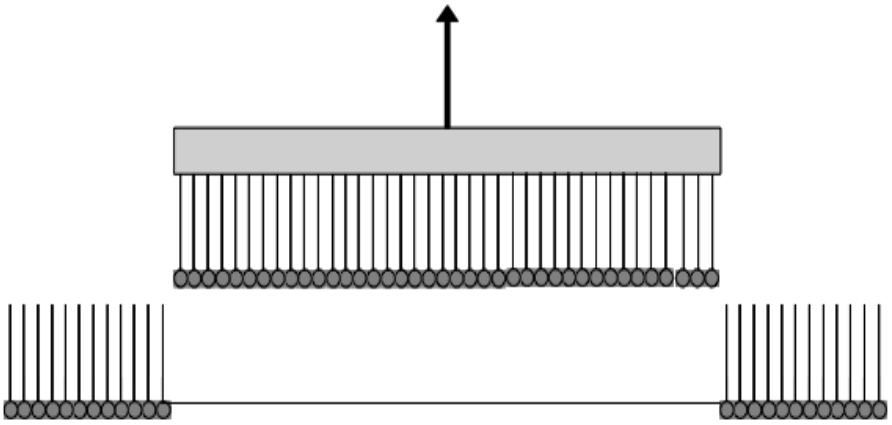

Figure 3.5 (b): Schematic diagram of Langmuir-Schaefer Technique [6]

3.5. Experimental Setup of Langmuir-Blodgett technique:

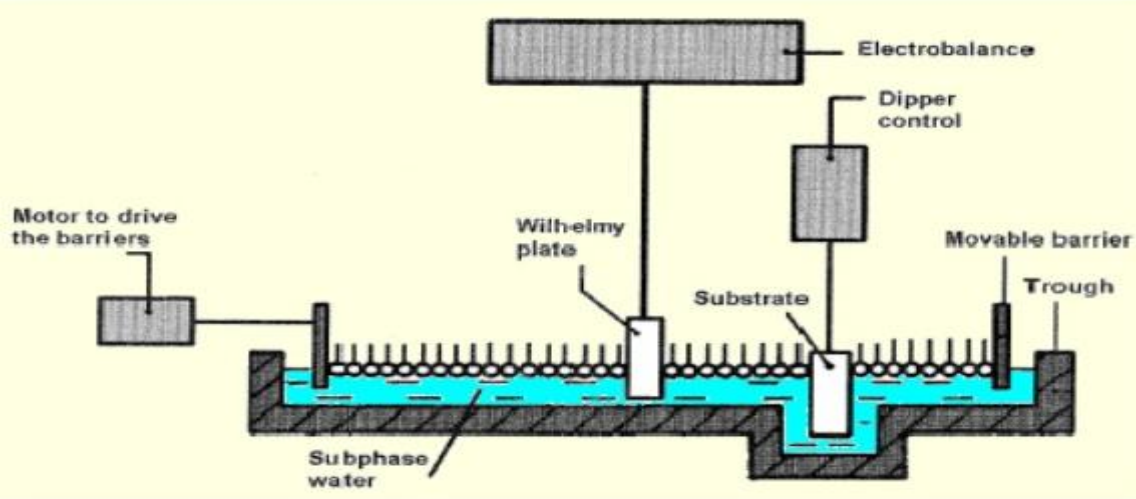

Figure 3.6 (a): Schematic diagram of Langmuir-Blodgett Technique [7]

Figure 3.6 (b): KSV-NIMA, Finland experiment set up of LB Technique

Various parts of the set-up:

1. **Trough:** Trough is made up of Teflon with a dipper well for dipping the substrate. It helps to prepare a monolayer of molecules and then compress these molecules on the surface of a liquid.
2. **Barriers:** Barriers are made up of Teflon and are in contact with the top of the fluid. The barriers are made out of hydrophilic material, which ensures that the film does not escape the barrier. The computer controlled stepper motors maintain the speed of the barriers.
3. **Balance:** The surface pressure is measured by the Wilhelmy plate (38mm×19.62mm×10mm) made up of platinum. Normally the position of the plate is such that one third of it is under the subphase. The force acting on the plate is measured by using the electro-balance.
4. **Dipper:** Holding the substrate into dipper clip vertically does the deposition of the film onto the solid substrate. Movement of the dipper is controlled through the computer controlled stepper motors. The speed of the motors can be controlled precisely.
5. **Bath/Circulator:** The whole set-up is located in a glass cabinet to avoid air and dust deposition and controls the temperature. The temperature is measured using a probe whose one side is dipped in trough and other is connected to interface unit.
6. **Layer Builder:** The Layer Builder interface unit is an interface between the computer and the various connected devices of the LB measurement system. The whole deposition is computerized through this interface unit, which displays barrier position (mm min^{-1}) and surface pressure (mN m^{-1}).

3.6. Modes of Langmuir Blodgett Deposition:

There are three modes of Langmuir-Blodgett Deposition i.e. X type, Y type and Z type mode. Among these three, Y-Type mode is the most common mode for depositing multilayers. In Y-type deposition, films are deposited with both upstroke and down stroke. In X-type deposition, films are deposited with downstroke only. In Z-type deposition, films are deposited with only upstroke. Figure 3.8 shows X, Y and Z modes of deposition of LB multilayers.

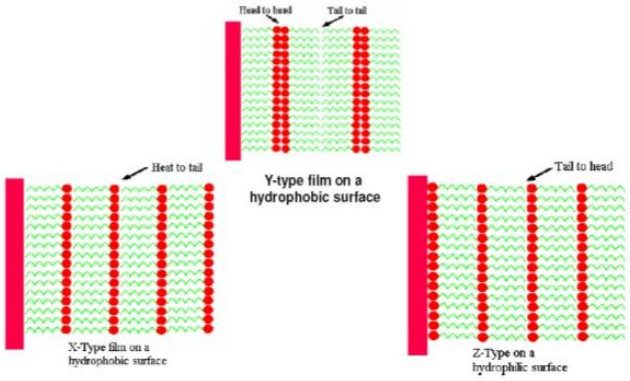

Figure 3.7: X, Y, Z modes of deposition of LB technique [8]

3.7. Transfer Ratio (TR):

Transfer Ratio is the ratio between the decrease in monolayer area (A_L) and area of the substrate (A_S). TR basically gives the information of the quantity and the quality of the monolayer material deposited on the solid substrate. Mathematically, it can be written as:

$$TR = A_L/A_S$$

For ideal transfer the TR is always equal to 1. The TR outside the range of 0.95 to 1.05 suggests poor film homogeneity. By successive up and down strokes of substrate, multilayers of desired thickness can be achieved.

3.8. Parameters affecting LB film:

When the Langmuir film is transferred onto the sample, its density, thickness and homogeneity properties are preserved. The important parameters that effects the deposition and growth of films are:

i. The pH, nature and concentration of the spread film.
ii. The composition and temperature of the subphase.
iii. The surface pressure during the deposition.
iv. The type and nature of the solid substrate.
v. The time for which the solid substrate is stored in air or in the subphase between the deposition cycles.

3.9. Advantages of LB technique:

Langmuir-Blodgett technique has many advantages over the other thin film depositing techniques. By using this technique ultrathin films can be formed. Also by changing compression parameters, the interspacing of molecules can be controlled. Using this technique the molecular orientation of the molecules can be determined. With LB technique, materials can be synthesized almost without any limitations and also with desired functionality.

3.10. Limitations of LB technique:

In LB deposition technique, after depositing each layer drying time is required so the process is slow to fabricate thick films. For the film deposition, substrate should be very smooth. Cleanliness is very important because any contamination can lowers the surface tension. Mechanical and Chemical stability is poor. These films have limited resistivity to high temperatures.

3.11. Applications of LB technique:

The LB films are ultra thin films and possess a high degree of structural order. This technique fabricates functional coatings, supported bilayers of phospholipids, and novel coatings of nanotubes, nanowires and graphene.

Organic and inorganic coatings: The various coatings that respond to changes in their environment can significantly change the surface properties of different materials. Also the Langmuir-Blodgett technique offers the possibility to fabricate and control the monolayer deposition in application areas. Some of them are:

- Smart and nano scale coatings
- Nanoparticles wires and nonlinear optics

Electronic industry: Depending on their composition, conductors, semiconductors and dielectric materials exhibit different properties. Langmuir-Blodgett deposition technique can be used to transfer high-quality molecular layers of different materials in electronic industry. Some examples are:

- Carbon-based nanoparticle applications
- Fuel and solar cells
- Semiconductor devices and material quality

Sensors: In general, sensors require a large surface for sufficient sensitivity and reversibility. For sensor applications, Langmuir-Blodgett deposition technique provides careful control of orientation and surface properties. Sensors based on LB films include applications such as:

- Volatile organic compound sensors
- Biosensors
- Ion sensors

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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 used:

The main chemicals and reagents used in this work are: Nickel (II) Sulfate (NiO_4S, Sigma Aldrich, Anhydrous with 99.99%, M.W. 154.76g/mol), Stearic acid ($C_{17}H_{35}COOH$, Sigma Aldrich, > 98.5%, M.W.284.48g/mol), Chloroform ($CHCl_3$, SDFCL, 99%, M.W.119.38g/mol), Ethanol (C_2H_6O, Loba Chemie Pvt. Ltd, 99.9%), Sodium Hydroxide Pellets (NaOH, Loba Chemie Pvt. Ltd, 98%, M.W. 40g/mol), Sulphuric acid (H_2SO_4, SDFCL, 98%, M.W. 98.07g/mol), Hydrogen Peroxide (H_2O_2, Loba Chemie Pvt. Ltd, M.W. 34.01g/ml). 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. Blue star glass slides cut in size of 2.3 X 2.3 cm were used as substrates.

4.2 Methods:

4.2.1 Cleaning of trough:

Cleaning of trough is very important. We used rubber gloves to minimize oils from the skin contaminating the apparatus. Firstly the trough was cleaned with ethanol using soft brush and then rinsed with deionized water (DI water). The trough was cleaned before and after every experiment. The pH of the water was ~6.0. To check the cleanliness of the trough, the trough was filled with deionized water and the surface pressure was monitored during the compression cycle. During the compression, if the surface pressure value remains below 1mN/m, the trough was considered to be clean and ready for use.

4.2.2. Cleaning of Substrates:

Blue Star glass substrates used for film deposition were cleaned using piranha cleaning method. The glass slides were carefully cleaned and were heated for one hour followed by sonication in DI water for five minutes. Furthermore the glass slides were

ultrasonicated with acetone, ethanol and deionized water for five minutes each. After it these were placed in Milli-Q water and were ready to use.

4.2.3. Preparation of Solution and spreading on Subphase:

Solution of stearic acid was prepared using chloroform. The solution was ultrasonicated for 5 minutes for proper dissolution and then was spread on the aqueous surface by Hamilton micro syringe. Small drops were placed uniformly above the subphase.

4.2.4. Preparation of subphase for isotherms and deposition:

The isotherms for the characterization of the Langmuir films were taken on DI water and Nickel Sulfate solution subphase (0.1mM). The Nickel Sulfate subphase solution was always maintained at 20^0C. The pH of the solution was modified using 0.1 M NaOH solution.

4.2.5. 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) was used as the spreading solution for the formation of Langmuir films. By Hamilton Micro Syringe, the 30 microlitres of the stearic acid solution was spreaded on the water surface. Solvent evaporation time of 15 minutes was given in each experiment before starting the compression process with barriers.

All the isotherms were taken at subphase temperature of 20^0C with barrier speed 7mm/min. The deposition of the LB films was done at 20mN/m. The films were allowed to stabilize for 10 minutes before deposition. For the deposition the dipping speed was maintained at 5mm/min for both up and down with a wait of 2 minutes for drying at the top. Transfer ratio close to 1.0 was maintained for all depositions to confirm complete transform of monolayers to substrate.

4.2.6 Drying and stepped heating protocol:

The films formed were dried in vacuum for 30 minutes using vacuum desiccators. The dried films were heated at 120^0C for one hour for removal of any absorbed water molecules.

After that step heating was done in furnace with rate of 5^0/min.

STEP 1:

Heat till 380^0C for removal and decomposition of stearic acid. This was followed by:

STEP 2:

Sample Name	Temperature	Time
NO1	450℃	4 hrs
NO2	450℃	7 hrs
NO3	600℃	4hrs

4.3. Characterization Techniques:

The techniques used for the characterization are Surface Pressure Area Isotherms, X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), Ultraviolet–visible spectroscopy (UV-VIS), and Fourier Transform Infrared (FT-IR) Spectroscopy. These are discussed as:

4.3.1. Surface Pressure(π) - Area (A) Isotherm:

The most basic characterization of Langmuir monolayer is the measurement of the surface pressure versus area isotherms. The Surface Pressure (π) –Area (A) isotherms are taken on Mini Trough. Generally an isotherm is taken by reducing the area with the barriers at a constant rate while continuously monitoring the surface pressure.

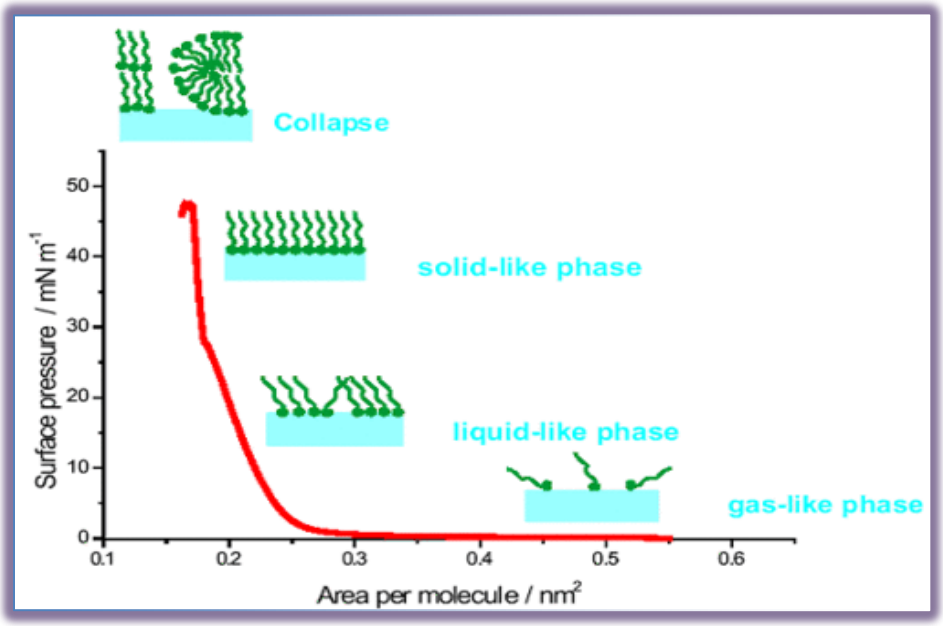


Figure 4.1. Surface Pressure-Area Isotherm[2]

When we examine the isotherm, different regions are formed which are known as phases. The various phase transitions occurring in the monolayer can be visualized through the given isotherm. The phase behaviour of the monolayer is mainly determined by:

1. The physical and chemical properties of the amphiphilic head.
2. The temperature and the composition of the subphase.

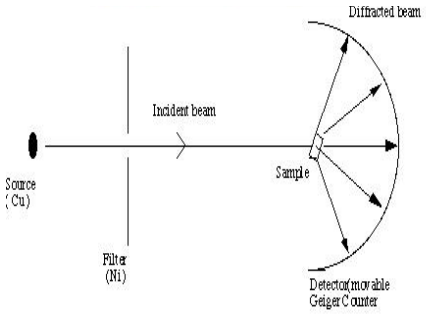
4.3.2. X-Ray Diffraction (XRD):

The XRD patterns were used for the study of structural and phase present of the crystalline materials in the bulk form. The intensity of diffraction peaks in the XRD pattern were recorded as a function of diffraction angle 2θ and indexed with different crystal systems. By using the Bragg's equation, we can calculate the values of interplanar spacing:

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

where n is the order of the reflection, λ is the wavelength of X-ray source and θ is the Bragg's angle for diffraction.

For the XRD studies we have used Philips XPERT- PRO MPD X-Ray Spectrometer.



(a)

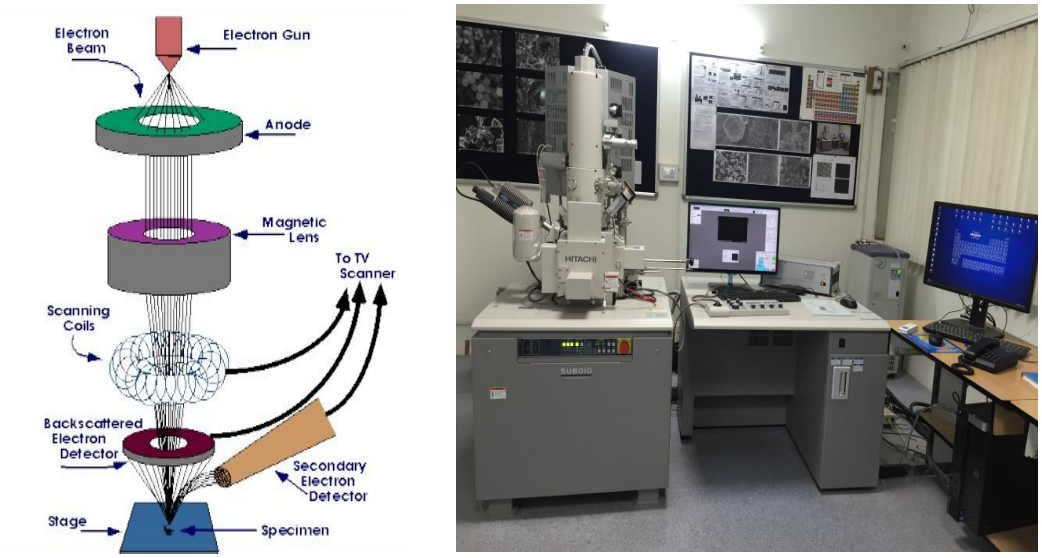
(b)

Figure 4.2: (a) Schematic diagram of X-ray diffraction [3] (b) Laboratory view of X-ray diffraction spectrometer

4.3.3. Field Emission Scanning Electron Microscopy (FESEM):

FESEM is a microscope, which uses electrons instead of light. These electrons are ejected by field emission source. Unlike the standard electron microscope, in FESEM no heating but a cold source is used for the ejection of electrons. Also Energy-dispersive spectroscopy (EDS) is done for elemental analysis of the film surface.

We have used HITACHI SU8010 Field Emission Scanning Electron Microscope for FESEM studies.



(a) **(b)**

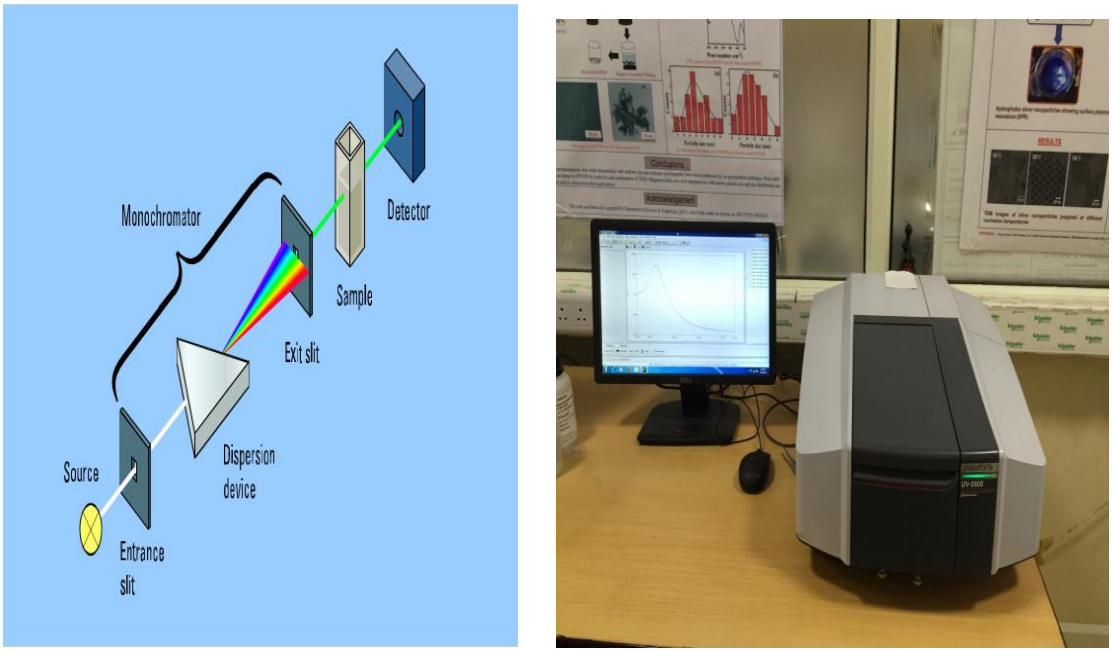
Figure 4.3: (a) Schematic diagram for FESEM [4] (b) Laboratory view of FESEM

It is basically used to observe small structures on the surface of cells and materials. FESEM has the more intensive and monochromatic electronic beam. That is why its resolution is better, than SEM.

4. 3.4. Ultraviolet–visible spectroscopy (UV-Vis):

The UV absorption spectrometry is one of the oldest techniques for the determination of micro and semi-micro quantities in a sample like band gap determination in semiconductors and nanomaterials, detection of impurities, functional groups etc. When the light passes through the sample then transmittance is measured and from transmittance absorbance can be calculated.

We have used SHIMADZU UV-2600 for UV-Vis studies.



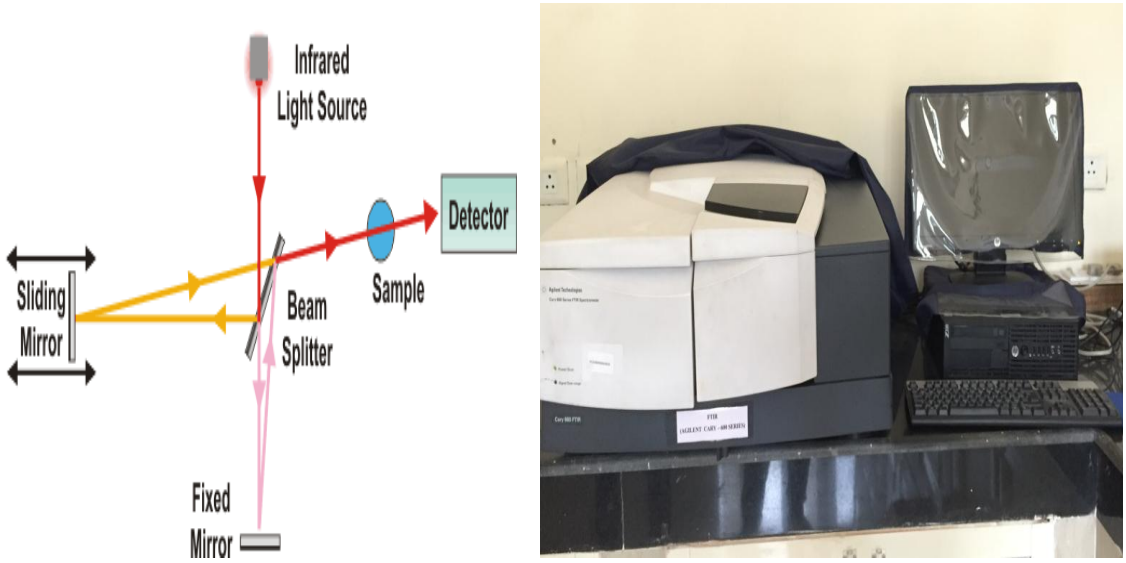
(a) **(b)**

Figure 4.4: (a)Schematic diagram of UV-Vis spectroscopy[5] (b) Laboratory view of UV-Vis Spectroscope

In our work the band gap and the dielectric characterization of the prepared samples were studied using UV Vis absorption spectroscopy. 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) **[6,7].**

4.3.5. Fourier Transform Infrared (FT-IR) Spectroscopy:

FTIR is an important characterization technique for determining the functional group and molecular structure. It can be applied for the analysis of solids, liquids and gases. The FTIR spectroscopy is a fingerprint of chemical structure of the material. It gives clear evidence of the bonding system in the material. Molecular bonds vibrate at different frequencies depending on the elements and the type of bonds. For a given bond, there are several vibrational frequencies corresponding to the ground state and several excited states. For the FTIR studies, Agilent Technologies Cary 660 FTIR was used for our work.



(a) **(b)**

Figure 4.5: (a) Schematic diagram of FT-IR [8] (b) Laboratory view of FT-IR

FTIR is used for some quantitative analysis because of strength of the absorption properties of the materials in this frequency range. The functional groups in the materials show their characteristic absorption peaks when frequency of IR radiation is equal to the natural frequency of molecular vibration. Thus an absorption peak in IR spectrum indicates the existence of functional group in the sample. FTIR is perhaps the most powerful tool for identifying types of chemical bonds. The infrared absorption spectrum is used to determine the chemical bonds. It is a non-destructive and time saving method to detect range of functional groups.

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CHAPTER 5

RESULTS AND DISCUSSION

Overview

In this chapter we present and discuss the various results that we have obtained in the current work. The results regarding surface pressure-area isotherms (π-A isotherms), XRD, FE-SEM, UV Vis, EDX, FTIR are discussed.

5.1. Surface Pressure (π) –Area (A) Isotherms:

Figure 5.1 shows the π-A isotherms for stearic acid on DI water and Nickel Sulfate solution subphase at different pH values. For all the isotherms the π-A isotherms shows three distinct regions: gas, liquid and solid. The transition pressure π_t between the liquid and the solid phase for DI water subphase is 12.7mN/m and the MmA in solid phase is 27.41 A^{02}. These results are in good agreement with the literature **[1]** and confirmed the purity and hence suitability of the procured Stearic Acid for further experiments. For the Nickel Sulfate subphase experiments the transition pressure between liquid and solid phase varies with the pH of the subphase. The data obtained is given in table 5.1.

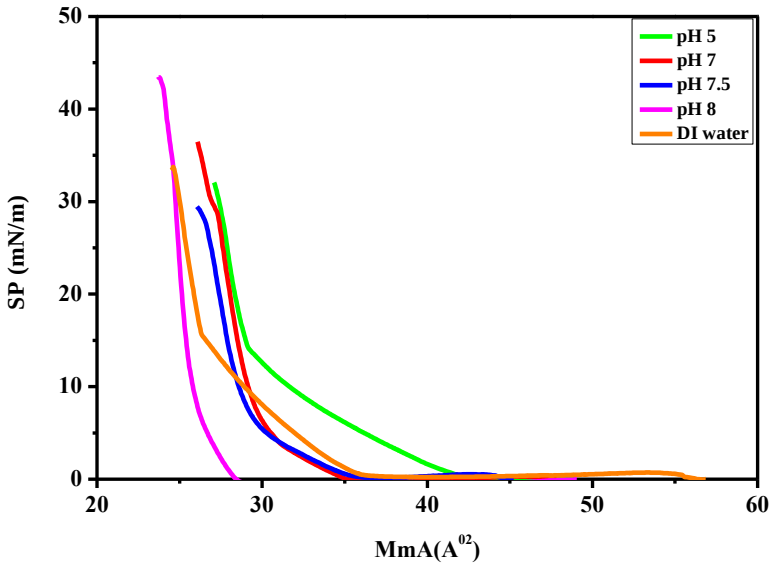


Figure 5.1: Surface Pressure area isotherms at different pH

Table 5.1: Mean molecular area and transition surface pressure from solid to liquid

pH	MmA for solid phase	Π_t liquid to solid phase
5	29.9	11.1
7	29.6	5.6
7.5	29.4	6.1
8	25.8	8.8
DI Water	27.41	12.7

For the Langmuir films formed on the nickel sulfate solution sub-phase the MmA becoming progressively less as the pH increases. This confirms the incorporation of Ni^{2+} ions in the film, which increases with increasing pH. So, all the films on the NiS solution subphase are mixture of stearic acid and nickel stearate (NS) with the stearate component increasing with increasing pH. The transition from liquid to solid phase also occurs for the Nickel sulfate solution subphase for a surface pressure, which is less as compared to that for DI water subphase. This indicates that the intermolecular forces are getting enhanced on the introduction of nickel ions in the film. We have used pH 8 for the dipping experiments since it has the maximum incorporation of Ni ions as indicated by the least mean molecular area. (Table 5.1)

5.2. Dipping:

Figure 5.2 shows the transfer ratios for the first 8 cycles for the deposition of the NS films on glass substrate. The image clearly shows that the NS deposits with Y-Type configuration.

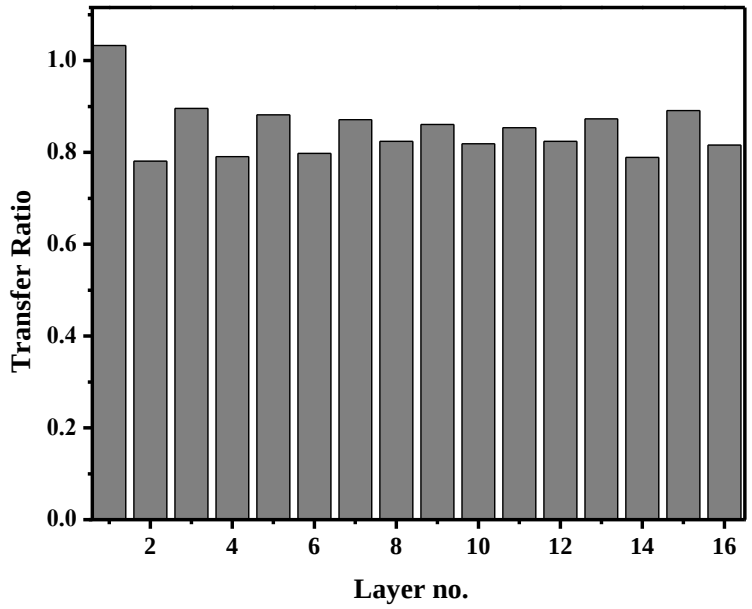


Figure 5.2: Transfer ratio for the deposition of NS films on glass substrate

The proposed structure of the transferred NS films is given in the Figure 5.3.

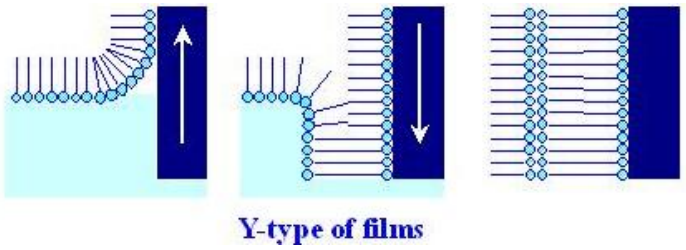


Figure 5.3: Proposed structure of the transferred NS films [3].

5.3 Fourier Transform Infrared Spectroscopy (FTIR):

The bonds present in the film are studied using the FTIR measurements in the transmission mode in the range 500-4500cm^{-1}. Figure 5.9 gives the normalized infrared spectra obtained for 20 layers of NiSt and NO3. The NiSt data shows the presence of the FTIR peaks for Stearic Acid at 2352cm^{-1}, 2845cm^{-1} and 2923cm^{-1} which are absent for NO3 sample. The peaks in the region from 500-760 cm^{-1} are due to Ni-O bond. The

variation between the two samples is clearly visible but the difference is very small. This is because even for the NiSt film the Ni-C bonds will be having peaks in the same region.

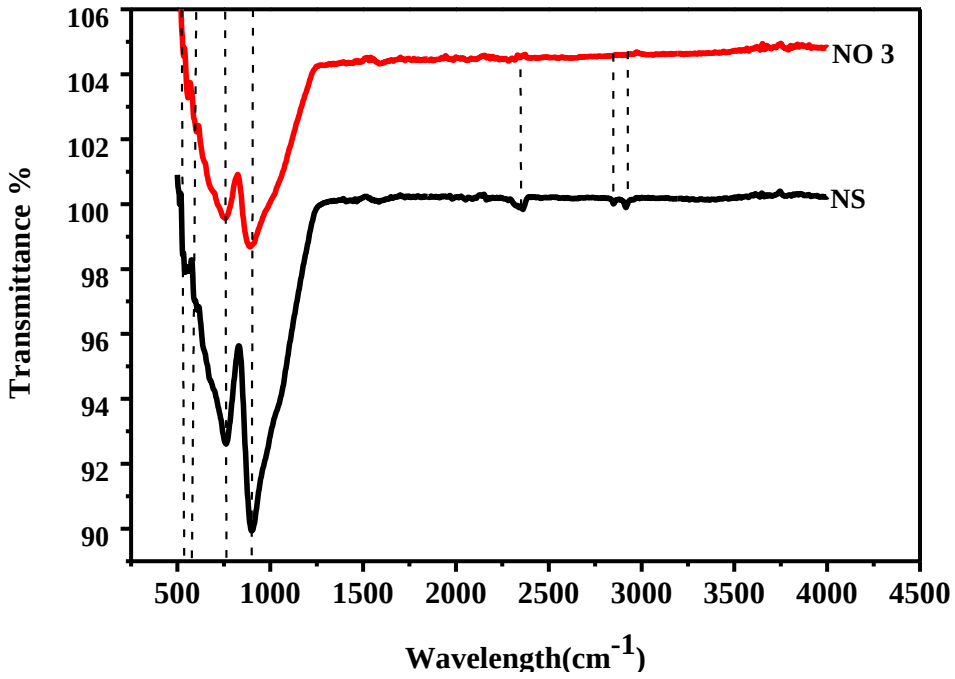


Figure 5.4: FTIR spectra of NO3 and NS.

5.4. X-Ray Diffraction (XRD):

Figure 5.4: shows the XRD diffraction pattern of thin films formed on glass substrate after annealing at different temperatures and times. For sample NO1 no characteristics peak is observed. For both NO2 and NO3 samples the peaks are seen which are getting enhanced for the NO3 sample. These peaks correspond to (101) and (002) planes for hexagonal phase of Ni_2O_3 (ICDD no: 000140481). This shows that the sample formed is Ni_2O_3 rather than NiO.

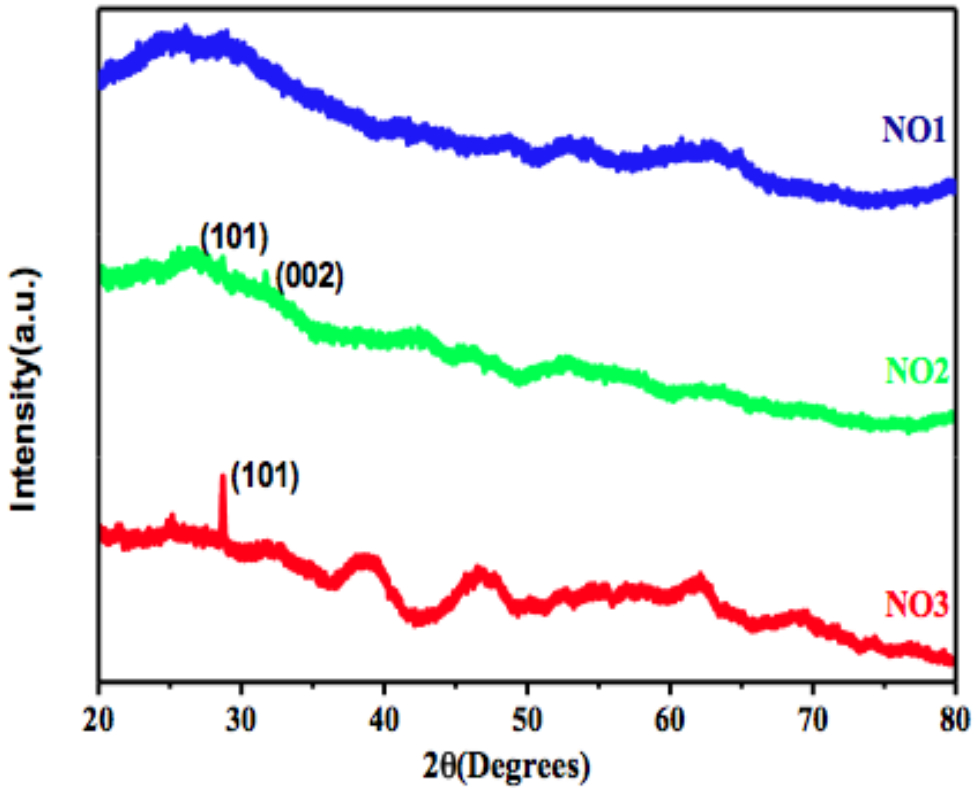
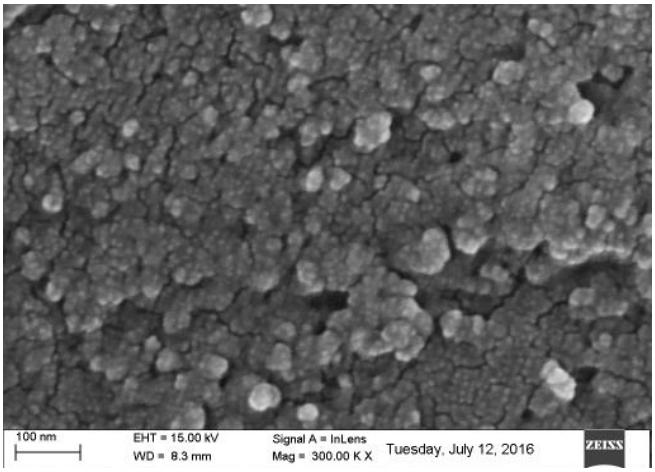


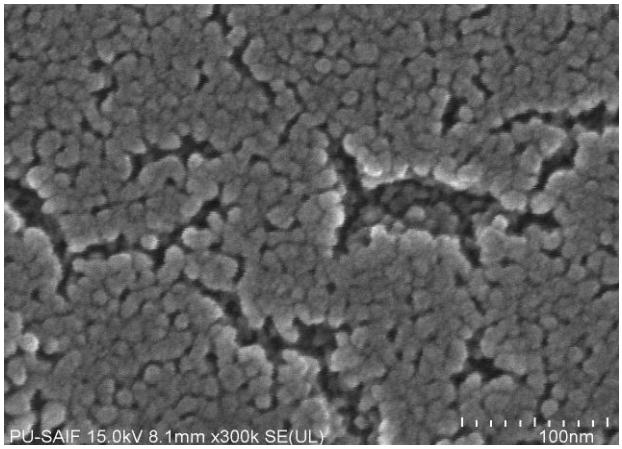
Figure 5.5: XRD pattern of Ni_2O_3 thin films on glass substrate for the NO1, NO2 and NO3.

5.5. Field Emission Scanning Electron Microscopy (FE-SEM):

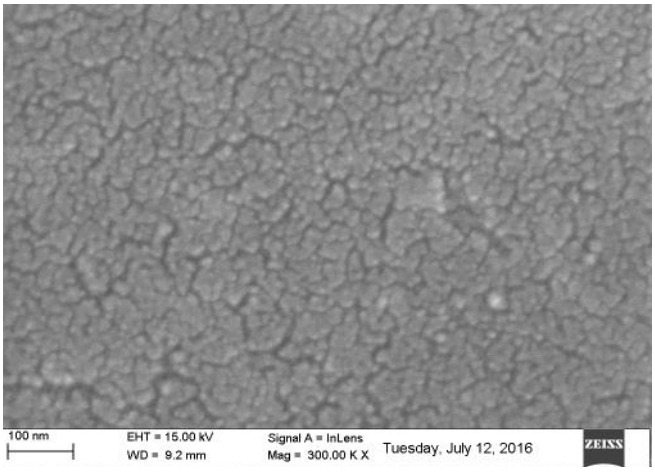
Figure 5.5 (a), 5.5(b), 5.5(c) shows the representative FE-SEM images of the samples NO1, NO2, NO3 respectively. Figure 5.5(d) shows the cross-sectional image of sample NO1. The film thickness is ~ 70nm. The FE-SEM images clearly show that the low temperature film is rougher with wide distribution of grain sizes. The films become denser as the temperature or time is increased. Figure 5.5 (e) shows the grain size distribution obtained from the image analysis of NO2 sample for ~300 grains. The graph shows that the grain sizes for the film follow gauss distribution with mean ~ 12.5 nm.



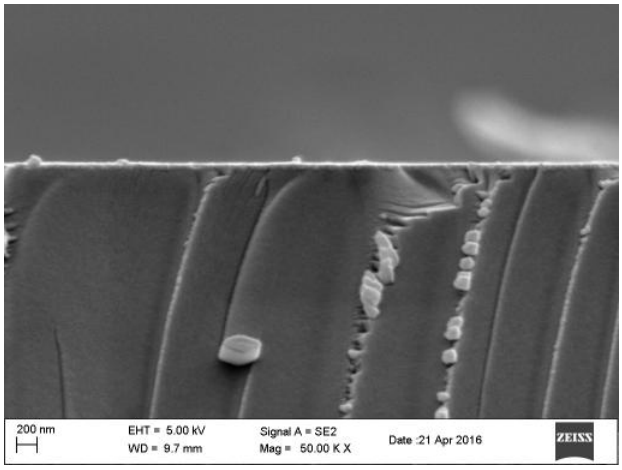
(a) NO1



(b) NO2



(c) NO3



(d) Cross-sectional image of NO1

Figure 5.6: (a), (b), (c) shows the FE-SEM images and (d) shows the cross-sectional image of FE-SEM

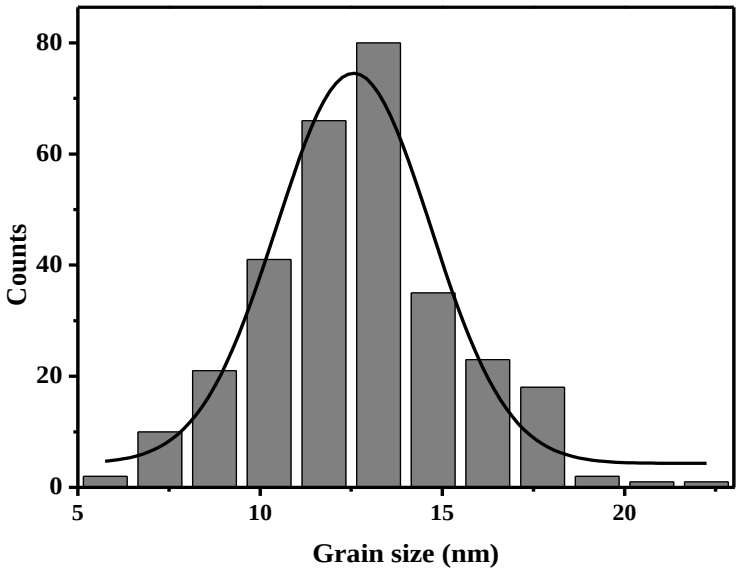
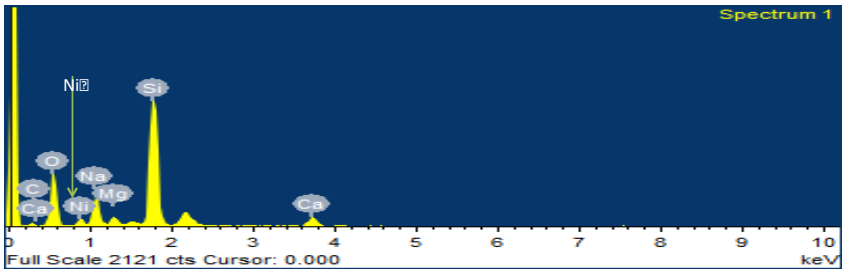


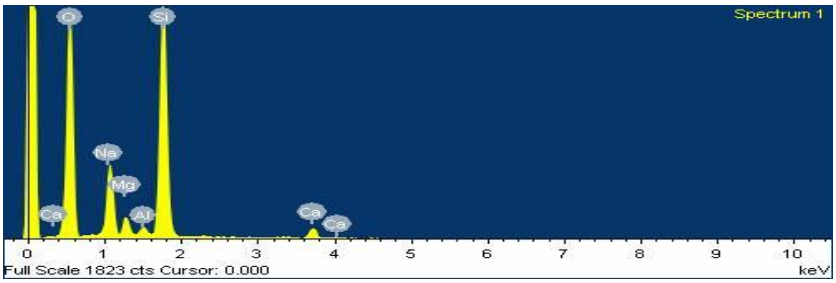
Figure 5.6(e): Grain size distribution for ~300 grains

5.6. Energy-dispersive X-ray spectroscopy (EDS):

Figure 5.6(a) shows the EDS spectra of NO1 sample clearly showing the presence of Ni. The same is absent from the EDS spectra of glass (Figure 5.6(b)).



(a) NO1



(b) Glass slide

Figure 5.7: (a) EDX of NO1 showing Ni and (b) EDX of glass slide

5.7. UV-Visible Spectroscopy (UV-Vis):

Figure 5.7(a) shows the transmittance spectra obtained from the UV-Visible spectroscopy of the deposited nickel oxide thin films. Samples annealed at higher temperature show higher transmittance which indicates that the improved crystalline nature of the film [4]. Figure 5.7 (b), (c), (d) shows the TAUC plot for the values of band gap of NO1, NO2, NO3.

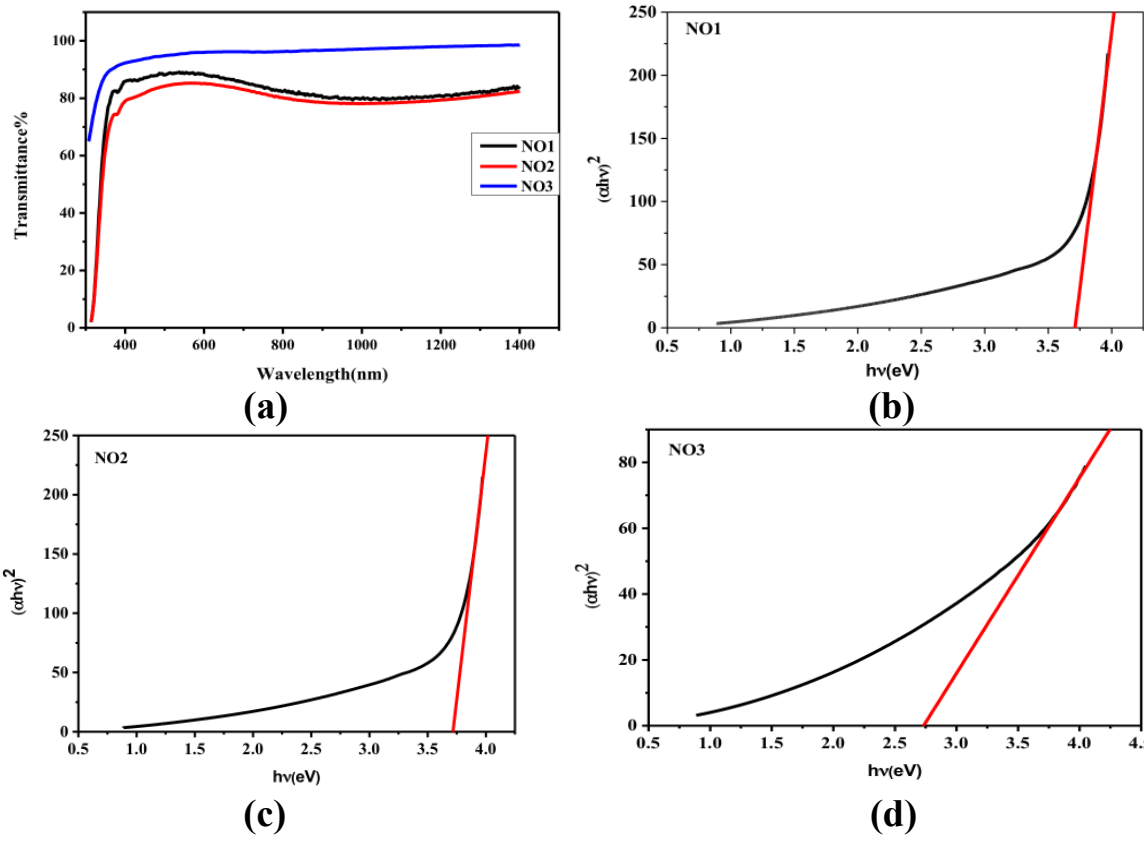


Figure 5.8: (a) The transmittance spectra of NO1, NO2, NO3
(b) TAUC plot for NO1 (c) TAUC plot for NO2 (d) TAUC plot for NO3

Table 5.2: Values of band gap of different samples

SAMPLE	BAND GAP
NO1	3.71
NO2	3.72
NO3	2.73

To determine the bandgap of the deposited films we have plotted $(\alpha h\nu)^2$ as a function of incident light energy. Table (5.2) shows the data obtained from the plots. XRD shows the formation of hexagonal Ni_2O_3. We believe that for NO3 sample, which has been synthesized at higher temperature, the decrease in bandgap is either due to removal of Ni^{2+} ions or due to the increase in the grain size.

5.8. Dielectric Studies:

Figure 5.8 shows the dielectric studies for NO1, NO2 and NO3. The real part of the dielectric constant ($\mathcal{E}_r'$) is enhanced at lower wavelengths for all the samples. Sample NO3 shows the smallest value of dielectric constant. A close analysis of the complete data shows that as the grain growth increases the value of transmittance increases and thus decreasing the value of dielectric constant.

For NO3 sample, we are getting the smallest values of $\mathcal{E}_r$'which shows that the conductivity of material is increased and thus polarization is decreased. This is also confirmed by FE-SEM and XRD data, which confirms grain growth.

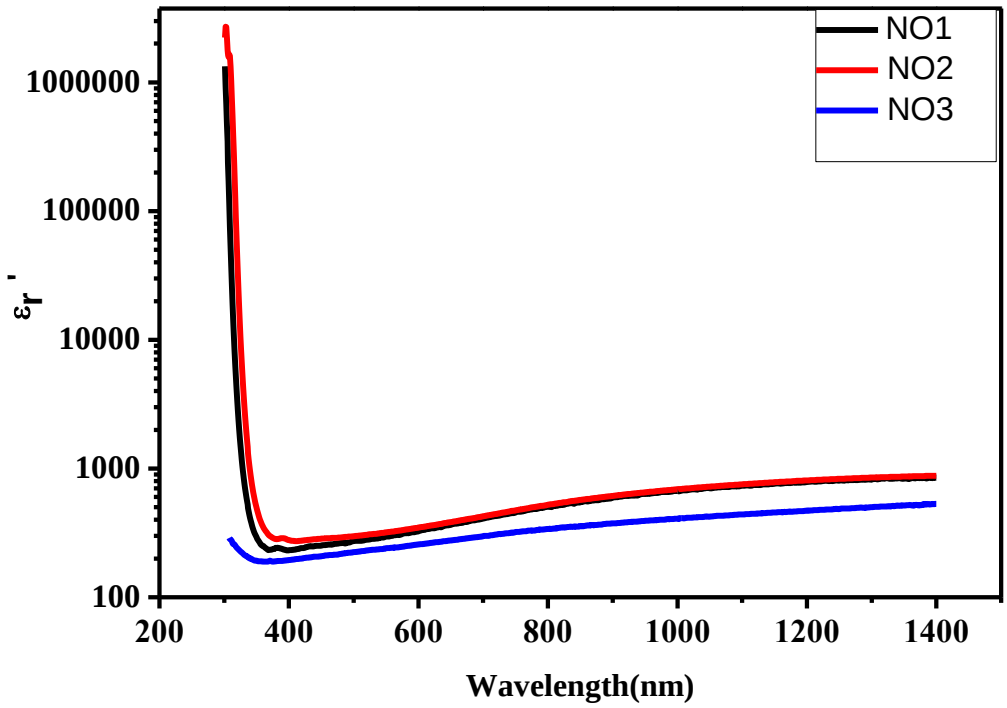


Figure 5.9: Variation of $\mathcal{E}_r$'with wavelength as obtained from the UV –Vis data for NO1, NO2, NO3.

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CHAPTER 6

CONCLUSIONS AND FUTURE SCOPE

6.1 Conclusions:

Nickel oxide is an important material in regard with its applications such as: electrochromic coatings, adhesive agents for enamels, in smart windows as counter electrode, as a catalyst for O_2 evaluation. Ni_2O_3 form of nickel oxide is not as well studied as the NiO. Ni_2O_3 has important applications as buffer layer for organic photovoltaics and as auto emission catalyst. We present here a novel method for the synthesis of transparent hexagonal Ni_2O_3 thin films using LB technique. The synthesis route involves the deposition of 200 layers of dense Nickel Stearate Langmuir layers followed by their decomposition and oxidation via stepped heating protocol. The characterization of the synthesized films shows that the Ni_2O_3 phase is enhanced at higher temperature with denser films and larger grain size. Increased grain size results in increased transmittance properties and reduced dielectric constant. The high temperature film shows greatly reduced bandgap of 2.7 eV. FTIR is used to confirm the complete removal of carbonaceous content, which may lead to defects and decrease the quality of the films.

6.2 Future Scope:

Ni_2O_3 is one of the least studied compounds of Nickel and oxygen where as it is gaining popularity as catalyst for auto emission. Ni_2O_3 has important applications as buffer layer for organic photovoltaics and as auto emission catalyst. So this work has a good scope for further studies. The as synthesized films need to be characterized for surface roughness and magnetic susceptibility. The reduction in bandgap for more crystalline sample needs to be further studied to understand the underlying phenomenon. For LB films the inclusion of Ni ions depends on pH so the porosity of the final film as a function of pH needs to be looked into. The conductivity as the function of grain growth and the annealing temperature also need to be calculated.