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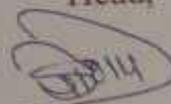
Smt. Kasturbai Walchand College, Sangli

Department of Physics

Class: - M.Sc.-II (2021-22)

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1	I	1) Musal Swaleha Farooque	18	Deposition of Nickel Cobalt thin film by Chemical route for Supercapacitor application
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2	II	1) Patil Prajkta Deepak	06	Deposition of Iron Oxide thin film by Chemical Bath method for Supercapacitor application
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3	III	1) Patil Rutuja Subhash	07	Synthesis and Characterization of Manganese Oxide thin film for supercapacitor application
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**“CHEMICAL SYNTHESIS AND
CHARACTERIZATION OF IRON OXIDE THIN FILM BY
CHEMICAL BATH DEPOSITION METHOD”**

A PROJECT SUBMITTED TO

SHIVAJI UNIVERSITY, KOLHAPUR

FOR THE DEGREE OF

MASTER OF SCIENCE

IN

PHYSICS

UNDER THE FACULTY OF SCIENCE BY

Miss. Maithili dattatray parekar

UNDER THE GUIDANCE OF

Miss. P. A. Desai

For the Year-2020-2021

CERTIFICATE

This is to certify that the project entitled **CHEMICAL SYNTHESIS AND CHARACTERIZATION OF IRON OXIDE THIN FILM BY CHEMICAL BATH DEPOSITION METHOD** which is being submitted herewith for the Degree MASTER OF SCIENCE IN PHYSICS of SHIVAJI UNIVERSITY, KOLHAPUR is the result of the original project work completed by **Miss. Maithili dattatray parekar** under my supervision and guidance. And to the best of my knowledge and belief the embodied in this project has not formed earlier the basis for the award of any Degree or similar title of this or other University or examining body.

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I hereby declare that the Project entitled“**CHEMICAL SYNTHESIS AND CHARACTERIZATION OF IRON OXIDE THIN FILM BY CHEMICAL BATH DEPOSITION METHOD**” completed and written by me has not formed earlier the basis for the award of any degree or similar title of this or any other University or Examining body.

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This is to certify that the project entitled "**CHEMICAL SYNTHESIS AND CHARACTERIZATION OF IRON OXIDE THIN FILM BY CHEMICAL BATH DEPOSITION METHOD**" being submitted here with for the award of the Degree of Master of Science in Physics under the faculty of Science SHIVAJI UNIVERSITY , Kolhapur. It is the result of the original research work completed by **Miss. Maithili dattatray parekar** under my supervision and guidance and to the best of my knowledge and belief the work embodied in this project has not formed earlier the basis for the award of any degree or similar title of this or any other university or examining body.

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CHAPTER - 1

Introduction and Theoretical Background

1.1 Introduction -

Iron oxides are chemical compounds composed of iron and oxygen. Iron oxides and oxyhydroxides are widespread in nature and play an important role in many geological and biological processes. They are used as iron ores, pigments, catalysts, and in thermite, and occur in hemoglobin. Iron oxides are inexpensive and durable pigments in paints, coatings and colored concretes. Colors commonly available are in the "earthy" end of the yellow/orange/red/brown/black range. When used as a food coloring, it has E number E172. i.e. Chemical methods such as chemical bath deposition method (CBD), successive ionic layer adsorption and reaction method (SILAR), electrodeposition etc. are simple, economic and convenient for the deposition of large area metallic oxide thin films. These are low temperature methods and hence avoid oxidation and corrosion of the substrates. The preparative parameters such as concentration, pH, nature of the complexing agent, temperature etc. are easily controllable.

In CBD, the film formation on substrate takes place when ionic product exceeds solubility product.]. chemical solution deposition (CSD), is a method to deposit thin films and nanomaterials, first described in 1869. It can be employed for large-area batch processing or continuous deposition. In 1933 Bruckman deposited lead(II) sulfide (PbS) thin film by chemical bath deposition, or solution growth method. This technique is extensively used to deposit buffer layers in thin film photovoltaic.

The major advantage of CBD is that it requires in its simplest form only solution containers and substrate mounting devices. One of the drawbacks of this method is the wastage of the solution after every deposition. Chemical bath deposition yields stable, adherent, uniform, and hard films with good reproducibility by a relatively simple process. The growth of thin films strongly depends on growth conditions, such as duration of deposition, composition, and temperature of the solution, and topographical and chemical nature of the substrate. Of all the thin film deposition methods, chemical bath deposition (CBD) is the simplest one that offers great scope for large area fabrication. This technique has been extensively used for the preparation of Fe_2O_3 thin films because of its application as a window layer material in Super capacitor Application.[3]

1.2 Literature Survey of Iron Oxide (Fe₂O₃) Thin Film -

Synthesis of iron oxide (Fe₂O₃) thin films on glass substrates was carried out by chemical bath deposition technique, with a view to investigate the effects of variation of temperature on the optical properties of the films. Structural characterization of the films obtained by X-ray diffraction (XRD), revealed that they were γ -Fe₂O₃. The optical property study revealed that the as deposited films had a transmittance of about 75–90% in the VIS-NIR regions of electromagnetic spectrum, but this was slightly reduced to a range of about 70–83% in the same regions when treated with heat. Their band-gap was found to be 2.38 eV for the unannealed, while it ranged from 2.55–2.68 eV for the annealed films. A variation in other optical properties – refractive index, extinction coefficient etc , was observed with heat treatment of the films, though not sequential. Their optical properties and band gaps make the films good materials for wide range of applications. [1].

Generally, Iron oxide exists in various crystallographic forms such as, FeO (wustite), α -Fe₂O₃ (Hematite), η -Fe₂O₃ (Maghemite) and Fe₃O₄ (Magnetite), based upon the atomic arrangements of Fe³⁺ and O²⁻ ions. Among various crystallographic forms, hematite (α -Fe₂O₃) is one of the most stable hexagonal corundum like structure [44,45]. In α -Fe₂O₃, the O²⁻ ions lie along (0 0 1) plane of a hexagonal closed-packed lattice, whereas the cation Fe³⁺ occupies two-thirds of the octahedral interstices in (0 0 1) basal planes. This cationic arrangement forms a pair of FeO₆ octahedrons with edges shared by three neighbouring octahedrons in the same plane. The α -Fe₂O₃ has been proved as a potential candidate for multifunctional applications such as, photoelec. Fe₂O₃ thin film can be deposited by Diffraints method .like Reflux ,CBD ,Silar ,hydrothermal method

The chemical bath deposition method is one of the cheapest method used to deposit thin films and prepare nanomaterial and is employed for large area batch processing or continuous deposition . Chemical deposition techniques are relatively low cost process and can be easily scaled up for industrial applications . Most of the chemical bath consists of one or more metal salts , source for the chalcogenide X (X = S Se Te) and typically a complexing agent.

1.2.1 Properties of Iron Oxide-

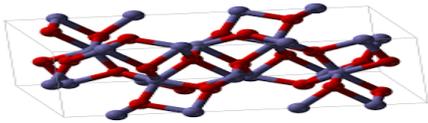
Iron oxide	
Iron oxide	
Structure (Rhombohedral)	
Names	
IUPAC names	Iron(II)iron(III) oxide oxo(oxoferriooxy)iron
Properties	
Chemical formula	Fe ₂ O ₃
Molar mass	159.687
Appearance	Red brown solid
Odour	distinct odour
Density	5.25 g/cm ³
Solubility in water	Insoluble
Band gap	1.95-2.35eV

Table -1 Properties of Fe₂O₃

Application of Iron Oxide- Applications of iron oxide nanoparticles include terabit magnetic storage devices, catalysis, sensors, superparamagnetic relaxometry, high-sensitivity biomolecular magnetic resonance imaging, magnetic particle imaging, magnetic fluid hyperthermia, separation of biomolecules, and targeted drug and gene delivery for medical diagnosis and therapeutics. These applications require coating of the nanoparticles by agents such as long-chain fatty acids, alkyl-substituted amines, and diols. They have been used in formulations for supplementation. Iron oxides and oxyhydroxides are widespread in nature and play an important role in many geological and biological processes. They are used as iron ores, pigments, catalysts, and in thermite, and occur in hemoglobin. Iron oxides are inexpensive and durable pigments in paints, coatings and colored concretes.

1.3 Purpose of work -

Thin Films of Fe_2O_3 are applicable in vast range of application. Our attempt is to prepare the Fe_2O_3 nanoparticles by Hydrothermal synomethod which is very inexpensive, simple and convenient deposition method and the thickness and other parameters can be easily controlled by this method .The thin film characterization will be studied by using x-ray diffraction, scanning electron microscopy, UV-Visible spectroscopy and contact angle measurement.

The x-ray diffraction will be used to determination of crystal structure; surface morphology of thin film will be studied by using scanning electron microscopy. The UV-VIS spectroscopy is used to determine band gap of thin film .Contact angle is measured by using Goniometer.

1.4 Plan of work -

The thin film of Fe_2O_3 will be deposited on glass substrate using CBD method. Optimization of deposition parameters to obtain uniform and well adherent Fe_2O_3 thin films. structural properties of well prepared thin films will be studied by using XRD method ,morphological ,optical and electrical properties will be studied by using Scanning electron microscopy and UV VIS spectroscopy respectively.

1.5 References -

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CHAPTER-2

Thin film deposition techniques

2.1 Thin Film: An Introduction

The field of material science and engineering community's ability to conceive the novel materials with extraordinary combination of chemical, physical and mechanical, properties has changed the modern society. There is increasing technological progress. Modern technology requires thin films for different applications. Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behavior of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films.

When we consider a very thin film of some substance, we have a situation in which the two surfaces are so close to each other that they can have a decisive influence on the internal physical properties and processes of the substance, which differ, therefore, in a profound way from those of a bulk material. The decrease in distance between the surfaces and their mutual interaction can result in the rise of completely new phenomena. Here the one dimension of the material is reduced to an order of several atomic layers which creates an intermediate system between macro systems and molecular systems, thus it provides us a method of investigation of the microphysical nature of various processes. Thin films are especially appropriate for applications in microelectronics and integrated optics. However the physical properties of the films like electrical resistivity do not substantially differ from the properties of the bulk material. For a thin film the limit of thickness is considered between tenths of nanometer and several micrometers[1].

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter.

Thin films are formed mostly by deposition, either physical or chemical methods. Thin films, both crystalline and amorphous, have immense importance in the age of high technology. Few of them are: microelectronic devices, magnetic thin films in recording devices, magnetic sensors, gas sensor, A. R. coating, photoconductors, IR detectors, interference filters, solar cells, polarizer's, temperature controller in satellite, superconducting films, anticorrosive and decorative coatings.

Thin films have been used in the study of the relationship between the structure of solid and their physical properties. A thin film is a layer of a material ranging[2] from fraction of a nanometer

to several micrometers in thickness. Thin films have very interesting properties that are quite different from those of the bulk material which they are made of. This is because of the fact that their properties depend on number of interrelated parameters, and also on the technique employed for their fabrication. Practical applications include electrical circuits, optical instruments and magnetic information storage devices. Thickness of thin film is usually discussed in term of Angstrom (\AA).

Thin films are formed by depositing material on a clean supporting substrate to build up film thickness, rather than by thinning down bulk material. An also thin film possesses wide range of applications in both civil as well as military sectors. “When the third dimension of the film that is the thickness on substrate is comparable with the mean free path of the electron in that film, then it is called thin film.” The thin solid films were first obtained by electrolysis in 1838. The conventional bulk material is characterized by three dimensional orders. In which the constructive atoms or molecules find themselves. This order or periodicity is responsible for the structure of the material. In case if thin films, the system possesses at most two dimensional orders or periodicity. The above two applications include their use for protection of material from corrosion, oxidation and wear, increasing transmission or reflection in a certain wavelength region and in filters, color separation, fire-resistance, high temperature superconductors, sectors are also discussed in the monograph. [3]

2.1.1 Properties of Thin Films-

1. Thin films may not be fully dense.
2. Thin films may be under stress.
3. Thin films have different defects structure from bulk.
4. Thin films are quasi two dimensional.
5. Thin films are strongly influenced by surface and interface effects.

2.1.2 Applications of Thin Film-

Depending on different properties, thin films have numerous applications in various fields that are tabulated below

Sr. No	Thin film property	Typical applications
1	Electrical	Solar Cell, Semiconductor devices, piezoelectric devices.
2	Optical	Reflective, Antireflective coatings, Decoration, Waveguides.
3	Chemical	Protect against corrosion and oxidation, Barrier to diffusion or alloying. Gas/Liquid sensors.
4	Mechanical	Coating
5	Magnetic	Memory disc

Table No.2.1- Applications of Thin film depending on its properties

2.2 Thin Film Deposition Methods:

Technological progress of our modern society mainly depends on material science with different extraordinary combination of physical and chemical properties of material. Modern material science study requires thin films for different uses. Thin film can be deposited by various physical and chemical techniques, and can be classified as shown in table. Among these some are explained above.

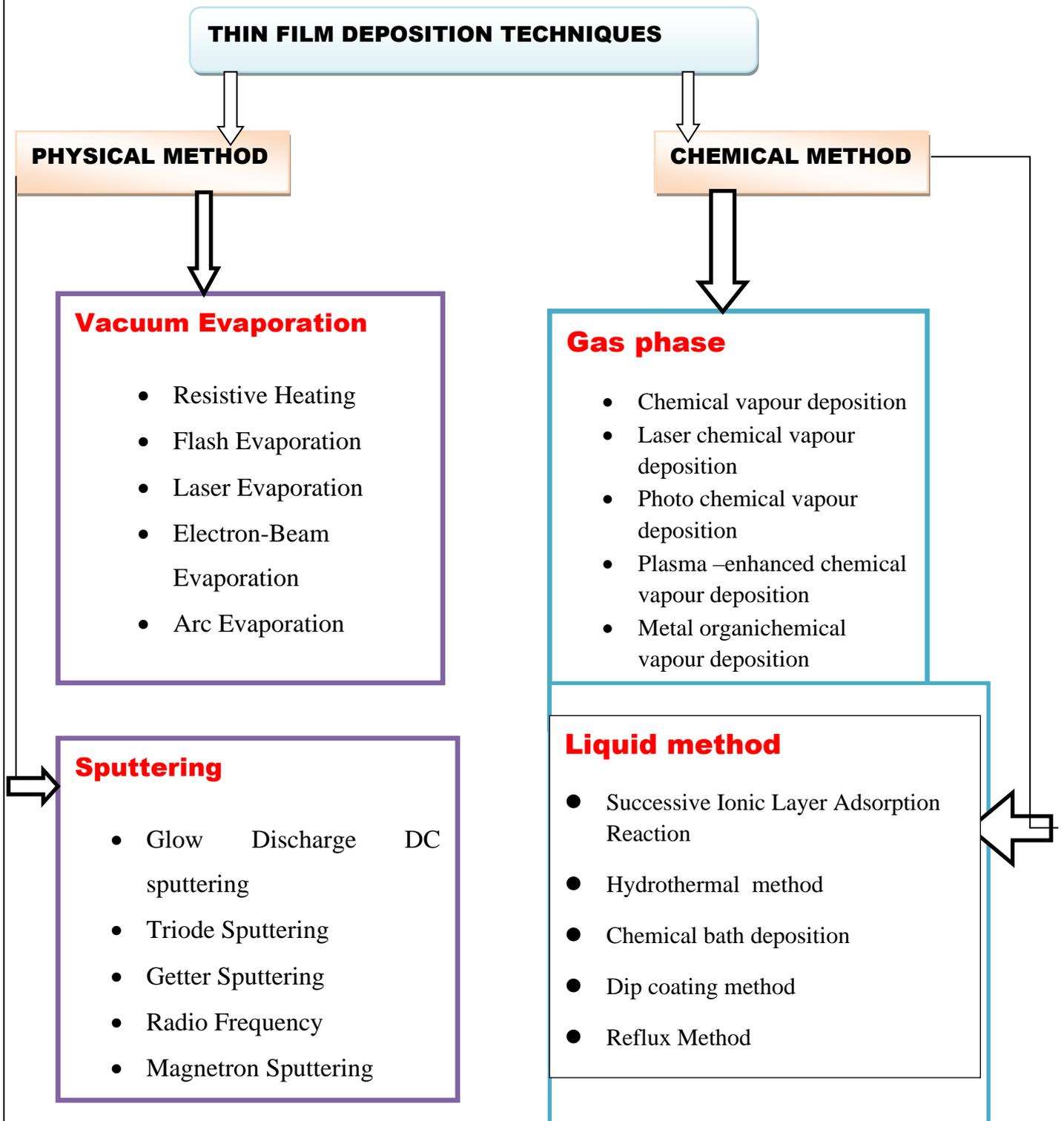


Table No 2-Thin film Deposition method

2.2.1 SILAR Method -

The SILAR method is mainly based on the adsorption and reaction of the ions from the solutions and rinsing between every immersion with distilled water (D. W.) to avoid homogeneous precipitation in the solution.

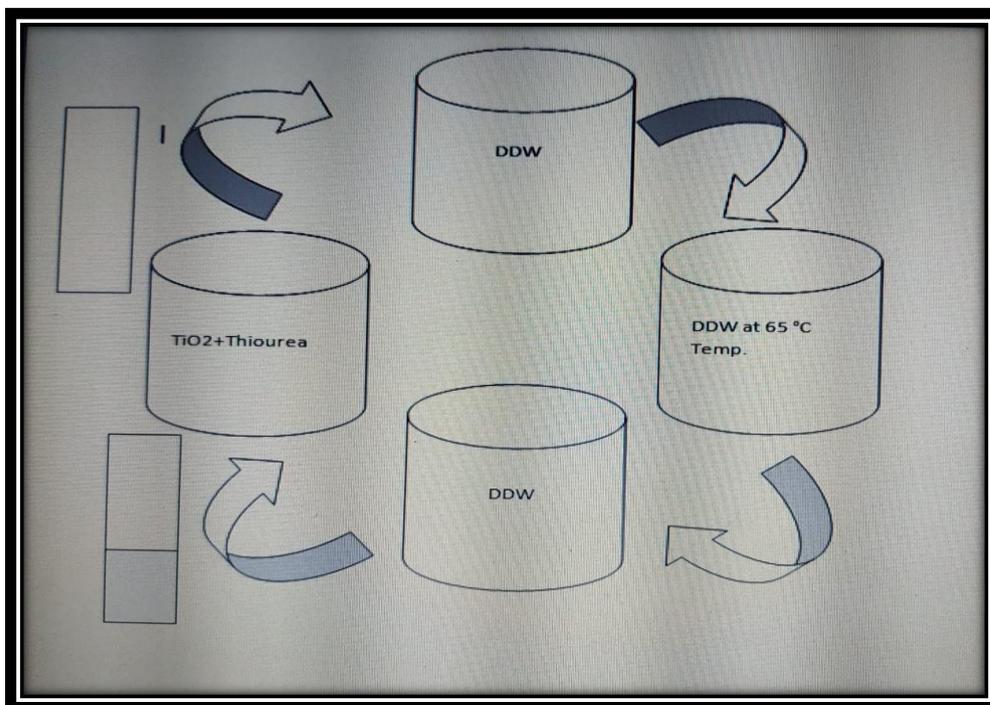


Fig. 2.1 Schematic diagram of SILAR method

Thin films have been obtained by adsorbed cations followed by reacting with anion from appropriate precursor solutions. The term adsorption can be defined as a collection of a substance on the surface of another substance, which is the fundamental building block of the SILAR method. Adsorption may be expected when two heterogeneous phases are brought in contact with each other. Hence, gas-solid, liquid-solid and gas-liquid are three possible adsorption systems. In SILAR method, the first step is mainly concerned with adsorption in a liquid-solid system. Adsorption is an exothermic process. The adsorption is a surface phenomenon between ions and the surface of the substrate and is possible due to attractive forces between ions in the solution and the surface of the substrate. These forces may be cohesive or Van-der Waals' or chemical attractive. Atoms or molecules of their kinds on all sides do not surround atoms or molecules of substrate surface. Therefore, they possess unbalanced or residual force and hold the substrate particles. Thus, adsorbed atoms (ad-atoms) can be holding on the surface of the substrate. In the second step, the adsorbed ion is reacted with anion, resulting in film formation [1].

The SILAR method involves four steps:

- 1) Adsorption
- 2) First rinsing
- 3) Reaction
- 4) Second rinsing.

1) Adsorption

In first step of SILAR method, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: first, the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative form the counter ions of the cations.

2) First rinsing

In this step, loosely adsorbed ions are rinsed away from the diffusion layer. This results into saturated electrical double layer.

3) Reaction

In this reaction step, the anions from anionic precursor solution are introduced to the system. Due to the low stability of ions reaction between cation and anion takes place leading to formation of solid phase over substrate.

4) Second rinsing

In last step of SILAR method, the excess and unreacted species and their reaction byproduct from the diffusion layer are removed. In this way, SILAR method culminated through adsorption of cations and reaction of newly adsorbed anions with preadsorbed cations, which leads to formation of thin film of desired material. The factors like temperature of solution, nature of the substrate, pH and concentration of solution, area of the substrate, dipping and rinsing time etc. affect the deposition process.

2.2. Chemical Bath Deposition Method -

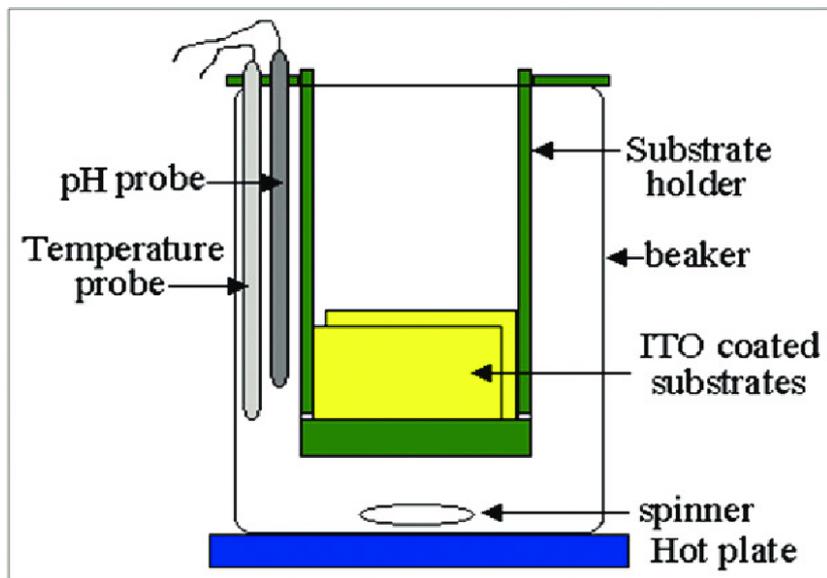


Fig2.2 Chemical Bath Method

Among the chemical methods of thin film depositions, chemical bath deposition (CBD) is probably the simplest method available for this purpose. The only requirements of these methods are a vessel to contain the solution and the substrate on which deposition is to be carried out. In addition to this various a specific and constant temperature are options that may be useful.

The mechanism of CBD method contains following types,

1. Simple ion by ion mechanism.
2. Simple Cluster (hydroxide) mechanism.
3. The complex decomposition ion by ion mechanism.
4. The complex decomposition cluster mechanism

The chemical bath deposition method is one of the cheapest methods used to deposit thin films and prepare nanomaterial and is employed for large area batch processing or continuous deposition. Chemical deposition techniques are relatively low cost processes and can be easily scaled up for industrial applications. Most of the chemical baths consist of one or more metal salts, source for the chalcogenide X (X = S Se Te) and typically a complexing agent.

Preparative Parameter -

1. Nature of Substrate -

The substrate plays major role in reaction kinetics and in the adhesion of deposited film . Hence cleaning of substrate is first important step in the film deposition rate and terminal thickness is obtained . When lattice parameter of substrate and deposited material match well with each other .

2. Temperature of solution -

It is another parameter which influences the rate of reaction the increasing temperature of solution both dissociates complex more efficiently . Therefore kinetic energy of molecules also increases leading to greater interaction ion . This is results in increase or decrease in terminal thickness depending on strength of supersaturation solution .

3. Complex agent -

In CBD method most of deposition is carried out in alkaline solution . Therefore to prevent precipitation of metal hydroxide complexing agent is added . It helps to reduce the concentration of free metal ions in both solutions , which avoids the rapid bulk concentration formation of desired product . The concentration of free metal ions decreases with increase in concentration of complexing agent . Subsequently rate of reduces that leads to larger terminal thickness .

2.2.3 Hydrothermal method -

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". The term "hydrothermal" is of geologic origin.^[1] Geochemists and mineralogists have studied hydrothermal phase equilibria since the beginning of the twentieth century. George W. Morey at the Carnegie Institution and later, Percy W. Bridgman at Harvard University did much of the work to lay the foundations necessary to containment of reactive media in the temperature and pressure range where most of the hydrothermal work is conducted.

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

Advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows if a steel tube is used.^[2] There are autoclaves made out of thick walled glass, which can be used up to 300 °C and 10 bar.

A large number of compounds belonging to practically all classes have been synthesized under hydrothermal conditions: elements, simple and complex oxides, tungstates, molybdates, carbonates, silicates, germanates etc. Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value. Some of the crystals that have been efficiently grown are emeralds, rubies, quartz, alexandrite and others. The method has proved to be extremely efficient both in the search for new compounds with specific physical properties and in the systematic physicochemical investigation of intricate multicomponent systems at elevated temperatures and pressures.^[3]

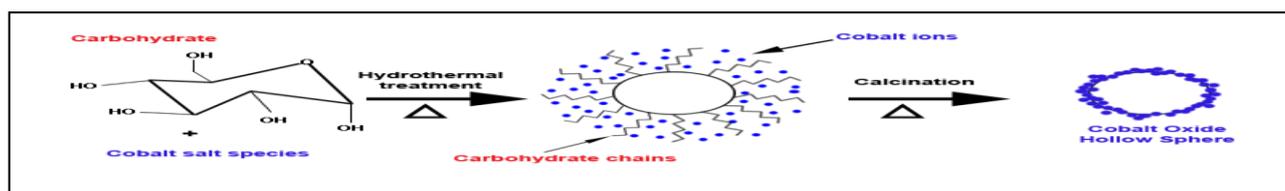


Fig 2.3 Hydrothermal Method

2.2.4 Dip Coating Method -

Dip Coating is with no doubt the easiest and fast method to prepare thin films from chemical solutions with the highest degree of control, making it highly appropriate for small scale production. In specific high technology cases, it is used to deposit coating on large surfaces.

The principle is as simple as dipping the substrate into the initial solution before withdrawing it at a constant speed. During which the solution naturally and homogeneously spreads out on the surface of the substrate by the combined effects of viscous drag and capillary rise. Evaporation then takes over and leads to solidification of the final coating.^[4]

2.3 References -

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CHAPTER-3

Thin Film Characterization Techniques

Characterization Techniques -

Recently nanostructured semiconducting materials are synthesized by different physical and chemical methods. The structural and electronic, optical properties are mainly depends on type of preparation method of thin film. Once the synthesis of an appropriate material is done, the first goal is to perform the characterization of particular material. In order to perform this in systematic way, one needs a diverse array of characterization technique. In this chapter we discussed some important characterization techniques which includes the basic principle of the characterization techniques in brief,

- X-Ray diffraction technique (XRD)
- Scanning electron microscopy (SEM)
- Ultra violet visible spectroscopy (UV-Vis)
- Contact angle measurement

The details of these method discussed in subsequent sections.

3.1 X-ray Diffraction -

X-ray diffraction has been use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a fingerprint or identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and material science.

We can determine the size and the shape of the unit cell for any compound most easily using X-ray diffraction.

Why XRD?

1. Measure the average spacing's between layers or rows of atoms.
2. Determine the orientation of a single crystal or grain.
3. Find the crystal structure of an unknown material.
4. Measure the size, shape and internal stress of small crystalline regions[1].

3.1.1 Bragg's Law -

English Physicists Sir W. H. Bragg and W. L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-rays beam at certain angles of incidence (θ). The variable d is the variable between atomic layer in a crystal and the variable λ is the wavelength of incident X-ray beam; in an integer. This observation is an example of X-ray wave interference.

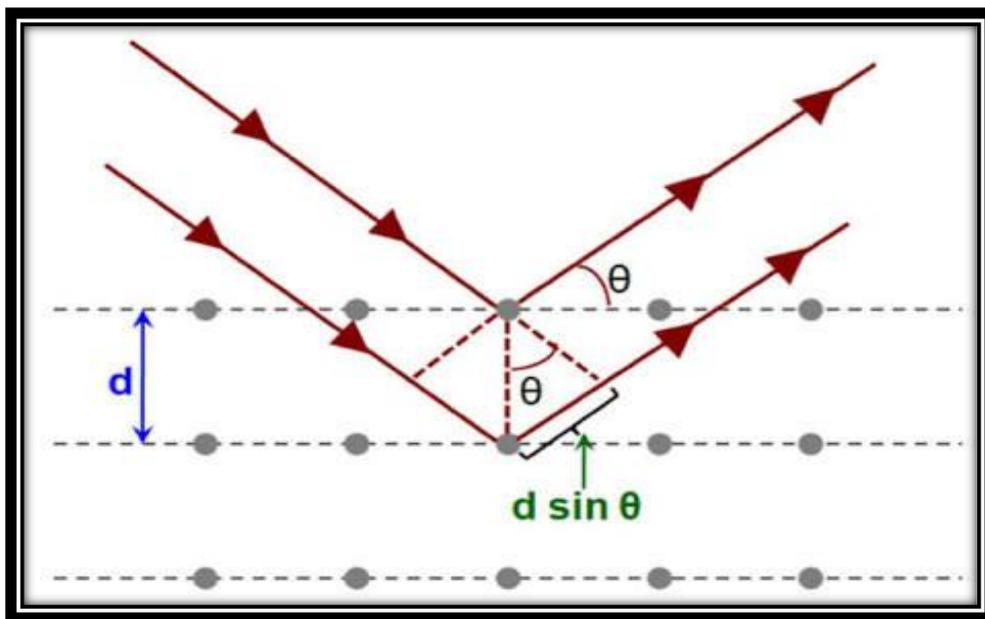


Fig3.1.A:- Reflection of X-rays from two planes of atoms in a solid

$X = d \sin(\theta)$The path difference between two waves

$$n\lambda = 2d \sin(\theta) \dots \dots \dots (1)$$

This is Bragg's Equation

3.1.2 Powder Method or Debye – Scherrer Method:-

When single crystal is not available, a simple technique may be used. The crystalline material is ground to a powder which then presents all possible orientations to a collimated X-rays beam consisting primarily of $K\alpha$ radiation.

The experimental apparatus is schematically drawn in fig.

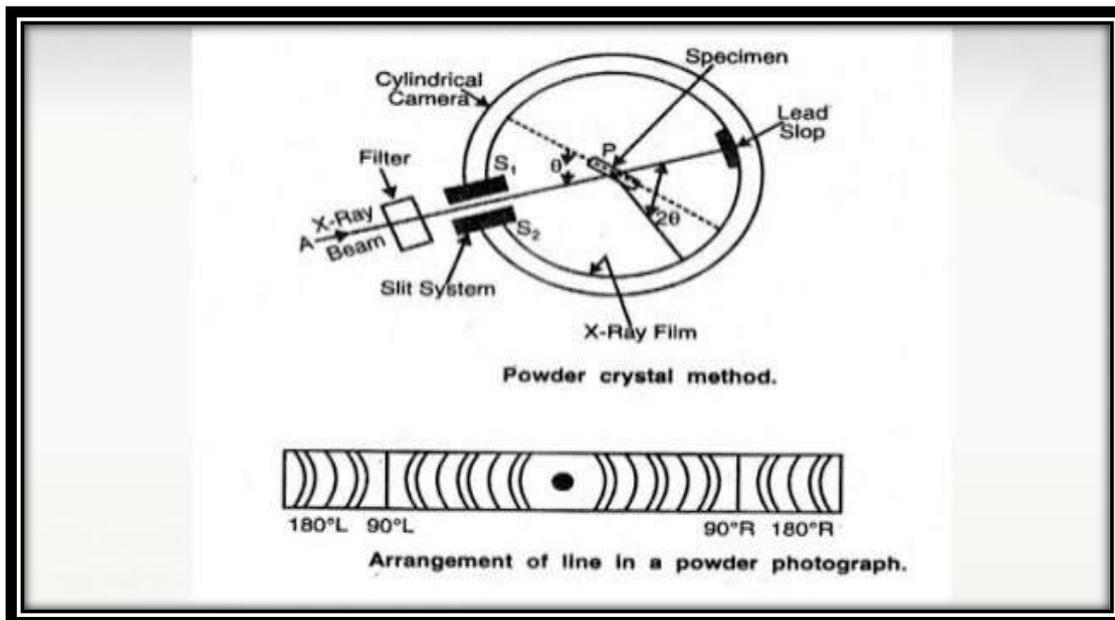


Fig3.1.B - Schematic representation of the X-ray Powder technique

If the crystals used are too coarse, the arcs in the powder pattern will appear specked instead of as firm lines. In this technique the powder may be composed into a rod sample when the tiny crystals have different orientations, and therefore possibility of interference which depends on the ratio of λ , d and Θ greatly increases. Because of this instead of individual spots whole series of spots are obtained on a stretched film these arcs appear as showing fig. The distances between symmetrical lines are designated as l_1, l_2, l_3 etc. And the diameter of the cylindrical film as D_1 the relation[2],

$$\Theta = \frac{90}{\pi D} \times l$$

OR

$$\Theta = K.l$$

Where, K is a constant factor for a particular chamber.

3.2 Scanning Electron Microscopy -

Principle

In technique, an electron beam is focused onto sample surface kept in a vacuum by electro-magnetic lenses (since electron possesses dual nature with properties both particle and wave, hence an electron beam can be focused or condensed like an ordinary light). The beam is rastered and scanned over the surface of the sample. The scattered electrons from the sample are then fed to the detector and then cathode ray through an amplifier, where the images are formed, which give the sample image. The scanning electron microscope (SEM) is used for observation of specimen surface. The scanning electron microscope (SEM) is used for observation of specimen surface.

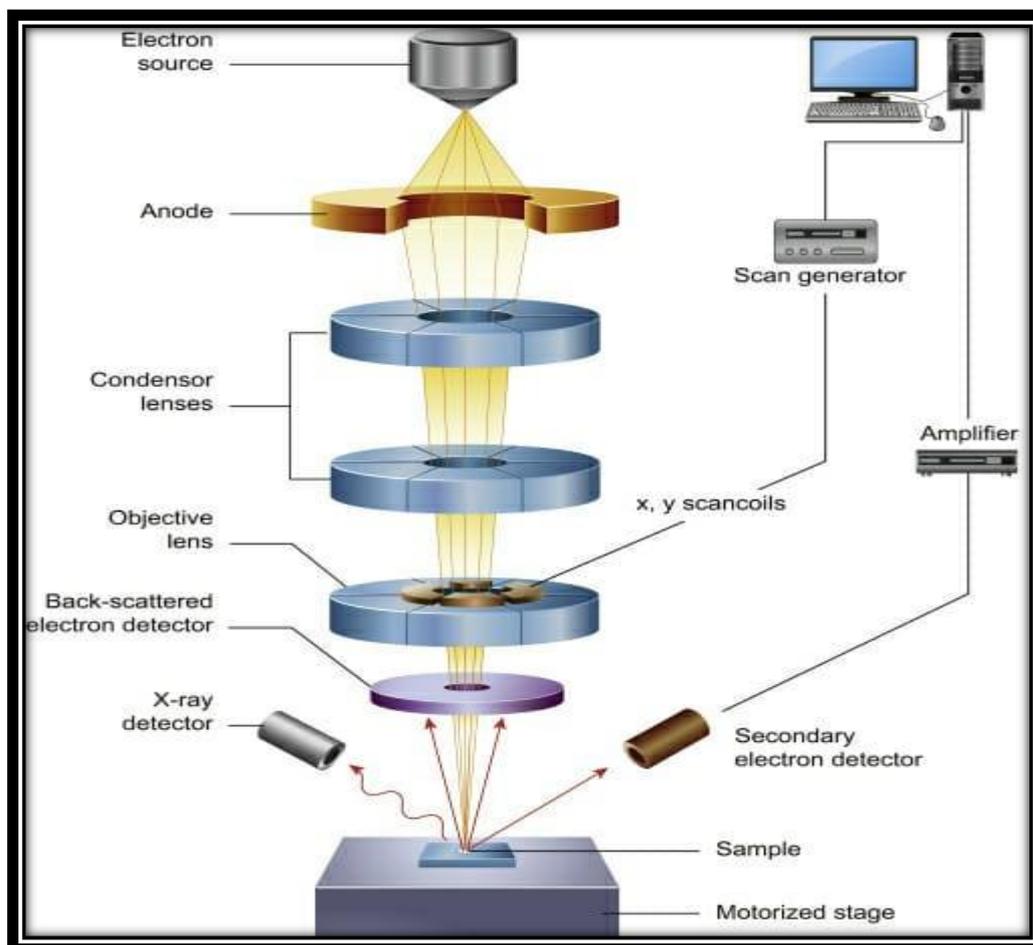


Fig 3.3- Scanning Electron Microscopy

Working of SEM -

1. The Electron Gun-

Thermoelectrons are emitted from a filament (cathode) made of a thin tungsten wire by applying a voltage (1 to 30 Kv) .The electron beam passes through anode.

2. Construction of Lens -

An electron microscope generally uses a magnetic lens. The main feature of the magnetic lens is that when you change the current passing through the coil, the strength of the lens is also changed .This is not achieved by an optical lens[3].

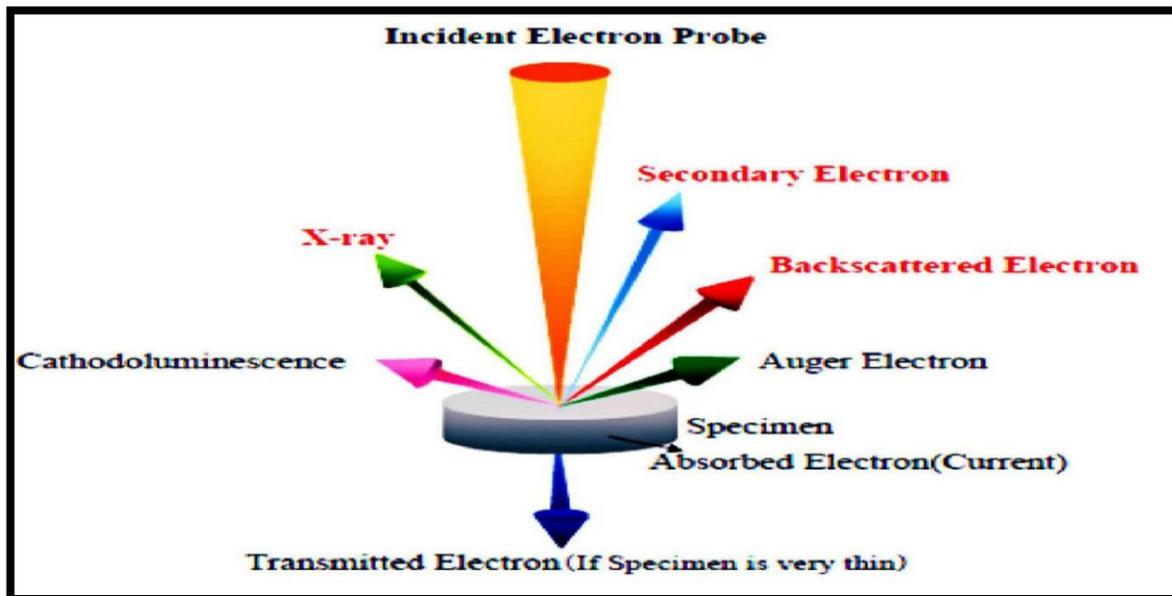


Fig 3.4 - The signals are transferred from point to point and signal map of the scanned area is displayed on a long persistent phosphor

3. Scanning Coil -

Magnification is controlled by current supplied to x,y scanning coils or voltage supplied to x,y deflector plates not by objective lens power.

Scanning coil is set of lenses which are moving the beam with very high precession. The beam passes through pairs of scanning coils deflects beam in x and y axes so that it scans in a raster fashion over rectangular area of the sample surface. As a result of the electron-sample interaction a no. of signals are produced. These signals are then detected by appropriate detectors.

As electrons interact with the sample, they produce secondary electrons, backscattered electrons, Auger electrons, and characteristic X-rays. These signals are collected by appropriate detectors to form image which are then displayed on the computer screen.

Advantages of SEM

1. The detailed three-dimensional and topographical imaging and the versatile information garnered from different detectors.
2. SEMs are also easy to operate with the proper training and advances in computer technology and associated software make operation user-friendly.
3. This instrument works fast, the technological advances in modern SEMs allow for the generation of data in digital form.
4. Although all samples must be prepared before placed in the vacuum chamber, most SEM samples require minimal preparation actions

3.3 UV-Visible Spectroscopy -

Ultraviolet- visible spectroscopy or ultraviolet-visible spectroscopy is the measurement of the attenuation of a beam of light it passes through a sample or after reflection from a sample surface

Principle of Ultraviolet-visible spectroscopy -

Ultraviolet absorption spectra obtained from transition of electron within a molecule from a lower level to a higher level. A molecule absorbs ultraviolet radiation of frequency (ν). Molecules containing π -electrons or non-bonding electrons can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons the longer the wavelength of light it can absorb.

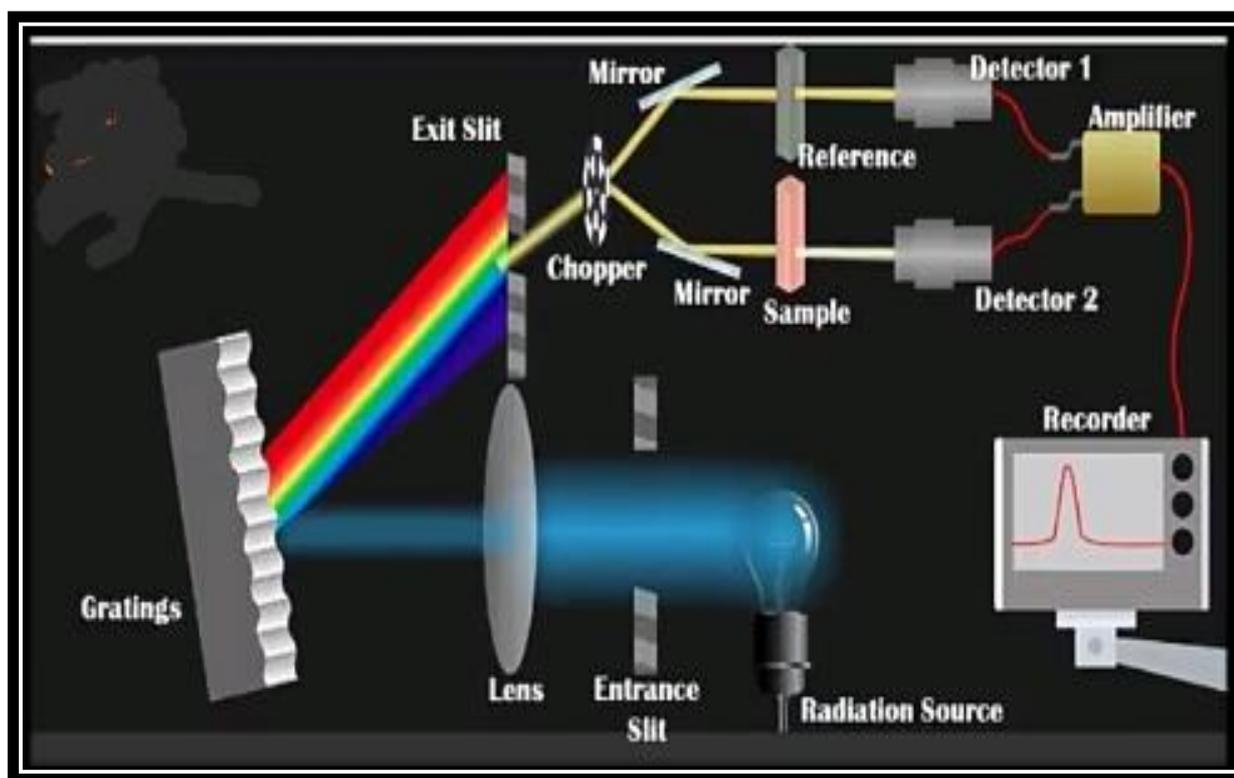


Fig3.5 - UV-Visible spectroscopy

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelength of light, and a detector. The radiation source is often a tungsten filament, a deuterium arc lamp, which is continuous over the ultraviolet region light emitting diodes for the visible wavelength. The detector is typically a photomultiplier tube, photodiode[4].

Single photodiode detectors and photomultiplier tubes are used with scanning monochromatic, which filter the light so that only light of a single wavelength reaches the detector at one time.

The scanning monochromator moves the diffraction grating to “step-through” each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromator are used with charge-coupled device and photodiode arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelength on different pixels or groups of pixels simultaneously.

Ultraviolet-Visible Spectrophotometer -

The instrument used in ultraviolet-visible spectroscopy is called a UV-Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through a sample (I_0). The ratio (I/I_0) is called the transmittance, and is usually expressed as a percentage (%T).

The absorbance ‘A’ is based on the transmittance:

$$A = -\log (\%T / 100\%)$$

The UV-visible spectroscopy can also be configured to measure reflectance. In this case, the spectrophotometer measures the intensity of light reflected from a sample (I), and compares it to the intensity of light reflected from a reference material (I_0). The ratio (I/I_0) is called the reflectance, and is usually expressed as a percentage (% R).

Why we use UV Spectroscopy?

- 1) Detection of band gap.
- 2) Detection of functional groups.
- 3) Detection of impurities
- 4) Qualitative analysis.
- 5) Single compound without chromophore.
- 6) It is help to slow the relationship between different groups, it is useful to detect the conjugation of the compound.

Application UV spectroscopy -

- 1) UV spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds and biological macromolecules, spectroscopy analysis is commonly carried out in solutions but solids and gases may also be studied.
- 2) Solutions of transition metal ions can be colored (i.e. absorb visible light) because electron within the metal atoms can be excited from one electronic state to another.
- 3) Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of electromagnetic spectrum.
- 4) While charge transfer complex also give rise to colors, the colors are often too intense to be used for quantitative measurement[4].

3.4 Contact Angle Measurement -

Principle -

The wettability property of a solid surface is one of the most important aspects in both theoretical research and industrial application. One of the fundamental methods of characterizing the hydrophobic properties of a solid surface is to determine the contact angle. The contact angle on the solid surface gets changed nearly by changing the chemistry of the outermost monolayer. Atoms on the surface have higher energy than those within the bulk, so there is energy associated with the existence of any interface.

Working -

When the specific energy (J/m²) of the solid-vapor interface, γ_{SV} , is greater than that of the solid-liquid interface γ_{SL} , liquid tends to flow over an exposed solid surface. When a small liquid droplet is put in contact with flat solid surface, distinct equilibrium regions may be found like partial wetting, the wetted portion of the surface is determined by certain contact line. A layer of liquid on a plane solid surface has two interfaces, solid-liquid line, A layer of liquid on a plane solid surface has two interfaces, solid-liquid ' γ_{SL} ' and liquid-vapor ' γ_{LV} ' so the change in energy (ΔE) produced by spreading of the liquid film is :

$$\Delta E = \gamma_{SL} + \gamma_{LV} - \gamma_{SV} \quad \dots\dots\dots (1)$$

If $\Delta E < 0$ the energy of the system is reduced so that the liquid will spread spontaneously (i.e. = 0), otherwise the solid-liquid-vapor will be characterized by a finite contact angle. The balance of the tensions at the point of interaction leads to a relationship between the surface tension that is known as Young's equation.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \gamma \quad \dots\dots\dots (2)$$

Hydrophobicity of the thin films was tested in terms of contact angle (γ) of the water droplet with the surface, using the formula.

$$\gamma = 2 \tan^{-1} (2h/b)$$

Where, h is the height

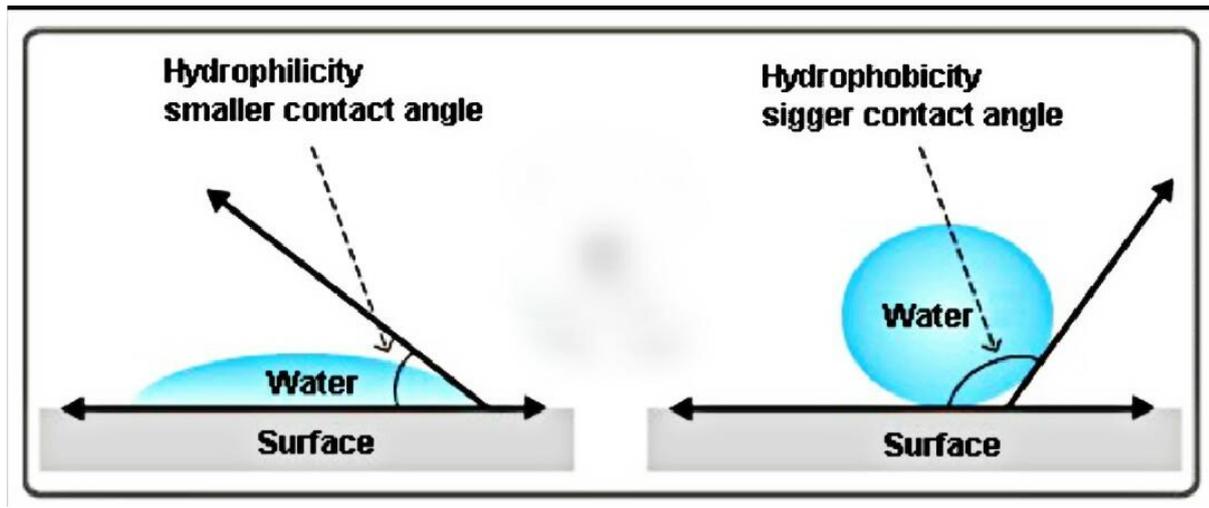


Fig 3.6 Interfacial tensions at the three phase contact line

Direct measurement by telescope-Goniometer -

The most widely used technique of contact angle measurement is a direct measurement of the tangent angle at the three phase contact point on a scale drop profile.



Fig. 3. 4 -Telescope Goniometer setup

Over the years, modification of the equipment have been to improve the accuracy and precision. A camera can be integrated to take photographs of the drop profile so as to measure the contact angle at leisure. The use of relatively high magnification enables a detailed examination of the intersection profile. A motor driven syringe can be used to control the rate of liquid addition and removal to study advancing, receding, or dynamic contact angles[5].

3.5 Fourier transform infrared -



Fig 3.5.A

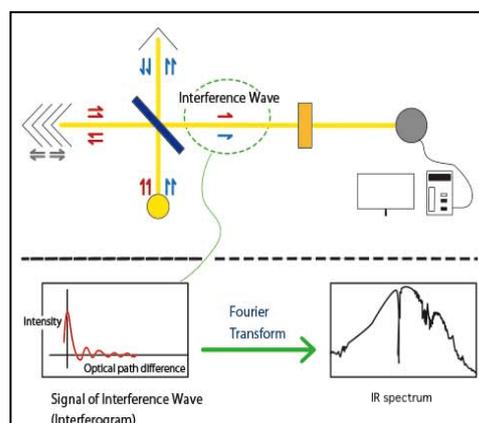


Fig 3.5. B

FTIR stands for Fourier transform infrared, the preferred method of infrared spectroscopy. When IR radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted). The resulting signal at the detector is a spectrum representing a molecular ‘fingerprint’ of the sample. The usefulness of infrared spectroscopy arises because different chemical structures (molecules) produce different spectral fingerprints. The FTIR uses interferometry to record information about a material placed in the IR beam. The Fourier Transform results in spectra that analysts can use to identify or quantify the material.

An FTIR spectrum arises from interferograms being ‘decoded’ into recognizable spectra

- Patterns in spectra help identify the sample, since molecules exhibit specific IR fingerprints

There are four major sampling techniques in FTIR:

- Transmission
- Attenuated Total Reflection (ATR)

- Specular Reflection
- Diffuse Reflectance

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Chaper - 4

SUMMARY AND CONCLUSION

Summary and Conclusion -

In the field of material research one is often confined with problem of material preparation and in order to reduce cost,a relative simply method is needed to able to assess quickly the various physio- chemical properties of material.

Preparation of the material in thin film relatively easy and less expensive as compared to that of growing in a single crystal.There are many method of thin film preparation,such as Electro deposition,spray pyrolysis, and so many high cost physical methods. Out of these methods Hydrothermal method is relatively simple, low cost and can be use for preparation of large area thin film.

In the present work, Iron Oxide film have been deposited using simply CBD method and film are characterized of prepared thin film is carried out using XRD,SEM,Angle of contact and UV-Visible Spectroscopy.

These work carried out is divided into three chapters.

Chapter-1

The general introduction of thin film and general survey of deposited Fe_2O_3 thin film is given. The purpose of project and plan of work is also stated there in this chapter.

Chapter-2

It deals with theoretical background of thin film deposition technique.

Chapter-3

In this chapter different characterization with working and principle were studied. In which XRD study was carried out. SEM micrograph reveals chemical composition of thin film, UV-Visible reveals band gap energy and surface wettability test shows angle of contact.



Latthe Education Society's

Smt. Kasturbai Walchand College,

Sangli

**Synthesis and characterization of Mn doped CuO thin
films for Super capacitor application**

A PROJECT SUBMITTED TO

SHIVAJI UNIVERSITY, KOLHAPUR

FOR THE DEGREE OF

MASTER OF SCIENCE

IN

PHYSICS

UNDER THE FACULTY OF SCIENCE BY

Mr. Kiran Gajanan Gurav

Seat No. [12470]

UNDER THE GUIDANCE OF

Miss. S. A. Gaikwad (M.Sc.)

For the Year. 2020-2021

CERTIFICATE

This is to certify that the project entitled “**Synthesis and characterization of Mn doped CuO thin films for Super capacitor application.**” which is being submitted herewith for the Degree MASTER OF SCIENCE IN PHYSICS of SHIVAJI UNIVERSITY, KOLHAPUR is the result of the original project work completed by **Mr. Kiran Gajanan Gurav** under my supervision and guidance. And to the best of my knowledge and belief the embodied in this project has not formed earlier the basis for the award of any Degree or similar title of this or other University or examining body.

Place: SANGLI

Project Guide

Date:

Miss. S. A. Gaikwad (M.Sc.)

Department of Physics,

Smt. KWC, Sangli.

Examiner

Dr. M. M.TONAPE

Head of Department

Smt. KWC, Sangli.

DECLARATION BY STUDENT

I hereby declare that the Project entitled “**Synthesis and characterization of Mn doped CuO thin films for Super capacitor application.**” completed and written by me has not formed earlier the basis for the award of any degree or similar title of this or any other University or Examining body.

Further I declare that I have not violated any of the provisions under Copyright Piracy/Cyber/IPR Act as and when amended from time to time.

Place: Sangli

Mr. Kiran Gajanan Gurav

Date:

Project Student

DECLARATION BY GUIDE

This is to certify that the Project entitled “**Synthesis and characterization of Mn doped CuO thin films for Super capacitor application.**” being submitted here with for the award of the Degree of Master of Science in Physics under the faculty of Science SHIVAJI UNIVERSITY , Kolhapur is the result of the original research work completed by **Mr. Kiran Gajanan Gurav** under my supervision and guidance and to the best of my knowledge and belief the work embodied in this Project has not formed earlier the basis for the award of any degree or similar title of this or any other University or examining body.

Place: Sangli

Miss S. A. Gaikwad

Date:

Project Guide

ACKNOWLEDGEMENT

On the day of completion of this project , the numerous memories are being rushed in my mind with full of gratitude to this encouraged and helped me a lot at various stages of this work .I offer sincere gratitude to all of them .

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My acknowledgement will be incomplete if I don't express my appreciation towards my mother, father, brother and all those who helped us directly-indirectly in completion of this work successfully.

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	3.2	Concept of solubility product	
	3.3	Advantages of SILAR over CBD	
	3.4	Mechanism of SILAR	
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	3.5.1	X ray Diffraction Study	
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CHAPTER4 Summary and Conclusion			



CHAPTER - 1

Introduction and Theoretical Background

Introduction

In synthesis and characterization of Mn doped CuO thin films we have prepared Mn doped CuO thin film by Successive Ionic Layer Adsorption and Reaction (SILAR) method.

1.1 Thin Film: An Introduction

The field of thin films has become evergreen in recent years. Thin films are important because they offer the potential for low-cost processing with minimal material usage while fulfilling application requirements. Importantly, this can enable cost-effective applications for expensive raw source materials. Thin films also can enable applications where low weight and mechanical flexibility are crucial.

Thin films have been used in the study of the relationship between the structure of solids and their physical properties. Practical applications include electrical circuits, optical instruments and magnetic information-storage devices. Thickness of the thin film is usually discussed in terms of angstrom units (Å). Thin films are formed by depositing material onto a clean supporting substrate to build up film thickness, rather than by thinning down bulk material.

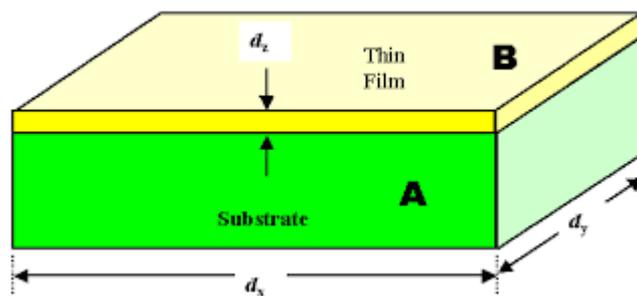
“A layer of material ranging from fractions of nanometer(monolayer)to several micrometers in thickness.”

OR

“Any solid or liquid system possesses at most two-dimensional order or periodicity is called as thin film.”

The thin solid films were probably first obtained by electrolysis in 1838. The conventional bulk material is characterized by three-dimensional order in which the constitute atoms or molecules find themselves. This order or periodicity is responsible for the structure/nature of the material, which in turn is at the heart of distinct physico-chemical properties of the materials. In case of thin films, the system possesses at most two-dimensional order or periodicity. This

accounts for the vast difference in physico-chemical properties between bulk material and its thin film counterpart. Applications of thin film technology have revolutionised the field of optics, electronics, sensors, energy storage device (supercapacitor) and magnetism. The need for new and improved optics, electronics and magnetic devices has stimulated the study of thin solid films of elements as well as binary and ternary systems, with controlled composition and specific properties.



The properties of thin films depend on the method of deposition. The required properties and versatility can be obtained by choosing proper method of thin films deposition. Thin film deposition methods can be broadly classified as either physical or chemical. Under physical methods, we have vacuum evaporation, and sputtering, where the deposition takes place after the material to be deposited has been transferred to a gaseous state either by evaporation or an impact process. Under chemical methods, we have the gas phase chemical processes such as conventional chemical vapour deposition (CVD), laser CVD, photo CVD, metal organo-chemical vapour deposition (MOCVD), and plasma enhanced CVD. Liquid phase chemical methods include electrodeposition, chemical bath deposition (CBD), modified chemical bath deposition (M-CBD), successive ionic layer adsorption and reaction (SILAR), electroless deposition, anodization, spray pyrolysis, liquid phase epitaxy, etc. The broad classification of thin film deposition techniques is

outlined in **Table. 1.1**

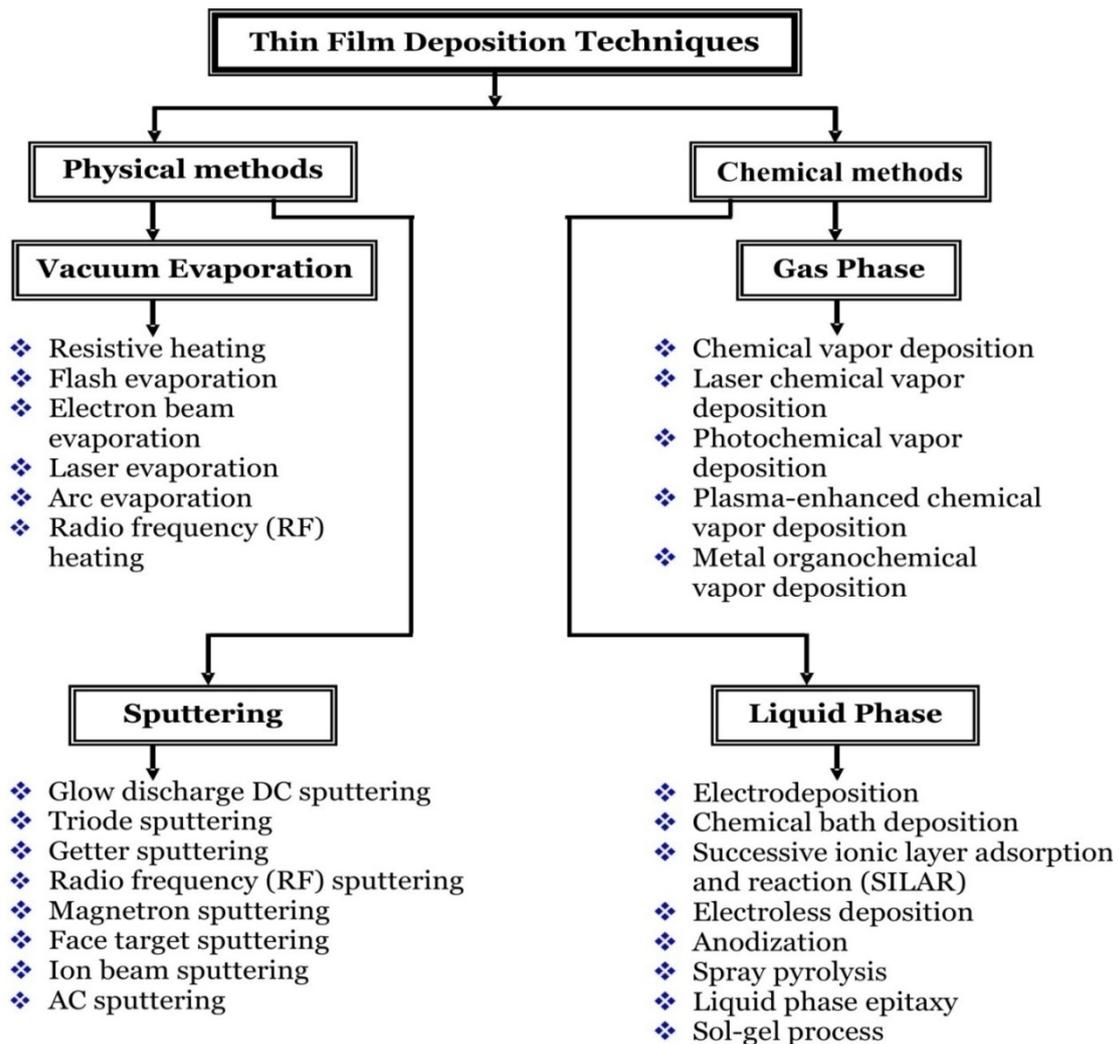


Table.1.1 Broad Classification of Thin Film Deposition Techniques Thin Film Deposition

Methods

1.2 Introduction to Supercapacitor

1.2.1 Various types of energy storage sources

A Ragone chart is a chart used for performance comparison of various energy-storing devices. On such a chart the values of specific energy (in W.h/kg) are plotted versus specific power (in W/kg). The Ragone chart was first used to compare performance of batteries. However, it is suitable to compare any energy-storing device.

Conceptually, the vertical axis describes how much energy is available, while the horizontal axis shows how quickly that energy can be delivered, otherwise known as power, per unit mass. Specific Energy = $(V \times I \times t) / m$ and Specific Power = $(V \times I) / m$, where V is voltage (V), I is electric current (A), t is time (s) and m is mass (kg).

Conventional capacitors have relatively high power densities, but relatively low energy densities when compared to electrochemical batteries and fuel cells. That is battery can store more total energy than capacitor, but it cannot deliver it very quickly, which means its power density is low. Capacitors, on the other hand store relatively less energy per unit mass or volume, but what electrical energy they do store can be discharged rapidly to produce a lot of power, so their power density is usually high.

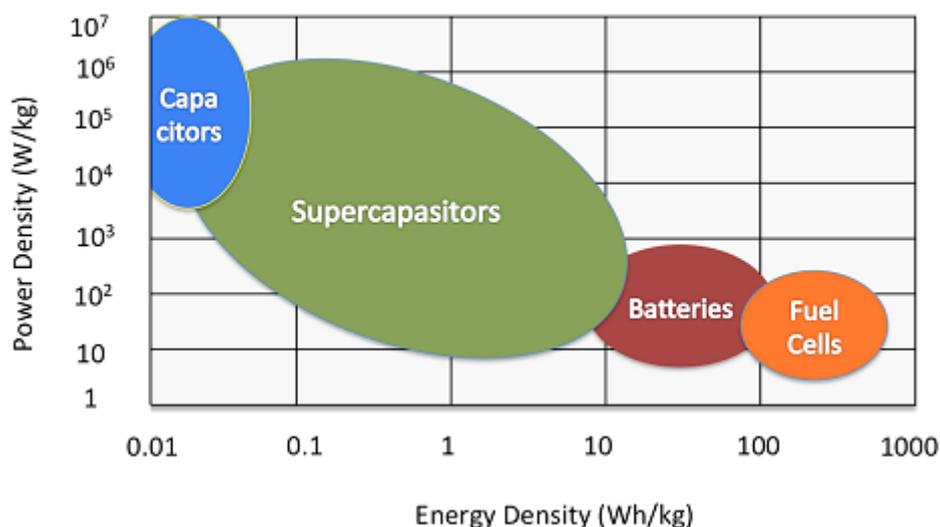


Fig.1.1 Ragone chart

1.2.2 Supercapacitors

Increasing demand in the need of global-energy drives the development alternative or non- conventional energy sources with high power and energy densities. Batteries, fuel cells and supercapacitors are typical non-conventional energy devices which are based on the principle of electrochemical energy conversion. They find widespread applications in consumer electronics ranging from mobile phones, laptops, digital cameras, emergency doors and hybrid vehicles etc. In these devices, chemical energy is converted in to electrical energy by means of electrochemical reactions. As far the fuel cells are concerned, as long as the fuel is fed, electrical energy can be obtained. In case of batteries, the stored energy can be drawn at the time of need. Supercapacitor is a typical energy storage device (similar to secondary battery) which possess high specific capacitance, high power density and long cycle life. Supercapacitors can be used in combination with batteries to meet the start-up power, usually high power density. Supercapacitors offer a promising alternative approach to meeting the increasing power demands of energy storage system and electronic devices. With their high power density, ability to perform in extreme temperature and millions of charge-discharge cycles capabilities. Supercapacitors can increase circuit performance and prolong the batteries. Depending on the mode of energy storage in supercapacitors, they are classified as in to electrical double layer capacitors (EDLC), pseudo-capacitors and hybrid capacitors.

1.2.3 Classification of Supercapacitor

Generally Supercapacitor are classified in to following two types,

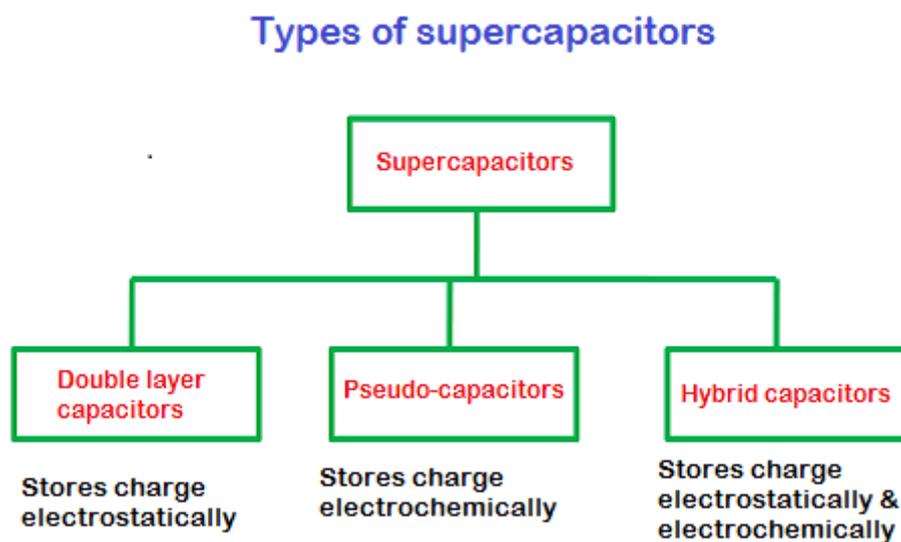


Table1.2 Types of supercapacitors

1. Electric double-layer capacitor

Electrostatic storage achieved by separation of charge in Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte. EDLCs do not have conventional dielectric. Instead of two plates separated by an intervening insulator, these capacitors use virtual plates made of two layers of the same substrate. Their electrochemical properties, the so called electrical double layer results in the effective separation of charge despite the vanishingly thin physical separation of the layers. The lack of need for a bulky layer of dielectric and the porosity of the material used permits the packing of plates with much larger surface area into a given volume, resulting in high capacitance in small packages.

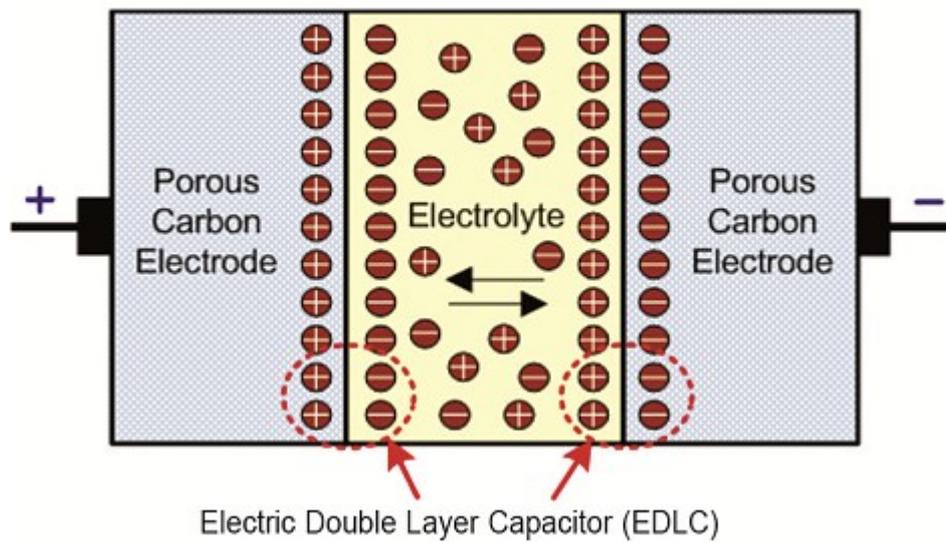


Fig.1.2 Schematic representation of electrochemical supercapacitors

2. Pseudo-capacitors

Pseudo capacitor is a hybrid between a battery and electric double layer capacitor. It also consists of two electrodes separated by an electrolyte. Charge storage occurs by chemical and electrostatic means. Chemical process involves charge transfer by means of reduction oxidation (redox) reactions. While the charge transfer is similar to that in battery, transfer rates are higher because of use of thinner redox material on the electrode or lower penetration of the ions from the electrolyte into the structure. Because of multiple processes acting to store charge, the capacitance values are higher in pseudo capacitors.

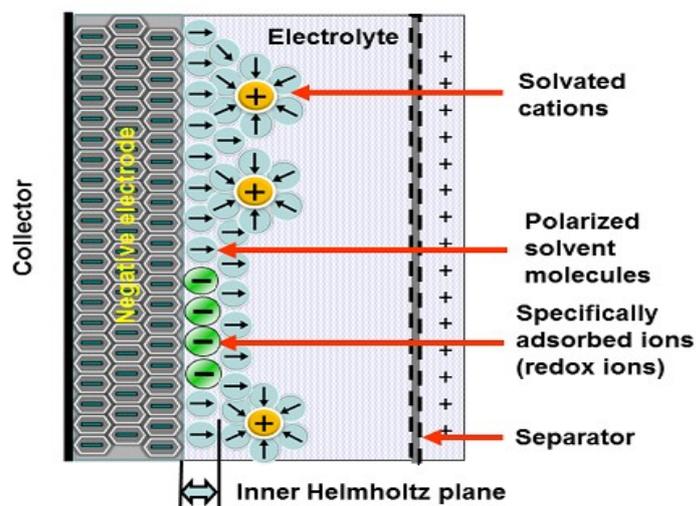


Fig. 1.3 Pseudo capacitance with specially adsorbed ions

3. Hybrid Capacitors

These are capacitors with asymmetric electrodes one of which exhibits electrostatic and other mostly electrochemical capacitance, such as Lithium ion capacitor. They are environmentally safe. The various materials that can be used for supercapacitors are activated carbon ,activated charcoal, carbon nanotubes, graphene, metal oxide etc.

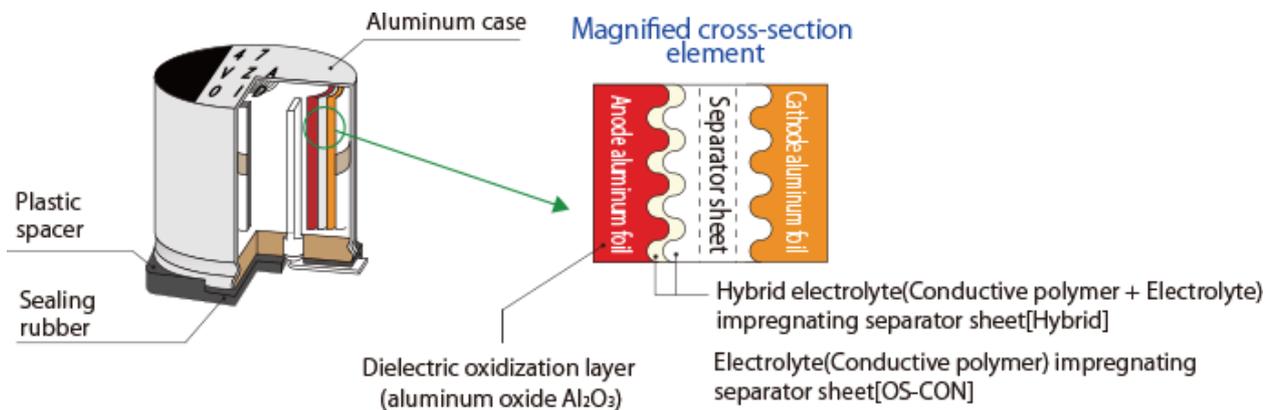


Fig.1.4 Hybrid capacitors

1.3 Literature survey

Metal oxide thin film preparation by successive ionic layer adsorption and reaction (SILAR) are simple, less expensive, low temperature and are convenient for large area deposition. A variety of substrates such as insulators, semiconductors or metals can be used. Very few p-type wide band gap materials were synthesized by these chemical methods. The synthesis and characterization of Copper Oxide (CuO) thin films via different techniques have attracted considerable attention due to their supercapacitor application. The different physical and chemical techniques that have been utilized to grow CuO thin films on glass and stainless steel substrates, it includes spray pyrolysis, electro deposition, CBD etc.

Copper Oxide present non-toxic, cost-effectively synthesized, abundant in nature, environmental stability, good potential stability and desirable electrical, optical, and electrochemical properties. It is P-type semiconductor material. Band gap energy is 1.2 eV at room temperature. It has Polycrystalline nature having monoclinic crystal structure.

SILAR method has emerged as one of the solution method to deposit a variety of compound materials in thin film form. The SILAR is inexpensive simple and convenient for large area deposition. A variety of substrates such as insulators semiconductors, metals can be used since the deposition is carried out at or near room temperature. As a low temperature it also avoids the oxidation and corrosion of substrates. The prime requisite for obtaining good quality thin film is the optimization of preparative parameters viz. concentration of the precursors, deposition cycles, temperature and deposition time etc. Copper Oxide thin film can be prepared by using various chemical deposition techniques such as sol gel, dip coating, CBD and physical vapor deposition techniques.

An emerging application of Copper Oxide is electrochemical supercapacitors. The supercapacitive behavior of Copper Oxide thin film was investigated by cyclic voltammetry in 1 M Sodium Sulphate electrolyte.

Ceramics International 39(2013) by Y. Gulen , F. Bayansal etc prepared Mn doped CuO thin films by SILAR method. They conclude from SEM that thickness and length of plate like nanostructures were affected by the Mn concentration. The XRD showed that all of the films have polycrystalline nature. Mn concentration increases optical transmittance and optical band gap

energy values. M. Lamari-Zeggar , M.S. Aida etc in JNTM Vol. 04, N^o 01 (2014)86-88 prepared CuO thin film by ultrasonic spray on glass substrate. They vary substrate temperature. At different substrate temperature Copper Oxide forms single phase and shows monoclinic structure. Paper published in Royal society of chemistry by Deepk P. Dubal , Vijay J. Fulari etc prepared Mn doped CuO thin films. They investigated that effect of Mn incorporation on the supercapacitive properties of CuO synthesized by SILAR method. At 3% Mn doping in CuO exhibits highest specific capacitance of 600Fg^{-1} at scan rate of 5mVs^{-1} . G. Dural , P. Kuppusaml and K. Viswanathan are performed Mn doped CuO thin films by RF magnetron sputtering method for improving supercapacitive performance. They showed that an enhancement of capacitance with the incorporation on Mn in CuO. From the GCD results the areal capacitance of the un doped CuO has increased from 49 to 87 mFcm^{-2} for the Mn doped CuO measured at constant current density of 1mAcm^{-2} .

1.4 Purpose of the research work

The Mn doped CuO thin films are applicable in various applications. Our attempt is to prepare the Mn doped CuO films by the SILAR method. The Mn doped CuO thin films will be deposited on stainless steel substrates by SILAR method. This method is mainly based on the immersion of the substrate on the separate cationic and anionic precursor solution with water to avoid homogeneous precipitation.

In the present work, Mn doped CuO are chemically deposited from simple aqueous solution using SILAR method. The effect of preparative parameters such as concentration, time, deposition cycles, etc will be studied and optimised to get uniform films.

The films characterization will be studied using X ray diffraction, optical, surface morphology properties. The X ray diffraction data will be used for determination of crystal structure. The surface morphology of thin films will be studied using field emission scanning electron microscope (FE-SEM). To study its electrochemical properties as electrode for supercapacitor application

1.5 Plan of project work

The Mn doped CuO thin films are applicable in various applications. Our attempt is to prepare the Mn doped CuO films by the SILAR method. The Mn doped CuO thin films will be deposited on stainless steel substrates by SILAR method.

Mn doped CuO are chemically deposited from simple aqueous solution using SILAR method. The effect of preparative parameters such as concentration, time, deposition cycles, etc will be studied and optimized to get uniform films.

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CHAPTER-2

Thin film deposition methods

2.1 Thin Film: An Introduction

The field of material science and engineering community's ability to conceive the novel materials with extraordinary combination of chemical, physical and mechanical, properties has changed the modern society. There is increasing technological progress. Modern technology requires thin films for different applications. Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behavior of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films.

When we consider a very thin film of some substance, we have a situation in which the two surfaces are so close to each other that they can have a decisive influence on the internal physical properties and processes of the substance, which differ, therefore, in a profound way from those of a bulk material. The decrease in distance between the surfaces and their mutual interaction can result in the rise of completely new phenomena. Here the one dimension of the material is reduced to an order of several atomic layers which creates an intermediate system between macro systems and molecular systems, thus it provides us a method of investigation of the microphysical nature of various processes. Thin films are especially appropriate for applications in microelectronics and integrated optics. However the physical properties of the films like electrical resistivity do not substantially differ from the properties of the bulk material. For a thin film the limit of thickness is considered between tenths of nanometer and several micrometers [1].

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter.

Thin films are formed mostly by deposition, either physical or chemical methods. Thin films, both crystalline and amorphous, have immense importance in the age of high technology. Few of them are: microelectronic devices, magnetic thin films in recording devices, magnetic sensors, gas sensor, A. R. coating, photoconductors, IR detectors, interference filters, solar cells, polarizer's, temperature controller in satellite, superconducting films, anticorrosive and decorative coatings.

Thin films have been used in the study of the relationship between the structure of solid and their physical properties. A thin film is a layer of a material ranging [2] from fraction of a nanometer to several micrometers in thickness. Thin films have very interesting properties that are quite different from those of the bulk material which they are made of. This is because of the fact that their properties depend on number of interrelated parameters, and also on the technique employed for their fabrication. Practical applications include electrical circuits, optical instruments and magnetic information storage devices. Thickness of thin film is usually discussed in term of Angstrom (\AA).

Thin films are formed by depositing material on a clean supporting substrate to build up film thickness, rather than by thinning down bulk material. An also thin film possesses wide range of applications in both civil as well as military sectors. “When the third dimension of the film that is the thickness on substrate is comparable with the mean free path of the electron in that film, then it is called thin film.” The thin solid films were first obtained by electrolysis in 1838. The conventional bulk material is characterized by three dimensional orders. In which the constructive atoms or molecules find themselves. This order or periodicity is responsible for the structure of the material. In case if thin films, the system possesses at most two dimensional orders or periodicity. The above two applications include their use for protection of material from corrosion, oxidation and wear, increasing transmission or reflection in a certain wavelength region and in filters, color separation, fire-resistance, high temperature superconductors, sectors[3] are also discussed in the monograph.

2.1.1 Properties of Thin Films:-

1. Thin films may not be fully dense.
2. Thin films may be under stress.
3. Thin films have different defects structure from bulk.
4. Thin films are quasi two dimensional.
5. Thin films are strongly influenced by surface and interface effects.

2.1.2 Applications of Thin Film-

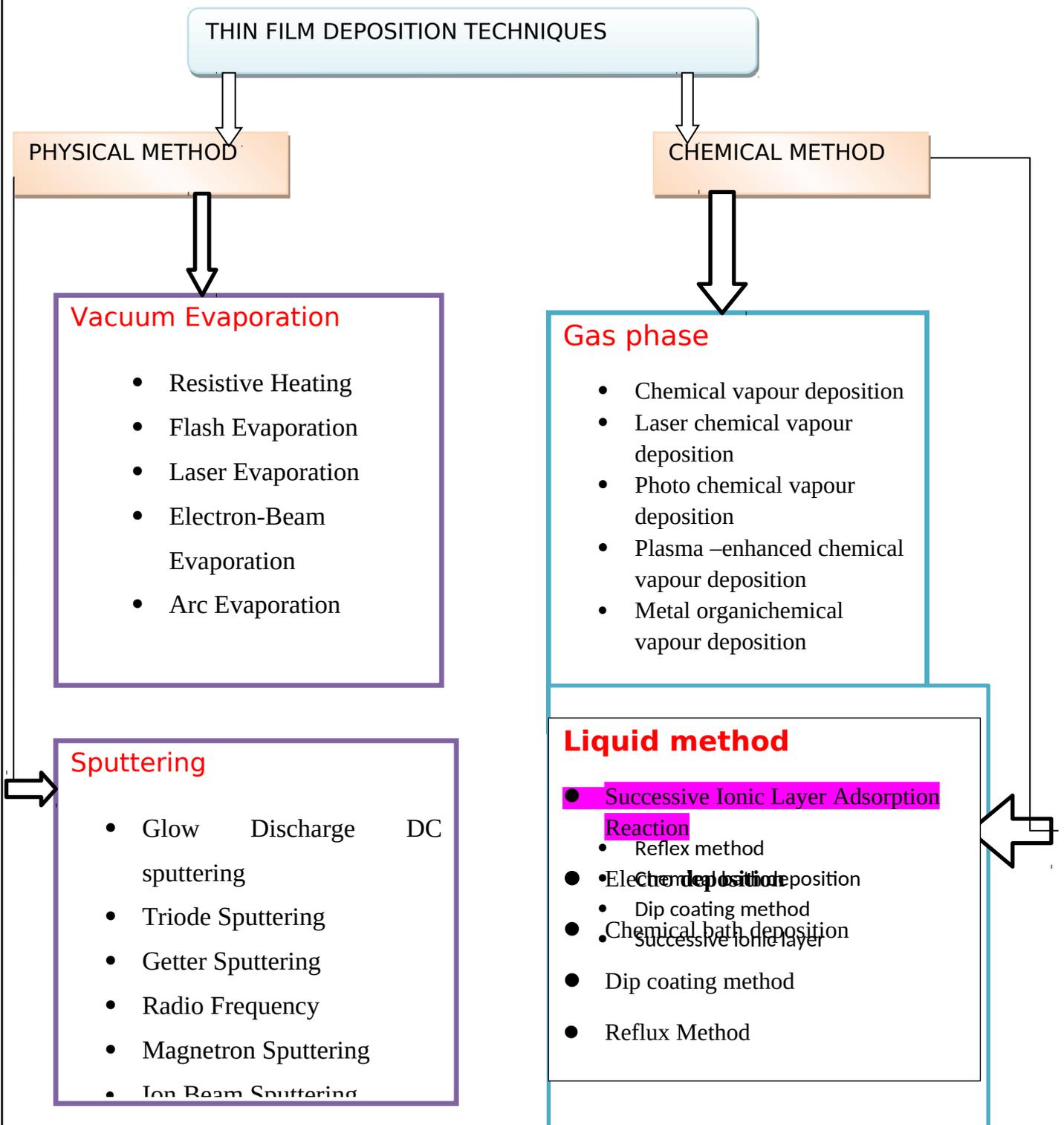
Depending on different properties, thin films have numerous applications in various fields that are tabulated below

Sr. No	Thin film property	Typical applications
1	Electrical	Solar Cell, Semiconductor devices, piezoelectric devices.
2	Optical	Reflective, Antireflective coatings, Decoration, Waveguides.
3	Chemical	Protect against corrosion and oxidation, Barrier to diffusion or alloying. Gas/Liquid sensors.
4	Mechanical	Coating
5	Magnetic	Memory disc

Table No.2.1 Applications of Thin film depending on its properties

2.2 Thin Film Deposition Methods:

Technological progress of our modern society mainly depends on material science with different extraordinary combination of physical and chemical properties of material. Modern material science study requires thin films for different uses. Thin film can be deposited by various physical and chemical techniques, and can be classified as shown in table. Among these some are explained above.



2.2.1 SILAR Method

The SILAR method is mainly based on the adsorption and reaction of the ions from the solutions and rinsing between every immersion with distilled water (D. W.) to avoid homogeneous precipitation in the solution

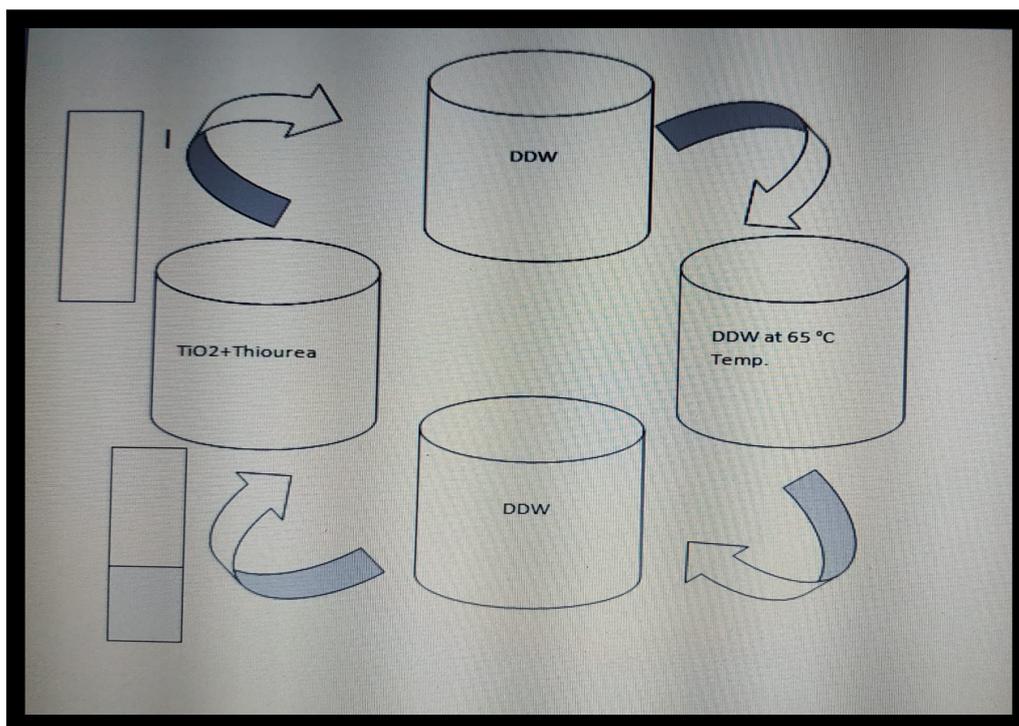


Fig. 2.2.1 *Schematic diagram of SILAR method*

Thin films have been obtained by adsorbed cations followed by reacting with anion from appropriate precursor solutions. The term adsorption can be defined as a collection of a substance on the surface of another substance, which is the fundamental building block of the SILAR method. Adsorption may be expected when two heterogeneous phases are brought in contact with each other. Hence, gas-solid, liquid-solid and gas-liquid are three possible adsorption systems. In SILAR method, the first step is mainly concern with adsorption in liquid-solid system. Adsorption is an

exothermic process. The adsorption is a surface phenomenon between ions and surface of substrate and is possible due to attractive force between ions in the solution and surface of the substrate. These forces may be cohesive or Van-der Waals or chemical attractive. Atoms or molecules of their kinds on all sides do not surround atoms or molecules of substrate surface. Therefore, they possess unbalanced or residual force and hold the substrate particles. Thus, adsorbed atoms (ad-atoms) can be holding on the surface of the substrate. In second step the adsorbed ion is reacted with anion, resulted into film formation[4].

The SILAR method involves four steps:

1) Adsorption 2) First rinsing 3) Reaction and 4) Second rinsing.

1) Adsorption

In first step of SILAR method, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: first, the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative form the counter ions of the cations.

2) First rinsing

In this step, loosely adsorbed ions are rinsed away from the diffusion layer. This results into saturated electrical double layer.

3) Reaction

In this reaction step, the anions from anionic precursor solution are introduced to the system. Due to the low stability of ions reaction between cation and anion takes place leading to formation of solid phase over substrate.

4) Second rinsing

In last step of SILAR method, the excess and unreacted species and the reaction by product from the diffusion layer are removed. In this way, SILAR method culminated through adsorption of cations and reaction of newly adsorbed anions with preadsorbed cations, which leads to formation of thin film of desired material. The factors like temperature of solution, nature of the

substrate, pH and concentration of solution, area of the substrate, dipping and rinsing time etc. affect the deposition process.

2.1.2.2 Effect of preparative parameters

The rate of deposition and terminal thickness depends upon the adsorption and reaction time in the solution. In SILAR method, growth kinetics depends on the concentration of ions, adsorption and reaction time, rinsing time, temperature and on complexing agent. The effect of various deposition conditions [4] on these parameters is discussed below:

a) Concentration of ions

The increase in compound concentration leads to an increase in cation and anion concentration and a film with larger thickness is obtained. Conversely, above a certain concentration of cation and anion when the rate of reaction becomes high and precipitation is leading to a lesser amount of material on the substrate then it lowers the thickness. Changing concentration of precursor solution, stoichiometry of the deposited material can be controlled.

b) Adsorption and reaction time

Adsorption and reaction time plays important role in formation of thin film. As the adsorption time is greater than that of reaction time the film formation takes place by assorted reaction it results higher terminal thickness. Equal adsorption and reaction time, result in to consistent reaction. Consistent growth provides uniform film formation.

c) Rinsing time

Rinsing between every immersion is significant to avoid the precipitation in the reaction bath. In rinsing bath the loosely bounded species peel off from the substrate surface. Sufficient rinsing time can provide a good quality film.

d) Temperature

The dissociation of complex and the anion of the compound depend on the temperature. At the higher temperatures, the dissociation is greater, which gives higher concentrations of cations and anions that result in higher rate of deposition.

e) Complexing agent

Release or adsorption of metal ion can be controlled by using the complexing agent. Due to the slow release of metal ions, it leads to slow growth rate of the film. Hence growth kinetics can be controlled by using complexing agent.

Similar to CBD method, SILAR method has the following advantages:

1. The thickness and morphology of the films can be easily controlled by varying the preparative parameters.
2. Relatively uniform films can be obtained on substrates of complex shape.
3. The equipment's needed are not expensive and does not require sophisticated instrumentation and vacuum.
4. The SILAR method is usually operated at low temperature.

Even with above advantageous points, SILAR method has interesting feature and additional advantage over CBD method is that, SILAR method saves material cost due to non-formation of precipitate in solution. SILAR method can be used for the deposition from aqueous or non-aqueous baths and it can be employed in the preparation of polymers, semiconductors or oxides.

2.2.2 Chemical Bath Deposition Method

Among the chemical methods of thin film depositions, chemical bath deposition (CBD) is probably the simplest method available for this purpose. The only requirements of these methods are a vessel to contain the solution and the substrate on which deposition is to be carried out. In addition to this various a specific and constant temperature are options that may be useful.

The mechanism of CBD method contains following types,

1. Simple ion by ion mechanism.
2. Simple Cluster (hydroxide) mechanism.
3. The complex decomposition ion by ion mechanism.
4. The complex decomposition cluster mechanism

2.2.3 Electrodeposition Method

Electrodeposition is process of depositing metal atoms on a conducting substrate by passing direct current through solution containing the metal ions to be deposited. The typical Electrodeposition set up consists of following,

1. Electrolyte
2. Cathode and Anode
3. Source of electricity

When direct current is passed through cathode and anode, immersed in electrolyte containing the metals ions, the metal ions get attracted towards the cathode, neutralized electrically by receiving electrons and get deposited on cathode. The deposition is controlled by monitoring the amount and the rate of charge passing through the electrolyte. Thus the electrical energy is used to cause chemical change.

2.2.4 Dip Coating Method:-

Dip Coating is with no doubt the easiest and fast method to prepare thin films from chemical solutions with the highest degree of control, making it highly appropriate for small scale production. In specific high technology cases, it is used to deposit coating on large surfaces.

The principle is as simple as dipping the substrate into the initial solution before withdrawing it at a constant speed. During which the solution naturally and homogeneously spreads out on the surface of the substrate by the combined effects of viscous drag and capillary rise. Evaporation then takes over and leads to solidification of the final coating.

2.2.5 SILAR METHOD:-

Thin film plays a vital role in the present day technology development. The different methods of thin films deposition offer a major key to the fabrication of micro and nanoscale devices.

The discussed in detail. Thin films formed using SILAR method will be further characterized by means of structural, surface morphology, optical and electrical measurements. It is necessary to study the basics involved in the characterization techniques of the materials in order to assess the scope for further improvement.

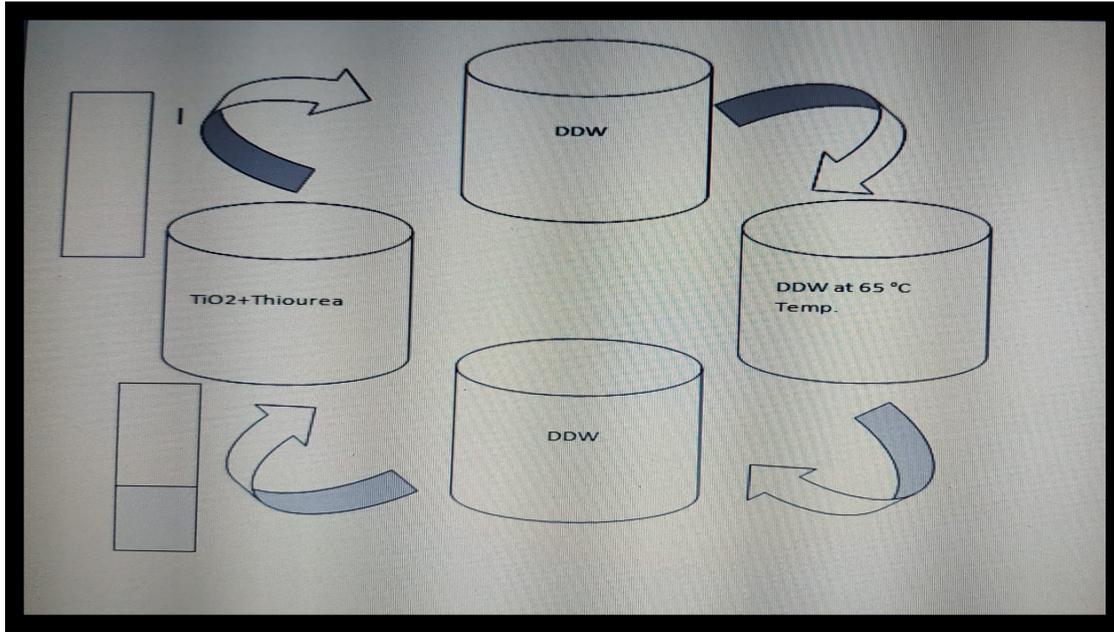


Fig.2.2.5 Schematic diagram of SILAR meth

2.3 References:-

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CHAPTER-3

Characterization techniques

3.1 Theoretical background of SILAR

Thin film plays vital role in the present day technology development, and methods of thin film deposition offer a major key to the fabrication of micro and nanoscale devices. Deposition of thin films by vacuum evaporation, spray pyrolysis, electrodeposition, anodization, electroless, chemical bath deposition (CBD), successive ionic layer deposition (SILAR) etc. are well known methods. Among these deposition methods, SILAR is simple, inexpensive and convenient for large area deposition.

For the sake of better understanding, the theoretical background and mechanism of SILAR is discussed in detail. Thin films formed by using SILAR will be further characterized by means of structural, surface morphological, optical and electrical measurements. It is therefore necessary to study the basics involved in the characterization techniques of the materials in order to assess the scope for further improvement and utility.

The successive ionic layer adsorption and reaction (SILAR) method is mainly based on the adsorption and reaction of the ions from the solutions and rinsing between every immersion with distilled

water to avoid homogeneous precipitation in the solution. The basics of SILAR are discussed in detail by Pathan H.M. et al. The collection of a substance on the surface of another substance is known as adsorption, which is the fundamental building block of the SILAR method. The term adsorption can be defined as the interfacial layer between two phases of a system. Adsorption may be expected when two heterogeneous phases are brought into contact with each other. Hence, gas–solid, liquid–solid and gas–liquid are three possible adsorption systems.

In SILAR method, we are only concerned with adsorption in liquid–solid system. Adsorption is an exothermic process. The adsorption is a surface phenomenon between ions and surface of substrate and is possible due to attraction force between ions in the solution and surface of the substrate. These forces may be cohesive forces or Van-der Waals forces or chemical attractive forces. Atoms or molecules of substrate surface are not surrounded by atoms or molecules of their kind on all sides. Therefore, they possess unbalanced or residual force and hold the substrate particles. Thus, ad atoms can be holding on the surface of the substrate. The factors like temperature of solution, pressure, nature of the substrate, concentration of the solution, area of the substrate etc affect the adsorption process. The reaction in pre-adsorbed (cations) and newly adsorbed (anions) forms the thin films of desired material.

3.2 Concept of solubility and ionic product

Sparingly soluble salt, AB, when placed in water, a saturated solution containing A^+ and B^- ions in contact with undissolved solid AB is obtained and equilibrium is established between the solid phase and ions in the solutions:



Applying the law of mass action,

$$K = [C_A^+ C_B^-] / C_{AB} \quad (2.2)$$

Where C_A^+ , C_B^- and C_{AB} are concentrations of A^+ , B^- and AB in the solution respectively. The concentration of pure solid is a constant number i.e.

$$C_{AB}(S) = \text{constant} = K, \quad (2.3)$$

$$K = [C_A^+ C_B^-] / K, \quad (2.4)$$

$$KK' = C_A^+ C_B^- \quad (2.5)$$

Since K and K' are constants, the product of KK' is also constant, say K_s , therefore (2.5) becomes

$$K_s = C_A^+ C_B^- \quad (2.6)$$

The constant K_s is called solubility product (SP) and $(C_A^+ C_B^-)$ is called the ionic product (IP). When the solution is saturated, the ionic product is equal to the solubility product. But when the ionic product exceeds the solubility product i.e

$$IP/SP = S > 1, \quad (2.7)$$

The solution is supersaturated ($S = \text{degree of supersaturation}$), precipitation occurs and ions combine on the substrate and in the solution to form nuclei. The rate of formation of nuclei forms on the surface of the substrate depends on the degree of supersaturation. It is assumed that the formation of stable growth center the surface $N(t)$ can be expressed as a function of total number of active sites on the surface N_0 by the law

$$N(t) = N_0 [1 - \exp(-At)], \quad (2.8)$$

Where A is nucleation rate constant.

Growth of particles already present in the solution takes place in second step, when nuclei or other seed particles are present. In case of ionic solids, the process involves deposition of cation and anion on appropriate sites.



Where n is the minimum number of A^+ and B^- required for giving stable phase $(AB)_n$. The growth rate is directly proportional to the supersaturation

Rate nucleation may occur through the precipitation process. As a result there are great numbers of centers upon which growth process can take place.

Where a is surface area of the exposed solid and K_0 is the constant which is a characteristic of the particular precipitate. If the supersaturation is maintained at low level throughout the precipitation

relatively few nuclei are formed. That will grow to give a small number of large particles with high supersaturation, many more nuclei are formed initially.

3.3 Advantages of SILAR over CBD

One of the newest solution methods for the deposition of thin film is successive ionic layer adsorption and reaction (SILAR) method, which is also known as modified version of chemical bath deposition. In spite of its simplicity, SILAR has a number of advantages:

- (i) It offers extremely easy way to dope film with virtually any element in any proportion by merely adding it in some form of the cationic solution
- (ii) Unlike vapor deposition method, SILAR does not require high quality target and/or substrates nor does it require vacuum at any stage, which is a great advantage if the method will be used for industrial application.
- (iii) The deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles
- (iv) Operating at room temperature can produce films on less robust materials.
- (v) Unlike high power methods such as radio frequency magnetron sputtering (RFMS) it does not cause local over heating that can be detrimental for materials to be deposited.
- (vi) There are virtually no restrictions on substrate material, dimensions or its surface profile.

Moreover, it is relatively inexpensive, simple and convenient for large area deposition. It can be carried out in glass beakers. The starting materials are commonly available and cheap materials. As it is a chemical method, a large number of varieties of substrates can be coated. Thus any insoluble surface to which the solution has free access will be a suitable substrate for the deposition. The deposition is carried out at or close to room temperature, avoids oxidation or corrosion of metallic substrates. Stoichiometric deposit is easily obtained. Since the basic building blocks are ions instead of atoms, the preparative parameters are easily controllable.

In chemical bath deposition (CBD) method, deposition of metal chalcogenide semiconducting thin films occurs due to substrate maintained in contact with dilute chemical bath containing metal and chalcogen ions. The film formation on substrate takes place when ionic product exceeds solubility product. However, this results into precipitate formation in the bulk of solution, which cannot be eliminated. This results in unnecessary formation of precipitation and loss of material. In order to

avoid such unnecessary precipitation, a CBD is modified and known as successive ionic layer adsorption and reaction (SILAR) method. In this modification, thin films are obtained by immersing substrate into separately placed cationic and anionic precursors and rinsing between every immersion with ion-exchanged water. The rinsing time in ion exchange water is critical for ionic layer formation.

Thus, precipitate formation i.e. wastage of material, is avoided in SILAR method. The successive ionic layer adsorption and reaction (SILAR) method is relatively a new and less investigated method, first reported in 1985 by Ristov *et al.* The name SILAR was ascribed to this method by Nicolau (1985).

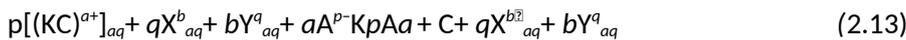
3.4 Mechanism of SILAR

The SILAR is based on sequential reaction at the substrate surface. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The SILAR process is intended to grow thin films of water insoluble ionic ion covalent compounds of the type $KpAa$ by heterogeneous chemical reaction at the solid solution interface between adsorbed cations, pK_a^+ and anion, aA_p^- , following the reaction



$$\text{With } ap=bq=bq, \quad (2.12)$$

where, K represents cation (Cd^{2+} , Zn^{2+} , Fe^{3+} , Cu^+ etc), p represents the number of cations, a represents the numerical value of charge on cation, X is a ion in cationic precursors having negative charge ($X = SO_4^{2-}$, I^- , NO_3^- etc), q represents the number of X in cationic precursors and b the numerical value of charges on X , b the number of Y in the anionic solutions, q the numerical value of charge on Y , Y the ion which is attached to chalcogen ion, A represents the anion (O , S , Se and Te), a the number of anions. A is the chalcogen ion. In the presence of complexing agent, above reaction can be written as



where C is complexing agent.

Figure 2.1. represents the basis of SILAR growth. It consists of at least four different steps: adsorption, rinsing (I), reaction and rinsing (II).

Adsorption: In this first step of SILAR process, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative form the counter ions of the cations.

Rinsing (I): In this step, excess adsorbed ions, pK^{a+} and aA^{p-} , are rinsed away from the diffusion layer. This results into saturated electrical double layer.

Reaction: In this reaction step, the anions from anionic precursor solution are introduced to the system. Due to the low stability of the material, $KpAa$, a solid substance is formed on the interface. This process involves the reaction of pK^{a+} surface species with the anionic precurs aA^{p-} .

Rinsing (II): In last step of a SILAR cycle, the excess and un reacted species aA^{p-} , X, Y, and the reaction by product from the diffusion layer are removed. By repeating these cycles, a thin layer of material, $KpAa$, can be grown. Following the above-mentioned steps the maximum increase in film thickness per one reaction cycle is theoretically one monolayer. This results into a solid layer of the compound $KpAa$.

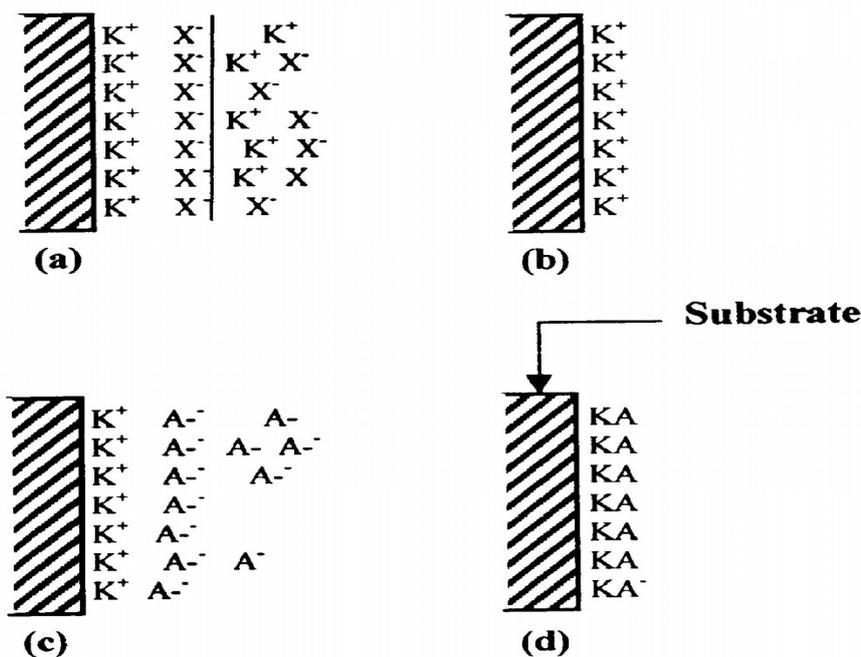


Fig.3.1 Schematic diagram of SILAR growth: (a) Adsorption of K^+X^- and the formation of electrical double layer, (b) rinsing (I) removes excess, unabsorbed K^+

and X, (c) reaction of A^- with pre-adsorbed K^+ ions to form KA and (d) rinsing (II) to remove excess and unreacted species and form the solid solution KA on surface of the substrate.

3.5 Thin film characterization techniques

The properties of the films can be best understood using different characterization techniques. Thickness measurement, X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Visible spectroscopy, contact angle measurement, two probe resistivity and thermo e.m.f. measurement techniques were utilized in the present study. Different techniques used in the present study with their utility to find out different properties are summarized in Table 2.

Table.2 Summary of different characterization techniques used in the present study to find properties of the films.

Sr. No.	Characterization techniques	Thin film properties
1	XRD	Crystal structure
2	FE-SEM	Surface morphology
3	EDAX	Elemental composition of materials
4	UV- VIS Spectrophotometer	Band gap energy
5	Contact angle	Nature of material
6	Cyclic Voltammetry	Specific Capacitance
7	Galvanostatic Charge discharge	Specific capacitance

Table.2.1 Characterization techniques

3.5.1 X ray Diffraction Study

The XRD is a well noising technique in order to examine the information of composition, phase and crystallite orientations of the material. The structural and phase confirmation, determination of lattice parameters and grain size, are based on the X-ray diffraction pattern. The recent X-ray diffractometer has the availability of commercial monochromators and intense micro focus X-ray sources, in order to employ X-ray diffraction technique valid for the films as thin as 100 \AA . The several researchers have explained X-ray diffraction system for its suitability to study the thin films. This technique uses a chromater, to offer a diffracted beam, which is further diffracted from the film surface oscillating about the mean diffraction position. The monochromatic radiation based X-ray diffraction technique is more significant, since the spacing of the planes (“d” spacing) can be estimated from the noticed diffraction angles. The phenomenon of X-ray diffraction can be measured as reflection of X-rays from the crystallographic planes of the lattice and is governed through the Bragg’s equation,

$$2d\sin\theta=n\lambda \quad (2.14) \quad \text{Where,}$$

d is lattice spacing,

λ is the wavelength of the monochromatic X-rays,

n is the order of diffraction and

θ is diffraction angle.

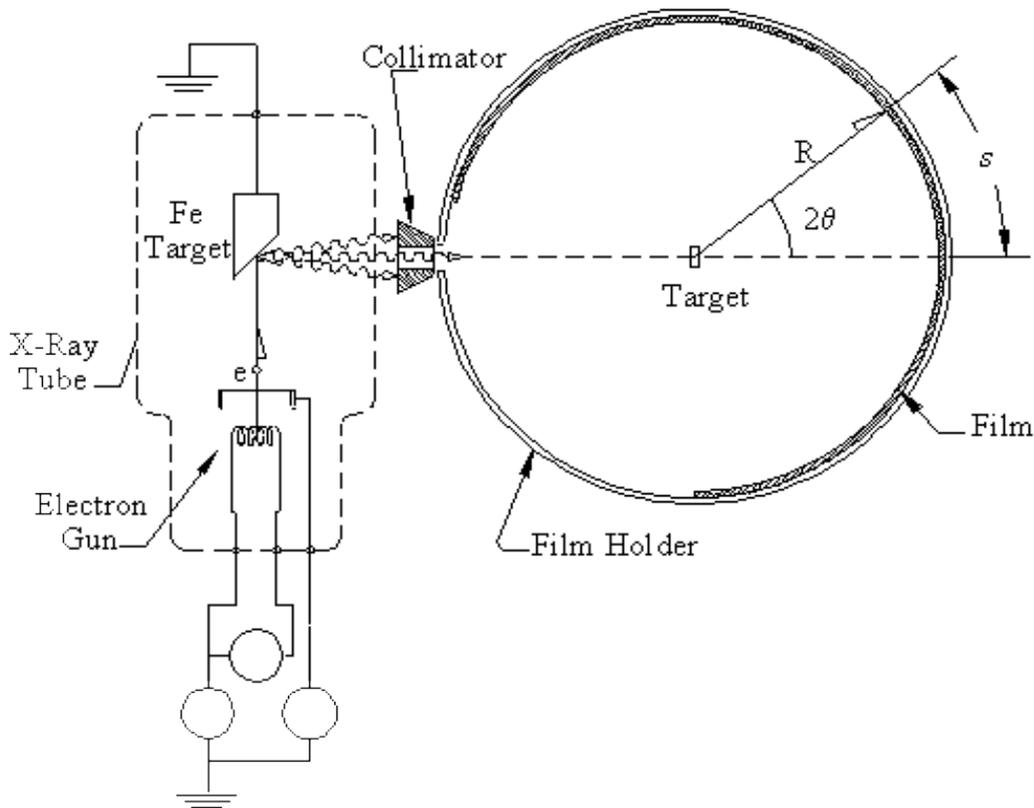


Figure 3.2 Schematics of X-ray diffractometer .

The ‘d’ values are computed through the above relation for known values of θ , λ and n . The X-ray diffraction data thus obtained is compared with American Standard for Testing of Materials (ASTM) or Joint Committee Powder Diffraction Standards (JCPDS) powder diffraction data to identify the unknown material. The sample utilized may be powder, single crystal or thin film.

The crystallite size of the material is measured using the full width at half maximum (FWHM) of the most intense diffraction line by Scherer’s formula as follows,

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \quad (2.15)$$

Where,

D is crystallite size,

λ is wavelength of X-rays used,

β is full width at half maxima of the peak (FWHM) in radians,

θ is Bragg's angle and

k is constant.

The value of k varies from 0.89 to 1.39, but mainly it is closer to 1. Though this technique is applicable for determination of crystal structure, lattice parameters, particle size etc, it is not practical for identification of individuals of multilayer's or percentage of doping material. This technique does not furnish any estimation about surface morphology.

3.5.2 Field Emission-Scanning Electron Microscopy (FE-SEM)

The FE-SEM is a tool, used to visualize the morphology of the sample at higher magnification, higher resolution and depth of focus as compared to an optical microscope and scanning electron microscope. Principally, it is used for topographical and compositional observations of surfaces, elemental analysis of specimen, internal structure observation, internal characteristics observation, crystalline structure and the observation of magnetic domain.

The electrons generated by a [field emission source](#) under [vacuum](#) are accelerated in a field gradient. The beam allows passing through [Electromagnetic Lenses](#), in order to focus onto the specimen. The different [types of electrons](#) are emitted from the specimen as a consequence of bombardment. Simultaneously, detector collects the secondary electrons and an image of the sample surface is traced through comparing the intensity of these secondary electrons to the scanning primary electron beam. Lastly, the image is displayed on a monitor. The ray diagram of FE-SEM is shown in Fig. 2.3 and emission of different types of signals during scanning is illustrated in Fig.2.4.

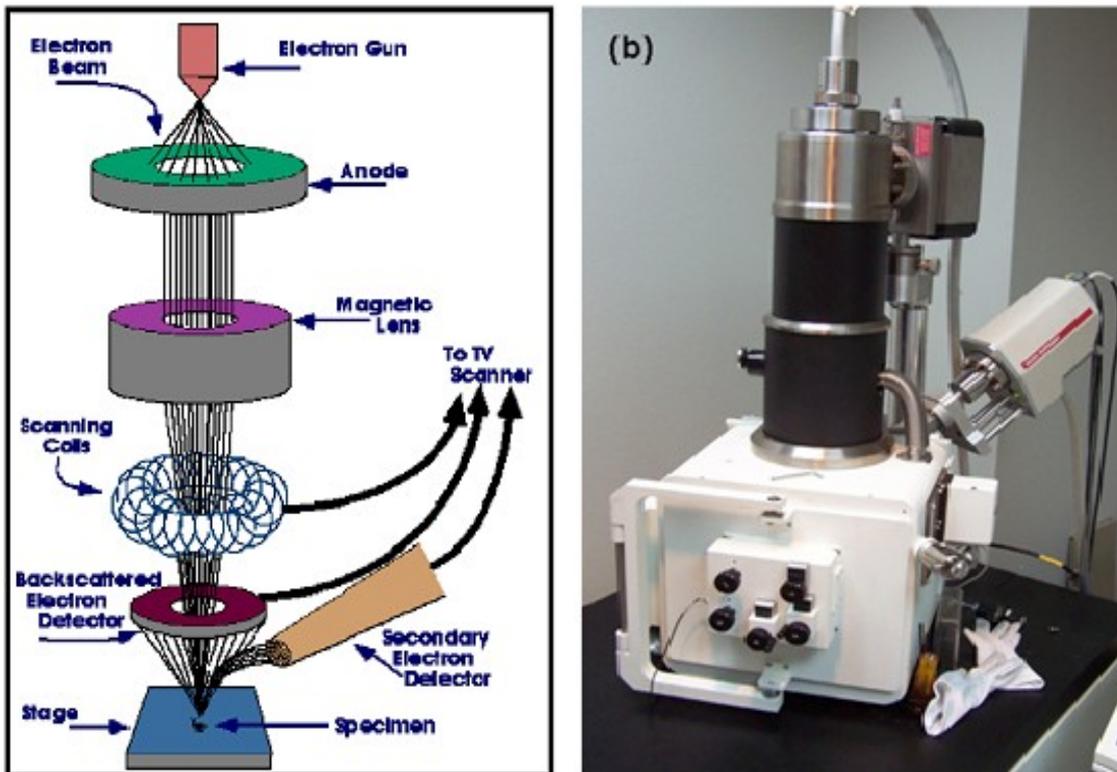


Fig.3.3 Field Emission-Scanning Electron Microscope.

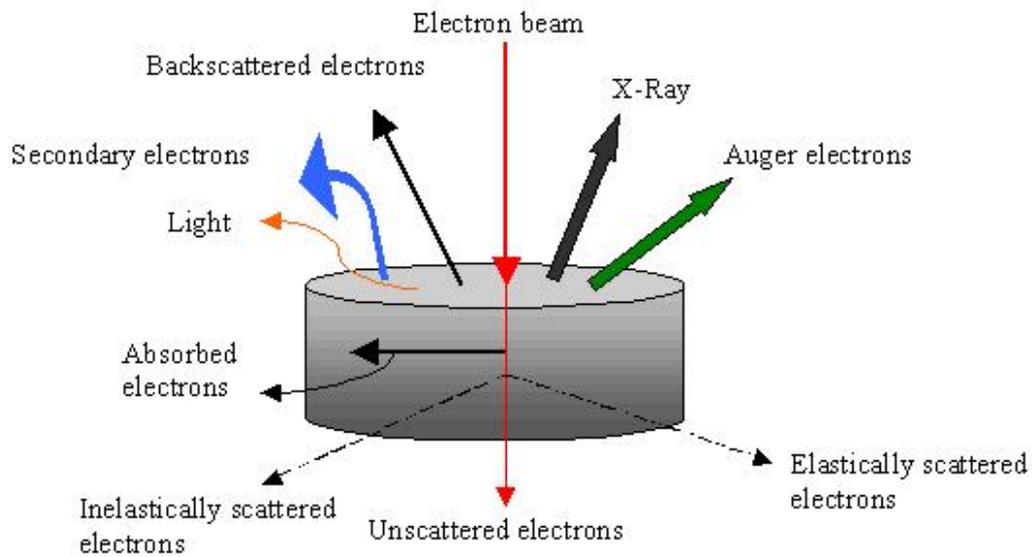


Fig.3.4 Ray diagram of emission of different types of electrons during scanning.

The FE-SEM can be assorted as a high vacuum instrument (less than 1×10^{-7} Pa). The vacuum permits electron movement along the column without scattering and helps to prevent discharges inside the instrument. The electron gun is used to offer a large and stable current in a small beam.

There are two types of emission sources

(a) Thermionic emitter and

(b) Field emitter,

which is the foremost difference between SEM and FE-SEM.

The thermionic emitters employ electrical current to heat up a filament; the two most common materials used for filaments are tungsten (W) and lanthanum hexaboride (LaB_6). The thermionic sources have relative low brightness, evaporation of cathode material and thermal drift during operation since the electrons can escape from the material only when the heat is sufficient to overcome the work function. Field Emission is one way of generating electrons that avoids these problems. A field emission source (FES); also called a cold cathode field emitter, does not heat the filament. The emission is reached through keeping the filament in a huge electrical potential gradient. The FES is generally a wire of tungsten (W) fashioned into a sharp point. The advantage of small tip radius (~ 100 nm) is that an electric field can be concentrated to an extreme level, becoming so big that the work function of the material is lowered and electrons can leave the cathode. FESEM uses Field Emission Source producing a cleaner image, less electrostatic distortions and spatial resolution < 2 nm (that means 3 or 6 times better than SEM). In order to resolve a feature on the specimen surface, the beam diameter must be smaller than the feature. So, there is need to condense the electron beam. To assist in the demagnification of the beam, electromagnetic lenses are employed. As the cross over diameter of the field emission source is smaller, a lower level of the beam condensation is essential. This achieves the highest resolution of the FE-SEM instrument. The changeable apertures are employed to refine the beam, since the large objective aperture size leads to a drop in the irradiation current and small objective aperture size will results into better resolution and good depth of field.

The specimen and the electron beam interact in both elastic and inelastic fashion giving different [types of signals](#). Elastic scattering events are those that do not influence the kinetic energy of the electron even when its trajectory had been affected. Inelastic scattering events are consequences of the energy transference from the electron beam to the atoms in the specimen, which result to energy loss electrons with small trajectory deviation. Some of the signals generated in this way are: secondary electrons (SE),

back scattered electrons, Auger electrons and X-Rays. Each of these signals gets specific information about topography, crystallography, surface characteristics, specimen composition and other properties.

3.5.3 Energy Dispersive X-Ray Analysis (EDX)

Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (**EDXMA**), is an analytical technique used for the [elemental analysis](#) or [chemical characterization](#) of a sample. It relies on an interaction of some [source](#) of [X-ray](#) excitation and a [sample](#). Its characterization capabilities are due in large part to the fundamental principle that each element has a unique [atomic structure](#) allowing a unique set of peaks on its electromagnetic [emission spectrum](#).

EDX is an analytical technique used for the elemental analysis or chemical Characterization of a sample. It is one of the variants of X-ray fluorescence spectroscopy which is based on the investigation of a sample through interactions between electromagnetic radiation and matter. Quantitative estimation is made by analyzing the X-rays emitted by the matter when it is bombarded with charged particles. Its characterization capabilities lie on the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another.

Accuracy of EDS spectrum can be affected by various factors. Many elements will have overlapping peaks (e.g., Ti K_{β} and V K_{α} , Mn K_{β} and Fe K_{α}). The accuracy of the spectrum can also be affected by the nature of the sample. X-rays can be generated by any atom in the sample that is sufficiently excited by the incoming beam. These X-rays are emitted in any direction, and so they may not all escape the sample. The likelihood of an X-ray escaping the specimen, and thus being available to detect and measure, depends on the energy of the X-ray and the amount and density of material it has to pass through. This can result in reduced accuracy in inhomogeneous and rough samples.

3.5.4 Optical Studies: UV- VIS Spectrophotometer

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. Fig.4 shows schematic of a single-beam UV-Vis spectrophotometer.

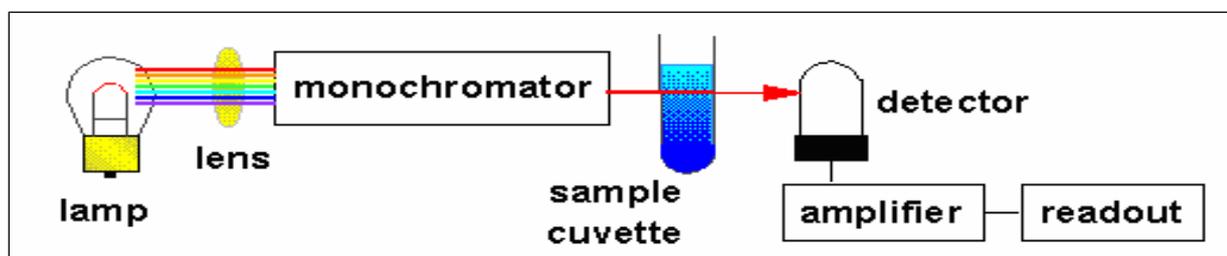


Fig.3.4 Schematic of a single-beam UV-Vis spectrophotometer.

The photons incident on any material may be reflected (**R**), transmitted (**T**) or absorbed (**A**). The quantity of radiation of wavelength λ absorbed by a material slab of thickness'' is measured in terms of optical density (α_i). Assuming negligible reflection ($R=0$), the energy absorbed can be given by Lambert's equation,

$$I = I_0 \exp (-\alpha_i) \quad (2.16)$$

Where,

I_0 and I - incident and transmitted intensities respectively.

In other words, optical absorption coefficient of films is evaluated from transmittance as,

$$T = A \exp(-\alpha_t t) \quad (2.17)$$

Where,

T - Transmittance, **t** - Film thickness, **A** - Coefficient related to the refractive index, which is nearly equal to unity at the absorption edge, **α_t** - absorption coefficient.

A photon absorption by a material is characterized by means of electron transition between energy states or bands according to quantum rules. An ideal semiconductor, at moderate temperature has small number of holes in the valance band electrons in the conduction band. Absorption of photons of sufficient energy tends to transfer the electrons from valance band to conduction band giving absorption maxima. Thus, the optical absorption edge at a certain incident photon energy, which can be attributed to the excitation of electrons from valance to conduction band separated by energy equal to the band gap energy (E_g). The photon energy dependence at the absorption edge is given by

$$(\alpha h\nu) = B (h\nu - E_g)^n \quad (2.18)$$

Where,

$h\nu$ - incident photon energy,

B - edge width parameter,

n - an exponent that determines the type of electronic transition causing absorption, which is $1/2, 3/2, 2, 3$ for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions, respectively.

Band gap:

Study of the optical properties of the films is necessary for applications of the films in opto-electronic devices. A considerable theoretical and experimental investigation on the optical behavior of thin films deals primarily with reflection, transmission and absorption properties and their relation to the optical photon incident on any material may be reflected, transmitted or adsorbed. The phenomenon of radiation absorption in a material is altogether considered to be due to—

- inner shell electrons
- Valance band electron

- Free carriers including holes as well as electrons and
- Electron bound to localized impurity centers or defects of some type.

In studies of fundamental property of the semiconductors, absorption by the second type of electron is of great importance. In an ideal semiconductor, at absolute zero temperature, the valence band would be excited to higher energy state from the valence band. Absorption of quanta of sufficient energy tends to transfer of electrons from valence band to conduction band.

For crystalline materials, the transition of electrons from valence band to conduction band can be grouped into direct and indirect process . In direct inter band optical transitions; the value of wave vector K for elements remains unchanged in E-K space and momentum also does not change as shown in figure 2.5(a), while in an indirect inter band transition the wave vector K for electrons changes in the E-K space as shown in figure 2.5 (b)

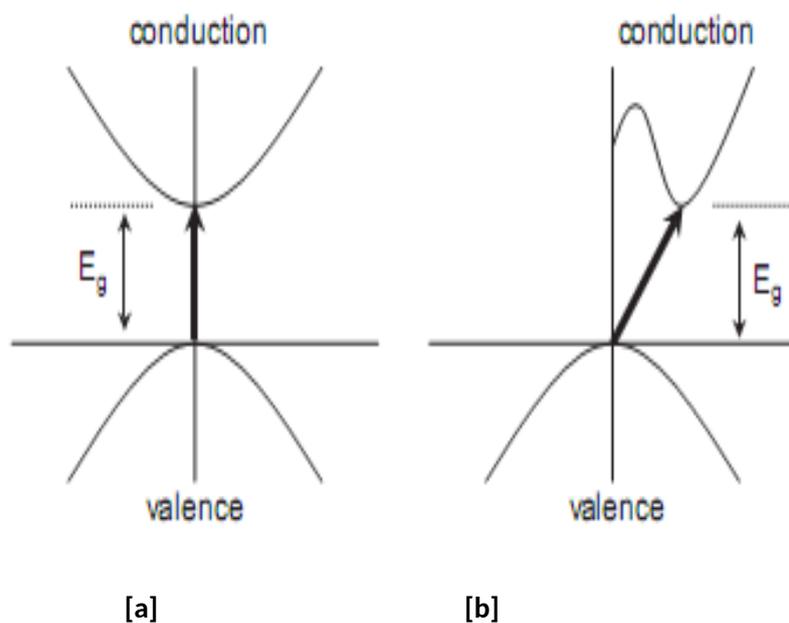


Fig.3.5 Interband optical transition for (a) direct band gap (b) indirect band gap semiconductor

Thus vertical transitions are important when the valence band and conduction band extreme are located at the same point in the Brillouin Zone. For indirect transition, band extreme differs in their positions in E-K space. It is possible to differentiate the nature of optical transition as direct allowed or direct forbidden by using classical relation -

$$\alpha = \alpha_0 (h\nu - E_g)^n / h\nu \tag{2.19}$$

where E_g is separation between bottom of conduction band and top of valance band, $h\nu$ is the photon energy, n is constant. For allowed direct transition $n = 1/2$ and allowed indirect transition $n = 2$. Thus if the plot of $(\alpha h\nu)^2$ against $h\nu$ is linear, then the transition is direct allowed. Band gap energy E_g is determined by extrapolating the linear portion of the curve to the energy axis at $\alpha = 0$

3.5.5 Contact angle measurement:

The contact angle is the angle at which a liquid/vapor interface meets the solid surface. The contact angle is specific for any given system and is determined by the interactions across the three interfaces. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. The shape of the droplet is determined by the Young relation.

$$0 = \gamma_{sv} - \gamma_{sl} - \gamma \cos \theta_c \quad (2.20)$$

Where, θ_c is the equilibrium contact angle, γ_{sv} denoted as the solid-vapor interfacial energy, γ_{sl} as the solid-liquid interfacial energy and γ is the liquid-vapor energy (i.e. the surface tension).

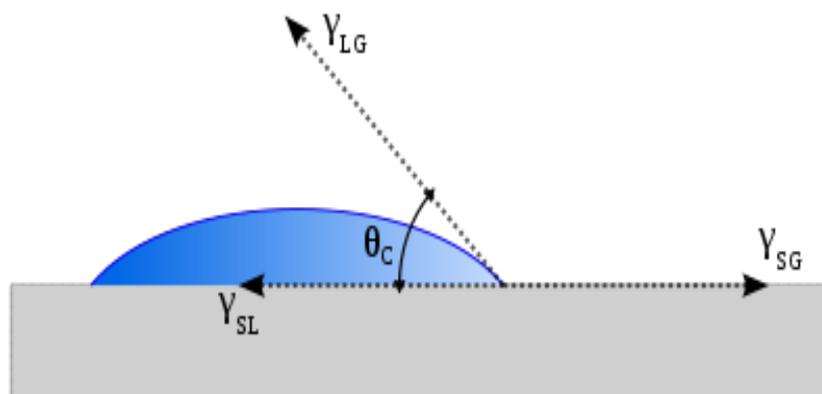


Fig.3.6 A contact angle of a liquid sample.

When a small water drop encounters a solid surface, for example, a raindrop on the hood of a car, a droplet is formed that consists of a sphere of water sectioned by the surface at a discrete, measurable contact angle. If the liquid is very strongly attracted to the solid surface (for example water on a strongly hydrophilic solid) the droplet will completely spread out on the solid surface and the contact angle will be close to 0° . Less strongly hydrophilic solids will have a contact angle up to 90° . On many highly hydrophilic

surfaces (superhydrophilic), water droplets will exhibit contact angles of 0° to 30°. If the solid surface is hydrophobic, the contact angle will be larger than 90°. On highly hydrophobic surfaces (superhydrophobic) the surfaces have water contact angles as high as 150° or even nearly 180°. On such surfaces, water droplets simply rest on the surface, without actually wetting to any significant extent.

$$\rho = (A/d) (V/l) \quad (2.21)$$

In case of semiconducting thin films, resistivity decreases with increase in temperature.

The thermal activation energy 'Ea' can be calculated by using relation,

$$\rho = \rho_0 \exp (-E_a/kT) \quad (2.22)$$

3.5.6 Cyclic voltammetry (CV)

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The potential wave form that is used in electrochemical experiments is the linear waveform i.e., the potential is continuously changed as a linear function of time.

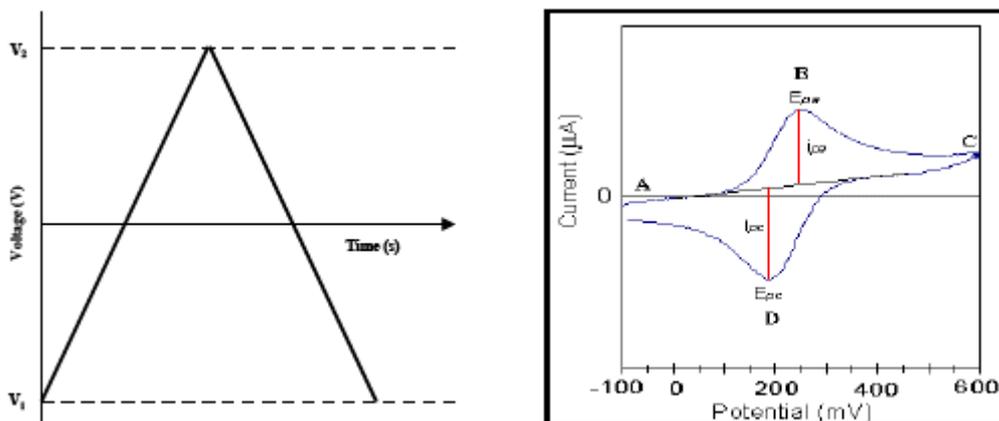


Fig.3.7(a-b) the response of a reversible redox couple during a single potential cycle.

The resulting current versus potential plot is termed a cyclic voltammogram. The Cyclic voltammogram is a time-dependent function of a large number of physical and chemical parameters. In this case the voltage is swept between two values fig.2.7 (a) at a fixed rate, however now when the voltage

reaches **V2** the scan is reversed and the voltage is swept back to **V1**. Here it is assumed that only the oxidized form O is present initially. Thus, a negative-going potential scan is chosen for the first half cycle, starting from a value where no reduction occurs.

As the applied potential approaches the characteristic E° for the redox process, a current begins to increase, until a peak is reached. After traversing the potential region in which the reduction process takes place, the direction of the potential sweep is reversed.



During the reverse scan, R molecules (generated in the forward half cycle, and accumulated near the surface) are reoxidized back to O and an anodic peak results.



The characteristic peaks in the cycle voltammogram are caused by the formation of the diffusion layer near the electrode surface. The basic shape of the current response for a cyclic voltammetry experiment is shown above. At the start of the experiment, the bulk solution contains only the reduced form of the redox couple (R) so that at potentials lower than the redox potential, i.e. the initial potential, there is no net conversion of R into O, the oxidized form (point A). As the redox potential is approached, there is a net anodic current, which increases exponentially with potential. As R is converted into O, concentration gradients are

set up for both R and O, and diffusion occurs down these concentration gradients. At the anodic peak (point B), the redox potential is sufficiently positive that any R that reaches the electrode surface is instantaneously oxidized to O.

Therefore, the current now depends upon the rate of mass transfer to the electrode surface and so the time dependencies qt resulting in an asymmetric peak shape. Upon reversal of the scan (point C), the current continues to decay with a Qt until the potential nears the redox potential. At this point, a net reduction of O to R occurs which causes a cathodic current, which eventually produces a peak shaped response (point D). It is assumed that only the oxidized ionic species O are present initially, the mass transfer under concentration gradient is diffusion controlled and Fick's law of diffusion holds good for both oxidized and reduced ionic species. The redox potentials are predicted by Nernst equation given by,

$$E = E_o + \frac{0.059}{n} \log \left(\frac{C_o}{C_r} \right) \quad (2.24)$$

where,

n is number of electrons transferred,

Co and Cr are concentrations of oxidized and reduced ionic species.

During a negative potential scan (coloration) in the first half cycle, as the applied potential approaches the characteristic reduction potential (Epc), predicted by Nernst equation, the cathodic current attains a peak value (Ipc). At least 90/n mV beyond the peak, the direction of applied potential is reversed. This helps in locating the presence of another reducible species in the bath. During the reverse positive scan (bleaching), the reduced ionic species get oxidized and with similar trend the anodic current attains a peak value (Ipa) at an oxidation potential (Epa). If the redox reaction is reversible i.e maintain the surface concentrations of oxidized and reduced species as per the Nernst equation, the voltammogram is symmetrical otherwise it is asymmetrical.

3.5.7 Galvanostatic charge-discharge

Galvanostatic charge- discharge (GCD) is the standard technique used to test performance and cycle-life of EDLCs and batteries. A repetitive loop of charging and discharging is called a cycle.

Most often, charge and discharge are conducted at constant current until a set voltage is reached. The charge of each cycle is measured and the capacitance C, in farads (F), is calculated,

$$C = \frac{Q}{V} \quad (2.25)$$

Where Q is the charge in coulombs, and V is the voltage window. Both are plotted as a function of cycle number.

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CHAPTER 4

SUMMARY AND CONCLUSION

Summary and Conclusion

There are many methods of thin films preparation, such as chemical bath deposition (CBD), electro deposition, successive ionic layer adsorption and reaction (SILAR). We studied Undoped and doped CuO thin films have been deposited on stainless substrate using SILAR method and films are characterized for their structure, surface morphology properties.

In chapter 1, the general introduction of thin films and various deposition techniques are mentioned and literature survey of CuO and Mn doped CuO is given. Also the purpose of research work is stated in it.

In chapter 2, deals with the theoretical background of SILAR method and details of other different methods for deposition of thin films.

In chapter 3, deals with the details of different characterization of film were carried out by x ray diffraction and field emission scanning electron microscopy (FE-SEM), Energy dispersive study, contact ,Cyclic voltammetry, Galvanostatic charge- discharge technique. For all of these characterization the CuO and Mn doped CuO thin films are deposited on stainless steel substrate.

This implies that Mn-doped CuO is suitable for supercapacitor application.



**Latthe Education Society's
Smt. Kasturbai Walchand College,
Sangli**

**“Synthesis and Characterization of Nickel ferrite Thin
Film By Chemical Bath Deposition Method”**

A PROJECT SUBMITTED TO
SHIVAJI UNIVERSITY, KOLHAPUR

FOR THE DEGREE OF
MASTER OF SCIENCE

IN
PHYSICS

UNDER THE FACULTY OF SCIENCE BY

Mr. Kaustubh Kumar Wadkar

UNDER THE GUIDANCE OF

Dr. M. M.TONAPE

For the Year 2020-2021

CERTIFICATE

This is to certify that the project entitled **Synthesis and Characterization of Nickel ferrite Thin Film By Chemical Bath Deposition Method** which is being submitted herewith for the Degree MASTER OF SCIENCE IN PHYSICS of SHIVAJI UNIVERSITY, KOLHAPUR is the result of the original project work completed by **Mr. Kaustubh Kumar Wadkar** under my supervision and guidance. And to the best of my knowledge and belief the embodied in this project has not formed earlier the basis for the award of any Degree or similar title of this or other University or examining body.

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Dr. M. M.TONAPE

Department of Physics,

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Head of Department

Smt. KWC, Sangli.

DECLARATION BY STUDENT

I hereby declare that the Project entitled “**Synthesis and Characterization of Nickel ferrite Thin Film By Chemical Bath Deposition Method**” completed and written by me has not formed earlier the basis for the award of any degree or similar title of this or any other University or Examining body.

Further I declare that I have not violated any of the provisions under Copyright Piracy/Cyber/IPR Act as and when amended from time to time.

Place: Sangli

Mr. Kaustubh Kumar Wadkar

Date:

Project Student

DECLARATION BY GUIDE

This is to certify that the Project entitled “**Synthesis and Characterization of Nickel ferrite Thin Film By Chemical Bath Deposition Method**” being submitted here with for the award of the Degree of Master of Science in Physics under the faculty of Science SHIVAJI UNIVERSITY , Kolhapur is the result of the original research work completed by **Mr. Kaustubh Kumar Wadkar** under my supervision and guidance and to the best of my knowledge and belief the work embodied in this Project has not formed earlier the basis for the award of any degree or similar title of this or any other University or examining body.

Place: Sangli

Date:

Dr. M. M. TONAPE

Project Guide

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CHAPTER – 1

Introduction and Theoretical Background

1.1 Introduction

Nickel ferrite is considered as one of the most attractive compound among the ferrite phases due to its fundamental chemical and physical properties, its use in energy-storage devices, electrochemical applications, and sensors. In this work, Nano crystalline Nickel ferrite thin films of different thicknesses were deposited on a glass substrate by a simple chemical method i.e. Chemical bath Deposition .

Chemical methods such as chemical bath deposition method (CBD), successive ionic layer adsorption and reaction method (SILAR), electrodeposition etc. are simple, economic and convenient for the deposition of large area metallic oxide thin films. These are low temperature methods and hence avoid oxidation and corrosion of the substrates. The preparative parameters such as concentration, pH, nature of the complexing agent, temperature etc. are easily controllable.

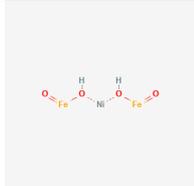
In CBD, the film formation on substrate takes place when ionic product exceeds solubility product.]. chemical solution deposition (CSD), is a method to deposit thin films and nanomaterials, first described in 1869. It can be employed for large-area batch processing or continuous deposition. In 1933 Bruckman deposited lead(II) sulfide (PbS) thin film by chemical bath deposition, or solution growth method. This technique is extensively used to deposit buffer layers in thin film photovoltaic.

The major advantage of CBD is that it requires in its simplest form only solution containers and substrate mounting devices. One of the drawbacks of this method is the wastage of the solution after every deposition. Chemical bath deposition yields stable, adherent, uniform, and hard films with good reproducibility by a relatively simple process. The growth of thin films strongly depends on growth conditions, such as duration of deposition, composition, and temperature of the solution, and topographical and chemical nature of the substrate. Of all the thin film deposition methods, chemical bath deposition (CBD) is the simplest one that offers great scope for large area fabrication. ... This technique has been extensively used for the preparation of NiFe_2O_4 thin films because of its application as a window layer material in Super capacitor Application.

1.2 Literature Survey of Nickel ferrite (NiFe₂O₄) thin Film

Nickel ferrite (NiFe₂O₄) is a well-known among the ferrite because of its properties such as high efficiency, low cost, physical and chemical stability, widespread availability and noncorrosive nature.. hutka,et. al(2010) In the present study ferrites with the spinel-type NiFe₂O₄ (NiF), CoFe₂O₄ (CoF) and hexagonal BaFe₁₂O₁₉ (BaM) structure were obtained using the auto-combusting reaction method.[1]. After the temperature-initiated auto-combusting reaction, different oxide mixtures were obtained. By calcinations of ferrite compounds gives a high level of purity . Auto-combustion reaction temperature was determined by thermogravimetry (TG) analysis. The crystalline phases and their crystallite size were investigated by X-ray diffraction (XRD) analysis.SU Hua, et . NiFe₂O₄ possesses p-type conductivity when the material contains cation vacancies and, consecutively, a corresponding amount of Ni³⁺ will be available at octahedral sites, apart from the cations Ni²⁺, and Fe³⁺, which are located at the octahedral sites. NiFe₂O₄ tend to attract oxygen during heating, and thus it is generally known as p-type semiconductor with cation vacancies It shows ferrimagnetism that originates from magnetic moment of anti parallel spins between Fe³⁺ ions at tetrahedral sites and Ni²⁺ ions at octahedral sites[2] The nickel ferrite in the ultra-fine form exhibit non collinear spin structure and magnetic moment at low temperature is appreciably lower than the value for the bulk material . The magnetic character of the nanoparticles used in various industries depends crucially on the size, shape, purity and magnetic stability (e.g. blocked unblocked state at particular operating temperature). These particles should be in single domain state, of pure phase, having high coercivity and moderate magnetization.[3]

1.2.1 Properties of Nickel ferrite

Nickel ferrite	
Nickel ferrite	
Structure	
Names	
IUPAC names	Nickel ferrite oxonickel
Properties	
Chemical formula	NiFe₂O₄
Molar mass	236.40
Appearance	Blackish
Odour	distinct odour
Density	3.25 g/cm³
Solubility in water	Insoluble
Band gap	2.84 to 2.94 eV

1.3 Purpose of work

Thin Films of NiFe_2O_4 are applicable in vast range of application. Our attempt is to prepare the NiFe_2O_4 nanoparticles by CBD method which is very inexpensive, simple and convenient deposition method and the thickness and other parameters can be easily controlled by this method. The thin film characterization will be studied by using x-ray diffraction, scanning electron microscopy, UV-Visible spectroscopy and contact angle measurement.

The x-ray diffraction will be used to determination of crystal structure; surface morphology of thin film will be studied by using scanning electron microscopy. The UV-VIS spectroscopy is used to determine band gap of thin film. Contact angle is measured by using Goniometer.

1.4 Plan of work

The thin film of NiFe_2O_4 have been deposited on glass substrate by using titanium trichloride and distilled water . using CBD method.

The synthesis will be characterization for the structure analysis using x-ray diffraction, film microstructure will be observed using SEM. UV-VIS spectroscopy used for measurement of optical properties like absorption coefficient and band gap. The contact angle and thickness of thin film will be measured.

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CHAPTER-2

Thin film deposition techniques

2.1 Thin Film: An Introduction

The field of material science and engineering community's ability to conceive the novel materials with extraordinary combination of chemical, physical and mechanical, properties has changed the modern society. There is increasing technological progress. Modern technology requires thin films for different applications. Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behavior of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films.

When we consider a very thin film of some substance, we have a situation in which the two surfaces are so close to each other that they can have a decisive influence on the internal physical properties and processes of the substance, which differ, therefore, in a profound way from those of a bulk material. The decrease in distance between the surfaces and their mutual interaction can result in the rise of completely new phenomena. Here the one dimension of the material is reduced to an order of several atomic layers which creates an intermediate system between macro systems and molecular systems, thus it provides us a method of investigation of the microphysical nature of various processes. Thin films are especially appropriate for applications in microelectronics and integrated optics. However the physical properties of the films like electrical resistivity do not substantially differ from the properties of the bulk material. For a thin film the limit of thickness is considered between tenths of nanometer and several micrometers[1].

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter.

Thin films are formed mostly by deposition, either physical or chemical methods. Thin films, both crystalline and amorphous, have immense importance in the age of high technology. Few of them are: microelectronic devices, magnetic thin films in recording devices, magnetic sensors, gas sensor, A. R. coating, photoconductors, IR detectors, interference filters, solar cells, polarizer's, temperature controller in satellite, superconducting films, anticorrosive and decorative coatings.

Thin films have been used in the study of the relationship between the structure of solid and their physical properties. A thin film is a layer of a material ranging[2] from fraction of a nanometer

to several micrometers in thickness. Thin films have very interesting properties that are quite different from those of the bulk material which they are made of. This is because of the fact that their properties depend on number of interrelated parameters, and also on the technique employed for their fabrication. Practical applications include electrical circuits, optical instruments and magnetic information storage devices. Thickness of thin film is usually discussed in term of Angstrom (\AA).

Thin films are formed by depositing material on a clean supporting substrate to build up film thickness, rather than by thinning down bulk material. An also thin film possesses wide range of applications in both civil as well as military sectors. “When the third dimension of the film that is the thickness on substrate is comparable with the mean free path of the electron in that film, then it is called thin film.” The thin solid films were first obtained by electrolysis in 1838. The conventional bulk material is characterized by three dimensional orders. In which the constructive atoms or molecules find themselves. This order or periodicity is responsible for the structure of the material. In case if thin films, the system possesses at most two dimensional orders or periodicity. The above two applications include their use for protection of material from corrosion, oxidation and wear, increasing transmission or reflection in a certain wavelength region and in filters, color separation, fire-resistance, high temperature superconductors, sectors are also discussed in the monograph. [3]

2.1.1 Properties of Thin Films:-

1. Thin films may not be fully dense.
2. Thin films may be under stress.
3. Thin films have different defects structure from bulk.
4. Thin films are quasi two dimensional.
5. Thin films are strongly influenced by surface and interface effects.

2.1.2 Applications of Thin Film-

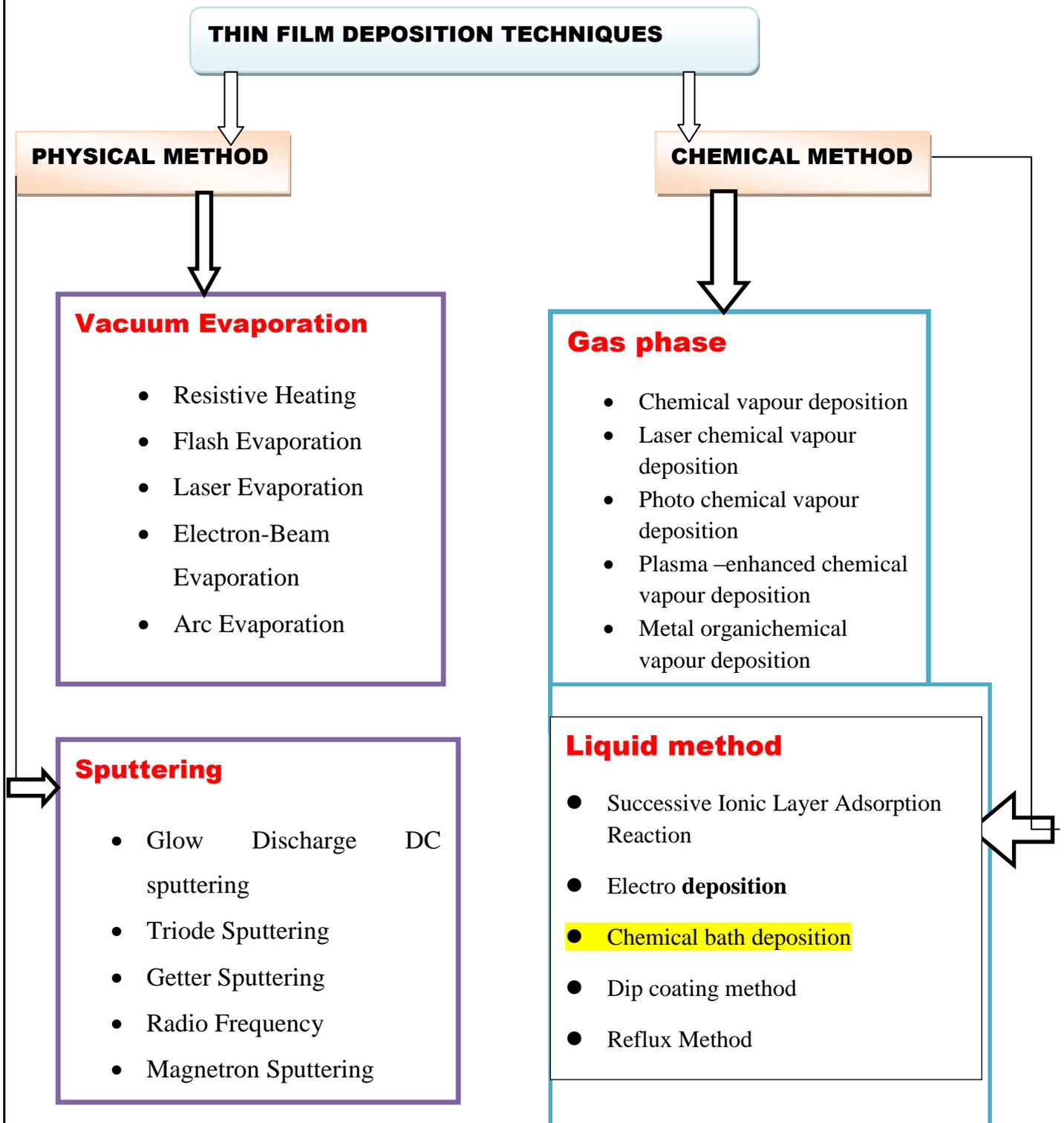
Depending on different properties, thin films have numerous applications in various fields that are tabulated below

Sr. No	Thin film property	Typical applications
1	Electrical	Solar Cell, Semiconductor devices, piezoelectric devices.
2	Optical	Reflective, Antireflective coatings, Decoration, Waveguides.
3	Chemical	Protect against corrosion and oxidation, Barrier to diffusion or alloying. Gas/Liquid sensors.
4	Mechanical	Coating
5	Magnetic	Memory disc

Table No.2.1 Applications of Thin film depending on its properties

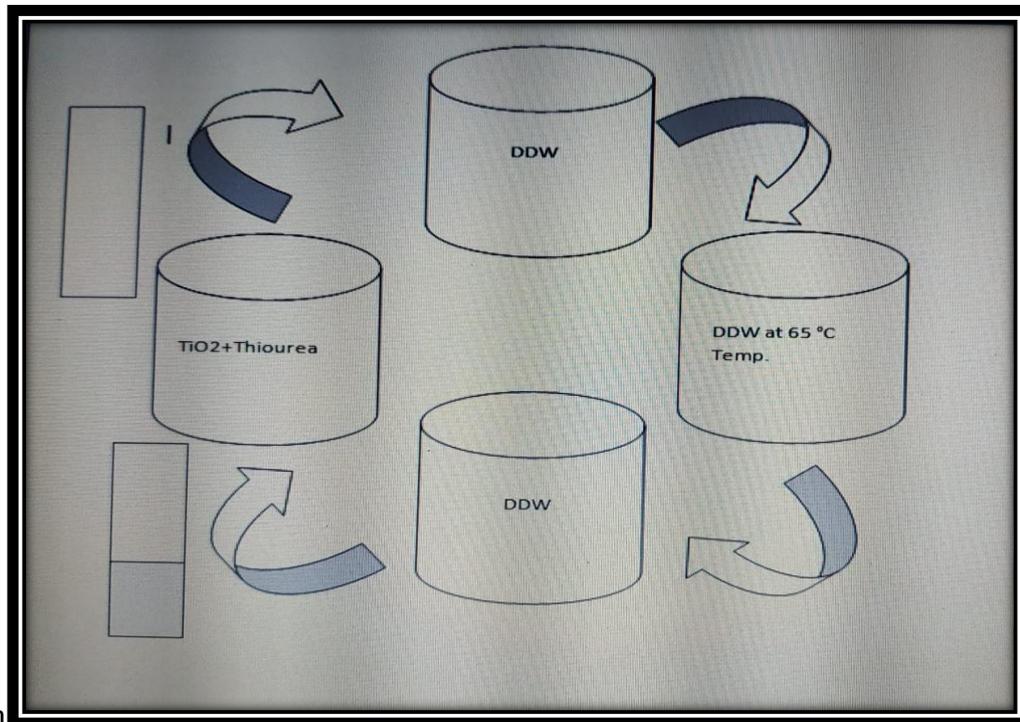
2.2 Thin Film Deposition Methods:

Technological progress of our modern society mainly depends on material science with different extraordinary combination of physical and chemical properties of material. Modern material science study requires thin films for different uses. Thin film can be deposited by various physical and chemical techniques, and can be classified as shown in table. Among these some are explained above.



2.2.1 SILAR Method

The SILAR method is mainly based on the adsorption and reaction of the ions from the solutions and rinsing between every immersion with distilled water (D. W.) to avoid homogeneous precipitation



in the solution

Fig. 2.2.1 Schematic diagram of SILAR method

Thin films have been obtained by adsorbed cations followed by reacting with anion from appropriate precursor solutions. The term adsorption can be defined as a collection of a substance on the surface of another substance, which is the fundamental building block of the SILAR method. Adsorption may be expected when two heterogeneous phases are brought in contact with each other. Hence, gas-solid, liquid-solid and gas-liquid are three possible adsorption systems. In SILAR method, the first step is mainly concerned with adsorption in a liquid-solid system. Adsorption is an exothermic process. The adsorption is a surface phenomenon between ions and the surface of the substrate and is possible due to attractive forces between ions in the solution and the surface of the substrate. These forces may be cohesive or Van-der Waals' or chemical attractive. Atoms or molecules of their kinds on all sides do not surround atoms or molecules of the substrate surface. Therefore, they possess unbalanced or residual force and hold the substrate particles. Thus, adsorbed atoms (ad-atoms) can be holding on the surface of the substrate. In the second step, the adsorbed ion is reacted with anion, resulting in film formation [4].

The SILAR method involves four steps:

1) Adsorption 2) First rinsing 3) Reaction and 4) Second rinsing.

1) Adsorption

In first step of SILAR method, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: first, the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative form the counter ions of the cations.

2) First rinsing

In this step, loosely adsorbed ions are rinsed away from the diffusion layer. This results into saturated electrical double layer.

3) Reaction

In this reaction step, the anions from anionic precursor solution are introduced to the system. Due to the low stability of ions reaction between cation and anion takes place leading to formation of solid phase over substrate.

4) Second rinsing

In last step of SILAR method, the excess and unreacted species and their reaction byproduct from the diffusion layer are removed. In this way, SILAR method culminated through adsorption of cations and reaction of newly adsorbed anions with preadsorbed cations, which leads to formation of thin film of desired material. The factors like temperature of solution, nature of the substrate, pH and concentration of solution, area of the substrate, dipping and rinsing time etc. affect the deposition process.

2.2.2 Chemical Bath Deposition Method

Among the chemical methods of thin film depositions, chemical bath deposition (CBD) is probably the simplest method available for this purpose. The only requirements of these methods are a vessel to contain the solution and the substrate on which deposition is to be carried out. In addition to this various a specific and constant temperature are options that may be useful.

The mechanism of CBD method contains following types,

1. Simple ion by ion mechanism.
2. Simple Cluster (hydroxide) mechanism.
3. The complex decomposition ion by ion mechanism.
4. The complex decomposition cluster mechanism

The chemical bath deposition method is one of the cheapest method used to deposit thin films and prepare nanomaterial and is employed for large area batch processing or continuous deposition . Chemical deposition techniques are relatively low cost process and can be easily scaled up for industrial applications . Most of the chemical bath consists of one or more metal salts , source for the chalcogenide X (X = S Se Te) and typically a complexing agent , in an aqueous solution M^{n+}

Prepartive parameter :-

1. Nature of Substrate :-

The substrate plays major role in reaction kinetics and in the adhesion of deposited film . Hence cleaning of substrate is first important step in the film deposition rate and terminal thickness is obtained . When lattice parameter of substrate and deposited material match well with each other .

2. Temperature of solution :-

It is another parameter which influences the rate of reaction the increasing temperature of solution both dissociates complex more efficiently . Therefore kinetic energy of molecules also increases leading to greater interaction ion . This is results in increase or decrease in terminal thickness depending on strength of supersaturation solution .

3. Complex agent:-

In CBD method most of deposition is carried out in alkaline solution . Therefore to prevent precipitation of metal hydroxide complexing agent is added . It helps to reduce the concentration of free metal ions in both solutions , which avoids the rapid bulk concentration formation of desired product . The concentration of free metal ions decreases with increase in concentration of complexing agent . Subsequently rate of reduces that leads to larger terminal thickness .

2.2.3 Electrodeposition Method

Electrodeposition is process of depositing metal atoms on a conducting substrate by passing direct current through solution containing the metal ions to be deposited. The typical Electrodeposition set up consists of following,

1. Electrolyte
2. Cathode and Anode
3. Source of electricity

When direct current is passed through cathode and anode, immersed in electrolyte containing the metals ions, the metal ions get attracted towards the cathode, neutralized electrically by receiving electrons and get deposited on cathode. The deposition is controlled by monitoring the amount and the rate of charge passing through the electrolyte. Thus the electrical energy is used to cause chemical change.

2.2.4 Dip Coating Method:-

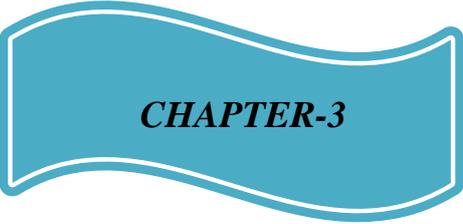
Dip Coating is with no doubt the easiest and fast method to prepare thin films from chemical solutions with the highest degree of control, making it highly appropriate for small scale production. In specific high technology cases, it is used to deposit coating on large surfaces.

The principle is as simple as dipping the substrate into the initial solution before withdrawing it at a constant speed. During which the solution naturally and homogeneously spreads out on the surface of the substrate by the combined effects of viscous drag and capillary rise. Evaporation then takes over and leads to solidification of the final coating.

Fig.2.2.5 Schematic diagram of SILAR meth

2.3 References:-

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CHAPTER-3

Thin Film Characterization Techniques

Characterization Techniques:-

Recently nanostructured semiconducting materials are synthesized by different physical and chemical methods. The structural and electronic, optical properties are mainly depends on type of preparation method of thin film. Once the synthesis of an appropriate material is done, the first goal is to perform the characterization of particular material. In order to perform this in systematic way, one needs a diverse array of characterization technique. In this chapter we discussed some important characterization techniques which includes the basic principle of the characterization techniques in brief,

- X-Ray diffraction technique (XRD)
- Scanning electron microscopy (SEM)
- Ultra violet visible spectroscopy (UV-Vis)
- Contact angle measurement

The details of these method discussed in subsequent sections.

3.1 X-ray Diffraction:-

X-ray diffraction has been use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a fingerprint or identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and material science.

We can determine the size and the shape of the unit cell for any compound most easily using X-ray diffraction.

Why XRD?

1. Measure the average spacing's between layers or rows of atoms.
2. Determine the orientation of a single crystal or grain.
3. Find the crystal structure of an unknown material.
4. Measure the size, shape and internal stress of small crystalline regions[1].

3.1.1 Bragg's Law:-

English Physicists Sir W. H. Bragg and W. L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-rays beam at certain angles of incidence (Θ). The variable d is the variable between atomic layer in a crystal and the variable λ is the wavelength of incident X-ray beam; in an integer. This observation is an example of X-ray wave interference.

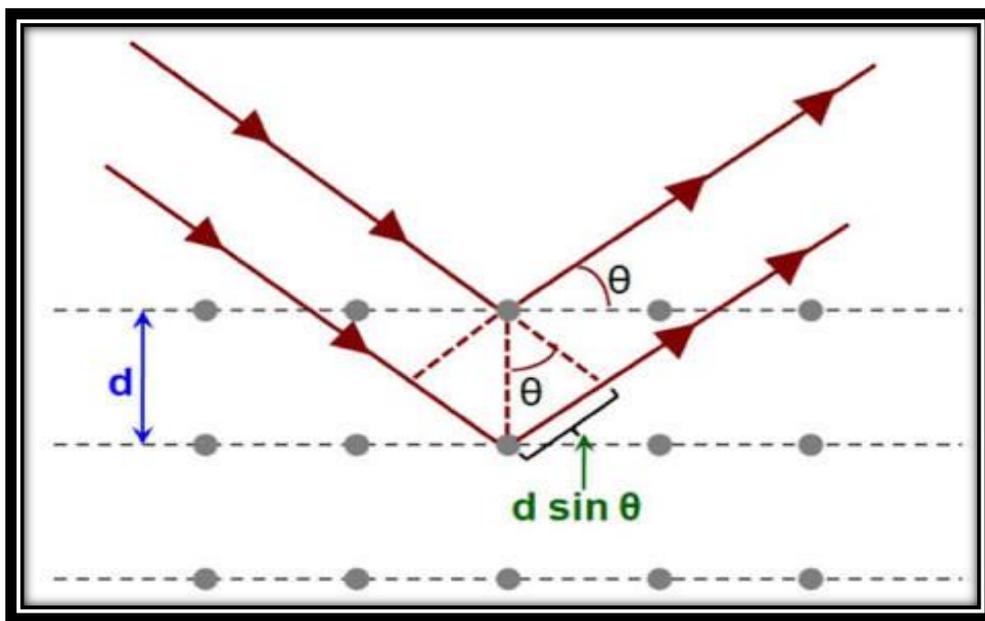


Fig4.1:- Reflection of X-rays from two planes of atoms in a solid

$X = d \sin(\Theta)$The path difference between two waves

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

This is Bragg's Equation

3.1.2 Powder Method or Debye – Scherrer Method:-

When single crystal is not available, a simple technique may be used. The crystalline material is ground to a powder which then presents all possible orientations to a collimated X-rays beam consisting primarily of $K\alpha$ radiation.

The experimental apparatus is schematically drawn in fig.

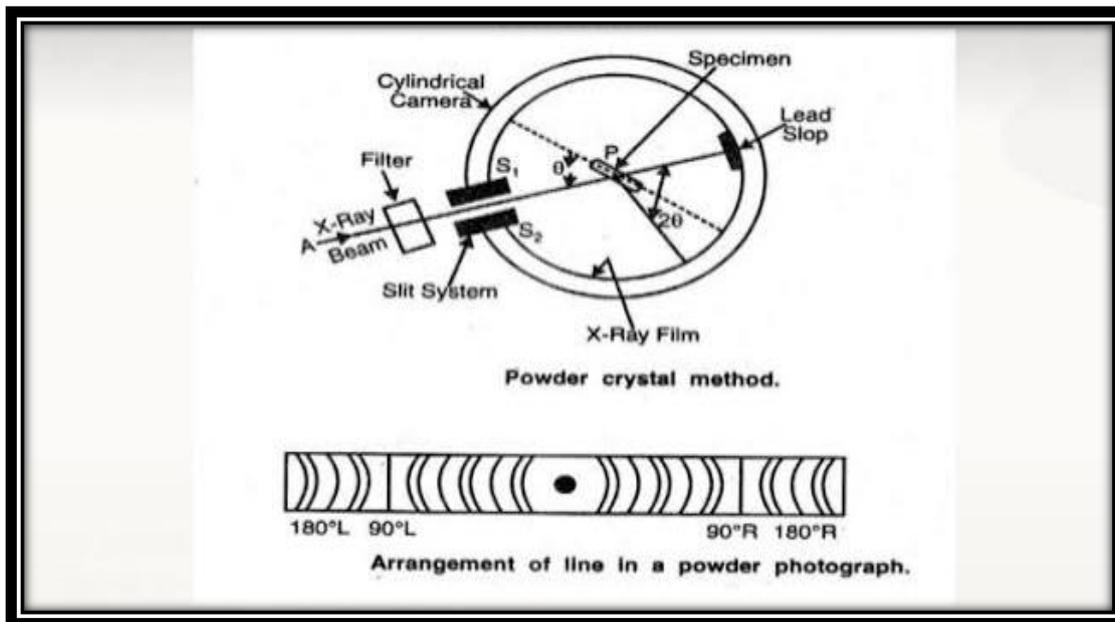


Fig4.2:- Schematic representation of the X-ray Powder technique

If the crystals used are too coarse, the arcs in the powder pattern will appear specked instead of as firm lines. In this technique the powder may be composed into a rod sample when the tiny crystals have different orientations, and therefore possibility of interference which depends on the ratio of λ , d and Θ greatly increases. Because of this instead of individual spots whole series of spots are obtained on a stretched film these arcs appear as showing fig. The distances between symmetrical lines are designated as l_1, l_2, l_3 etc. And the diameter of the cylindrical film as D_1 the relation[2],

$$\Theta = \frac{90}{\pi D} \times l$$

OR

$$\Theta = K.l$$

Where, K is a constant factor for a particular chamber.

3.2 Scanning Electron Microscopy:-

Principle

In technique, an electron beam is focused onto sample surface kept in a vacuum by electro-magnetic lenses (since electron possesses dual nature with properties both particle and wave, hence an electron beam can be focused or condensed like an ordinary light). The beam is rastered and scanned over the surface of the sample. The scattered electrons from the sample are then fed to the detector and then cathode ray through an amplifier, where the images are formed, which give the sample image. The scanning electron microscope (SEM) is used for observation of specimen surface. The scanning electron microscope (SEM) is used for observation of specimen surface.

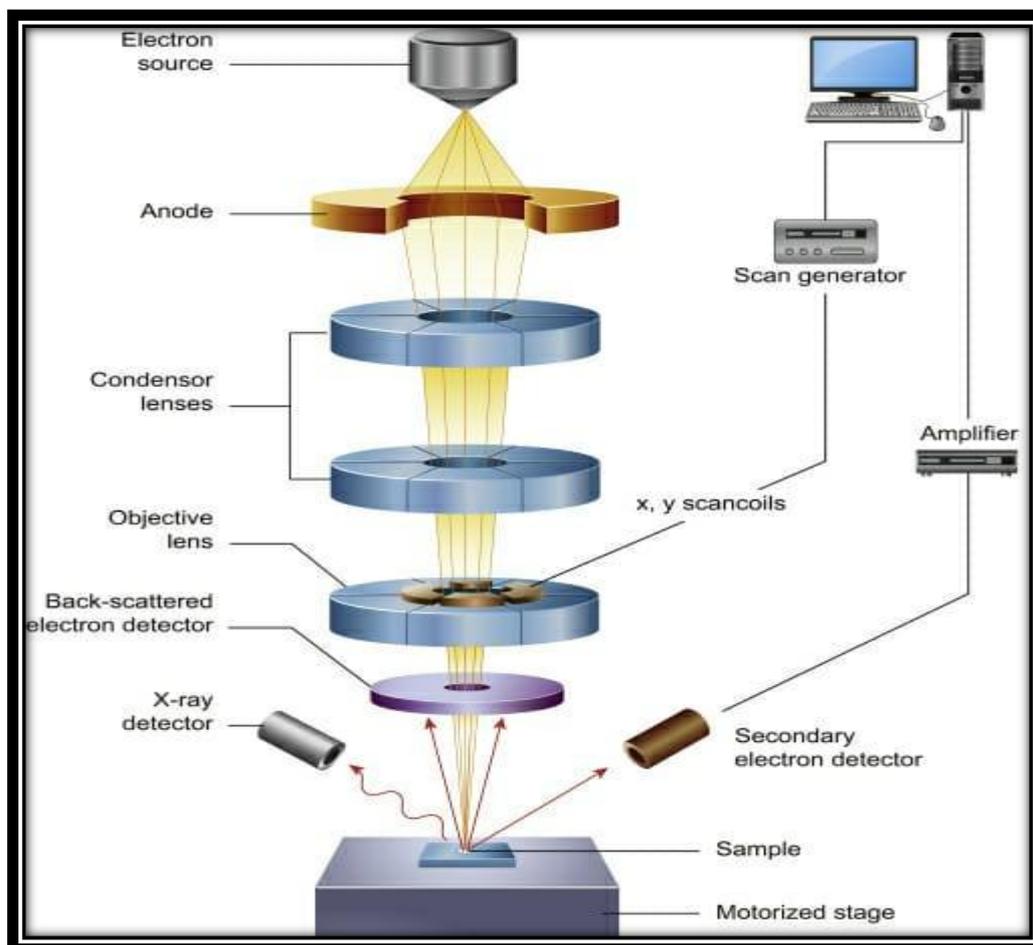


Fig 3.3 Scanning Electron Microscopy

Working of SEM:

1. The Electron Gun:-

Thermoelectrons are emitted from a filament (cathode) made of a thin tungsten wire by applying a voltage (1 to 30 Kv) .The electron beam passes through anode.

2. Construction of Lens:-

An electron microscope generally uses a magnetic lens. The main feature of the magnetic lens is that when you change the current passing through the coil, the strength of the lens is also changed .This is not achieved by an optical lens[3].

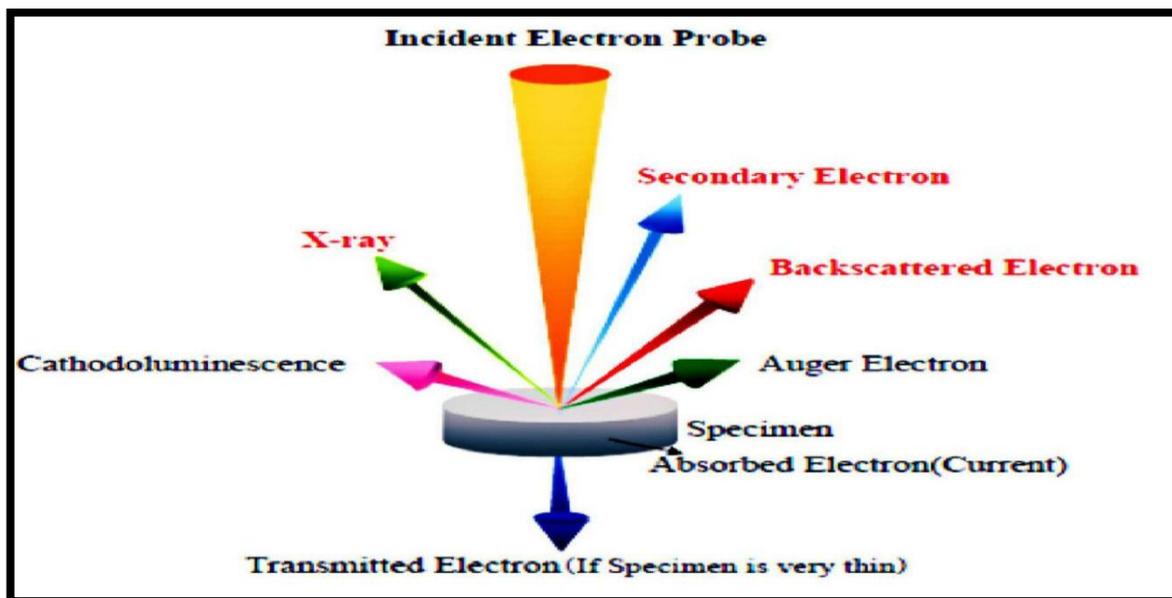


Figure 3.4: The signals are transferred from point to point and signal map of the scanned area is displayed on a long persistent phosphor

3. Scanning Coil:-

Magnification is controlled by current supplied to x,y scanning coils or voltage supplied to x,y deflector plates not by objective lens power.

Scanning coil is set of lenses which are moving the beam with very high precession. The beam passes through pairs of scanning coils deflects beam in x and y axes so that it scans in a raster fashion over rectangular area of the sample surface. As a result of the electron-sample interaction a no. of signals are produced. These signals are then detected by appropriate detectors.

As electrons interact with the sample, they produce secondary electrons, backscattered electrons, Auger electrons, and characteristic X-rays. These signals are collected by appropriate detectors to form image which are then displayed on the computer screen.

Advantages of SEM

1. The detailed three-dimensional and topographical imaging and the versatile information garnered from different detectors.
2. SEMs are also easy to operate with the proper training and advances in computer technology and associated software make operation user-friendly.
3. This instrument works fast, the technological advances in modern SEMs allow for the generation of data in digital form.
4. Although all samples must be prepared before placed in the vacuum chamber, most SEM samples require minimal preparation actions

3.3 UV-Visible Spectroscopy:-

Ultraviolet- visible spectroscopy or ultraviolet-visible spectroscopy is the measurement of the attenuation of a beam of light it passes through a sample or after reflection from a sample surface

Principle of Ultraviolet-visible spectroscopy:-

Ultraviolet absorption spectra obtained from transition of electron within a molecule from a lower level to a higher level. A molecule absorbs ultraviolet radiation of frequency (ν). Molecules containing π -electrons or non-bonding electrons can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons the longer the wavelength of light it can absorb.

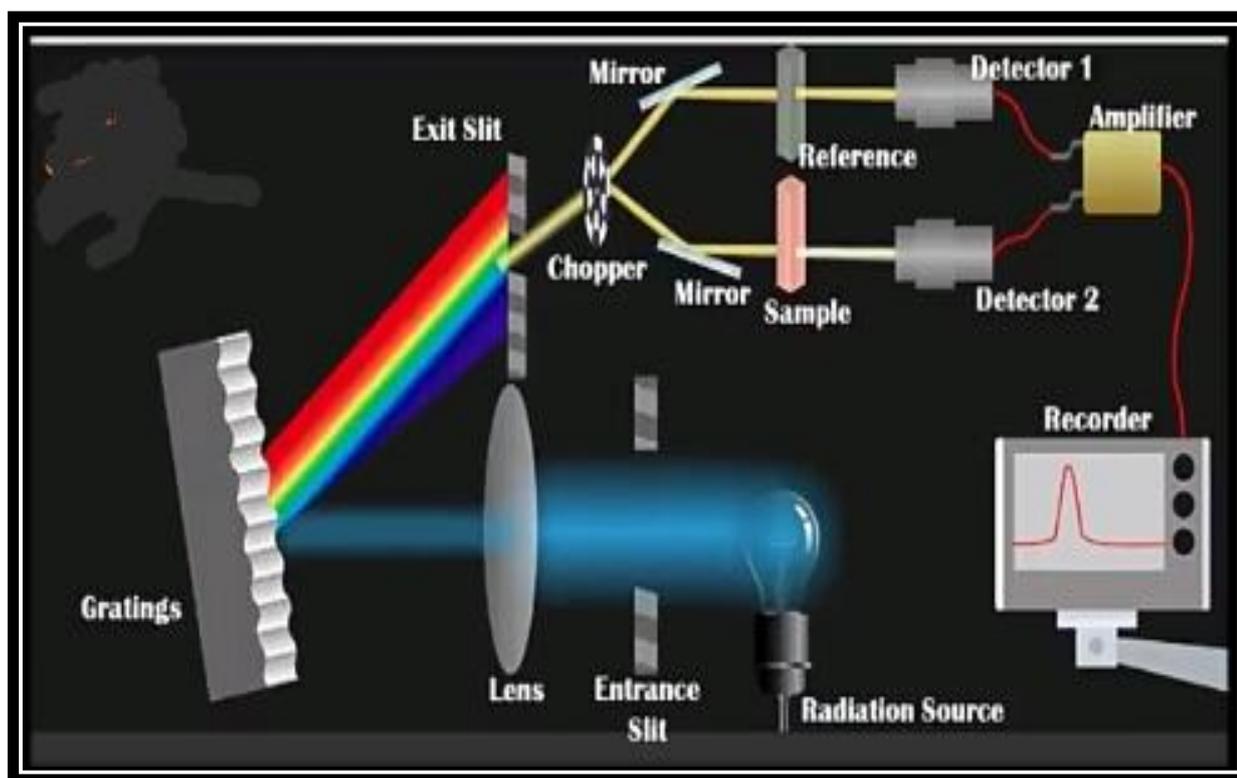


Fig3.5:- UV-Visible spectroscopy

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. The radiation source is often a tungsten filament, a deuterium arc lamp, which is continuous over the ultraviolet region light emitting diodes for the visible wavelength. The detector is typically a photomultiplier tube, photodiode[4].

Single photodiode detectors and photomultiplier tubes are used with scanning monochromator, which filter the light so that only light of a single wavelength reaches the detector at one time.

The scanning monochromator moves the diffraction grating to “step-through” each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromator are used with charge-coupled device and photodiode arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelength on different pixels or groups of pixels simultaneously.

Ultraviolet-Visible Spectrophotometer:-

The instrument used in ultraviolet-visible spectroscopy is called a UV-Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through a sample (I₀). The ratio (I/I₀) is called the transmittance, and is usually expressed as a percentage (%T).

The absorbance ‘A’ is based on the transmittance:

$$A = - \log (\%T / 100\%)$$

The UV-visible spectroscopy can also be configured to measure reflectance. In this case, the spectrophotometer measures the intensity of light reflected from a sample (I), and compares it to the intensity of light reflected from a reference material (I₀). The ratio (I/I₀) is called the reflectance, and is usually expressed as a percentage (% R).

Why we use UV Spectroscopy?

- 1) Detection of band gap.
- 2) Detection of functional groups.
- 3) Detection of impurities
- 4) Qualitative analysis.
- 5) Single compound without chromophore.
- 6) It is help to show the relationship between different groups, it is useful to detect the conjugation of the compound.

Application UV spectroscopy: –

- 1) UV spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds and biological macromolecules, spectroscopy analysis is commonly carried out in solutions but solids and gases may also be studied.
- 2) Solutions of transition metal ions can be colored (i.e. absorb visible light) because electron within the metal atoms can be excited from one electronic state to another.
- 3) Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of electromagnetic spectrum.
- 4) While charge transfer complex also give rise to colors, the colors are often too intense to be used for quantitative measurement[4].

3.4 Contact Angle Measurement:-

Principle:-

The wettability property of a solid surface is one of the most important aspects in both theoretical research and industrial application. One of the fundamental methods of characterizing the hydrophobic properties of a solid surface is to determine the contact angle. The contact angle on the solid surface gets changed nearly by changing the chemistry of the outermost monolayer. Atoms on the surface have higher energy than those within the bulk, so there is energy associated with the existence of any interface.

Working:-

When the specific energy (J/m^2) of the solid-vapor interface, γ_{SV} , is greater than that of the solid-liquid interface γ_{SL} , liquid tends to flow over an exposed solid surface. When a small liquid droplet is put in contact with flat solid surface, distinct equilibrium regions may be found like partial wetting, the wetted portion of the surface is determined by certain contact line. A layer of liquid on a plane solid surface has two interfaces, solid-liquid line, A layer of liquid on a plane solid surface has two interfaces, solid-liquid ' γ_{SL} ' and liquid-vapor ' γ_{LV} ' so the change in energy (ΔE) produced by spreading of the liquid film is :

$$\Delta E = \gamma_{SL} + \gamma_{LV} - \gamma_{SV} \quad \dots\dots\dots (1)$$

If $\Delta E < 0$ the energy of the system is reduced so that the liquid will spread spontaneously (i.e. $\gamma = 0$), otherwise the solid-liquid-vapor will be characterized by a finite contact angle. The balance of the tensions at the point of interaction leads to a relationship between the surface tension that is known as Young's equation.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \gamma \quad \dots\dots\dots (2)$$

Hydrophobicity of the thin films was tested in terms of contact angle (γ) of the water droplet with the surface, using the formula.

$$\gamma = 2 \tan^{-1} (2h/b)$$

Where, h is the height

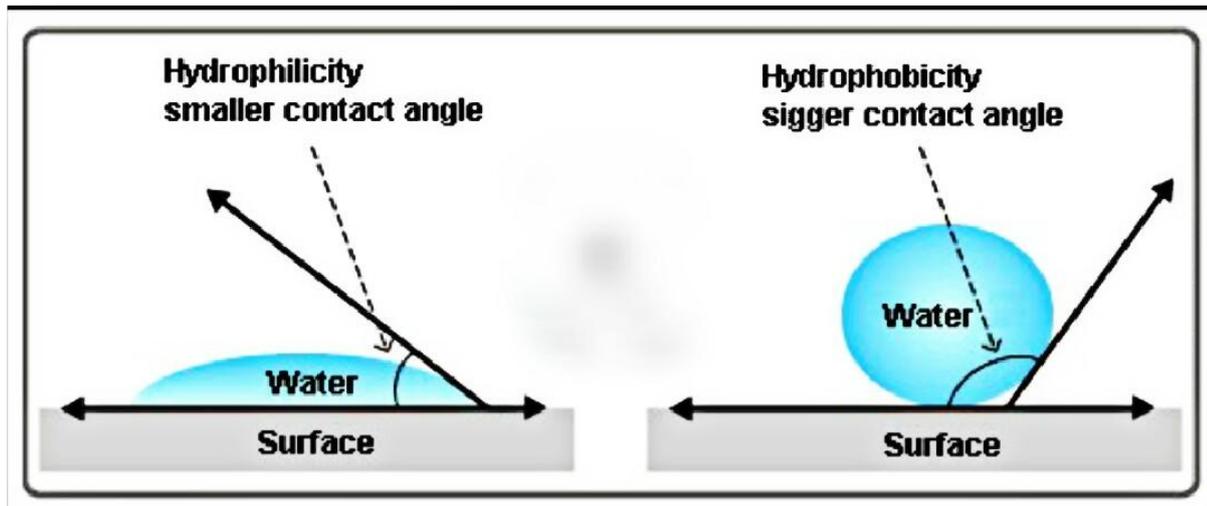


Fig 4.6 :- Interfacial tensions at the three phase contact line

Direct measurement by telescope-Goniometer:-

The most widely used technique of contact angle measurement is a direct measurement of the tangent angle at the three phase contact point on a scale drop profile.



Fig. 3.7:- Telescope Goniometer setup

Over the years, modification of the equipment have been to improve the accuracy and precision. A camera can be integrated to take photographs of the drop profile so as to measure the contact angle at leisure. The use of relatively high magnification enables a detailed examination of the intersection profile. A motor driven syringe can be used to control the rate of liquid addition and removal to study advancing, receding, or dynamic contact angles[5].

3.5 Fourier transform infrared:-

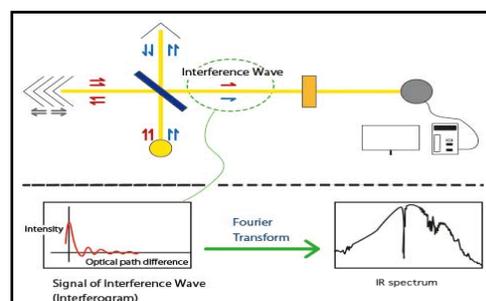
FTIR stands for Fourier transform infrared, the preferred method of infrared spectroscopy. When IR radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted). The resulting signal at the detector is a spectrum representing a molecular 'fingerprint' of the sample. The usefulness of infrared spectroscopy arises because different chemical structures (molecules) produce different spectral fingerprints.

The FTIR uses interferometry to record information about a material placed in the IR beam. The Fourier Transform results in spectra that analysts can use to identify or quantify the material.

- An FTIR spectrum arises from interferograms being 'decoded' into recognizable spectra
- Patterns in spectra help identify the sample, since molecules exhibit specific IR fingerprints

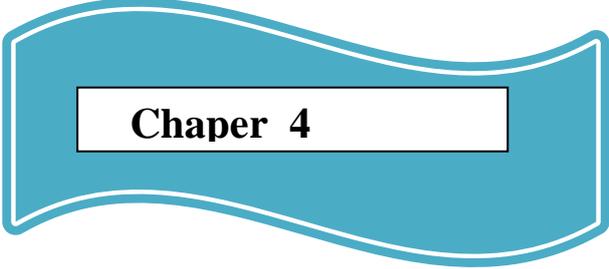
There are four major sampling techniques in FTIR:

- Transmission
- Attenuated Total Reflection (ATR)
- Specular Reflection
- Diffuse Reflectance



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Chaper 4

SUMMARY AND CONCLUSION

Summary and Conclusion

In the field of material research one is often confined with problem of material preparation and in order to reduce cost,a relative simply method is needed to able to assess quickly the various physio- chemical properties of material.

Preparation of the material in thin film relatively easy and less expensive as compared to that of growing in a single crystal.There are many method of thin film preparation,such as Electro deposition,spray pyrolysis, and so many high cost physical methods. Out of these methods CBD is relatively simple,low cost and can be use for preparation of large area thin film.

In the present work, cadmium sulfide film have been deposited using simply CBD and film are characterized of prepared thin film is carried out using XRD,SEM,Angle of contact and UV-Visible Spectroscopy

These work carried out is divided into three chapters.

Chapter-1

The general introduction of thin film and general survey of deposited NiFe_2O_4 thin film is given. The purpose of project and plan of work is also stated there in this chapter.

Chapter-2

It deals with theoretical background of thin film deposition technique.

Chapter-3

In this chapter different characterization with working and principle were studied. In which XRD study was carried out. SEM micrograph reveals chemical composition of thin film, UV-Visible reveals band gap energy and surface wettability test shows angle of contact.