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Shri Swami Vivekanand Shikshan Sanstha's

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Department of Physics

M.Sc. II (2019-20)

Research Project Title

Roll No.	Name of Students	Name of Guide	Title of Project
1701	Bote Sushant Suresh	Prof. S. V. Malgaonkar	Synthesis and Characterization of Nickel Ferrite by Microwave combustion method
1702	Deshmukh Aishwarya Ramesh	Dr. M. M. Karanjkar	Preparation of Magnesium Cadmium Ferrite by Sintering method
1703	Deshmukh Mahesh Baburao	Prof. S. V. Malgaonkar	Synthesis and Characterization of MgCd Ferrite by Microwave combustion method
1704	Jadhav Amit Ashok	Prof. S. V. Malgaonkar	Preparation of Ni-Zn Ferrite by Microwave Assisted Combustion method
1705	Jadhav Shivprasad Kiran	Prof. S. V. Malgaonkar	Preparation of Mg-Zn Ferrite by Microwave Combustion method
1706	Kadam Ketki Prakash	Dr. M. M. Karanjkar	Preparation of Nickel Cadmium Ferrite by Sintering method
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1709	Nirmale Pooja Ganesh	Dr. M. M. Karanjkar	Synthesis of Zinc Ferrite by Sintering Technique
1710	Patil Ashutosh Madhkar	Dr. M. M. Karanjkar	Preparation of Ni-Zn Ferrite and Structural Study
1711	Patil Asmita Viraj	Dr. M. M. Karanjkar	Synthesis of Cuo thin film by Reflux Method
1712	Patil Manisha Aniruddha	Dr. M. M. Karanjkar	Synthesis of Polyaniline thin film by CBD method

1713	Patil Swati San•a	Dr. M. M. Karanjkar	Thin Film by MnO_2 by Silar method
1714	Patole Anuradha Vilas	Dr. M. M. Karanjkar	Synthesis of CuO thin film By Hydrothermal Technique
1715	Phadatare Dhanshri Chandrakant	Dr. G.J. Navathe	Synthesis of MnO_2 as Supercapacitor by Electrodeposition method
1716	Patil Pranit Gunvant	Prof. S. V. Malgaonkar	Synthesis and Characterization of MgCd Ferrite by Microwave combustion method
1717	Sherala Dinesh Naresh	Dr. S. I. Inamdar	Study of ZnO thin films using spray pyrolysis technique for gas sensing application
1718	Shinde Amruta Chandrashekhar	Dr. M. M. Karanjkar	Thin film deposition of MnO_2 as supercapacitor by using chemical bath deposition
1719	Tamboli Asif Jahangir	Dr. M. M. Karanjkar	Preparation of Fe_2O_3 by Silar method
1720	Tamke Vaishnavi Ramchandra	Dr. M. M. Karanjkar	Preparation of Magnesium Cadmium Ferrite by Sintering method

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VIVEKANAND COLLEGE KOLHAPUR (Autonomous) ESTD JUNE 1964

PREPARATION OF FE_2O_3 BY SILAR METHOD

A Dissertation Report Submitted to

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For the Partial Fulfillment of

Degree of Master of Science

In

PHYSICS

Under the Faculty of Science

by

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2019-2020

DECLARATION

I hereby declare that, the project entitled "PREPARATION OF FE_2O_3 BY SILAR METHOD" completed and written by me has not previously formed the basis for the award of any Degree or Diploma or other similar title of this or any other University or examining body.

Place: Kolhapur

Date: 11/09/2020.

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CERTIFICATE

This is to certify that the project entitled "PREPARATION OF FE_2O_3 BY SILAR METHOD" which is being submitted herewith for the award of the Degree of **Master of Science** in **Physics** of **Vivekanand College (Autonomous), KOLHAPUR,** is the result of the original project work completed by **Mr. ASIF JAHANGIR TAMBOLI** under our supervision and guidance and to the best of our 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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Mr. ASIF JAHANGIR TAMBOLI.

M.Sc. II (Physics)

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CHAPTER :- 1

1. Introduction And Theoretical Background

Various mathods and relative technology for preparing thin film can described for research and development . Thin film means the layer of the material. The range of the thickness of material is very few nanometer to micrometer. Thin film deposioin techniques are relavent to change the physical properties of the surface by using very thin layer. By using thin film we can modify the optical properties of substrate and also its electrical conductivity. Advanced thin film technology can be used in many fields like optical instrument, flat display pannel, microcircuits, biomedical devices, solar cell sensors. There are many deposition techniques that offers fabrication of micro and nanoscale devices. In all these techniques, SILAR was very much simple, priseless, and much convinient for large area deposition. The thin films established by using the SILAR method is characterised by means of structural, optical and electrical measurements, surface morphological.

- **THIN FILM DEPOSITION METHODS :-**

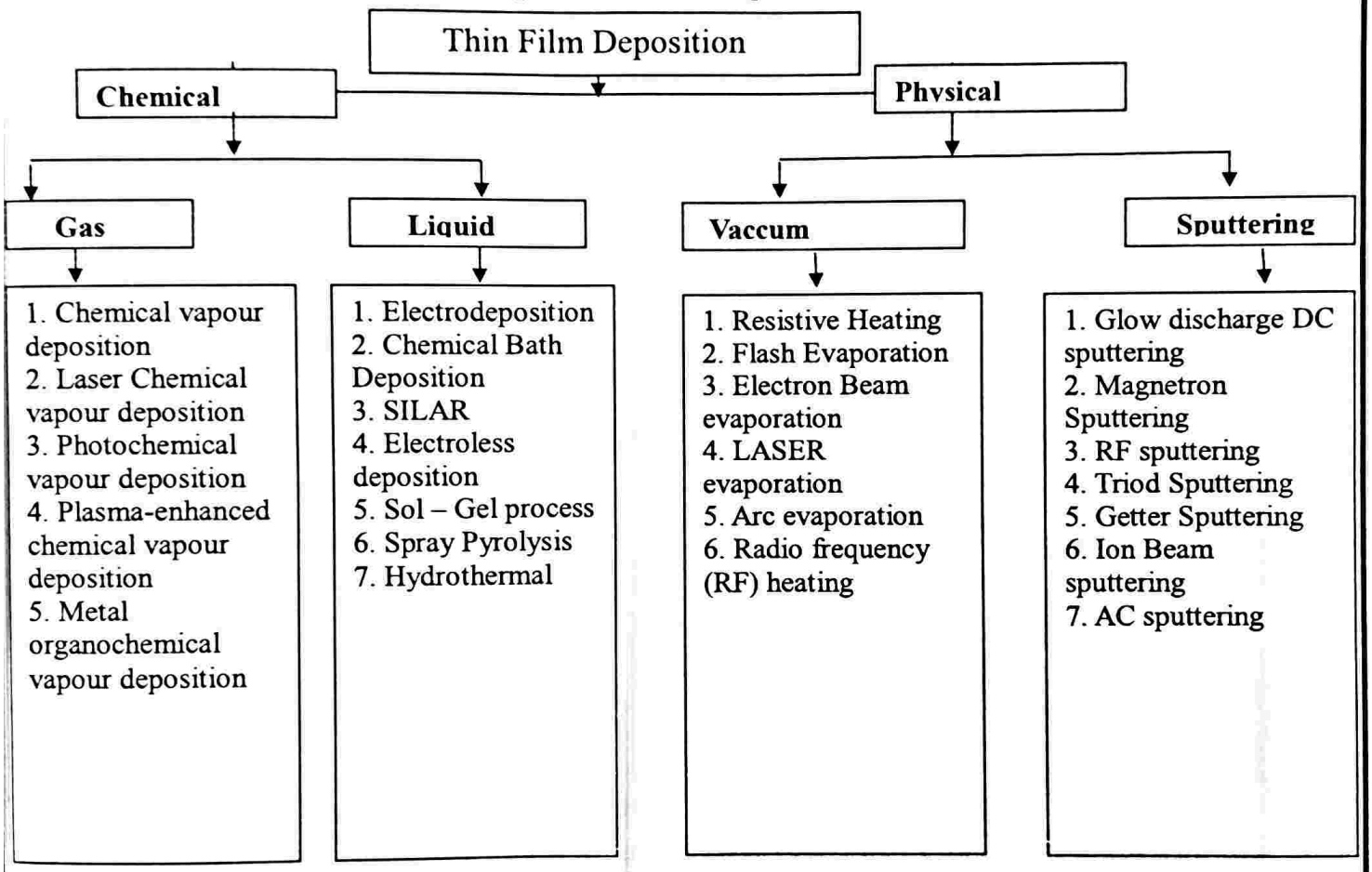
There are mainly two types of deposition methods,

1] PHYSICAL METHOD.

2]CHEMICAL METHOD.

They also have many sub methods as shown below

Deposition Techniques



- **PHYSICAL METHOD :-**

A] GAS PHASE :-

1] CVD :-

CVD stands for Chemical Vapor Deposition. CVD is very simple very useful technique in thin film deposition.we get the depotion on substrate by using the vapor of chemical. In CVD, variety of materials, compounds and elements are used on various variety of substrate. It offers many of advantages than the othe techniques of deposition. Main application of CVD is in semiconductor integrated electronic circuits.

2] MOCVD :-

MOCVD means Metal Organic Chemical Vapor Deposition. By using this technique we can deposited very thin layer on the substrate. We can produce polycrystalline thin films by using MOCVD.

3] PECVD :-

PECVD stands for Plasma Enhanced Chemical Vapour Deposition. It is versatile technique for depositing wide variety of thin film materials. PECVD of thin film material has many reactor designs and different expriemental conditions. The primary role of the plasma is to promote chemical reaction.

4] LCVD :-

Now a day Laser Chemical Vapor Deposition technique is developed. In this technique deposite the material by using laser. LCVD Is modification of convetional CVD. The chemical reaction which is initiated by the laser beam for the deposition has mainly two mechanisms, which are photolysis and pyrolysis.

- **B] LIQUID PHASE :-**

1] SILAR :-

SILAR stands for Successive Ionic Layer Adsorption and Reaction. Its is based on the adsorbtion and reaction of ions. The operations to deposite thin film by SILAR method is cations are adsorbed, then rinsing with the distilled water, then reaction between adsorbed cations and anions, and then again rinsing with the double distilled water.

2] CBD :-

CBD means Chemical Bath Deposition. It is also called as solution growth. It dose not reqired sophisticated materials. It is low budget ans simple method. This methos has beakers, hot plate, temperature sensor.

3] Spray pyrolysis :-

Spray pyrolysis is very simple and useful deposition technique, that we can deposited broad range of thin films. By using spray pyrolysis we can deposit nano thin films. In this process, films are deposited by spraying a solution on hot plate.

- **PHYSICAL METHOD :-**

Vacuum evaporation is mainly divided into two parts,

A] VACUUM EVAPORATION.

B] SPUTTERING.

A] VACUUM EVAPORATION :-

1] ELECTRON BEAM EVAPORATION :-

In electron beam evaporation, electron beam accelerate to the material to convert it into vapor for a deposition. When electrons incident on the surface of matrial then electrons lose their energy rapidly then material melts and evaporate. Electron gun can be classified into two categories which are thermionic and plasma electron. In this mathod liquid cooled crucible is used.

2] LASER EVAPORATION :-

In laser evaporation, to vaporise the evaporant material the thermal source is used which is laser. High vacuum technique is used for the preparation of thin films by laser evaporation, where the source is at outside the vacuum system. The substrate for the deposition is placed in front of the material inside the chamber. Laser evaporation has many advantages.

3] RADIO FREQUENCY (RF) HEATING :-

In this method a cruicible is used which is support crucible. In RF heating, material inside the cruicible which has RF coils around the crucible. This mathod is much expensive and want heavy equipment. The evaporation rate of evaporant is much difficult to control so this method is not commonly used for preparation of the thin film.

4] FLASH EVAPORATION :-

In flash evaporation, evaporant material is in powder form. We can take two or more materials deposion in this method. The materials which are in powder form ans present in small quantities is dropped at the heated boat and evaporate. The temprature of the hot boat is set at the large melting point of that material which deposited.

B] SPUTTERING :-

1] GLOW DISCHARGE DC SPUTTERING :-

The arrangement of this method is very simple than other. This system is at the vacuum chamber. In this chamber neutral gas is present and glow amd discharge is iniciated. In chamber there is only anode and substrate is used. The pressure in vacuum chamber is about 10^{-1} to 10^{-2} torr. The plate of substrate is connected to the negative voltage supply.

2] ION BEAM SPUTTERING :-

In ion beam sputtering, ion source produce ion beam. Thin beam was extracted into the high vacuum system by extraction voltage then it goes to target of the material, which is sputter and deposit on substrate. From the ion production process, greater isolation of substrate allows by ion beam sputtering. Ion beam sputtering has accurate scanning and focusing. In this process, energy and current of ion bean can be controlled. Mainly the kaufman and duoplasmatron are the sources which is used for the ion beam sputter deposition.

3] TRIOD SPUTTERING :-

In this method, there are plates which is substrate, anode and target. Also the coils are placed at both the side of the system. All the plates are placed inside the vacuum chamber. Also the filament is present in it. Which is produce the electrons. For good deposition filament is very important.

4] RF SPUTTERING :-

RF sputtering means Radio Frequency sputtering. In other sputtering process, metal is used as the target but in RF sputtering insulator is used as the target. In this process two electrolyte is used which insulator is in between them. In rf sputtering process, the deposition rate of metal films are about 1000 A/min.

- **APPLICATION OF THIN FILM :-**

There are mainly six applications of the thin film, which are as follows

1] DECORATIVE COATING :-

The uses of decorative coating in thin film is an one of the oldest application. The thin film materials which have high refractive index, variable thichness are applied for decorative coating. Titanium dioxide is an example for it. The surface which is intransparent gold colour may be prepared by sputtering of gold.

2] OPTICAL COATING :-

Optical coating is used in both reflective and refractive systems. Refractive lenses are used in microscope and camera which are optical instruments. Development in optical system by thin film technology is a few mm wide lenses. Thin lenses is used in mobile cameras. And also the anti-reflective coating on eyeglass and solar panels.

3] PROTECTIVE COATING :-

Thin film deposition can be used to protect work piece from external influences. To reduce the diffusion from the exterior medium to the work piece protective coating is used.

4] ELECTRICALLY OPERATING COATING :-

Metal layers like copper, silver, gold, etc and alloys have various applications in electrical devices. They have high electrical conductivity . Because of their high electrical conductivity they are able to transport electrical currents or supply voltage. These metal deposition thickness range of a few 100 nm.

5] THIN-FILM PHOTOVOLTAIC COATING :-

Now a days thin films are developed and reduce the cost of solar cell. In printed electronic process, this type of thin film is used. Other thin film techniques, which are in research or limited availability, are classified as third generation photovoltaic cells that include polymer solar cell, quantum dot, nanocrystal.

6] THIN-FILM BATTERIES :-

To create unique batteries for specialised applications, thin film printing technology is used to apply solid state lithium polymers. Thin film batteries can deposited directly on the chips.

- **ADVANTAGES :-**

1] Thin films are lower in costs.

2] They have higher efficiency potential.

3] low material consumption.

LITERATURE SURVEY

In chapter deals with the low and what we refer for the study of thin film deposition of Fe_2O_3 (ferric oxide) by SILAR method. For this project there are various websites are used. And also some research papers from sci-hub , google scholar. From thesis of author M.R. Belkhedkar, A.U. Ubale, Y.S. Sakhare found that mn doped Fe_2O_3 thin films were successfully synthesised by successive ionic layer adsorption and reaction method .

In the present investigation, the applicability of Fe2O3 thin films as anode and cathode electrodes respectively in supercapacitors has been systematically studied. Fe2O3 thin films are synthesized by simple and cost effective chemical methods and further more all-solid-state symmetric (Fe2O3) and asymmetric (Fe2O3) supercapacitor devices are fabricated. The electrochemical properties (cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), electrochemical impedance spectroscopy (ESR), etc.) of these devices are studied using two electrodes system. The asymmetric supercapacitor shows improved performance with maximum operating potential window of 2.0 V and specific capacitance of 79 F g_1 at 2 mA cm_2 current density. The maximum energy density and power density of 23Wh and 19 kW are obtained for asymmetric supercapacitor. In addition, the asymmetric supercapacitor demonstrates the excellent flexibility with capability retention of 89% over bending at an angle of 180.

Initially, Fe2O3 thin lms are prepared by the successive ionic layer adsorption and reaction (SILAR) . The detail processes of preparation of these lms are explained in ESI.† Further, these lms are characterize during different physico-chemical techniques to get information regarding the surface morphology, crystal structure and electrochemical features. shows the XRD patterns for Fe2O3 thin lms on stainless steel substrate. The indexed peaks are well matched with the JCPDS Fe2O3 .

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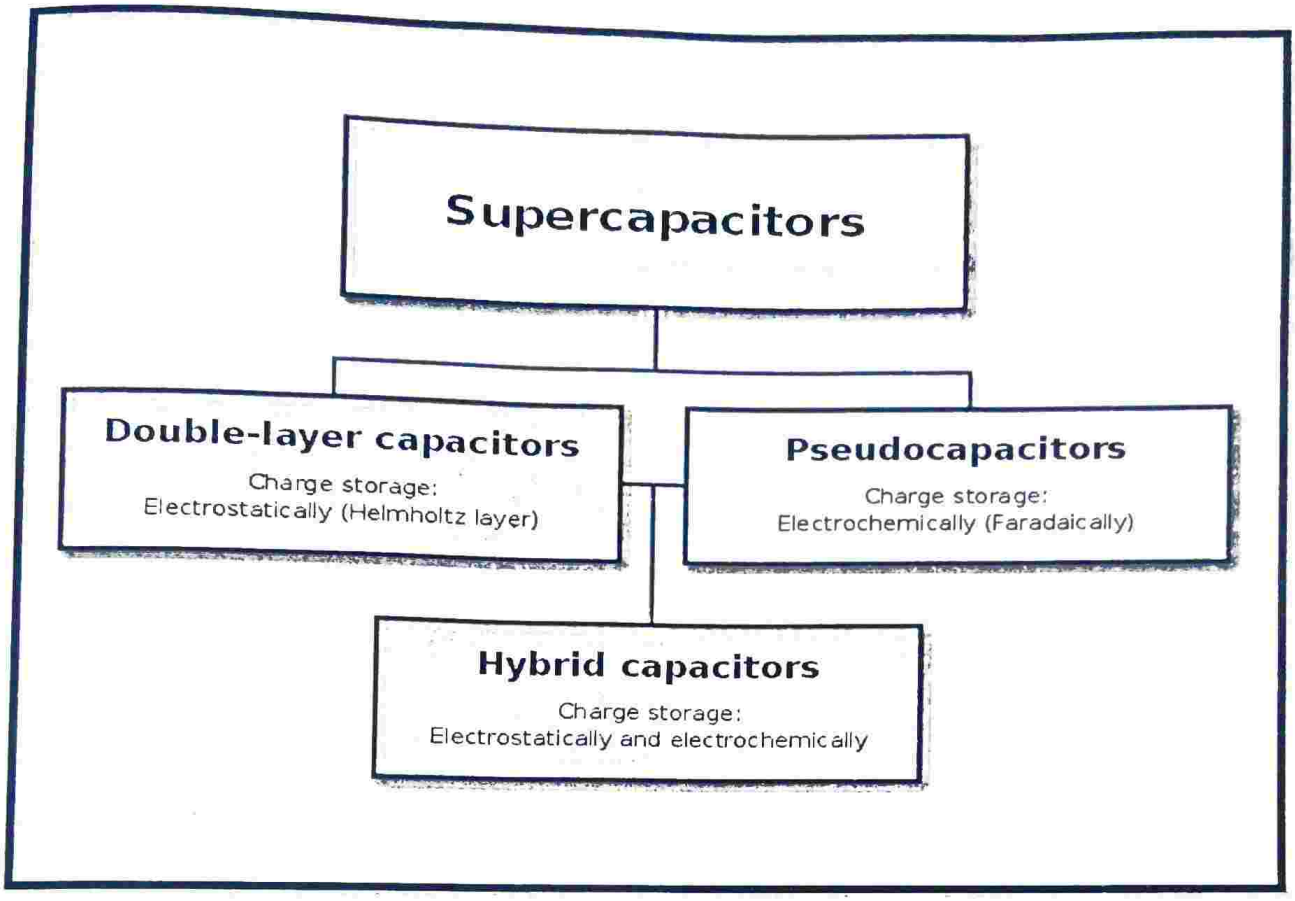
CHAPTER :- 2

SUPERCAPACITOR

- ## INTRODUCTION :-

A super capacitor, which has high capacity electrochemical capacitor. It has many advantages. Many of times it acts like ultra capacitor. Super capacitors charging time is fast and also discharge time is also fast. Super capacitor hava large conducting value which is greater than capacitor. Super capacitor can be store energy than the electrolytic capacitor, which is 10 to 100 times more than capacitor. Supercapacitor can discharge itself. Supercapacitors has many limitations. It is expensive and also discharge itself. Supercapcitors can be store 10 to 100 times more energy per unit unit volume than electrolytic capacitor. Supercapacitors can be charge fast and also discharge fast than the other batteries. They can deliver charge much faster. The charging and discharging cycle life was also more. They are used in the requirement of many charging-discharging cycle, that is short term energy storage

- **TYPES OF SUPRCAPACITORS :-**



- **Double layer capacitor :-**

Double layer capacitor can also called as, electrostatic double layer capacitor (EDLC). In electrochemical capacitor, there are two electrodes present. These two electrodes are seprated by the separator. They are ionically connect with each other through a electrolyte. The electrolyte is a mixture of negative and positive ions which is dissolved in solvent which is water. The formula for calculating capacitance for conventional plate capacitors,

$$C = \epsilon . A / d.$$

In EDLC, the carbon material is used as electode. The carbon material which is used is in solid form and electrolytic fluid is a liquid. When these two materials are come in contact with each other, then negative and positive poles are disturb and relative to each other for an very short distance. This is called as electric layer. In EDLC, ther is no chemical reaction happen like other batteries. This technology is environment friendly.

- **Pseudo capacitor :-**

There are two basic reactions, which lead to electrochemical cell. Both occur at the interface between a conductor and an electrolyte and both benefit from very high specific areas at the electrode. Surface area around 2000 m2/g is commonly available for carbons while 140 m2/g commonly available for metal oxide. The first mechanism commonly referred to as charge separation, which is well documented as a non-faradic mechanism and is the basis for EDLC. The charges are basically blocked at the electrode/electrolyte interface, preventing charges to diffuse. The second reaction commonly referred to as an oxidation reduction reaction (redox) due to faradic mechanism, which is the basis for pseudocapacitance

- **Hybrid Super capacitor :-**

With asymmetric electrodes, one of which exhibits mostly electrostatic and the other mostly electrochemical capacitance, such as lithium-ion capacitors, Because double-layer capacitance and pseudocapacitance both contribute inseparably to the total capacitance value of an electrochemical capacitor, a correct description of these capacitors only can be given under the generic term. The concepts of supercapattery and supercabattery have been recently proposed to better represent those hybrid devices that behave more like the supercapacitor and the rechargeable battery.

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CHAPTER : - 3

CHARACTERISATION

- **Characterisation Technique :-**

Characterisation is an important role to develop the material. To determine the properties of materials, the characterisation of a material consists of phase analysis, surface characterisation, structural elucidation, composional characterisation, micro-structural analysis. In this chapter, we are using different analytical instrumental techniques to characterise our thin films.

Characterisation techniques are as follows :-

1] XRD .

2] SEM.

3] CV

4]CD

- **X-Ray Differaction Technique :-**

The atomic planes of a crystal cause an incident beam of X-rays to interfece with one another as they leave the crystal. This phenomenon is known as X-ray differaction.

In 1985, X-rays were discovered by scientist Wilhelm Conrad Roentgen. He found new form of radiations and he didn't know that what is it, so he called it X-rays. X-rays are the form of high energy electromagnetic radiation. X-ray differaction is very powerful technique to determine crustal structure and lattice parameters. The wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers when differaction occurs. This type of differaction is bragg's law, which given as,

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

Where,

λ = Wavelength of X-ray.

d = Interplaner spacing.

Θ= Diffraction angle.

n = Order of diffraction.

- **Why X-RD is used ?**

1. To find the crustal structure of any or unknown material.
2. To measure the sixe, shape and internal stress of very smanll crystalline region.
3. To measure the average spacing between layers.
4. To determine the inclination of a single crystal or gain.

- **APPLICATIONS OF X- RAY DIFFERACTION :-**

1] Determine the atomic arrangement.

2] To measure the thickness of thin films.

3] X-RD is a non-destructive technique.

4] To identify crystalline phases and orientation.

5] To determina the structural properties : Lattice parameters, strain, grain size, etc.

There are three methods of X-ray differaction,

1) Laue's Method
2) Rotating Crystal Method
3) Powder Method

1. Laue's Method:

In the Laue method single crystal is irradiated by a beam of continuous wavelength x-ray. X-ray is emitted at angles and wavelength for which the Laue equations are satisfied. These equations are derived by consideration the x-ray beam as reflected from the surface of the crystal as though from a diffraction grating.

A flat film receives the diffracted beams and the diffraction patterns is composed a series of spot that shows the symmetry of the crystal. This Laue method is used extensively for the rapid determination of crystal orientation, such as direction within a crystal, and of symmetry. In the formal case, the crystal is oriented in a Goniometer and rotated until a desired direction is found, as indicated by the x-ray pattern.

Thus the Laue method enables us to investing the summery of the crystals lattice and to determine the orientation of planes which were cut from a crystal at unknown angles to the elements of symmetry of the crystal.

2] Powder Method :-

When single crystals are not available, a simple technique may be used. The crystalline material is ground to a powder which then present all possible orientations to a controlled X-Ray beam consisting primarily of Ka radiation.

If the crystal 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 compressed into a rod sample when the tiny crystal have different orientations and therefore possibility of interference which depends on the ratio of 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

3] Rotating crystal method:

It is combination of both Laue and powder method. It requires a small crystal. In the rotating crystal methods a single crystal is oriented so that a monochromatic x-ray beam is perpendicular to a direct lattice axis. Rotation of the crystal causes different atomic plane to different atomic plane to different x-ray whenever the value of θ is satisfies the Bragg's equation since different levels of reciprocal lattice point are normal to the direct axis, the rotation about the axis causes each level of points to intersect the sphere of reflection in a circle.

The diffracted rays pass from the center of the sphere through these circles forming cones. the zero level is a flat cone with other cone axes coincident and parallel to the rotating axis. In order to record the diffracted x-ray, film is normal cylindrical around the sample and concentrically with rotating sample holder. The x-ray beam passes through the crystal at right angles to the film and crystal holder. X-ray diffraction from all plane parallel to the rotation x is occur as reflected spots in a horizontal line on the film. Other planes cause diffraction both above and below the horizontal plane. These reflected spots occurring in line are called layer line

- **SCANNING ELECTRON MICROSCOPY (SEM) :-**

Scanning electron microscopy (SEM) is the powerful technique to study the surface properties of the material. This technique is widely used in the field of material science, metallurgy, geology, biology, medicine etc. SEM uses highly energetic electrons to generate variety of signals from the surface of the sample. These signals are generated from the interaction between the energetic electron and the sample and provide the information about the surface morphology (texture), chemical composition, crystalline structure and orientation of material.

Principle of the SEM :-

Accelerated electrons emitted from the electron gun carry large amounts of kinetic energy, and this energy is used to generate the variety of signals by electron- sample interactions when the incident electrons are slowed down on the solid sample. Generated signals shown in Fig. 2.7 include secondary electrons, backscattered electrons, diffracted backscattered electrons, photons, visible light and heat. The secondary electrons and backscattered electrons are used to produce surface morphology or topography of the sample.

Secondary electrons are important for the morphology and the backscattered electrons for illustrating contrasts in composition of multiphase samples. The diffracted backscattered electrons are useful for the determination of the crystallographic structures and orientations of specimen under consideration. [16]. The X-rays are generated by inelastic collisions of the incident electrons with electrons in discrete shells of atoms in the specimen. As these excited electrons return to lower energy states, emits X-rays with a certain fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element present in the specimen.

CHAPTER :- 4

Experimental Details of preparation of FE_2O_3 Thin film

3.1 Introduction

Among this thin film deposition methods, successive ionic layer adsorption and reaction (SILAR) method is relatively simple and offers wide range of advantages over other expensive methods of thin film deposition such as

1) It the process in which the deposition and thickness of the film can be easily controlled over a wide range by changing the deposition cycle.

2) Relatively uniform films can be obtained on substrates of any shape there is no restriction on substrate material, dimensions or its surface profile.

3) Unlike vacuum based deposition method, SILAR method does not require any expensive and sophisticated instruments and also vacuum at any stage which is a great advantage in the thin films have been obtained by adsorption cations followed by reacting with anion from appropriate precursor solution. The term adsorption can be defined as a collection of a substances on the surface of another substances, which is the fundamental building block of the context of an industrial application

4) The SILAR method usually requires low operating temperature. Apart from the obvious advantages in terms of energy saving, low deposition temperature avoids high temperature avoids high temperature effects involved in different processes such as inter diffusion, contamination and dopant redistribution.

- **Instrumentation :-**

The substantive components of the Scanning Electron Microscope are electron gun, magnetic lenses, sample Stage, display/data output devices. The electron gun produces highly energetic beam of electrons. The thermionic emission occurs when the thin tungsten filament is heated at high temperature (about 2800K) and thermoelectrons are produced.

The fine electron beam is required for the analysis of SEM. The electron beam is passed through the metallic plates maintained at positive potential (1 to 30 kV). The magnetic lenses are placed below the electron gun to adjust the beam of the diameter. The specimen stage is required to support the motion and to move the specimen in various directions like horizontal movement (x-y), vertical movement (z) and rotation movement. The output signal from detector are amplified and transferred to the display unit.

3.2.1 The SILAR method involves four steps :-

1] Adsorption.
2] First rinsing.
3] Reaction.
4] Second rinsing.

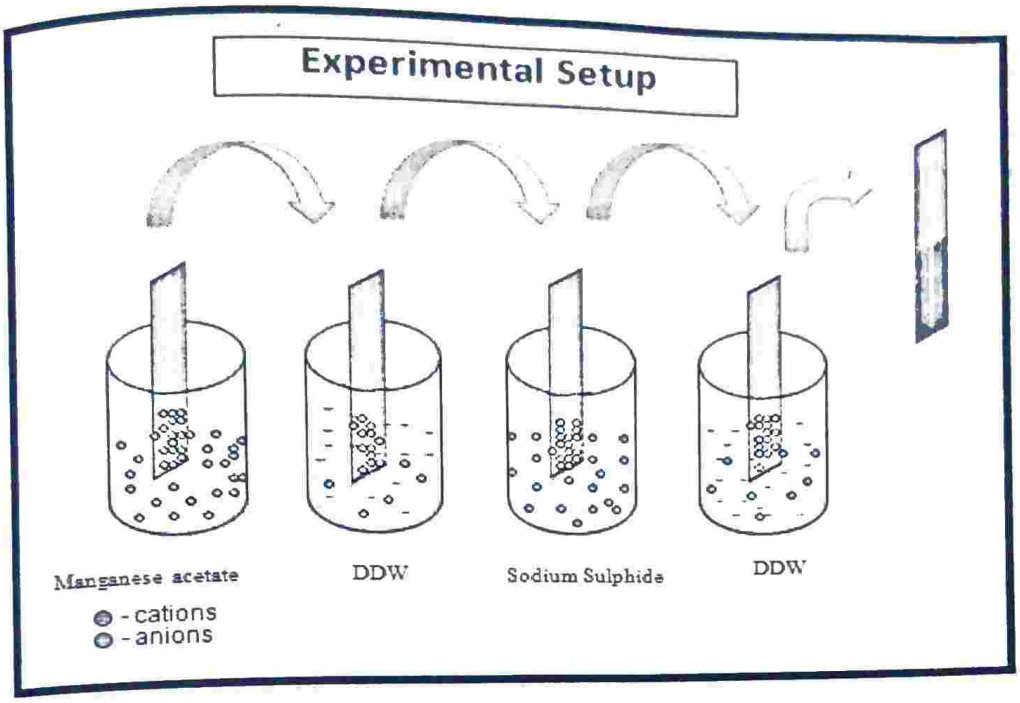


Fig 3.1 Successive Ionic Layer Adsorption and Reaction process.

1. Adsorption

In first step of SILAR method, the cations present in the precursor solution are absorbed on the surface of the substrate and form the Helmholtz electric double layer. The 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 anion from anionic precursor solution is introduced to the system. Due to the 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 un reacted species and 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 pre adsorbed cation. This leads to formation of thin film of desired material. The factors like temperature of solution. Nature of the substance, ph and concentrated of solution, area of the substrate, dipping and rinsing time etc. Affect the deposition process substrate, dipping and rinsing time etc. Affect the deposition process.

Effect of preparative parameters :-

The rate of deposition and terminal thickness depends upon 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 complexing agent. The effect of various deposition conditions on these parameters is discussed below

A) Concentration of ions :-

The increases in compound concentration lead to an increases in cation and anion concentration and film with larger thickness is obtained. Conversely, above a certain concentration of cation and anion when the rate of reaction become high and precipitation is leading to a lesser amount of material on the substrate then it lower 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 the formation of thin film. As the adsorption time is greater than that of reaction time the film formation takes place by assorted reaction to results higher terminal thickness. Equal adsorption and reaction time, results into consistent reaction. Consistent growth provides inform film formation.

C) Rinsing time :-

Rinsing between every immersion is significant to avoid the precipitation in the reaction bath. In rising 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 compound depend on the temperature. At the higher temperatures, the dissociation is greater, which gives higher concentration of cation 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.

3.2 Experimental details:

SILAR method, adsorption may be expected when two heterogeneous phases are brought in contact with each other. Hence, gas-solid, liquid-solid, gas-liquid are three possible adsorption systems. In SILAR method, the first step 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 Vander Waal or chemical attractive. Atoms or molecules of their kinds on all sides do not surround atoms or molecules of substrate surface. Therefore, they posses unbalanced or residual forces and holds the substrate particles. Thus, adsorbed atoms (ad-atoms) can be holding on the surface of the substrate. In second step the adsorbed step the adsorbed ion is reacted with anion, resulted into film formation.

Advantages of SILAR method :-

1. It is simple, convenient and inexpensive method for large area deposition.
2. The SILAR method is usually operated at low temperature.
3. Slow process which facilities better orientation of crystalline with improved growth structure.
4. SILAR does not require high quality target or substrate and vacuum at any stage.
5. The deposition rate and thickness of thin film can be easily controlled over a wide range by changing the deposition cycle.
6. It offers extremely easy way to dope films.

CHAPTER :- 5

Synthesis and Result:

For synthesis of Fe_2O_3 thin film, analytical grade ferric chloride and sodium hydroxide were used. 0.1 molar concentration of ferric chloride and sodium hydroxide dissolved in 50ml double distilled water. Beakers are arranged according to requirements of SILAR method. First beaker is of ferric chloride, second of double distilled water, third is of sodium hydroxide, and fourth is of double distilled water. In first and third beaker slide deep for 10 sec. In second and fourth beaker slide rinsing for 5 sec respectively.

- **Characterization:**

1. X-ray diffraction (XRD):

After synthesis Fe_2O_3 thin film is used for further characterization. To identify the structural information of the synthesized film, we measured X-ray diffraction (XRD) pattern Fe_2O_3. The XRD patterns of the Fe_2O_3 thin film sample is shown in Figure. The XRD pattern of Fe_2O_3 thin film indicates diffraction peaks at about 37.48°,43.56 , 63.30° ,75.90 ° and 79.98 ° correspond to the diffractions from (111) , (200) , (220) ,(311) and (222) crystal planes, respectively. So values of **a=b=c=4.15 Å** and **$\alpha = \beta = \gamma = 90°$**, indicating the formation of the perovskite phase in the cubic phase as supported by the Reference code - **01-074-2282.**

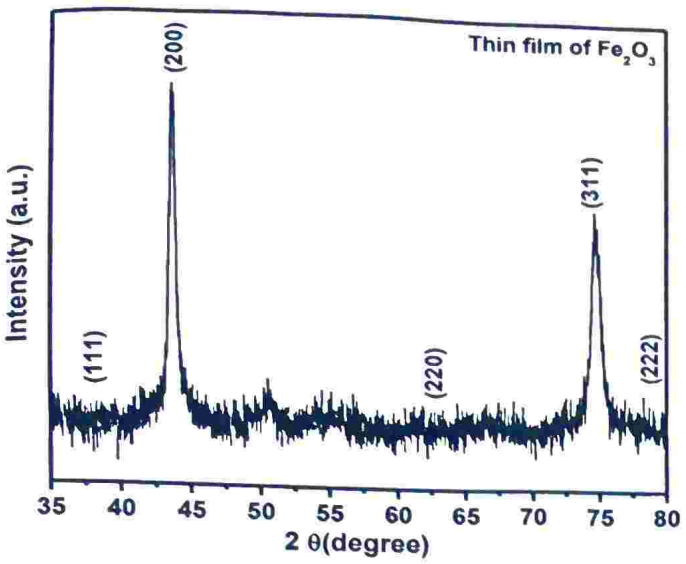


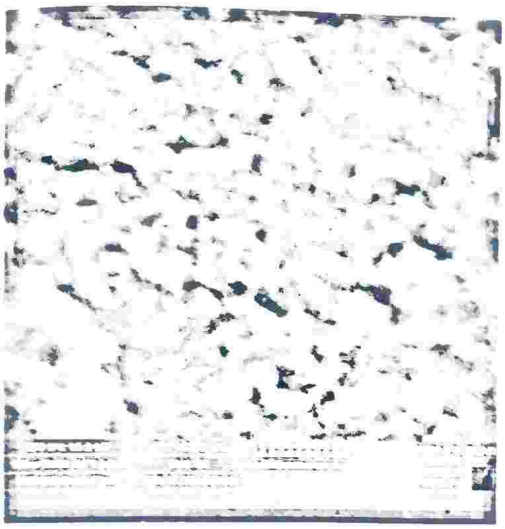
Fig:- X-Ray diffraction pattern of synthesized Fe_2O_3 thin film

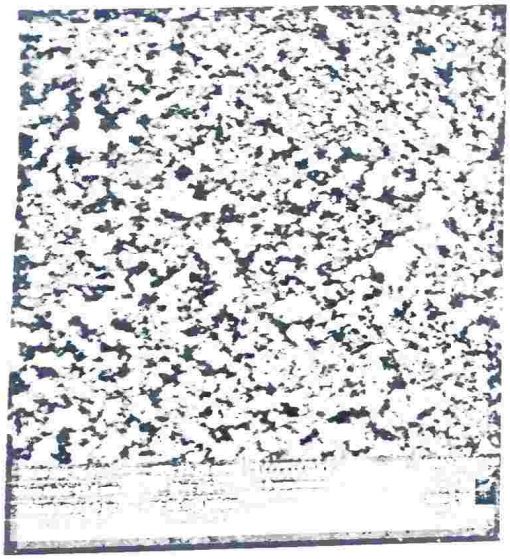
Results :

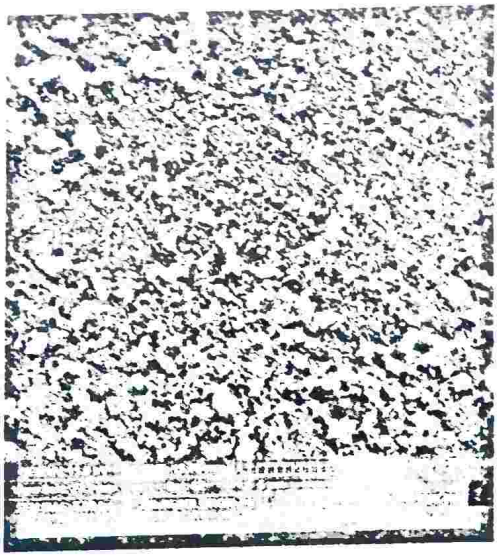
By using SILAR method, we have successfully synthesized Fe_2O_3 thin film. After synthesis Fe_2O_3 thin film used for characterizations like X-Ray diffraction. X-Ray diffraction pattern of Fe_2O_3 thin film shown in figure and indicating the crystalline nature of Fe_2O_3 thin film, we conclude that values of **a=b=c=4.15 Å** and **$\alpha = \beta = \gamma = 90°$**, confirms Fe_2O_3 thin film has Cubic structure and supported by the Reference code - **01-074-2282.**

Scanning Electron micrograph of Fe_2O_3 films :-

A SEM image of Fe_2O_3 thin film at various magnifiction are shown in following figures. The film compactness is high. From the result nanoparticles are found. The grain size is generally small and the grain size is generally narrow.







CHAPTER :- 6

SUMMARY AND CONCLUSION

In first chapter, a general introduction of the thin film is explained. The various thin film deposition techniques and theoretical background are mentioned in this chapter. And also the literature survey of Fe2O3 thin film deposition is given. The purpose of the project is starts from this chapter.

In second chapter, the main property of the material is mentioned which is supercapacitor. The mainly three types of supercapacitor is explained in detail. How they work and how material help to them is given.

In third chapter, the characterizations are explained very well.all the details of X-RD and how its work...how we find the crytaline structure is given. Also the SEM technique is explained.

fourth chapter is experimental details of preparation of FE_2O_3 thin film. In this chapter, how SILAR method works is given. What is the process of SILAR method and what steps are used for the preparation of thin fil is metioned.

Fifth chapter is synthesis and result. In this chapter, what we actually done in process to get a thin film is given. And what results find with this method and the material for thin film is given.

conclusion :

The X-RD study was carried out for Fe2O3 thin film deposited on the stainless still substrate. And also Scanning Electron Microscopy characterization is studied.

PREPARATION OF FE_2O_3 BY SILAR METHOD

A Dissertation Report Submitted to

Vivekanand College (Autonomous),
KOLHAPUR.

For the Partial Fulfillment of

Degree of Master of Science

In

PHYSICS

Under the Faculty of Science

by

ASIF JAHANGIR TAMBOLI.
M.Sc.

Under the Guidance of

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Kolhapur.

2019-2020

DECLARATION

I hereby declare that, the project entitled "PREPARATION OF FE_2O_3 BY SILAR METHOD" completed and written by me has not previously formed the basis for the award of any Degree or Diploma or other similar title of this or any other University or examining body.

Place: Kolhapur

Date: 11/09/2020.

Mr. ASIF JAHANGIR TAMBOLI.

M.Sc. II (Physics)

Department of Physics,

Vivekanand College (Autonomous),

Kolhapur.

2018-2019

CERTIFICATE

This is to certify that the project entitled "PREPARATION OF FE_2O_3 BY SILAR METHOD" which is being submitted herewith for the award of the Degree of **Master of Science** in **Physics** of **Vivekanand College (Autonomous), KOLHAPUR,** is the result of the original project work completed by **Mr. ASIF JAHANGIR TAMBOLI** under our supervision and guidance and to the best of our 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: Kolhapur.

Date: 11/09/2020.

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2018-2019

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On the day of completion of this project, I offer sincere gratitude to those who encouraged and helped me a lot at various stages of this work.

I have great pleasure to express my deep sense of indebtedness and heart full gratitude to **Dr. M. M. Karanjkar**, Professor, Department of Physics, Vivekanand College (Autonomous), Kolhapur, for his expert and valuable guidance and continuous encouragement given to me during the course of my project work. He has already been a source of strength for me. I find in him a real researcher who through his own example and devotion for scientific work inspired me towards a common goal of achieving scientific knowledge and pursuit.

I wish to express my appreciation to **Prof. S. V. Malgaonkar, Prof. C. J. Kamble, Prof. G. J. Navathe** for discussion and co-operation in each and every movement of my project work.

My acknowledgement will be incomplete if I don't express my appreciation towards my family members whose good will & inspiration helped us a lot in completing this project work.

Mr. ASIF JAHANGIR TAMBOLI.

M.Sc. II (Physics)

INDEX

CHAPTER :- 1

1. Introduction And Theoretical Background

Various mathods and relative technology for preparing thin film can described for research and development . Thin film means the layer of the material. The range of the thickness of material is very few nanometer to micrometer. Thin film deposioin techniques are relavent to change the physical properties of the surface by using very thin layer. By using thin film we can modify the optical properties of substrate and also its electrical conductivity. Advanced thin film technology can be used in many fields like optical instrument, flat display pannel, microcircuits, biomedical devices, solar cell sensors. There are many deposition techniques that offers fabrication of micro and nanoscale devices. In all these techniques, SILAR was very much simple, priseless, and much convinient for large area deposition. The thin films established by using the SILAR method is characterised by means of structural, optical and electrical measurements, surface morphological.

- **THIN FILM DEPOSITION METHODS :-**

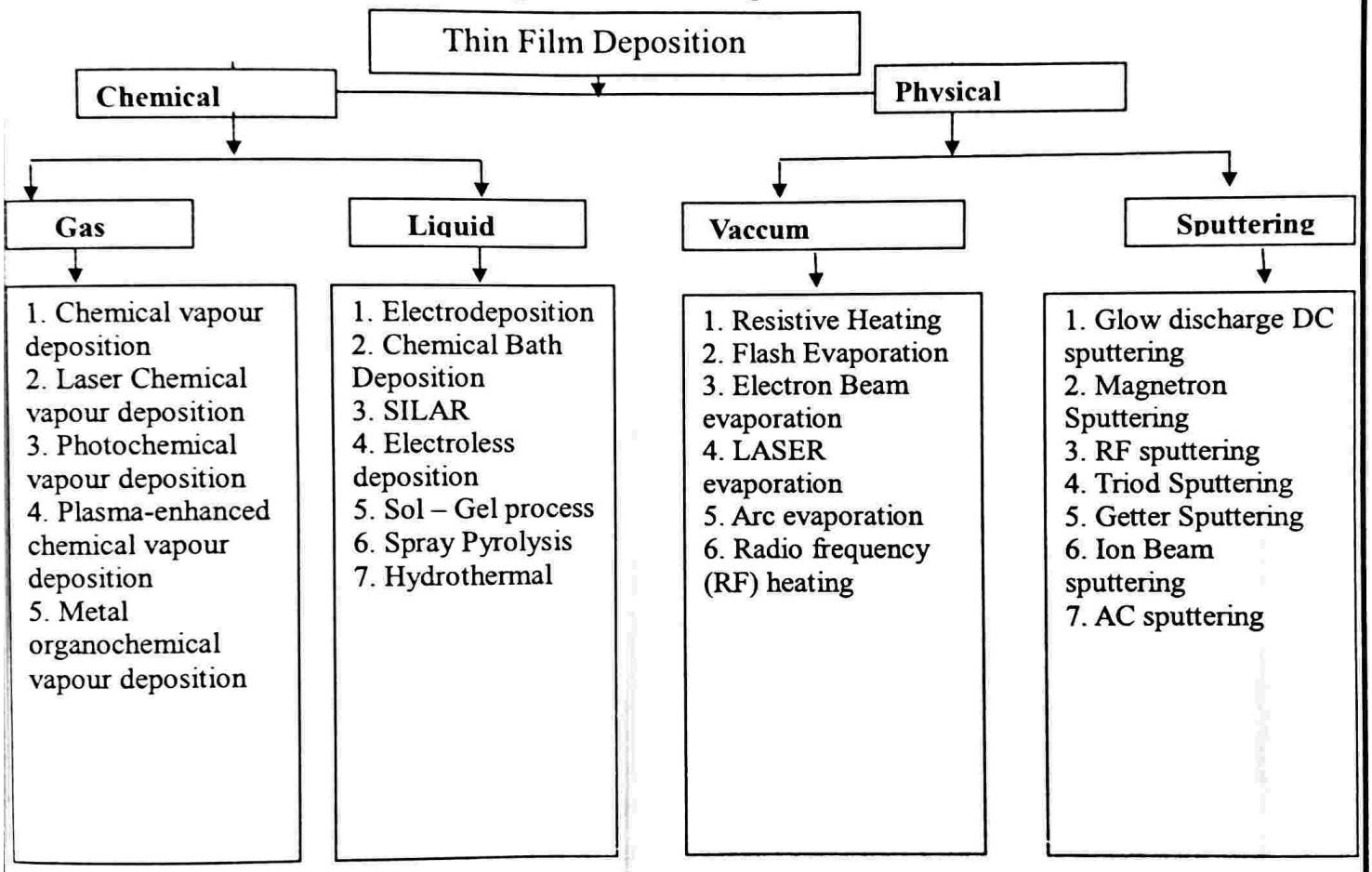
There are mainly two types of deposition methods,

1] PHYSICAL METHOD.

2]CHEMICAL METHOD.

They also have many sub methods as shown below

Deposition Techniques



- **PHYSICAL METHOD :-**

A] GAS PHASE :-

1] CVD :-

CVD stands for Chemical Vapor Deposition. CVD is very simple very useful technique in thin film deposition.we get the depotion on substrate by using the vapor of chemical. In CVD, variety of materials, compounds and elements are used on various variety of substrate. It offers many of advantages than the othe techniques of deposition. Main application of CVD is in semiconductor integrated electronic circuits.

2] MOCVD :-

MOCVD means Metal Organic Chemical Vapor Deposition. By using this technique we can deposited very thin layer on the substrate. We can produce polycrystalline thin films by using MOCVD.

3] PECVD :-

PECVD stands for Plasma Enhanced Chemical Vapour Deposition. It is versatile technique for depositing wide variety of thin film materials. PECVD of thin film material has many reactor designs and different expriemental conditions. The primary role of the plasma is to promote chemical reaction.

4] LCVD :-

Now a day Laser Chemical Vapor Deposition technique is developed. In this technique deposite the material by using laser. LCVD Is modification of convetional CVD. The chemical reaction which is initiated by the laser beam for the deposition has mainly two mechanisms, which are photolysis and pyrolysis.

- **B] LIQUID PHASE :-**

1] SILAR :-

SILAR stands for Successive Ionic Layer Adsorption and Reaction. Its is based on the adsorbtion and reaction of ions. The operations to deposite thin film by SILAR method is cations are adsorbed, then rinsing with the distilled water, then reaction between adsorbed cations and anions, and then again rinsing with the double distilled water.

2] CBD :-

CBD means Chemical Bath Deposition. It is also called as solution growth. It dose not reqired sophisticated materials. It is low budget ans simple method. This methos has beakers, hot plate, temperature sensor.

3] Spray pyrolysis :-

Spray pyrolysis is very simple and useful deposition technique, that we can deposited broad range of thin films. By using spray pyrolysis we can deposit nano thin films. In this process, films are deposited by spraying a solution on hot plate.

- **PHYSICAL METHOD :-**

Vacuum evaporation is mainly divided into two parts,

A] VACUUM EVAPORATION.

B] SPUTTERING.

A] VACUUM EVAPORATION :-

1] ELECTRON BEAM EVAPORATION :-

In electron beam evaporation, electron beam accelerate to the material to convert it into vapor for a deposition. When electrons incident on the surface of matrial then electrons lose their energy rapidly then material melts and evaporate. Electron gun can be classified into two categories which are thermionic and plasma electron. In this mathod liquid cooled crucible is used.

2] LASER EVAPORATION :-

In laser evaporation, to vaporise the evaporant material the thermal source is used which is laser. High vacuum technique is used for the preparation of thin films by laser evaporation, where the source is at outside the vacuum system. The substrate for the deposition is placed in front of the material inside the chamber. Laser evaporation has many advantages.

3] RADIO FREQUENCY (RF) HEATING :-

In this method a cruicible is used which is support crucible. In RF heating, material inside the cruicible which has RF coils around the crucible. This mathod is much expensive and want heavy equipment. The evaporation rate of evaporant is much difficult to control so this method is not commonly used for preparation of the thin film.

4] FLASH EVAPORATION :-

In flash evaporation, evaporant material is in powder form. We can take two or more materials deposion in this method. The materials which are in powder form ans present in small quantities is dropped at the heated boat and evaporate. The temprature of the hot boat is set at the large melting point of that material which deposited.

B] SPUTTERING :-

1] GLOW DISCHARGE DC SPUTTERING :-

The arrangement of this method is very simple than other. This system is at the vacuum chamber. In this chamber neutral gas is present and glow amd discharge is iniciated. In chamber there is only anode and substrate is used. The pressure in vacuum chamber is about 10^{-1} to 10^{-2} torr. The plate of substrate is connected to the negative voltage supply.

2] ION BEAM SPUTTERING :-

In ion beam sputtering, ion source produce ion beam. Thin beam was extracted into the high vacuum system by extraction voltage then it goes to target of the material, which is sputter and deposit on substrate. From the ion production process, greater isolation of substrate allows by ion beam sputtering. Ion beam sputtering has accurate scanning and focusing. In this process, energy and current of ion bean can be controlled. Mainly the kaufman and duoplasmatron are the sources which is used for the ion beam sputter deposition.

3] TRIOD SPUTTERING :-

In this method, there are plates which is substrate, anode and target. Also the coils are placed at both the side of the system. All the plates are placed inside the vacuum chamber. Also the filament is present in it. Which is produce the electrons. For good deposition filament is very important.

4] RF SPUTTERING :-

RF sputtering means Radio Frequency sputtering. In other sputtering process, metal is used as the target but in RF sputtering insulator is used as the target. In this process two electrolyte is used which insulator is in between them. In rf sputtering process, the deposition rate of metal films are about 1000 A/min.

- **APPLICATION OF THIN FILM :-**

There are mainly six applications of the thin film, which are as follows

1] DECORATIVE COATING :-

The uses of decorative coating in thin film is an one of the oldest application. The thin film materials which have high refractive index, variable thichness are applied for decorative coating. Titanium dioxide is an example for it. The surface which is intransparent gold colour may be prepared by sputtering of gold.

2] OPTICAL COATING :-

Optical coating is used in both reflective and refractive systems. Refractive lenses are used in microscope and camera which are optical instruments. Development in optical system by thin film technology is a few mm wide lenses. Thin lenses is used in mobile cameras. And also the anti-reflective coating on eyeglass and solar panels.

3] PROTECTIVE COATING :-

Thin film deposition can be used to protect work piece from external influences. To reduce the diffusion from the exterior medium to the work piece protective coating is used.

4] ELECTRICALLY OPERATING COATING :-

Metal layers like copper, silver, gold, etc and alloys have various applications in electrical devices. They have high electrical conductivity . Because of their high electrical conductivity they are able to transport electrical currents or supply voltage. These metal deposition thickness range of a few 100 nm.

5] THIN-FILM PHOTOVOLTAIC COATING :-

Now a days thin films are developed and reduce the cost of solar cell. In printed electronic process, this type of thin film is used. Other thin film techniques, which are in research or limited availability, are classified as third generation photovoltaic cells that include polymer solar cell, quantum dot, nanocrystal.

6] THIN-FILM BATTERIES :-

To create unique batteries for specialised applications, thin film printing technology is used to apply solid state lithium polymers. Thin film batteries can deposited directly on the chips.

- **ADVANTAGES :-**

1] Thin films are lower in costs.

2] They have higher efficiency potential.

3] low material consumption.

LITERATURE SURVEY

In chapter deals with the low and what we refer for the study of thin film deposition of Fe_2O_3 (ferric oxide) by SILAR method. For this project there are various websites are used. And also some research papers from sci-hub , google scholar. From thesis of author M.R. Belkhedkar, A.U. Ubale, Y.S. Sakhare found that mn doped Fe_2O_3 thin films were successfully synthesised by successive ionic layer adsorption and reaction method .

In the present investigation, the applicability of Fe2O3 thin films as anode and cathode electrodes respectively in supercapacitors has been systematically studied. Fe2O3 thin films are synthesized by simple and cost effective chemical methods and further more all-solid-state symmetric (Fe2O3) and asymmetric (Fe2O3) supercapacitor devices are fabricated. The electrochemical properties (cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), electrochemical impedance spectroscopy (ESR), etc.) of these devices are studied using two electrodes system. The asymmetric supercapacitor shows improved performance with maximum operating potential window of 2.0 V and specific capacitance of 79 F g_1 at 2 mA cm_2 current density. The maximum energy density and power density of 23Wh and 19 kW are obtained for asymmetric supercapacitor. In addition, the asymmetric supercapacitor demonstrates the excellent flexibility with capability retention of 89% over bending at an angle of 180.

Initially, Fe2O3 thin lms are prepared by the successive ionic layer adsorption and reaction (SILAR) . The detail processes of preparation of these lms are explained in ESI.† Further, these lms are characterize during different physico-chemical techniques to get information regarding the surface morphology, crystal structure and electrochemical features. shows the XRD patterns for Fe2O3 thin lms on stainless steel substrate. The indexed peaks are well matched with the JCPDS Fe2O3 .

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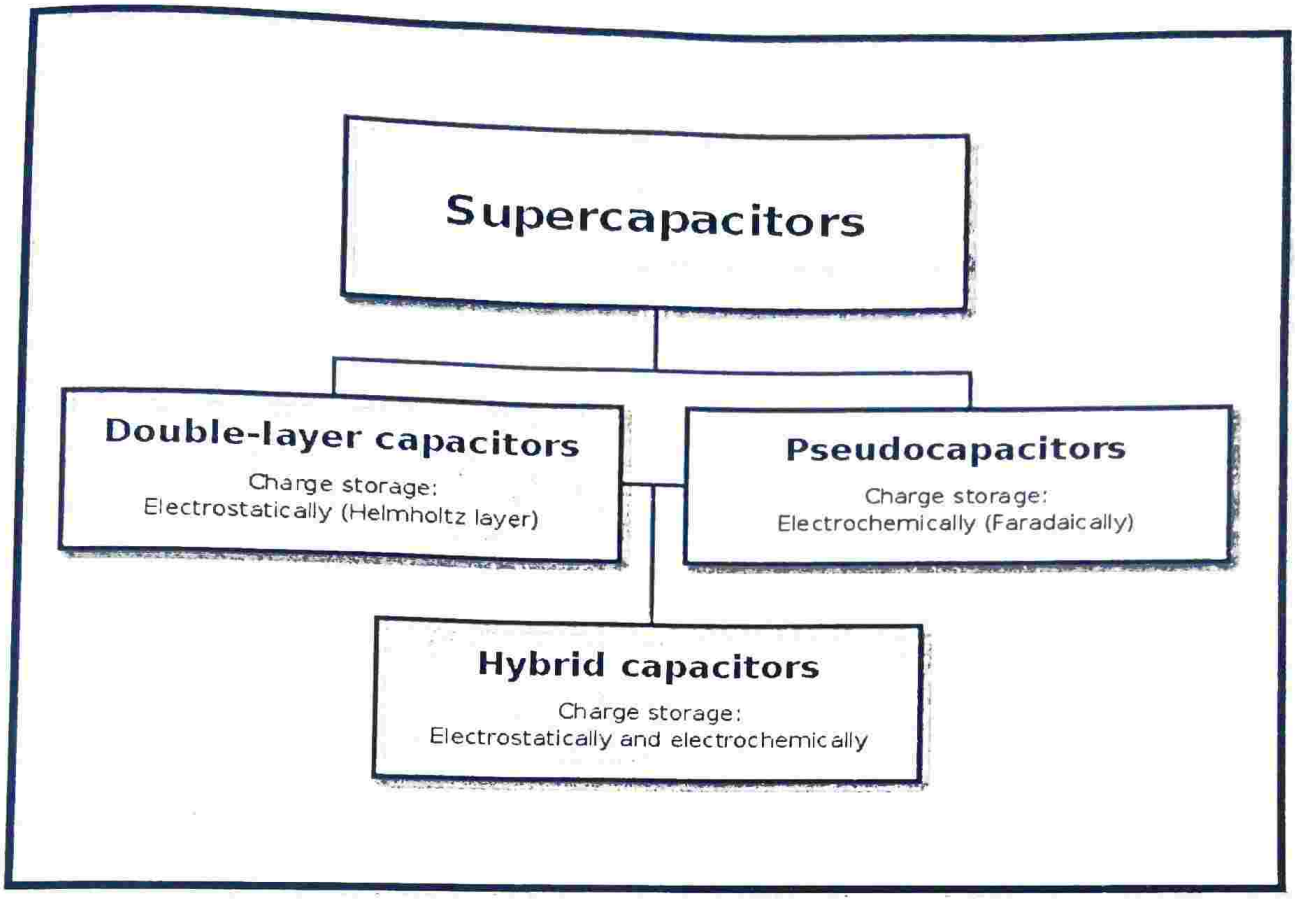
CHAPTER :- 2

SUPERCAPACITOR

- ## INTRODUCTION :-

A super capacitor, which has high capacity electrochemical capacitor. It has many advantages. Many of times it acts like ultra capacitor. Super capacitors charging time is fast and also discharge time is also fast. Super capacitor hava large conducting value which is greater than capacitor. Super capacitor can be store energy than the electrolytic capacitor, which is 10 to 100 times more than capacitor. Supercapacitor can discharge itself. Supercapacitors has many limitations. It is expensive and also discharge itself. Supercapcitors can be store 10 to 100 times more energy per unit unit volume than electrolytic capacitor. Supercapacitors can be charge fast and also discharge fast than the other batteries. They can deliver charge much faster. The charging and discharging cycle life was also more. They are used in the requirement of many charging-discharging cycle, that is short term energy storage

- **TYPES OF SUPRCAPACITORS :-**



- **Double layer capacitor :-**

Double layer capacitor can also called as, electrostatic double layer capacitor (EDLC). In electrochemical capacitor, there are two electrodes present. These two electrodes are seprated by the separator. They are ionically connect with each other through a electrolyte. The electrolyte is a mixture of negative and positive ions which is dissolved in solvent which is water. The formula for calculating capacitance for conventional plate capacitors,

$$C = \epsilon . A / d.$$

In EDLC, the carbon material is used as electode. The carbon material which is used is in solid form and electrolytic fluid is a liquid. When these two materials are come in contact with each other, then negative and positive poles are disturb and relative to each other for an very short distance. This is called as electric layer. In EDLC, ther is no chemical reaction happen like other batteries. This technology is environment friendly.

- **Pseudo capacitor :-**

There are two basic reactions, which lead to electrochemical cell. Both occur at the interface between a conductor and an electrolyte and both benefit from very high specific areas at the electrode. Surface area around 2000 m2/g is commonly available for carbons while 140 m2/g commonly available for metal oxide. The first mechanism commonly referred to as charge separation, which is well documented as a non-faradic mechanism and is the basis for EDLC. The charges are basically blocked at the electrode/electrolyte interface, preventing charges to diffuse. The second reaction commonly referred to as an oxidation reduction reaction (redox) due to faradic mechanism, which is the basis for pseudocapacitance

- **Hybrid Super capacitor :-**

With asymmetric electrodes, one of which exhibits mostly electrostatic and the other mostly electrochemical capacitance, such as lithium-ion capacitors, Because double-layer capacitance and pseudocapacitance both contribute inseparably to the total capacitance value of an electrochemical capacitor, a correct description of these capacitors only can be given under the generic term. The concepts of supercapattery and supercabattery have been recently proposed to better represent those hybrid devices that behave more like the supercapacitor and the rechargeable battery.

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CHAPTER : - 3

CHARACTERISATION

- **Characterisation Technique :-**

Characterisation is an important role to develop the material. To determine the properties of materials, the characterisation of a material consists of phase analysis, surface characterisation, structural elucidation, composional characterisation, micro-structural analysis. In this chapter, we are using different analytical instrumental techniques to characterise our thin films.

Characterisation techniques are as follows :-

1] XRD .

2] SEM.

3] CV

4]CD

- **X-Ray Differaction Technique :-**

The atomic planes of a crystal cause an incident beam of X-rays to interfece with one another as they leave the crystal. This phenomenon is known as X-ray differaction.

In 1985, X-rays were discovered by scientist Wilhelm Conrad Roentgen. He found new form of radiations and he didn't know that what is it, so he called it X-rays. X-rays are the form of high energy electromagnetic radiation. X-ray differaction is very powerful technique to determine crustal structure and lattice parameters. The wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers when differaction occurs. This type of differaction is bragg's law, which given as,

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

Where,

λ = Wavelength of X-ray.

d = Interplaner spacing.

Θ= Diffraction angle.

n = Order of diffraction.

- **Why X-RD is used ?**

1. To find the crustal structure of any or unknown material.
2. To measure the sixe, shape and internal stress of very smanll crystalline region.
3. To measure the average spacing between layers.
4. To determine the inclination of a single crystal or gain.

- **APPLICATIONS OF X- RAY DIFFERACTION :-**

1] Determine the atomic arrangement.

2] To measure the thickness of thin films.

3] X-RD is a non-destructive technique.

4] To identify crystalline phases and orientation.

5] To determina the structural properties : Lattice parameters, strain, grain size, etc.

There are three methods of X-ray differaction,

1) Laue's Method
2) Rotating Crystal Method
3) Powder Method

1. Laue's Method:

In the Laue method single crystal is irradiated by a beam of continuous wavelength x-ray. X-ray is emitted at angles and wavelength for which the Laue equations are satisfied. These equations are derived by consideration the x-ray beam as reflected from the surface of the crystal as though from a diffraction grating.

A flat film receives the diffracted beams and the diffraction patterns is composed a series of spot that shows the symmetry of the crystal. This Laue method is used extensively for the rapid determination of crystal orientation, such as direction within a crystal, and of symmetry. In the formal case, the crystal is oriented in a Goniometer and rotated until a desired direction is found, as indicated by the x-ray pattern.

Thus the Laue method enables us to investing the summery of the crystals lattice and to determine the orientation of planes which were cut from a crystal at unknown angles to the elements of symmetry of the crystal.

2] Powder Method :-

When single crystals are not available, a simple technique may be used. The crystalline material is ground to a powder which then present all possible orientations to a controlled X-Ray beam consisting primarily of Ka radiation.

If the crystal 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 compressed into a rod sample when the tiny crystal have different orientations and therefore possibility of interference which depends on the ratio of 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

3] Rotating crystal method:

It is combination of both Laue and powder method. It requires a small crystal. In the rotating crystal methods a single crystal is oriented so that a monochromatic x-ray beam is perpendicular to a direct lattice axis. Rotation of the crystal causes different atomic plane to different atomic plane to different x-ray whenever the value of θ is satisfies the Bragg's equation since different levels of reciprocal lattice point are normal to the direct axis, the rotation about the axis causes each level of points to intersect the sphere of reflection in a circle.

The diffracted rays pass from the center of the sphere through these circles forming cones. the zero level is a flat cone with other cone axes coincident and parallel to the rotating axis. In order to record the diffracted x-ray, film is normal cylindrical around the sample and concentrically with rotating sample holder. The x-ray beam passes through the crystal at right angles to the film and crystal holder. X-ray diffraction from all plane parallel to the rotation x is occur as reflected spots in a horizontal line on the film. Other planes cause diffraction both above and below the horizontal plane. These reflected spots occurring in line are called layer line

- **SCANNING ELECTRON MICROSCOPY (SEM) :-**

Scanning electron microscopy (SEM) is the powerful technique to study the surface properties of the material. This technique is widely used in the field of material science, metallurgy, geology, biology, medicine etc. SEM uses highly energetic electrons to generate variety of signals from the surface of the sample. These signals are generated from the interaction between the energetic electron and the sample and provide the information about the surface morphology (texture), chemical composition, crystalline structure and orientation of material.

Principle of the SEM :-

Accelerated electrons emitted from the electron gun carry large amounts of kinetic energy, and this energy is used to generate the variety of signals by electron- sample interactions when the incident electrons are slowed down on the solid sample. Generated signals shown in Fig. 2.7 include secondary electrons, backscattered electrons, diffracted backscattered electrons, photons, visible light and heat. The secondary electrons and backscattered electrons are used to produce surface morphology or topography of the sample.

Secondary electrons are important for the morphology and the backscattered electrons for illustrating contrasts in composition of multiphase samples. The diffracted backscattered electrons are useful for the determination of the crystallographic structures and orientations of specimen under consideration. [16]. The X-rays are generated by inelastic collisions of the incident electrons with electrons in discrete shells of atoms in the specimen. As these excited electrons return to lower energy states, emits X-rays with a certain fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element present in the specimen.

CHAPTER :- 4

Experimental Details of preparation of FE_2O_3 Thin film

3.1 Introduction

Among this thin film deposition methods, successive ionic layer adsorption and reaction (SILAR) method is relatively simple and offers wide range of advantages over other expensive methods of thin film deposition such as

1) It the process in which the deposition and thickness of the film can be easily controlled over a wide range by changing the deposition cycle.

2) Relatively uniform films can be obtained on substrates of any shape there is no restriction on substrate material, dimensions or its surface profile.

3) Unlike vacuum based deposition method, SILAR method does not require any expensive and sophisticated instruments and also vacuum at any stage which is a great advantage in the thin films have been obtained by adsorption cations followed by reacting with anion from appropriate precursor solution. The term adsorption can be defined as a collection of a substances on the surface of another substances, which is the fundamental building block of the context of an industrial application

4) The SILAR method usually requires low operating temperature. Apart from the obvious advantages in terms of energy saving, low deposition temperature avoids high temperature avoids high temperature effects involved in different processes such as inter diffusion, contamination and dopant redistribution.

- **Instrumentation :-**

The substantive components of the Scanning Electron Microscope are electron gun, magnetic lenses, sample Stage, display/data output devices. The electron gun produces highly energetic beam of electrons. The thermionic emission occurs when the thin tungsten filament is heated at high temperature (about 2800K) and thermoelectrons are produced.

The fine electron beam is required for the analysis of SEM. The electron beam is passed through the metallic plates maintained at positive potential (1 to 30 kV). The magnetic lenses are placed below the electron gun to adjust the beam of the diameter. The specimen stage is required to support the motion and to move the specimen in various directions like horizontal movement (x-y), vertical movement (z) and rotation movement. The output signal from detector are amplified and transferred to the display unit.

3.2.1 The SILAR method involves four steps :-

1] Adsorption.
2] First rinsing.
3] Reaction.
4] Second rinsing.

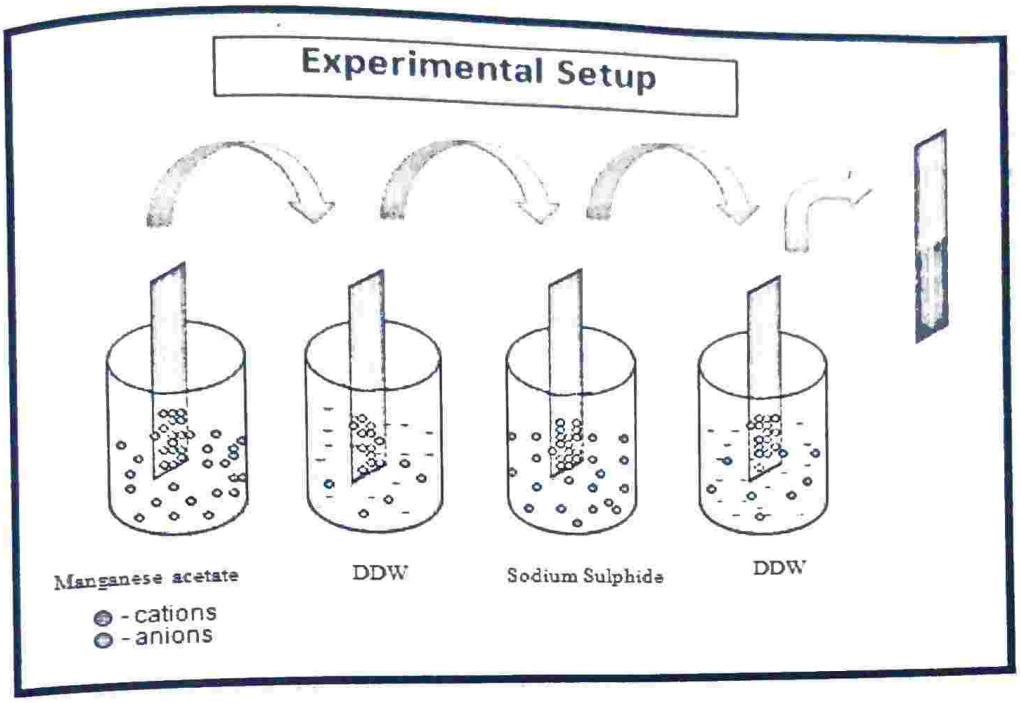


Fig 3.1 Successive Ionic Layer Adsorption and Reaction process.

1. Adsorption

In first step of SILAR method, the cations present in the precursor solution are absorbed on the surface of the substrate and form the Helmholtz electric double layer. The 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 anion from anionic precursor solution is introduced to the system. Due to the 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 un reacted species and 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 pre adsorbed cation. This leads to formation of thin film of desired material. The factors like temperature of solution. Nature of the substance, ph and concentrated of solution, area of the substrate, dipping and rinsing time etc. Affect the deposition process substrate, dipping and rinsing time etc. Affect the deposition process.

Effect of preparative parameters :-

The rate of deposition and terminal thickness depends upon 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 complexing agent. The effect of various deposition conditions on these parameters is discussed below

A) Concentration of ions :-

The increases in compound concentration lead to an increases in cation and anion concentration and film with larger thickness is obtained. Conversely, above a certain concentration of cation and anion when the rate of reaction become high and precipitation is leading to a lesser amount of material on the substrate then it lower 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 the formation of thin film. As the adsorption time is greater than that of reaction time the film formation takes place by assorted reaction to results higher terminal thickness. Equal adsorption and reaction time, results into consistent reaction. Consistent growth provides inform film formation.

C) Rinsing time :-

Rinsing between every immersion is significant to avoid the precipitation in the reaction bath. In rising 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 compound depend on the temperature. At the higher temperatures, the dissociation is greater, which gives higher concentration of cation 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.

3.2 Experimental details:

SILAR method, adsorption may be expected when two heterogeneous phases are brought in contact with each other. Hence, gas-solid, liquid-solid, gas-liquid are three possible adsorption systems. In SILAR method, the first step 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 Vander Waal or chemical attractive. Atoms or molecules of their kinds on all sides do not surround atoms or molecules of substrate surface. Therefore, they posses unbalanced or residual forces and holds the substrate particles. Thus, adsorbed atoms (ad-atoms) can be holding on the surface of the substrate. In second step the adsorbed step the adsorbed ion is reacted with anion, resulted into film formation.

Advantages of SILAR method :-

1. It is simple, convenient and inexpensive method for large area deposition.
2. The SILAR method is usually operated at low temperature.
3. Slow process which facilities better orientation of crystalline with improved growth structure.
4. SILAR does not require high quality target or substrate and vacuum at any stage.
5. The deposition rate and thickness of thin film can be easily controlled over a wide range by changing the deposition cycle.
6. It offers extremely easy way to dope films.

CHAPTER :- 5

Synthesis and Result:

For synthesis of Fe_2O_3 thin film, analytical grade ferric chloride and sodium hydroxide were used. 0.1 molar concentration of ferric chloride and sodium hydroxide dissolved in 50ml double distilled water. Beakers are arranged according to requirements of SILAR method. First beaker is of ferric chloride, second of double distilled water, third is of sodium hydroxide, and fourth is of double distilled water. In first and third beaker slide deep for 10 sec. In second and fourth beaker slide rinsing for 5 sec respectively.

- **Characterization:**

1. X-ray diffraction (XRD):

After synthesis Fe_2O_3 thin film is used for further characterization. To identify the structural information of the synthesized film, we measured X-ray diffraction (XRD) pattern Fe_2O_3. The XRD patterns of the Fe_2O_3 thin film sample is shown in Figure. The XRD pattern of Fe_2O_3 thin film indicates diffraction peaks at about 37.48°,43.56 , 63.30° ,75.90 ° and 79.98 ° correspond to the diffractions from (111) , (200) , (220) ,(311) and (222) crystal planes, respectively. So values of **a=b=c=4.15 Å** and **$\alpha = \beta = \gamma = 90°$**, indicating the formation of the perovskite phase in the cubic phase as supported by the Reference code - **01-074-2282.**

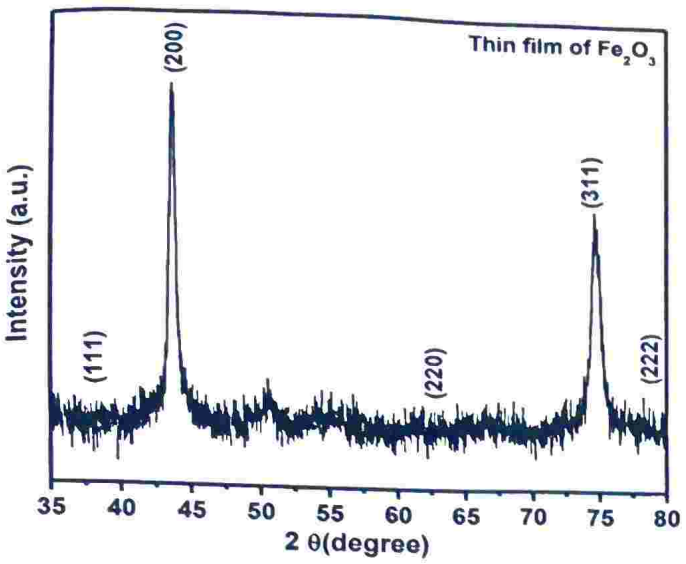


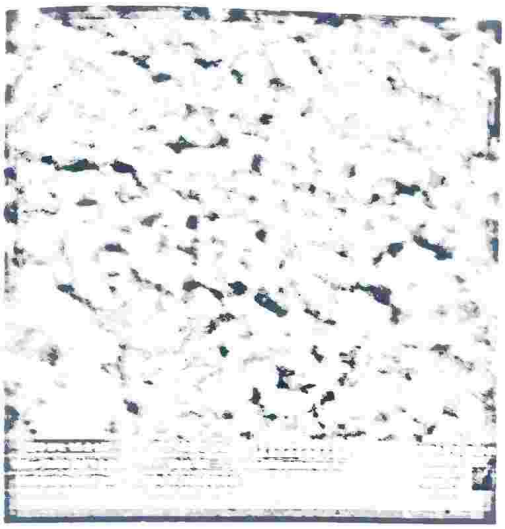
Fig:- X-Ray diffraction pattern of synthesized Fe_2O_3 thin film

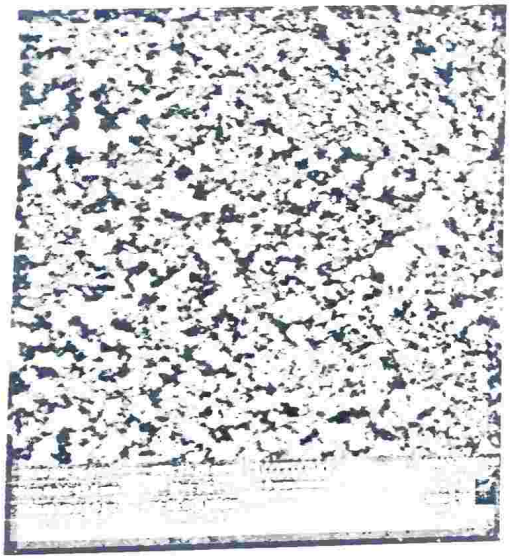
Results :

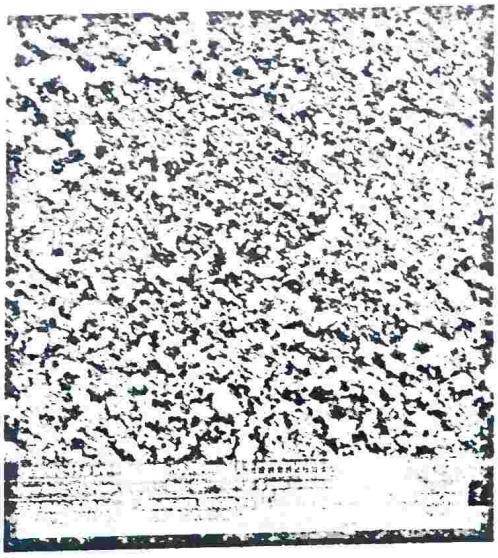
By using SILAR method, we have successfully synthesized Fe_2O_3 thin film. After synthesis Fe_2O_3 thin film used for characterizations like X-Ray diffraction. X-Ray diffraction pattern of Fe_2O_3 thin film shown in figure and indicating the crystalline nature of Fe_2O_3 thin film, we conclude that values of **a=b=c=4.15 Å** and **$\alpha = \beta = \gamma = 90°$**, confirms Fe_2O_3 thin film has Cubic structure and supported by the Reference code - **01-074-2282.**

Scanning Electron micrograph of Fe_2O_3 films :-

A SEM image of Fe_2O_3 thin film at various magnifiction are shown in following figures. The film compactness is high. From the result nanoparticles are found. The grain size is generally small and the grain size is generally narrow.







CHAPTER :- 6

SUMMARY AND CONCLUSION

In first chapter, a general introduction of the thin film is explained. The various thin film deposition techniques and theoretical background are mentioned in this chapter. And also the literature survey of Fe2O3 thin film deposition is given. The purpose of the project is starts from this chapter.

In second chapter, the main property of the material is mentioned which is supercapacitor. The mainly three types of supercapacitor is explained in detail. How they work and how material help to them is given.

In third chapter, the characterizations are explained very well.all the details of X-RD and how its work...how we find the crytaline structure is given. Also the SEM technique is explained.

fourth chapter is experimental details of preparation of FE_2O_3 thin film. In this chapter, how SILAR method works is given. What is the process of SILAR method and what steps are used for the preparation of thin fil is metioned.

Fifth chapter is synthesis and result. In this chapter, what we actually done in process to get a thin film is given. And what results find with this method and the material for thin film is given.

conclusion :

The X-RD study was carried out for Fe2O3 thin film deposited on the stainless still substrate. And also Scanning Electron Microscopy characterization is studied.