

**PHOTOLUMINESCENCE (PL) CHARACTERIZATION
OF PURE ZnO AND Mg DOPED ZnO THIN FLIM BY
SILAR METHOD**

A PROJECT REPORT

Submitted by

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Reg.No:20211062521125

In partial fulfillment for the award of the degree of

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IN

PHYSICS



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CERTIFICATE

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This is to certify that the project work entitled **“PHOTOLUMINESCENCE (PL) CHARACTERIZATION OF PURE ZnO AND Mg DOPED ZnO THIN FLIM BY SILAR METHOD”** M.RAJESHWARI (20211062521125) of II M.SC PHYSICS in partial fulfillment of the award of the degree of MASTER OF SCIENCE IN PHYSICS of the Kamarajar Government Arts College affiliated to the Manonmaniam Sundaranar University is a bonofide work carried out under my guidance during the academic year 2022-2023.

Signature of the Research Supervisor

Dr. J. Asbalter

Supervisor

DECLARATION

I hereby declare that this project work entitled “ PHOTOLUMINESCENCE CHARACTERIZATION OF PURE ZnO AND DOPED Mg THIN FILMS BY SILAR METHOD” has been submitted to the department of physics, Kamarajar Government Arts College, Surandai in partial fulfillment of the requirements for the award of the degree of the MASTER OF SCIENCE IN PHYSICS, it is record of original project work and that it has not formed the basis for the award of any degree, diploma or any other similar title so far any other universities or Institution.

Place: Surandai

Signature of the candidate

Date:

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ABSTRACT

Zinc oxide and Magnesium doped zinc oxide thin films have been deposited by using by simple SILAR method in an aqueous alkaline medium in room temperature. Thin films of ZnO& Mg doped ZnO were characterized by Photoluminescence (PL) measurement. The band gap of the ZnO and Mg doped ZnO thin films were found to be 3.17eV and 3.1eV

Keywords: thin films, silar, Mg doped ZnO, photoluminescence, ZnO

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CHAPTER –I

INTRODUCTION



CHAPTER – I

THIN FILM TECHNOLOGY

1.1. INTRODUCTION

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications. [1]

Advances in thin film deposition techniques during the 20th century have enabled a wide range of technological breakthroughs in areas such as magnetic recording media, electronic semiconductor devices, integrated passive devices, LEDs, optical coatings (such as antireflective coatings), hard coatings on cutting tools, and for both energy generation (e.g. thin-film solar cells) and storage (thin-film batteries). It is also being applied to pharmaceuticals, via thin-film drug delivery. A stack of thin films is called a multilayer.

In addition to their applied interest, thin films play an important role in the development and study of materials with new and unique properties. Examples include multiferric materials, and superlattices that allow the study of quantum phenomena.

1.2. HISTORY

In the following, a brief history of thin film technology is given for the sake of completeness:

- ~1650: Observation and interpretation of interference patterns (e. g. oil on water) by R.Boyle, R.Hooke, I.Newton.
- ~1850: Development of first deposition techniques (M.Faraday; W.Grove; T.A.Edison) and of methods of thickness determination (Arago, Fizeau; Wernicke; Wiener)

- Commercial introduction of electrochemistry (Galvanic) for gold plating of uniform-accessories.
- Thin Film Technology/Physics of Thin Films.
- ~1940: Industrial manufacturing of coatings for optical, electronical and mechanical applications (mostly military).
- ~1965: Thin film technology developed as an integral part of the mass manufacturing processes in semiconductor and optical industry.
- ~1990: Thin films of High T_c-Superconductors.
- ~1995: Thin film processing allows for the tailoring of microstructures of atomic and mesoscopic dimensions (“Quantum-Dots” by PVD, “Cu-technology”)
- Electrochemistry applied to integrated circuits.
- ~2000: Manufacturing of nanocrystalline materials with defined composition and structure for applications as protective coatings and in tribology. Deposition of highly ordered two and three dimensional objects with sizes in the nm range.
- ~2004: Upscaling of complex reactive coating processes for industrial applications (coatings on glass, thermal management). Combinatorial investigation of ternary and quaternary material systems.
- ~2006: Investigation of organic coatings leads to the emergence of organic electronics (OLED, printable circuits).
- ~2010: Preparation and characterization of the prototype two dimensional (2d) material, Graphene. Introduction of reliable solid state touch screens to communication media (Smartphone).
- ~2015: Generation of heterostructures made from 2d materials. Approaches to manufacture flexible electronic devices consisting of ultrathin materials [2].

Thin film has become an essential aspect of human life, so that hardly one can find any field of activity where they are not present. The first use of thin films for optical purposes can be dated to exactly 1912. Pohl and Pringsheim published the famous work about the production of mirrors using a vaporization process of metals like Ag and Al out of a MgO crucible in high vacuum.

After that, thin film coatings use has extended to many other applications in the optics industry like e.g. anti-reflective coatings, scratch-resistant coatings, UV- and IR-reflective coatings. In parallel, many other technological fields began to benefit from this technology: decorative coatings, tribologic coatings, biomedical coatings, self-cleaning coatings. Thin film market demand is shown in Fig.1.1. Thin film usage in different countries in different years is shown in Fig 1.2. Thin film classification based on its thickness is shown in Fig 1.3.

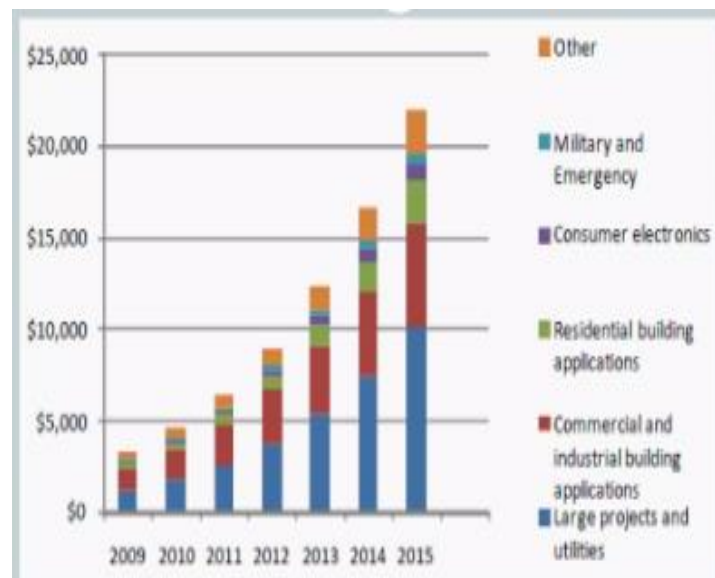


Fig1.1 Thin Film Market Demand [3]

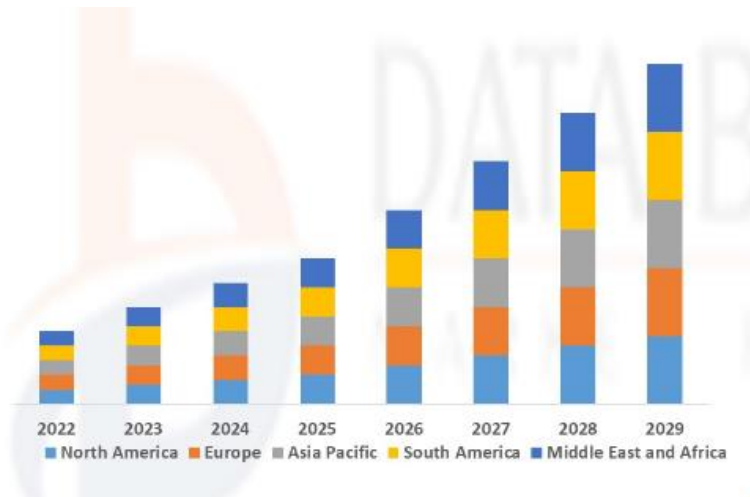


Fig1.2Thin Films Usage[4]

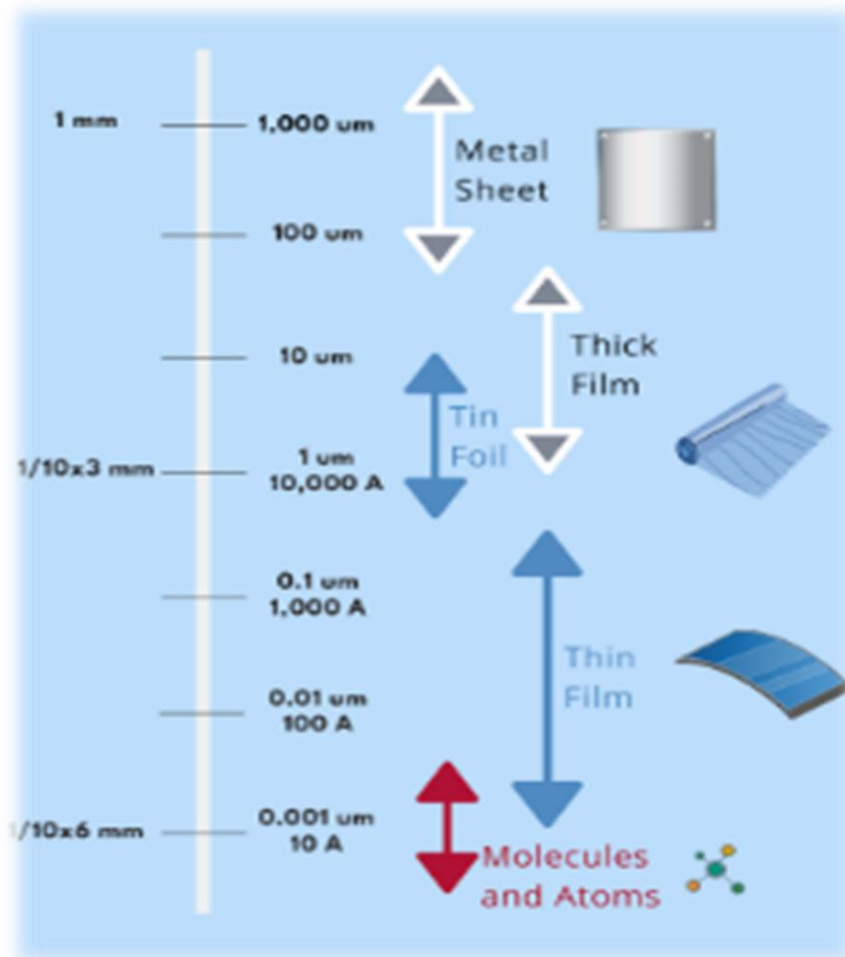


Fig 1.3Thin filmclassification[5]

Film Thickness:

Thin film science has received tremendous attention in the recent years for their applications in diverse fields such as, electronic industries, military weapon systems space science, and solar energy utilization. Thin films are used as optical and super conducting film materials, high memory computer elements, sensors. The film properties mainly depend upon the preparative conditions, film structures, presence of defects, impurities and film thickness. Various physical constants related to the bulk material properties may not often be the same for corresponding films prepared from the bulk. However, with increasing film thickness these tend to assume corresponding bulk values. Numerous applications of films lead to intense studies of these especially to develop and prepare better films with specialized properties for newer compounds or composite materials.

A thin film may be defined as a solid layer having thickness varying from a few angstroms to about 10 micrometer or so. Further it may broadly be classified in three subdivisions according to its thickness as,

I) Ultra-thin (50- 100 Å)

II) Thin (100- 1000 Å)

III) Comparatively thick one (greater than 1000 Å)

Thickness plays an important role in thin films it is an important parameter, which affects the optical, electrical, structural properties of metals considerably. Reproducible characteristics can be obtained by choosing specific thickness and proper combination of deposition parameters for a particular material.

To make sure that coatings which were produced by a given process satisfy the specified technological demands a wide field of characterization, measurement and testing methods is available.

The physical properties of a thin film are highly dependent on their thickness. The determination of the film thickness and of the deposition rate therefore is a fundamental task in thin film technology.

In many applications, it is necessary to have a good knowledge about the current film thickness even during the deposition process, as e.g. in the case of optical coatings.

Therefore one distinguishes between thickness measurement methods which are applied during deposition ("in situ") and methods by which the thickness can be determined after finishing a coating run ("ex situ") [6].

1.3. PURPOSE OF THIN FILMS:

Thin films are generally used to improve the surface properties of solids. Transmission, reflection, absorption, hardness, abrasion resistance, corrosion, permeation and electrical behavior are some of the properties of a bulk material surface that can be improved by using a thin film.

One of the fields where thin films are not only useful, but also they constitute the key manufacturing technology, is the industry of semiconductors, which includes: telecommunications devices, integrated circuits (I.C), transistors, solar cells, LEDs, photoconductors, LCDs, magneto-optic memories, compact discs, electro-optic coatings, memories, flat-panel displays, smart windows, computer chips, magneto-optic drives, microelectromechanical systems (MEMS), and multifunctional coatings.

1.4. APPLICATIONS OF THIN FLIMS:

1.4.1Thin films in optical coating

Optical coating involves depositing one or more layers of a metallic and/or ceramic material over an optical material such as a glass- or plastic-made lens, aiming to alter its transmission and reflection properties. The use of anti-reflective coating is an example of optical coating which reduces reflection of optical surfaces, e.g. photographic lenses. This effect can be obtained without significantly altering the cost of the component, since the substrate material, and the relative manufacturing technologies remains the same, while the cost of the coating itself is remarkably low.

1.4.2Thin film polarizers

Another application of thin film in the optical coating fields is in thin film polarizers. Thin film polarizers are optical polarizers that are based on the interference effect in a thin film dielectric layer; they are used, for example, to reduce glare and flare in optical systems, or as a fundamental component of LCD displays.

1.4.3 Thin films in preventing corrosion and wearing

Thin films help in preventing the corrosion of metallic parts of many devices as well as protect against wear. Materials such as jewelry, wrist watches, and knives are often coated to avoid corrosion. Thin film coatings are used also as anti-tarnish protection for some sensitive materials, like silver, in jewelry applications.

Metals such as chromium and zinc are commonly used for the coating to prevent corrosion, while some extremely hard ceramic materials like titanium

nitride, chromium nitride and alumina are used for preventing wearing of devices and tools.

1.4.4 Thin film in a semiconductor

Integrated circuits and also discrete semiconductor devices are made from a stack of thin films of conductive, semiconductor, as well as insulating materials. Thin films are deposited on a very flat substrate when making an integrated circuit, often made of silicon or silicon carbide. Then, a carefully designed stack of thin films is deposited over this substrate which is also known as the “wafer”, while each layer is carefully patterned using lithographic technologies, thus allowing for the manufacturing of a very large number of active and passive devices at the same time.

Each tiny device is in turn made from the interconnection of differently-doped thin film layers, and the interconnection between different devices is managed by the use of thin-film metallic layers, usually made with aluminum or copper. This technology led to the possibility of miniaturization of many fundamental semiconductor devices, like BJTs, FETs, MOSFETs and diodes, which -in turn- allowed for the manufacturing of the modern computers, memories and high-performance integrated circuits.

1.4.5 Thin films in Optoelectronics

Another field where thin film technology has become fundamental is optoelectronics. With technologies similar to that employed for the manufacturing of integrated circuits (deposition/lithography), the manufacturing of some very important devices in today’s life is possible: LED and OLED devices for lighting and for display applications, LCDs, CMOS sensors for video cameras.

Remarkably, thin film technology allows also for the deposition of electrically conductive, transparent films: for example, indium tin oxide (ITO) coatings are often used in the form of plain and see-through electric conductive electrodes. Thin film technology has also been used to produce thin-film batteries which have been then be inserted into chips.

1.4.6 Thin film in protective and decorative coatings

Thin films are used for protecting the surface of much material, especially optical elements, from wear, scratches, fingerprints, and even from corrosion. A protective thin film coating can also possess secondary functions, like e.g. a decorative effect, modifying the surface glossiness, its apparent color, and its texture.

Sometime, thin films are used purely for decorative purposes, like in the case of metallic coatings made over a plastic substrate, which can be made also using evaporation processes, under high-vacuum conditions, avoiding the harmful traditional processes base on galvanic deposition.

1.4.7 Thin film in solar cells

The depletion of fossil fuels and climatic change has made the use of renewable energy sources more prominent. For what concerns the use of solar energy as a viable mean for the production of energy with sustainable processes, there are two established technologies available: thermal solar, and photovoltaic.

Thermal solar systems convert energy from the sun (radiant energy) into thermal energy with the help of a energy exchanger called the solar collector. The solar collector is of two types; concentrating and non-concentrating. Thin films play a role in the coating of the solar collector which enhances the photo-thermal conversion efficiency.

The second technology i.e. photovoltaic is dominated by the use of silicon-based cells, which -in their manufacturing process- need the deposition of some thin-film functional layers to enhance their efficiency. Moreover, the niche technology of thin-film solar cells contributes to the manufacturing of very-high efficiency photovoltaic cells, which are used in room-critical applications (e.g. telecom satellites, military, etc.), where high reliability and efficiency are the key figures of merit.

1.4.8 Thin film in the Nanotechnologies

The application film in nanotechnology is one of the most recent advances in the study of thin films. This involves coating with nanocomposite materials thereby giving the materials improved mechanical properties due to a so-called “size effect”. The final functional effects which can be obtained are: oxidation resistance, high adherence, low thermal conductivity, wear-resistance, higher toughness, and hardness. In this field, primarily the magnetron sputtering method is used for deposition, due to the high purity and low level of defects which are allowed by this process.

In conclusion, the role thin films play in our day to day lives is endless as many more inventions are being made in the study of thin films. Thin film technology has been used so far from the textile or fabrics industry, to the gadgets, utensils, vehicles, tools, constructions (roads), medical examination, decoration, all of which are products very useful in our every day’s life. Thin film technologies have played a vital role in making life easier for everybody [7].

1.5 THIN FLIM DEPOSITION TECHNIQUES

Various thin film deposition techniques are as shown in Fig 4.1.

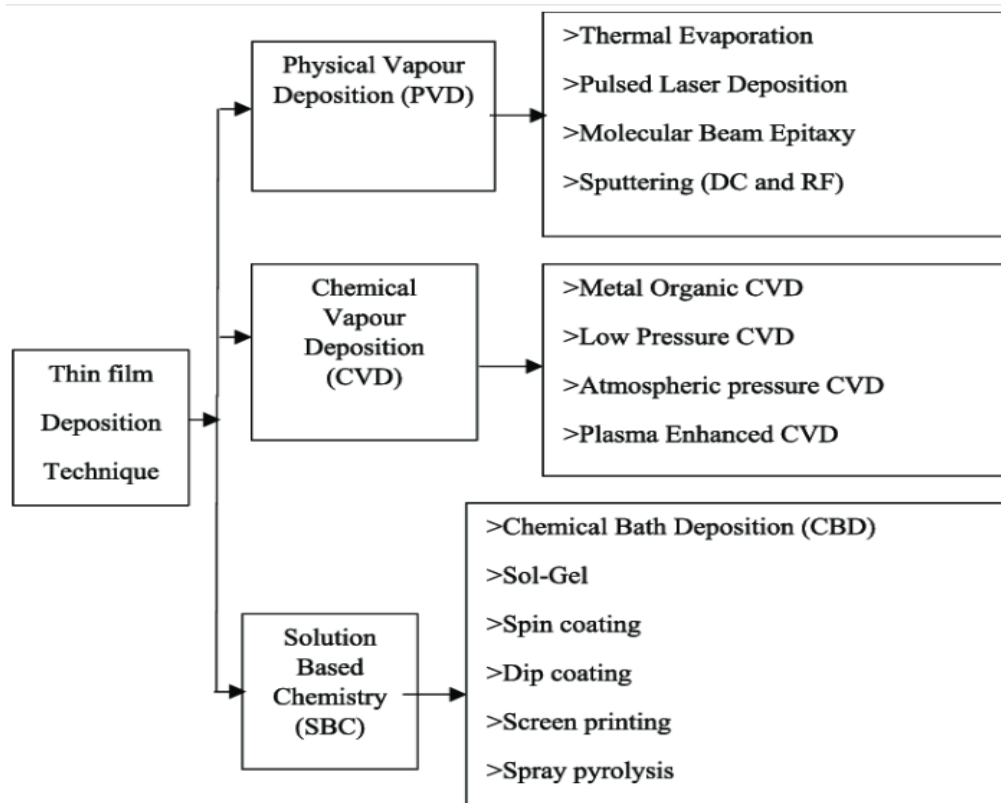


Fig 1.4Thin Film Deposition Techniques[8]

1.5.1 CHEMICAL BATHDEPOSITION METHOD

Thin films deposition methods that use chemically vaporized solids evaporating liquids and gases are classified as chemical deposition techniques. The various chemical deposition processes are as follows and discussed briefly

- Chemical vapour deposition
- Electro deposition
- SILAR

1.5.2 SILAR

One of the newest solution methods for the deposition of thin films is successive ionic layer and reaction (SILAR) method, which is also known as modified version of chemical bath deposition. SILAR method was first introduced by Nicola and Restov in 1985. 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 chemical method, a large number of varieties of substrate can be coated.

In order to avoid such necessary precipitation, a CBD is modified and known as SILAR method. In the 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 precipitation formation i.e. wastage of materials, is avoided in SILAR method.

ADVANTAGES OF SILAR METHOD:

SILAR has a number of advantages:

- ❖ 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.
- ❖ Unlike closed vapor deposition methods, SILAR does not require high quality target and or substrate not does require vacuum at any stage, which is great advantage if the method will be used for industrial application.
- ❖ The deposition rate and the thickness of the film can be controlled over a wide range by changing the deposition cycles.

- ❖ Operating at room temperature can produce films on less robust materials.
- ❖ Unlike high power methods, such as radiofrequency magnetron sputtering(RFMS), it does not cause local over heating.
- ❖ There are virtually no restriction on substrate materials, dimensions or its surface profiles.

Various applications of thin film technology is shown in Fig 1.5.

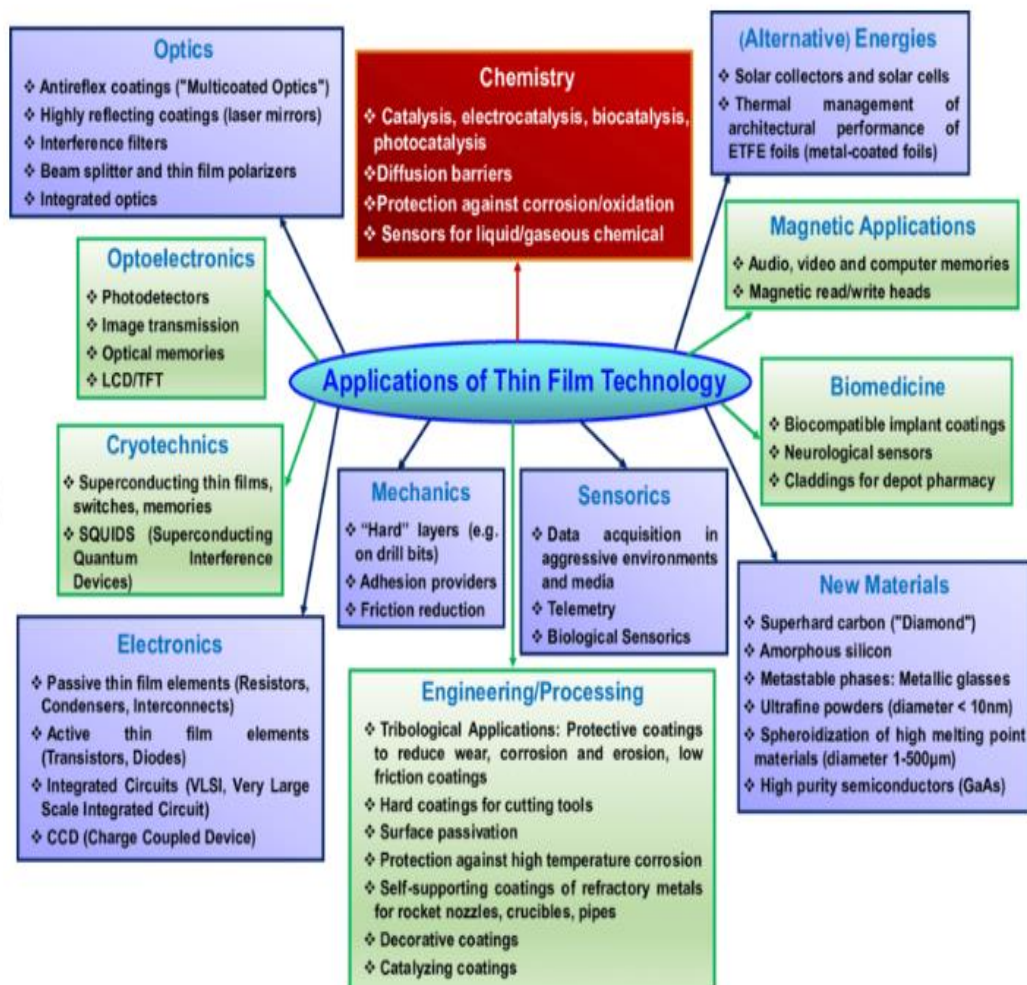


Fig1.5. Application of thin film technology[9]

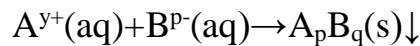
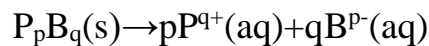
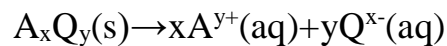
1.6 THEORY AND PROCESS MECHANISM

SILAR is one of the simplest techniques in terms of the better flexibility of the substrate choice, capability of large-area fabrication, deposition of stable and adherent film, low processing temperature for the film fabrication as well as reproducibility. This technique is very budget friendly since it does not require any sophisticated equipment.

Moreover, various fabrication parameters such as solution concentration, precursors, the number of cycles during immersion, pH, annealing, doping, and growth temperature affect the rate of fabrication as well as the structural, optical, and electrical properties of the fabricated thin films led the technique unique to study in an extensive manner.

SILAR is widely used, simple technique to fabricate high-quality thin films. During deposition, successive ionic layer adsorption and reaction of the ions take place at the solid-solution interface of the substrate.

Thus, the thin film of the compound, A_pB_y is deposited on to the substrate surface by dint of the adsorbed cations, xA^{y+} and anions, qB^{p-} due to the following heterogeneous chemical reactions:



where x, y, p, q and y^+, q^+, x^-, p^- are the number and charges of the corresponding ions A (metal ions), P (cationic precursor), Q (anionic precursor), and B (anions) respectively .

The solution having the first element containing the final target material can be thought as the compound A_xQ_y fully dissociated in the chosen solvent such as in water (Reaction 3). Usually, A_xQ_y is a metal salt where A^{y+} represents cations such as Zn^{2+} , Cu^{2+} , Mn^{2+} , Cd^{2+} , Bi^{3+} , and B^{p-} represents anions such as NO_3^- , Cl^- , SO_4^{2-} .

Hence, a basic SILAR cycle comprises four different steps, correlating alternate immersion of the substrate into cationic and anionic precursor solution followed by rinsing in every immersion cycle to eliminate loosely adhered particles as shown in Fig. 1.6. and described below:

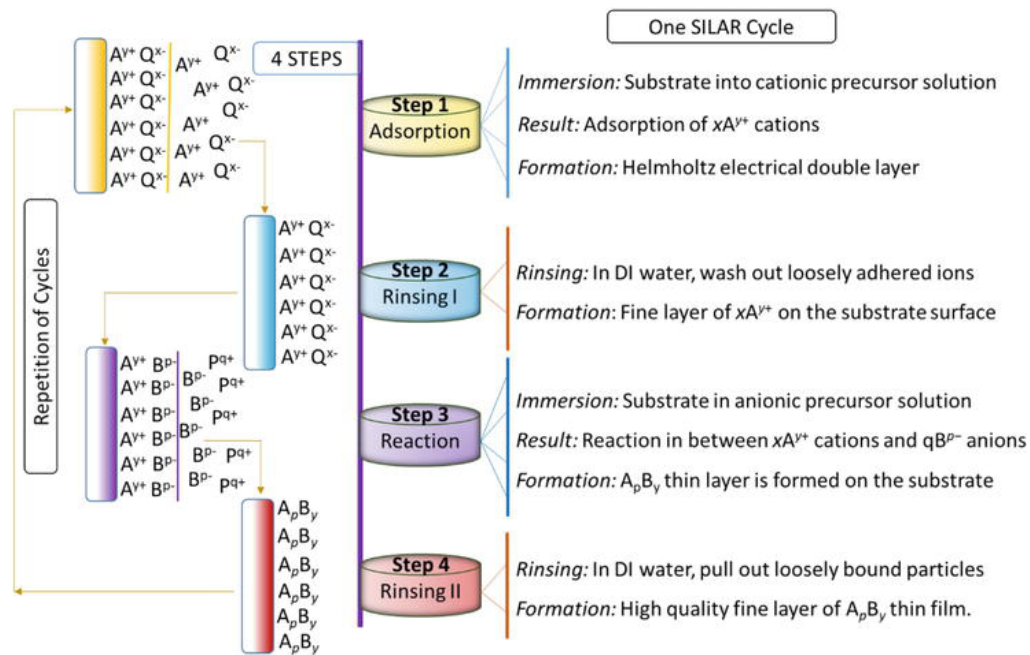


Fig 1.6 Representation Of Different Steps During A SILAR Cycle.[10]

Adsorption

First step of the SILAR process is the formation of the Helmholtz double layer, which is due to the initial adsorption of cationic precursor, $x A^{y+}$, on the surface of the substrate. This layer is generally composed of two charged layers, the positively charged inner layer and negatively charged outer layers.

The positive (+ve) layer consists of the cations, $x\text{A}^{y+}$, while the negative (-ve) layer, $y\text{Q}^{x-}$, is the counter ions of the cations.

Rinsing I

In the second step, excessive adsorbed ions, $x\text{A}^{y+}$ and $y\text{Q}^{x-}$, are rinsed away from the diffusion layer toward the bulk solution and a hypothetical monolayer is formed. This results in a saturated electrical double layer showing an ideal scenario of the process.

Reaction

In the reaction stage, the anions, $q\text{B}^{p-}$, from anionic precursor solution are introduced into the system. A solid substance, A_pB_q , is formed on the interface due to the low stability of the material. This process employs the reaction of $x\text{A}^{y+}$ surface species with the anionic precursor, $q\text{B}^{p-}$.

Rinsing II

In the final step of a SILAR cycle, the excess and unreacted species ($y\text{Q}^{x-}$, $p\text{P}^{q+}$) and the reaction by product from the diffusion layer are removed leaving expected films[10].

1.7. USES OF THIN FILMS TODAY

Idea of coating a surface with another substance is nothing new.

Jewellers have been plating cheaper metals with gold and silver for centuries, and many grandmothers have cooked with enameled crockery since cast iron became popular.

Coating technology has advanced rapidly, and we now have the ability to coat almost any substrate with almost any material imaginable.

From ceramics to metals and superconductors, thin film technology is indispensable in many industries, and its role in future advancements is certain. Manufacturers use thin films to alter or enhance the properties of an existing substrate or combine several coatings for unique effects.

The common uses of thin films today include:

- Hard coatings for cutting tools
- Corrosion protection
- Highly reflective coatings for laser mirrors
- Anti-reflective coatings for optics
- Photodetectors in infra-red devices
- Active and passive thin-film elements in electronic components
- Integrated circuits
- Friction reduce
- Coatings and adhesives in manufacturing
- Liquid or gas sensors
- Biocompatible implant coatings
- Photovoltaic coatings for solar panels
- High-purity semiconductors

Almost any field including medicine, magnetism, and alternative energy, takes advantage of the benefits that thin-film technology provides. Thin film technology plays a massive role in cutting-edge research by allowing researchers to alter the properties of existing materials in a highly-controlled and granular manner.

Advances in nanotechnology, photovoltaics and energy storage, medical devices, and electronics would have been impossible without the ability to lay down multiple layers of atom-thick coatings.

While most of the major problems facing thin film deposition technology are resolved, plenty of space still exists for innovation.

Computer simulations are becoming a staple in thin film deposition, where a manufacturer can model the entire process and outcome before going ahead with physical experimentation.

Novel modeling techniques such as multiscale and hybrid methods allow researchers to combine different simulation methods into one technique, speeding up the modeling process and improving its accuracy.

Thin film technology has already made a massive impact and sped up advances in fields such as engineering, optics, electronics, and medicine.

It offers an exciting and sustainable alternative to environmentally harmful plating techniques while helping manufacturers cut costs and increase output. The future is bright for thin-film technology, and we can't wait to see what it brings [11].

1.8 .THIN FILM CHARACTERISTIC

These are three characteristics of the thin film.

- Adsorption
- Desorption
- Surface diffusion

Adsorption

Adsorption is the transfer of atoms, ions, or molecules from a liquid or gas to a surface. A film of the adsorbate is created on the surface of the adsorbent by this process. This process is different from absorption, in which a fluid is dissolved by a liquid.

Desorption

The physical process of desorption involves the release of a previously adsorbed substance from a surface. This happens when a molecule gains enough energy to overcome the activation barrier of the bounding energy that keeps it on the surface.

Surface diffusion

A general process involving the motion of adatoms, molecules, and atomic clusters at solid material surfaces is called surface diffusion [12].

CHAPTER –II

LITERATURE REVIEW



LITERATURE REVIEW

1. Magnesium oxide (MgO) thin films were grown by successive ionic layer adsorption reaction (SILAR). As a result of Fe doping, modifications of the morphological, structural and optical properties of MgO thin films were reported. UV–Vis spectroscopy, photoluminescence (PL), X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses were performed to investigate the consequences of Fe doping. The energy band gap for the un-doped MgO and Fe doped MgO thin films were obtained to be between 3.57 and 4.00 eV. The density of PL spectrum peaks were observed to decrease with the addition of Fe which shifted to the UV region of the spectrum. All in all, pure MgO and Fe doped MgO nanostructures were successfully produced in the light of variable characterization techniques [13].
2. In this present work, pure and Sr doped ZnO films were systematically coated SILAR method is debated. The influence of Sr doping content on microstructure, surface morphology, elemental composition, photoluminescence and ammonia vapor sensing properties of these coated films were analyzed before and after incorporation of Sr. The effect of Sr doping revealed a change in crystal orientation from the (0 0 2) to the (1 0 1). SEM analysis reveals the formation of flower-like morphology formed by a number of nanowires with doping concentration. With the increase in Sr concentration, the bandgap values are increased from 3.02 to 3.20 eV. The addition of Sr also induces a rapid response towards ammonia gas sensing [14].
3. The undoped and 1%, 2%, and 3% Cd-doped MgO nanostructures were grown by SILAR method on the soda lime glass substrate. X-ray

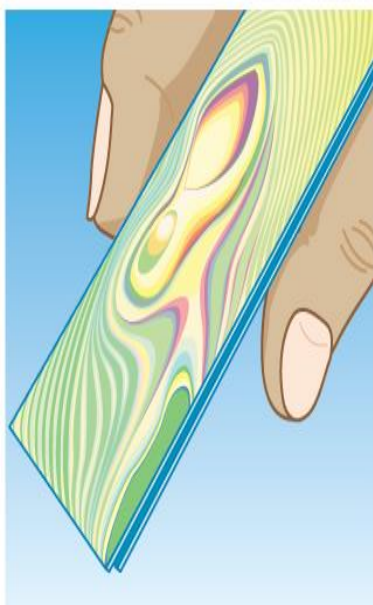
diffractometer (XRD), ultraviolet–visible spectrometer, scanning electron microscope, photoluminescence (PL), and X-ray photoelectron spectroscopy measurements were taken to investigate Cd doping effects on the structural, optical, and morphological properties of MgO nanostructure. PL measurements show that undoped and Cd-doped MgO thin films can radiate in the visible emission region[15].

4. In the present study, pure and zinc (Zn) doped tin oxide (SnO_2) thin films were grown by successive ionic layer adsorption and reaction method on the soda lime glass slides at 293 K. The prepared samples were examined to observe the impact of Zn doping on structural, morphological, electrical, and optical properties of SnO_2 crystal lattice. The x-ray diffractometer (XRD), ultraviolet–visible spectrometer, energy dispersive x-ray analysis (EDAX), scanning electron microscope (SEM), Raman, x-ray photoelectron spectroscopy (XPS), and photoluminescence (PL) spectra measurements were conducted. And, two probe detection method was applied to find the shift in resistance values corresponding to varying temperatures. The PL spectra displayed that the emission intensity decreased with the introduction of impurities into the SnO_2 lattice.[16]
5. Highly *c*-axis oriented Ga-doped ZnO films (GZO) have been grown on sapphire (0001) substrates by pulsed laser deposition (PLD) method. Photoluminescence (PL) spectra indicate that Ga atoms have a large effect on the luminescent properties of ZnO films. PL spectra of GZO films show near band edge (NBE) emissions and broad orange deep-level emissions. The NBE emission shifts to higher energy region and the intensity decreases with the increase of Ga concentration. The blue shift of NBE emission results from Burstein-Moss effect. The quenching of NBE emission is ascribed to the nonradiative recombination. The orange emission is related to the oxygen vacancies [17].

6. Highly oriented and transparent ZnO thin films have been fabricated on ultrasonically cleaned quartz substrates by the sol-gel technique. X-ray diffraction, UV-VIS, FTIR, photoluminescence and SEM are used to characterize ZnO thin films. X-ray diffraction study show that all the films prepared in this work have hexagonal wurtzite structure, with lattice constants $a = b = 3.260$ Å, $c = 5.214$ Å. The optical band gap energy of the thin films is found to be direct allowed transition ~ 3.24 eV. The FTIR spectrum of the film has the characteristics ZnO absorption band at 482 cm^{-1} . The photoluminescence spectrum of the samples has an UV emission peak centred at 383 nm with broad band visible emission centred in the range of 500 - 600 nm [18].
7. Undoped and Mg-doped ZnO thin films were deposited on Si(1 0 0) and quartz substrates by the sol-gel method. The thin films were annealed at 873 K for 60 min. Microstructure, surface topography and optical properties of the thin films have been measured by X-ray diffraction (XRD), atomic force microscope (AFM), UV-vis spectrophotometer, and fluorophotometer (FL), respectively. The XRD results show that the polycrystalline with hexagonal wurtzite structure are observed for the ZnO thin film with Mg:Zn = 0.0, 0.02, and 0.04, while a secondary phase of MgO is evolved for the thin film with Mg:Zn = 0.08. The ZnO:Mg-2% thin film exhibits high c -axis preferred orientation. AFM studies reveal that rms roughness of the thin films changes from 7.89 nm to 16.9 nm with increasing Mg concentrations. PL spectra show that the UV-violet emission band around 386–402 nm and the blue emission peak about 460 nm are observed[19].

CHAPTER – III

METHODS AND METERIALS



CHAPTER- III

METHODS AND MATERIALS

3.1 SUBSTRATE CLEANING

Glass slides 25mmx75mmx1mmdimensions are used as substrate. The glass substrate should be cleaned before the deposition. The following steps are:

1. The glass substrate is washed in soap by scrubbing the surface with the cotton swap in liquid soap to remove the oil, grease.
2. The substrate was rinsed in distilled water to remove the soap solution left on the surface followed by acetone.
3. The substrate was boiled on chromic acid in 2hours.
4. Finally, the substrate is rinsed thoroughly in deionized water dried in hot air oven.

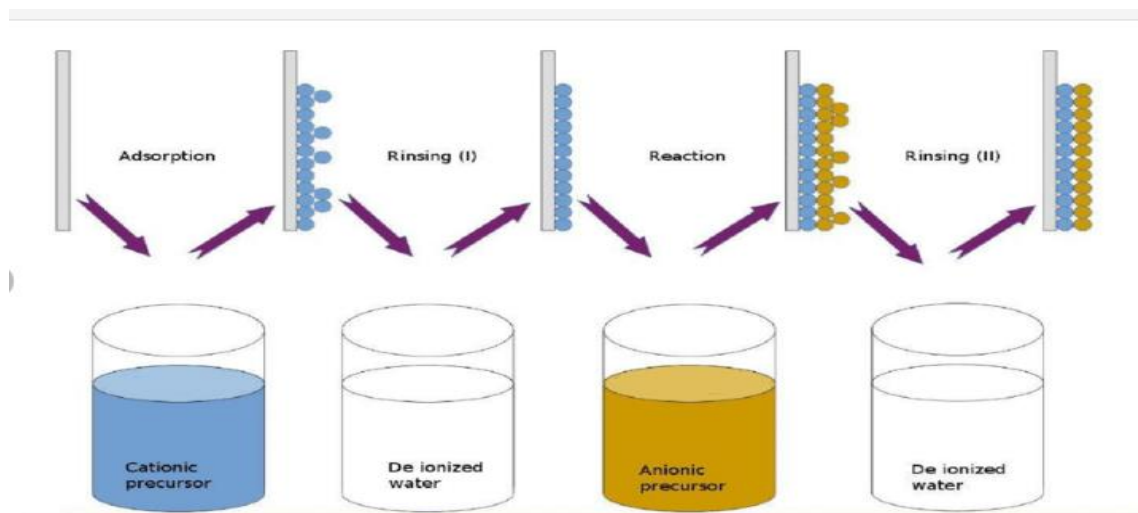


Fig3.1SilarMethod Setup[20]

3.2 PREPATION OF PURE ZnO THIN FILMS

The cationic solution was prepared by dissolving 0.2M of Zincsulphate(ZnSO_4) in 50 ml distilled water under constant stirring for 10 minutes. A quantity of 1M of sodium hydroxide (NaOH) was added to the cationic solution to make Sodium Zincate complex. Then the pH of the solution maintained at 10. Hot distilled water maintained 90°C taken as anionic solution. Glass substrate was immersed the cationic solution for 5s. It was then immersed in the anionic solution for 5s, to remove the excessive OH ions and dried in air 5s. This forms one SILAR deposition cycle. For 80 cycles we have obtained deposition of pure ZnO thin film. The prepared thin film was annealed at 300°C for three hours. The various steps in the preparation of ZnO thin films is shown in the Fig 3.2.

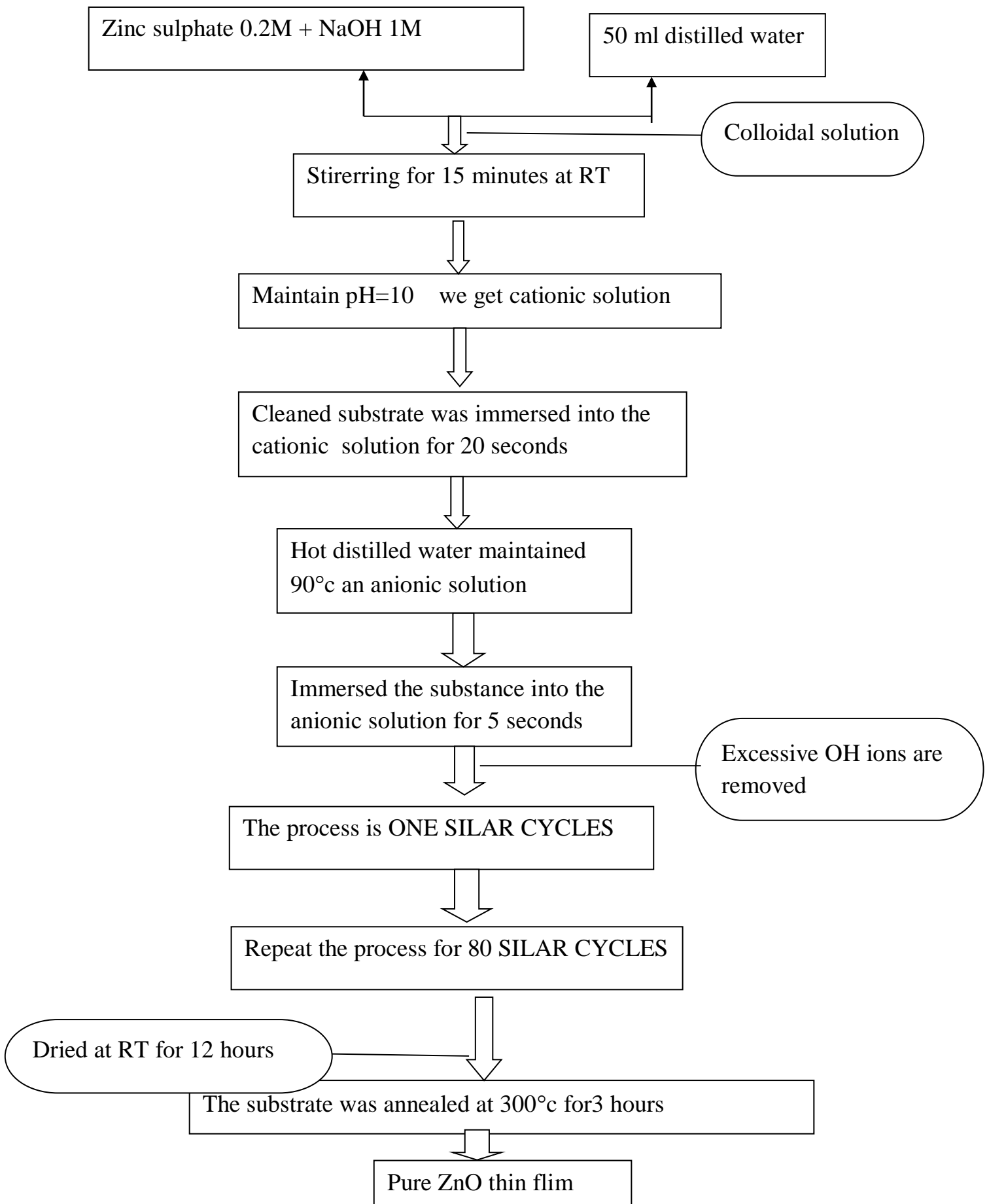


Fig 3.2 Various steps in the preparation of ZnO thin films

3.3 PREPATION OF Mg DOPED ZnO THIN FLIMS

The cationic solution was prepared by dissolving 0.2M of Zinc sulphate(ZnSO_4) and 1M of sodium hydroxide (NaOH) in 50 ml distilled water under constant stirring for 10 minutes. A quantity of 2% magnesium sulphate(MgSO_4) was added to the cationic solution which the pH of the solution maintained at 10. MgSO_4 is the doped source of Mg. Hot distilled water maintained 90°C taken as anionic solution. Glass Substrate was immersed in the cationic solution for 5s.

It was then immersed in the anionic solution for 5s, to remove the excessive OH^- ions and dried in air for 5s. This forms one SILAR deposition cycle. For 80 cycle we have obtained deposition of pure ZnO thin film. The prepared thin film was annealed at 300°C for three hours. The preparation of Mg doped ZnO thin films is as shown in Fig 3.3.

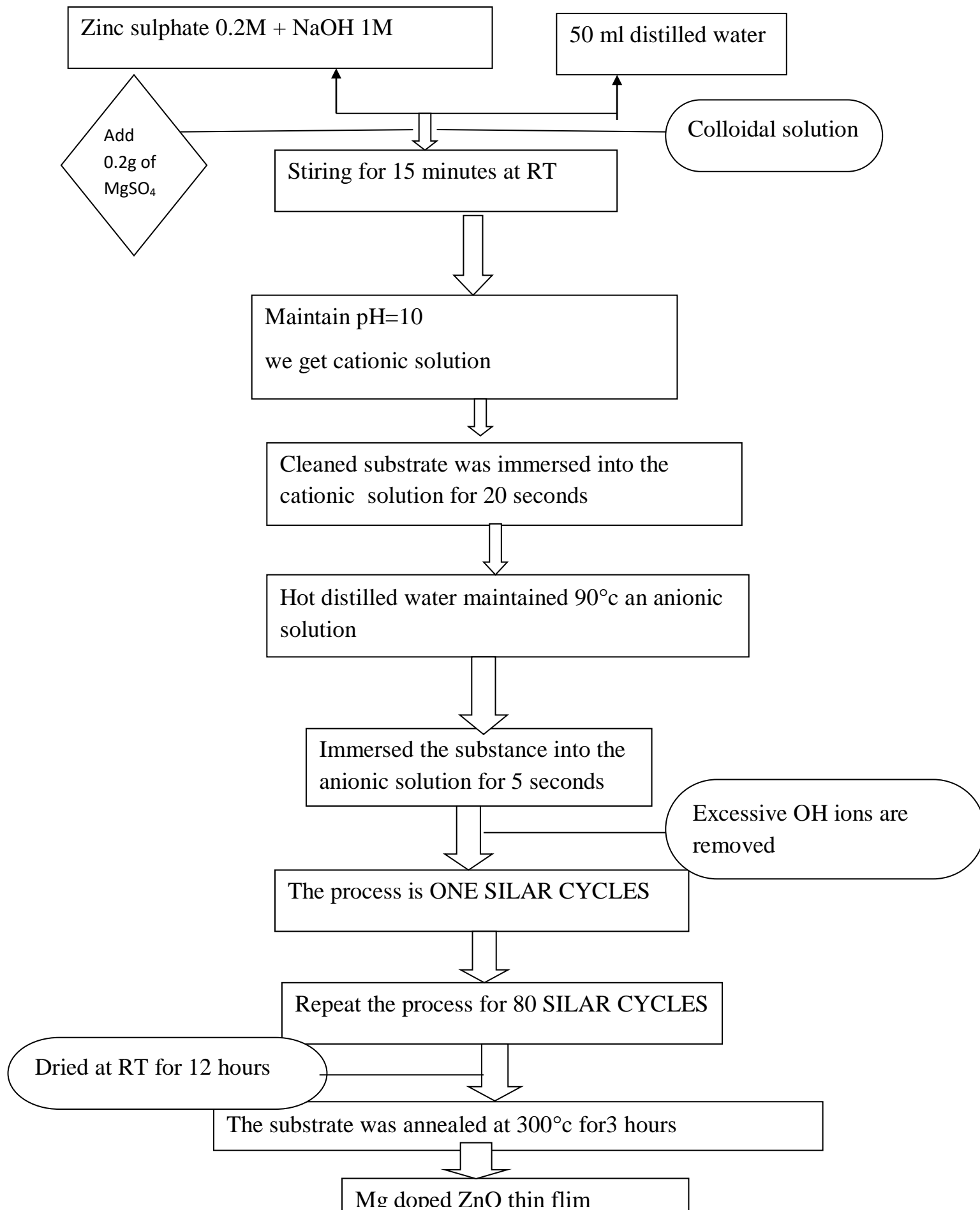


Fig 3.3 Thepreparation of Mg doped ZnO thin films

3.4 ZnO PROPERTIES

Zinc oxide (ZnO) is a versatile and inexpensive semiconductor with a wide direct band gap that has applicability in several scientific and technological fields. Zinc oxide thin films have attracted much attention in the recent years as alternative transparent conducting oxide because of their lower cost and comparable properties to those of conventional ITO films. ZnO possess novel properties such as wide band gap, good conductivity, high transparency, in addition to low deposition temperature, low cost and nontoxicity. At ambient conditions, ZnO exhibits a hexagonal wurtzite structure with a tetrahedral coordination typical of sp^3 covalent bonding, but has considerable ionic character. The unit cell is composed of two interpenetrating hexagonal-closed-packed (HCP) sublattices, where each Zn atom is surrounded by four O atoms in a tetrahedral coordination, and vice versa. There is a deviation from the ideal wurtzite crystal due to lattice expansions and ionicity. Lattice expansions are attributed to free charges, point defects, and threading dislocations.

Thus, undoped ZnO is typically non-stoichiometric and shows n-type conductivity. ZnO exhibits a direct and large bandgap, which allows it to sustain large electric fields and higher breakdown voltages. In addition, lower noise generating, high temperature, high power devices can be fabricated. ZnO has not yet shown its full potential because some challenges remain unsolved. It is seen particularly in the failure to fabricate a stable, competent and reproducible p-type doped material.

CHAPTER – IV

CHARACTERIZATION



CHAPTER- IV

CHARACTERIZATION

4.1 PHOTOLUMINESCENCE:

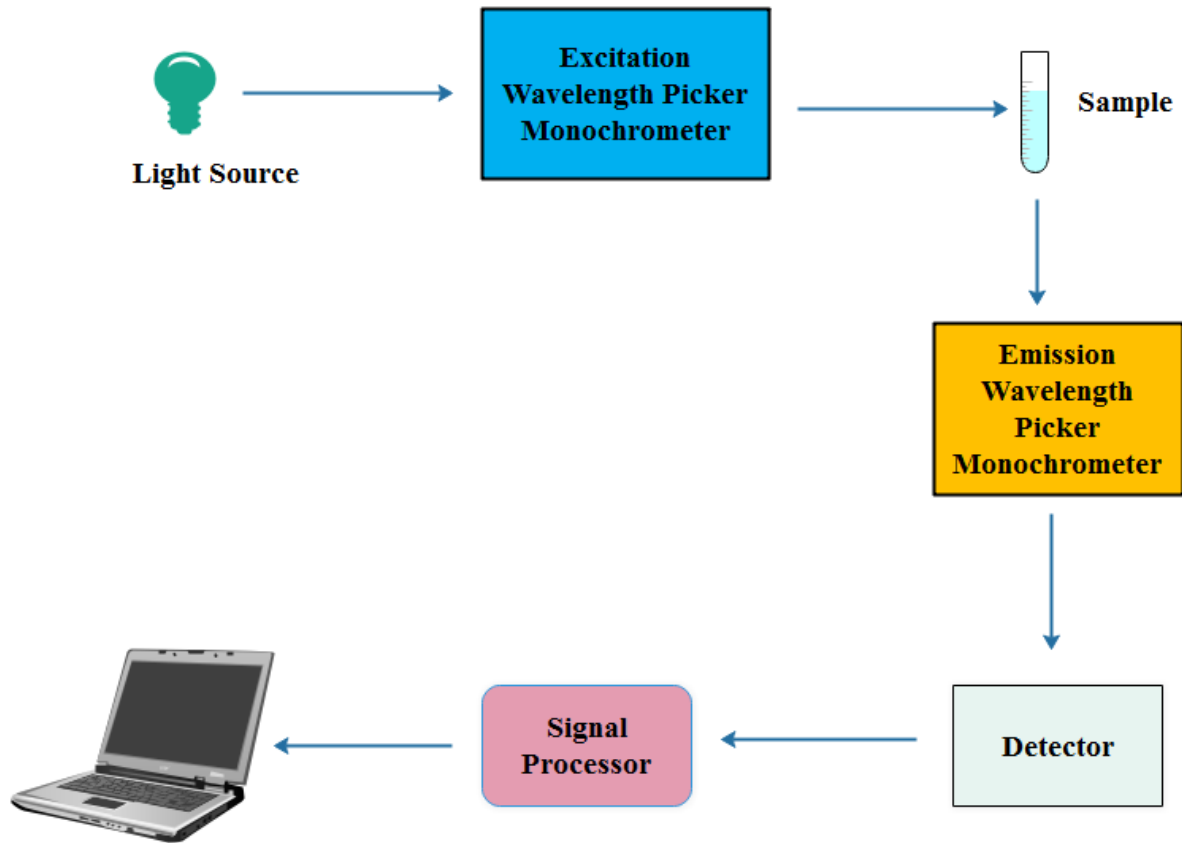


Fig 4.1 Block diagram of Photoluminescence set up[22]

Working

Photoluminescence which investigates optical property of luminescent semiconductor materials is a strong and nondestructive invention. As per analytic information of photoluminescence, we can know the type of impurities, bandgap, and impurity activation energy etc. from the spectra.

We can approximate the structure of the compound from the apex intensity of PL spectra.

Utilizing photoluminescence, the internal interface of hetero-structure can be investigated which common physical or electronic measurements cannot measure. Luminescence process comprises of three procedures:

- (1) Excitement
- (2) Heat balance
- (3) Recombination

Incident light produces electron-hole pairs and recombines to produce photons after heat stabilization. Contaminations and imperfections in structure form different energy levels in the bandgap and their relating energy will create radiation by radiation recombination process or produce absorption by nonradiative recombination process.

In PL, a material gets energy by absorbing photon at some wavelength by advancing an electron from a lower to a higher energy level. This might be depicted as making a shift from ground state to an energized state of an atom or a molecule or from the valance band to conduction band of a semiconductor crystal. The system at that point experiences a nonradiative internal relaxation including interaction with crystalline or molecular vibration modes. After a characteristic life time in the energized state, electron will come back to the ground states.

In the luminescence material the energy discharged during the final shift is as light, for this condition the relaxation is known to be radiative. It caught to be noticed that relying upon the characteristic life time of emission, quick PL with life time of sub-micro seconds is known as fluorescence, whereas slower one are pointed out as phosphorescence.

PL spectrum of all the samples were obtained at room temperature through shimadzu RF-5301 PC spectro-fluoro-photometer under the condition that the excitation wavelength λ is 325 nm and the emission spectra was recorded at the wavelength range of 350–550 nm. Also Ozone free Xenon-quartz light of 150 W was applied for excitation.

USES OF PL:

- ✚ To Measure purity
- ✚ To find Crystalline quality
- ✚ To Identify impurities

Type	Name	Wavelength
Ultraviolet	UV-C	100nm-280nm
	UV-B	280nm-315nm
	UV-A	315nm-400nm
Visible light	Purple	400nm-435nm
	Blue	435nm-480nm
	Patina	480nm-490nm
	Blue green	490nm-500nm
	Green	500nm-560nm
	Yellow green	560nm-580nm
	Yellow	580nm-595nm
	Orange	595nm-610nm
	Red	610nm-750nm
	Red purple	750nm-800nm
Infrared	IR-A	800nm-1400nm
	IR-B	1400nm-3000nm
	IR-C	3000nm-100萬nm

Fig4.2. PL colour[22]

4.2 APPLICATIONS OF PL SPECTROSCOPY:

- ❖ PL spectroscopy is not considered a major structural or qualitative analysis tool, because molecules with subtle structural differences often have similar fluorescence spectra.
- ❖ Used to study chemical equilibrium and kinetics
- ❖ Fluorescence tags/ markers
- ❖ Important for various organic-inorganic complexes
- ❖ Sensitivity to local electrical environment polarity, hydrophobicity
- ❖ Track(bio-)chemical reactions
- ❖ Measure local friction(micro-viscosity)
- ❖ Track salvation dynamics
- ❖ Measure distances using molecular rulers: fluorescence resonance energy transfer(FRET)
- ❖ Bandgap of semiconductors
- ❖ Nanomaterials characterization

Photoluminescence Spectrophotometer

Model : Cary-Eclipse

Make : Agilent

Facility Description:

Photoluminescence spectroscopy is a widely used technique for characterization of the optical and electronic properties of semiconductors and molecules. The technique its self is fast, contactless, and nondestructive.



Facility Specifications:

- ✓ *Type: 450 W ozone-free xenon arc lamp*
- ✓ *Spectral Range: 230 nm- > 1000 nm*
- ✓ *Options Ozone generating lamp with spectral range: 200 nm – >1000 nm*
- ✓ *Light Source: 150 W CW Ozone-free Xenon arc lamp*
- ✓ *Monochromators; Czerny-Turner with plane gratings for accurate focus at all wavelengths and minimum stray light*
- ✓ *Spectral Coverage – Excitation: 230 nm - 1000 nm*
- ✓ *Spectral Coverage - Emission: 200 nm - >870 nm*

Fig 4.3 Photoluminescence spectrophotometer[23]

CHAPTER-V

RESULTS AND DISCUSSSION



CHAPTER-V

RESULT AND DISCUSSION

5.1 PHOTOLUMINESCENCE STUDIES

The optical properties of the ZnO thin films were investigated using photoluminescence (PL). Photoluminescence is a common technique used to characterize the optoelectronic properties of semiconductors and other materials. Its principle is simple: electrons are excited from the valence to the conductance band of the material by a laser with an energy larger than the bandgap.

Luminescence is the process of emission of light by atoms or molecules excited. A molecule in the ground state is raised to the excited state due to the absorption of photons that have enough energy. The excited molecules undergo a vibrational relaxation of the level of energy toward the lowest excited state by nonradiative processes and then return to ground state by emitting photons.

The phenomena of fluorescence and phosphorescence fall within this definition, and therefore, the two phenomena are often referred by the general term photoluminescence. PL spectroscopy technique involves measuring the energy distribution of emitted photons after the optical excitation.

5.2 RESULT AND DISCUSSION

The PL spectra of the ZnO films and Mg doped ZnO is shown in Fig 5.1.

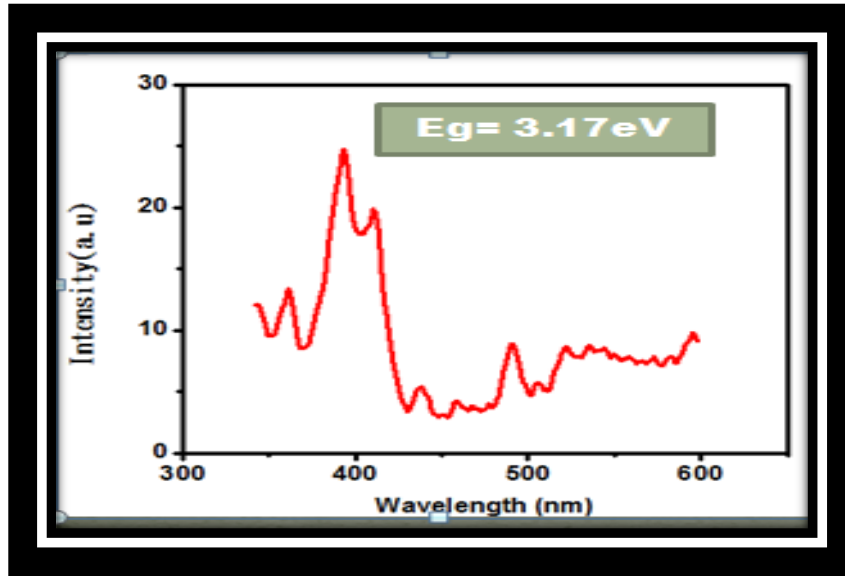


Fig5.1 .Pure ZnO Thin FlimPL Sample

The excitation wavelength is observed at 340nm. The peak observed at 360nm is due to UV emission. The sharp peak observed at 390 nm is due to visible violet emission. The peak observed at 490 nm is due to blue emission. The photoluminescence spectra of Mg doped ZnO thin film is shown in Fig 5.2. The excitation wavelength is observed at 340 nm as in pure ZnO thin film. The sharp peak observed at 360 nm is due to UV emission. The sharp peak observed at 390 nm as in undoped ZnO thin films is due to visible violet emission. The peak observed at 490 nm is due to blue emission. The doping of Mg does not alter much the emission peaks. The energy band for both the undoped ZnO and doped ZnO Mg are same as 3.1 eV.

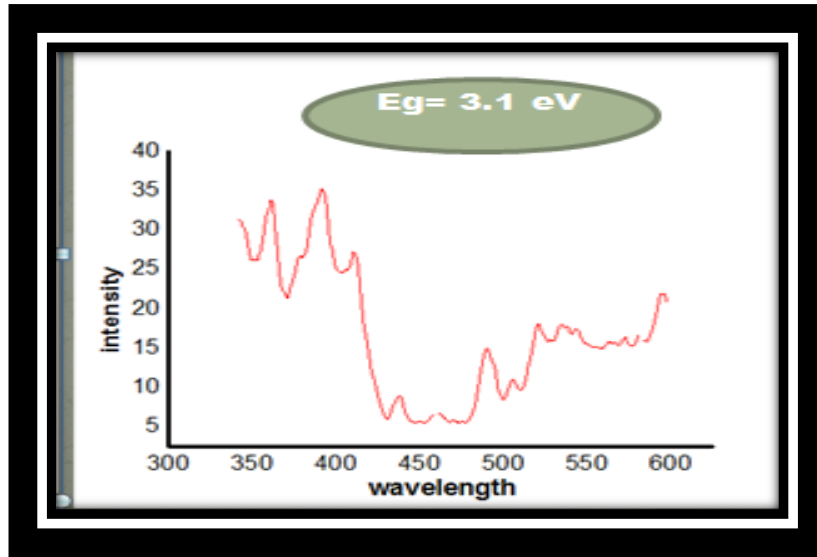


Fig 5.2 Photoluminescence Spectra of Mg Doped ZnO Thin Film

The below table shows the theoretical and experimental band gap energy value of the undoped and doped samples.

Sample	Theoretical Band gap	Experimental band gap
Pure ZnO	3.10eV to 3.37eV	3.17 eV
Mg Doped ZnO	3.155eV to 3.217eV	3.1 eV

It is observed that the theoretical and observed band gap energy values are found to be same. Therefore it is clear that the doping of Mg with ZnO does not alter the energy band gap.

CHAPTER –VI

CONCLUSION



Chapter –VI

Conclusion:

Zinc oxide thin film deposited by silar method at the room temperature and annealed at 300°C. The sharp peak is observed at 390nm and its optical band gap is found to be 3.17eV. Magnesium doped Zinc oxide thin film deposited by silar method at the room temperature and annealed at 300°C. The sharp peak is observed at 390 nm and its optical band gap is observed at 3.1 eV.



CHAPTER –VII



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CHAPTER- VI

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