

**SYNTHESIS AND CHARACTERIZATION OF
 $Zn_{1-x}Mn_xS$ THIN FILMS DEPOSITED BY
SPRAY PYROLYSIS TECHNIQUE**

Submitted By

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CANDIDATE'S DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

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Session : October, 2009

*Dedicated
To
My Parents and Teachers*

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ABSTRACT

Diluted magnetic semiconductor (DMS) thin films ($A_{1-x}M_xB$) are prepared by doping a particular amount of magnetic element (M) into II (A)-VI (B) semiconductor. $Zn_{1-x}Mn_xS$ with varying Manganese (Mn) concentrations or $x = 0.00, 0.10, 0.30, 0.50$ and 0.70 mole were synthesized on glass substrates using Spray Pyrolysis Deposition (SPD) technique. An aqueous solution containing Zinc acetated, Manganese acetated and thiourea for Zinc ions (Zn^{+2}), Manganese ions (Mn^{+2}) and sulfide ions (S^{-2}) respectively were used to deposit $Zn_{1-x}Mn_xS$ thin films at $350^{\circ}C$ substrate temperature. The ratio of Zinc acetated, Manganese acetate and thiourea were 1:1:2.

The films were characterized by Scanning Electron Microscopy (SEM), energy dispersive X-ray spectrometer (EDX), X-ray diffractometer (XRD), ultraviolet visible light (UV-vis) spectroscopy and Van-der Paw method for electrical property. The results showed that deposition time, temperature, and Mn doping concentration can affect the composition, surface morphology, crystallinity, grain size, and transmission spectra of the films. All the films were annealed at $450^{\circ}C$ and $550^{\circ}C$ for 1h.

All as deposited films showed amorphous in nature and annealed films showed crystalline nature. SEM micrographs showed that the surface morphology of as-deposited $Zn_{1-x}Mn_xS$ films was inhomogeneous and after annealing the films became homogeneous. Some fibrous like structure was found into the annealed ZnS and $Zn_{1-x}Mn_xS$ films showed some crystallographic shape which confirmed the presence of Mn into ZnS.

EDX spectra revealed the presence of Zn, Mn and S peaks in the films. All XRD patterns showed that crystallinity of the films increased with increasing Mn concentration. The size of the particles increased as the annealing temperature was increased. XRD patterns of the $550^{\circ}C$ annealed samples with different Mn concentrations (0.00, 0.10, 0.30, and 0.50 mole) showed polycrystalline nature.

UV-vis transmission spectroscopy showed that the films were highly transparent (>80%) in the visible region. The optical direct band gap of as-deposited films was decreased from 3.51 eV to 3.01eV and indirect band gap from 3.02eV to 1.85eV with increasing Mn concentrations. This indicated that the presence of Mn in the system greatly affected the optical band gap.

The electrical conductivity and activation energy increased with increasing Mn concentrations. The dc conductivity was 10^{-3} order and activation energy changed from 0.14 eV to 0.45 eV. Also the increase of electrical conductivity with the increase of temperature indicated semi conducting behavior of as-deposited films.

CONTENTS

	Pages
Declaration	I
Dedication	II
Acknowledgements	III
Abstract	IV-V
List of Contents	VI-X
List of Figures	130-132
List of Table	132
Appendix	133-146

List of Contents

CHAPTER –I: GENERAL INTRODUCTION	1-16
1.1 Introduction	3-4
1.2 Characteristics of semiconductor thin films	5
1.3 Diluted Magnetic Semiconductor(DMS) Thin films	5-6
1.3.1 Properties of DMS	6-7
1.4 Application of Thin Films	7-8
1.4.1 Spintronics	8-10
1.4.2 Antireflective coating	10
1.5 Information of Zinc, Manganese, and Zinc Sulphide.	11-12
1.5.1 Information of Zinc and Manganese	11
1.5.2 Properties of Zinc Sulphide	11-12
1.6 Review of the present Work	13-14
1.7 Aim of the present Work	14-15
References	15-16

CHAPTER –II: THIN FILM DEPOSITION TECHNIQUES	17-31
2.1 Introduction	19
2.2 Classification of the deposition process	19-23
2.3 Various deposition techniques	23-29
2.3.1 Pulsed Laser Deposition (PLD)	23
2.3.2 Vacuum Evaporation	24-25
2.3.2.1 Electron beam evaporation	24
2.3.2.2 Resistive evaporation	25
2.3.3 Spin Coating	25-26
2.3.4 Sputtering	26-27
2.3.5. Molecular Beam Epitaxy	27-28
2.3.6 Spray Pyrolysis	28-29
2.4 Advantages Spray pyrolysis Deposition (SPD) technique	30
References	30-31
CHAPTER –III: EXPERIMENTAL DETAILS	32-52
3.1 Introduction	34
3.2 Experimental Equipments	34-37
3.2.1 Preparation of Masks	34
3.2.2 Heater	35
3.2.3 The Design of the Reactor	35
3.2.4 The Fume chamber	35-36
3.2.5 Air Compressor	36
3.2.6 Spray Head/ Nozzle	36
3.2.7 Choice and Cleaning of Substrate	36-37

3.3	Film Preparation	37-43
3.3.1.	Working Solution	37
3.3.2	Estimation of compound composition	37-39
3.3.3	Film Deposition Parameters	39-40
3.3.4	Sample Deposition	40-42
3.3.5	Rate of Deposition	42
3.3.6	Thickness Control	42
3.3.7	Optimization of the Deposition Process	43
3.4	Film Characterization Methods	40-48
3.4.1	Surface Morphology and Structural Characterization	44-48
3.4.1.1	Scanning Electron Microscopy (SEM)	44-46
3.4.1.2	Energy Dispersive X-ray (EDX) spectroscopy	46
3.4.1.3	Bragg's diffraction Method	46-47
3.4.1.4	X-ray Diffraction (XRD) powder method	47-48
3.4.2	Method for film thickness measurement (Fizeau fringes method)	48-49
3.4.3	Van-der Pauw's method for Electrical Characterization	49-51
	References	51-52
	CHAPTER –IV: THEORETICAL PERSPECTIVE	53-79
4.1	Introduction	55-57
4.2	Formation of Thin Films	58-63
4.2.1	Particle preparation by spray method	58-59
4.2.2	Different Stages of Film Formation	59-62
4.2.2.1	Condensation	59-60
4.2.2.2.	Nucleation	60-62
4.2.2.3	Growth	62-63
4.2.3	Formation of $Zn_{1-x}Mn_xS$ thin film	58-59
4.3	Theory of Film Characterization	63-79
4.3.1	Optical properties of thin films:	63- 69
4.3.1.1	Measurement of absorption coefficient	64
4.3.1.2	Energy Band Gap	64-69

4.3.1.3	Refractive index, extinction coefficient, dielectric constant	70-71
4.3.1.4	Dielectric losses	72-73
4.3.2	Structural Analysis	73-76
4.3.2.1	Indexing of (hkl) by Hess- Lipson technique	73-74
4.3.2.2	Calculation of lattice parameters (a and c)	74-75
4.3.2.3	Calculation of crystallite size	76
4.3.3	Electrical Properties	76-78
4.3.3.1	DC Resistivity and Conductivity Measurement	76-77
4.3.3.2	Sheet Resistance	77
4.3.3.3	Activation Energy	77-78
References		78-79
CHAPTER –V: RESULTS AND DISCUSSION		80-121
5.1.	Introduction	82
5.2	Deposition of Pure ZnS and Zn _{1-x} Mn _x S Thin Films	82
5.3	Thickness Measurement	82-83
5.4.	Surface Morphology and Structural Investigation	83-94
5.4.1	Scanning Electron Microscopy (SEM)	83-87
5.4.2	Energy Dispersive X-ray (EDX) studies	87-89
5.4.3	X-ray diffraction (XRD) Study	89-94
5.5.	Optical Properties	
5.5.1	Optical Properties of as deposited Zn_{1-x}Mn_xS thin films	94-107
5.5.1.1	Optical Transmittance	94-95
5.5.1.2	Optical band gap (Direct and Indirect)	95-99
5.5.1.3	Optical Absorbance	99-100
5.5.1.4	Reflectance	101
5.5.1.5	Extinction coefficient	101-103
5.5.1.6	Refractive index	103-104
5.5.1.7	Dielectric constants	104-105
5.5.1.8	Dielectric loss	106
5.5.1.9	Optical conductivity	107
5.6	Effect of annealing temperature on Zn _{1-x} Mn _x S films	108-110
5.6.1	Transmittance of Zn _{1-x} Mn _x S films annealed at 550°C	108
5.6.2	Direct band gap of Zn _{1-x} Mn _x S films annealed at 550°C	108-109

5.7	Effect of annealing temperature on $Zn_{0.70}Mn_{0.30}S$ films	109-113
5.7.1	Transmittance of $Zn_{0.70}Mn_{0.30}S$ thin film	109-110
5.7.2	Direct Band gap of $Zn_{0.70}Mn_{0.30}S$ thin film	110-113
5.8.	Electrical Properties	113-119
5.8.1	Variation of DC Resistivity with Temperature	113-114
5.8.2	Variation of Conductivity with Temperature	114-116
5.8.3	Variation of Sheet Resistance with Temperature	116-117
5.8.4	Activation Energy	117-119
	References	119-121

	CHAPTER –VI: CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK	122-127
6.1	Conclusions	124-126
6.2	Suggestions for future work	127

CHAPTER - I
GENERAL INTRODUCTION

At a glance Chapter-1

- 1.1. Introduction**
 - 1.2. Characteristics of semiconductor thin films**
 - 1.3. Diluted Magnetic Semiconductor(DMS) Thin films**
 - 1.3.1 Properties of DMS**
 - 1.4. Application of Thin Films**
 - 1.4.1 Spintronics**
 - 1.4.2 Antireflective coating**
 - 1.5. Information of Zinc, Manganese, and Zinc Sulphide.**
 - 1.5.1 Information of Zinc and Manganese**
 - 1.5.2 Properties of Zinc Sulphide**
 - 1.6. Review of the present Work**
 - 1.7. Aim of the present Work**
- References**

CHAPTER-I

GENERAL INTRODUCTION

1.1 Introduction

Thin films of II–VI binary compound semiconductor have drawn scientists' attention more than four decade. Such attention is related to possibility of creation number of high-performance electronic devices on basis of thin layers. But, at the same time, in most cases expectations of researchers still remain unjustified. It is largely conditioned by the structural specialty of chalcogenide thin films, which, in turn, determine electro-physical and optical properties of layers [1]. Among the family of II–VI binary compound semiconductors, ZnS, ZnSe, ZnTe CdS, ZnO, CdTe, etc. are the fore most candidates. [2]. Materials containing zinc are interesting because of their applications in many areas of modern technology. In the past 10 years, extensive attention has been paid to the preparation and characterization of semiconductor sulfides as a consequence of their interesting properties and potential applications. Among those ZnS is a commercially important semiconductor with a wide band gap about 3.60-3.70eV [3] which makes it suitable as a transparent material in the visible region. They exist mainly in two forms, (hexagonal wurtzite structure) and (cubic sphalerite structure). it is a potentially important material to be used as an antireflection coating for hetero-junction solar cells.

ZnS doped with transition-metal element (Fe, Mn, Co, Ni, cu, Sc, Ti, V, Cr) or rare-earth element (Eu, Gd, Er) has also been used as effective phosphor material. ZnS doped with Mn is also an equally important electroluminescent material. Bhargava et al. first reported luminescence properties of Mn-doped ZnS nanocrystals prepared by a chemical process at room temperature, [4] Ternary derivatives of ZnS have generated a lot of research interest for applications in the field of optoelectronic devices. One such ternary compound is Zinc Manganese Sulphide ($Zn_{1-x}Mn_xS$). $Zn_{1-x}Mn_xS$ ternary compounds are promising materials for a variety of optoelectronic device applications, such as electroluminescent, photo luminescent and photoconductor devices and especially in photovoltaic cells. In recent years nanocrystalline $Zn_{1-x}Mn_xS$ attracted much attention

because the properties in nano form differ significantly from those of their bulk counterparts. Therefore much effort has been made to control the size, morphology and crystallinity of $Zn_{1-x}Mn_xS$ thin film.

Several techniques have been used to produce $Zn_{1-x}Mn_xS$ thin film such as Molecular Beam Epitaxy (MBE,) Pulsed Laser Deposition (PLD) Chemical Solution Deposition (CSD), Spray Pyrolysis Deposition (SPD), Chemical Vapor Deposition (CVD), sputtering. Every thin film deposition technique has its own advantages and disadvantages. Recently more attention has been bestowed on the development of cost effective thin films deposited techniques, especially in the field of photovoltaic technology, for the preparation of device quality alternative absorber or buffer layer over large areas in order to economize the technology. In view of this, a simple spray pyrolysis deposition technique is developed for the preparation of $Zn_{1-x}Mn_xS$ film in the present investigation. This is a low cost and non-wet technique that has good control over the rate of deposition. This technique of film preparation is very attractive because it is inexpensive, simple and capable of getting a deposition of optically smooth and homogenous layers of amorphous or crystalline ZnS and $Zn_{1-x}Mn_xS$ films

Although much work has been done on the electronic and optical properties of polycrystalline ZnS, less information is available on the ternary $Zn_{1-x}Mn_xS$ system. Thin films of $Zn_{1-x}Mn_xS$ are known to have properties in between those of ZnS and MnS. Its band gap can be tailored from 3.1eV (MnS) to 3.7eV (ZnS) [5]. This makes the material much more attractive for the fabrication of solar cells. It is demonstrated that the chemically sprayed films have high carrier densities and sensitivities. Both the energy gap and the film composition depend on the spraying solution composition. In this article, the optical, structural and electrical properties of $Zn_{1-x}Mn_xS$ thin films prepared using the chemical spraying method are investigated by varying the concentrations of Mn in the range $x = 0.00$ M to $x = 0.90$ M.

1.2 Characteristics of Semiconductor Thin Films

Thin film technology is an important special branch of Physics in which the characteristics of different metals, semiconductors and insulators are investigated in thin

film form. The word “Thin” gives a relative measurement of any dimension but not to any absolute value and “Film” means a coating of layer of a material onto another material (called substrate) which is non-reactive except for sufficient adhesion. The word “Thin Film” is defined as a material created by the random nucleation and growth processes of individually condensing or reacting atomic / ionic / molecular species on a substrate. When a thin layer of solid material is formed on a solid substrate and if the layer thickness becomes comparable in magnitude with mean free path (~10 nm-100 nm) of the conduction electrons of solid material then this layer is termed as “Thin Film”.

During the past seventy years a new branch of science has been introduced. Stimulated by the need for few and improved optical and electronic devices in industrial and military applications, and also by the exiting possibilities opened up for basic research into the physics and chemistry of interfaces. This new branch of science has become known as “Thin solid films” and the field has been developed very rapidly since 1940. The process of thin film deposition involves one or more phase transition and a study of the thermodynamics and kinetics of these phase transformations can give the knowledge about the formation of a thin film. The properties of thin films are something different from that of the bulk material due to the various reasons. The properties of thin film changes appreciably when it is cooled to a very low temperature or heated at a higher temperature (above room temperature). The study of the changes in the properties of thin film with temperature provides a great deal of information about the properties of thin films Imperfections are formed on both vitreous and crystalline substrate, but a high temperature oriented single crystal films are formed on crystalline substrates.

1.3 Diluted Magnetic Semiconductor (DMS) Thin films

Dilute magnetic semiconductors have recently been a major focus of magnetic semiconductor research. These are based on traditional semiconductors, but are doped with transition metals instead of, or in addition to, electronically active elements. Magnetic semiconductors are semi conducting materials that exhibit both ferromagnetic and semiconductor properties. If implemented in devices, these materials could provide a new type of control of conduction. Whereas traditional electronics are based on control of

charge carriers (n- or p-type), practical magnetic semiconductors would also allow control of quantum spin state (up or down). This would theoretically provide near-total spin polarization which is an important property for spintronics applications, e.g. spin transistor. There is a wide class of semi conducting materials which is characterized by the random substitution of a fraction of the original atoms by magnetic atoms. The materials are commonly known as semi magnetic semiconductors (SMSC) or diluted magnetic semiconductors (DMS). The most common DMS are II-VI compounds (like CdTe, ZnSe, ZnS, CdSe, CdS, etc.), with transition metal ions (e.g. Mn, Fe or Co) substituting their original cations.

1.3.1 Properties of DMS

Several of the properties of DMS materials may be tuned by changing the concentration of the magnetic ions. The ternary nature of DMS provides the possibility of tuning parameters such as the band gap and the lattice constant by varying the composition of the material. A change in the concentration of the magnetic ions alters the magnitude of several magneto optical effects and influences the magnetic properties of the material. It has been possible to grow the bulk crystals with structures of the form $A_{1-x}Mn_xB$, where A and B are atoms from the second and the sixth group (II-VI) of the periodic table of elements respectively within the wide range of compositions $x < 0.7$. Many spectacular features of SMSC are induced by the interaction between the localized electrons of d shells of the magnetic ions and delocalized band carrier states (of s or p origin). The fact that the s-d interaction is in the ferromagnetic coupling of the spins of transition metal ions and conduction band electrons. The p-d interaction is in the spins of the valence band electrons to that of the magnetic ions, the hybridization is anti ferromagnetic for all Mn, Fe or Co-based II-VI DMS. Theoretical considerations have pointed out the possibility of ferromagnetic p-d interaction for transition metal ions with less than half-filled p-d shells. There are three types of semiconductors:

- (a) Nonmagnetic semiconductor, which contains no magnetic ions;
- b) Diluted magnetic semiconductor (DMS), i.e., a cross between a nonmagnetic semiconductor and a magnetic transition-metal (TM) element, in a paramagnetic state;
- (c) DMS with ferromagnetic order mediated by charge carriers (holes).

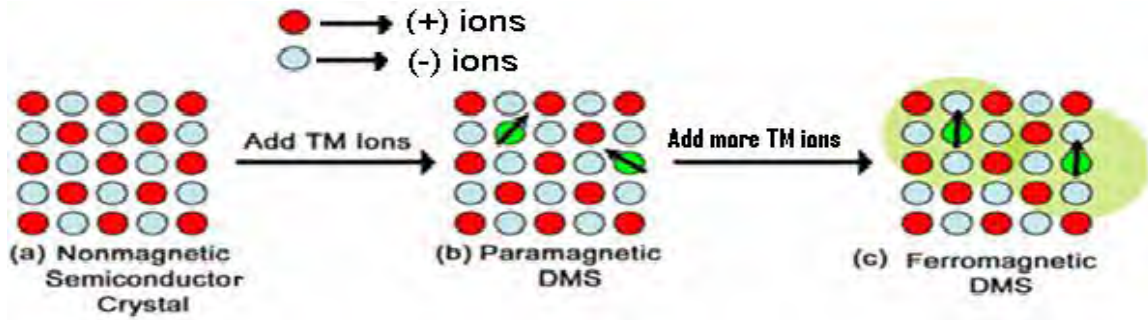


Fig-1.1: Interaction among the spins leads to ferromagnetic order at low temperature (300K)

These semiconductor alloys may be considered as containing two interacting subsystems. The first of these is the system of delocalized conduction and valence band electrons. The second is the random, diluted system of localized magnetic moments associated with the magnetic atoms. The fact that both the structure and the electronic properties of the host crystals are well known means that they are perfect for studying the basic mechanisms of the magnetic interactions coupling the spins of the band carriers and the localized spins of magnetic ions. The coupling between the localized moments results in the existence of different magnetic phases (such as paramagnets, spin glasses and antiferromagnets). The wide variety of both host crystals and magnetic atoms provides materials which range from wide gap to zero gap semiconductors, and which reveal many different types of magnetic interaction.

1.4 Application of Thin Films

II-VI compound Metal sulphide semiconductors have immense technological importance in different applied branches of science and technology. Zinc sulphide (ZnS) is one of the most important II-VI semiconductor Metal sulphide thin film. Consequently, it is a potentially important material to be used as an antireflection coating. Particularly, ZnS is believed to be one of the most promising materials for blue light emitting laser diodes and thin film electroluminescent displays. Here some application is given for heterojunction solar cells [6]. It is an important device material for the detection, emission and modulation of visible and near ultra violet light [7]. They are described as bellow

1.4.1 Spintronics

Spintronics is a rapidly developing field in which the charge and the spin of electrons are utilized in electronic devices. Some new spintronics devices are:

(I). Spin transistor

Similar to typical metallic semiconductor transistor, spin transistors may function as switches or amplifiers, or for data storage. A spin transistor is a device which uses the fact that electrons (fermions) naturally exist in one of two spin states, spin up or spin down. The electrons are set in a particular spin state to store information, for example spin up and spin down being analogous to a 1 and a 0 in binary numbering. Spin states are advantageous because once applied to an electron they are semi-permanent and can be detected or even altered in some cases without the application of an electric current. These characteristics allow for devices utilizing spin which require much less power to function, as well as potential non-volatile solid state memory storage due to spin permanent

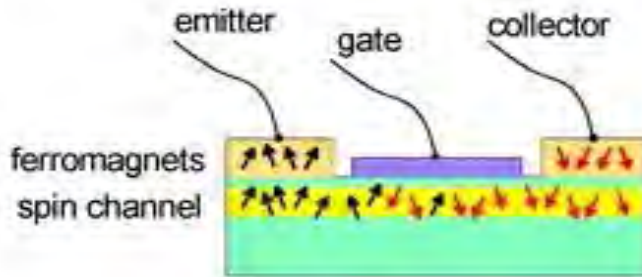


Fig-1.2: Spin Transistor

(II). Spin valve

A spin valve is a device which utilizes the Giant Magneto resistive effect. The device functions by alternating its electrical resistance depending on the alignment of the magnetic layers. The device can be made to be highly resistive or highly conductive depending on the direction of the applied magnetic fields in the conducting layers. The resistive setting functions by applying a particular spin to electrons in one layer and the

opposite in the other layer with an applied potential difference across the device. When electrons of one spin encounter the other layer they are forced to flip their spin, requiring extra energy and causing the device to become highly resistive to electron flow. Due to this property, a spin valve may act as a magnetic switch which is activated by a magnetic field - when the magnetic orientation of the plates is opposite, the device is highly resistive, and when the fields are aligned it is highly conductive. This technology offers very fast switching speeds and reduced power consumption.

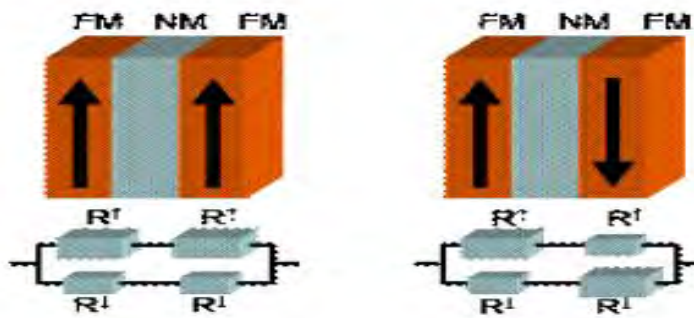


Fig-1.3 Spin valve

(III) Spin light emitting diode (LED)

The function LED is simply by injection of a charge carrier, usually an electron, from a Ferro magnet into a semiconductor layer where it combines with a hole supplied by the substrate, resulting in the emission of light.

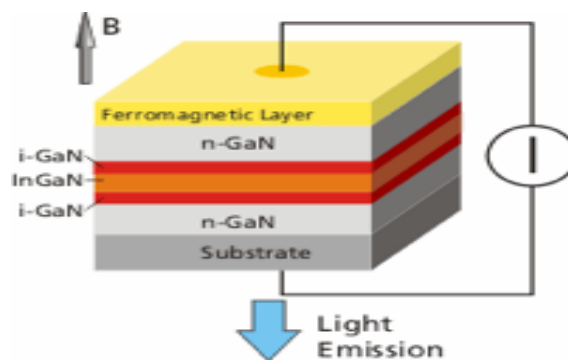


Fig-1.4: Spin LED

The emitted light will then possess a polarization dependent on the spin-polarization of the charge carriers involved in the recombination additionally, spin LEDs can be used in the study and development of other spintronics devices where analysis of the polarization

of the emitted light provides information about the spin states of the charge carriers in the device.

1.4.2. Anti-reflective coatings

Anti-reflective coatings are used in a wide variety of applications where light passes through an optical surface, and low loss or low reflection is desired. Examples include anti-glare coatings on corrective lenses and camera lens elements.

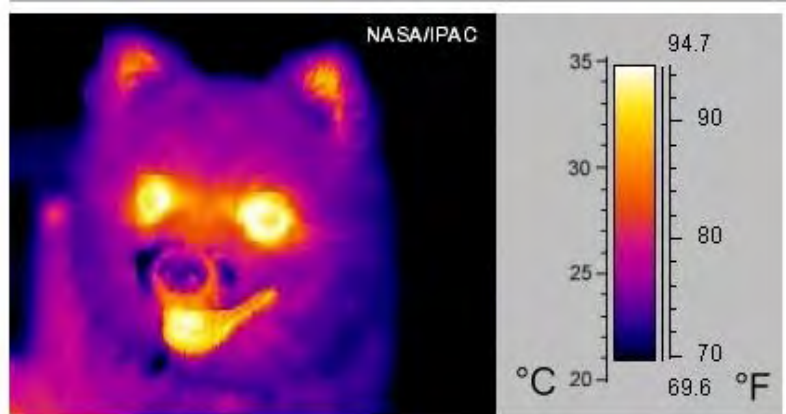


Fig-1.5: Moth eye

Moths' eyes have an unusual property: their surfaces are covered with a natural nanostructure film which eliminates reflections. This allows the moth to see well in the dark, without reflections to give its location away to predators [8].

The structure consists of a hexagonal pattern of bumps, each roughly 200 nm high and spaced on 300 nm centers. This kind of antireflective coating works because the bumps are smaller than the wavelength of visible light, so the light sees the surface as having a continuous refractive index gradient between the air and the medium, which decreases reflection by effectively removing the air-lens interface. Practical anti-reflective films have been made by humans using this effect; this is a form of biomimicry

1.5 Information of Zinc, Manganese, and Zinc Sulphide

1.5.1 Information of Zinc and Manganese

Table 1.1: Properties of Zn and Mn

	Zinc	Manganese
Symbol	Zn	Mn
Crystal structure	Hexagonal	Cubic
Classification	Metal	Transition metal
Density at 300K	7.133 gm.cm ⁻¹	7.43 gm.cm ⁻¹
Ionic radius	0.74 Å	0.83 Å
Atomic radius	1.53 Å	1.79 Å
Atomic volume	9.2 cm ³ .mol ⁻¹	1.39 cm ³ .mol ⁻¹
Electron work function	4.33 eV	4.10 eV
Electron configuration	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ²	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁵ 4s ²

1.5.2 Properties of Zinc Sulphide

Zinc sulphide) is a chemical compound with the formula ZnS. It is p-type semiconductor. It is typically encountered in the more stable cubic form, known also as zinc blende or sphalerite. and hexagonal form also known as a synthetic material and mineral wurtzite. Some physical properties of ZnS are mentioned below [9].

Table 1.2: Basic properties of ZnS

	Cubic	Hexagonal
Density at 300K	4.11gm.cm-1	3.98 gm.cm-1
Lattice parameter at 300K	a = b = c = 0.541nm	a = b = 0.3811 nm & c = 0.6234 nm
c / a ratio	-----	1.636
Nearest Neighbour Dist. at 300K	0.234 nm	0.234 nm
Dielectric Const. low frequency	8.9	9.6
Refractive index	2.368	2.356
Band Gap at 300K, Direct	3.68 eV	3.911 eV

Zinc Blend (Cubic) crystal structure of ZnS - The structure of cubic ZnS may be viewed as a CCP lattice of anions ($Z = 4$), with the smaller cations occupying every other T_d hole ($Z = 4$).

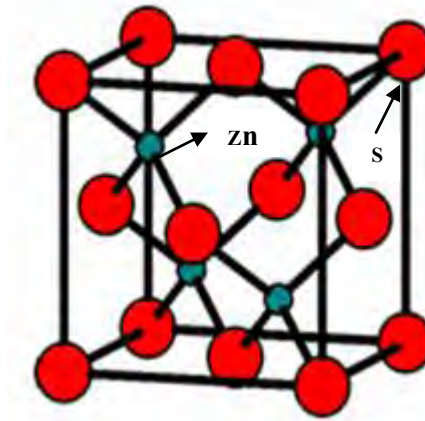


Fig-1.6: Zinc Blend ZnS

Zinc Blend lattices - The lattice of cations in zinc blende is a FCC lattice of the same dimension as the anion lattice, so the structure can be described as interpenetrating FCC lattices of the same unit cell dimension. Note that the only difference between the halite and zinc blende structures is a simple shift in relative position of the two FCC lattices.

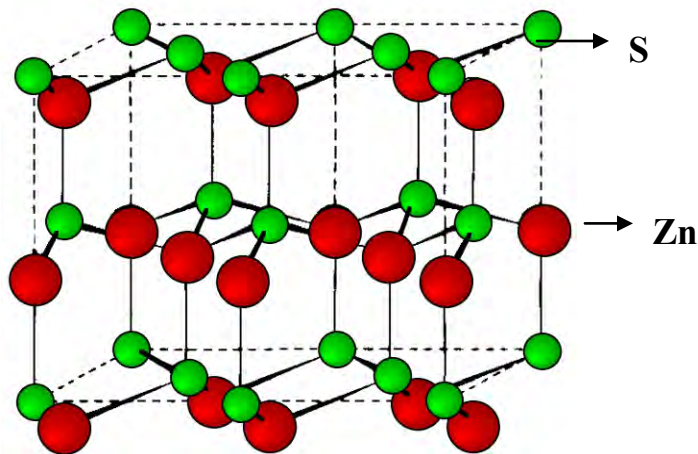


Fig-1.7: Hexagonal (wurtzite.) ZnS

Hexagonal (wurtzite.) crystal structure of ZnS - The structure of Hexagonal ZnS may be viewed as a hcp lattice of anions (S^{2-}) and cations (Zn^{+2}) occupying half of T_d hole. There are two T_d holes for each atom in hcp array.

1.6 Review of the present Work:

During the last few years several authors reported the properties of semiconductor thin films deposited by different methods. Here in this section a survey on the reported works are given.

In 1991, Ying Wang and Norman Herron characterized $Zn_{1-x}Mn_xS$ DMS Clusters [10] and they prepared $Zn_{0.93}Mn_{0.07}S$ sample with a slight Zn and Mn (9.6×10^{-4} mole/100g). The concentration of the cluster was 4.56 wt%. They investigated distinct peaks at 2θ of 28.7° , 47.5° , and 56.5° corresponding to the (111), (220), and (311) planes. **In 2000, A. D. Dins more, D. S. Hsu, S. B. Qatari, J. o. Cross, T. A. Kennedy, H. F. Gray, and B. r. Ratna** characterized Mn doped ZnS nanoparticles [11]. They investigated that the crystallite size of unannealed samples were approximately 3.5nm, with some size variation (~ 0.5 nm) from sample to sample. After annealing at $300^\circ C$ and $350^\circ C$ the average crystallite sizes were 6.0nm and 8.4nm respectively and (100) and (101) peaks were visible. **In 2002, B Bhattacharjee and S chaudhuri** synthesized Mn doped ZnS in sol- gel method [12]. They investigated optical absorption and optical band gap in the wave length range 200-800nm. They noticed that band gap of ZnS was 3.6 eV and band gap increased with 5% Mn doping and the grain size was ~ 3 nm for ZnS and ~ 2.5 nm for 5% doped films. **In 2005, Subhajit Biswas, Soumitra Kar, and Subhadra Chaudhuri** synthesized Mn doped ZnS thin films by Solvothermal Process [13]. They investigated the $Zn_{1-x}Mn_xS$ films in hexagonal wurtzite structure and 0.24, 2.49, and 5.58 atom % Mn was detected for 1%, 6% and 20% doped ZnS films. **In 2007, A U Ubale, V S Sangawar and D K Kulkarni** deposited ZnS thin films by chemical bath deposition technique [14]. They investigated that the grain size was changed from 6.9-17.8nm as film thickness was changed from 76-332nm. and band gap was increased from 3.68-4.10 eV as thickness was reduced from 332-76 nm

In 2009, Ravisharma, B. P. Chandra, and D. P. Bisen deposited Mn doped ZnS by chemical routs [15]. They observed that the band gap energy of the samples corresponding to the absorption edge was found in the range 4.5eV-4.8eV with increasing capping agent concentration and from XRD studies, the samples was cubic structure having peaks at (111),(220),(311)planes and lattice parameter was 5.31Å, close

to standard value 5.42Å. Taejoon Kang and Bongsoo Kim synthesized ZnS doped with Mn/Fe and Co and investigated that the Fe doped ZnS thin films exhibit the largest magnetization value, H_c was ~ 130 Oe [16]. **In 2010, Elham Mohaghehpour and Mohammadreza Tahriri** synthesized $Zn_{1-x}Mn_xS$ $x=0.0001, 0.007, 0.02, 0.03, 0.055, 0.09$ and 0.13 [17] and investigated that lattice parameter of pure cubic ZnS is 0.5414Å, close to standard value 0.5415Å and $Zn_{1-x}Mn_xS$ is 0.5420 where ionic diameter of Mn^{2+} is 0.83 nm and Zn^{2+} is 0.74 nm. **In 2011, Mohannad Syuhaimi Ab-Rahman and Noor Azie Mohd Arif** deposited $Zn_{0.9}Mn_{0.1}S$ thin film [18] and they investigated that the film showed above 90% transmittance in wave length range of 200-1000nm and band gap was 4.7eV. The electrical conductivity was in the range of $10^{-5} (\Omega)^{-1}$.

1.7 Aim of the present Work:

The aim of the present work is to develop DMS $Zn_{1-x}Mn_xS$ thin films and to measure the band gap of the films with varying Mn concentrations (x) and annealing temperature, increase transmission of light, type of carrier can be changed and resistivity decrease. The study of $Zn_{1-x}Mn_xS$ is motivated by its applications as a solid state gas sensor material, in photovoltaic or photo thermal devices, optics, as absorber coating, spintronics, quantum dot device, integrated components for telecommunication, photodiodes, etc.. This review describes the physical and chemical properties that make $Zn_{1-x}Mn_xS$ a suitable material for these purposes. Thin film process techniques and research are strongly related to the basic research activities in technology. Achieving high optical transparency and electrical conductivity simultaneously in thin film is governed by the deposition parameters, the dopants, and controlled non-stoichiometry. From the practical point of interest, the main objective of this research is to synthesize $Zn_{1-x}Mn_xS$ thin films in different doping concentrations by spray pyrolysis deposition system to reduce the preparation cost as well as the structural, optical and electrical characterizations of these as deposited thin films will be studied in details to explore its potential applications. It will be optically transparent and uniform homogeneous thin film.

Recent researches have shown that simple (binary) semiconductor films in many cases did not have a combination of properties, necessary for the fabrication of the gas sensors,

satisfying the requirements such as high sensitivity and good selectivity at high temporal stability of operating characteristics. Good controllability of the thin films from aqueous solutions has great advantages of economy, convenience and capacity of large area deposition for production design. a wide band gap of semiconductor, such as ZnS, can be made highly conducting, when sufficiently doped by transition metal. It has the desirable property of being transparent through most of the visible spectrum. Therefore, it is optimized that optically transparent and low resistivity, homogeneous and stoichiometric Mn doped thin films with high efficiency to be grown by using this low cost technique and thus it is expected that energy band gap of the resulting ternary $Zn_{1-x}Mn_xS$ alloys should lie between 3.1eV and 3.7 eV.

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CHAPTER - II

THIN FILM DEPOSITION TECHNIQUE

2.1 Introduction

The act of applying a thin film to a surface is known as thin-film deposition. Thin-film deposition is any technique for depositing a thin film of material onto a substrate or onto previously deposited layers. "Thin" is a relative term, but most deposition techniques allow layer thickness to be controlled within a few tens of nanometers, and some (molecular beam epitaxy) allow single layers of atoms to be deposited at a time. [1] Modern thin film technology has evolved into a sophisticated set of techniques used to fabricate many products. Applications include very large scale integrated (VLSI) circuits [2], electronic packaging, sensors, and devices; optical films and devices; as well as protective and decorative coatings. Generally thin films are prepared by depositing the film material, atom by atom on to a substrate. One of the examples is the condensation of vapor to give a solid or liquid film. Such process of deposition involves a phase transformation. It is useful in the manufacture of optics (for reflective or anti-reflective coatings, for instance), electronics (layers of insulators, semiconductors, and conductors form integrated circuits), packaging (i.e., aluminum-coated PET film), and in contemporary art. Similar processes are sometimes used where thickness is not important: for instance, the purification of copper by electroplating, and the deposition of silicon and enriched uranium by a CVD-like process after gas-phase processing.

2.2 Classification of the deposition process

There are three categories of thin film processes:

- (I) Physical Vapor Deposition (PVD)
 - (II) Chemical Vapor Deposition (CVD)
 - (III) Chemical Bath Deposition (CBD)
- (I) Physical Vapor Deposition (PVD)**

Physical vapor deposition (PVD) is fundamentally a vaporization coating technique involving transfer of material on an atomic level. It is an alternative process to

electroplating. It is a process by which a thin film of material is deposited on a substrate according to the following sequence of steps:

- 1) The material to be deposited is converted into vapor by physical means;
- 2) The vapor is transported across a region of low pressure from its source to the substrate;
- 3) The vapor undergoes condensation on the substrate to form the thin film. In VLSI fabrication, the most widely-used method of accomplishing PVD of thin films is by sputtering. [3]

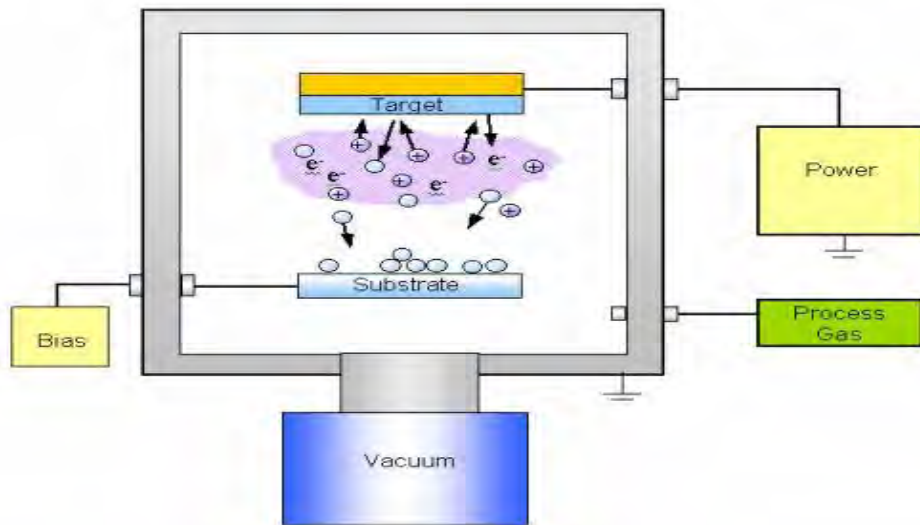


Fig-2.1: Physical vapor deposition method

PVD covers processes such as:

1. Sputter coating
2. Pulsed laser deposition (PLD)
3. Cathode arc deposition

Advantages of the Physical vapor deposition process as materials can be deposited with improved properties compared to the substrate material, almost any type of inorganic material can be used as well as some kinds of organic materials, the process is more environmentally friendly than processes such as electroplating etc. and some disadvantages of the physical vapor deposition process as it is a line of sight technique

meaning that it is extremely difficult to coat undercuts and similar surface features, high capital cost, some processes operate at high vacuums and temperatures requiring skilled operators, the rate of coating deposition is usually quite slow.

(II) Chemical Vapor Deposition (CVD)

Precursor gases (often diluted in carrier gases) are delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase and which are deposited onto the substrate.

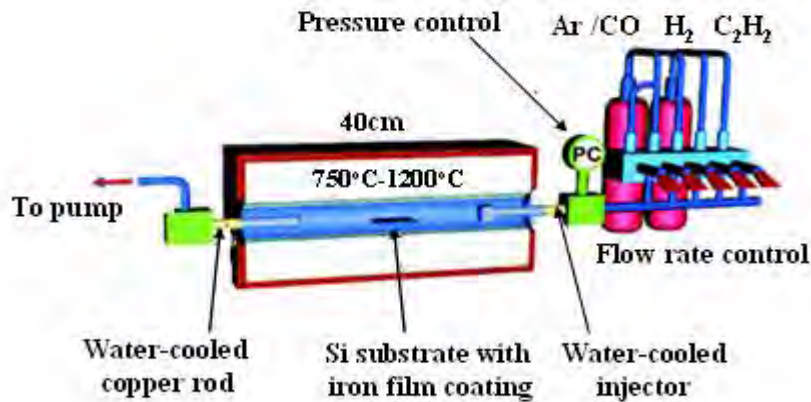


Fig-2.2: Chemical Vapor Deposition Process

The substrate temperature is critical and can influence what reactions will take place. CVD covers processes such as:

1. Atmospheric Pressure Chemical Vapor Deposition (APCVD)
2. Metal-Organic Chemical Vapor Deposition (MOCVD)
3. Plasma Enhanced Chemical Vapor Deposition (PECVD)
4. Photochemical Vapor Deposition (PCVD)
5. Chemical Beam Epitaxy

CVD coatings are usually only a few microns thick and are generally deposited at fairly

slow rates, usually of the order of a few hundred microns per hour. CVD is an extremely versatile process that can be used to process almost any metallic or ceramic compound. Some of these include: Elements, Metals and alloys, Nitrides Carbides, Borides, Oxides, intermetallic compounds [4].

(III) Chemical Bath Deposition (CBD)

The technique of CBD involves the controlled precipitation from solution of a compound on a suitable substrate. The technique offers many advantages over the more established vapor phase synthetic routes to semiconductor materials, such as CVD, MBE and spray pyrolysis.

Typical CBD processes for sulfides employ an alkaline media containing the chalcogenide source, the metal ion and added base. A chelating agent is used to limit the hydrolysis of the metal ion and impart some stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation. The extent of the heterogeneous reaction on the substrate surface is limited by two major factors, the competing homogeneous reaction in solution (which results in massive precipitation in solution) and deposition of material on the CBD reactor walls.

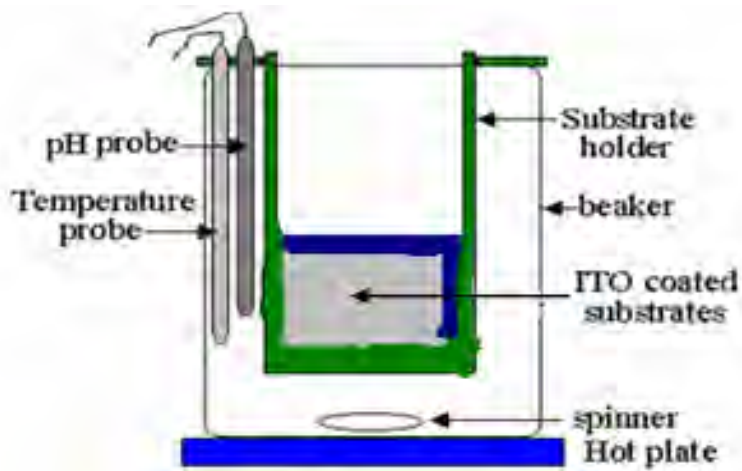


Fig-2.3: Chemical Bath Deposition Process

This deposition takes place in a beaker with DI water where it is heated between temperatures of 85 C to 90 C. Chemicals needed for preparing materials are poured individually and its chemical reaction results in the deposition of materials onto all

surfaces in the bath, including the surfaces of the ITO coated glass. Typically, for a 20-minute run, a thickness of 800-1000 Å can be achieved. The substrate is usually annealed before another deposition of other materials takes place. We have more deposition processes as Molecular beam epitaxy (MBE), Reactive sputtering etc.

2.1 Various deposition techniques

Different kinds of deposition techniques are described as bellow:

2.1.1 Pulsed Laser Deposition (PLD)

The principle of pulsed laser deposition, in contrast to the simplicity of the system set-up, is a very complex physical phenomenon. It does not only involve the physical process of the laser-material interaction of the impact of high-power pulsed radiation on solid target, but also the formation plasma plume with high energetic species and even the transfer of the ablated material through the plasma plume onto the heated substrate surface.

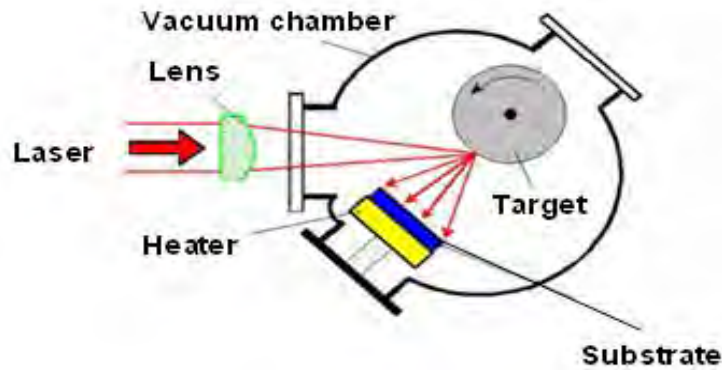


Fig- 2.4: Schematic diagram of pulsed laser deposition technique

Thus the thin film formation process in PLD generally can be divided into the following four stages.

1. Laser radiation interaction with the target
2. Dynamic of the ablation materials
3. Deposition of the ablation materials with the substrate
4. Nucleation and growth of a thin film on the substrate surface

Each stage in PLD is critical to the formation of quality epitaxial crystalline, stoichiometric, uniform and small surface roughness thin film. [5-7]

2.1.2 Vacuum Evaporation

In evaporation the substrate is placed inside a vacuum chamber, in which a block (source) of the material to be deposited is also located. The source material is then heated to the point where it starts to boil and evaporate. The vacuum is required to allow the molecules to evaporate freely in the chamber, and they subsequently condense on all surfaces. This principle is the same for all evaporation technologies, only the method used to the heat (evaporate) the source material differs. There are two popular evaporation technologies, which are e-beam evaporation and resistive evaporation each referring to the heating method.

2.1.2.1 Electron beam evaporation

In e-beam evaporation, an electron beam is aimed at the source material causing local heating and evaporation. A schematic diagram of a typical system for e-beam evaporation is shown in the figure below.[8]

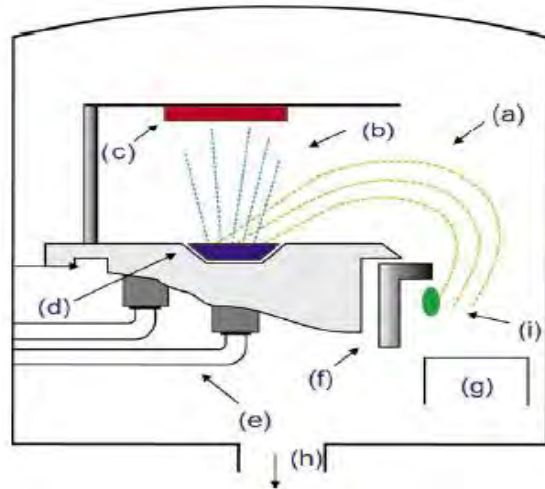


Fig- 2.5: Electron beam evaporation set up used for thin films preparation

(a) Electron Beam, (b) Material Vapor, (c) Substrate, (d) Target Material, (e) Water Cooling Lines, (f) Shield, (g) Magnet, (h) To Vacuum Pumps, (i) Tungsten Filaments.

2.1.2.2 Resistive evaporation

In resistive evaporation, a tungsten boat, containing the source material, is heated electrically with a high current to make the material evaporate. Many materials are restrictive in terms of what evaporation method can be used (i.e. aluminum is quite difficult to evaporate using resistive heating), which typically relates to the phase transition properties of that material.

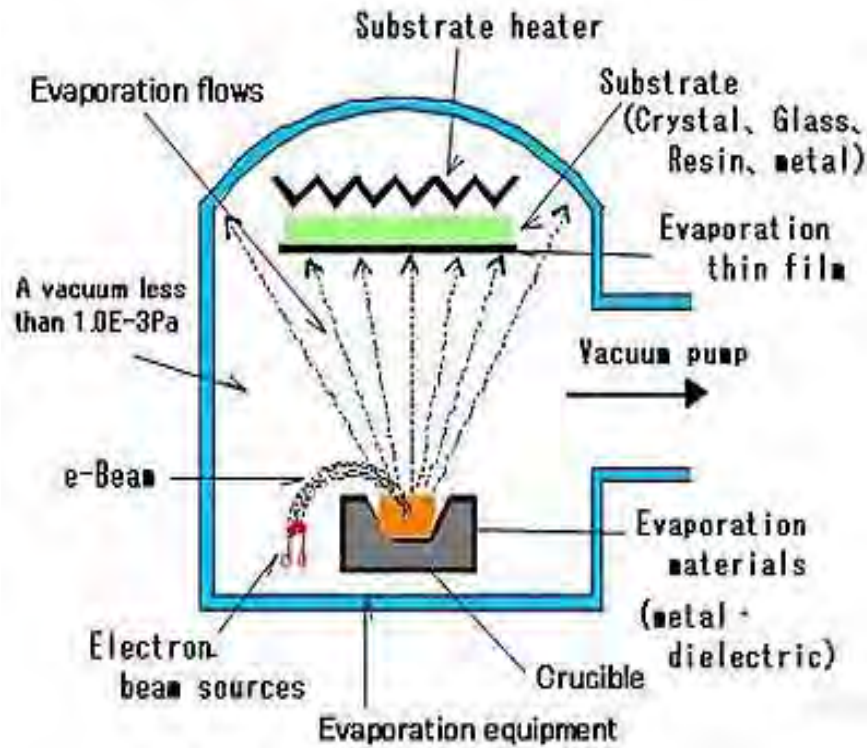


Fig- 2.6 : Typical system for resistive evaporation of materials.

2.1.3 Spin Coating Process

Spin coating has been used for several decades for the application of thin films. A typical process involves depositing a small puddle of a fluid resin onto the center of a substrate and then spinning the substrate at high speed (typically around 3000 rpm). Centripetal acceleration will cause the resin to spread to, and eventually off, the edge of the substrate leaving a thin film of resin on the surface.

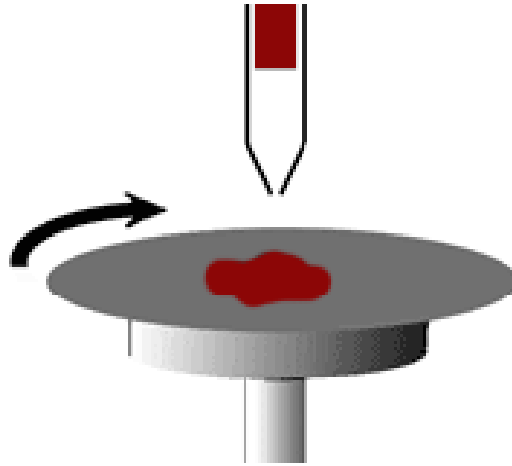


Fig 2.7 : Schematic diagram of the spin coating process

Final film thickness and other properties will depend on the nature of the resin (viscosity, drying rate, percent solids, surface tension, etc.) and the parameters chosen for the spin process. Factors such as final rotational speed, acceleration, and fume exhaust contribute to how the properties of coated film are defined. One of the most important factors in spin coating is repeatability. Subtle variations in the parameters that define the spin process can result in drastic variations in the coated film

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2.3.4 Sputtering

Sputtering is a technology in which the material is released from the source at much lower temperature than evaporation. The substrate is placed in a vacuum chamber with the source material, named a target, and an inert gas (such as argon) is introduced at low pressures. Gas plasma is struck using an RF power source, causing the gas to become ionized. The ions are accelerated towards the surface of the target, causing atoms of the source material to break off from the target in vapor form and condense on all surfaces including the substrate. As for evaporation, the basic principle of sputtering is the same for all sputtering technologies. The differences typically relate to the manner in which the ion bombardment of the target is realized. [9].

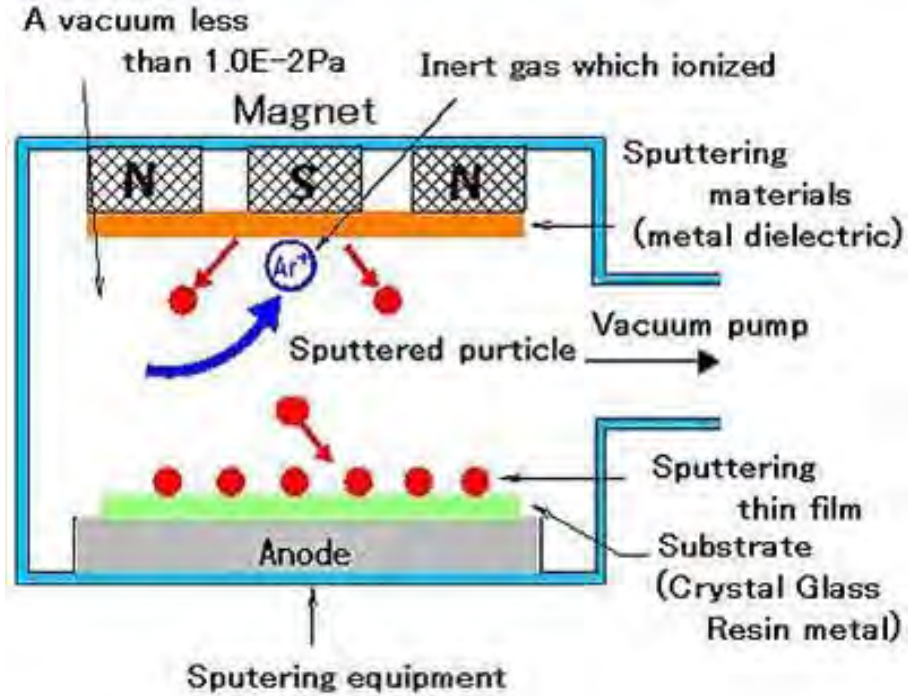


Fig -2.8: Schematic diagram of sputtering

2.3.5. Molecular Beam Epitaxy

Epitaxy means growth of film with a crystallographic relationship between film and substrate. Molecular beam epitaxy is a technique for epitaxial growth via the interaction of one or several molecular or atomic beams that occurs on a surface of a heated crystalline substrate. In Fig.2.9 a scheme of a typical MBE system is shown.

The solid source materials are placed in evaporation cells to provide an angular distribution of atoms or molecules in a beam. The substrate is heated to the necessary temperature and, when needed, continuously rotated to improve the growth homogeneity. Ultra high vacuum (UHV) is the essential environment for MBE. Therefore, the rate of gas evolution from the materials in the chamber has to be as low as possible. Focusing on the possibility that, despite the fact that MBE processes occur under strong nonequilibrium conditions, for the III/V elements, a thermodynamic approach can be used on the basis of equations for mass action in combination with the equations describing the conservation of the mass of the interacting elements.

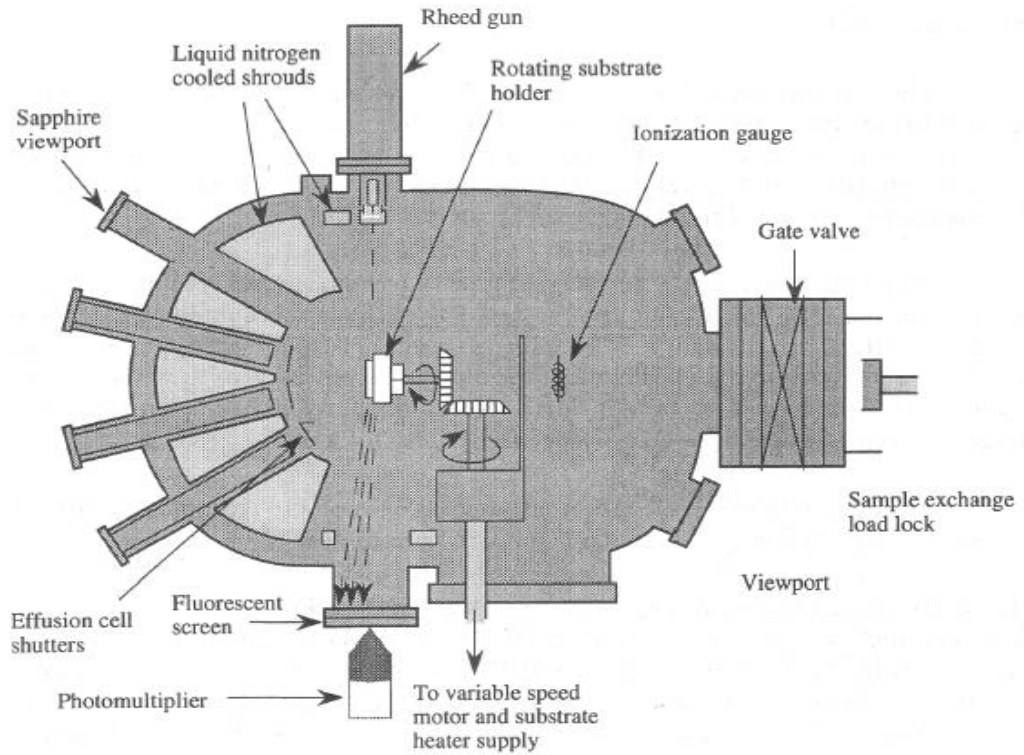


Fig -2.9 : Schematic diagram of Molecular Beam Epitaxy

2.3.6 Spray Pyrolysis

Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition.[10] The spray pyrolysis technique has been applied to deposit a wide variety of thin films. These films were used in various devices such as solar cells, sensors, and solid oxide fuel cells. The properties of deposited thin films depend highly on the preparation conditions. An extensive review of the effects of spray parameters on film quality is given to demonstrate the importance of the process parameters. The substrate surface temperature is the most critical parameter as it influences film roughness, cracking, crystallinity etc [11]. The design of the reactor is shown in Fig 2.10 It is a vertical batch type reactor composed of a heater , heat susceptor, thermocouple, Spray nozzle. [12] For the rapid expulsion of the by product gases there are opening at the side and at the top of the reactor. It helps focusing the

incoming sprayed solution towards the substrate and also provides a chimney action to the exhaust gas upwards.

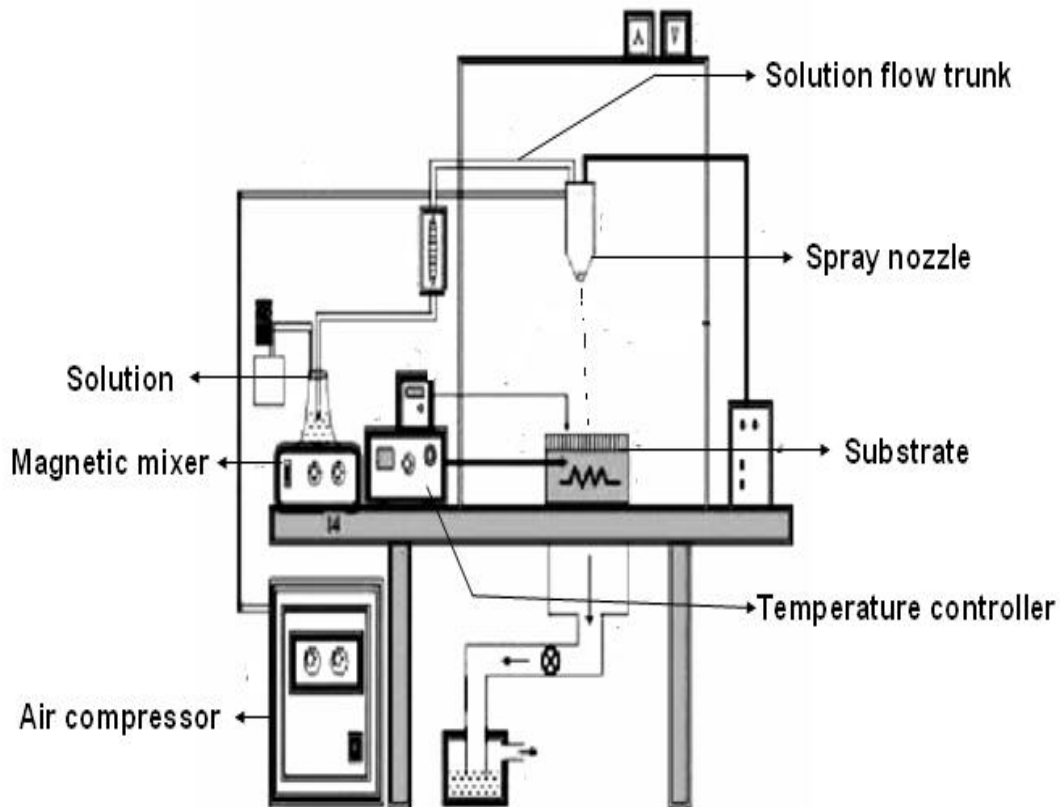


Fig -2.10: Spray pyrolysis system

It provides for flow measurement of both the propellant gas and the liquid. With spraying areas of a few square centimeters, liquid flows of 1-20 ml/min have been reported. Sufficiently low-flow commercial pneumatic spray heads are not readily available, and a needle is needed to restrict the flow. Acidic solutions attack stainless steel to the extent that iron contamination of the deposit is a problem. A pyrex glass spray head can be used with success. Other atomizers, such as a resonant cavity or a piezoelectric transducer, can be used. The substrate heater is a metal block; a liquid metal bath with a thermocouple, and a controller, or infrared (IR) lamps. A 1-kW heater typical. Air is the usual propellant, typically at 20 psi with a flow rate of 20 liters/min. When oxygen contamination is a problem, an inert gas with an enclosure is used.

2.2 Advantages Spray pyrolysis Deposition (SPD) technique

Spray pyrolysis is a convenient, low-cost, very simple and rapid method for the deposition of thin films [13], and is suitable for industrial applications and has been used for about 30 years for the manufacture of conductive glass. It is also an excellent method for preparing films of semiconductor alloys and complex compounds. Because individual droplets evaporate and react very quickly, grain sizes are very small, usually less than 0.1- μ m. The small grains are a disadvantage for most semiconductor applications.[14] The use of low concentration and slow spray rates to improve film quality tends to frustrate the low-cost processing objective, but post deposition heat treatment of small-grain. Films can improve stoichiometry and crystallinity. The process is sensitive to variables, particularly temperature, and the measurement at the surface is uncertain. Not only do the physical and electronic properties of the film vary with temperature, but the deposition efficiency decreases with increased temperature; stoichiometry is also affected, particularly for alloys. In spite of these difficulties, spray pyrolysis is an excellent method for the deposition of large-area thin films.

In all processes, the significant variables are the ambient temperature, carrier gas flow rate, nozzle-to-substrate distance, droplet radius, solution concentration, solution flow rate, and--for continuous processes--substrate motion. To this list one should add the chemical composition of the carrier gas most importantly.

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CHAPTER - II
THIN FILM DEPOSITON TECHNIQUE

At a glance Chapter-2

2.1 Introduction

2.2 Classification of the deposition process

2.3 Various deposition techniques

2.3.1 Pulsed Laser Deposition (PLD)

2.3.2 Vacuum Evaporation

2.3.2.1 Electron beam evaporation

2.3.2.2 Resistive evaporation

2.3.3 Spin Coating

2.3.4 Sputtering

2.3.5. Molecular Beam Epitaxy

2.3.6 Spray Pyrolysis

2.4 Advantages Spray pyrolysis Deposition (SPD) technique

References

CHAPTER -III
EXPERIMENTAL DETAILS

At a glance Chapter-3

3.1 Introduction

3.2 Experimental Equipments

- 3.2.1 Preparation of Masks**
- 3.2.2 Heater**
- 3.2.3 The Design of the Reactor**
- 3.2.4 The Fume chamber**
- 3.2.5 Air Compressor**
- 3.2.6 Spray Head/ Nozzle**
- 3.2.7 Choice and Cleaning of Substrate**

3.3 Film Preparation

- 3.3.1. Working Solution**
- 3.3.2 Estimation of compound composition**
- 3.3.3 Film Deposition Parameters**
- 3.3.4 Sample Deposition**
- 3.3.5 Rate of Deposition**
- 3.3.6 Thickness Control**
- 3.3.7 Optimization of the Deposition Process**

3.4 Film Characterization Methods

- 3.4.1 Surface Morphology and Structural Characterization**
 - 3.4.1.1 Scanning Electron Microscopy (SEM)**
 - 3.4.1.2 Energy Dispersive X-ray (EDX) spectroscopy**
 - 3.4.1.3 Bragg's diffraction Method**
 - 3.4.1.4 X-ray Diffraction (XRD) powder method**
- 3.4.2 Method for film thickness measurement (Fizeau fringes method)**
- 3.4.3 Van-der Pauw's method for Electrical Characterization**

References

CHAPTER -III EXPERIMENTAL DETAILS

3.1 Introduction

Thin films can be prepared from a variety of materials such as metals, semiconductors, insulators or dielectrics etc., and for this purpose various preparation techniques has also been developed. Spray pyrolysis is the most commonly used technique adopted for the deposition of metals, alloys and many compounds.

This chapter deals mainly with the description of the apparatus and the preparation of the sample. In this chapter we will discuss the preparation of $Zn_{1-x}Mn_xS$ thin films on glass substrate by spray pyrolysis process. Various steps of the film deposition procedure of the spray pyrolysis method have been discussed in this chapter.

3.2 Experimental Equipments

3.2.1 Preparation of Masks

The direct deposition of thin film pattern requires a suitably shaped aperture, commonly referred to as a mask. For the purpose of various experimental studies, film of specific size and shape are required. Mask was made from stainless steel plate with the desired pattern cut into it. The aperture was made in a bath machine

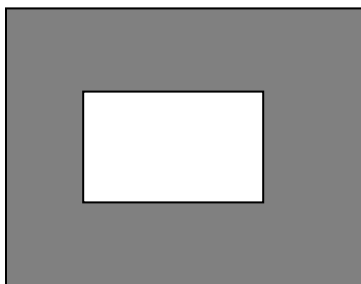


Fig. - 3.1: Mask for the sample

The mask is placed in proximity to the substrate, thereby allowing condensation of the evaporate only in the exposed substrate areas. The mask was prepared in such a way that

the edge of the mask is smooth so that it is helpful for determining the film thickness accurately.

3.2.2 Heater

The heater is an ordinary hot plate 2k-watt nichrome wire heater. The top of the plate is covered with a piece of asbestos sheet having a small open area at the center where a mica sheet is attached. A thick stainless steel plate) is placed on this mica sheet. Substrate is placed on this susceptor plate to have a uniform temperature throughout the substrate surface. An electrical voltage variac controls the heater power.

3.2.3 The Design of the Reactor

It is a vertical batch type reactor composed of a galvanized iron enclosure heater and heat susceptor For the rapid expulsion of the by-product gases there are opening at the side and at the top of the reactor. It helps focusing the incoming sprayed solution towards the substrate and also provides a chimney action to the exhaust gas upwards.



Fig- 3.2: Design of the Reactor

3.2.4 The Fume chamber

It is a large type chamber with a slanting top and is provided with a chimney. There is an exhaust fan fitted at the mouth of the chimney to remove the unused gases from the chamber. The slanting top and the sidewalls are made of glass and wood. There are airtight doors in the front side. The chamber has purging facilities. The whole spray

system and the reactor are kept inside this fume chamber at the time of film deposition because of the safety grounds and to check air current disturbances at the deposition site. These two points just stated are very important for the spray process when deposition is carried out in open- air atmosphere.

3.2.5 Air Compressor

It is reservoir type electrical air compressor. A rotary pump in this section mode draws atmospheric air and keeps it reserved in a large capacity air tank. At the outlet of the tank a pressure gauge is attached which records the pressure of the air at the time of supplying it from the tank. There is a by pass control valve which can keep the output pressure constant.

3.2.6 Spray Head/ Nozzle

The single spray nozzle consists of capillary tubes (stainless steels) fitted perpendicular to the other tube. When compressed air is passed rapidly through the tube in direction tangential to the mouth of the, a partial vacuum is created at the front part of the tube whose other end is kept immersed in the spray liquid. Due to this partial vacuum the liquid rises up through the tube and the compressed air drives it away in the form of fine spray particles. The thinner spray nozzle would give the finer spray particles [1]. A very fine needle shaped capillary tube was used for the spray nozzle and it may vary from nozzle to nozzle.

3.2.7 Choice and Cleaning of Substrate

The Choice and cleaning of substrate has a major influence on the properties of the thin film deposited onto them. Thin films cannot support themselves; and thus some carriers must be provided. This carrier, or substrate, would ideally have no interaction with the thin film except for sufficient adhesion to provide support. Glass, quartz and ceramic substrates are commonly used for polycrystalline films. Single crystal substrates of alkali halides, mica, MgO, Si, Ge etc. are used for epitaxial growth. The commonly used glass substrate (3 cm × 2.5 cm) having thickness 1 mm were used in the present work. Surface contaminations manifest it in pinholes, which can cause open resistor or localized high resistance.[2,3]

The following procedures were used for substrate cleaning. The gross contamination of each of the substrates were first removed by luke warm aqueous solution of sodium carbonate and then washed with distilled water. After washing in distilled water, the substrates were dipped at first into nitric acid for some time and again washed in distilled water. These were then dipped into chromic acid for some time. Taking them out of chromic acid bath one by one and then these were washed and thoroughly rinsed with deionized water for several times. Finally, these were dried in hot air and preserved for use. During the whole process the substrates were always held by slide holding forceps.

3.3 Film Preparation

3.3.1 Working Solution

The working solution was prepared by taking Zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] as a source material. As [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] dissolves in water at room temperature, water was taken as solvent. Since the spray system used in the present experiment operates via a partial vacuum path as the mouth of the spray nozzle, the concentration of the solution prepared by the solvent was made in such a way that it could be at least be drawn by the nozzle. The higher the solution concentration the lower the spray rate. A typical value of solution concentration 0.1 M was used in this work. Also in order to prepare the $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ thin film An aqueous solution containing 0.1M Zinc acetated [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], 0.1M Manganese acetated [$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] and 0.2M thiourea (NH_2CSNH_2) for Zinc ions (Zn^{+2}), Manganese ions (Mn^{+2}) and sulphide source (S^{-2}) respectively were used as the precursor solution. at 350°C substrate temperature. In our work the ratio of concentration of Zinc acetated, Manganese acetated and thiourea were 1:1:2.

3.3.2 Estimation of compound composition

Formula for compound composition: $\text{Zn}_{1-x}\text{Mn}_x\text{S}$

Chemical symbol:

Zinc acetate (aq): $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

Manganese acetate (aq): $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$

Thiourea : NH_2CSNH_2

Atomic weight:	Zn = 65.39 gm	O = 15.999 gm
	H = 1.0079 gm	N = 14.00674 gm
	C = 12.011 gm	Mn = 54.999 gm
	S = 32.066 gm	

Molecular Weight:

$$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = 65.39 + 2 (12.011 \times 2 + 1.0079 \times 3 + 15.999 \times 2) + 2 (1.0079 \times 2 + 15.999)$$

$$= 219.507 \text{ gm / mole}$$

Actual Weight = **219.49 gm / mole**

$$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = 54.999 + 2 (12.011 \times 2 + 1.0079 \times 3 + 15.999 \times 2) + 4 (1.0079 \times 2 + 15.999)$$

$$= 245.08465 \text{ gm / mole}$$

Actual Weight = **245.09 gm / mole**

$$\text{NH}_2\text{CSNH}_2 = 14.00674 \times 2 + 1.0079 \times 4 + 12.011 + 32.066$$

$$= 76.11848 \text{ gm / mole}$$

Actual Weight = **76.04 gm / mole**

Doping rate in gms/mole:

“For 100cc 0.1m solutions in $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ ”:-

For x = 00,

$$\text{ZnS} = (219.507 \times 0.1 \times 100) / 1000 = 2019507$$

For x = 0.01,

$$\text{Zn}_{0.99}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = (219.507 \times 0.99 \times 100) / 1000 \times 10 = 2.1731$$

$$\text{Mn}_{0.01}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = (245.08465 \times 0.01 \times 100) / 1000 \times 10 = 0.0245$$

For x = 0.03,

$$\text{Zn}_{0.97}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = (219.507 \times 0.97 \times 100) / 1000 \times 10 = 2.1292$$

$$\text{Mn}_{0.03}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = (245.08465 \times 0.03 \times 100) / 1000 \times 10 = 0.0735$$

For x = 0.05,

$$\text{Zn}_{0.95}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = (219.507 \times 0.95 \times 100) / 1000 \times 10 = 2.0853$$

$$\text{Mn}_{0.05}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = (245.08465 \times 0.05 \times 100) / 1000 \times 10 = 0.1225$$

For x = 0.10,

$$\text{Zn}_{0.90}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = (219.507 \times 0.90 \times 100) / 1000 \times 10 = 1.9756$$

$$\text{Mn}_{0.10}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = (245.08465 \times 0.10 \times 100) / 1000 \times 10 = 0.2451$$

For x = 0.30,

$$\text{Zn}_{0.70}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = (219.507 \times 0.70 \times 100) / 1000 \times 10 = 1.5365$$

$$\text{Mn}_{0.30}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = (245.08465 \times 0.30 \times 100) / 1000 \times 10 = 0.7353$$

For x = 0.50,

$$\text{Zn}_{0.50}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = (219.507 \times 0.50 \times 100) / 1000 \times 10 = 1.0975$$

$$\text{Mn}_{0.50}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = (245.08465 \times 0.50 \times 100) / 1000 \times 10 = 1.2254$$

For x = 0.70,

$$\text{Zn}_{0.30}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = (219.507 \times 0.30 \times 100) / 1000 \times 10 = 0.8780$$

$$\text{Mn}_{0.70}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = (245.08465 \times 0.70 \times 100) / 1000 \times 10 = 1.4705$$

For x = 0.90,

$$\text{Zn}_{0.10}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = (219.507 \times 0.10 \times 100) / 1000 \times 10 = 0.2195$$

$$\text{Mn}_{0.90}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} = (245.08465 \times 0.90 \times 100) / 1000 \times 10 = 2.2058$$

[Calculation theme: According to definition of molar concentration,

$$1000\text{cc } 1\text{M } \text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} = 219.507\text{gm}$$

$$100\text{cc } 1\text{M } \text{,,} = 219.507 \times 100 / 1000$$

$$\text{,, } 0.1\text{M } \text{,,} = 219.507 \times 0.1 \times 100 / 1000$$

$$100\text{cc } 0.95\text{M } \text{,,} = 219.507 \times 0.95 \times 0.1 \times 100 / 1000]$$

3.3.3 Film Deposition Parameters

In the chemical spray deposition technique the structure, composition and other characteristics of the deposited films depend on a number of process variables [deposition parameters]. The variable quantities such the substrate temperature, solution and gas flow

rate, deposition time, quality of the substrate material, size of atomized particles, solution concentration, and substrate to spray outlet distance, etc. are affected on the film properties. It is obvious that the substrate temperature is the most important deposition parameter and it is control with grate care. For the deposition of ZnS thin film, all the above mentioned parameters except

- (I) Substrate temperature (T_s)
- (II) Deposition time (t_d)
- (III) Solution concentration (C)
- (IV) Spray rate (S_r)
- (V) Spray outlet to substrate distance (d_s) and
- (VI) Carrier air pressure (P_a),

To study the effect of any one of these six parameters on the film properties the remaining other were kept constant.

3.3.4 Sample Deposition

It has been stated earlier that spray pyrolysis method for preparing ZnS thin films is an economically attractive method, which consist basically of spraying solution on a heated glass substrate. The apparatus needed to carry out the chemical spray process consists of a device to atomize the spray solution and a substrate heater.

A considerable amount of (100 ml) solution was taken in the beaker fitted with the spray nozzle. The clean substrate with a suitable mask was put on the susceptor of the heater. The distance between the tip of the nozzle and the surface of the glass substrate was kept 25 cm.

Before supplying the compressed air the substrate temperature was to be kept at a level slightly higher than the required substrate temperature because at the onset of spraying a slight fall of temperature is likely. The temperature of a substrate was controlled by controlling the heater power using a variac. The substrate temperature was measured by placing a copper constantan thermocouple on the substrate. Fig 3.3 shows a schematic diagram of spray pyrolysis technique.

When compressed air is passed through air compressor at constant pressure (1 bar), a fine $Zn_{1-x}Mn_xS$ was produced and was automatically carried to the reactor zone where film was deposited on the heated substrate. We have adjusted a situation such that 08 minutes of spray produces $Zn_{1-x}Mn_xS$ thin film, thickness of the range 627 to 793 nm keeping substrate temperatures kept at $350^{\circ}C$

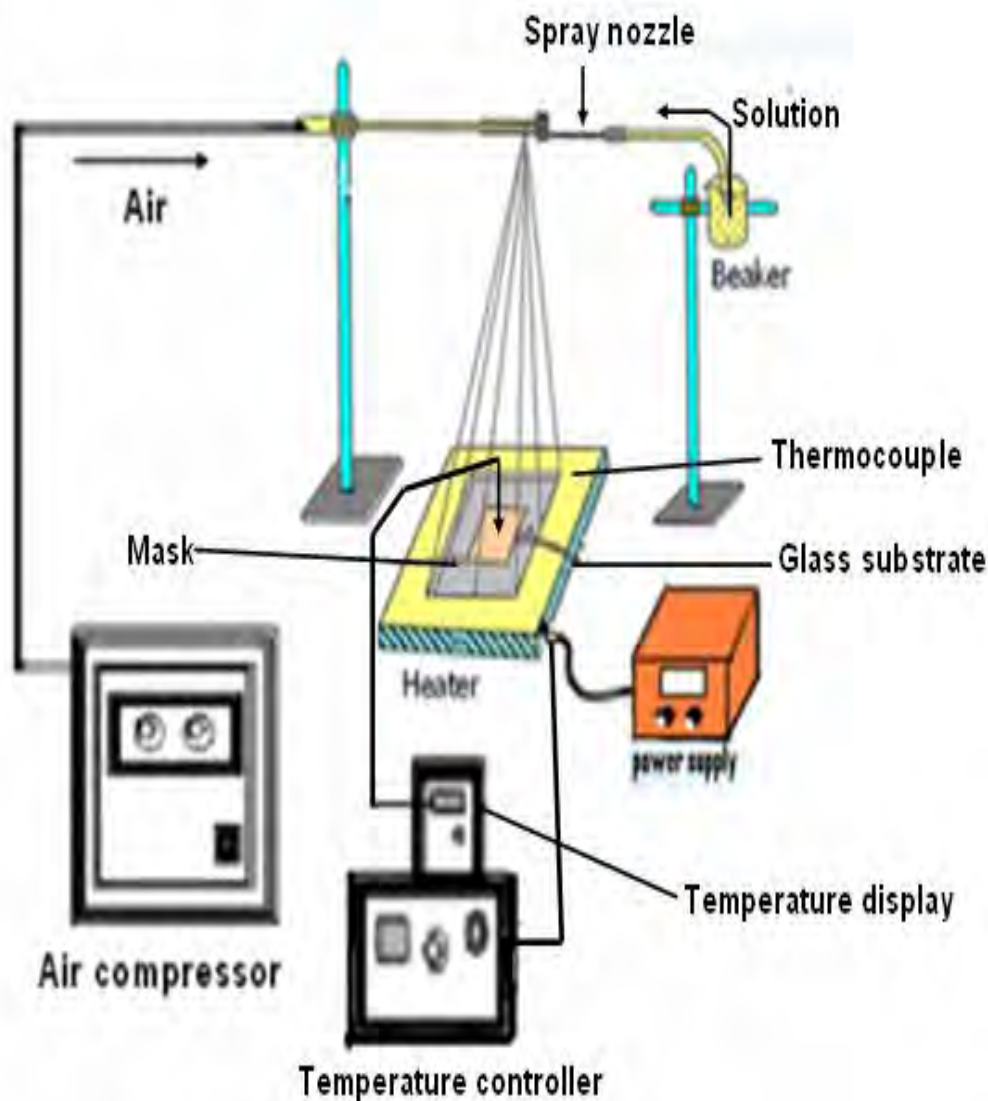
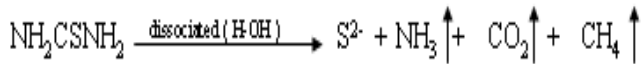
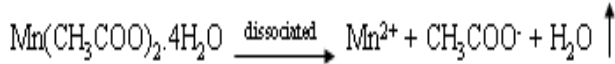
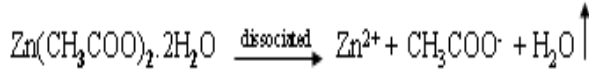


Fig. 3.3: Schematic diagram of spray pyrolysis technique.

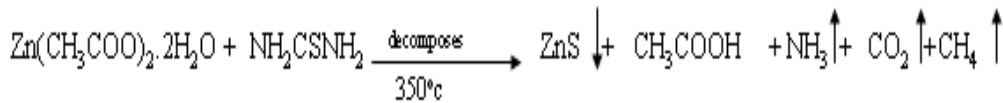
Possible chemical reaction

The possible chemical reaction that takes place on the heated substrate to produce $Zn_{1-x}Mn_xS$ may be as follows

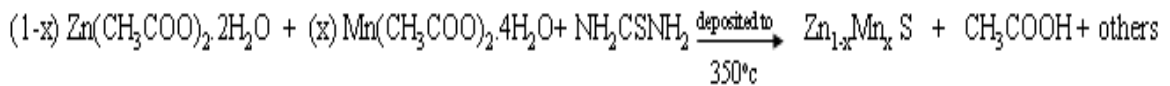
In aqueous solution,



Therefore, ZnS nucleate due to the reaction between Zn^{2+} and S^{2-} as



Due to variable Mn concentration, Zn / Mn acetate mixtures with NH_2CSNH_2 can be considered as :



3.3.5 Rate of Deposition

The rate of flow of the working solution can be controlled by a suitable nozzle and adjusting the airflow rate. Spray rate is a parameter that influence the properties of the films formed. The crystallinity, surface morphology, resistivity and even thickness are affected by the change of spray rate [4].

3.3.6 Thickness Control

In the present spray deposition process, the deposition time is the main factor for the thickness control, provided the other parameters, remain constant. Since the deposition is carried out in normal atmosphere a direct and insitu control of thickness is not so easy. To control the film thickness therefore calibration chart may be used. These charts are generally plots of deposition time vs. thickness, and can be prepared at different constant substrate temperatures prior to the preparation of particular experimental samples using the same solution and deposition variables.

3.3.7 Optimization of the Deposition Process

To obtain the optimum condition of the film deposition process, it is essential to select at first the requirements with respect to which the process should be optimized. The optimization process is very lengthy because there are a number of process variables. The basic requirement was to get a film of high transparency as well as high electrical conductivity.

For the process of optimization following set of films have been deposited. The first set of films was deposited at various substrate temperatures, keeping all other deposition parameters constant at an arbitrary level. From the set of films the optimum substrate temperature T_s was selected with respect to the best conducting and transparent films.

After obtaining the optimum value of T_s , second set of films were deposited by varying the substrate to spray outlet distance, d_s using the optimized T_s and other parameters were kept constant to the arbitrary level as they were in the first set. From this second set of films the optimum distance d_s was selected corresponding to the best film.

Fixing the distance d_s and substrate temperature T_s , a third set of films were deposited by varying the pressure of the carrier gas P_a . From this set, optimum carrier air pressure was selected. Keeping T_s , d_s and P_a as fixed fourth set of films were deposited by taking spray rate S_r as variable parameters. From this set, optimum spray rate S_r was selected. The fifth set of films were deposited keeping T_s , d_s , P_a and S_r at their optimum values. In this case, the solution concentration C was varied for selecting the optimum concentration of the working solution.

Thus in all cases the optimum values of the parameters (T_s , d_s , P_a , S_r and C) were selected for deposition of films that exhibit good conductivity and high transparency. The resulting optimization is undoubtedly a tentative one because the process variables are in some degree mutually interdependent.

3.4 Film Characterization Methods

Thin films are usually characterized by their surface morphology, elemental composition, structural, optical, electrical and mechanical properties. In this section, the characterization methods used in this work are reviewed briefly. These techniques include Optical microscope, Energy Dispersive X-ray (EDX) Diffraction for

compositional study, X-ray diffraction (XRD) for structural characterization, Absorption spectra, for the optical characterization.

3.4.1 Surface Morphology and Structural Characterization

The techniques employed for structural analysis of thin films may be classified under two groups, one dealing primarily with the “surface” structure and the other with “volume and surface” structure. This arbitrary classification is obviously meaningless for ultra thin films.

3.4.1.1 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a powerful microscope that uses electrons rather than light to form an image of objects such as fractured metal components, foreign particles and residues, polymers, thin films electronic components, biological samples, and countless others. The shorter wavelength of electrons permits image magnifications of up to 100,000X, as compared to about 2,000X for conventional light microscopy.



Fig 3.4: SEM with EDX (Philips XL30)

An SEM also provides a greater depth of field than a light microscope, allowing complex, three-dimensional objects to remain sharp and in focus. This capability reveals details that cannot be resolved by light microscopy

Scanning electron microscopy (SEM) is a very versatile technique employed for the examination and analysis of the microstructure characteristics of solid objects. SEM is capable of high resolution (values of the order of 10 nm), and its greater depth of focus allows more three-dimensional information to be gathered than optical microscopy. The technique uses a rastered electron beam (typically 2 to 30kV) to strike a solid sample and cause secondary electrons, back-scattered electrons, x-rays and Auger electrons to be emitted. The intensities of the emitted secondary electrons vary with topography and may be detected and displayed using a cathode ray tube screen, producing a detailed image of the surface

Scanning process of SEM

Electron Microscopes function exactly as their optical counterparts except that they use a focused beam of electrons instead of light to "image" the specimen and gain information as to its structure and composition. The basic steps involved in all Electron Microscopes are shown in fig 3.5.

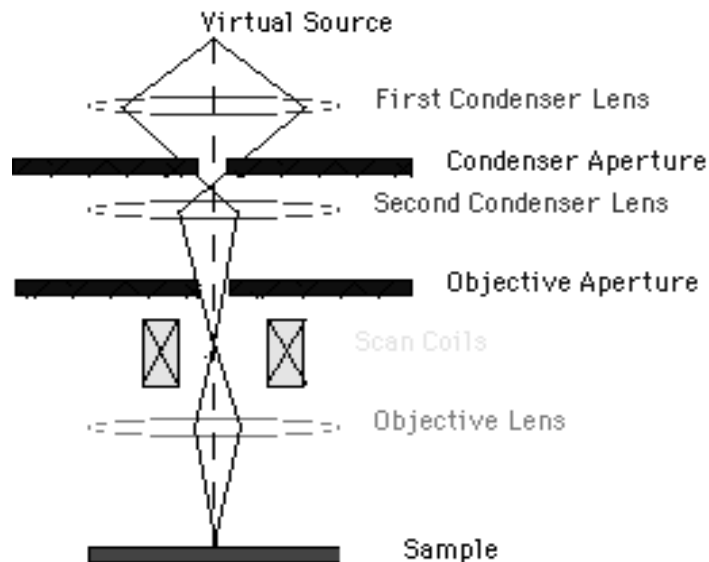


Fig.3.5: Schematic diagram of a Scanning electron microscope

electrons are harmonically emitted from a tungsten or lanthanum hex boride (LaB_6) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest

vapour pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 0.4 nm to 5 nm. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron optical column, typically in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electrons' landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation, which can be detected to produce an image.

A stream of electrons is formed by the Electron Source and accelerated toward the Specimen using a positive electrical potential. This stream is confined and focused using metal apertures and magnetic lenses into a thin, focused, monochromatic beam. This beam is focused onto the sample using a magnetic lens. Interactions occur inside the irradiated sample, affecting the electron beam. These interactions and effects are detected and transformed into an image.

3.4.1.2 Energy Dispersive X-ray (EDX) analysis

EDX describes the compositional analysis of the thin films. This is done by the scanning electron microscopy (SEM) by focusing the X-ray beam on the full frame or a particular spot of the thin films. The analysis represents the individual weight (%) of the element that is present in the thin films.

3.4.1.3 Bragg's diffraction Method

Bragg reflection is coherent elastic scattering in which the energy of the X-ray is not changed on reflection. If a beam of monochromatic radiation of wavelength λ is

incident on a periodic crystal plane at an angle θ and is diffracted at the same angle as shown in Fig. 3.6, the Bragg diffraction condition for X-rays is given by

$$2d \sin\theta = n\lambda \quad (3.1)$$

where d is the distance between crystal planes and n is the positive integer which represents the order of reflection. Equation (3.1) is known as Bragg law. This Bragg law suggests that the diffraction is only possible when $\lambda \leq 2d$ [5]. For this reason we cannot use the visible light to determine the crystal structure of a material. The X-ray diffraction (XRD) provides substantial information on the crystal structure.

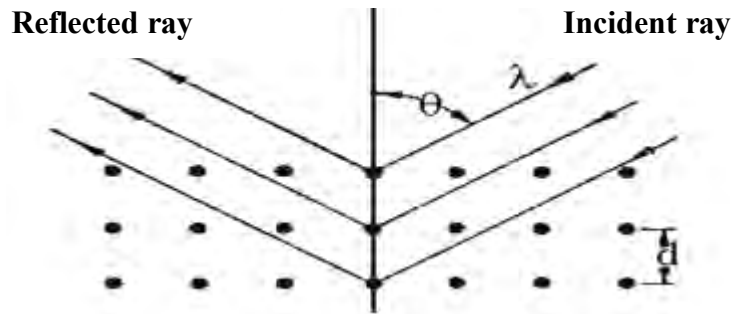


Figure 3.6. Bragg law of diffraction.

3.4.1.4 The powder diffraction method

The methods, which are commonly employed for the determination of the atomic arrangements and lattice parameters of different crystals, are based on diffraction of X-rays, electrons or neutrons. The most common method of structure determination is the technique of X-ray diffraction.

The Powder method derived by Debye and Scherrer and independently by Hull in 1919 is the most widely used method in the field of applied X-rays. When the crystalline material is not available in the form of discrete single crystals then X-ray diffraction patterns are obtained of aggregation of crystals usually of the form of fine powder using a powder camera or diffractometer.[6] Basically the method involves diffraction of monochromatic X-rays by a powdered or a fine-grained polycrystalline specimen and if properly employed can yield a great deal of structural information about the material under

investigation. Each particle, a grain in the specimen, is tiny crystal oriented at random with respect to the incident beam. There is fair chance that a certain (hkl) plane will be correctly oriented to reflect the incident beam. Thus a variation of θ is obtained, not by rotating a single crystal about one of θ its axis but through the presence of many small crystals randomly oriented in space in the specimen.

In powder diffractometry diffraction peaks appear at 2θ positions, which are recorded by a chart recorder. From the chart recorded diffraction pattern the Bragg angle as well as the heights (peak intensity) can be read out. The, d values corresponding to each peak can be calculated using the Bragg's relation. The interpretation of the powder diffraction pattern requires identification, i.e., determination of (hkl) values corresponding to each diffraction peak. This is known as indexing which leads to the determination of the crystal structure. Below we describe the indexing of powder pattern by the reciprocal lattice concept.

3.4.2. Method for film thickness measurement (Fizeau fringes method)

Optical interference method is one of the film thickness methods by which the thickness of the thin film can be determined accurately. In this method two reflecting surfaces are brought into close proximity to produce interference fringes.

Weiner was the first to use interference fringes for the measurement of the film thickness. Later on using Fizeau fringes, Tolansky developed this method (interferometric method) to a remarkable degree and is now accepted as a standard method.

For the experimental setup a low power microscope, a monochromatic source of light, a glass plate and an interferometer are required. To see the Fizeau fringes of equal thickness in a multiple beam interferometer a thin absorbing film on a glass substrate with an auxiliary reflecting coating on the film surface is required. For a transparent film with a very smooth surface no such auxiliary coating is necessary. [7]

The film whose thickness is to be measured is required to form a step on a glass substrate and over it another plane glass plate (Fizeau plate) is placed. This type of interferometer is shown in Fig. 3.7. When the interferometer is illuminated with a parallel

monochromatic beam of light (sodium light) at normal incidence, a fringe system is produced and is viewed with a low power microscope. Dark fringes are also observed against a white background. The displacement “h” of the fringe system across the film-substrate step is then measured to calculate the film thickness (t), using the relation

$$t = \frac{\text{step height}}{\text{fringe spacing}} \times \frac{\lambda}{2} = \frac{h}{I} \times \frac{\lambda}{2} \quad \dots \dots \dots (3.2)$$

Where, λ is the wavelength of the monochromatic light (sodium light), I is the fringe-spacing. In this method, thickness from 3nm to 2000 nm can be measured with an accuracy of ± 5 nm.

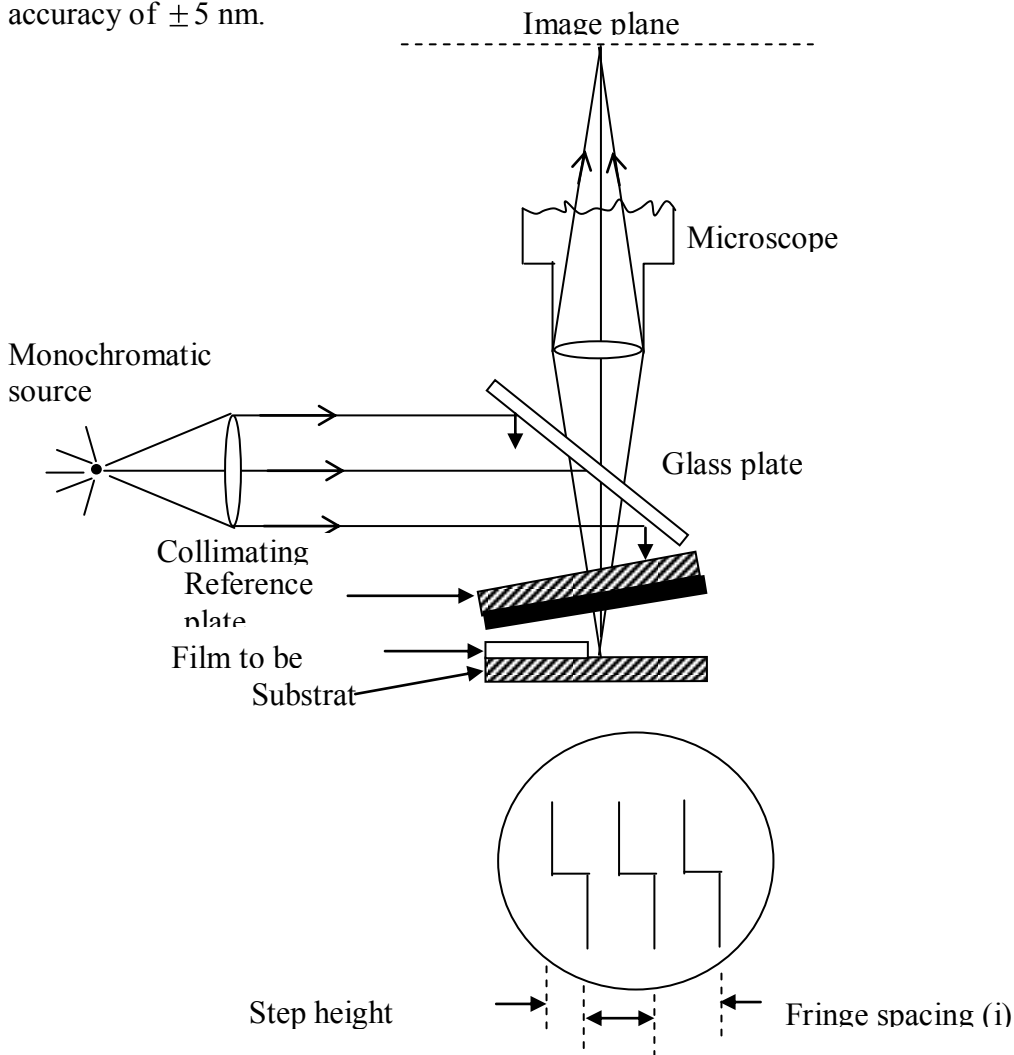


Fig. 3.7: Interferometer arrangement for producing reflection Fizeau fringes of equal thickness

3.4.3 Van-der Pauw’s method for Electrical Characterizations

The resistivity of a film having any arbitrary shape can be uniquely determined by Van-der Pauw [8] method. A brief account of this method is given below because in our measurement we have used Van-der Pauw method.

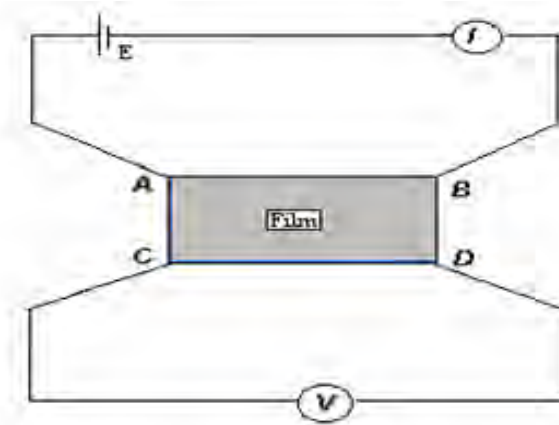


Fig- 3.8: Circuit arrangement of Van der Pauw's technique

At first we select a region on the sample where four electrical contacts were made at four corners, say A, B, C, and D as shown in Fig. 2.2D. Silver paste or indium was used to the contact. If a current I_{AB} entering the specimen through the contact A and leaving through the contact, B produces a potential difference $V_D - V_C$ between C and D then the resistance $R_{AB,CD}$ is defined as

$$R_{AB,CD} = \frac{V_D - V_C}{I_{AB}} = \frac{V_{CD}}{I_{AB}} \dots \dots \dots (3.3)$$

Similarly,

$$R_{BC,DA} = \frac{V_A - V_D}{I_{BC}} = \frac{V_{DA}}{I_{BC}} \dots \dots \dots (3.4)$$

$$R_{CD,AB} = \frac{V_B - V_A}{I_{CD}} = \frac{V_{AB}}{I_{CD}} \dots \dots \dots (3.5)$$

$$\text{and } R_{DA,BC} = \frac{V_C - V_B}{I_{DA}} = \frac{V_{BC}}{I_{DA}} \dots \dots \dots (3.6)$$

The resistivity of a thin film can be expressed by the equation

$$\rho = \frac{\pi t}{\ln 2} \left[\frac{R_{ABCD} + R_{BC,AD}}{2} \right] \times f \left[\frac{R_{ABCD}}{R_{BC,DA}} \right] \dots \dots \dots (3.7)$$

$$\rho = 4.53t \times \left[\frac{R_{ABCD} + R_{BC,DA}}{2} \right] \times f \left[\frac{R_{ABCD}}{R_{BC,AD}} \right] \dots \dots \dots (3.8)$$

Where t is the thickness of the film and the function f can be evaluated from the equation

$$\left[\frac{R_{ABCD} - R_{BC,DA}}{R_{ABCD} + R_{BC,DA}} \right] = \frac{f}{\ln 2} \operatorname{arccosh} \frac{\exp(\ln 2 / f)}{2} \dots \dots \dots (3.9)$$

If $R_{AB, CD}$ and $R_{BC, DA}$ is almost equal, f may be approximately equal to unity and then the equation (2.12) takes the form,

$$\rho = 2.265 t (R_{AB, CD} + R_{BC, DA}) \text{ ohm-cm} \dots \dots \dots (3.10)$$

It is very difficult to get f, so we have taken the value of f from the chart for different ratio greater than unity.

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