TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY

Department of Materials and Environmental Technology

DEPOSITION AND PROPERTIES OF ZNS:MN THIN FILMS AND NANOSTRUCTURED LAYERS BY SPRAY PYROLYSIS METHOD

PIHUSTUSSADESTUSE MEETODIL ZNS:MN ÕHUKESTE KILEDE NING NANOSTRUKTUURSETE KIHTIDE SÜNTEES NING OMADUSED

MASTER THESIS

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AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.

No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

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THESIS TASK

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PREFACE

From the depth of my heart, I give God all the glory, the maker of the whole universe and the owner of my life without whom it would have been impossible to complete my Masters program.

My deepest gratitude goes to my ever attentive and supportive supervisor in the person of Dr Tatjana Dedova and gratitude to Dr Atanas Katerski and Prof. Malle Krunks for their support throughout the cause of this work. Also to Dr. V. Mikli for recording the SEM images.

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List of abbreviations and symbols

ZnS	Zinc Sulphide
eV	Electron volts
FET	Field effects transistors
CSP	Chemical spray pyrolysis
XRD	X-ray diffraction
SEM	Scanning Electron Microscopy
Zn	zinc
A	Armsrong
nm	Nanometers
ALD	Atomic Layer method
CVD	Chemical Vapour Deposition
SILAR	Successive ionic layer adsorption and reaction
EL	Electroluminescence
ELD	Electroluminescent displays
LCD	Liquid crystals displays
OLEDs	Organic Light-emitting diode
LEDs	Light Emitting Diodes
PL	Photoluminescence
α	optical absorption coefficient
hv	photon energy
A	critical absorption
Eg	optical band gap

INTRODUCTION

In recent years , the study of nanomaterials and nanostructures have not only become the most studied materials but they have also gradually became part of our daily life. This quote "If I were asked for an area of science and engineering that will most likely produce the breakthroughs of tomorrow, I would point nanoscale science and engineering" made by the US President Advisor for Science and Technology aptly highlights the great potentials inherent in nanoscience in the coming decades[1-2]

Nanostructured materials are group of new class materials having dimensions ranging from 1-100nm with immense potentials and importance in the industrail sector. In the quest to improve existing products by creating smaller components with better performance ,material all at a lower price, less power consumption, faster response, higher density of integration etc. Companies that will manufactuture "nanoproducts" will grow fast and will soon make up for the majority of companies across the industries[3-4].

The efforts to enhance the electrical, optical and magnetic properties of nanostructured semicondutors have made it one of the extensively investigated material over the decade. Zinc Sulphide (ZnS) an important semiconductor with a band gap of 3.68 eV as one of the first discovered semiconductor. Due to its electronic and optoelectronic capability, its a good candidate for diverse applications such as light emitting diodes, Field effects transistors (FET), sensors, photocatalyst[3]. Additionally, It is also applicable as field emitters, flat panel displays and in lasers[4].

Nevertheless, ZnS can be prepared by both the physical and chemical technique which includes the Magnetron sputterring technique[5], Electrochemical deposition[6], Chemical spray pyrolysis(CSP)[7], Sol-gel technique[8], hydrothermal synthesis[9], Chemical bath deposition[10].

Among the methods listed, CSP is a solution based method that allows the mixing of solutions before deposition making it an effective method to use in the doping of a wide range of materials. It is relatively simple and economically suitable method for depositing of thin films on different substrates for a large scale production of various electronic devices. CSP method is an attractive technique for the preparation of thin films because of its simplicity and easy to operate, film thickness and deposition parameters are easy to control, operation at moderate temperatures, does not require vacuum and does not select choice of substrates[11]. CSP offers the opportunity to deposit uniform and compact films for a wide range of device applications. The properties of the films strongly depend on the precursor reagent, precursor concentration, temperature, deposition time and velocity [12].

This thesis is aimed at fabricating Zinc Sulphide nanorods and Zinc sulphide thin films doped with Manganese by CSP method of deposition, owing to the fact that doping of Zinc sulphide nanorod with manganese is a novel and promising material. Also we would like to obtain material with enhanced photoluminescence properties through the incorporation of Manganese into the Zinc Sulphide rod like crystals.

The structural properties were carried out by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). UV-VIS and Photoluminescence were used for its optical investigation.

1 LITERATURE REVIEW

1.1 Zinc Sulphide

Zinc Sulphide (ZnS) is an inorganic semiconductor with a zinc (Zn) metal which is the first element in the group 12 of the periodic table. Zn is the 24th most abundant elements in the earth crust and it has five stable isotopes. ZnS is a highly important semiconducting material belonging to the group II-IV wide band gap semiconductors that has been largely researched over the years. Its characteristic wide band gap (3.68ev), non-toxicity, safety to environment and high transparaency has made it probably one of the most important electronic and optoelectronic material with outsatnding applications[13].

ZnS has a varying band gap with its cubic form ranging from 3.54-3.6ev while the band gap of its hexagonal form ranging between 3.74 – 3.87ev [14]. It also has a dielectric constant of 8.9 and lattice constant of 5.4093 A. It can be doped as both the n-type and the p-type semiconductor which is uncommon among the group II-IV semiconductors. Zinc Sulphides have the capacity to form electroluminescent, Photolumiscent and cathode lumiscence emission with a variety of elements including Manganese, Copper, Sodium, Silver, Gold, Gallium etc.

The general properties of Zinc Sulphide are as tabulatedi Tables 1.1a - 1.1f.

Table 1.1a: Chemical Properties

Chemical Formular	ZnS
Molecular weight	97.46g/mol
Group	Zinc-12 Sulphur-16
Crystal structure	Cubic
Lattice constant	5.4093A

Table 1.1b: Electrical Properties

Band Gap	3.54Ev
Electron mobility	180cm^2/vs
Hole Mobility	5cm^2/vs
Electronic configuration	Zinc : [Ar] 3d^{10} 4s^2
	Sulphur:[Ne] 3s^2 3p^4

Table 1.1c: Thermal Properties

Heat of Fussion	390J/g
Heat of formation	477Kj/mol
Thermal coefficient of expansion	6.36µm/m°C
Thermal Conductivity	25.1W/mk
Specific heat Capacity	0.472J/g°C

Table 1.1d: Mechanical properties

Density	4.079g/cm3
Boiling Point	1185°C
Melting point	1850°C
Flexural Strenght	103Mpa
Modulus of Elasticity	75Gpa
Poison ratio	0.27

Table 1.1e Physical Properties

Solubility in water	Insoluble
Appearance	Grey white to yellow powder
Odour	Sulphurous Odour

Table 1.1f: Optical Properties

Refractive Index	2.356

1.1.1 Crystal structures and properties of ZnS polymorphs

ZnS is observed in nature to exist in two crystallographic forms namely; Zinc blend and Wurzite. Zinc blend also known as Sphalerite. Its a mineral that is the chief ore of zinc consisting largely of zinc sulphide in crystalline form but a variable amount of Iron. It has a cubic lattice structure closely related to the structure of diamond. The lattice constant in the zinc blend crystal structure is 0.541nm calculated from the geometry and ionic radii of 0.074nm (zinc) and 0.184nm(Sulphide). All natural sphalerites contains finite concentrations of various impurities of element. These generally substitutes for the zinc position in the lattice, the most common been Cd and Mn. Economically, it is the most important ore of zinc with 95% of primary zinc obtained from sphalerites and also an important source of many minor minerals such as gallium[15] and indium[16] . Wurtzite is a less frequently encountered mineral form of sphalerite with about 80% variable iron content. It was first described in 1861 for an occurence in San Jose mine in oruro Bolivia, named after the French chemist Charles-Adolphe Wurtz. It has hexagonal lattice structure system. Both the zinc blend and the wurtzite have atoms in the bulk crystallographic forms being four-coordinated and having a tetrahedral coordination. Figure 1.1 clearly highlights zinc blend and wurzite structure.

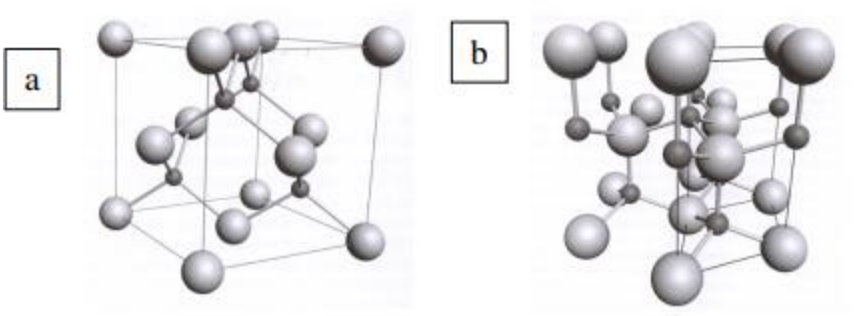


Figure 1.1. (a) zinc blend (b) wurzite crystal structure of ZnS

Table 1.2: ***Basic Properties of zinc blend and wurzite.***

Property	**Zinc Blend**	**Wurtzite**
Crystal structure	Cubic	Hexagonal
Atom per unit cell Z	4	2
Lattice parameters	a= 5.41	a=b= 3.82 c=6.26
Refractive index	2.37	2.37 2.38
Optical properties	Isotropic	Uniaxial
Diaphaneity	Transparent to Translucent	Translucent

1.2. ZnS thin films

ZnS exist in different forms among which are powder, nanoparticles, nanorods, fibres and thin films. These forms of ZnS can be prepared using different techniques. For the purpose of this research work, ZnS thin film and nanostructured layers will be reviewed.

1.2.1 Deposition of ZnS thin film

ZnS thin film can be obtained using a variety of both physical and chemical methods, the methods makes use of the modern technology and they have been widely used in the deposition of ZnS thin film. Amongst the methods in use are the Atomic Layer method (ALD) Chemical Vapour Deposition (CVD) Sol-gel technique, Chemical bath deposition, Chemical Spray Pyrolysis, Magnetic sputtering, Successive ionic layer adsorption and reaction (SILAR).

The most widely used physical method of depositing ZnS thin film is the Magnetron sputtering technique this method has developed rapidly over time to the point where it has become the prefered method of deposition of a wide range of industrially important coatings. Magnetron sputtered materials are applicable in variety of areas such as hard-wear resistant coatings, corossion resistant coatings, low friction coatings and coatings with specific electrical and optical properties. Zinc Sulphide thin film from magnetron sputtering without using any matrix is scanty. Magnetron sputtering compared to other techniques has number of advantages for example, both conducting and non-conducting materials can be sputtered via magnetron sputtering as ZnS is poorly conducting material. It is performed at a low pressure and hence sources of contamination are negligible. Large area thin films could be achieved easily which is suitable for industrial application. The method is also a cost effective method of deposition[18-19].

However, chemical methods are widely used for the deposition of ZnS thin film. The chemical vapour deposition (CVD) characterize with its ability to uniformly coat a complex substrate, versatility and can be use to obtain high density material formation at low melting point. Films obtained by CVD are pure and economically viable. It was also reported that ZnS thin films having cubic configuration with Eg of 3.4Ev and 3.6Ev and refractive indices of 2.19-2.26 were obtained using the CVD method[18][19].

Similarly, Chemical based deposition which is a solution based technique is also one of the method used in depositing ZnS thin film. CBD is a method for directly depositing large area films of semiconductors at low temperature compared to others, it allows films to be deposited on substrates that might not be otherwise stable at high temperature. The technique yields stable, adherent uniform and hard films with good reproductibility by a relatively simple process. Its major limitation been the wastage of solution after deposition. Thin films from this technique are now applicable in areas such as the solar energy and other photonic applications. In this process the growth of thin films depends on a number of conditions which includes duration of deposition composition and temperature of solution and the chemical nature of substrates[20].

Furthermore, Sucessive ionic layer adsorption and reaction (SILAR) method which is also one of the newest methods for depositing a thin film. The SILAR method is relatively new and less investigated method of depositing of thin film, It was first reported in by Ristov et al [21] in 1985, and the name of the process is ascribed to Nicolau and Mernard in their research work[22] which deals with ZnS, CdZnS and CdS thin film. These methods is suitable for the deposition of various chalcogenide group such as the I-VI, II-VI binary group and I-III-VI, II-VI tertiary chalcogenides and composite films. Figure 1.2 clearly highlights different thin film deposition methods.

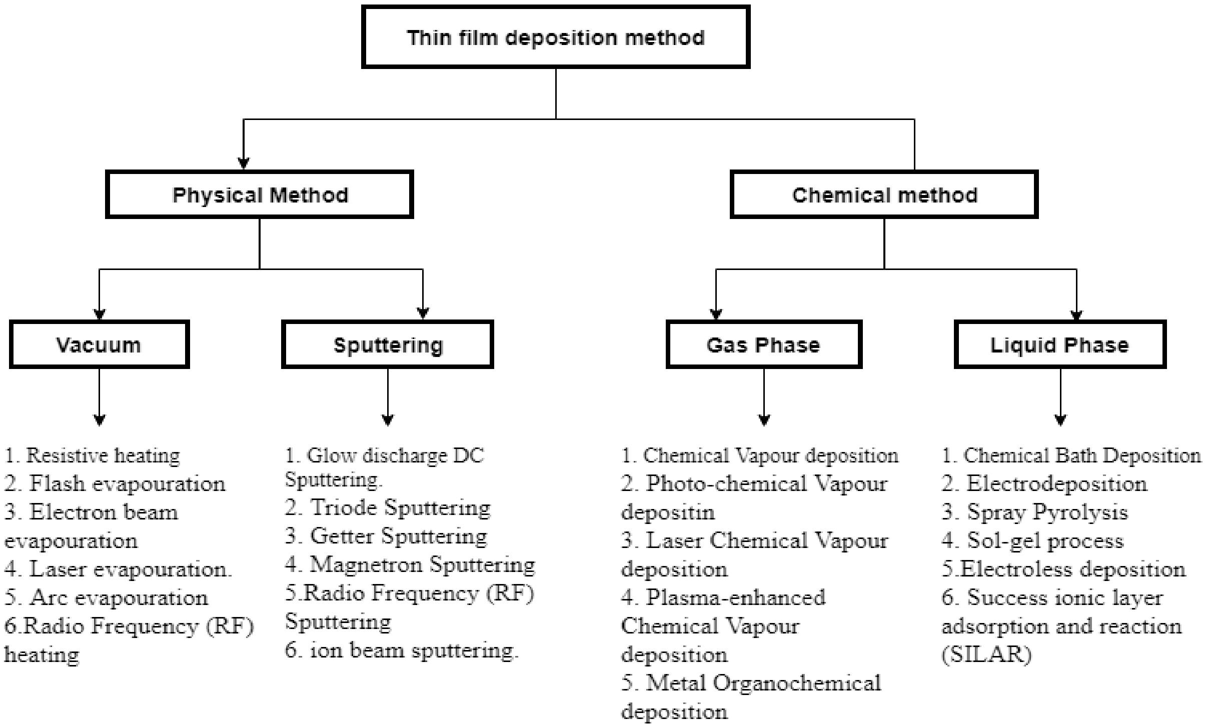


Figure 1.2. Classification of thin film deposition methods

The methods illustrated above have their advantages and disadvantages. For instance, the physical methods of deposition are expensive, this is because they require vacuum for the process. Wet chemical deposition methods such as Chemical Bath deposition, Spray pyrolysis, electrodeposition are found to be attractive due to their simplicity, low cost and possibility of large scale production. For the purpose of this work, Spray Pyrolysis which is the method been used for this work will be described in the subsequent chapter.

1.3 Chemical Spray Pyrolysis

The method of deposition was first introduced in 1966 by Chamberlin and Skarmann for the deposition of Cadmium Sulphide and Cadmium Sulphide films[25].

CSP is a solution based technique which has no limitations to the choice of substrate particle size and surface profile. It has been used in growing of varieties of conducting and semiconducting materials[26-27]. The basic principle of the CSP technique is that, when droplets of the spraying solution gets in contact with the hot substrate, due to the pyrolytic decomposition of solution and the free pin-hole, the film is deposited uniformly on the substrates (Figure 1.3). The other volatile by-products and excess solvent escape in the form of vapours. The thermal energy for decomposition and subsequent recombination of the species and sintering, recrystalliation of the crystallites is provided by the hot substrate. Though, this is different for different materials and solvents used in the spray pyrolysis.

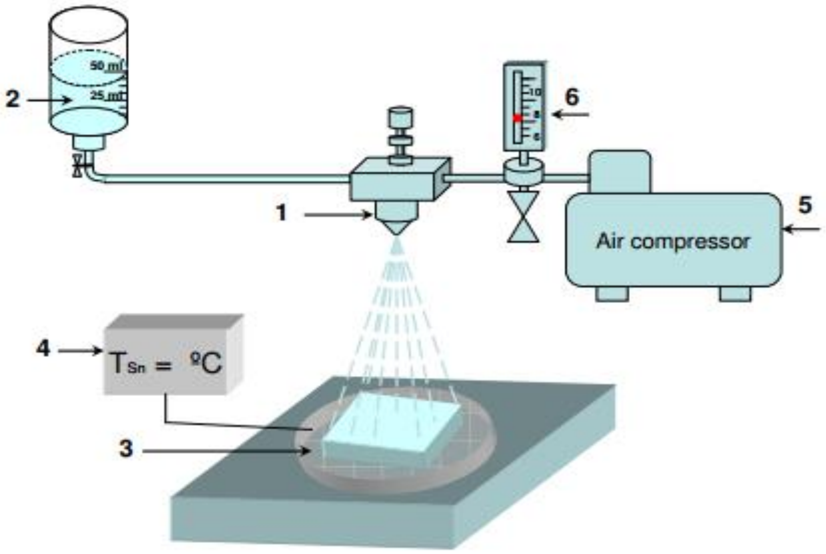


Figure 1.3 . Set-up of the chemical spray pyrolysis system used for this work

CSP is advantageous in a variety of ways when compared to other technique, amongst which includes:

- Its capability to produce large area, high quality adherent films of uniform thickness

- It is simple and a cost effective technique for preparation of semiconductor thin films
- Capable to operate at moderate temperature (100 - 500°C) and produce good films
- Spray parameters can be changed to control the deposition rate and thickness of the film.
- It offers an extremely easy way to dope films with virtually any elements in any proportion, by merely, adding it in some form to the spray solution.
- Spray pyrolysis does not require high quality targets or substrates nor does it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications.

The CSP technique have been used in time past to prepare thin film on various substrates such as glass, ceramic or metallic. In previous years spanning to decades, researchers have in their studies of the CSP technique and the mechanism of thin film formation and the influence of varieties of parameters on the film formation process have been comprehensively reviewed in the literature[28] due to its simplicity and its ability to produce in a large scale is an attractive method for the formation of differnt oxides ranging from thin metal oxides[26] to binary chalcogenides[27]

Thin film formation by using the CSP technique depends on various parameters. However, there are factors that govern this technique in the formation of thin fim and those factors includes:

- The automation of the spray solution into a spray of fine droplets which depends on the geometry of the spraying nozzle and pressure of a carrier gas.
- The properties of thin films depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also on the cooling rate after deposition.
- The film thickness depends on the distance between the nozzle and substrate, solution concentration, quantity and substrate temperature.
- The film formation depends upon the process of droplet landing, reaction and solvent evaporation which are related to droplet size and its moment

Furthermore, the deposition in spray pyrolysis are processed using the following steps;

Precursor Solution: This plays a major role in the formation of various compounds. Examples of aerosol precursors are sols, true solutions, emulsions, colloidal suspensions. However aqueous solutions are usually used due to its safety, low cost and availaibility in of a wide range of water soluble metal salts. The solute must have a high solubility which increases in particle yield of the process[28].

Atomization: Different atomization techniques have been used in the formation of aerosol solution, they include the pneumatic, ultrasonic and electrostatic. These techniques differ from another in their droplet size, rate of atomization and droplet velocity. It is important to note that the velocity of the droplet when it leaves the droplet is important. This is because it helps in determining the heating rate and the time of the droplet during spray pyrolysis. For Pneumatic or pressure nozzles, the size of droplets decreases when the pressure across the nuclei is increased. For a specific atomizer the droplet characteristics depend on the solution density, viscosity and surface tension[28].

Evaporation: During the spray pyrolysis process, evapouration of the solvent from the surface of the droplets, diffusion of the solvent vapour from the droplet in the gas phase, change in temperature and diffusion of solute towards the centre of the droplet all play a vital role in the formation of the thin film[28].

Despite all this factors that affect CSP technique, CSP has been used in depositing a varieties of thin films materials such as Tin Oxide[29], NiO[30]and MoO_3[31]

1.3.1 Chemically sprayed ZnS nanostructured layers

The properties of CSP deposited ZnS nanostructured layer have been investigated and reported in time past, Dedova et al[32] in her report stated that concentration and the amount of solution are the main parameters that influences the dimensions of rods, using concentration of $ZnCl_2$ C=0.05 and 0.1mol/L these were optimal for the growth of seperately elongated ZnS rods and a higher concentration C=0.1mol/L with solution amount of 100-150ml led to the formation of large and very compacted ZnS crystals. It was further reported that the ZnS layers grown at temperature of 520-580°C showed a highly composed c-axix oriented, well-alligned perpendicilerly standing ZnS rods and higher concentration of sulphur in the solution (Zn:S 1:4 or 1:6) resulted in lower intensity as reveled by the PL study

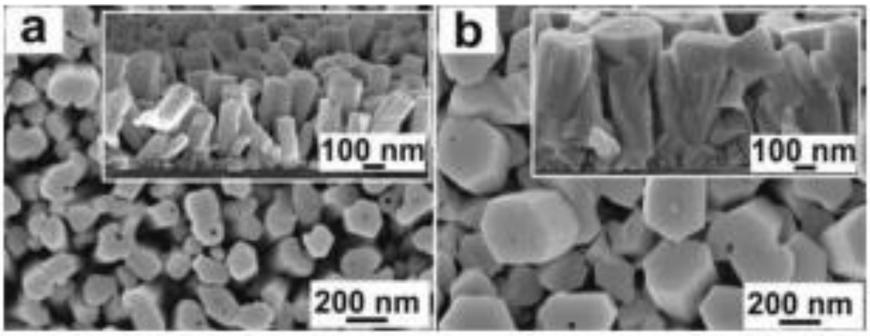


Figure 1.4: SEM images of the ZnS rods deposited on SGL from 150ml solution concentration of $ZnCl_2$ (a) c=0.05mol/L and (b) C=0.1mol

Furthermore, it was also revealed in the report by Dedova et a l[33] that the precursor spray ratio in spray solution is an important parameter controlling the phase composition and the morphological properties of sprayed ZnS thin films. It was revealed that ZnS films produced from 1.1 solution at 500°C possess predominantly cubic structure at band gap of 3.54Ev while those deposited at temperature of 550°C at same solution ratio becomes a mixture of ZnS and ZnO, the ZnO due to oxidation on the part of $ZnCl_2$ not taking part in the complex formation. The report also stated that spraying of the thiocarbimide solution (Zn:S= 1:3) allows to obtain ZnS layersat temperature up to 600°C whereas at growth temperature of 550°C and above, ZnS layers comprising c-axis oriented nanorods with a diameter of approximately 80nm and length of 300nm were grown.

In conclusion, there have been no study that reveals the doping of ZnS nanorods with a foreign metal such as Manganese.

Precursor Solution: The precursor source of Zinc is very important for the deposition of ZnS film by spray method. Precursors such as zinc acetate or zinc chloride have been researched upon. The precursor salt commonly used are generally classified as organo-metallic compounds. This compounds with their characteristic solubility both in polar and non-polar solvent with organic content are easily pyrolysed leaving no residue[34][35]. Additives usually a chelating agent are needed to prevent hydrolysis, this helps in either stabilizing or complexing the precursor solution. The additives or chelating agent such as acetic acid, acetylacetone among others have been reported to have effect on film morphology, thickness and the crystallization of the material[36][37].

The solvent, concentration of precursor solution and the quantity of precursor solution sprayed and the additives added all influences the physical and chemical properties of the ZnS film.

Deposition Temperature: This is another key parameter that affects ZnS film morphology, optical and other properties. Increasing the deposition temperature, the morphology of the film can be changed from a well adherent thin film to a cracked layer or a porous film. At a fixed temperature of 450°C, using zinc choloride as zinc source and thioucarbamide (tu) as sulphur source. It was reported[38][39] that films deposited at temperature below 300°C were amorphous while those deposited at higher temperature up to 500°C were polycrystaline with cubic crystals. Ahmad et al [39] using the spray pyrolysis method also reported that the band gap of ZnS films decreases with a slight increase in sustrate temperature.

Substrate Material: Substrate materials such as glass, quartz, silicon etc is also an important parameter in ZnS film deposition owing to the fact that it controls the nucleation and crystal growth which have a significant influence on the properties of the final product. Abdulazeez et al [41] depositing thin films of ZnO vis the CSP technique using different substrates (glass, quartz and ITO coated glass) reported that the quartz gave a better lattice matching and the ITO coated glass substrate gives higher transmittance than glass and quartz.

1.3.2. Applications of ZnS.

Zinc Sulphide nanocrystals are one of the most interesting and important group of semiconducting materials used in the production of electronic and optelectronic devices.

Zinc Sulphide has a potential application in field emission of electron induced by external electromagnetic field. The large work function of ZnS (7.0eV) other than materials like Si (3.6eV) ZnO (5.3eV) makes it a good candidate for field emitting material. It was established that ZnS exhibited enhanced field emission properties such as emission current, stability, turn on field and field enhancement factors. Filed emitters have great applications in high brightness electron sources, flat panel displays and microwave devices[42][43].

Also, due to its chemical stability against oxidation and hydrolysis when exposed to violent environment, zinc sulphide are interesting materials for catalytic application. They can be used as important catalyst in environmental protection by removing organic and toxic water pollutants. They have also be used for the photocatalytic degradation of organic pollutant such as dyes halogenated benzene derivatives in waste water treatment[42].

Zinc Sulphide is considered important for application in light emitting diodes (LEDs). The properties of LEDs such as its high efficiency, low power consumption environmentally friendly, long lifetimes, fast response to time etc and their optical properties such as broad absorption easy control of the emission and superior luminescence efficiency have made it an attractive choice for the next generation of displays[44].

Other applications of zinc sulphides includes its use in Sensors[45], Laser Solar[46], Solar Cells[47], Cell imaging[48], amongst others.

1.4 Electroluminescence devices

Electroluminescence (EL) as the name suggest is an an electrical and an optical phenomenum. This is the characteristics of a material that emits light when an electric current is passed through it, or when subjected to strong electric field. This phenomenum occurs due to radiative recombination of holes and electrons of the concerned material usually a semiconductor. The excited electrons release their energy as photons which results in light. Before the recombination electrons and holes may be seperated either by doping the material to form a p-n junction or through excitation by impact of high energy electrons accelerated by a strong electric field.

Unlike incandescence (light generation through heat) chemiluminescence (Light generation due to chemical reaction) mechanoluminescence (Light generation due to mechanical action) and sonoluminescence (Light generation due to sound) electroluminesce is one of the rare instance in which direct conversion of electric energy to light occurs without generation of heat.

Electroluminescence in crystals can be achieved mainly in two ways: Intrinsically and charge injection. The two techniques differ in two ways with no net current passin through the elctroluminescent material in the first case and in the second Luminescence only last until the passage of the electric current.

An electroluminescence device is similar to a laser in the fact that photons are produced by the material when there is a change from ground state to an excited state. The difference between an electroluminescence device and a laser lies in the fact that less energy is required to operate an electroluminescent device and it also does not provide coherent light.

Electroluminescent devices are manufactured from either organic or inorganic electroluminent materials. The active material are generally semiconductors of wide enough bandwith to allow exit of the light. The most typical inorganic thin film is Zinc sulfides doped with Manganese with yellow-orange emission. Other examples includes powdered zinc sulphide doped with copper(producing greenish light) or Silver (producing bright blue light), thin film zinc sulphide doped with Manganes (Producing orange -red collour). Semiconductors containing group iii and group iv elements such as indium phosphide (InP), Gallium Arsenide (GaAs).

1.4.1 Applications of Electroluminescense devices

Electroluminescence is suitable for a number of applications which includes

- Backlights
- Liquid Crystals displays
- Electroluminescent lightings
- Nights lamps
- Organic light-emitting diodes (OLEDs)

1.4.2 Electroluminescent displays (ELD)

Electroluminescent displays is a category of flat panel displays created by sandwiching a thin film of electroluminescent material between two plates. This display method makes use of the phenomenum of electroluminescence. Though not commonly used as other displays they are used in industrial instrumentation and transportation application.

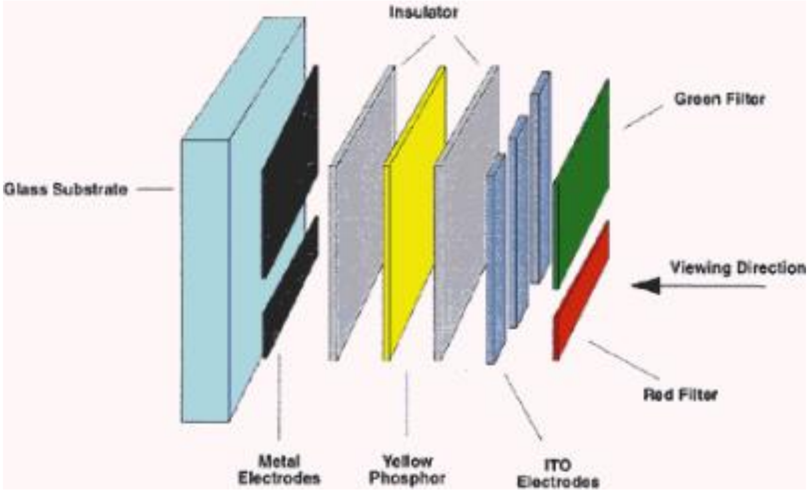


Figure 1.5: Schematics of Electroluminiescent display.

Electroluminescent displays are similar to capacitors in many ways but they differ in the sense that in electroluminescence phosphor layers are laid in between the material. In ELD, alternating current is normally used for its operation and the ELD provides a wide viewing angle as well as a clear and sharp image. Most electroluminescence displays are monochromatic.

1.4.3 Liquid crystals displays (LCD)

This is a type of display technology that makes use of liquid crystal that open or close when stimulated by an electric current. This phenomenum are based on LCD technology. It was first discovered in 1972 in Pittsburg and in 2008, LCD have replaced the cathode ray tubes in television production. The LCD works in taidem with temperature to which it is exposed by changing from solid to liquid. The crystals are arranged in a matrix groups of three crystals of the colour red, blue and green forming a segment known as pixels thereby forming numbers, letters or shape which are arranged in rows or columns.

LCD is applicable in modern display devices such as smartphones, Laptops, LCD television, computers and they are prefered ahead of others because they are thinner, lighter and uses less power.

1.4.4 Organic Light-emitting diode (OLEDs)

An organic light-emitting diode (OLED) is a solid state light device that makes use of the flat light emitting technology with the help of two conductors between which a series of organic thin film are kept. Unlike other display modes an OLED does not require backlighting because of its low power consumption and great brightness. OLED is used as backlight source in LCD displays, electronic equipment, signalling as well as general lighting.

There are basically two types of OLED which are light-emitting polymers (LEPs) which uses large plastic molecules called polymers and traditional OLEDs use small organic molecules deposited on glass to produce light.

OLEDs are alsp applicable in Television, computer screens, MP3 and cell phone displays. Their thinness, greater brightness and better colour makes it an exciting prospect for future applications.

1.4.5 Light Emitting Diodes (LEDs)

This is a semiconducting device that emits visible light when an electric current passes through it. It is essentially PN junction opto-semiconductor that emits a monochromatic (single colour) light when operated in a forward biased direction. The LED work in the principle of movement of electrons when sufficient voltage is applied to the chip across the leads of the LED, electrons can move easily in only one direction across the junction between the p and n region. In the P region there are many more positive than negative charges.

The energy of the light emitted by a LED is related to the electric charge (q) of an electron and the voltage(V) required to light the LED by expression.

$$E = q\ V \text{ Joules}$$

Some of the applications of LEDs includes

- Sensors examples medical instrumentation, Bar code readers
- Mobile applications examples includes Digital camera, mobile phones, laptops
- LED signals examples tower lights, rail traffic, sign applications

Zinc sulphide is considered important for application in Light Emitting Diodes (LEDs). The properties of LEDs such as its high efficiency, low power consumption, environmentally friendly, long lifetimes, fast response time etc. Their optical prperties includes broad absorption, easy control of the emission and superior luminescence efficiency have made it an attractive choice for next generation of display.

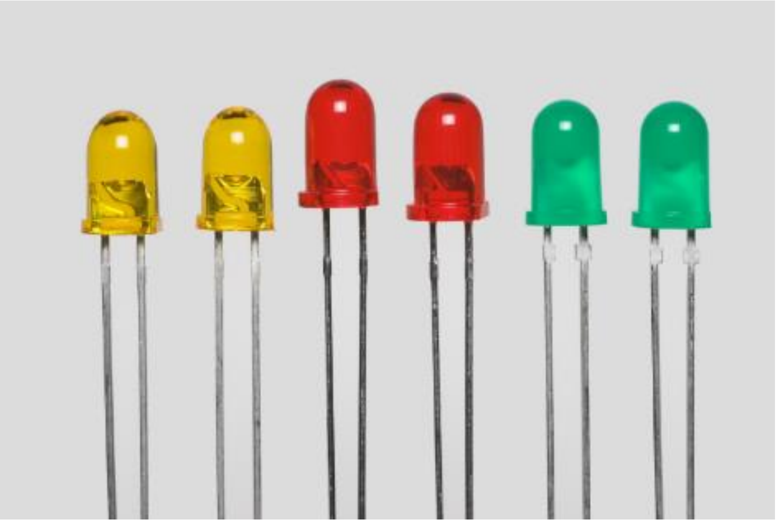


Figure 1.6: Exmple of a Light emitting diode crystal.

1.5 ZnS doping

The wide band gap of ZnS which makes it suitable for use as a host material for variety of dopants and its diverse applications such as electroluminescence devices, light emitting diodes, solar cells and optoelectronic devices have attracted the attention of a large number of researchers. The doping of ZnS is one of the most efficient methods to improve its use in electroluminescence devices, Solar cells and other applications. The dopant introduced into ZnS lattice can be cationic or anionic, which modifies its crystalline and electronic structure for improved applications. Different elements have been used in time passed to dope ZnS. ZnS: Cu[49], ZnS: Pb[50], ZnS:Ga[51].

The numerous effect and phenomena observed when matter interacts with light in an optical experiment are distinctive to the particular material system. This interaction process reveals the difference in the physical properties of materials. These are the reasons for the use of optical techniques for precise characterization of the quality of material. Optical techniques have proven to be very sensitive tool and also a non-destructive technique for studying the growth process, structural defects, impurities etc. Nevertheless, much efforts have been made to control the size, morphology and polycrystallinity of the ZnS nanocrystals in order to increase their physical properties[52]

In principle, the role of dopants atom in ZnS matrix is considered to be

- Improving the numbers and types of charge carriers
- Increase the conductivity of the material
- Change the electronic properties in a controllable way.
- Doping also helps to produce two groups of semiconductors, the negatively and positively charged

1.5.1 Doping of Zinc Sulphide with manganese (ZnS:Mn)

Due to their unique properties and technological applications, luminescent semiconducting nanocrystals especially those of the group II-VI semiconductors have attracted a greal deal of attention. The most extensively investigated doped semiconductor being Mn doped ZnS nanocrystals. In Mn doped ZnS, the doping ions (Mn^{2+} ions) act as recombination centre for the excited electron-hole pairs and this result in strong and characteristics luminescence. Mn doped ZnS semiconductor material has also been studied to be applicable in diverse area such as optical coatings, electro-optic modular, photoconductors, UV light emitting diode, efficient phosphor in flat panel displays, photovoltaic devices etc[53]. ZnS doped with Mn has potential applications field emission devices (FED)and also used also as phosphors and thin film in electroluminescence devices[54][55].

In the doped semiconducting compounds, the impurity states plays major role in affecting the electronic energy structures an the transition probabilities[56] which is not same with the un-doped semiconducting material. Mn doped ZnS have high quantum efficiency and luminescence intensity[57] and the band structure of the semiconducting material changes with decreasing particle size. The change in the properties of the nanoparticles are driven mainly by two factors which are the increase in the surface to volume ratio and the change in the electronic structure of the material due to quantum confinement effect.

The effect of Mn^{2+} substitution on the photoluminescence properties of doped samples is also studied and doped ZnS:Mn showed enhanced luminescence property compared with that of the undoped ZnS nanoparticles[58]. Similarly, ZnS doped with Mn which emits a yellowish orange under excitation is one of the most important phosphor used in displays and its conventionally produced by solid state process at high temperature (900°C - 1200°C) as bulk materials[59]. It was also reported by Ummartyotin et al[60] that the presence of a dopant in the ZnS lattice exhibited intense and stable emission.

Anions such as Nitrogen(N) Carbon(C), Boron (B) Chlorine (Cl_2) and Fluorine (F) have also been used for doping by researchers to improve both chemical and physical properties of semiconductors. However, there are limited publications on the doping with non-metals. The other types of dopant is called the cationic dopants. It consist of the elements of the transition metals such as Ag, Cu, Pb, Co, Zr amongst others which have been investigated as suitable dopants to improve the properties of ZnS materials.

Transition metal-doped ZnS materials have received a great amount of attention from researchers due to its vast applications in electronics and optoelectronics. Since the first report of ZnS semiconductor doped with Mn by Bhargava et al[61]. Several research work have been conducted on ZnS:Mn[62][63][64].

Bhargava et al[61] reported that the doping of Mn into ZnS nanocrystals result in the enhancement of its luminescent efficiency and the lifetime shortening when compared to the bulk material, his results were explained on the bases of the sp electron of the host (ZnS) and the 3d electrons of the impurity(Mn) under the quantum confinement of the Sp states.

Tanaka et al[65] after analysing photolumisnescence excitation (PLE) spectra in ultra-violet and visible regions of ZnS:Mn nanoparticles samples using different sizes concluded that the luminescence of Mn^{2+} under the inter-band excitation occurs mostly by energy transfer from electron hole pairs delocalized inside the ZnS host nanocrystals.

Studying the optical properties of Mn doped ZnS semiconductor nanoclusters various samples of ZnS:Mn were characterised using characterization methods Hoa et al[66]. reported that the PL spectra of ZnS doped with Mn at room temperature exhibit both the 495nm blue defect related emission and 587nm orange Mn^{2+} emission. The blue emission dominant at low temperature while orange emission dominant at low temperature which further interpret photoluminescence behaviour of ZnS doped with Mn.

Bodo et al[67] in its report of the synthesis and characterization of ZnS:Mn using chemical co-precipitation method at room temperature, the optical and structural prperties of ZnS:Mn particles were determined by XRD, SEM, UV-Visible and PL analysis concluded that the Mn incorporated into ZnS nanoparticles results in changing its morphological structure and optical properties.

There are several methods to deposit ZnS nanoparticles with various Mn^{2+} concentrations such as Sol gel, Chemical vapour deposition, hydrothermal method, Chemicl Co-precipitation and Chemical Spray Pyrolysis. Among the different deposition processes, spray pyrolysis method is used because of its vast advantages which includes its simplicity, conveniency, cost effectiven, capable of producing large scale. Till now there are many reports on the ZnS:Mn using spray pyrolysis technique.

Rangath et al[68] in its report of properties of ZnS: Mn thin films by improved spray method using distilled water as the solvent and stock solutions of anhydrous zinc chloride ($ZnCl_2$) Manganese tetrahydrate ($MnCl_2 . 4H_2O$) and thiourea [$SC(NH_2)_2$] at different Mn doping concentrations of 1 at %, 3 at %, 6 at %, 8 at % and 12 at % deposited on an ordinary glass substrate. It was concluded that thin films doped with Mn with 3 at % concentration in the solution exhibited the best properties. Furthermore, the Mn doped thin films showed two peaks one associated with self activated center at 2.53eV and other at 2.10eV (590nm yellow orange emission) associated with Mn^{2+} ions in ZnS films.

The intensity of blue emission was dominant at 0 at % and was found to decrease with Mn doping concentration, the yellow orange emission intensity showed maximum at 3 at %.

BinXia et al[69] using three types of precursor nitrates, chlorides and acetates of Zn^{2+} and Mn^{2+} as cationic sources, Thiourea used as the sulphur source reported that they chloride products have a higher crystallinity and the photoluminescence of ZnS:Mn is strongly dependent on the synthesis conditions. The nitrate product has the strongest emission while the acetate product shows a high emission and a unique particle morphology. It could be readily fabricated into devices for use in phosphor applications.

Falcony et al[70] with solutions 0.1M $Zn(C_2H_3O_2)_2$ and 0.1M $C_3H_8N_2S$ in a mixture of three parts of isopropyl alcohol and one part of deionized water with Mn doping achieved by mixing $MnCl_3$ in spraying solution at varied temperature of 340-500°C with Mn concentration in the range of 0-20 at %. Two peaks of 490nm and 590nm spectra were shown. It was also reported that luminescence intensity of this centers started to increase as the Mn concentration increases and above center in concentration 3 at % Mn in the spraying solution, which is also similar to others reported by other techniques.

Table . Common synthesis methods of Mn doped ZnS and applications

Sample Morphology	Method	Chemistry	T°C	PL	Application	Ref
ZnS films	CBD	$Zn(CH_3COO)_2.2H_2O$ $CH_3COONH_4.2H_20$ $Mn(CH_3COO).2H_2O$ Mn:Zn=1:1 to 1:4	50 to 80°C	Intense 592nm Low 342nm I_{Red}/I_{NBE}=1.25	Flat panel Displays	[71]
ZnS films	Improved Spray Pyrolysis	$ZnCl_2$ $[SC(NH_2)]_2$ $MnCl_2.4H_2O$ Mn:Zn=1:3	450°C	Intense 590nm Low 490nm I_{Red}/I_{NBE}=4.0	Optoelectronic Application	[68]
ZnS nanoclusters	Hydro-thermal Process	$Zn(CH_3COO)_2.2H_2O$ $[SC(NH_2)]_2$ $Mn(CH_3COO).2H_2O$ Mn:Zn=1:3	200°C	Intense 587nm, Low 495nm I_{Red}/I_{NBE}=1.3	Optical Properties	[66]
ZnS film	ALD	$ZnCl_2$ $Mn(thd)_3$	300°C-400°C	–	Electrolumini-Nescence Device	[72]

ZnS nanocrystals	Two step Thermochemical method	$Zn(NO_3)_2$ $Na_2S_2O_3$ $Mn(NO_3)_2$ Mn:Zn=1at%	96°C	Intense 585nm, Low 254nm I_{Red}/I_{NBE}=4.0	Electrolumini-Nescence Device	[73]
ZnS film	Spray Pyrolysis	$Zn(C_2H_3O_{2)2}$ $[SC(NH_2)]_2$ $MnCl_3$ Mn:Zn=1:3	340°C – 500°C	Intense 590nm, Low 490nm I_{Red}/I_{NBE}=4.5	Lumininescent Material	[70]
ZnS films	CBD	$Zn(CH_3COO)_2.2H_2O$ $[SC(NH_2)]_2$ $MnCl_2.4H_2O$ Mn:Zn=1:6	90°C	Intense 585nm Low 438nm I_{Red}/I_{NBE}=6.0	Optoelectronic Industry	[74]
ZnS Nanoparticles	Chemical Co-precipitation Method	$ZnCl_2$ Na_2S $MnCl_2$ Mn:Zn=1:10	300°C	Intense 598nm Low 396nm I_{Red}/I_{NBE}=5.0	Radiation Measurement Device	[75]
ZnS nanoparticle	Solid State Method	$Zn(CH_3COO)_2.2H_2O$ $Na_2S.9H_2O$ $Mn(CH_3COO)_2.2H_2O$ Mn:Zn=3 at%	900°C	Intense 580nm Low 345nm I_{Red}/I_{NBE}=4.0	Phosphor Material & Luminescence device	[59]
ZnS films	Co-sprayed	$Zn(CH_3COO)_2.2H_2O$ $[SC(NH_2)]_2$ Zn:Mn=1:2	380°C	Intense 585nm Low 386nm I_{Red}/I_{NBE}=5.0	Electroluminiscent Device	[76]
ZnS film	Spray Pyrolysis	Zn (C2H3O2)2 C3H8N2S MnCl3	340°C-500°C	Intense 585nm Low 386nm	Electroluminiscent Device	[70]

1.6 Characterization methods of thin films and nanostructured layers

The materials synthesized can be implemented effectively in their various fields of applications based on their physical and chemical properties.

The complete characterization of any materials comprises its phase analysis, structural clarification, compositional, optical and surface characterization amongst others. All these plays a crucial role in evaluating the properties of a material. Characterization techniques also helps in categorising and marking the prepared materials properly in accordance with its area of suitability in applications. The methods also helps in explaining reasons behind various phemena and assist to establish scientific support to the proposed theories for future references.

This section of this report aptly explains different characterization methods used, their operation and working principle.

In this thesis, Scanning Electron Microscopy (SEM) X-ray Diffraction (XRD) Photoluminescence (PL) and Ultraviolet Visible Spectroscopy (UV-Vis) were used. These characterization methods are further discussed.

1.6.1 Scanning Electron Microscopy (SEM)

Electron microscopes are scientfic instruments that uses a beam energetic electrons to examine objects on a very fine scale. This source of illumination were developed due to the limitations of light microscopes which are limited by the physics of light. During the early 1930s the desire to scientifically see the fine details of the interior structures of organic cells such as nucleus, mitochondria etc which require magnifications greater than 10,000(ten thousand) but could not be achieved by simple light/optical microcopy because the wavelenght of electrons can be up to 10,000 times shorter than that of visible light photons, the electron microscope has a higher resolving power than light microscope and can reveal the structure of smaller objects. This led to the development of a SEM in 1931 which waslater commercialised after about thirty years (30years) later.

Scanning Electron Microscopy (SEM) is a type of electron microscopy that images a sample by scanning it with a high energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the samples surface topography, composition and other properties such as electrical conductivity. SEM can be used to determine the Topography, Morphology, Composition and Crystallographic information of materials.

Characteristics that can be viewed on SEM

Topography: The surface feature of an object or “how it looks“. Its texture direct relation between these features and materials properties.

Morphology: The shape and size of the particle making up the object, direct relation between these structures and material properties.

Composition: The elements and compounds that the object is composed of and the relative amount of them, direct relationship between composition and materials properties.

Crystallographic Informations: How the atoms are arranges in the object; direct relationship between these arrangement and material properties.

Applications and the Limitations of SEM

Applications:

- Virology- for the investigations of virus structure
- Cryo-electron microscopy- I mages can be made of the surface of frozen materials.
- 3D tissue Imaging
    - Helps to know that cells are organized in a 3D network
    - Their organization determines how cells can interact.
- Forensics- SEM reveals the presence of materials on evidences that is otherwise undetectable.

Limitations:

- SEMs are expensive and large
- Special trainings is required to operate an SEM
- The preparation of samples can result in artifacts.
- SEMs are limited to solid samples.
- SEMs carry a small risk of radiation exposure associated with the electrons that scatter from beneath the sample surface

Figure 1.7: ZEISS HR FE-SEM Ultra 55 Scanning Electron Microscope

However, a typical SEM set-up consists of five units which are: electron gun unit, demagnification unit, scanning unit, focus unit, and detector unit. A beam of scattered electron is produced by an electron gun which is then narrowed down by the condenser lens in the demagnification unit. The produced electron is collimated and it is focused on the sample with the help of an electromagnetic lens in the focusing unit which then scans the sample. Images are produced as a result of the ejected electrons (backscattered or secondary electron) from the surface of the sample being detected in the detector unit.

1.6.2 X-ray Diffraction (XRD)

X-rays are electromagnetic wave of high energy and very short wavelenght between ultraviolet light and gamma rays, which is able to pass through many materials opaque to light. Most x-rays have wavelenght ranging from 0.001 to 10 nanometers, corresponding frequencies in the range of 30petahertz to 30 exahertz and energy levelsranging from100Ev to 100keV. The German physicist Wilhelm Rontgen is credited as the discovere of X-rays in 1895 because he was the first to systematically study them.

Diffraction on the otherhand, is the process by which a beam of light or other system of waves is spread out as a result of passing through a narrow aperture or across an edge, typically accompanied by interference between the waves form produced. Diffraction occurs with electromagnetic waves such as light and radio waves and also in sound and water waves. The most conceptual form of diffraction is the double slit diffraction, that is why light diffraction is firstly remembered.

X-rays is a novel and non-destructive method for chemical analysis and a variety of x-ray techniques are available in practice amongst which includes X-rays Absorption, X-rays fluorencence and X-ray Diffraction. For the purpose of this study, we shall be dwelling on X-rays diffraction as a case study.

X-ray Diffraction is a technique use to determine the atomic and molecular structure of crystals in which the crystalline atoms cause a beam of incident x-rays to diffract into many specific directions. The atomic planes of a crystal cause an incident beam of x-trays to interfer with one another as they leave the crystal. The phenomenum is called X-ray diffraction. A stream of xrays directed at a crystal diffract and scatter as they encounter atoms, the scattered rays interfare with each other and produce spots of different intensities that can be recorded on film.

To determine the structural and phase composition of the material, the instrument used to obtain XRD patterns was ULTIMA IV Rigaku D/max 2500 diffractometer and strip of silicon detector D/Tex ultra with Cu Kα radiation source operated at 40KV and 40Ma. The diffraction patterns were measured in the 2θ range from 20 to 60 degrees wit a step of 0.002 degree and scanning rate of 5 degrees per minute. Using the Bragg-Brentano`s equation expressed below, the planes of the crystal that are parallel to the substrate was determined.

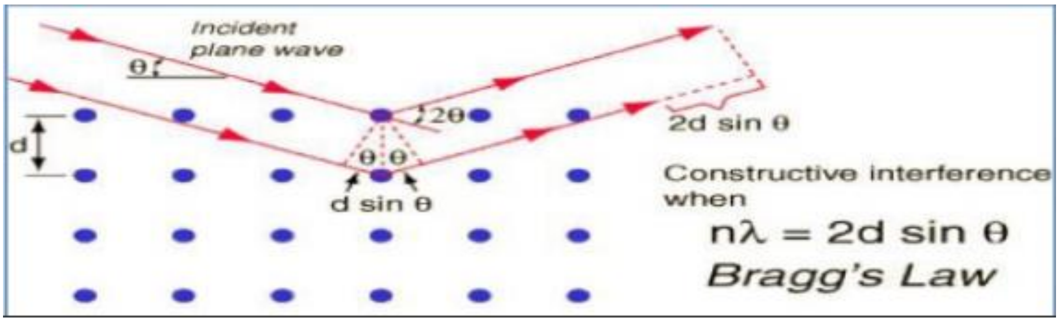


Figure 1.8: Sample of XRD Diffraction techniques.

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

Where n is an integer of positive value, λ is wave length in Angstrom (10^{-10} m), d is the spacing between crystals, and θ is the diffraction angle.

Information such as crystallite size and crystallinity, phase composition, unit cell parameter, lattice type, and orientation of the crystallites was determined from the diffractograms. For phase analysis, peaks observed were often compared with those published in international data base, for example, International Centre for Diffraction Data (ICDD). The mean crystallinity size was evaluated by the Debye-Scherrer equation expressed below.

$$ŧ= K\lambda/ß\cos\theta$$

where ŧ is the mean crystallite size, K is a dimensionless shape factor given as 0.94, λ is the wave length of the X-ray, ß is the full width at half maximum (FWHM) value in radian, and θ is the Bragg's angle.

Applications of XRD

- XRD is a non-destructive technique to identify crystalline phases and orientation
  Obtain XRD pattern, measure d-spacings, obtain integrated intensities.
  Compare data with known standards in the JCPDS file.
- To measure the thickness of the films and multilayers
- To determine atomic arrangement
- To determine the strutural properties
  Lattice parameters, grain size, epitaxy, phase composition, prefer strained orientation, thermal expansion.
- XRD can be used to determine whether the compound is solvated or not
- The Powder XRD pattern may be thought of as finger print of the single crystal structure and it may be used conduct qualitative and quantitative analysis.

1.6.3 Ultraviolet – Visible Spectroscopy (UV - VIS)

Spectroscopy is the branch of science that deals with the study of interaction of matter with light of the branch of science that deals with the study of interaction of electromagnetic radiation with matter.

Spectroscopy began with Isaac Newton's optics experiment (1666-1672). Newton applied the word ´´Spectrum`` to describe the rainbow of colours. During the early 1800's Joseph Von Fraundlofer made experimental advances with dispersive spectrometer that enables spectroscopy to become a more precise and quantitative scientific technique. Since then Spectroscopy has played and continues to play a significant role in chemistry, physics and astronomy.

Spectroscopy is the most powerful tool available for the study of atomic and molecular structure and its is used in the analysis of a wide range of samples. Atomic spectroscopy is concerned with the interactin of electromagnetic radiation with atoms commonly in the lowest energy called the ground state while Molecular Spectroscopy deals with the interaction of electromagnetic radiation with molecule

Ultraviolet and Visible (UV-VIS) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption surface can be at single wavelength or over an extended spectral range. UV spectroscopy can be used for various reasons which includes;

1. Detection of functional group
2. Detection of impurities
3. Qualitative analysis
4. Quantitative analysis
5. Single compound with chromophore
6. Drugs with chromophic agent
7. It helps to show the relationship between different groups. It is also useful to detect the conjugation of the compoun

Applications of UV-Visible Spectroscopy

- **Detection of impurities**; this is one of the best method use to determine impurities in organic compounds. Additional peaks can be observed due to impurities in the samle and it can be compared to the standard raw material.
- **Structure elucidation of organic compounds**: From the location of peaks and combinations of peaks, it can be concluded whether the compound is saturated or unsaturated, heteroatoms are present or not etc.
- **Qualitative Analysis**: it helps to characterise compounds which absorbs UV radiation. Identification is done by comparing the absorption spectrum with the spectra of the known compounds.
- **Quantitative Analysis**: It is used for the quantitative determination of compounds that absorbs UV radiation.
- **Molecular weight determination**: Molecular weight of compounds can be measured spectrophotometrically by preparing the suitable derivatives of this compounds.
- Detection of functional groups in a compound
- Quantitative analysis of pharmaceutical substances

Figure 1.9 : Jasco V-670 UV-VIS NIR model Spectrophotometer

Optical spectra were used to calculate the optical bandgap (Eg) and the haze factor (HF): HF = DR/TR. The band gap energy of the film was evaluated using the expression below;

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where α is the optical absorption coefficient, *h*v is the photon energy, *A* is a constant called critical absorption, *n* value varies depending on the band transition whether it is direct transition or indirect, but in our case n = 0.5 for direct transition and *Eg* is the optical band gap. The value of *Eg* for the materials obtained were obtained by plotting $(\alpha h\nu)^2$ against the photon energy and extrapolating the linear part of the curve to the photon energy axis.

1.6.4 Photoluminescence (PL)

Photoluminescence is a contactless nondestructive spectroscopic technique commonly used for the study of intrinsic ans extrinsic properties of both bulk semiconductors and nanostructures. In essence, light is directed onto a sample where it is absorbed and imparts excess energy onto the material in a process called photo-excitation.

The photo-excitation causes the material to jump to a higher electronic state and will then release energy(photons) as it relaxes and returns back to lower energy level. The emission of light or luminescence through this process is what is refered to as Photoluminescence (PL)

An excitation wavelenght is selected by one monochromator and luminescence is observed through a second monochromator, usually positioned at ninety degrees (90) to the incident light to minimise the intensity of scattered light reaching the detector. If the excitation wavelenght is fixed and the emitted radiation is scanned and emission spectrum is produced.

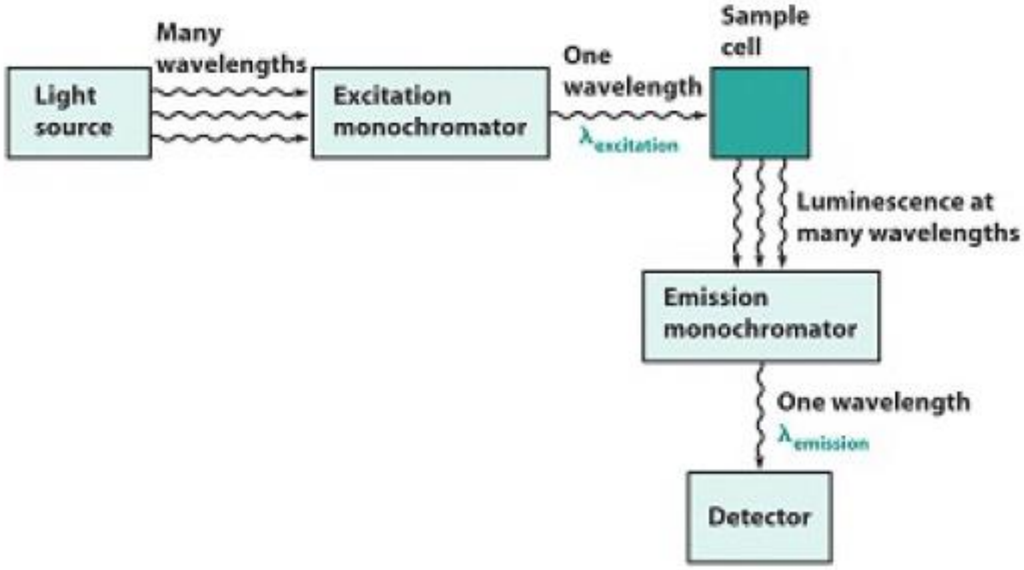


Figure 1:10 Working principle of photoluminescence device

Applications of Photoluminescence

PL spectroscopy is of a great significance in many field of analysis expecially semiconductors. It includes;

Band gap determination: This is the energy difference between the states in the conduction band and the valence band of the radiative transition in semiconductors. The spectral distribution of PL from a semiconductor can be analysed to non-destructively determine the electronic bandgap. This provides a means to quantify the elemental composition of compound semiconductor and its a vitally important material parameter influencing solar cell device efficiency.

Impurity level defects: Radiative transitions in semiconductors involves localized defects levels. The PL energy level associated with these levels can be used to identify specific defects and the amount of PL can be used to determine their concentration. The PL spectrum at low temperature often reveals spectra peaks associated with impurities contain within the host material. The high sensitivity of this technique provides the potential to identify extremely low concentrations of intentional and unintentional impurities that can strongly affect material quantity and device performance.

Recombination Mechanism: The quantity of PL emitted from a material is directly related to the relative amount of radiative and non radiative recombination rates, Non radiative rates are typically associated with impurities and thus, this technique can quanlitatively monitor changes in materials quality as a function of growth and processing conditions.

Other applications of PL includes

- Material quality
- Surface structure and excited states.

Figure 1:11: ***KIMMON IK series He-Cd laser with the wavelength of 325 nm***

Summary of literature review and aims of study

According to the literature survey ZnS thin films have been extensively researched on and various deposition methods including the CSP have been used for its synthesis, it has also been used in diverse fields of application like optical coatings, phosphors, electroluminescence displays and other light emitting materials. Different precursor solutions have also been used to deposit Zns films such as nitrate, acetates, chlorides. Also from the survey, lots of research work have been done on the synthesizes of ZnS thin films doped with Mn deposited using different deposition techniques and CSP have been proven to also be a good technollogical attractive method to deposite ZnS thin films doped with Mn.

To the best of my findings, there is limited or no publication on the ZnS rods doped with Mn using the spray pyrolysis method of deposition.

1.7 Aims of study

The following are the aims of the study:

1. To deposit ZnS thin films and nanorods doped with Mn using the CSP method of deposition
2. To study the optical, structural, morphological properties of ZnS films and nanorods doped with Mn.
3. To find out the relationship between the rods properties and Mn concentration
4. To find out the optimal deposition parameters for ZnS that could be applicable for electroluminescent device

2 MATERIALS AND METHODS

2.1 Experimental details

The ZnS layers have been deposited by spray pyrolysis deposition technique. The detailed description of the preparation procedure is presented in this chapter.

2.1.1 Substrate preparation

The substrates used for the experiment is Soda lime glass (SGL) substrates. The substrates were mechanically cut into coupons of same dimensions and they were cleaned for 5mins with acetone plus 5minutes with ethanol and 5minutes with water in an ultrasonic bath. They were finally dried in air and kept in a clean petri-dish.

2.1.2 Preparation of Precursor Solution

Aqueous solution of $ZnCl_2$ and doubly recrystallised thiacarbanide were used as precursor. 50ml volume of precursor solution were to be synthsized. The molar ration of $ZnCl_2$ and tu (Zn:S) was fixed at 1:6 using substrate temperature (T_S) of 550°C. Air flow ratewas 8L/min and the solution deposition rate was 24Lmin using continuous spray mode.

Mn doped ZnS was prepared by adding quantitative amount of MnCl2 corresponding to the Mn/Zn mole ratio. The mixture is then transfered into an ultra-sonic both for 15mins to ensure complete desssolution and homogenous makin. Series of Mn doped ZnS precursor solution were prepared by varying Mn/Zn mole ratio (5,10,20,40%).

Chemicals

The following reagents were used: acetone, zinc chloride, Thiourea, Manganese chloride and deionised water. Details regarding the reagents were presented in the table.

Table 3.1. Details about the chemicals used in the experiment

Reagent name	Chemical formulae	Molecular weight (g/mol	Company	Purity (%)
Acetone	CH_3COOCH_3	58.08	Sigma-Alorich	96.6
Manganese (II) Chloride	$MnCl_2$	125.84	Sigma-Alorich	98.0
Zinc Chloride	ZnC_{l2}	136.29	Sigma-Alorich	98.0

Thiourea	CH_4N_2S	76.12	Merck	98.0
Deionised water	H_2O	18	Millipore	>18.2Mohms.cm

2.2 Film deposition

The cleaned substrates were placed on a tin bath maintained at 450°C and the prepared solution was sprayed using a pneumatic spray set-up at the spraying rate of 2.5 ml/min (adjusted with ethanol) using compressed air as the carrier gas. The flow rate of the carrier gas was 8 L/min. The nozzle of the spray set was tilted in a way such that the flowing aerosol reached the surface of the heated substrate at an angle of almost 60 degrees. One spray cycle consisted of 60s spraying plus 60s pause and ten spray cycles were made from each solution. The precursor solution decomposes to form thin film on the substrate and the solvent evaporate simultaneously.

The experimental details on Sprayed ZnS layers are as summarised in the table xxx below

Table 3.2 : Experimental composition of the layers

Sample name	Dopant, Mn^{2+}	Morphology	Concentrations			T$_S$, °C
			ZnCl2	Tu	MnCl$_2$	
MnZnS$_R$-0	0%	Rod	0,1 mol/l	0,6 mol/l	–	570
MnZnS$_R$-1	1%	Rod	0,1 mol/l	0,6 mol/l	0,001 mol/l	570
MnZnS$_R$-3	3%	Rod	0,1 mol/l	0,6 mol/l	0,003 mol/l	570
MnZnS$_R$-5	*5%*	Rod	0,1 mol/l	0,6 mol/l	0,005 mol/l	570
MnZnS$_F$-0	0%	Film	0,1 mol/l	0,6 mol/l		400/450
MnZnS$_F$-1	1%	Film	0,1 mol/l	0,6 mol/l	0,001 mol/l	450
MnZnS$_F$-3	3%	Film	0,1 mol/l	0,6 mol/l	0,003 mol/l	450

2.3 Characterization methods

2.3.1 Scanning Electron Micrope (SEM)

The Surface morphology and cross-sections of the deposited layers were examined by scanning electron microscopy (SEM) using a high-resolution SEM Zeiss HR FESEM Ultra 55 at an accelerating voltage of ca. 4 kV. Crystals density was evaluated from the SEM surface images, from area of 2.6 µm×2.1 µm.

2.3.2 X-ray Diffraction (XRD) Study

X-ray powder diffraction (XRD) was used to examine the crystal structure, phase composition and crystallite orientation. XRD measurements were performed on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5406 A, 40 kV at 40 mA) using silicon strip detector ˚ D/teX Ultra.

2.3.3 Ultraviolet – Visible Spectroscopy (UV - VIS)

The optical parameters of the ZnS, such as total transmittance (TT), diffuse reflectance (DR) and total re- flectance (TR) were recorded on Jasco V-670 UV-VIS-NIR spectrophotometer equipped with an integrating sphere. Spectra were recorded in the wavelength range of 300– 2500 nm. Optical spectra were used to calculate the optical bandgap (Eg) and the haze factor (HF): HF = DR/TR. Optical band gaps (Eg) were calculated from the intercept of the straight-line portion of (αhν) 2 vs. hν graph on hν-axis when (αhν) 2 -axis value is 0.

2.3.4 Photoluminescence (PL) Study

The PL measurements were carried out at room temperature using KIMMON IK series He-Cd laser with the wavelength of 325 nm (3.8 eV) for excitation. The PL spectra were recorded by using a computer controlled SPM-2 monochromator (f = 40 cm) together with a photomultiplier tube and a DSP Lock-In amplifier SR 810.

3 RESULTS AND DISCUSSION

3.1 SEM study. Surface morphology of ZnS layers

Images obtained from SEM were used to study the influence of varying Mn concentration in precursor solution on film morphology and thickness. Figure (3.1) shows the SEM images of the undoped ZnS and Mn doped ZnS films at different concentrations i.e (1%, 3%). It can be seen from SEM, the undoped ZnS film (figure a and b) has a very uniform and compacted surface composing of fine grains with dimensions of about 10-15nm. However, with the addition of small amount of Manganese (1%) to the spraying solution, it was noticed that the sufaces (figure c and d) become more structured and composed of clearly pronounced grains with diameters of 90nm. Tiny pinholes could also be noticed from the surface of the structure. It was also observed that on addition of 3% Manganese dopants in the solution, (figure e and f) shows a compact structure consisting of large and tiny grains was seen on the surface of the structure with dimensions of about 75nm and 20nm.

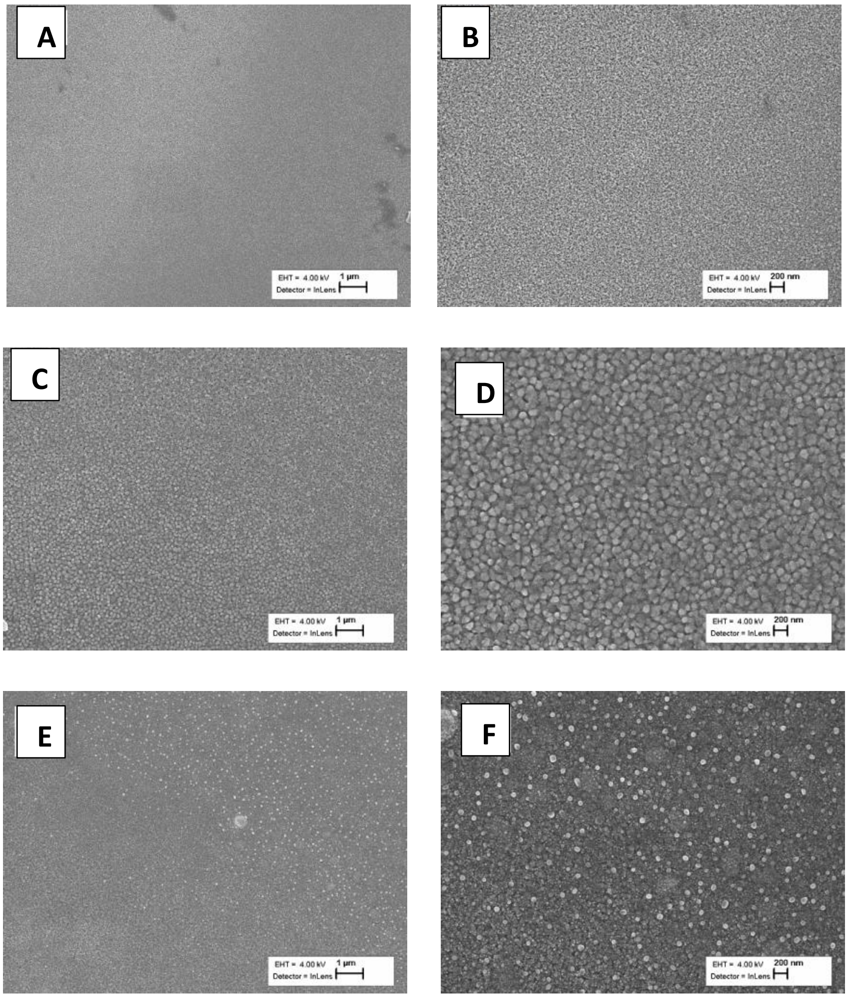


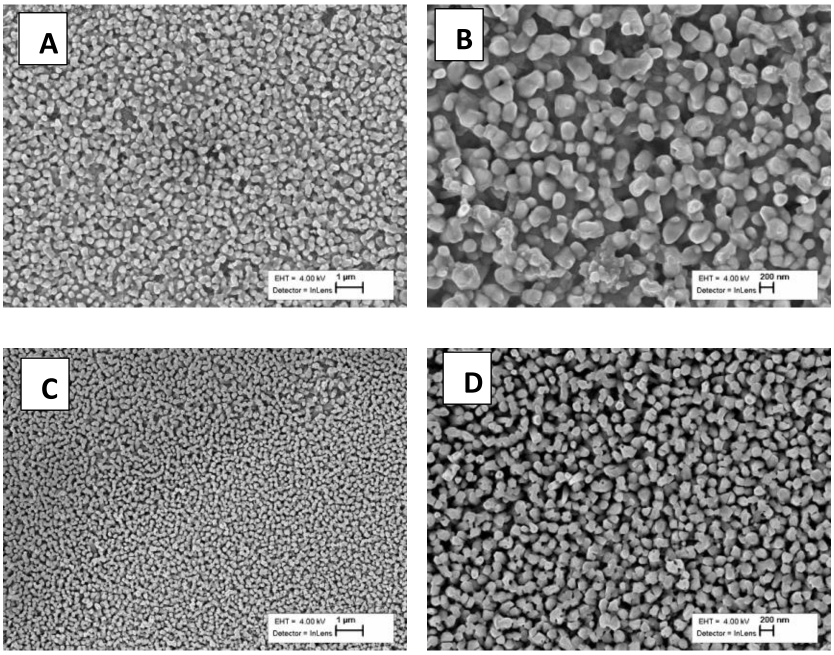
Figure 3.1 SEM images of undoped and doped ZnS thin films at different Mn concentration

(A) (B) Undoped ZnS films, bar 1μm (A) and 200 nm (B); **C) D)** ZnS:Mn 1at% films, bar 1μm (C) and 200 nm (D); **E) F)** ZnS:Mn 3at% films, bar 1μm (E) and 200 nm (F).

The figure (3.2) shows the SEM images of undoped and doped ZnS nanorods at different concentration. The undoped ZnS nanorods (figuure 3.2 a and b) shows a layer composed of seperately standing rod-like crystals with diameter about 80-100nm and length of 450nm. ZnS nanorods doped with 1% Mn have a very good morphology consisting of seperately standing crystals with average diameter of 110nm and length 700nm. It can be seen from the (figure c and d) that the distribution of the crystal is dense and perpendicular to the substrate.

Higher concentration content of Manganese at 3% leads to a remarkable change in its morpholgy resulting in the structured surfaces with large crystal (diameter = 280nm Length=500nm). However, (figures e and f) show from high magnification that the crystals noticed have tiny particles on their side facets with average dimensions of 30nm with some of those particles having sharp top edge.

Furthermore, on addition of more dopant concentration of manganese at 5%, the structure was shown to be closely packed in clusters of crystals with non-uniform dimensions and shape and majority of the crystals having sharp top edge (figuure 3.2 g and h).



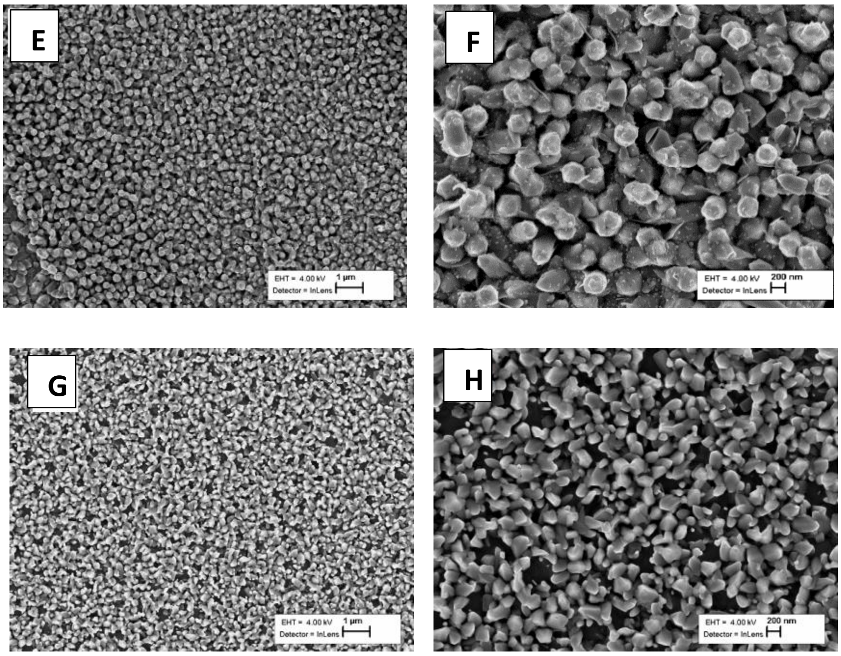


Figure 3.2 SEM images of undoped and doped ZnS nanorods at different Mn concentration.

(A) And (B) Undoped ZnS rods, bar 1μm (A) and 200 nm (B); **C) D)** ZnS:Mn 1at% rods, bar 1μm (C) and 200 nm (D); **E) F)** ZnS:Mn 3at% rods, bar 1μm (E) and 200 nm (F), **G) H)** ZnS:Mn 5at% rods, bar 1μm (G) and 200 nm (H).

3.2 Transmittance, reflectance and Eg of ZnS layers. UV-VIS study

Optical transmittance and reflectance spectra of Mn doped ZnS thin films and nanorods was carried out in the wavelenght range of 350nm – 850nm as shown in figure (3.3 and 3.4)

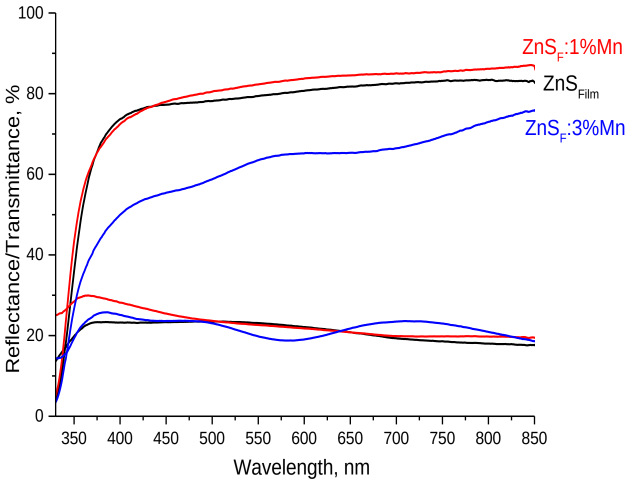


Figure 3.3: Optical transmittance and reflectance spectra of Mn doped ZnS thin films

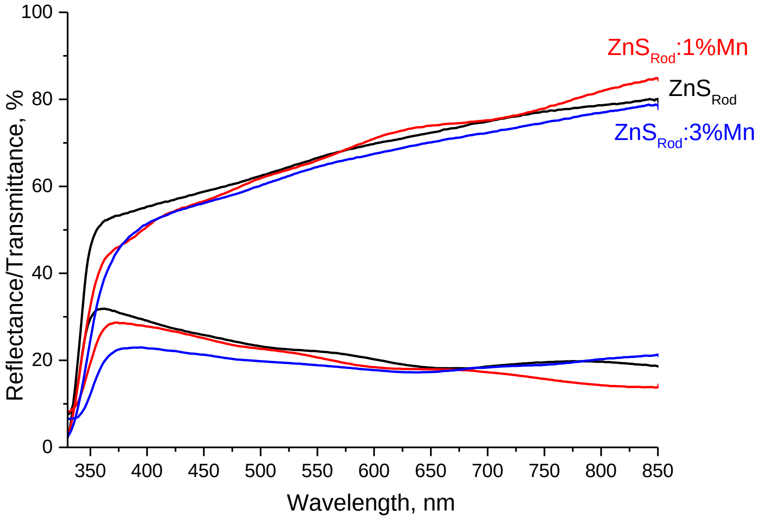


Figure 3.4: Optical transmittance and reflectance spectra of Mn doped ZnS rods

It was observed that a low optical transmittance of 50% at low wavelengths and a high optical transmittance of 75% was observed for all the nanorods layers. However, it was observed that undoped ZnS thin film sample has a transmittance of about 75-80% in the visible spectrum region. On addition of 3% concentration of dopant, the doped ZnS film had a low transmittance of 65%. It was observed that there was a significant difference in the transmittance of the film like structure for the doped and the undoped.

The change in the mean optical transmittance with Mn doping concentration was attributed to variation in the film thickness. In addition, an increase in the concentration of grains led to higher surface roughness[77] which decreases optical transmittance.

As shown in the SEM structures the surface of the samples with rod-like structures was overed with densely packed grains. The overall transmittance of the nanorod structure was seen to be lower when compared to the thin film.

The optical direct band gap (Eg) of the deposited film can be calculated by applying the expression stated below and summarized in the table

Table 3.1: Bandgap energy of ZnS thin film and narods at different dopants concentration.

Sample Name	Band gap (Eg)
ZnS_{rod}	3.67
ZnS_{rod} +1%	3.65
ZnS_{rod} +3%	3.59
ZnS_{rod} +5%	3.66
ZnS_{film}	3.7
ZnS_{film} +1%	3.66
ZnS_{film} +3%	3,64

$$\alpha hv=A(hv - Eg)^n$$

where α is the optical absorption coefficient, hv is the photon energy, A is a constant called critical absorption, n value varries depending on the band transition whether it is direct transition or indirect trnsition and Eg is the optical band gap. The energy bandgap (Eg) can be obtained by plotting $(\alpha hv)^2$ against the photon energy and extrapolating the liner part of the curve towards the photon axis.

Furthermore, independent of the dopant concentration and the morphology of the layer, it was observed from the total transmittance spectra that the material showed a direct band gap of 3.66Ev which is in good correspondence with those found in literature of ZnS prepared by chemical bath deposition. The transmittance of 80% is like those reported by[75] For the films grown by spray pyrolysis

3.3 Structural properties of ZnS layers. XRD study

The figures 3.5 and 3.6 shown below show the XRD patterns for thin films and nanostructured layers. The XRD measurement reveals that the nanocrystalline of ZnS has zinc blende having plane (100), (101) (102),(103), (110) and (112). Irrespective of the method of preparation and the dopant concentrations, it was observed that all the layers are highly structured c-axis oriented hexagonal ZnS [PDF 01-079-2204].

It was observed that the strongest ZnS peak appeared on the 2θ of 28.27° which corresponds to the (002) plane. However, other smaller peaks for ZnS were found at 2θ of 26.96° for plane (100), 30.58° for plane (101), 39.65° for plane (102), 47.51° for plane (110), 52.51° for plane (103) and 56.60° for plane (112).

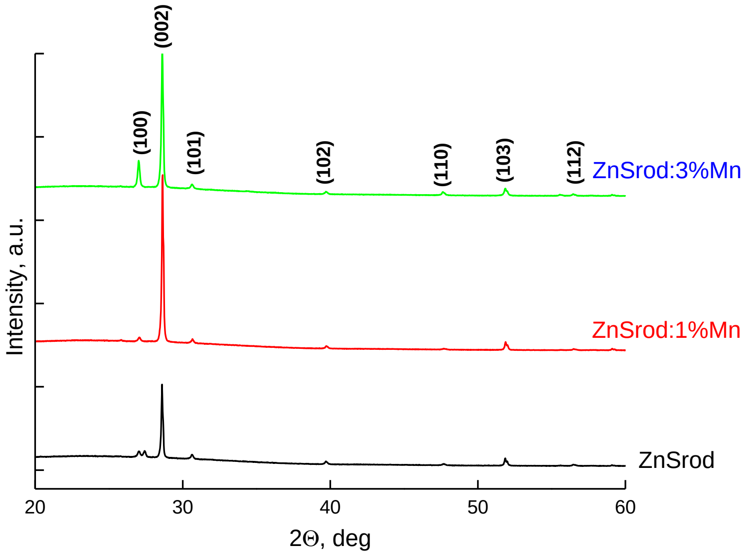


Figure 3.5: XRD patterns of ZnS and ZnS:Mn thin films

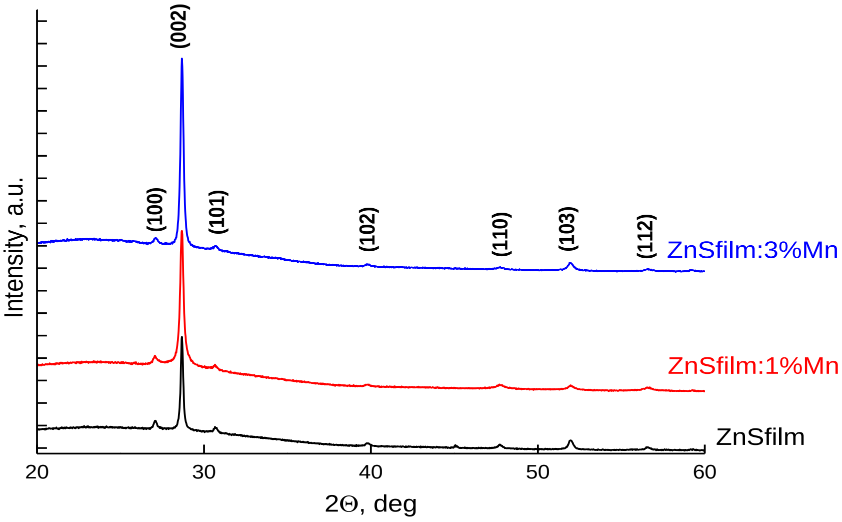


Figure 3.6: XRD patterns of ZnS and ZnS:Mn rods

Similarly, the intensity ratios measured for the ZnS nanorods and at different concentration of Mn dopants (ZnS_{rods}, ZnS_{rods}+ 1%, ZnS_{rods} +3%) were calculated to be 14, 33 and 36 respectively. While the intensity ratio of the ZnS thin film and at different concentration of Mn dopants ($ZnS_{film,}$ ZnS_{film} +1%, ZnS_{film} +3%) were calculated to 12, 20 and 36 respectively.

Therefore, this indicates that all the layers are highly c-axis oriented ZnS crystals when compared to the ZnS powder diffraction file [PDF 01-079-2204] where intensity ratio is approximately 0.4.

In conclusion, the intensity ratios of doped layers are higher than the un-doped material revealing that small addition of dopant accompanies the crystallization process which improves the crystallinity. It is also important to note that there was no reflection from other phases than ZnS as it was found in the XRD patterns independent of the dopant inclusion or morphology of the layer.

Table 3.2: Intensity ratio and crystalline sizes of ZnS films and nanorods

Sample name	I(002)/I(101)	Crystallite sizes, nm
ZnSrod	14	47
ZnSrod:1%	33	74
ZnSrod:3%	26	50
ZnSfilm	12	40
ZnSfilm:1%	20	43
ZnSfilm:3%	36	47

3.4 Photoluminescence (PL) study

The figure 3.7 shows the room temperature photoluminescence (PL) spectra of Mn doped ZnS thin film and nanostructured material under the excitation of 320nm. It was observed that there were no remarkable emission from the samples of the ZnS thin film.

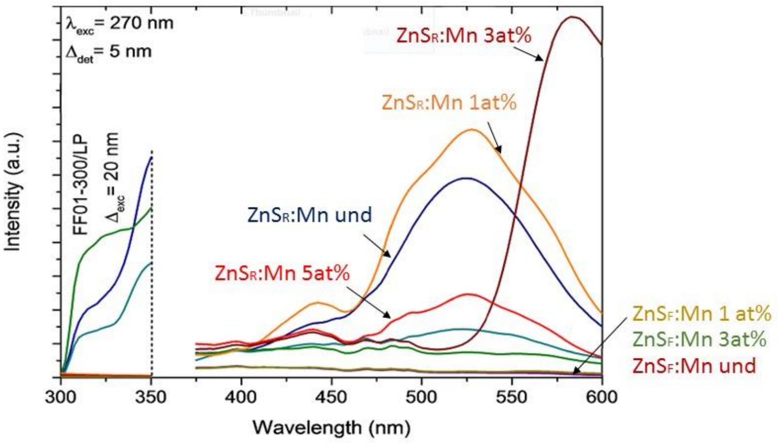


Figure 3.7: The room temperature photoluminescence (PL) spectra of Mn doped ZnS thin film and nanostructured material under the excitation of 320nm

However, the nanostructured ZnS layers showed different emissions in the visible spectrum range. This emissions were significantly governed by the presence of Mn dopant and the concentrations in the ZnS nanostructured layer. The PL spectrum of the un-doped ZnS and the 1% Mn doped ZnS layer shows a broad peak centered at 525nm (2.7Ev) under the excitation of 320nm which corresponds to the orange emission. This emission could be attributed to the donor-acceptor pair (DAP) to the valence band[78]. As it has been reported previously[79][78] the prominent orange emission in the un-doped and 1% Mn doped ZnS layer could be due to the DAP transitions. The emission could be attributed to the electron transfer from sulphur vacancies (Vs) to interstitial sulfur state[80] which appears mostly on the surface of the defects of the nanocrystals.

Dopants plays a vital role in the host (ZnS) this can effectively alter a materials microstructure, properties and functions. It can be observed that 3% Mn dopant in the ZnS shifts the enrgy transition, turning the primary orange emission (525nm) into an intense red emission at 580nm under an ultraviolet (UV) excitation. The intense red emission at 580nm can be attributed to the characeristics $^4T_1$-^6A_l transition of Mn^{2+} ions in the ZnS lattice[69].

Morever, the PL spectra as observed showed two distinct strong emission bands centered at 525nm and 580nm for the Mn doped nanostructured layers. The orange emission centered at 525nm was due to the characteristic luminescence of un-doped ZnS. In pure ZnS, the UV emission was due to band edge transition while the orange emission is associated with defect related transitions in the host matrix[81][78] while in the case of Mn doped ZnS the d electron of the Mn2+ ion state can act as luminescent centers because they strongly interact with the s.p electronic states of the hos matrix[78][79].

Sample name	Dopant, Mn^{2+}	Morphology	PL emission	PL emission intensities
$MnZnS_R$-0	0%	Rod	orange emission	I_{orange}/I_{NBE}=0.9
$MnZnS_R$-1	1%	Rod	orange emission	I_{orange}/I_{NBE}=5.3
$MnZnS_R$-3	3%	Rod	Intense red emission	I_{Red}/I_{NBE}=14.5
$MnZnS_R$-5	*5%*	Rod	small orange emission	I_{orange}/I_{NBE}=1.5
$MnZnS_F$-0	0%	Film	no emission	-
$MnZnS_F$-1	1%	Film	no emission	-
$MnZnS_F$-3	3%	Film	nearly no emission	-

The strong intense emission band centered at 580nm ($^4T_1$-^6A_l) observed, strongly suggests the successful incorporation of Mn^{2+} ions into the ZnS lattice. Further increase of the dopant concentration, the emission intensities decreases which could be attributed to concentration quenching effect. The strong intensity of Mn^{2+} ions at 580nm suggest the non-radiative energy transfer from ZnS to Mn^{2+} ions[82]. The obtained high PL emission highlights its importance in the application of Light emitting diodes and photonic devices.

4 CONCLUSIONS

In this thesis, chemical spray pyrolysis method of deposition was implemented and studied which is a very promising technique characterised for its simplicity, cost effective, better homogenity for deposition of Mn doped ZnS thin film and nanorods. The physical and chemical properties of the CSP deposited Mn doped ZnS thin films and nonostructured layers were investigated and the effect of varying the Mn dopant concentration on the properties of both ZnS thin film and nanostructured layers were duly studied. The conclusions drawn from this research work were solely based on what was observed experimentally and was supported to other results from available literature on Mn doped ZnS films and nanostructured layers prepared by other techniques.

1. Very uniform ZnS thin films and ZnS nanostructured layers composing of rod-like crystals undoped and doped with manganese have been prepared by spray pyrolysis method
2. The XRD analysis and data revealed that independent of the morphology and the deposition temperature, all the obtained ZnS layers are highly crystalline along the (002) oriented axis with wurtzite type ZnS.
3. According to UV-VIS study, ZnS thin film have high optical transparency of approximately 80% when compared to ZnS nanostructured layer with total transmittance around 65-70%. The energy band gasp obtained for all ZnS layers were close 3.66 eV which is close to the theoritical Eg value of ZnS monocrystal.
4. The PL study revealed that the layers with thin film morphology did not emit any radiation despite the dopant concentration. However, nanostructured ZnS layers showed an intense red emission after been doped with 3% Mn concentration. Also nanostructured ZnS layer also showed orange PL emission (un-doped, 1% Mn and 5% Mn doped samples)

Finally, it was observed that dopant concentration of 3% Manganese was optimal for the preparation of highly luminescent ZnS nanostructured sample with intense red emission at 595nm (I_{red}/I_{NBE}= 14.5). Therefore, CSP is proposed as a suitable method for the deposition of Mn doped ZnS nanostructured layer which can be used as an electroluminescence device.

Abstract

Mn doped ZnS thin films have been extensively reported in several fields of applications such as Solar cells, Electroluminescence devices, Flat panel displays. Deposition methods such as Chemical Bath deposition, Sol-gel technique, Sputtering amongst others have been used in deposition the ZnS thin film.

In this study, simple and cost-effective pneumatic spray pyrolysis set-up was used to obtain ZnS layers. Aqueous solution of $Zncl_2$ (Aldrich> 98.0% purity) and double recrystallized thiocarbamide (Merck > 98.0% purity) were used as precursor. To the best of our knowledge no publications on Mn doped ZnS nanorods by Chemical Spray Pyrolysis have been reported so far.

The aim of this thesis is to deposit and study the optical, structural, morphological properties of undoped and Mn doped ZnS thin films and nanostructured layer by chemical spray pyrolysis method.

According to SEM analysis very uniform ZnS films and ZnS nanostructured layer were formed. The XRD analysis and data revealed that independent of the morphology and the deposition temperature, all the obtained ZnS layers are highly crystalline along the (002) oriented axis with wurtzite type ZnS.

ZnS thin films (un-doped and 1% Mn doped) posess high optical transmittance approximately 80%. Films are more transparent when compared to ZnS nanostructured layers (65-70% optical transmittance). The energy band gaps obtained were close 3.66 eV independent of the morphology which is close to the theoritical Eg value for ZnS.

Finally, it was observed that dopant concentration of 3% Manganese was optimal for the preparation of highly luminescent ZnS nanostructured sample with intense red emission at 595nm (I_{red}/I_{NBE}= 14.5). Therefore, CSP is proposed as a suitable method for the deposition of Mn doped ZnS nanostructured layers which can be used as an electroluminescence device.

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