CHAPTER-II
REVIEW OF LITERATURE

2.1. INTRODUCTION

Thin films of a group II –VI semiconductor, ZnS having a large direct band gap near UV region [1]. It’s well known to be an important device material, which can be used for detector, emitter, and modulator in optoelectronics [2, 3] and blue light emitting laser diode [4]. Also, it can be applied to a transparent dielectric material [5, 6]. The excellent optical properties make them suitable for the fabrication of solar cells.

For this wide variety of usage, it has been prepared by various methods such as chemical bath deposition [CBD] [7, 8], Spray pyrolysis, [9, 10], solution growth technique. Among them, spray pyrolysis method is known to obtain quality thin films with less impurities and uniform thickness. In the following section a brief literature survey relating the methods of preparation of sulphides of Zinc are described.

2.1.1. ZnS FILMS BY AN IMPROVED METHOD FOR CBD.

It has been reported that ZnS thinfilms with stoichimetry uniform morphology and optical properties [11]. The nucleation, growth and morphology of the thin films can be greatly affected by the thermodynamic
conditions of the interfaces between the substrates and the reaction solution with modulating the activity energy of the formation of thin film nucleus. Avoiding the use of cadmium compounds is desirable from the viewpoint of environmental safety[12].

The Hexagonal structure for ZnS thin film by CBD Method [13] ZnS nucleation is more liable to occur due to the higher interfacial activity induced by the preheating of the substrates, and hence the formation of ZnS grains dominates the whole solution reaction. SEM images of ZnS thin films deposited by original method consists of big grains and a lot of pinholes on the surface. Built the samples synthesized by improved method has a uniform and compact morphology. Optical properties of the samples indicate that the films have a good homogeneity in the shape and size of the grains and lower defects density near the band edge [14]. This material has potential applications in electroluminescent devices and photovoltaic cells.

2.1.2. ZnS FILM BY ELECTROSTATIC INTERACTION

A self-assembly technique was extended by Decher et al. [15] from the pioneering work of Iler et al. [16]. Briefly, oppositely charged polyelectrolytes were
alternately adsorbed on to the ionic substrate based on electrostatic interaction as driving force [15, 16]. This technique was characterized by several advantages: [17] the preparative procedure is simple and no elaborate instrument is required; [18] a large variety of polyanions can be used [19] the thickness of individual layer can be controlled by many factors, [14] any charged surface is employable. It was proved by this technique was another alternative to assemble inorganic colloids [20, 21].

It has been reported that electrostatic interaction in the preparation of ZnS Powders [22] leads nano materials [50ml of 1.0x10^-3 mol/l Zn[NO₃]₂ and 2ml of 2.0x10^-3 mol/l AgNO₃ mixed solution was degassed with N₂ before use. After which 5 ml of 2.0x10^-3 mol / l HS CH₂ COOH was added, the pH was adjusted to 8.2 with 0.1 mol/l NaOH then 4.5 mil of 1.0x10^-5 mol/l Na₂S was added to the basic mixture with stirring, the pH of the resulting colloid was adjusted to 4.5 by drop wise addition of 0.01 mol/l HNO₃ along with flushing for 20 min by N₂.

2.1.3. ZnS FILM BY PLASMA ASSISTED MOCVD

Metal organic chemical vapour deposition has greatest potential in preparing thin films because of its merit in preparing at low temperature. Also the cations and anions which are set free in an excited state by
thermal decomposition from their corresponding organic vapour molecules can “snap together” by chemical bond forces to form a diamond lattice at temperatures so low that the forces exerted by random thermal impacts [which are the cause of vacancy formation] are still largely below the threshold.

Many workers [23-35] have reported the growth of II-IV films by MOCVD and found remarkable photoluminescent and electro luminescent properties, but efficient large area p-n. Electroluminescence in polycrystalline layers is still difficult to produce.

It has been reported that polycrystalline ZnS films [36] of micrometer thickness were grown on 50mm diameter soda lime glass substrates at 623°K at about $10^3$ Pa pressure by epitaxial pyrolysis of diethyl zinc and hydrogen sulphide gas mixtures without premature reaction using a simplified plasma assisted metal organic chemical vapour deposition apparatus employing only a gas ballast fore pump and a tesla spark tester. The reaction rate was strongly increased by a gas discharge. The films became strongly n type on doping with aluminum from added trimethyl aluminium vapour. The blue photoluminescence of the films was impaired by their
contamination with chromium from the stainless steel vessel and tubing employed.

2.1.4. ARSENIC ACTIVATED ZNS POWDER

It has been reported that arsenic activated ZnS shows that these emission band when exited by UV light [or] cathode ray [37].

The Zinc sulfide, together with 5% by weight of sodium chloride and an appropriate quantity of arsenic trisulfide, was fired in quartz test tubes which in turn were placed within larger quartz tubes through which either nitrogen or hydrogen was passed. The firing temperatures were usually in the neighborhood of 900°C. During the firing considerable quantities of arsenic were lost so that in every case the amount of arsenic remaining is the finished phosphor was much smaller than the quantity added to the unfired mix. It produce from the first firing was not always completely homogeneous in its luminescent properties. By regrinding the phosphor, and then refiring it for a short period of time, a fairly homogeneous product resulted. Microscopic examination of the phosphor under excitation with 3650 A° ultraviolet light indicated that the greater part of the grains had the same fluorescence color, although there were some having redder fluorescence and a still smaller number.
having a blue fluorescence. The finished phosphor was finally washed free of the flux with hot distilled water.

### 2.1.5. AEROSOL JET DEPOSITION OF ZnS THIN FILM

An Aerosol has been used to prepare ZnS thin films in an open atmosphere [38]. It has been reported that the aqueous precursor solution were prepared by dissolving the stoichiometric chemicals in $\text{H}_2\text{O}$ with the molar concentration of 0.01 to 0.05M. Optical glass slides were used as true substrates. The deposition temperature was verified from 250° to 500°C. The band gap values for ZnS film from reported value (3.66 eV Vs 3.31 eV). [Depending on the process conditions, heterogeneous and/ or homogeneous reactions can take place [39].] The advantages of using aerosols are relatively low equipment costs and wider options for precursor materials. Oxide thin films can be deposited in an open atmosphere without the need for sophisticated vacuum equipment. Unlike CVD process, precursor materials with high vapour pressures are not required in the aerosol deposition, especially for multicomponent materials, as long as the precursors can be dissolved in a solution. There are several ways to generate aerosol. For example, pressure atomization, both hydraulic and pneumatic, are capable of producing aerosol with droplet size of ca. 10 μm [40]. While
ultrasonic atomization can generate aerosol with droplet size <5 μm. However, both techniques require at large volume of carrier gas (normally >1 l/min) to deliver the aerosol onto the substrate during film deposition. The large flow of carrier gas results in turbulence near the substrate which will adversely affect the efficiency of deposition and the uniformity of the resultant films. Electrostatic spraying, on the other hand, has recently been used for film deposition [41]. Finer droplet size [2 μm] with monodispersed size distribution can be achieved under proper conditions [42]. Changing can cause the spraying droplets to drift apart, whereby avoid the coalescence. In addition, no carrier gas is needed to transport the aerosol. The electrostatically charged droplets can be attracted towards a grounded substrate by a columbic force. However, the rate of aerosol generating is very low (ca < 0.5 ml/min) because of the use of capillary and the process is difficult to scale up. Siefert [43] reported a corona spray pyrolysis technique which combined atomization with corona discharge to deposit thin films.

2.1.6. ZnS FILMS BY PHOTOCHEMICAL DEPOSITION

Photochemical deposition has been developed to deposit compound semiconductor thin films from an
aqueous solution and it is a very advantageous technique for solar cell fabrication [44-46].

ZnS thin films have been deposited on a glass substrate by photochemical depositors from an aqueous solution with varying pH [47].

In the XRD analysis, it is found that the ZnS film is formed in cubic phase. The films have been annealed in an inert atmosphere from 100°C to 500°C in steps of 100°C for about 45 min and XRD pattern was recorded. The intensity of the diffraction peaks increases with the annealing temperatures, which confirm the improvement of crystallinity of the films by annealing. The broad signal observed in the 2θ ranges from 16°C to 30°C is due to the glass substrate.

The surface morphology of the as-deposited and annealed films (100°C to 500°C) has been studied by the optical microscope. The surface morphology and crystallinity of the film increases enormously by annealing the film at high temperatures.

2.1.7. ZnS FILMS BY PULSED ECD.

The Electrochemical deposition ECD is very attractive and inexpensive method for obtaining ZnS thin films for various applications has been reported [48].
Electrochemical deposition (ECD) is the simplest of the chemical methods [49]. In this work the deposited ZnS, which is an n-type semiconductor with a wide direct band gap (3.7 eV at room temperature). ZnS is very suitable as a window layer in heterojunction photovoltaic solar cells, because the wide band gap will decrease the window absorption losses and improve the short circuit current of the cell [50]. ZnS can also be used for light emitting diodes in the blue ultraviolet region.

ZnS thin films are prepared by using pulsed electro-deposition. Although normal dc electro-deposition was used in the earlier trials [51-54], the use of pulsed electrode position improves the deposit quality. Pulsed electro-deposition gives wide range of parameters which can be changed independently to obtain high quality films, such as the pulse type, the pulse height, the on time, and the off time [49] the high instantaneous current density allows many atoms to arrive at the substrate surface.

2.1.8. MORPHOLOGY OF ZnS THIN FILMS

It has been reported that the films were prepared using different ZnS ratios (between 1:1 and 1:6) [55] and in different growth solutions: (A), zinc chloride and thiourea and (B) dehydrated zinc acetate and thiourea, both in distilled water.
By varying the Zn:S ratio in the films, the optical properties (absorption and photo-luminescence) show that different species are created during the film growth. This was deducted from the wide emission band appearing in the green region of the photoluminescence spectra, and from the change in band gap, which varies between 3.2 and 3.5 eV. Films formed from solution. (A) With a Zn:S ratio 1:3 or 1:4 show the best morphology and transmission. ZnS has a wider band gap than other conventional II-VI semiconductors utilized in various electronic and optical devices and can be expected to provide a useful window layer of solar cells which leads to an improvement in overall efficiency by decreasing absorption loss.

The spray pyrolysis technique offers interesting possibilities because it is a large area technique, with a relatively low cost, and a capacity to deposit optically smooth, uniform and homogeneous layers. However, this technique has not been used frequently to prepare materials of this kind. Several of the structural and optical characteristics of ZnS thin films have been reported. Nevertheless, their chemical properties have not been widely studied in order to reach the bulk and surface composition.
The optical properties of the films deposited on silica substrates were determined from transmission measurements in the 250-750nm range. The transmission spectra as deposited ZnS films for the two sets of solutions were used. Film thickness was approximately 900nm for solution A and approximately 1200nm for solution B. The results show that optical transmission was close to 80% for samples from solution A, and 70% for solution B, in the visible range.

Based on the optical transmittance obtained, the square of the absorption coefficient ($a^2$) is plotted as a function of the photon energy ($h\nu$). The films from solution A have a better defined steep optical absorption feature than those from solution B, indicating an improved homogeneity in the film and a lower density of defects near the band edge. Similarly, from solution A, the film with the 1:4 Zn:S ratio presents the sharpest and steepest absorption of photons with energies above the band gap. This indicates good stoichiometry.

The band gap is obtained by extrapolating the straight portion of the curve to the zero absorption coefficients. The band gap values are somewhat lower than the typical value of the bulk ZnS (~3.65eV). The shift in the band gap towards lower values is thought to be due
to the presence of oxygen appearing in the XPS analysis. Oxygen can combine with zinc to form ZnO, which has a lower energy gap of approximately 3.2eV.

The ZnS thin film prepared from solution A, with its (Zn:S) ratio equal to (1:4), was assigned in a previous work [56] as the best compromise in terms of the desired properties of ZnS film, the low intensity in the PL spectra may very well be an indication of such characteristics. The presence of non-radiative centers (impurities), or the absence of emissive centers in the defects region, are the two contributors possibly quenching the PL signal. Absorption analysis shows that this sample presents the best stoichiometry, as corroborated by the decrease in PL emission corresponding to the defects region in the spectra.

2.1.9. COPPER–DOPED SPRAYED ZnS THIN FILMS

In optoelectronics, it can be used as light-emitting diode in the blue to ultraviolet spectral region due to its wide band gap at room temperature (RT). Furthermore, ZnS films are used as light source for viewing screens and buffer layer for Cu (In, Ga) (S,Se)2 solar cells [57, 58]. There are many studies about different properties of electroluminescent devices based on ZnS:Cu structures [59-61].
ZnS is one of the well-known II-VI compound semiconductors suitable to be used as host matrix for large variety of dopants because of its wide direct energy band gap (≈3.7 eV). ZnS phosphors have a broadband luminescence from the near ultraviolet (UV) to the near infrared (IR). Therefore, it has been often used in the field of opto-electronic devices, such as for light emitting diodes and flat-panel displays [62]. Especially, when ZnS is doped with a small amount of metallic ions, it emits a light in the visible region which is characteristic of the incorporated impurity. Therefore, it forms a very important class of phosphors for the fabrication of thin film electroluminescent devices. For ZnS:Cu turned out to be a good CRT phosphor and is applied in, for example, color TV and oscilloscopes doped with metallic ions have been discussed extensively in the literature and the properties of such phosphors can be found in many references dealing with luminescence [99-101]. Vij studied the structural, electrical, optical and thermoluminescence (TL) properties of undoped and copper doped ZnS spray deposited thin films deposited by spray pyrolysis [66].

The XRD of undoped ZnS thin film is found to be polycrystalline with preferential orientation along the
(002) plane, the other secondary peaks visible are (220) and (103). All the peaks are associated with hexagonal ZnS and no major zinc or sulfide peaks are found. The lattice parameter $a$ is determined from Bragg's formula for the hexagonal systems and using the angles $2\theta=28.5^\circ$, $48.13^\circ$ and $51.85^\circ$. The lattice constant calculated from XRD trace is found to be 5.29Å. The small differences in the lattice constants of the ZnS thin films given here and in Ref [67] can be caused by the different ZnS thin film preparation techniques. The XRD shows a hexagonal structure with a preferred orientation along the (002) plane. No major difference is observed in X-ray patterns of the as-deposited and Cu doped samples. In doped films, the sharpness of the peak increases which in turn decreases the full width of the half maximum (FWHM).

2.1.10. GOLD ACTIVATED ZnS MATERIAL

The greenish fluorescence of gold activated zinc sulfide is well known [68-70] but the properties of the luminescent centers have been investigated only limitedly. It was generally assumed that they differed considerably in character from the centers of copper and silver in zinc sulfide. This was attributed to theoretical possibility of gold being incorporated in the trivalent as well as the monovalent state. By using trivalent metals as
co-activators instead of halogens, Kroger and Dikhoff [71] showed that the gold band was composed of two bands at 470 and 530µ, and that the latter became predominant by co-activation.

Copper [72] and Silver [73] are known to give two emission bands each in CdS gold produces three distinct bands. Two bands are found at 640µ and 800µ when gold alone is used as an activator. The third band appears as the only band at 1150µ when the gold activator is balanced by a trivalent co-activator such as aluminium. The same emission band is also found when indium is used instead of aluminum. On cooling to liquid nitrogen temperature it shows only a slight shift toward longer wave lengths and no other emission bands appear. When zinc is substituted for cadmium in the host lattice this band is displaced in a regular manner toward shorter wave lengths and appears at 530 µ is zinc sulfide. Thus the 1150µ co-activated gold emission is CdS corresponds very well to the emission bands of co-activated silver and copper at 730 and 1020µ, respectively.

The optical absorption of the co-activated gold center in CdS extends beyond the fundamental absorption edge and gives the powder a reddish brown body color. In
this respect, too, the co-activated gold centers resemble closely the co-activated centers of copper and silver. Thus gold activated in ZnS shown to produce three emission bands [74] in CdS at 640, 800 and 1150 μm. The 1150μm band in CdS is shown to correspond to the 530μm gold band in ZnS.

2.1.11 NANO ZnS DOPED WITH Mn BY CHEMICAL PRECIPITATION METHOD.

It has been reported that ZnS [75] is a very good luminescence material used in displays, sensors and lasers apart from applications in photocatalysis [76,77]. Nanodimensional ZnS is found to excellent optical and optroelectronic properties which differ greatly from the bulk ZnS [78-80]. ZnS doped with Mn is also an equally important electroluminescent material. The first reported luminescence properties of Mn-doped Nanocrystals prepared by a chemical process at room temperature[81].

Paramagnetic behaviour in ZnS:Mn nanosystems prepared by co-precipitation method[82]. There is not much work on ZnS:Mn, particularly, on magnetic properties but focused on the efficient luminescent properties. New spintronic materials exhibiting room temperature ferromagnetism has finding
Optical absorption studies reveal that the nano ZnS has a band gap of 3.9 eV blue shifted from bulk.

2.2. GROWTH OF ZnS FILM BY R.F. SPUTTERING:

ZnS thin films are usually prepared by electron beam evaporation, R.F. sputtering and chemical method to obtain reproducible properties. R.F. sputtering has merits on producing defect free thin film due to controlled R.F. field in the plasma of source material. It has been reported that the initial growth of ZnS thin film deposited by R.F. sputtering [84] on to Cadmium Stannate substrates are traced. Showing how a chemical interface is developed.

Four different plants were used employing chambers and targets of different sizes but all with target to substrate distances of 4-5 cm. Pressed powder targets containing 0.6 at 10% Mn where used substrates clipped to a holder were heated by twin quartz iodine lamps. The chamber was pumped to a base pressure of 3x 10⁻⁷ Torr before the introduction of the working gas, 90% Ar – 10% H₂. The substrate temperature was raised to 400°C and maintained for 30 min. While continuing to pump to 3 x
$10^{-7}$ Torr; it was then allowed to fall to 200°C before striking the plasma.

The target was pre-sputtered for 10-15min at a pressure of $5 \times 10^{-3}$ Torr and a flow rate of 10 standard cm$^3$ min$^{-1}$, using an R.F. power of 100W; For a film of normal device thickness, 0.75 μm, the deposition time was 120 min. corresponding to an overall deposition rate of about 60 Å min$^{-1}$.

The ZnS films were heated to 450° C in a stream of argon (atmospheric pressure, 21 min$^{-1}$) and immediately allowed to cool to obtain homogeneous film.

2.2.1. ULTRA THIN ZnS FILMS STUDY OF NANOSTRUCTURE

It has been reported that the fundamental band gap increases experimentally with a decrease in the size of the quantum confinement [85]

The effects of quantum confinement are observed when the confined size is of the order of a Bohr diameter. In semiconductors, in general, the exact radius is about 5-10nm whereas the radii of the excited states of the above mentioned impurities are quite small, of the order of 0.1 – 1nm. Quantum confinement will affect the properties of impurity atoms only when the size of the nanostructure is of the order of 1-3nm.
Some experimental work on the doped quantum dots has already been reported [86-90]. The electronic structure of ultra thin film of ZnS, both cleaned and passivated either by H or O. The thickness of the films is varied from 2.7 Å to 29.1Å

2.2.2. EFFECT OF ANNEALING ON OF ZnS THIN FILM

It has been reported that the crystalline structure of the films[91], concentration of dopant and the effect of Cu incorporation into the lattice of ZnS influence on the operating parameters and degradation stability of ACTFEL devices [ Alternating current thin film electro luminescent].

The XRD patterns of ZnS glass and ZnS / Ba TiO₃ structures deposited from three types of the targets revealed that ZnS films had only cubic crystal structure with preferred orientation in <111> direction. For two types of the ZnS:Cu, Cl ,glass films prepared from ZnS films by annealing in the ZnS-Cu, Cl powder with different ratio of Cu and Cl at 600°C a phase transformation and change in the texture were not observed. The XRD patterns of ZnS /Ba TiO₃ and ZnS Cu/BaTiO₃ films annealed in S₂ rich atmosphere with and without Ga vapors at 950° C did not show any changes in crystal structure through the annealing temperature was very close to the ZnS phase transformation temperature
of 1020°C. Strong phase transformation for ZnS:Cu, Cl/BaTiO₃ film was observed after the annealing in the ZnS:Cu, Cl powder at 800°C. After two steps of annealing the phase transformation for ZnS:Cu, Ga film was also observed. The fraction of grains, which were transformed, depends on the temperature of the second annealing in the S²-rich atmosphere with Ga vapors. After the second annealing at the higher temperature of 950°C the film has the hexagonal structure with preferred orientation in <100> direction almost in whole volume.

The improvement of electroluminescent [EL] characteristic of ZnS:Cu films were developed [92] and also reported that effective powder EL material must contain both sphalerite and wurtzite phases [93-94].

2.3. LUMINESCENCE OF UNDOPED ZnS THIN FILMS.

Zinc Sulphide is a commercially important II –VI semiconductor having a wide optical band gap, rendering it a very attractive material for optical application especially in nano crystalline form. The size dependent physical property in this form makes ZnS an active area of extensive research [95-105]. Optical and luminescent properties of nano crystalline ZnS prepared in the forms of thin film, powder and colloid using different synthesis techniques such as sputtering [95], co-evaporation [96],
wet chemical [97-99], sol gel [100,105] solid state [106], microwave irradiation [107,108], ultrasonic irradiation [109] or synthesis under high gravity environment[110] were studied in detail. Luminescence measurements were identified as one of the most important techniques to reveal the energy structure and surface states of these particles [97]. Localized trap states inside the band gap were studied [111] in detail to recognize the sub-band gap energy levels. It was found that the defect levels play an important role in determining the luminescence characteristics of the ZnS nanoparticles [112] and most of the nanoparticles exhibit broad and stokes shifted luminescence arising from the deep traps of the surface states [95,97]. Only clusters with good surface passivation may show high band edge luminescence [113]. Visible luminescence from ZnS was achieved mainly by adding appropriate dopants in it [114, 115].

Red emission from silica coated ZnS nanoparticles and their blue shifting with increasing annealing temperature [116] and or time were also observed by Zhu et al [117].

2.3.1. OPTICAL PROPERTIES OF ZnS THIN FILMS

Zinc Sulphide (ZnS) is a semiconductor with a large band gap, which becomes a highly efficient luminescent
material, when doped with manganese, copper or other ions [118]. ZnS thin films have also been widely studied due to their employment in many optoelectronic devices such as blue and green emitting laser diodes or electro luminescent displays.

It has been reported that the XRD investigation of ZnS films, as they were grown under standard conditions did not reveal any diffraction peak indicating that ZnS layer is disordered. The X-ray diffraction pattern of thermally treated ZnS/glass/ ZnS structures shows a well defined (002) reflection at $2\theta = 33^\circ$C, indicating a highly textured layer with (002) direction of the ZnS phase (wurtzite –type) with crystallite dimensions of about 14nm. The very broad diffraction at $2\theta = 26^\circ$, is caused by Nanosize Crystallites and the lattice strains [119] faults.

2.3.2. ELECTRONIC PROPERTIES OF ZnS THIN FILMS.

It has been reported that the films obtained by this method [120] were uncolored, smooth, homogeneous and adherent. X-ray diffraction for ZnS layers grown on glass and glass /SnO$_2$ at different time deposition has not revealed diffraction peaks, which is indicative of highly disordered materials. Result is in agreement with the findings of Dona and all [121]. However, X-ray diffraction
for samples formed by three successive layers deposited for 60 min every one by dipping in several reaction baths reveal a (111) diffraction peak corresponding to the cubic structure of β-ZnS phase [122].

Auger studies are useful in order to get information on the surface layer composition and a possible contribution of some parameters (heat treatment, time deposition, etc.,) to this composition. Auger studies are only used to obtain qualities information on the role of these parameters and to deduce the main features of the surface layer.

2.3.3. PHOTO ELECTRICAL PROPERTIES OF ZnS THIN FILMS.

ZnS is an n-type semiconductor with a wide direct band gap (3.7 eV at room temperature), and it is very suitable as a window layer in heterojunction photovoltaic solar cells deposited ZnS thin films on Sn-doped In$_2$O$_3$ coated glass substrate using pulsed electrodeposition from aqueous solutions containing Na$_2$S$_2$O$_3$ and ZnSO$_4$ with two different compositions, the first group grown from ZnSO$_4$ rich solution, and the second grown from Na$_2$S$_2$O$_3$ rich solution. Naglaa Fathy & Masaya Ichimura investigated electrical properties of the ZnS thin films and properties of contacts with different metals evaporated on the surfaces. Au and In contacts have Ohmic-like
characteristics to ZnS. Photoconductivity of the ZnS thin films by means of photo electrochemical (PEC) measurements. It has been reported that for both the groups of ZnS thin films, the as deposited film shows weak photosensitivity and after annealing at 300°C the photosensitivity improved [123].

2.3.4. PHOTOLUMINESENCE OF Mn DOPED ZnS THIN FILM.

Photo luminescent properties of manganese doped Zinc Sulphide films deposited at room temperature by spray Pyrolysis are reported [124] these films were deposited on pure glass substrates at atmospheric pressure using air as a carrier gas. All films were polycrystalline with a wurtzite [hexagonal] structure. The manganese doping was achieved by mixing MnCl$_3$ with the starting solution to deposit ZnS. The photoluminescence spectra were measured at room temperature as a function of the different deposition parameters and the Mn concentration. Besides the characteristic light emission associated with Mn impurities in a ZnS matrix, a peak associated with the self activated emission was also observed under certain deposition conditions [low substrate temperatures and or long deposition times]. The presence of chlorine impurities in the films is suggested to be associated with this emission.
The Mn luminescence presents a quenching effort with the Mn concentration. This quenching effect is similar to the reported on films deposited by other techniques. The light emission at this center has activation energy of 0.71 ± 0.05 eV with the deposition temperature. This energy is proposed to be related with the energy required by the Mn along to find a proper site during the growth process to form a Mn$^{2+}$ center.

2.3.5. ZnS THIN FILM ON BORO SILICATE SUBSTRATE

ZnS thin films have a vast potential for use in short wavelength optoelectronic device such as electroluminescent devices. It has been reported that the XRD pattern of film prepared by thermal decomposition method [125] leads to amorphous at a substrate temperature below 420°C. The crystallization occurred at temperature above 450°C.

The XRD pattern of the films prepared shows that heating at a temperature lower than about 420°C make the film amorphous. The crystallization occurred at a temperature above 450°C.

The XRD pattern of the film annealed at 550°C for 30mm in a nitrogen atmosphere after thermal decomposition of raw material at 400°C in air shows
number of peak of ZnO is observed, and the intense
diffraction pears of ZnS show the development of better
crystallinity. The XRD pattern suggests that the crystal
structure is hexagonal phase.

The optical energy gap of the ZnS thin film was
estimated from the optical absorption measurements for
crystalline films 130mm thick and amorphous films 85 mm
thick. The optical energy gaps $E_g$ of 3.45 eV for
crystalline ZnS [direct transition] and 3.5 eV , for
amorphous ZnS. The value of $E_g$ indicates that the
crystalline film is cubic [$E_g=3.5$ eV] and not hexagonal
[$E_g=3.7eV$]. The combination of this result with that
obtained from the XRD pattern strongly suggests that the
film is a mixture of hexagonal and cubic phases and that
the optical transmittance is dominated by the energy gap
of cubic phase, which is smaller than that of hexagonal
phase.

2.3.6. ZnS PHOSPHORS BY ION BOMBARDMENT

It has been reported that the trapping level of ZnS
phosphor changes due to positive ion bombardment [126]
a decay method which consisted of measuring the amount
of visible light emitted by the ZnS:Ag phosphor 5.0 msec
after excitation by weak ultraviolet, studies were made of
the changes in trap distribution on the surface of
phosphor crystals which previously had been bombarded by $\text{Ar}^+$, $\text{H}_2^+$, and $\text{O}_2^+$ ions. Interpretation of results was limited to first order kinetics.

The results showed that bombardment by ions caused an increase in the number of traps at the lowest trapping level, 0.28 eV deep, as well as the creation of new traps at depths slightly greater and slightly less than 0.28 eV. This effect was independent of the ion used for bombardment. In addition, ion bombardment caused new traps to appear at deeper trapping levels: 0.37 eV for $\text{Ar}^+$ ion bombardment, 0.38 eV for $\text{H}_2^+$ ion bombardment, and 0.39 eV for $\text{O}_2^+$ ion bombardment. For the latter, the peak in the difference curve is quite sharp and clearly located at 345°K, locating its depth at 0.39 eV. This corresponds to the next trapping level with increasing depth reported in the literature and thus may indicate that this trapping level is caused by the presence of oxygen in ZnS phosphors.

2.3.7. ELECTROLUMINESCENCE OF THULLIUM DOPED ZNS

The ac electroluminescence of thullium doped ZnS [127] embedded in boric acid matrix was investigated. The El emission spectra were recorded as a function of voltage, frequency, and temperature. The emission spectra at all temperatures show only strong sharp
emission lines which were assigned to transitions within the 4f shell of Tm$^{3+}$ ion. The emission spectra consisted of five groups of lines centered around 483 nm [$^1G_4 - ^3H_6$], 661.7 nm [$^1G_4 - ^3H_4$], 710.5 nm [$^3F_3 - ^3H_6$], 785 nm [$^1G_4 - ^3H_5$], 805.5 nm [$^3F_4 - ^3H_6$]. The emission intensities $I$ of different peaks were recorded as a function of the applied voltage $V$. The plot of natural logarithm of $I$ vs. $V^{-1/2}$ shows a straight line characteristic over many orders of emission intensity which indicates that the direct impact excitation mechanism is a dominant process. The experimental values of the 483 emission line [transition $^1G_4 - ^3H_5$] intensity $I$ vs. the applied voltage were reproduced theoretically on the basis of the direct impact excitation mechanism.

### 2.3.8. EMISSION SPECTRA OF ZnS MATERIAL

Zinc sulfide type phosphors are well known to display may different emission spectra depending on the phosphor matrix, the impurities, the conditions of excitation, etc. With the exceptions of edge emission, which ordinarily can be observed only at very low temperatures, and of the complex line spectra due to incorporated rare earths, all spectra consist of structureless broad bands of various widths and peak positions. Even a single activator e.g., copper in ZnS, may cause
several emission bands to appear simultaneously, often with considerable overlap, so that an analysis of such spectra is not simple. However, zinc sulfide type phosphors emitting only, or primarily, in a single emission band can be prepared, and these spectra are more accessible to a quantitative study.

Single emission bands of ZnS-type phosphors are represented [128] as Gaussian curves. The width [at half maximum amplitude] of the emission bands of almost all ZnS and [Zn, Cd] S phosphors activated by Cu or Ag and containing various co-activators is 0.36eV. The colours of single emission bands, and of superposition's of the two main bands in case of copper activation, are represented in colour diagrams. A red shift of the green copper emission band of ZnS phosphors with increasing high concentrations of activator and co-activator, as reported by Froehlich for ZnS:Cu, Al, has also been observed in [Zn, Cd] S phosphors and with many different co-activators.

2.3.9 OPTOELECTRONIC PROPERTIES OF ZnS NANOSTRUCTURED THIN FILM

It has been reported that ZnS films [129] were prepared on glass substrate by varying the deposition parameters and PH of the solution.
Zinc Sulphide (ZnS) is an important II-VI semiconductor material with a wide direct band gap $E_g = 3.68\text{eV (bulk)}$ [130]. ZnS has been studied due to its wide applications as phosphors and catalysts [131]. It is also applicable for a variety of other applications such as electro-luminescent devices, solar cells, and many other optoelectronic devices.

Zinc Sulphide (ZnS) is also currently used as a shell (or) capping layer in core / ZnS core / shell structure [132]. Thickness of the film was measured by gravimetric method using highly sensitive electronic microbalance I-V characteristic is recorded using Keithley electrometer and Hioki variable power supply. SEM images indicate that as-synthesized thin film consists of ZnS nanoparticle of spherical shape.

2.3.10. SPRAY PYROLYTICALLY PREPARED ZnS THIN FILMS

Spray Pyrolysis has been used in the glass industries for several decades for the purpose of decorative and abrasion resistance coating in the form of ferric and stannous oxide [133].

It has been reported that ZnS films [134] prepared from a mixture of 0.1M Zinc chloride and thiourea solution as a precursors solution for spraying. Dry, clean
compressed air at a flow rate of 15ml min$^{-1}$ was used. Deposition was carried out on fused silica and glass substrates [2.5x1.5x0.1cm$^3$] heated by a cylindrical stainless steel block furnace electrically controlled with an accuracy of ±2°C. The spray time [10-30 min] and substrate temperature [300-500°C] were varied while the other spray parameters were kept constant.

The studies referred the thickness of the films is found to decrease with increasing substrate temperature. The decrease in film thickness is attributed to an increase in the rate of re-evaporation initial constituent with increasing substrate temperature [135, 136]
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