



# A Comprehensive Review on Zinc Sulphide Thin Film by Chemical Bath Deposition Techniques

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## ABSTRACT

Nowadays, the synthesis of metal chalcogenides has received wide attention because of their suitability, simplicity and cost-effectiveness for large scale deposition by the selection of suitable chemical methods. Predominantly, thin-film technology has led to large-scale deposition techniques, using the variety of substrates such as insulators, semiconductors and metals. These methods are applicable at low temperatures, reducing the chances of oxidation and corrosion of the substrate. Among the various methods, Chemical Bath Deposition is highly attractive, owing to its advantages over conventional thin film deposition method. Moreover, it does not require high temperature as well as sophisticated and expensive equipment. Most researchers focused on the metal sulphides; they have a wide range of applications like sensors, modulators, dielectric filters, LEDs, efficient phosphors in flat panel display and buffer layers in the solar cells. A comprehensive review has been attempted in this work with necessary background theory for the thin film depositions. The Chemical Bath Deposition method has been reviewed in detail to obtain well-adherent and uniform zinc sulphide thin films. Bath parameters and structural, morphological, optical, and electrical properties were highlighted.

**Keywords:** Chemical bath deposition; Metal chalcogenides; Thin films; Zinc sulphide.

## 1. INTRODUCTION

Transition metals with group 16 elements are generally known as metal chalcogenide (Palve *et al.* 2019). Metal chalcogenides are wide band-gap semiconducting materials and metal chalcogenides thin films have novel applications in various fields such as superconducting films, anti-corrosive films, diamond films, surface modification, hard coatings, photoconductors, Infrared detectors, solar cells, solar selective coatings, optical imaging, magnetic films, optical mass memories, temperature control of satellites, wave-guide coatings, sensors, fabrication of large area photodiode arrays and catalysts. The usage of thin film-based solid state electronic devices rapidly increased as well as integrated chips for monolithic and hybrid microelectronics. Today, numerous techniques are available for the growth/deposition of metal sulphide thin films: vacuum evaporation, electro-deposition, electro-conversion, dip growth, spray pyrolysis (Hernández-Fenollosa *et al.* 2008), sputtering, successive ionic adsorption and reaction, chemical bath deposition method (Roy *et al.* 2006), sol-gel method, solution-gas interface technique, thermal oxidation, molecular beam epitaxy, etc. Among these methods, chemical vapour deposition (Lee *et al.* 2005), spray pyrolysis (Hernández-Fenollosa *et al.* 2008) and

vacuum evaporation methods require consciousness of high temperature for specific and useful deposition of chalcogenides thin films. On the other hand, some of the chemical solution methods need very low temperature for the successful deposition of chalcogenides thin films. Recently, numerous researcher reported that Chemical bath deposition (CBD) played a major role in deposition of thin films (Biswas *et al.* 2005; Roy *et al.* 2006; Prabahar *et al.* 2009a; Prabahar *et al.* 2009b; Kathirvel *et al.* 2011; Srikanth *et al.* 2011; Jeyachitra *et al.* 2014; Gallanti *et al.* 2016), owing to its easily attainable temperature, simplicity, convenience for large scale deposition and cost-effectiveness.

Many researchers established and reported a versatile and environmental friendly solution approach for the fabrication of a variety of metal sulphide thin films because of the easy availability and low cost of the starting materials. Metal hydroxides, metal oxides, metal chlorides, metal acetylacetonates and metal acetates were used as the starting materials (Tian *et al.* 2014). They dissolved in thioglycolic acid and ethanalamine, forming many types of metal organic precursor solutions.

This work provides a comprehensive review of recent researches towards ZnS thin film preparation using CBD technique. Light has been thrown upon the

major properties of ZnS film, the benefits of employing CBD method for ZnS thin film preparation and observed variations in its properties like film growth rate, crystalline nature, surface morphology and optical spectra.

## 2. BASIC PROPERTIES OF ZnS

Among all metal chalcogenides, ZnS is an important semiconductor compound of II–VI group with excellent physical properties and direct wide band-gap energy of 3.7 eV at 300 K; it has attracted great attention (Salim et al. 2012; Palve et al. 2019). The two basic types are: cubic phase (sphalerite) and hexagonal phase (wurtzite). ZnS thin film act as a “buffer” and “window” layer in hetero-junction solar cells. It has numerous applications in optoelectronics (Xiong et al. 2004; Daniels et al. 2006), solar cells, lasers (Biswas et al. 2008) ultraviolet light emitting diodes (Luo et al. 2008), phosphor host (Wang et al. 2000), optical sensors (Biswas et al. 2005) and luminescence (Zhu et al. 2003; Goswami et al. 2007); because of high refractive index (2.35), it is used in anti-reflection and coating (Liu et al. 2009).

**Table 1. Some important parameters and their effects on various properties of ZnS thin films by CBD method (Sinha et al. 2018)**

S. No.	Name of the parameter	Properties of ZnS films
1.	Zinc salt and [Zn]/[S] ratio	Crystalline behaviour, morphology, film growth
2.	Complexing agent	Crystalline behaviour, morphology, optical transmittance, thickness and roughness
3.	Stirring speed	Thickness and roughness, film growth rate
4.	pH value	Crystalline behaviour, optical transmittance, band-gap, film growth rate
5.	Deposition temperature	Thickness, optical transmittance, band-gap, pH of solution, morphology
6.	Deposition time	Crystalline behaviour, thickness, band-gap
7.	Humidity	Crystalline behaviour, morphology, optical transmittance
8.	Annealing	Crystalline behaviour, morphology, optical transmittance

**Table 2. Properties of ZnS (Navneet et al. 2016)**

Name of property	Name of the parameter	Parameter value
Chemical Properties	Chemical formula	ZnS
	Molecular weight	97.46 g/mol
	Group	Zinc-12 Sulphur-16
	Crystal Structure	Cubic
	Lattice Constant	5.4093 Å
Electric Properties	Dielectric Constant	8.9
	Electronic configuration	Zinc:[Ar] 3d <sup>10</sup> 4s <sup>2</sup> Sulphur:[Ne] 3s <sup>2</sup> 3p <sup>4</sup>
	Band Gap	3.54 eV
	Electron Mobility	180 cm <sup>2</sup> /Vs
	Hole Mobility	5 cm <sup>2</sup> /Vs
Thermal Properties	Heat of Fusion	390 J/g
	Heat of Formation	477 KJ/mol
	Thermal coefficient of Expansion	6.36 µm/m °C
	Thermal Conductivity	25.1 W/mK
	Specific heat capacity	0.472 J/g °C
Mechanical Properties	Density	4.079 g/cm <sup>3</sup>
	Boiling Point	1185 °C
	Melting Point	1850 °C
	Flexural Strength	103 MPa
	Modulus of Elasticity	75 GPa
Optical Properties	Poisson’s Ratio	0.27
	Refractive Index	2.356
Physical Properties	Solubility in water	Insoluble
	Appearance	Grey-white to yellow powder
	Odour	Sulphurous odour

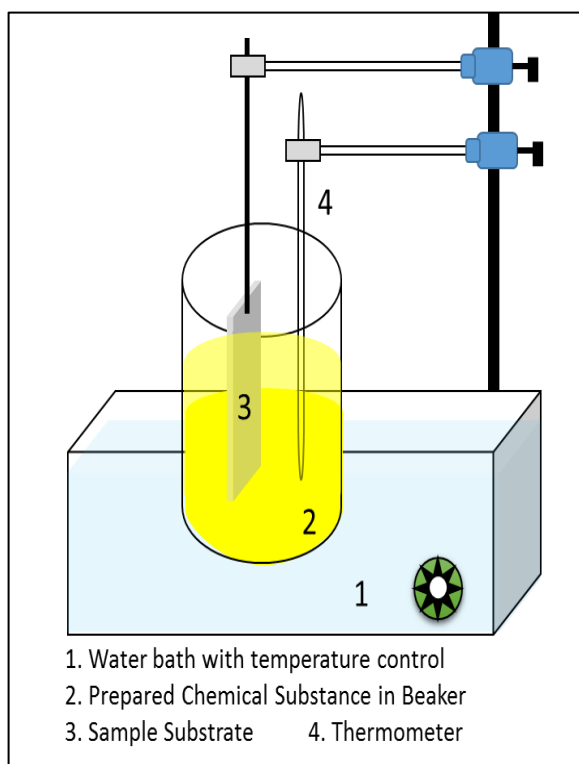
### 3. PREPARATION TECHNIQUE: CHEMICAL BATH DEPOSITION (CBD) METHOD

This review is confined to the deposition of ZnS thin films mainly by CBD technique. A collection of various preparation procedures and deposition of ZnS thin film, based on CBD technique in recent days are given in Table 3.

Moreover, this method gives stable, adherent, uniform and hard films with good reproducibility by a relatively simple process, only it requires a small and portable apparatus (fig.1) setup. And during deposition, for the shaking of sample compartment, closed and isolated apparatus is more desirable to become an ,

**Table 3. Details on preparative conditions and properties of ZnS thin films (CBD method)**

Bath Composition	pH value	Prepared film thickness (nm)	Deposition		Selected Substrate	Remarks	Reference
			Temp. (°C)	Time			
ZnSO <sub>4</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH, N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	-	-	70	2 h	Soda-lime glass	-	(Wei et al. 2013)
ZnSO <sub>4</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	-	-	80	40 min	Microscopic glass	-	(Mukhamale et al. 2013)
ZnSO <sub>4</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH	10	-	80	1 h	Glass	-	(Al-khayatt et al. 2014)
ZnSO <sub>4</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH	-	-	80	2 h	Glass	-	(Zhou et al. 2009)
ZnSO <sub>4</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	2, 3, 4	759.7	80	100 min	Glass	-	(Min et al. 2011)
ZnCl <sub>2</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH, N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	10-11.5	600 to 320	90	3 h	Glass	Transmittance=70% and E <sub>g</sub> =3.78 to E <sub>g</sub> =3.67 eV	(Ben Nasr et al. 2006)
ZnCl <sub>2</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH, N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	11.5	-	90	3 h	Glass	-	(Eid et al. 2010)
ZnCl <sub>2</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH, N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	11.5	-	90	1-3 h	Glass	-	(Salim et al. 2012)
Zn(CH <sub>3</sub> COO) <sub>2</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH, N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	8-9	84-85	70	24 h	Glass	-	(Sarma et al. 2015)
Zn(CH <sub>3</sub> COO) <sub>2</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>8</sub> .2H <sub>2</sub> O	-	60	80	1 h	Glass	E <sub>g</sub> =3.75 eV	(Mallick et al. 2019)
Zn(CH <sub>3</sub> COO) <sub>2</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH	10.5	1300	30	3 days	Glass	E <sub>g</sub> =3.851 eV	(Mukherjee et al. 2015)
ZnSO <sub>4</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH	-	70, 89, 118, 160 nm	65, 70, 75, 80	20, 30, 40, 50 min	Glass	E <sub>g</sub> =4.05 – 3.97 eV ZnS NPs radius = 1.9, 2.3, 2.45, 2.51 nm	(Zein et al. 2019)
ZnSO <sub>4</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH, N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	-	-	80	10–60 min	Silicon	Substrate tilting angle = 30 - 60°	(Gangopadhyay et al. 2004)
Zn(CH <sub>3</sub> COO) <sub>2</sub> , CS(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH, N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	10	220 nm	80	4 h	Glass	E <sub>g</sub> = 3.53 eV	(Cheng et al. 2003)
ZnSO <sub>4</sub> , SC(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH, N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	-	570 nm	90	1 h	Glass	-	(Kamoun Allouche et al. 2010)
ZnCl <sub>2</sub> , SC(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH, N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	-	700 nm		2 h			



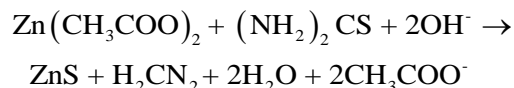
**Fig. 1: Schematic diagram of CBD Method**

Deposition of ZnS thin film by CBD method refers to the main reaction between  $Zn^{2+}$  and  $S^{2-}$  ions. The precursors of zinc solution are commonly zinc acetate [ $Zn(CH_3COO)_2$ ], zinc sulphate ( $ZnSO_4$ ), or zinc chloride ( $ZnCl_2$ ). Most preferably, thiourea [ $CS(NH_2)_2$ ] is used as sulphur ions reagent. Both are mixed together and hence it called as one-pot preparation method. In addition, to maintain a constant pH value, one or more complexing agents such as ammonia solution ( $NH_4OH$ ), tri-sodium citrate (TSC) ( $Na_3C_6H_5O_7$ ), triethanolamine (TEA) ( $C_6H_{15}NO_3$ ),  $Na_2$ -EDTA ( $Na_2C_{10}H_{16}N_2O_8$ ) or hydrazine hydrate (HH) ( $N_2H_4$ ) are used, giving uniformity to the as-prepared ZnS thin films, even though, the purity of chemicals is another essential factor which will have a significant effect on the results.

The main feature of CBD technique is that the reaction starts only when the solution with the substrate dipped inside the solution, placed in a bath is maintained within a suitable temperature range depending on the demand of material formation. During deposition process, at temperatures below the room temperature, it is very difficult to deposit a ZnS thin film by CBD method. Alternatively, a water bath is used for deposition in the CBD process. Hence, in CBD equipment, a container is filled with heated water and then sample is placed in the water bath at a constant temperature over a certain period of time. Therefore, the CBD method can control the structural and optical properties of the prepared films by changing the bath temperature, pH value of the prepared solution, stirring speed, concentration of reagents, complexing agent, deposition time and annealing conditions.

#### 4. RESULTS AND DISCUSSION - REVIEW OF LITERATURE

Lădar *et al.* 2007 prepared and reported for monolayer and multilayer of ZnS thin films by CBD techniques in the alkaline medium using zinc acetate and thiourea. They employed the sodium citrate as a complexing agent for the preparation of ZnS thin films and reaction involved in the analysis was as given below:



They investigated the influence of the sodium citrate complexing agent on the thickness of ZnS films at constant zinc acetate and thiourea concentration. In addition, the concentration of complexing agent influences the film quality and growth rate. Hence, the thickness of ZnS films grown onto glass substrates is dependent on deposition time. For the typical CBD techniques, when the deposition time is double, the thickness does not increase twice. Because, the initial growing rate decreases with time and thickness tends to level off. Moreover; the total deposition time is the same for the monolayer ZnS thin films having smaller thickness as that of multilayer ZnS thin films. They also reported the XRD, photoluminescence of prepared ZnS films. They concluded that further investigations are needed in order to explain the observed properties and to obtain more optimum luminescent ZnS layers.

Gallanti *et al.* 2016 developed a new bath technique for the preparation of photo-chemical deposition of ZnS thin film on CIGSe substrate for solar cell applications. They studied the effect of the deposition time on the thickness of the deposited films and reported the growth of the films with three stages, *viz.* i) an induction time at the beginning of the process where no observable growth occurs, ii) an approximately linear region and iii) a termination step where no further growth occurs. They studied the morphology of as-prepared ZnS films deposited on a CIGSe substrate in 25 minutes and then obtained the homogeneous ZnS film with a thickness of 20 nm. They also studied the optoelectronic properties of the prepared solar cells with the deposition time varied between 10 and 50 minutes. They optimized the efficiency for deposition time rate between 25 and 30 minutes. Therefore, they reported that the method has a higher efficiency for the solar cell preparation; moreover, the as-prepared solution could be re-used four times consecutively, which is a great main advantage. They mainly achieved the better fill factor and short-current density. Finally, they concluded that the ZnS buffer layer deposition on CIGSe substrate has no need to heat the prepared solution and no need to prevent precipitation of various species using complexing agent and it is easy to implement for low reactant concentrations.

Ben Nasr *et al.* 2006 reported the pH contribution for the structure and growth of deposited zinc sulphide thin films on glass substrates by CBD technique. They analysed and reported thin films using the XRD, SEM and optical studies. The researchers analysed by changing the pH in the chemical bath which induced the layer of crystallinity of the ZnS thin films and they found the best pH value as 10. In the XRD analysis, they observed the two main peaks at the diffraction angles of 28.8° and 47.7° which were assigned to both cubic and hexagonal phases of the planes (111)<sup>cub</sup> / (002)<sup>hex</sup> and (220)<sup>cub</sup> / (110)<sup>hex</sup>. Moreover, the other characteristic peaks of (100), (101), (102), (103) and (200) planes of hexagonal were not present in all spectra. Hence, the prepared ZnS films were having cubic structure (h-ZnS), irrespective of the tested pH values. In the optical transmission analysis, the band gap energy was obtained and it varied from 3.67 to 3.88 eV. Particularly, the band gap energy was 3.78 eV for the crystalline structure of film at pH=10 in chemical bath. Also, it closely agrees with the ZnS thin films obtained by CBD technique. Moreover, these studies have shown that the pH contributes for the growth and the structure of deposited thin films. They particularly observed and found the best crystallinity of the ZnS thin films at a pH of 10 and then analysed.

Oliva *et al.* 2010 investigated single-phase ZnS films prepared by CBD method and the prepared films were transparent, pale-white in colour and had good adherence. Under light reflection, these films appeared in golden colour. They studied the structural, morphology and optical band gap energy. In this method higher KOH concentrations were used for CdS films deposition by changing the pH of the bath (Cd salt by a Zn salt). The chemical bath's optimal pH was 11.5 with the KOH reagent. The pH value in the chemical bath was a key factor, because concentrations below 1.0 M do not produce conditions for ZnS films deposition. This effect was also reported by Antony et al. [10] for a chemical bath with Zn(NO<sub>3</sub>)<sub>2</sub> and NH<sub>4</sub>OH as the salt reagent and the source of OH radicals, respectively. Annealing treatments at 200 °C and 400 °C on ZnS films were done in order to study their effects. Small changes were obtained on the optical properties of ZnS films with the annealing treatment, as demonstrated by the reduction of the band gap energy value for higher annealing temperatures. However, they found that the annealing process did not produce important changes on the crystalline structure of the films. The optical direct band gap energy of ZnS films was found by spectrophotometry technique and calculated from the absorption spectra through the relation:

$$\alpha^2(h\nu) = A^2(h\nu - E_g)$$

where  $\alpha$  is the optical absorption co-efficient,  $E_g$  is the energy of the incident light,  $h$  is the Planck's constant and  $\nu$  is the light frequency. By plotting  $\alpha^2$  vs  $h\nu$ , the

bandgap energy of the initial absorption edge line when  $\alpha=0$ . They calculated the ZnS optical transmittance between 70-80% in the visible light spectrum range. The deposited films change the band gap energy values from 3.70 eV to 3.45 eV for as-grown and for annealed films, respectively. The films' stoichiometry ratio (Zn:S) was close to 1.0:1.2 both for punctual and zone analysis.

Liu *et al.* 2012 developed the uniform ZnS thin film composed of nano-crystallines with CIGS solar cell deposited by CBD technique. The deposition morphology, growth rate, structure and optical properties of ZnS thin films within 100 nm thickness was investigated by a Field emission scanning electron microscope (FE-SEM), Transmission electron microscope (TEM), X-ray diffractometer (XRD), Atomic force microscope (AFM) and Ultraviolet visible light spectroscope (UV/Vis.). FESEM morphologies / images showed the impact of even and dense ZnS films deposited on soda lime glass used to high concentration ratio of thiourea. The ZnS thin film grow rate was 0.88 nm/min. The TEM diffraction patterns and XRD patterns revealed that ZnS films were nano-crystallines, of which FCC (111) phase dominated over others. The transmittance and band gap of ZnS thin films are over 80% in the range of 300-800 nm and 3.83-3.85 eV, respectively. The ZnS/CIGS/FTO structure and Al:ZnO/ZnO/ZnS structure in CIGS solar cell formed by wet processes showed good hetero-interfaces.

Zhou *et al.* 2009 reported the structural characterization of zinc sulphide (ZnS) thin films deposition by CBD on glass substrates. The solution concentration and annealing condition played a very important role on homogeneity, crystal and transmissivity of ZnS thin films. Spectrophotometer, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS) and digital four-point probe resistance measurement were used to characterize their properties and composition.

- The trend of the transmissivity was upward within the range of 300–600 nm wavelength of incident light; then it would be stable above 600 nm. Transmissivity of the ZnS films were more than 80%. Transmissivity of the ZnS films without annealing was greater than that at 200 °C and higher than that at 300 °C, for 1 h. As concentration of ZnSO<sub>4</sub> was lower between 0.020 and 0.030 mol/L, transmissivity of the ZnS film was higher.
- The films' structure was basically amorphous or microcrystalline; after annealing, the main diffraction peaks due to ZnS (III) planes were corresponding to sphalerite-type ZnS.
- The particles of the films surface were almost spherical and homogeneous, and there were some white spots.

- The resistance of the ZnS films without annealing reduced with the increasing concentration of ZnSO<sub>4</sub>.

Bian *et al.* 2008 have adopted CBD method to form ZnS thin films which were deposited on glass substrates at 80–82 °C temperature. When the film deposition is in process, they added the complexing agents namely, ammonia or ammonia-hydrazine hydrate; they influenced the quality of as-deposited films and the substrate was in vibration condition. They reported the role of hydrazine hydrate for the growth of ZnS thin films. It has improved the homogeneity, specularity and the growth rate of films. Also, the addition of hydrazine hydrate led to a few white grains of film. Moreover, vibration of substrate reduced the formation of pinholes and improved the uniformity of the films. The physical and optical properties of as-prepared films were characterized using XRD, SEM and UV-Vis. spectroscopy. From the XRD analysis, ammonia-hydrazine was found to be a better complexing agent compared with other agents and it has shown a hexagonal crystallization structure with (008) diffraction peak. The prepared ZnS films exhibited good optical properties with high transmittance (~80%) in the visible region and the band gap value was estimated in the range of 3.5–3.70 eV.

In 2017, González-Chan *et al.* 2017 have analysed the physico-chemical process of zinc sulphide (ZnS) thin films by chemical bath deposition (CBD). They have investigated the performance of the ZnS solution contained zinc chloride, potassium hydroxide, ammonium nitrate and thiourea. These chemical compound permitted the physico-chemical analysis of ZnS thin film deposition. Then the solubility curves and species distribution diagrams have been utilized to obtain the best conditions for ZnS thin film deposition and the various concentration of the bath temperatures in the range of 25 to 90 °C at different deposition time rate (González-Panzo *et al.* 2014). The results indicated the necessity to adjust the thiourea solution concentration according to the bath temperature; it helps the formation of ZnS thin film deposition in order to contribute with enough amounts of sulphur ions in the bath solution. They also reported the thiourea concentrations with respect to the bath temperatures like 2.25 M (25 °C), 1.25 M (40 °C), 0.6 M (60 °C) and 0.2 M (90 °C). The impact of thiourea at low concentration, in the formation of ZnS thin films was the poor quality obtained due to the excess of zinc hydroxi-complexes. Moreover, the detailed relative properties such as optical, stoichiometric and morphological have been reported at different concentration of thiourea.

**Table 4. Comparison of samples prepared at different temperatures**

Sample preparation temp.	Thiourea concentration	Zn/S ratio	Bandgap energy
25 °C	2.25 M	0.96	3.72 eV
40 °C	1.25 M	0.90	3.69 eV
60 °C	0.60 M	1.11	3.66 eV
90 °C	0.20 M	1.15	3.65 eV

The ratio of Zn/S close to 1, homogeneous surfaces with similar grains size, optical transmission between 80 and 85%, and bandgap energy close to the bulk value of 3.72 eV were obtained for all the thin films deposited with the proper conditions of thiourea at different concentration with four different temperatures *viz.* as 25 °C, 40 °C, 60 °C and 90 °C with optimized deposition time rate. Thus, as-deposited ZnS thin films have good quality at the wide range of bath temperatures, but adequate chemical conditions are required. Finally, they reported that the solubility curves and species distribution diagrams proved the best physico-chemical conditions.

Patel *et al.* 2018; Khatri *et al.* 2018 investigated the properties of ZnS thin films deposited on glass substrate by using CBD technique at 70 °C bath temperature with the effect of post annealing at 350°C temperature for 1 h. XRD confirmed hexagonal phase for both as-grown and annealed ZnS thin films. The average crystallite size was 331 nm for as-grown and 643 nm for annealed thin films using Debye-Scherrer equation. TGA analysis has shown that 350 °C is suitable for annealing process of ZnS thin film and optical measurement has shown that the transmittance of film was in the range of 5-35% in the visible region. Also, the films have direct bandgap, which increased from 3.80 to 4.18 eV with annealing at 350 °C for 1 h. Finally, they reported that the materials can be potentially used in electroluminescence devices and photovoltaic cells. For doping on ZnS, as-prepared thin films have been developed for huge number of applications. Doped ZnS may have either cubic or hexagonal structure as Zinc Blende (ZB) or Wurt Zite (WZ), which depends on its synthesis conditions like sample prepared temperature, precursor type and concentration. For Co, Cu, Fe and Sn, doped in ZnS thin film, properties have been given in Table 5 (Shakil *et al.* 2018).

**Table 5. Comparison of Cu, Sn, Co and Fe doping in ZnS for some properties (Mukherjee et al. 2017; Shakil et al. 2018)**

Property	Co-doped	Cu-doped	Fe-doped	Sn-doped
Atomic No.	27	29	26	50
Band Gap (eV)	3.6	3.47	3.94	3.90
Crystallite size (nm)	12	11	10.38	12
Structure	Zincblende (ZB)		Wurtzite(WZ)	
Structure type	Cubic		Hexagonal	

From Table 5, it can be inferred that due to change of doping element, the energy band gap, structure as well as crystallite size may vary with respect to the selection dopant; also, it may vary with the concentration of doping element also.

### 5. CHARACTERIZATION OF THE FILMS - MEASUREMENTS

Film thickness are measured with different methods such as surface profiler and gravimetric method. Generally, film are deposited on only one side of the substrate and thickness is calculated by (Oriaku et al. 2008),

$$t = \frac{m}{\rho A}$$

where, m is the mass of the deposited film measured with a very sensitive electronic balance, A is the area and ρ is the density of the film obtained from crystallographic data.

#### 5.1 X-ray Diffraction (XRD)

Grain size of the crystalline structure of the prepared film is obtained by substituting values of Full Wave Half Maximum (FWHM) in the well-known Debye-Scherrer formula (Jones et al. 1938):

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where, D is crystalline size, K is the Scherrer constant (= 0.94), λ is the wavelength (=1.54059Å) of the X-ray source used, β is the full width at half maximum intensity in radians and θ is the angle of diffraction at the peak or Bragg's angle.

#### 5.2 Lattice Constant

The lattice constant for both doped and un-doped thin films are determined from the relation,

$$a = d\sqrt{(h^2 + k^2 + l^2)}$$

where, d is the spacing between the crystal planes. The lattice parameter a, for ZnS structure was obtained from the d interplanar spacing of different peaks by the equation,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

The precise value of lattice parameter a can be estimated from Nelson-Riley function (Long et al. 2008),

$$F(\theta) = \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}$$

where, θ is the Bragg's angle.

### 5.3 Optical Characterizations

#### 5.3.1. Absorbance of the Film

The spectrophotometer used to obtain the optical information for the absorbance of the film. The absorbance α is obtained from the relation:

$$\alpha = \frac{2.30A}{t}$$

Where, t is the thickness of the deposited film, A is the absorbance and reflectance is neglected for highly transmitting film.

#### 5.3.2. Bandgap Estimation

The bandgap of materials is a very important parameter that determines the application of the films. It is evaluated using the formula (Ezekoye et al. 2005),

$$\alpha = \left(\frac{A}{hv}\right)(hv - E_g)^n$$

where, n=1/2 for allowed direct bandgap transition materials. The plot of α<sup>2</sup> or (αhv)<sup>2</sup> versus photon energy hv (in eV) with extrapolation of the straight-line portion of the curve to zero shows that the absorption coefficient (hv axis) gives the direct bandgap energy of materials. n=2 shows the allowed indirect bandgap transition. The plot of α<sup>1/2</sup> or (αhv)<sup>1/2</sup> versus photon energy hv (in eV) with extrapolation of the straight-line portion of the curve to zero shows that the absorption coefficient (hv axis) gives the indirect bandgap energy of materials. n=2/3 indicates that forbidden direct transition and n=3, the forbidden indirect transition (Ezekoye et al. 2005).

### 5.4 Optical Measurement

From UV-Vis. region spectrometer operated in the wavelength range of 400-700 nm, the optical absorption coefficient, α, was calculated from the values

of Tand Rusing, using the following relation (Ezekoye et al. 2005),

$$\alpha = \frac{1}{t} \ln \left[ \left( \frac{(1-R)^2}{2T} + \frac{(1-R)^4}{4T^2} + R^2 \right)^{1/2} \right]$$

where,  $t$  is the film thickness and  $k$  is the extinction coefficient  $\left( k = \frac{\alpha \lambda}{4\pi} \right)$ . The refractive index,  $n$ , can be calculated using the relation:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

From the spectral variation of the refractive index and the extinction coefficient for ZnS films of different thickness, it is seen that the refractive index of ZnS films increase with the increase in the film thickness. In order to deduce the band gap of the thin films, the absorption coefficient of the investigated ZnS films are analyzed using the equation (Pankove et al. 1971),

$$(ah\nu) = A(h\nu - E_g)^p$$

where,  $h\nu$  is the photo energy,  $A$  is a parameter that depends on the transition probability,  $E_g$  is the optical band gap and the exponent  $p$  depends on the type of the optical transition between the valence and the conduction band, direct or indirect transition (Pankove et al. 1971).

### 5.5 Applications of Zinc sulphide thin film

It has numerous applications such as ZnS nanostructures being used as field emitters, field effect transistors (FETs), catalyzers, fuel cells, electroluminescence devices, solar cells, UV-light and chemical sensors, humidity and gas sensors, biosensors and nanogenerators.

### 6. CONCLUSION

A comprehensive review related to the necessary background theory of ZnS thin film deposition has been attempted in this work. Light has been thrown upon the usage of Chemical bath deposition method for well-adherent and uniform zinc sulphide (ZnS) thin film formation, the parameters involved and the structural, morphological, optical and electrical properties. Moreover, the mathematical relations have been given for the measurement of various parameters of the prepared thin films.

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### CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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