

2019

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Gashaw Hone, Fekadu and Abza, Tizazu (2019) "Short Review of Factors Affecting Chemical Bath Deposition Method for Metal Chalcogenide Thin Films," *International Journal of Thin Film Science and Technology*. Vol. 8 : Iss. 2 , Article 3.

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Short Review of Factors Affecting Chemical Bath Deposition Method for Metal Chalcogenide Thin Films

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Received: 2 Feb. 2019, Revised: 7 Apr. 2019, Accepted: 15 Apr. 2019

Published online: 1 May 2019

Abstract: Thin film materials are important because of their potential low cost processing with minimal material usage while fulfilling application requirements. Thin films also enable applications where low weight and mechanical flexibility are decisive. A number of studies verified that their physical and chemical properties are highly dependable on the deposition methods. Thin films can be synthesized by varieties of physical and chemical deposition techniques. Among these techniques chemical bath deposition (CBD) is one of the most suitable routes to get uniform, well adherent and good reproducibility thin films. Moreover, currently it attracts considerable attention due to its low temperature compatibility, large area deposition with better homogeneity and cost effectiveness. But there are lots of factors affecting the deposition mechanism and the quality of the thin films. Hence, it is very helpful to know about these different factors which influence CBD method. The intention of this review paper is to present a screening of different works carried out so far to achieve a better understanding of the major factors affecting chemical bath deposition method in order to get the best out of this deposition technique.

Keywords: Chemical bath deposition, Metal chalcogenide thin films, Solubility Product, Semiconductor.

1 Introduction

Chemical bath deposition (CBD) has been used as synthesis method for over 140 years [1] and in the recent two decades it has been widely applied successfully for the synthesis of different types of chalcogenide (CdS, SnS₂, CdSe, PbS), chalcopyrite (CuInS₂, CuInSe₂), and oxide (ZnO, CdO, TiO₂) thin film materials for different optoelectronics and solar cell devices. Thin film is a traditional well established material technology. However, thin film technology is still being developed on a daily basis since it is a key in the twenty first century development of new materials such as nanometer materials and/or a man-made super lattices [2].

Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry, and structure of the film [3]. Thin films have very interesting properties that are quite different from those of the bulk materials which they are made of. As the film becomes thinner, the surface properties become more important than the bulk. The other Cause of interest is the miniaturization of elements such as

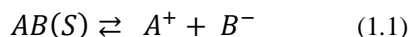
Electronic resistors, thin film transistors and capacitors. The thin films are characterized by a number of interrelated parameters like the thickness, crystalline orientation and multilayer aspects. These film natures highly influenced by the deposition technique. Chemical bath deposition method (CBD) is one of the well-established thin film deposition techniques so far. In CBD, deposition of thin films takes place from aqueous solutions at low temperatures (Room temperature to 90 °C) by a chemical reaction between dissolved precursors, with the help of a complexing agent (or ligand) [4]. Amongst the various methods available for the synthesis of thin films, the chemical bath deposition method have a several advantages and widely used for thin film deposition because it is relatively inexpensive, convenient for large area deposition and ability of tuning thin film properties by adjusting and controlling the deposition parameters [5]. The starting chemicals are commonly available and cheap. It gives pin-hole free and uniform deposits of films since solution and substrate are in contact during deposition process. With CBD method, a large number of substrates can be also coated in a single run with a proper chemical bath design. Electrical conductivity of the substrate is not the necessary requirement. The low temperature deposition avoids

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oxidation and corrosion of metallic substrates [6]. It is also a method free of the many inherent problems associated with high temperature techniques such as MOCVD [7]. Another attractive feature of the CBD method is that, ternary and quaternary compounds can be easily synthesized without the use of any sophisticated instrumentation and process control [8]. However CBD have a lot of advantages there are several factors affect thin film deposition process which should need serious attention. For instant the rate of deposition and terminal thickness depend upon the number of nucleation centers, supersaturation of the solution and rate of stirring. The growth kinetics depends on the concentration of ions, their velocities and nucleation and growth processes on immersed substrates. In CBD deposition, the key is to control the reaction rate so that they occur slowly enough to allow progressive deposition on the substrates. Hence, it is really important to know how we control the deposition rate by considering different factors which influence it. Therefore, in this review paper attempt has been made to point out the major factors which affect the chemical bath deposition method which may alter the final chemical and physical properties of the deposited thin films.

2 Basic principles of CBD and Concept of Solubility Product

The basic working principle behind the CBD process is similar to those for all precipitation reactions and it is based on relative solubility of the product. At a given temperature when the ionic product (IP) of reactants exceeds the solubility product (K_{sp}), precipitation occurs. Whereas if the ionic product is less than the solubility product, then the solid phase produced will dissolve back to the solution resulting in no net precipitation [9]. A central concept necessary to understanding the mechanisms of CBD is that of the solubility product (K_{sp}). The solubility product gives the solubility of a sparingly soluble ionic salt (this includes salts normally termed "insoluble"). Sparingly soluble salt, $AB(S)$, when placed in water, a saturated solution containing A^+ and B^- ions in contact with undissolved solid AB is obtained and equilibrium is established between the solid phase and ions in the solution as:



Applying the law of mass action,

$$K = \frac{[A^+][B^-]}{[AB]} \quad (1.2)$$

where K is stability constant, $[A^+]$, $[B^-]$ and $[AB]$ are concentrations of A^+ , B^- and AB in the solution,

respectively. The concentration of pure solid is a constant number, i.e.

$$C_{AB}(S) = \text{constant} = K^* \quad (1.3)$$

$$K = \frac{[A^+][B^-]}{K^*} \quad (1.4)$$

$$KK^* = [A^+][B^-] \quad (1.5)$$

Since K and K^* are constants, the product of KK^* is also a constant, say K_{sp} , [6]. Therefore equation (1.5), becomes

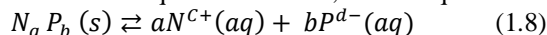
$$K_{sp} = [A^+][B^-] \quad (1.6)$$

The constant, K_{sp} , is called solubility product (SP) and $[A^+][B^-]$ is called the ionic product (IP). When the solution is saturated, the ionic product is equal to the solubility product. But when the ionic product exceeds the solubility product ($IP/SP = S > 1$), the solution is supersaturated (where S is degree of supersaturation), precipitation occurs and ions combine on the substrate and in the solution to form nuclei.

There are three main factors which affect the solubility product these are temperature, solvent and particle size [10]. The equilibrium between a precipitate and its ions in solution will shift according to whether the heat of solution is endothermic or exothermic [11]. Using a solvent of lower dielectric constant, the solubility of moderately insoluble substance in water is reduced by the addition of alcohol or some other water miscible solvent. As particle size decreases, solubility appears to increase.

Solubility constants have been reported by using different methods which includes calorimetric, cation exchange, conductivity, ion exchange, polarography, thermodynamic data, rate of reaction etc. The solubility constants are found to be dependent on temperature, medium and method of measurements and therefore a difference of several orders of magnitudes in solubility constants of a material has been reported in the literature [6].

A complexing agent acting as a catalyst is usually employed in a bath to control the reaction otherwise spontaneous reaction and sedimentation of materials will be obtained [9]. The more soluble the salt is, the greater the ion product and the greater the K_{sp} . However, K_{sp} also depends on the number of ions involved, for any formation of thin film there is some minimum number of ions or molecules, which produce a static phase in contact with solution, called nucleus. Nucleation on the substrate of surface starts at local homogeneity. The rate at which nuclei forms on the surface of the substrate, depends on the degree of supersaturation [12]. K_{sp} can be derived theoretically from the free energies of formation of the species involved in the dissolution equilibrium. Thus, for the equilibrium



where N_a and P_b are sources of cations and anions. The free energy of the dissolution is given by

$$\Delta G^0 = a\Delta G^0(aN^{c+}(aq)) + b\Delta G^0(P^{d-}(aq)) - \Delta G^0(N_a P_b(s)) \quad (1.9)$$

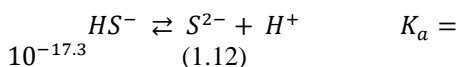
Since

$$\Delta G^0 = -RT \ln K \quad (1.10)$$

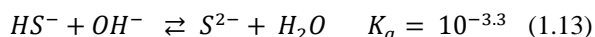
Then

$$\ln K_{SP} = -\frac{\Delta G^0}{RT} \quad (1.11)$$

Since K_{SP} is a thermodynamic quantity, the ionic product that should result in precipitation may not necessarily do so for kinetic reasons (hence the term used earlier to qualify precipitation: "in principle". This would be a case of supersaturation. In practice, however, the solubility product does give a fairly good idea of when precipitation will occur in most cases [13]. The preparation of metal sulphides by introducing S^{2-} ions into aqueous solution of metal salt to effect chemical precipitation is well established. In actual fact, in all but highly alkaline solutions most of the sulphur ion will be in the form of HS^- rather than S^{2-} . This is due to the equilibrium between the two species:



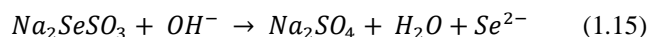
or alternatively, in terms of hydroxide concentration which is related to the hydrogen ion concentration through the ion product of water:



Thus at a pH of 11, a common value in chemical deposition (CD), which gives a value for $[OH^-]$ at room temperature of 10^{-3} M, the S^{2-} concentration will be

$$[S^{2-}] = 10^{-3.3} [HS^-][OH^-] = 10^{-6.3} [HS^-] \quad (1.14)$$

Therefore the main sulphur ion in solution will be HS^- . Similarly, selenium ions are generated by dissolving inorganic sodium selenosulphate in an alkaline solution as given by the reaction [14].



If high concentration of S^{2-} or Se^{2-} ions exists locally such that the solubility product is exceeded, localized spontaneous precipitation of a sulphide or selenide may occur as the case may be. This situation can be avoided by generating chalcogen ions slowly and uniformly throughout the volume of the solution. In general the principle of CBD technique is to control the chemical reaction so as to effect the deposition of a thin film by precipitation [13].

Chemical deposition reactions sometimes proceed via a metal hydroxide intermediate; the concentration of OH^-

ions in the solution is particularly important in such cases. Since almost all CD reactions are carried out in aqueous solutions, the pH of the deposition solution will give this concentration. The OH^- concentration increases (decreases) by one order of magnitude for every unit increase (decrease) in pH [13]. This means that the formation of a metal hydroxide (whether as a colloid or as a precipitate) in aqueous solution will be strongly dependent on temperature when the product of the free metal ions and OH^- ions is close to the hydroxide solubility product, although increase in K_{SP} with temperature may partially offset this effect [15].

3 Factors Which Will Affect Chemical Bath Deposition Method

3.1 Effect of Chemical Bath Solution pH

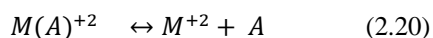
The reaction rate as well as rate of deposition depends on the supersaturation condition and rate of the formation of MX (where M and X is the number of metals and O/ OH^- ions respectively). If the concentration of OH^- ions in the solution is higher, the M ions concentration will lower and the reaction rate will be slow [16]. At a certain pH, the concentration of M ion decreases to a level such that the ionic product of M and X becomes less than the solubility of MX and a film will not be formed. For the growth of good quality thin films, the hydroxy ions in precursor solution are necessary. The thin film formation depends on the pH of the reaction mixture and pH depends on OH^- ions. The decrease in pH results in porous, non-reflecting, powdery and weakly adhered thin films on the substrates. At higher pH metal ion concentration will be lower and the reaction rate will be slow. When an increase in pH make the metal ion concentration decreased, as a result the rate of film formation will be decreased [16, 17]. Films of the same material but deposited at acidic and basic medium may have different properties. The other aspect in which pH influences is that of the equilibrium between the complexing agents and water. The equilibrium in the aqueous solution gives rise to OH^- ions, if OH^- ions are part of the complex, (as with the intermediate of ZnO) an increase in pH increases OH^- ion concentrations hence making the complex more stable thus reducing the concentration of free metal ions. T. Ben Nasr et al [20] deposited ZnS thin films using CBD method by changing the pH of the bath solution fixing the other deposition parameters constant. Their results suggested that the pH contributes had noticeably effects on the growth and crystal structure of deposited ZnS thin films. It was particularly observed that the best crystallinity of the ZnS thin films was obtained at pH of 10. The decreasing of the pH value from 10.99 to 10 is related with the increasing of the (111) diffraction peak intensity. The optical transmission coefficient was found to increase when the pH increased from 10 to 11.5. This may be interpreted by the decrease of

the film thickness. ZnS film prepared at pH 11.5 shows a high transmission coefficient (70%) and a wide band gap of 3.67 eV. The influence of pH (9, 10.5, 11 and 12.5) on an aqueous alkaline chemical bath deposition of PbS thin films were studied by A.N. Chattarki, et al [19]. They reported that the film growth is found to be dependent on the pH of the reaction bath. The EDX results revealed that the PbS samples were less stoichiometric for a low pH value (< 10.5) and slants in the direction of stoichiometry as the pH value increased (> 10.5). The observed average ratio of Pb/S was 1.05 for pH=10.5, which indicated that the product composition of Pb^{2+} and S^{2-} is at approximate ratio of 1:1. The SEM study verified that at low pH values, growth of the crystallites is not clear compared to the growth at higher pH values. The densely packed embedded crystallites appear to be randomly oriented with irregular and spherical shapes of similar sizes.

In most examples of CBD from alkaline solution, the deposition rate increases with increase in pH. This is due to both the greater rate of decomposition of the chalcogenide precursor at higher pH (this decomposition usually involves hydroxide ions) and, in many cases, the greater probability of solid hydroxide formation (as long as this is not excessive). The hydrated metal hydroxy complex is a soluble species. However, if the pH is sufficiently high, the metal hydroxide, which is relatively insoluble for most metals (apart from the alkali group metals) will precipitate. [13].

3.2 Effect of Complexing Agent

Complexing agents, also known as ligands, are typically added to the chemical bath to control the availability of the free cation through thermodynamic equilibrium. The concentration of the complexing agent is typically tuned together with that of the metal salt to achieve desired film properties such as deposition rate, adhesion, and roughness [20]. It is also greatly influences the structural, electrical, morphological and optical properties of the thin films [21, 22]. In CBD technique the process depends on the slow release of chalcogenide ions into an alkaline/acidic solution in which the free metal ion is buffered at a low concentration [7]. The free metal ion concentration is controlled by the formation of complex species according to the general reaction:



Where M is the metallic ion sources and A is the complexing agent; here concentration of the free metal ions at a particular temperature is represented by the relation:

$$K = \frac{[M^{+2}][A]}{[M(A)^{+2}]} \quad (2.21)$$

Where K being the instability constant of the complex ion. The instability constant is different for different complexing agents. As the instability constant increases,

more number of ions will be released. The stability of the complex also depends on temperature and pH of the reaction bath. Increase in temperature of the solution will make the complex less stable; whereas an increase in pH generally makes it more stable [13]. Film formation occurs by combination of released metal ions from complex metal ion source and chalcogen source. It helps to limit the hydrolysis of the metal ion and impart some stability to bath otherwise it undergoes rapid hydrolysis and precipitation [17]. In general complexing agents usually form complexes with metal ions used to increase the bath stability, control deposition rate and good quality films, it also greatly influence the structural and electro-optical properties of the thin film [13, 23]. Nature of complexing agents may influence the final products. For example, when ammonia was used as a complexing agent for the preparation of ZnS thin film, it was found to result in ZnO/Zn(OH)₂ phase rather than ZnS. However when two complexants ammonia and hydrazine were used, the oxide and hydroxide phases could be avoided to a great extent [7]. In a recent studies, Carrillo-Castillo et al. [21] have investigated the effect of hydrazine and hydrazine-ammonia complexing agents on PbS thin film growth. They suggested that complexing agent reduces the deposition rate due to the higher complexation and the slow release of Pb^{2+} ions. K.C. Preetha et al. [24] deposited PbS thin films from three different complexing agents i.e triethanolamine, diethanolamine and hexamine. They found the best crystallinity and high adhesion PbS thin film from hexamine complexing agent. Moreover, they recommended this thin film for solar control coating. Jun Liu, et al [22] were deposited ZnS thin films on glass substrates via the CBD technique using tri-sodium citrate or hydrazine hydrate as the complexing agent. The effects of the different complexing agents and their concentrations on the structure, composition, morphology, optical properties and growth mechanism of the ZnS thin films were investigated. The ZnS thin films prepared using tri-sodium citrate were composed of a large number of uniform but not very dense particles with diameters of approximately 100–200 nm. However, the ZnS thin films prepared using hydrazine hydrate were composed of very uniform and dense fine particles with diameters of 20 to 30 nm. The optical band gap increased from 3.72 eV to 3.87 eV with an increase in the tri-sodium citrate concentration from 0.2 M to 0.8 M and from 3.74 eV to 3.88 eV with an increase in the hydrazine hydrate concentration from 0.16 M to 0.82 M. The nucleation density of Zn(OH)₂ nuclei on a substrate plays an important role in the growth of high-quality ZnS thin films. If a compound containing more than one cation is to be deposited, complexation could be used to offset the difference in *K_{sp}* between the individual metal compounds. S.B. Patil and A.K. Singh [25] were deposited CdS thin films from two complexing agents i.e. ammonia and triethanolamine and they compared their photoelectrochemical (PEC) performance. They found that triethanolamine complex led to better crystallinity and

marigold flower-like morphology. The improved crystallinity, as well as, surface area led to enhanced optical absorption. Due to increased surface area and optical absorption, in case of triethanolamine complex, the short circuit current density, as well as, open circuit voltage were increased which in turn increased overall conversion efficiency. In our recent work [26] we also observed that the concentration of ethanolamine (ETA) complexing significantly affects the structural, optical, morphological and electrical properties of PbS thin films deposited by CBD method. It is observed from the fig.1 that the resistivity decreased as ETA molar concentration increased.

conductivity ($\approx 1.58 \times 10^{-4}$) was observed for PbS thin film deposited from 1.64M molar concentration. The variations of conductivity and resistivity with crystalline size was also investigated and it was observed that conductivity has a direct relation with crystalline size while inverse relation with resistivity. Relatively high resistivity value founds at 0.41M molar concentration may be due to its poor crystallinity which indicates the presence of few atomic layers of disordered atoms. Improvement in crystallinity reduces the resistivity of PbS thin films due to reduced grain boundary scattering.

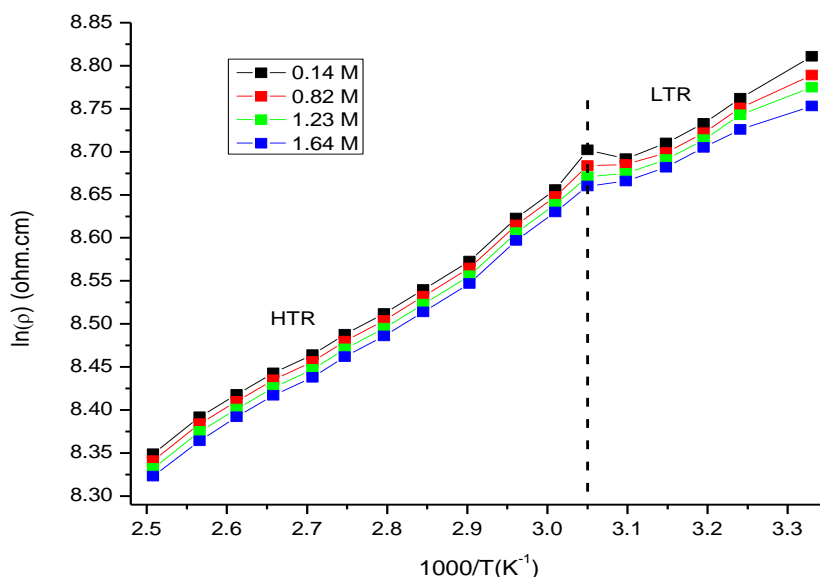


Fig.1: Relation between $\ln \rho$ and the reciprocal of the absolute temperature ($1000/T$) of PbS thin films for various ETA molar concentration [26].

3.3 Effect of Bath Temperature

The rate of chemical reaction in the bath can also be influenced by the bath temperature. As temperature increases dissociation of the complex increases hence the kinetic energy of the molecules also increases leading to greater interaction between ions and subsequent deposition at volume nucleation centers of the substrate [27]. This will result in increase or decrease of terminal thickness, depending on the extent of super saturation of the solution of the bath. Stirring basically brings fresh parts of the solvent into contact with the solute and particles are forced to connect and the presence of temperature assists the entire process for effective desired results [28].

This behavior may be attributed to an increase in mobility due to increasing crystallite size with ETA molar concentration.

The experimental data also verified that a better

Bath temperature has an important effect on crystal size. In most cases higher temperatures allow more grain growth whereas, lower temperatures gives very small nuclei in solution that are thermodynamically unstable. However, if the cluster is smaller than the critical nucleus size, then there is the possibility that the nucleus will redissolve. [Srinivasan and Rajesh [29]], studied the effect of temperature on the structural and optical properties of PbS thin films. Their result revealed that the crystallinity of films were improved when the temperature was increased from 30 °C to 60 °C with the preferred orientation growth along the (200) plane and the band gap energy decreases linearly from 1.2 eV to 0.9 eV. Effect of deposition temperature on the structural, morphological and optical band gap of chemically deposited PbSe thin films were studied by F. G. Hone and F. K. Ampong [30]. The samples were deposited at the bath temperatures of 60, 75 and 90 °C respectively and characterized. The XRD results

revealed that the PbSe thin film deposited at 60 °C was amorphous in nature. Films deposited at higher temperatures exhibited sharp and intense diffraction peaks, indicating an improvement in crystallinity. The deposition temperature also had a strong influence on the preferred orientation of the crystallites as well as other structural parameters such as microstrain and dislocation density. From the SEM study it was observed that film deposited at 90 °C had well defined crystallites, uniformly distributed over the entire surface of the substrate. The EDAX analyses confirmed that the samples deposited at the higher temperature had a better stoichiometric ratio. The optical study revealed that the optical band gap decreased from 2.26 eV to 1.13 eV as the bath temperature varied from 60 °C to 90 °C.

In most cases chemical bath deposition can be used to carefully control the crystallinity of the thin film semiconductors by adjusting the deposition temperature. The lifetime of the nucleus will then depend on its size and also on the temperature; lower temperatures will slow the redissolution step. Thus lower temperature increases the chance that a subcritical nucleus will eventually grow to a stable size rather than redissolve. In PbS thin film the band gap increases with increasing temperature, in contrast to the normal semiconductor band gap dependence on temperature [1, 31].

3.4 Effect of Deposition Time

Deposition time is one of the parameter which affects thin film deposition in CBD method. In most cases it has a great influence on structural, morphological and optical properties of thin films. F. G Hone et al [32], showed that deposition time strongly influenced the preferred orientations of the crystallites as well as structural parameters such as average crystallite size, strain and dislocation density for PbS thin films. In this study the optical band gap of PbS thin films also decreased from 1.32 eV to 1.10 eV with increasing deposition time. O'Brien and Saed, used ethylenediamine as complexing agent, higher deposition temperatures and glass as a substrate and found that the thickness of the CdS thin film increased linearly with deposition time [13]. In general, the growth of good quality semiconductor thin films by the chemical bath deposition technique proceeds at a slow pace. Higher deposition rates and higher films thicknesses are usually accompanied by powdery deposits and a lack of specular reflection. Nair et al [33] has studied intensively the effect of deposition period on film thickness by fixing all the other parameters for different semiconductor thin films and for most cases (not always) the film thickness increase with deposition time see Figure 2.

F.Göde et al [34] were studied the structural, optical, electrical and TSL properties of the PbS thin films prepared by CBD with different deposition times of 100, 115, 130

and 145 min. The optical band gap of the films decreased from 2.65 eV to 2.50 eV with increasing deposition time. The electrical conductivity of the PbS films increased from $1.791 \times 10^{-6} (\Omega\text{cm})^{-1}$ to $1.655 \times 10^{-3} (\Omega\text{cm})^{-1}$ with increasing deposition time. The TSL study of PbS films with different deposition times were indicated that for all films, three main deconvoluted peaks (P_1 , P_2 and P_3) were obtained using the CGCD method. The trap energy levels for the main glow peak (P_3) decreased from 0.50 eV to 0.45 eV with increasing deposition time. Trapping centers in grown PbS thin films with activation energies of 0.50, 0.48, 0.46 and 0.45 eV were detected by the TSL technique. These levels can be attributed to defects created during the crystals growth and/or unintentional impurities.

In our recent work on PbSe thin films, [35] we noticed that the film thickness which was controlled by varying the deposition time had a strong influence on the structural, chemical composition, optical, and surface morphology of the PbSe thin films synthesized by CBD method. The XRD results demonstrated that film thickness had a strong influence on the average crystalline size, texture of coefficients and dislocation density of PbSe thin films see Fig.3.

The EDAX analyses confirmed that varying the film thickness had a significant effect on the stoichiometric ratio of PbSe thin films. The atomic ratio of Se/Pb improved from 0.55 to 0.81 as the film thickness increased from 198 to 451 nm (deposition time increased from 40 to 80 min). The optical absorption spectroscopy study revealed that the optical band gap of the PbSe thin films tuned over a wide spectral range by simple and cost effective route from 1.07 eV to 1.50 eV. The photoluminescence study verified that increasing the film thickness enhances the emission intensity and broadens of the emission rang.

3.5 Effect of Concentration of Cation and Anion Sources

Chemical bath composition is critical for synthesis of good quality of thin films. The nature of the reactants influences the whole physical and chemical properties of the deposited thin film. By changing the composition of the reactive solution, competition between the processes of homogeneous and heterogeneous nucleation could be altered to favor thin film growth [13]. Nature of the reactants influences the composition of the products.

The deposition of good quality, adherent, specular and crystalline CdSe has usually been associated with supersaturated bath with respect to the precipitation of cadmium hydroxide species, irrespective of the substrate. According to P. P. Hankare et al.[16] the growth under These circumstances give Se^{-2} ions into an alkaline solution, where the free metal ions are buffered.

Thus, low concentration of bath ingredients usually favors the nucleation in the first stage. Indeed, the bath concentration plays an important role in the substrate

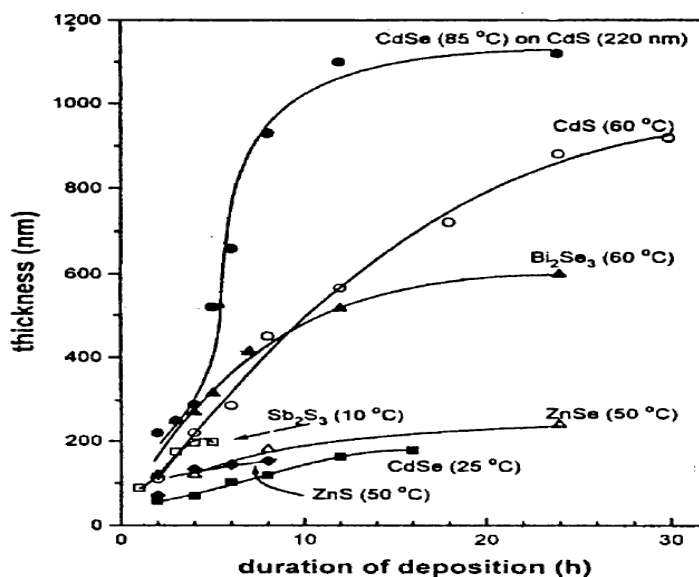


Fig. 2: Dependency of film thickness on deposition time for some selected semiconductor thin films [33].

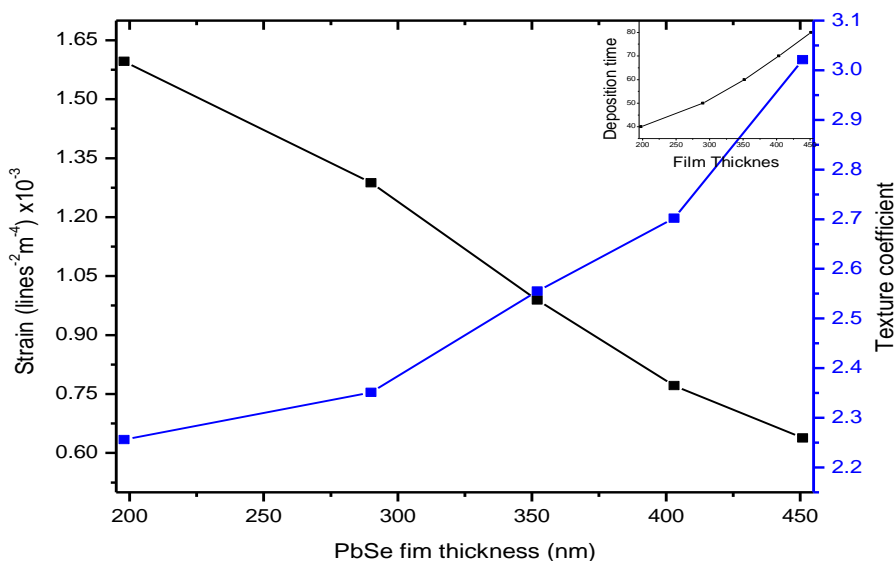


Fig. 3: Dependence of microstrain and texture coefficient on the thickness of PbSe thin films. (Inset: Variation of deposition time with film thickness) [35].

interaction with growing particles. For high concentrations, the films formed were thicker, indicating stronger interaction. Under these circumstances, the growth process becomes cluster-by-cluster rather than ion-by-ion nucleation. On the other hand, at low concentration, the films formed were too thin and nonuniform. This may be attributed to the fact that the required number of ionic species is not available in the solution to get better quality film. In the preparation of lead sulphide thin films by [36], using different cationic precursors; it was observed that

lead sulphide thin film prepared with lead acetate as cationic precursor was found with very good structural, morphological and optical properties compared to lead sulphide thin films deposited from lead chloride, lead nitrate, and lead sulphate cationic precursors. Liua et al [37], showed the effect of different thiourea concentrations in bath for ZnS thin film. In this study the surface morphologies of ZnS thin films prepared in baths with a concentration ratio of ZnSO₄/SC(NH₂)₂ of 1:1, 1:2, and 1:3 were quite smooth and compact. When the concentration

ratio of $\text{ZnSO}_4/\text{SC}(\text{NH}_2)_2$ were 1:4 and 1:5, cracks appeared on the surface of ZnS thin films. [Mousa and Ali [38]] also studied the effect of concentration of lead acetate for PbS thin films. Their result showed that the film thickness goes on decreasing as the concentration of lead acetate increases because this parameter attained a state of higher super saturation earlier, generating precipitate instead of thin film. V. Nirmal Kumar et al [39] deposited ternary $\text{Cu}_{1-x}\text{Cd}_x\text{S}_2$ thin films on glass substrates from precursor solution that had various concentrations of cation and anion sources. The XRD analyses revealed the hexagonal structure of deposited films and change of lattice parameters upon varying the composition. The SEM image showed continuous coating of thin films with morphology changed from spherical to sheet like structure owing to cluster growth process of Cd rich films. EPMA measurement showed the composition of S remains same and cation compositions change. Increase in binding energies of Cu 2p, Cd 3d and S 2p levels were observed as the composition of cadmium increases owing to shift in valance band structure from Cu_xS to CdS. Band gap of $\text{Cu}_{1-x}\text{Cd}_x\text{S}_2$ thin film increases from 1.46 eV to 1.85 eV for Cu to Cd rich composition. Raman peaks were observed at 298.9, 601.8 and 473.3 cm^{-1} owing to vibration modes of its binary phases CdS and Cu_xS , respectively. The carrier concentration of CuCdS_2 thin films decreased as the composition of Cd increased in deposited thin films. The same material, CuCdS_2 thin films exhibited two different type conductivities, p and n-type owing to composition of cations. Cu rich film showed p-type conductivity, whereas Cd rich samples showed n-type conductivity.

3.6 Effect of Types of Precursor Sources

Varies studies verified that using different types of cation and anion precursor sources during film deposition play a vital role on the final physical and chemical properties of the thin films. In the preparation of cadmium sulphide, [40] investigated the effect of different cadmium salts. The results have shown tangible difference in growth kinematics and properties of the thin films. Hani Khallaf et al [42] studied the effect of four differ cadmium sources on physical properties of CdS thin films deposited by chemical bath deposition method. The result revealed that film thickness was found to decrease in the order CdSO_4 , $\text{Cd}(\text{CH}_3\text{COO})_2$, CdCl_2 , CdI_2 . However, the band gap was found to decrease in the order CdSO_4 , $\text{Cd}(\text{CH}_3\text{COO})_2/\text{CdI}_2$, CdCl_2 . All films were found to be cubic, regardless of the Cd salt used. The grain size decreases in the order CdSO_4 , CdCl_2 , $\text{Cd}(\text{CH}_3\text{COO})_2$, CdI_2 . The RBS data showed that usage of CdCl_2 and CdI_2 results in highly stoichiometric films (S:Cd ratio = 1:1). More Cd was detected when CdSO_4 and $\text{Cd}(\text{CH}_3\text{COO})_2$ were used. The S:Cd ratio and carrier concentration were found to decrease in the order CdSO_4 , $\text{Cd}(\text{CH}_3\text{COO})_2$, $\text{CdI}_2/\text{CdCl}_2$. CdCl_2 -based films were found to have a better transmission and much smoother surfaces than other films. Using CdSO_4 as Cd

source leads to the highest growth rate, band gap, carrier concentration, and mobility. The effect of using different anion Zn sources for chemically deposited ZnS(O,OH) films were studied by K. Ernits et al [42]. The study revealed that the growth rate and composition of ZnS(O,OH) layer depend on the instability constant value of Zn complex in chemical bath solution. The ZnS(O,OH) film's growth rate and ZnS concentration in films increased with the increasing value of Zn precursor's instability constant up to the $\text{Zn}[\text{NH}_3]^{2+}$ complex but decreased after that. The analogous effect of chemical nature of anion was detected for solar cell current densities and efficiencies. The highest solar cell current densities and efficiencies were achieved with ZnS(O,OH) buffer layers with the highest growth rate and ZnS content, deposited from $\text{Zn}(\text{Ac})_2$. The only exception was solar cell with ZnS(O,OH) deposited from $\text{Zn}(\text{NO}_3)_2$ containing bath, which results in ZnS(O,OH) with the widest band gap (3.8 eV) and the highest transmission. Films from ZnI_2 with relatively high resistivity and high impurity content in the films have the lowest current densities. L. Beddek et al. [43] were investigated the effect of the lead source and the thiourea concentration on structural and optical properties of PbS thin films synthesized by CBD method. They reported that films were formed through the ion by ion process when using the acetate lead source and through the complex-decomposition process when using nitrate source. Furthermore, lead acetate yields dense films with larger crystallite size (from 4 to 16 nm), however lead nitrate produces rough films with smaller crystallite size (from 1 to 4 nm). Increasing the thiourea concentration causes the crystallinity improvement when using lead acetate and, oppositely, its degradation when using lead nitrate.

3.7 Ageing of the Stock Solution

Ageing of the stock solution is one of the overlooked factors which affect the reproducibility of the CBD method and quality of the deposited thin films. Sarkar et al. [44] were reported that the age of the selenosulphate solution is often important in PbSe deposition. This solution is relatively unstable and fresh selenosulphate often results in rapid precipitation of PbSe when the selenosulphate solution is added. They found it more reproducible and controllable to use a selenosulphate solution which has been aged for about 2 days. Similar observation has been reported by [45] for the deposition of CdSe thin films.

3.8 Nature of Substrates and Their Separation

The nature of the substrate is another important factor that plays a major role in the reaction kinetics. Moreover, nucleation and crystal growth also takes place on it during thin film deposition [46]. Substrate should be cleaned properly with a standard procedure before being immersed in the reactant mixture. One of the advantages of CBD is that thin films can be deposited on any surface. Moreover, shape and electrical conductivity of the substrates are a

usually not important very irregularly shaped substrates can be used. However, the nature of the substrate is usually important in order to obtain an adherent film [6, 47]. Glass is one of the most commonly used substrates with different adhesion in CBD, however, metals make good substrates in general, either because chalcogenides tend to adsorb strongly on many metals, or the non-noble metals are covered with a (hydroxylated in the deposition solution) oxide layer. If the metal in the deposition solution has a sufficiently negative potential, an internal electrochemical reduction may occur [13]. A large variety of CBD thin films have been also deposited on different polymer surfaces. Deposition sometimes is satisfactory on the clean polymer with various activation treatments, such as treatment with permanganate, have been used to improve the adhesion and homogeneity [48]. Apart from adhesion, the crystallographic properties of chemically deposited films are sometimes dependent on the nature of the substrate. One example is epitaxial deposition on a crystallographically-ordered substrate [49]. The kinetics of growth has also been observed to depend sensitively on the nature of the substrate surface. Higher deposition rates and

under similar conditions, higher rates and thickness have been observed on Ge substrate rather than on glass substrate because of better matching of the lattice parameters of PbSe with those of Ge because no incubation period for nucleation is required competing to the glass. In addition of substrate cleanness and types, its separation during deposition has significant effect on film thickness. Readigos et al [51] explained this phenomenon by considering film thickness as a function of separation between substrates in batch production. They observed that, film thicknesses reach an asymptotic maximum with increase in substrate separation. This behavior is explained on the basis of the existence of a critical layer of solution near the substrate, within which the relevant ionic species have a higher probability of interacting with the thin film layer that contribute to precipitate formation. Actually, the critical layer depends on the solution composition, the temperature of the bath, as well as the duration of deposition. For instant in the case of CdS thin film, this critical layer was found to extend from 0.5 mm to 2.5 mm from the substrate surface depending to deposition [9]

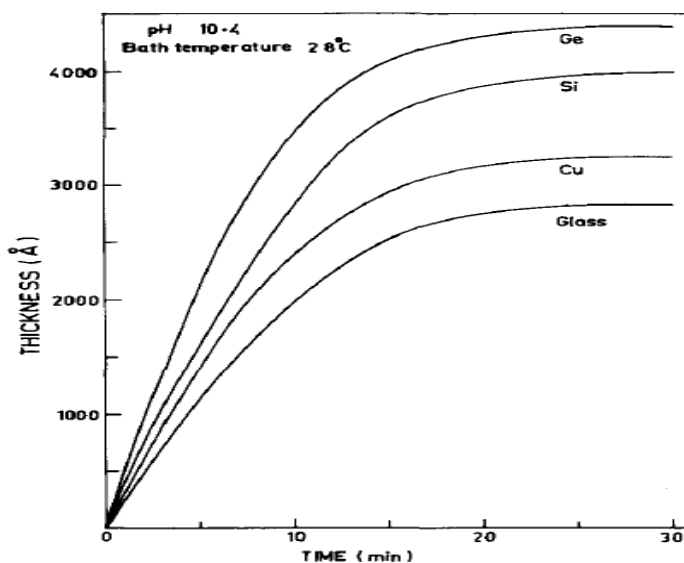


Fig. 4: Thickness as a function of deposition time for PbSe films grown at 28 °C on different substrate materials [50].

4 Conclusions

In the present review paper, attempt has been made to highlight the basic principle of chemical bath deposition method and major factors which influence the final physical and chemical properties of the synthesized metal chalcogenide thin films. The reviewed results also suggested that this method is relatively inexpensive and very suitable to synthesize quality thin films for various Terminal thickness are observed for those substrates whose lattices and lattice parameters match well with those of the deposited material. During deposition of PbSe thin films

optoelectronic and solar cell devices. Moreover, the semiconductor properties of the thin films deposited by this technique are highly comparable with other semiconductor materials deposited by sophisticated deposition techniques like MBE, thermal evaporation, PLD etc as long as the deposition parameters are controlled systematically.

Acknowledgements: The authors wish to acknowledge Hawassa University department of physics.

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