Analysis of Thin Chalcogenide PbS Films Prepared from Chemical Bath.

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ABSTRACT

Thin chalcogenide films of PbS were deposited on glass substrates at room temperature (300K) by chemical bath deposition (CBD) technique. The optimized thin films were then annealed at different temperatures (373K, 473K, and 573K), and their optical constants were determined from absorption measurements, using a spectrophotometer (model UV-2102 PC) at normal incidence of light in the UV-VIS-NIR region. The thin film structures were characterized using XRD and photomicroscope. Measured crystallite sizes of the films were between 1.36nm and 12.72nm. The films exhibited fairly high absorbance and narrow direct transition band gaps (0.65eV – 1.10eV), making them potential materials for photothermal systems, antireflection coatings, and micro-electronics applications.

(Keywords: thin films, chalcogenide films, chemical bath deposition, CBD, photothermal materials)

INTRODUCTION

The chemical bath deposition (CBD) technique has been used extensively for the deposition of thin chalcogenide films [1, 4]. This is largely because the technique possesses a number of advantages such as low cost, low working temperature, and easy coating of large surfaces, over other thin film deposition methods [16]. A CBD technique also offers the advantage of being able to deposit films on different kinds, shapes, and sizes of substrates [2].

CBD technique has also been found to be a very suitable method for deposition of polycrystalline PbS thin films with good photoconductive properties [16]. The photoconductive effect of PbS thin films may be attributed [15] to an amorphous to crystalline transformation during annealing. It has been found that the properties of chemically deposited PbS thin films depend strongly on the growth conditions [18].

In this paper, the deposition of chalcogenide thin films of PbS on glass substrates using CBD technique from aqueous solution of lead acetate and thiourea as starting materials is reported. Also, the structure and optical properties of the annealed PbS thin film samples are investigated.

Deposition of PbS Chalcogenide Films

The chemicals in the reaction bath for the deposition of PbS thin films consist of lead acetate [$Pb(CH_3COO)_2.3H_2O$], thiourea [$(H_2N)_2CS$], sodium hydroxide (NaOH), triethylene-amine (TEA), and distilled water. All reagents used were of analytical grade. The volumetric composition of the bath was obtained as follows: 2.5ml of 0.5M of lead acetate was measured with a clinical syringe and poured into a 50ml beaker. Then 3.5ml of 2M sodium hydroxide was added to the bath and then stirred to obtain a milky solution. To this was added 3ml of 1M thiourea, followed by 1ml of 1M TEA. The resulting solution was thoroughly mixed and stirred. Finally, 36ml of distilled water was added to make up the bath solution, while stirring continued. Cleansed glass substrate was then inserted vertically into the beaker, and the bath was left undisturbed for 3 hours at room temperature.

Fast precipitation implies that a thin film cannot deposit on the substrate immersed in the bath [4, 6]. Therefore using TEA as complexing agent slows down the precipitation action and enables the deposition of PbS on the substrates. For the purpose of optimizing the PbS thin films, several reaction bath constituents were employed by varying the bath parameters as shown in Table 1. The films were successfully deposited in 3 hours.

Table 1: Composition of Bath for PbS Thin Films.

Bath Sample	$Pb(COO)_2.3H_2O$		Thiourea		NaOH		TEA		Distilled Water	Dip Time
	M	ml	M	ml	M	ml	M	ml	ml	(hr)
AP1	0.5	2.5	1.0	3.0	2.0	3.5	1.0	1.0	36.0	3.0
AA4	0.5	2.5	1.0	3.5	2.0	4.0	1.0	1.0	36.0	3.0
AA6	0.5	2.5	1.0	4.0	2.0	3.0	1.0	1.0	35.0	3.0

After deposition, the substrates were withdrawn, rinsed thoroughly with distilled water, and dried in air under ambient condition.

The deposition of PbS thin films took place in a basic medium provided by sodium hydroxide. This deposition is based on the reaction between lead acetate [$Pb(CH_3COO)$] and thiourea [$(H_2N)_2CS$] which were the sources of Pb^+ ions and S^- ions respectively. The ligand or complexing agent used slowed down the precipitation action and enabled the formation of PbS thin films on the substrates.

The stepwise reactions involved in the complex ions formation and film deposition process leading to PbS thin films are as follows:

$$Pb(CH_3COO)_2.3H_2O + TEA \rightleftharpoons \{Pb(TEA)]^{2+} + 2(CH_3COO)^-$$

$$[Pb(TEA)]^{2+} \rightleftharpoons Pb^{2+} + TEA$$

$$[(H_2N)_2CS] + OH^- \rightleftharpoons CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \rightleftharpoons H_2O + S^{2-}$$

$$Pb^{2+} + S^{2-} \rightleftharpoons PbS$$

After the thin film deposition, they were characterized to determine their optical and solid state properties.

Optical and Solid State Studies

The absorbance (**A)** of the deposited thin films was measured using a double beam (Pye-Unico UV–2102 PC) spectrophotometer. Absorbance of the films was determined in the ultraviolet, visible, and near infrared regions of the electromagnetic spectrum. Optical constants; absorption coefficient (α), refractive index (n), extinction coefficient (K), complex dielectric constant (ε) and optical conductivity (σ_0) were deduced using relations adopted by [3, 13]. The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band [8], was used to determine the nature and value of the optical energy band gap. The relationship between the absorption coefficient (α) and incident photon energy ($h\upsilon$) can be written as [5, 8];

$$(\alpha h\upsilon)^{1/n} = A\,(h\upsilon - E_g) \qquad \textbf{(1)}$$

where A is a constant, h is the Planck's constant, and n is a constant which depends on the type of transition. For direct allowed transition n = 2, indirect allowed transition n = ½.

To determine the possible transitions, $(\alpha h\upsilon)^{1/n}$ versus ($h\upsilon$) was plotted. The corresponding band gap energies were obtained from extrapolating the straight portion of the graphs on the $h\upsilon$ axis at [2]:

$$(\alpha h\upsilon)^{1/n} = 0 \qquad \textbf{(2)}$$

CHARACTERIZATION OF THE PBS THIN FILM STRUCTURES

The XRD technique was used to ascertain a wide variety of structural information including; crystal inter-atomic spacing, Bragg diffraction angle, and crystallite size of the deposited films. The XRD patterns were obtained using a mini-diffractometer (model MD–10) using Cukα radiation (λ = 1.54056A^0) in the 2θ scanning mode. Crystallite sizes of the films were estimated using Sherrer's formula [10, 11]:

$$D = k\lambda/\beta\cos\theta \qquad \textbf{(3)}$$

where, D = crystallite size, k = constant = 0.9, λ = wavelength of the X-ray source, θ = Bragg's

diffraction angle in degrees, β = Full-Width-at-Half-Maximum (FWHM). The thin film surface microstructure was obtained by the use of optical microscope (Olympics BH) attached to an Olympics digital camera (Model C – 4040 zoom).

RESULTS AND DISCUSSIONS

The spectral absorbance values (Figure 1) of sample AP_1 annealed at 373K showed peak of about 0.54 corresponding to wavelength of about 375nm in the ultra violet region of the electromagnetic spectrum. Sample AA4 annealed at 473K showed maximum absorbance of about 0.80 at 437nm in the visible region. Sample AA6 annealed at 573K exhibited absorbance with peak of about 0.82 corresponding to wavelength of 431nm. The peak optical and solid state properties of the deposited films are summarized on Table 2.

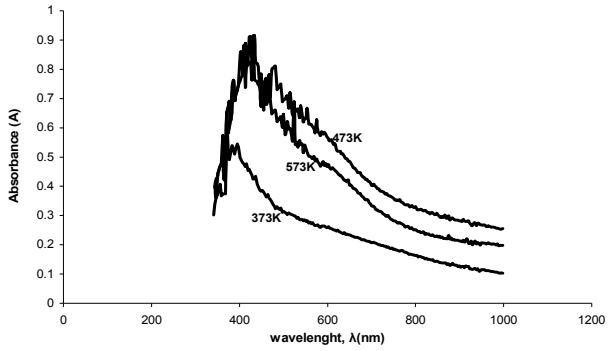


Figure 1: Absorbance Spectra of PbS Thin Films.

Optical absorbance spectra of the deposited thin films are shown in Figure 1. Figures 2 to 9 represent the plot of optical and solid state properties against photon energies (hυ).

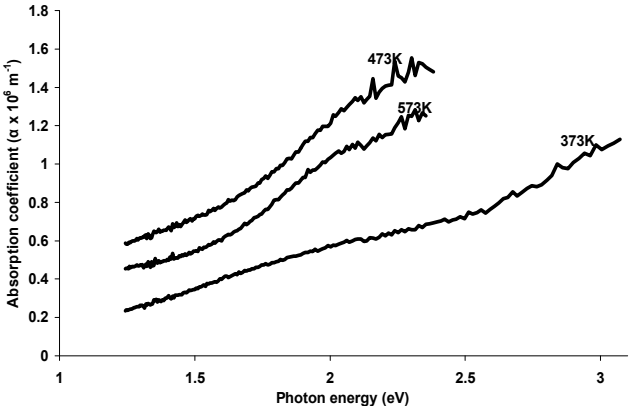


Figure 2: Plot of Absorption Coefficient versus Photon Energy.

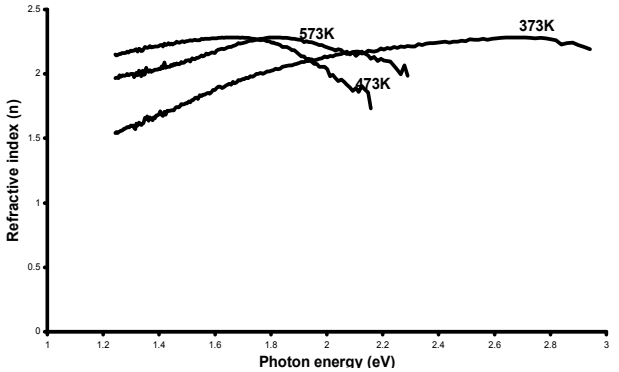


Figure 3: Plot of Refractive Index versus Photon Energy.

Table 2: Values of Peak Optical and Solid State Properties of the Deposited PbS Thin Films.

Bath	σ_o x $10^{14}s^{-1}$	α x 10^6m^{-1}	n	K	E_g^d (eV)	E_g^i (eV)	ε_r	ε_i
AP1	0.59	1.13	2.28	36.35	1.10	2.44	5.21	156.89
AA4	0.60	1.25	1.79	54.24	0.65	1.75	5.20	224.99
AA6	0.60	1.55	1.62	67.67	0.75	1.60	5.21	247.14

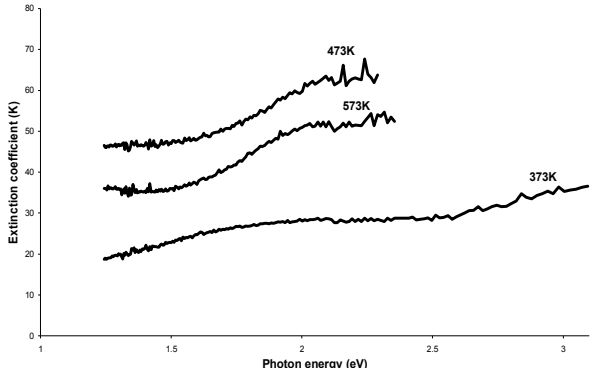


Figure 4: Plot of Extinction Coefficient versus Photon Energy.

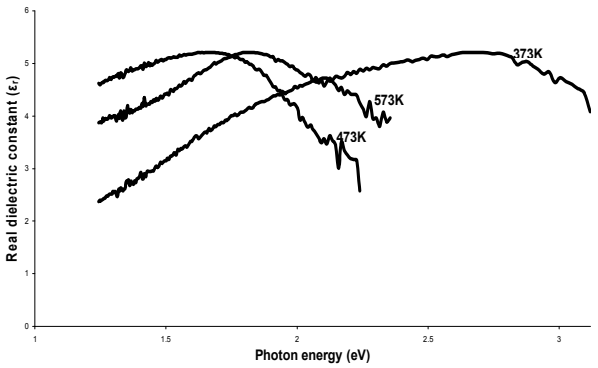


Figure 5: Plot of Real Dielectric Constant versus Photon Energy.

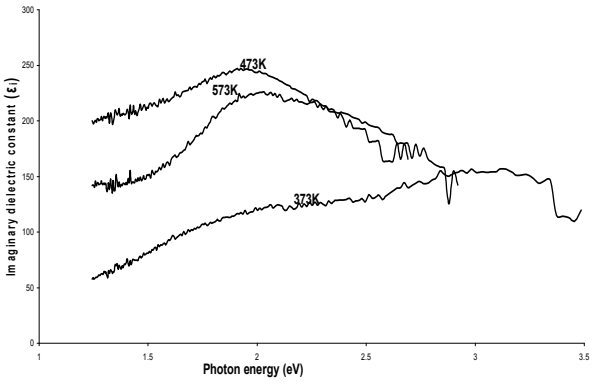


Figure 6: Plot of Imaginary Dielectric Constant versus Photon Energy.

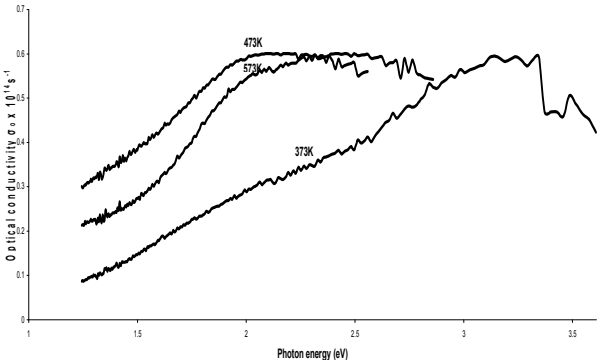


Figure 7: Plot of Optical Conductivity versus Photon Energy.

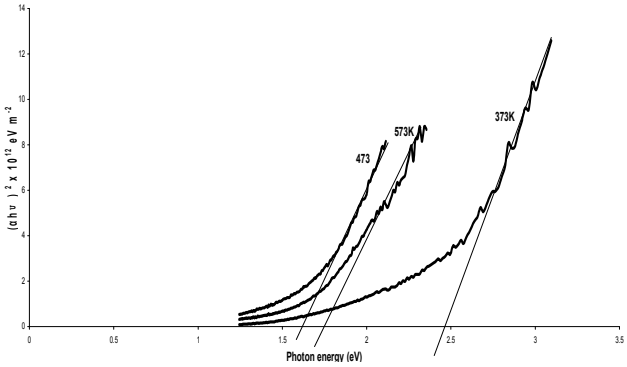


Figure 8: Plot of $(\alpha h_v)^2$ x10^{12} eVm^{-2} versus Photon Energy.

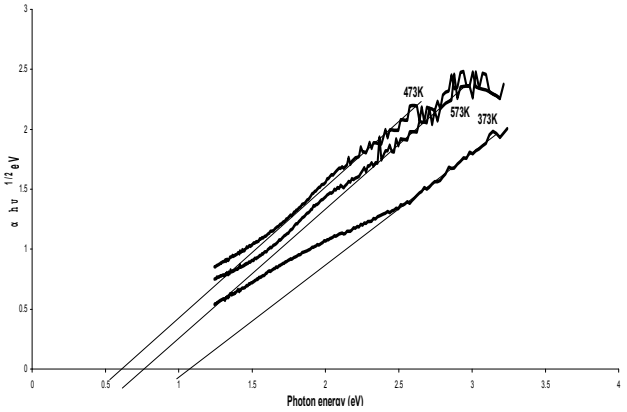


Figure 9: Plot of Plot of $\alpha\ h_v^{1/2}$ versus Photon Energy.

The X-ray diffraction patterns (diffractograms) of all the samples (Figures 10, 11, and 12) showed diffraction peaks corresponding to certain Bragg's diffraction angles $2\theta^{o}$. Some of these peaks exhibited by the samples are broad peaks. The presence of broad diffraction peaks indicate that the thin films deposited on the substrates are of nano-sizes [8, 12].

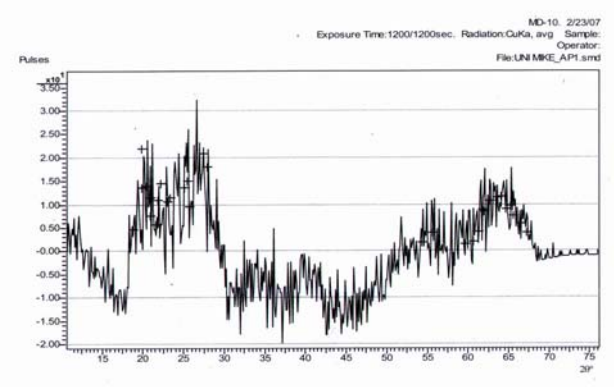
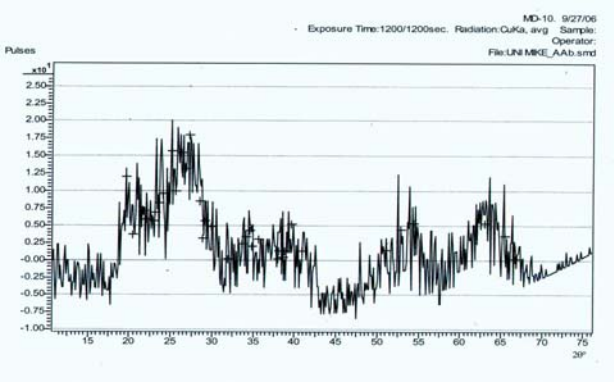


Figure 10: XRD Pattern for PbS Thin Films Annealed at 373K.



Figures 11: XRD Pattern for PbS Thin Films Annealed at 473K.

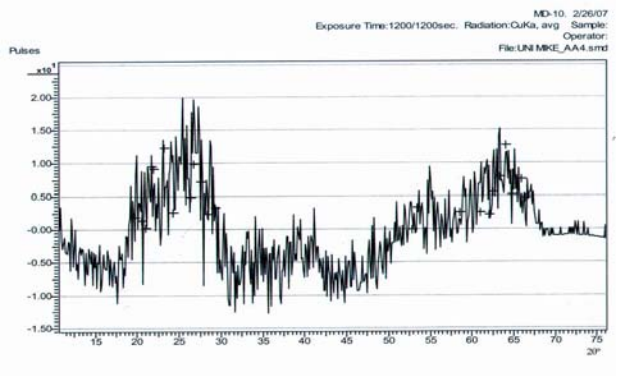


Figure 12: XRD Pattern for PbS Thin Films Annealed at 573K.

Nanocrystalline thin films are of significant interest for a large variety of electronic and optoelectronic devices [17]. The thin film samples exhibited varied polycrystalline and not well defined structural arrangement (Figures 13, 14, and 15).

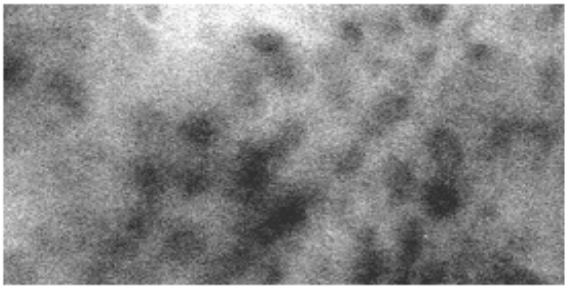


Figure 13: Optical Micrograph of PbS Films (X400) Annealed at 373K.

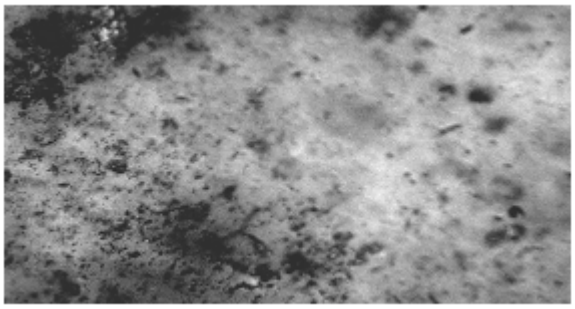


Figure14: Optical Micrograph of PbS Films (X400) Annealed at 473K.

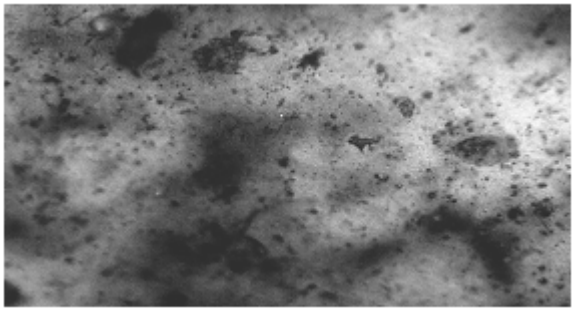


Figure 15: Optical Micrograph of PbS Films (X400) Annealed 573K.

It can be observed that the annealing temperature appreciably affected both the microstructures and crystallite sizes of the films. Sample AP_I annealed at 373K showed more amorphous structure than sample AA_6 and AA_4 annealed at 473K and 573K, respectively.

Sample AA4 annealed at 573K showed the largest crystallite size of 12.72nm (Table 3). This shows that annealing of thin film modifies its grain boundaries and consequently increases the grain size [7].

At room temperature, PbS thin film has an energy band gap of approximately 0.37eV – 0.4eV [14]. The direct transition band gap energy of 0.65eV obtained for sample AA_4 is in good agreement with E_g=0.60eV earlier reported [16] for nanocrystalline PbS thin films. The value of energy band gap is however low when compared with E_g=3.6eV – 3.8eV reported [9] for PbS thin films.

Table 3: XRD Crystallograhic Properties of PbS Thin Films Deposited.

SAMPLES	INTERATOMIC DISTANCE (A°)	FWHM (β)	CRYSTALLITE SIZE, D (nm)
AP_1	4.46330	0.074212	1.8968
AA_4	4.51386	0.011037	12.7206
AA_6	3.48485	0.10457	1.3596

CONCLUSIONS

Thin Chalcogenide films of PbS was deposited using the CBD method. The annealed films were studied using X-ray diffraction (XRD), spectrophotometry and optical microscopy. XRD result revealed the films are nanocrystalline, with crystallite size enhanced by thermal annealing. Optical micro-structural studies of the films showed that the films crystalline structure can be improved by annealing. The Optical properties of the films within the UV-VIS- NIR indicate these films can be useful in photothermal systems, antireflection coatings and microelectronics.

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