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Research Article

EFFECT OF SULFUR ION CONCENTRATION ON STRUCTURAL AND OPTICAL PROPERTIES OF LEAD SULFIDE THIN FILMS OBTAINED BY CHEMICAL BATH DEPOSITION METHOD

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ABSTRACT. In the present investigation Lead sulfde thin films were synthesized on glass substrate with various thiourea concentrations from 0.1 M to 0.2 M by chemical bath deposition method. The XRD analyses revealed that the average crystalline size was decreased from 21.12 to18.7 nm with increasing thiourea concentration. The preferential orientation was along the (111) plane for 0.1 and 0.15 M whereas it was changed to (200) for 0.2 M. The SEM study showed that the film consists of nearly spherical shaped grains, with different grain size. EDX analysis showed that the film was consistent with the formation lead sulfide compounds on glass slide substrate in the desired stoichiometric ratio. The optical characterization of the sample revealed that the optical band gap energy was increased from 0.95 to 1.3 eV with increasing thiouera concentration.

Keywords: *semiconductor, nonmaterial, characterization*

INTRODUCTION

Lead sulfde (PbS), is one of the IV–VI group semiconductors with its unique optical, structural, and morphological properties, has been used in different technological areas such as sensors, solar cells, laser diodes and optoelectronic devices because of these characteristics [1, 2]. Lead sulfide (PbS) is a semiconductor material having FCC structure, small direct band gap of 0.4 eV at 300 K and a relatively large exciton Bohr radius of 18 nm [3]. Lead sulfide exhibits strong quantum size effects below excitonic Bohr radius, this allows the band gap of its nanocrystals to tuned anywhere between 0.41 eV and 5 eV [4]. Due to these properties, it can be useful in light-emitting devices, detectors in the infrared spectral region and photovoltaic devices [5, 6].

The interest in the synthesis and application of semiconductor nanomaterials is increased since their properties are size and shape dependent [2]. There are different synthesis techniques that used to yield high-quality of PbS thin films such as, electron beam evaporation, pulse laser, ion beam sputtering and Chemical bath deposition (CBD) [7]. Among these techniques CBD Method has significant advantages over the other methods due to its cost effectiveness, large area production and simplicity in instrumental operation [8]. The properties of chemically deposited thin films is influenced by various factors like Bath temperature, Nature and concentration of the precursors, Nature and concentration of complexing agent, pH of the mother solution, Deposition time and Nature of the substrate [8, 9]. The optimization of these deposition parameters leads to nano particles with different size and shapes exhibiting different structural, optical, and electrical properties [21].

Literature review showed that the effects of lead ion precursor's concentration,

complexing agents, and bath temperature on chemically deposited PbS thin films were reported. While, to the best of our knowledge, few studies dealing with the concentration of sulfur precursors were carried. Hence, the lack of studies related to the effect of sulfur ion concentration on PbS thin films motivates the present work. In this study, the effects of sulfur ion precursor concentration on the properties of PbS thin films were investigated.

MATERIALS AND METHODS

The experiments were conducted according to literature with slight modification [12, 18]. Freshly prepared lead acetate was used in the chemical bath as a source of lead ion while thiourea for sulfur ion. PbS thin films had been grown by the reaction between lead ions and sulfur ions. In this work, PbS thin films were deposited by the following procedures: firstly, 30 ml of lead acetate and 30 ml of ammonia solution (as both a complexing agent and pH adjuster) were mixed in 150 ml beaker. The pH of the solution was adjusted at 10.96. Then a 0.1 M of thiourea solution was added and distilled water was also added to a final volume of 90 mL solution. Then the solution was immersed in water bath and the mixture was stirred by magnetic stirrer. The pre-Cleaned substrates were vertically immersed in the chemical bath beaker containing different concentration of thiouera from 0.1 M to 0.2 M per step of 0.05 M, placed on hot plate maintained at 80 ^0C. After 1 hr all samples were subjected to remove from the solution, washed with distilled water and dried under ambient conditions before film characterization. The crystallographic structure of PbS thin films were characterized by Bruker D8 advance diffractometer with CuKα (0.15406 nm) radiation and the machine was operated at 40 mA and 40 Kv. The surface morphology and elemental composition of the sample were investigated using Oxford X-MaxN energy dispersiveX-ray analysis (EDX) attached with a Tescan VEGA3. The Optical properties were analyzed by using a Shimadzu UV-3600 Plus UV-VIS-NIR Spectrophotometer within the wavelength range of 700 nm -1800 nm.

RESULTS AND DISCUSSION

X-ray diffraction analyses

The structural analyses of as deposited PbS thin films were carried out by X-ray diffraction in the range of 2θ value between 20^0 to 70^0 and Figure 1.0 presents the X-ray diffractograms of PbS films made by CBD.

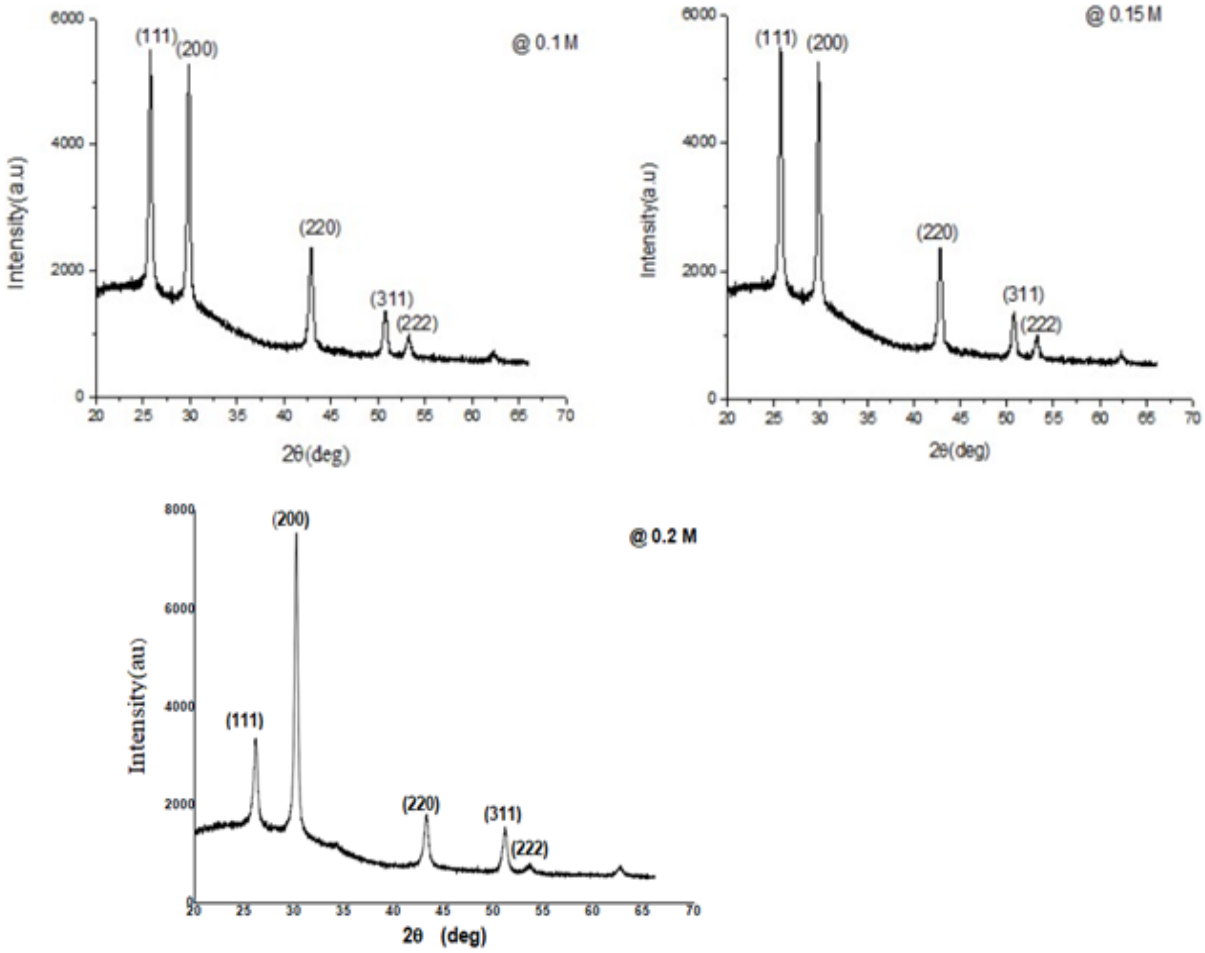

Fig. 1. *XRD pattern of deposited PbS thin films at different sulfur ion concentration*

The possible peaks observed in all samples were (111), (200), (220), (311) and (222) around the 2θ values of 25.964^0, 30.075^0, 42.841^0, 50.978^0 and 53.213^0 respectively, with preferential orientation mainly along (200) and (111) planes. The sample synthesized from 0.1 M and 0.15 M has a preferential orientation along the (111) plane while from 0.2 M was along (200) plane. This variation of preferential orientation is due to the change of the total system free energy during the film growth [19]. Furthermore, any peak referring to impurity phases were not detected. This may confirm the formation of high purity PbS films [10]. As shown in figure 1.0 all diffraction peaks were strongly agreed with standard data of Joint Committee on Powder Diffraction Standards (JCPDS:00-005-0592) data for face centered cubic structure. The sharpness of peaks in figure 1.0 revealed that the synthesized samples were well crystalline. It can be also noticeable from the XRD pattern that the peaks of deposited films are sequential (i.e. a pair of peaks are followed a single peak, which is again followed a pair of peaks and continuous periodical). This is a typical characteristic of a face centered cubic structure [11]. The lattice parameters of the samples were calculated using (1 1 1) and (200) orientations for the cubic structure, which is given by:

$$\alpha = d\sqrt{h^2 + k^2 + l^2} \quad \text{.....eq (1)}$$

The calculated value of the lattice constant is in good agreement with its standard value of 0.5932 nm.

The crystalline size was determined from the major peaks using the Scherrer's equation [12].

$D=K\lambda / \beta(\cos\theta)$ ……eq.(2)

Where k is a constant, whose value is taken as 0.94, β is the full width at half maximum (FWHM) intensity of the peak in radian, θ is the Bragg's diffraction angle and λ is the wavelength of X-ray(0.15406nm). The crystallite sizes were observed to be decrease with increasing sulfur ion concentration in bath solution as shown in Table 1. This may be due to increasing the growth rate rather than nucleation rate, at fast deposition rate growing species (ions) has not enough time to be organized and found a favorable [13].

Table 1. D*ifferent crystallographic parameters of the prepared sample*

PbS samples	2Θ(degree)	d – space (nm)		Lattice parameter (nm)		Crystalline size (nm)
		standard	observed	standard	observed	
0.1M	25.75	0.3429	0.346	0.59362	0.5985	21.12
	29.82	0.2969	0.299			
0.15M	25.75	0.3429	0.346	0.59362	0.598	21
	29.84	0.2969	0.30			
0.2M	26.00	0.3429	0.342	0.59362	0.594	18.7
	30.07	0.2969	0.297			

Morphological and Compositional Analysis

The SEM images of chemically deposited PbS thin films at 0.1, 0.15 and 0.2M are displayed in figure 2.0. The surface morphology of the PbS thin film is homogeneous and covered the substrate very well (see figure 2.0 a). From figures, it is seen that PbS film surface is compact and well covered with smooth, irregular shaped spherical grains of random sizes. These irregular shaped nanograins are inter- connected with each other to form a cluster.

An exceedingly small dispersed spherical structures can also be observed (see Fig. 2b), which seem to be formed by cluster of microparticles [22]. This condition is less marked for a sulfur ion concentration equal to 0.1 M. Nevertheless, the pyramidal crystallites are uniformly distributed on the surface make thin film with strong compactness.

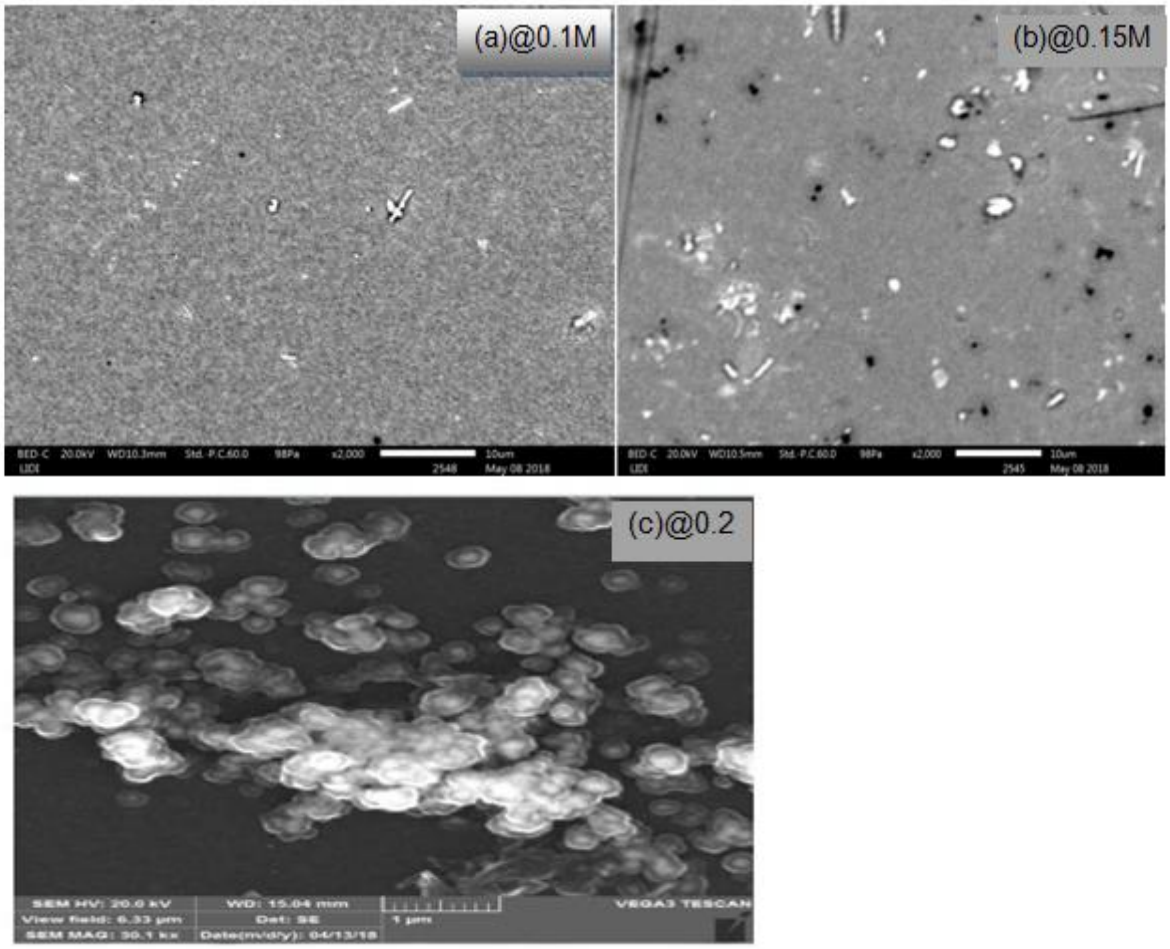

Fig. 2. *SEM images of the deposited sample*

The films deposited at 0.2 M consists of nearly agglomerated spherical shaped grains with different size. The grain increased slightly in size with an increase in the molar concentration of thiouera. Most of the grains are interconnected to each other. Those large size grains were observed over the compacted surface of the film. These may be due to grain which are initially grown homogeneously within the reaction solution and adsorbed to the thin films surface at the final phase of deposition [14]. The micrographs confirmed the dominance of adsorption of homogeneously grown grains on the substrate over heterogeneous film growth process.

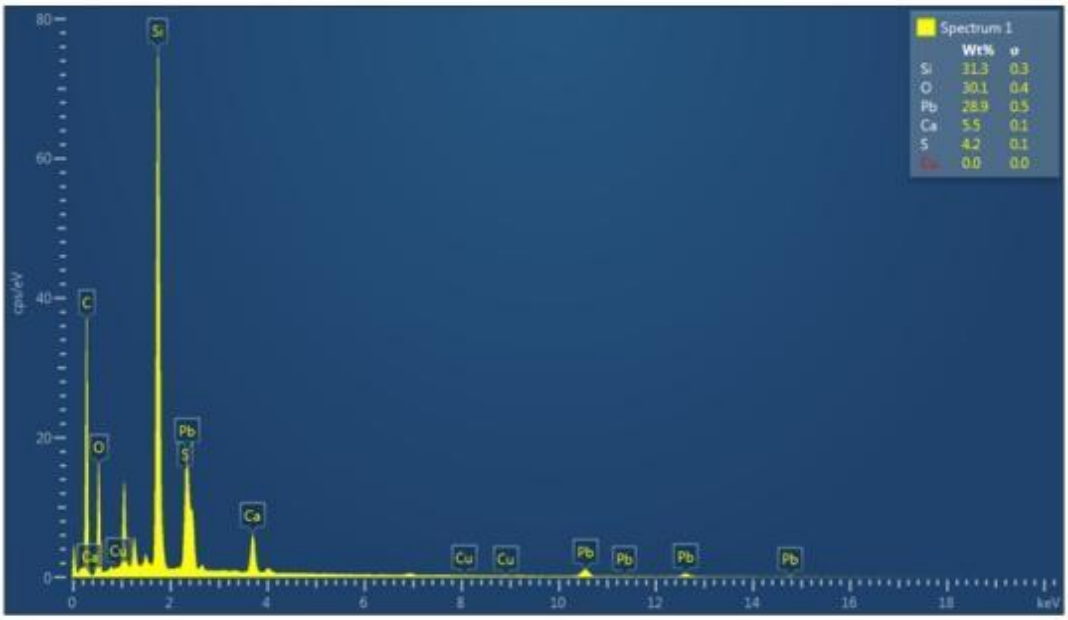

Fig. 3. *Images of EDX spectrum of PbS thin films at 0.2M*

The Elemental analysis were performed by using EDX. From figure 3, it can be observed that the emission lines of Pb and S were present in EDX spectra indicating the presence of PbS films. The sample percentage ratio of Pb to S is 51.52:48.48, which is nearly 1:1, this shows that films had the desired stoichiometric ratio. The presence of oxygen, calcium and silicon in the EDX spectrum of deposited PbS thin films may be due to the composition of glass substrate that used for deposition of thin films [18].

Optical Characterization

Band gap energy (Eg) is very important parameters to be considered while studying the optical properties of materials. In this work, Eg of the films was determined from the absorption measurements by using UV-vis spectrophotometer in the range of 700-1800 nm wavelength and its value was estimated by applying tauc plot analysis from absorbance data [15].

As seen from figure 4.0 the estimated Eg of the films prepared from 0.1 to 0.2 M are 0.95, 1.0 and 1.3 eV respectively. It is important to note that the absorption edge of the all sample shows a blue shift compared with the bulk sample. It was observed that the optical band gap energy of the deposited films increased from 1.0 to 1.3 eV with sulfur ion precursor concentration. Similar results were reported by Beddek et. al. [13]. This increase in Eg value may be due to the improvement in the crystallinity and the decrease in structural disorder and lattice strain. [17]. It can be seen from Table 1. that the crystallite size value decreases from 21.12 to 18.7nm and the band gap of the sample increased from 1.0 to 1.3 eV. This could be attributed to quantum confinement effect in nano crystalline films [16, 18, 20].

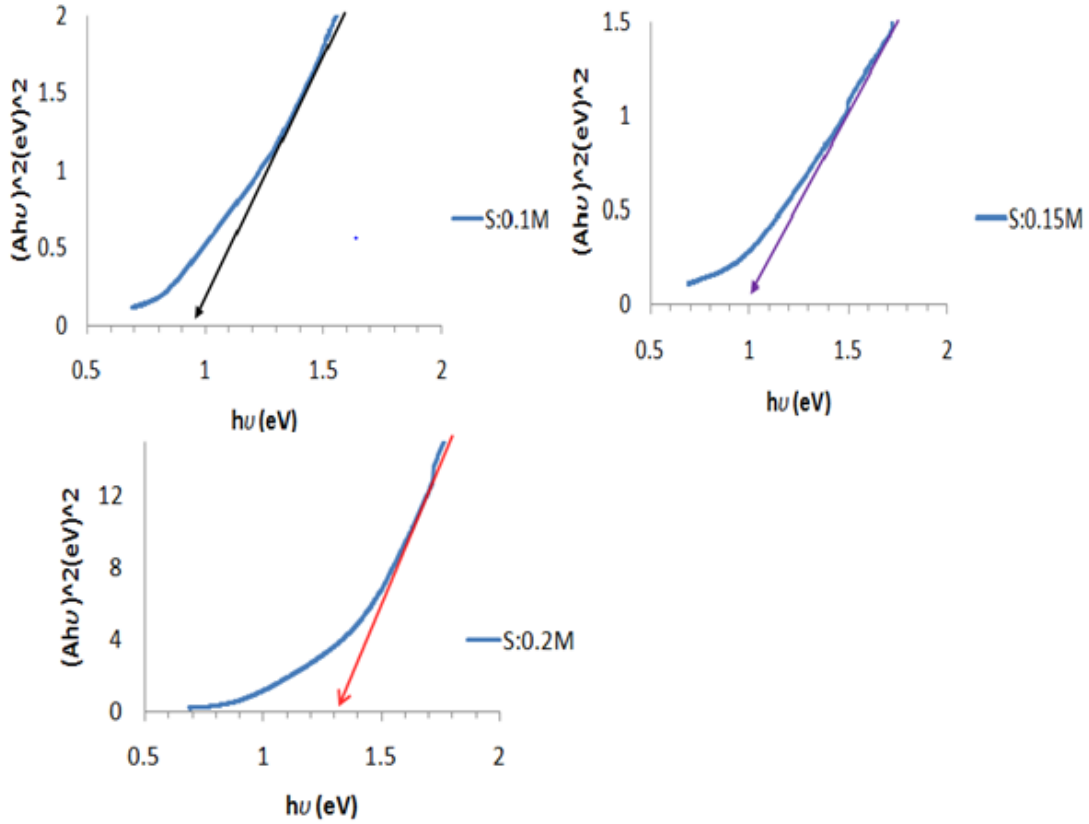

Fig. 4. *The graph of $(Ahv)^2$ versus hv and band gap determination for PbS thin films*

The band gap energy of all deposited films are corresponds to light wavelengths in the near infrared region. Semiconductor materials with band gap energy lies in the range of 1-1.3 eV are suitable for solar cells absorber components [17]. This possibility for Eg variation in PbS thin films presents the opportunity for the design of solar cells. So, PbS thin films deposited at this condition may be considered as a profound material for solar cell applications.

CONCLUSION

Lead sulfide thin films were successfully deposited on glass substrate by chemical bath deposition technique using 30ml of ammonia both as a complexing agent and pH adjuster and various molarities of thiouera from 0.1 to 0.2M as per step of 0.05M with constant heating at 80 ^0C. The deposited films were adherent to the substrate and dark in color. The XRD analysis revealed that FCC structure of polycrystalline films with orientation mainly along the (200) and (111) planes were deposited. However, at high concentration specifically at 0.2M the intensity of peak along the (200) plane was more intense than the (111) plane. The crystalline size was decreased from21.12 to 18.7nm with increasing thiouera concentration. The SEM micro graphs showed that the films surface has spherically shaped grains. The elemental composition analysis of the film confirmed the existence of Pb and S and their ratio Pb:S is very close to one. The optical characterization revealed that the band gap energy increased from 0.95 to 1.3eV as sulfur ion concentration increase.

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