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Nanocrystalline Lead Sulphide Thin Film Fabrication and Characterization

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Abstract— *Nanocrystalline lead sulphide thin films were deposited on clean glass substrates by chemical bath deposition technique. For the sources of Pb^{+2} and S^{-2} ions lead acetate and thiourea were used. To obtain a sample with uniform morphology and pure composition, we investigated and optimized the amounts of experimental variables such as thiourea and lead acetate concentrations, deposition time, pH, and bath temperatures. The size, structure and morphology of Nanocrystalline lead sulphide thin films were systematically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-VIS spectroscopy techniques.*

Keywords— *Nanocrystalline, structural properties, thin film morphology.*

I. INTRODUCTION

Recent advances in the synthesis and the characterization of semiconductor nanocrystals (NCs) have greatly improved the ability to tailor their electronic and optical properties, making them suitable for several applications [1]. The nanoparticles possess the best physicochemical, optical and biological properties which can be manipulated suitably for desired applications [2]. Nanocrystalline thin films are significant interest for a large variety of electronic and optoelectronic devices. The quantum effects that come up when the crystal size drops below 30 nm change in a fundamental way the material properties, which can be used to design a new generation of devices. Different morphologies can play roles in the properties. They include nanocrystals, nanorods, nanotubes, nanocubes, star shapes, dendrites, and flower-like crystals. All can be prepared by different methods [1-3].

Among different methods, Chemical Bath Deposition (CBD) technique has several advantages compared to other techniques such as uniform film deposition, inexpensive, convenient for large area deposition and does not require sophisticated instrument. The deposition parameters such as pH value, deposition temperature, concentration of lead and sulphur ions are optimized to obtain good quality of films. Thus the growth techniques used to obtain nanocrystalline materials and the investigation of their properties are thus of considerable interest [4-6].

Lead chalcogenide nanocrystals show very strong quantum confinement and broad-band absorption that make them attractive for applications in photovoltaic (PV) cells, photodetectors, light-emitting diodes, and thermoelectric devices. Among this group of materials, the lead sulfide (PbS) nanoparticles have wide applications in many fields such as solar cells, solar absorbers, photographs, lasers, LED devices, telecommunications, detectors, optical switches, optical amplification, and also as gas- sensing agents in the solid-state sensors. Only a few reports about using PbS as a gas-sensing agent are available [4-6]. In the present investigation, we have prepared nanocrystalline PbS thin films by chemical bath deposition and studied their structural, surface morphological, and optical properties.

II. EXPERIMENTAL PROCEDURE

In this study lead acetate ($PbC_4H_6O_4.3H_2O$), thiourea (CH_4N_2S), and deionized water were used as raw material. CBD technique has been proved to be a good approach for synthesis of PbS thin films. Corning glass was chosen as substrates for PbS thin films grown using a CBD technique. To investigate the effect of material concentration on the properties of PbS films, experiments were performed for different molarity ratio under the constant growth parameters. The substrates were cleaned with washing detergent, acetone, ethanol and deionized water, respectively to remove adsorbed dust and surface contamination. In order to fabricate PbS thin films, 50 mL aqueous solutions composed of lead acetate ($PbC_4H_6O_4.3H_2O$) (0.1M&0.2M) and Thiourea (CH_4N_2S) (0.1M &0.2M) were used as precursor source for the growth of PbS films. The molar ratio of ($PbC_4H_6O_4.3H_2O$) and (CH_4N_2S) were kept to be 1: 1.

Firstly, lead acetate ($PbC_4H_6O_4.3H_2O$) and thiourea (CH_4N_2S) was weighed. Lead acetate and thiourea were mixed 25ml of de-ionized water by molarity ratio. Lead acetate solution became milky white solution and thiourea solution was pure solution after stirring 10 minutes. Each solution was filtered by qualitative filter paper. Then the two solutions were mixed and stirred, milky white mixture solution was obtained. This mixture solution was stirred with magnetic stirrer for 1 h the milky white solution was changed to dark brown colour. After stirred with magnetic stirrer again with the temperature of 40°C for 15min, dark brown solution was changed into dark aqueous solution. The test pH level of aqueous solution was 7.26.

To fabricate PbS thin film, the cleaned glass substrate was immersed into the aqueous solution. The beaker was subsequently put into an oven kept at 60°C for 3h. All the growth parameters (pH, growth temperature and time) have been optimized for obtaining a high aspect ratio and well-defined crystalline shape of the PbS films. At the end of the growth, the substrates were taken out of the solution and rinsed several times with deionized water, and dried at room temperature. After that it was dried at 60°C for 30 min. Finally, deposited films were annealed with 300°C for 1h. Samples preparation conditions were listed in table 1. In this

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research paper, material concentration dependence of PbS films structure, microstructural properties and film thickness were firstly studied. After that the optical properties of PbS thin films was studied by UV/VIS spectroscopic measurement. Block diagram of experimental procedure was pictured in figure 1.

TABLE I. Samples preparation conditions.

Deposition time	3 h
pH level	7.26
Deposition temperature	60°C ± 5°C
Precursor concentration	0.1M (PbS 1), 0.2M (PbS 2)
Deposition Method	Chemical Bath Deposition(CBD)
Process temperature	300°C

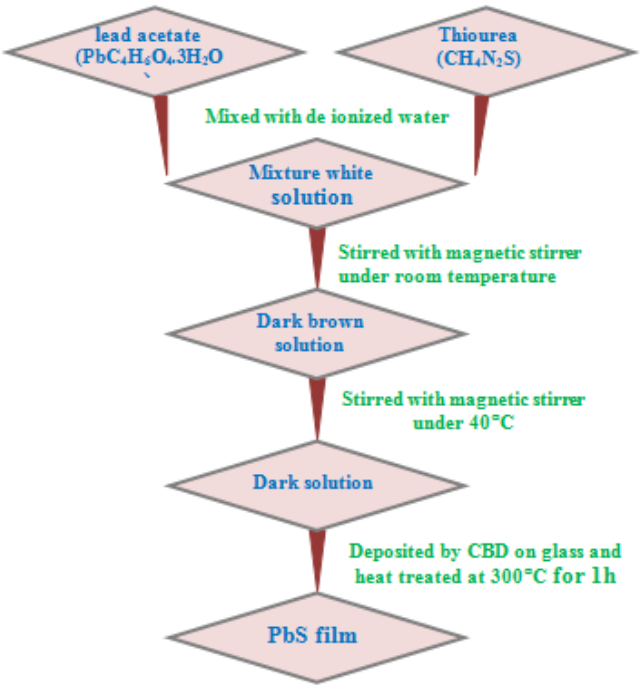

Fig. 1. Schematic diagram of experimental procedure for PbS film.

III. Results and Discussion

A. XRD Studies

XRD technique was used to investigate the crystallographic properties and make the plane identification of fabricated sample. It was performed using monochromatic Cu-Kα radiation (λ = 1.54046Å) operate at 40 kV (tube voltage) and 40 mA (tube current). Sample was scanned from 10° to 70° in diffraction angle, 2θ with a step-size of 0.01°. The XRD spectrum of PbS samples were indicated as shown in figure 2(a&b). Upper side of XRD profile was represented the observed profile while the lower side indicated the standard/ reference profile was JCPDS (Joint Committee on Powder Diffraction Standards) library file. In these XRD patterns, three peaks were clearly observed. They were (111), (200), and (220) respectively. Some extra peaks were observed in figure 2(a), due to the formation of impurities. The three observed diffraction patterns were consistent with standard. The sharp peaks of the XRD pattern indicated that the synthesized PbS nanoparticles were well crystalline. All the diffraction peaks can be indexed to face centered cubic phase of PbS with calculated lattice constant a=5.9394 Å. It is in good agreement with the standard value (JCPDS file no. 65-0892).

The crystallite sizes of the nanocrystalline PbS was estimated by using Scherrer's formula. The value of the crystallite sizes G varies within the range 55.52 to 102.94 nm. For all the crystallites the size is small in a direction perpendicular to (111) plane. X-ray diffractograms of the PbS films, shown in figure 2(b), exhibit broadened diffraction profiles confirming formation of PbS nanocrystals.

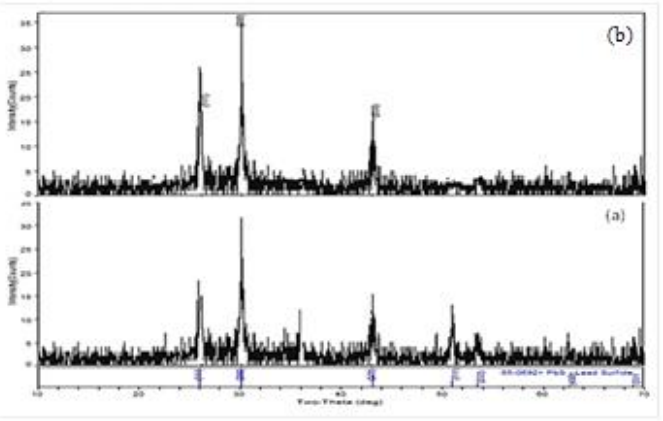

Fig. 2. XRD pattern of (a) PbS 1 and (b) PbS 2 sample.

B. Determination of u-Parameter and Bond Length

In molecular geometry, bond length or bond distance is the average distance between nuclei of two bonded atoms in a molecule. It is a transferable property of a bond between atoms of fixed types, relatively independent of the rest of molecule. Bond length is related to bond order, when more electrons participate in bond formation the bond will get shorter. Bond length is also inversely related to bond strength and the bond dissociation energy, as a stronger bond will be shorter. In a bond between two identical atoms half the bond distance is equal to the covalent radius. Bond lengths are measured in the solid phase by means of X-ray diffraction, or approximated in the gas phase by microwave spectroscopy. A set of two atoms sharing a bond is unique going from one molecule to the next. In this section the position parameter (u) and the bond length (B.L) were calculated and the values were 0.5833 and 1.69 Å.

C. Microstructural Characterization

The microstructural properties of PbS thin film was characterized by Scanning Electron Microscopy (SEM). The scanning electron images (SEI) of two different films deposited using solutions of two different molarities were shown in figure 3(a&b). From the micrograph in figure 3(a) it was observed that grain sizes are not much uniformity. Film surface was rough and the maximum degree of surface density was observed in low material concentration. Grain distribution was not clear but non-crack.

In figures 3(b), the regular grain was formed and the agglomeration was homogeneously distributed on SEM image. The film became smooth and non-cracked. This image consisted of circular feature in microstructure. All grains were

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clearly formed and uniformly distributed. But the connectivity between grains was observed. The density of film was lower compare to the figure 3(a).

As additional analysis of SEM image, it was observed that the average grain sizes determined by SEM were comparatively larger than measured by XRD. This larger value of grain sizes may be due to the agglomeration of grains. Further, the broadening of XRD line profile is not entirely due to smaller crystallite sizes, presence of non-uniform strain in the sample also have some contribution, however, small may be. The average grain sizes of the films were found to vary from 0.576 to 0.475 µm.

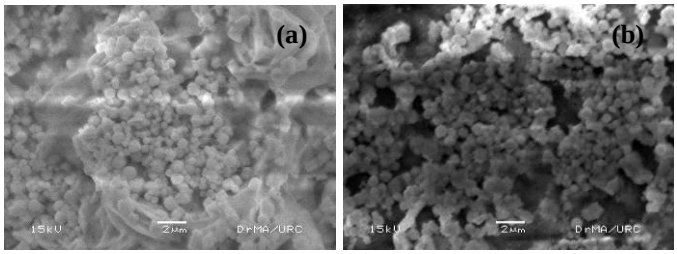

Fig. 3. Scanning electron image of (a) PbS1 and (b) PbS2 film.

D. Film Thickness Calculation

Film thickness of PbS thin film with the two different material concentrations were studied by weighing method. The calculated values of film thickness were 1.195 µm and 0.546 µm for PbS1 and PbS2 thin films.

E. Optical Absorption Studies

UV visible spectrum has been widely used to characterize the semiconductor nanoparticles. As the particle size decrease, absorption wavelength (λ_{max}) will be shifted to shorter wavelength, since the band gap increases for the nano sized particles. This is the quantum confinement effect of the semiconductor nanoparticles.

The optical absorption and transmission spectra for a range of samples of PbS thin films were obtained in UV/ VIS region (up to 1100 nm) using a SHIMADZU U-1800 UV/ VIS Double Beam Spectrophotometer with bare (uncoated) glass slide as the reference.

The wavelength range of spectrum laid between 190 nm to 1100 nm. The related absorbance spectrums were shown in figure 4(a&b). Figure 4(a) showed the absorption spectrum of PbS 1 film. It was found that the film showed good absorption level between 300 nm to 500 nm wavelength. Figure 4(b) showed the absorption spectrum of PbS 2 film. In this spectrum, λ_{max} was observed at 295 nm. This indicated that the absorption shift towards the shorter wavelength, because of the particle size reduction. From this spectrum, it was observed that the PbS nanoparticles exhibit the significant blue shift. This is an indication of strong quantum confinement.

The transmittance spectra for PbS thin films were shown in figure 5(a&b). It is clearly observed that these films have low transmittance. It can be positively concluded that the material is of highly absorbing nature.

From UV spectrum, the band gap of the PbS nanoparticles film have been calculated as 2.57eV and 3.34 eV. It shows that the optical band gap of this material was highly enhanced. This reveals that, when the size of the particle is reduced to very low, the energy states separation is too high (i.e, energy gap).

The values of *Eg* so obtained vary from 2.57 to 3.34 eV indicating increase of band gap with decrease of crystallite size with the exception of the film deposited with molarity equal to 0.2. This increase of band gap is consistent with theoretically shown band gap dependence on crystallite size.

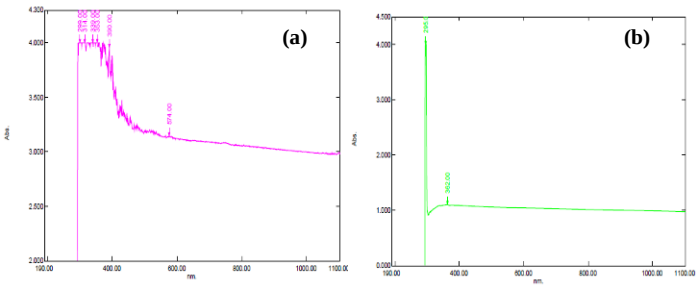

Fig. 4. Absorption spectrum of (a) PbS1 and (b) PbS 2film.

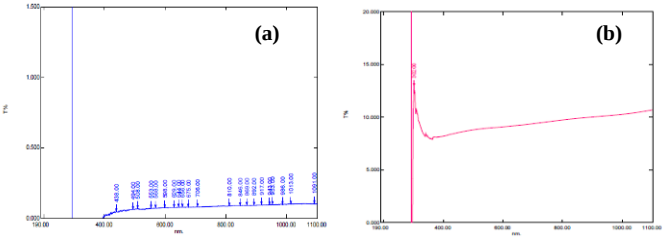

Fig. 5(a)Transmission spectrum of (a) PbS1 and (b) PbS2 film.

IV. Conclusion

PbS nanoparticle films have been successfully implemented by chemical bath deposition method. According to the XRD results, it was obvious that PbS sample was clearly formed with face centre cubic symmetry. The lattice constant was calculated to be 5.9394 Å. The minimum crystallite size was calculated to be about 55.54 nm for PbS sample. Micro grain of PbS sample was uniformly distributed and high dense. The absorption edges were observed that the wavelengths of PbS films were caused between 300 nm and 500 nm respectively. The energy band gap values were determined to be 2.57 eV and 3.34 eV for PbS films with 0.1M and 0.2M. The absorption spectrum of PbS 1 film was broader and weaker compare to those of PbS 2. That is to say, stabilized PbS nanoparticles still exist in coatings after depositing and drying. Due to their liability, PbS particles grow or agglomerate further, and the size distribution broadens slightly during film preparation, resulting in peak broadening. From the experiment results it was observed that the structure, microstructure and optical properties of the PbS nanocrystals in the deposited film is affected by the molarity of the solutions.

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