Nano-Crystalline Lead Sulfide Thin Films using The Chemical Bath Deposition: Synthesis and Characterization

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Abstract - **Nanocrystalline lead sulfide (PbS) thin films have been successfully grown on glass substrate using the chemical bath deposition technique. Microwave oven was used as a heating source to facilitate the growth process of the thin films. Aqueous solutions of lead nitrate $Pb(NO_3)$ and thiourea $[SC(NH_2)_2]$ were used as lead and sulfur ion sources, respectively. Structural, morphological and optical analyses revealed good quality growth of nanocrystalline PbS thin films. This study introduced a facile and low cost method to prepare high quality nanocrystalline PbS thin films in a relatively short growth time for optoelectronic applications.**

Keywords **-** Nanocrystalline; PbS; thin films; Chemical bath deposition.

I. INTRODUCTION

Narrow band-gap semiconductors, such as lead sulfide (PbS), are of interest for photovoltaic (PV) solar energy conversion as they can absorb the "IR tail" of the solar spectrum, which is not absorbed by commonly used PV materials [1]. The use of such absorbers in semiconductor-sensitized solar cells allows the integration of low cost device configurations and broad spectral response, which may also be utilized in IR and near-IR (NIR) photodetectors. PbS thin films can be prepared using various techniques such as molecular beam epitaxy [2], chemical vapor deposition [3], solid-vapor deposition [4] and atomic layer epitaxy [5]. Such techniques require expensive and sophisticated instruments. Chemical bath deposition (CBD) is a promising technique that produces homogeneous and high quality PbS thin films [6]. CBD is a simple and cost effective method. However, PbS thin films prepared using CBD require a long preparation time. Heat is usually transmitted from outside to the inside of the material, leading to an uneven distribution of temperature in the solution, which may affect the quality of the deposited thin films. Microwave irradiation has been widely applied as a heating method in chemistry and material syntheses. Using microwave, the heat is created from inside the material unlike conventional methods where heat flows inward [7]. The direct interaction between the radiation and materials facilitate very short reaction times, moreover less energy is consumed during the process. The integration of microwave irradiation and CBD technique is referred to as microwave-assisted chemical bath deposition (MA-CBD). This work aims to produce high quality nanocrystalline PbS thin films which could be promising materials for optoelectronic applications.

II. MATERIALS AND METHOD

Aqueous solutions of lead nitrate $Pb(NO_3)$ and thiourea $[SC(NH_2)_2]$ were used

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as sources of (Pb^{2+}) and sulfur (S^{2-}) ions, respectively. Ammonium acetate (NH_4CH_3COO) was added as a buffer solution to control the release of ions and to assure a slow deposition rate [8]. For the synthesis of PbS thin films, first, 10 ml of lead nitrate (concentration of 0.1 M) was added into a 100 ml beaker, after that, appropriate quantity of 0.5 M ammonium acetate was added under continuous stirring. After 5 min stirring, 10 ml of thiourea (concentration of 0.1 M) was added dropwise to the solution. Deionized (DI) water (resistivity ~18.2 MΩ.cm) was then added to the solution to achieve total volume of 100 ml. pH of the final solution was fixed at 12 by adding 0.5 M sodium hydroxide (NaOH) solution. Prior to the deposition, glass substrates were cleaned with soap and hot distilled water. After rinsing with distilled water, substrates were soaked in an aqua regia solution for 30 min followed by thorough rinsing with distilled water and dried with pure nitrogen gas. The clean substrates were then fixed vertically inside the beakers; beakers were covered and heated in a microwave oven at 65 °C for 20 min. Samples were washed and ultrasonicated with DI water for 1 min to remove the remaining salts and loosely adherent particles, and then they were dried with nitrogen gas. Mirror-like dark gray with highly adherent PbS thin films on the substrates were obtained.

Structural, morphological and optical properties for the grown thin films were studied using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectroscopy (EDX) installed, and UV-Vis-NIR spectrometer at wavelengths ranging from 500 to 2500 nm, respectively.

III. RESULTS AND DISCUSSION

3.1 Structural Properties

The XRD pattern for the grown PbS thin films are shown in Fig. 1. The pattern shows the formation of a polycrystalline PbS phase with good crystallinity stirring All the observed diffraction peaks were indexed within a cubic (rock salt) structure as confirmed using a standard JCPDS card (ICCD-PDF4 No. 00-005-0592). No additional phases appeared, indicating no oxidation occurred during the preparation, which resulted in the good quality of the formed thin films. The high intensity diffraction peaks indicated well crystalized thin films.

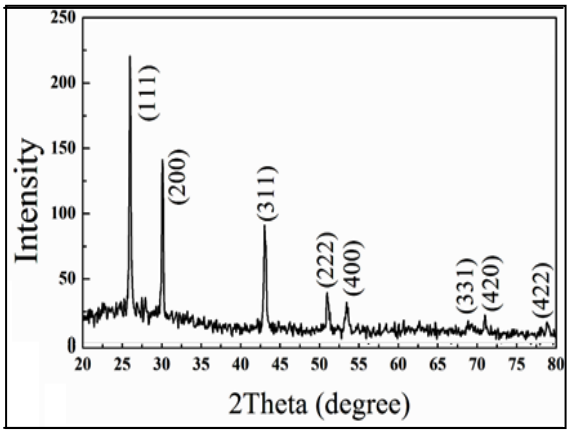

Fig. 1 XRD pattern for the grown PbS thin films using 0.1M concentration of precursors.

The crystallite size (D) for the nanocrystalline PbS thin films calculated using the Debye–Scherrer formula [9]:

$$D = 0.94\lambda / \beta \cos \Theta \quad (1)$$

where, D is the average crystallite size (nm), λ is the wavelength of the X-ray (0.15418 nm), β is the full-peak width at half maximum (FWHM) of the XRD spectrum of PbS thin films (radians), and Θ is the diffraction angle (radians). The crystallite size of the prepared PbS thin films were calculated and found to be 43 nm.

3.2 Morphological Characterization: FESEM and EDX Analysis

Fig. 2 shows FESEM analysis of the prepared PbS thin films by MA-CBD. The inset inside the figure demonstrates a higher

magnification for PbS thin film surface morphology. As shown in the figure, thin film surface appeared to be compact and uniform throughout all the regions without the presence of voids, pinholes or cracks. [10]. EDX analyses confirmed the presence of lead and sulfur for the prepared samples. Analysis shows the prepared thin films are stoichiometric in composition with a Pb/S ratio of 1:02. The small nano-sized cubes clearly indicated their nanocrystalline nature.

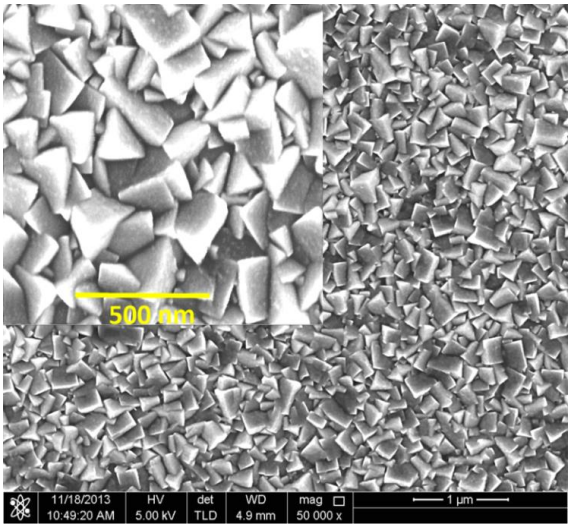

Fig. 2 FESEM images for the grown PbS thin films prepared by the MA-CBD. The insets showed images with higher magnification.

3.3 Optical Properties: UV-Vis Measurements

Fig. 3 shows the optical transmission spectra of the deposited PbS thin film over wavelengths range of 500 to 2500 nm. The deposited thin film exhibits low transmittance, which it could be due to the strong absorbance of light in this region [11].

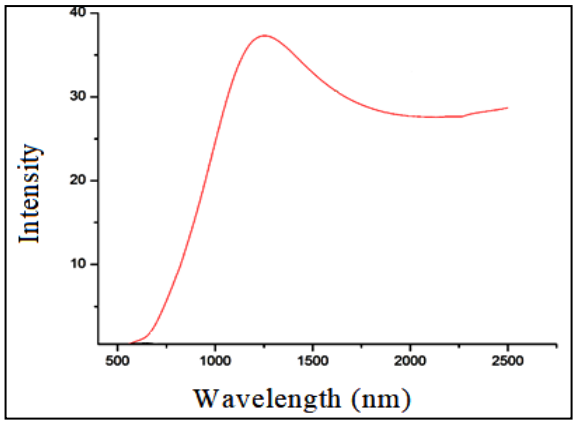

Fig. 3 Transmission spectrum of nanostructured PbS thin films prepared by the MA-CBD.

IV. CONCLUSIONS

Nanocrystalline PbS thin films were successfully grown on glass substrates using MA-CBD. Structural and morphological analyses revealed that good quality PbS thin film characteristics were obtained using 0.1 M of lead nitrate and thiourea. Thin film surface morphology is uniform and compact throughout all the regions, no voids or cracks were observed. Besides, structural analysis revealed high diffraction peaks intensity indicating an improvement in thin film crystallinity. This study produced a simple and cost effective way to prepare polycrystalline PbS thin films which could be a remarkable candidate for optoelectronics applications.

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