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XRD, AFM and UV-Vis Optical Studies of PbSe Thin Films Produced by Chemical Bath Deposition Method

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Abstract. *PbSe thin films have been deposited on microscope glass substrates by chemical bath deposition technique. The chemical bath consisted of lead nitrate, sodium selenate and triethanolamine solutions. The influence of bath temperature on the properties of PbSe films was investigated. The X-ray diffraction, atomic force microscope and UV/Vis Spectrophotometer were used to obtain the structural characterization, surface morphological and absorbance data, respectively. Based on the X-ray diffraction results, the thin films obtained were found to be polycrystalline in nature with cubic structure. The intensity of the (111) peak showed a significant increased as the bath temperature was increased from 40 to 80° C. The films deposited at 80° C indicated that the crystallinity was improved and more PbSe peaks were observed. On the other hand, the grain size, film thickness and surface roughness were increased while band gap energy decreased as could be observed in atomic force microscope and UV-Vis optical studies, respectively.*

Keywords: *Lead selenide; X-ray diffraction; Optical properties; Chemical bath deposition; Thin films.*

INTRODUCTION

Lead selenide is an important semiconductor material with interesting properties such as direct band gap and abundance in nature. Thus, lead selenide thin films have been widely used in a variety of fields such as solar cells, thermoelectric cooling, optical recording, light emitting diodes, sensors, laser and thin film transistors. Several techniques have been applied to obtain lead selenide thin films such as electrodeposition [1], chemical bath deposition [2], electrochemical atomic layer epitaxy [3], photochemical [4], molecular beam epitaxy [5], pulsed laser deposition method [6] and vacuum evaporation [7]. Basically, thin films prepared by chemical methods such as chemical bath deposition method and electrodeposition method are generally less expensive than those prepared by the capital-intensive physical technique. The chemical bath deposition method is an electroless method that is attractive as a simple, low cost instrumentation and potential for large-scale production. Up-to-date, chemical bath deposition method has been successfully used to deposit various thin films including NiSe [8], PbS [9], CdTe [10], $AgIn_5S_8$ [11] and Cu_4SnS_4 [12].

The present work reports the preparation and physical characterization of PbSe thin films onto microscope glass substrates using chemical bath deposition method. The chemical bath contains lead nitrate and sodium selenate which provides Pb^{2+} and Se^{2-} ions, respectively, while triethanolamine act as complexing agent. It is the first time, we report the influence of bath temperature ranging from 40 to 80°C on the PbSe thin films. The results of the investigation on structural, morphological and optical properties of thin films have been carried out using X-ray diffraction, atomic force microscopy and UV-Vis spectroscopy methods, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the X-Ray Diffraction (XRD) patterns of lead selenide thin films deposited at different bath

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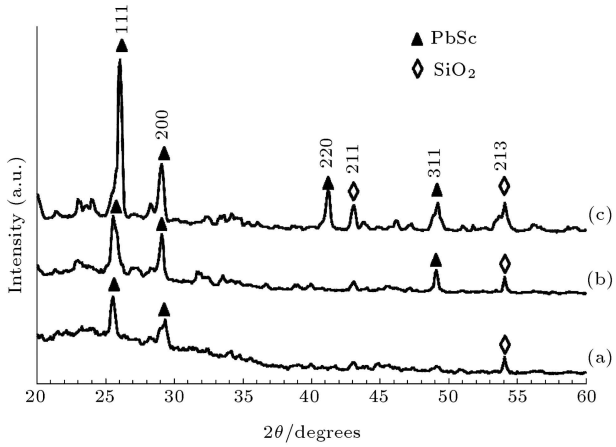

Figure 1. X-ray diffraction patterns of PbSe thin films deposited at various bath temperatures. (a) 40°C, (b) 60°C, and (c) 80°C.

temperatures ranging from 40 to 80°C. All the samples are found to be polycrystalline in nature. For the films prepared at 40°C, two peaks at $2\theta = 25.5°$ and 29.0° are observed. The corresponding interplanar distances are well in agreement with JCPDS data (Reference code: 00-065-1040) [13] of 3.55 and 3.06 Å which attributed to the (111) and (200) planes, respectively. As the bath temperature is increased to 60 and 80°C, the PbSe peaks increased to three and finally four, respectively. All these peaks are related to the compound of PbSe of cubic structure. The lattice parameter values are $a = b = c = 6.128$ Å. On the other hand, as the bath temperature is increased from 40 to 80°C, the intensities of the peaks attributable to PbSe improved. Diffraction along the (111) plane shows the highest intensity with well-defined sharp peak, indicating high crystallinity of the material prepared. Similar prominent plane has been reported for the chemical bath deposited PbSe thin films on GaAs substrate [2].

The presence of the silicone dioxide [14] (JCPDS reference No.: 01-074-0201) peaks in the XRD patterns are due to the microscope glass substrate used during deposition. Two peaks occurred at 2θ values of 43.3° and 53.8° corresponding to (211) and (213) planes are obtained. Based on the XRD patterns, the peaks marked with solid triangles are associated with reflections of the cubic structure of PbSe and those marked with open diamonds can be ascribed to the orthorhombic structure of silicon dioxide.

The PbSe thin films were morphologically characterized using Atomic Force Microscopy (AFM) technique. Figure 2 shows the three-dimensional representation of 20 × 20 μm area of the PbSe thin films deposited at different bath temperatures. The PbSe thin films prepared at lower bath temperature (40°C) indicate that the growth of small grains distributed across the surface of the substrate. The size of the

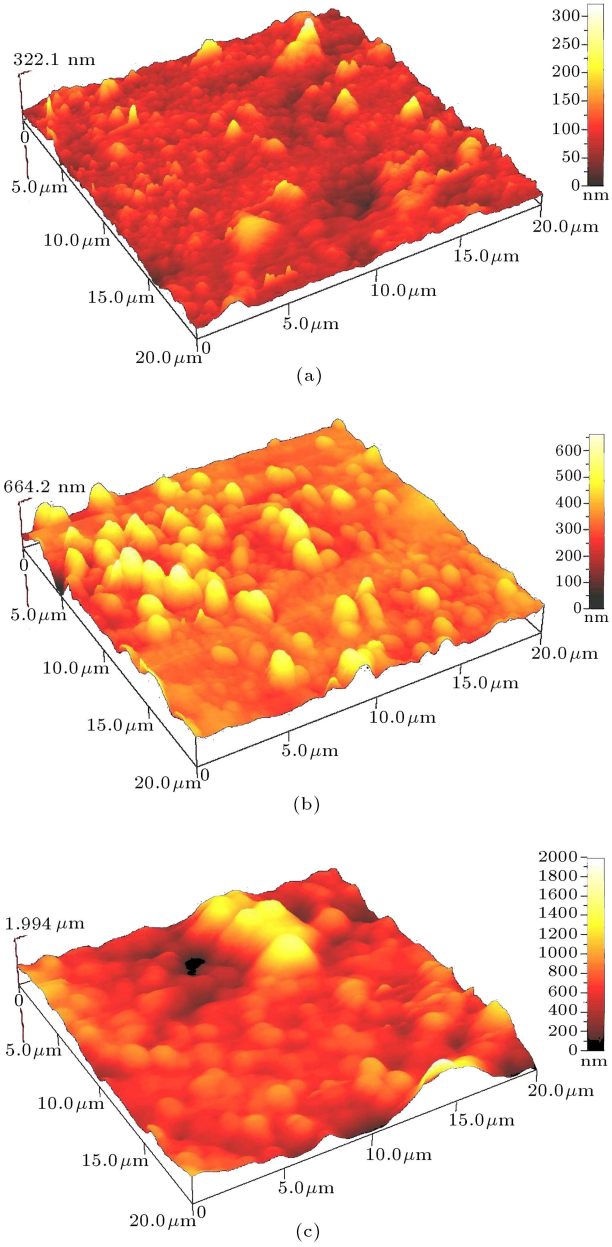

Figure 2. The atomic force microscopy images of PbSe thin films deposited at various bath temperatures. (a) 40°C, (b) 60°C, and (c) 80°C.

grains is rather different from each other indicating irregular growth rate of the grains. The granules are made of different sizes varying from 0.3-0.5 μm. However, the sizes of the grains are noticed to increase as the bath temperature is increased to 60 (1.3-1.5 μm) and 80°C (2-3 μm), respectively. The films deposited at higher bath temperature (80°C) show compact morphology. Based on AFM image (Figure 2c), the grain density reduced indicating the smaller grains agglomerate together to form larger grains of PbSe.

On the other hand, the thickness and surface roughness of the films were measured using AFM

technique. The thickness values of 322, 664 and 1994 nm have been observed for the samples prepared at 40, 60 and 80°C, respectively. Similarly, the corresponding values of surface roughness are 24, 63 and 225 nm, respectively. Root Mean Square (RMS) surface roughness defined as the standard deviation of the surface height profile from the average height is the most commonly reported measurement of surface roughness [15]. The surface roughness is unavoidable since the grains are grown with different sizes. It can be seen that the surface roughness and thickness values increase with increasing the bath temperature indicating an increase in the grain size. We can conclude that the bath temperature plays a vital role on the properties of the PbSe thin films.

The fundamental absorption which corresponds to electron excitation from the valence band to conduction band can be used to determine the nature and value of optical band gap [16]. The relation between the absorbance (A), band gap energy (E_g) and the photon energy ($h\nu$) can be written as [17] shown below (Equation 1):

$$A = \frac{[k(hv - E_g)^{n/2}]}{hv}, \tag{1}$$

where v is the frequency, h is the Planck's constant, k equals a constant, and n is a constant and carries the value of either 1 or 4. The $n = 1$ for the direct transition [18] while $n = 4$ for indirect transition [19], respectively. The absorption spectra of the samples are recorded in the wavelength range 350-800 nm using a UV-Vis spectrophotometer. For the direct band gap semiconductor, the $(Ahv)^{2/n}$ versus hv graph is predicted to be a straight line with a photon energy axis intercept giving the value of band gap [20,21]. The plots of $(Ahv)^2$ against the photon energy (hv) for the lead selenide thin films is presented in Figure 3.

The band gap values are found to be 1.3, 1.2 and 1.1 eV for the films deposited at 40, 60 to 80°C, respectively. It is clear that the band gap decreases when the bath temperature is increased. At higher bath temperature, enhancement in crystallinity of the films leads to larger grains, and causes a reduction in the band gap energy of the materials [22,23]. The band gap of lead selenide thin films obtained in this work is in agreement with the value reported for the chemical bath deposited PbSe thin films on GaAs substrate [24].

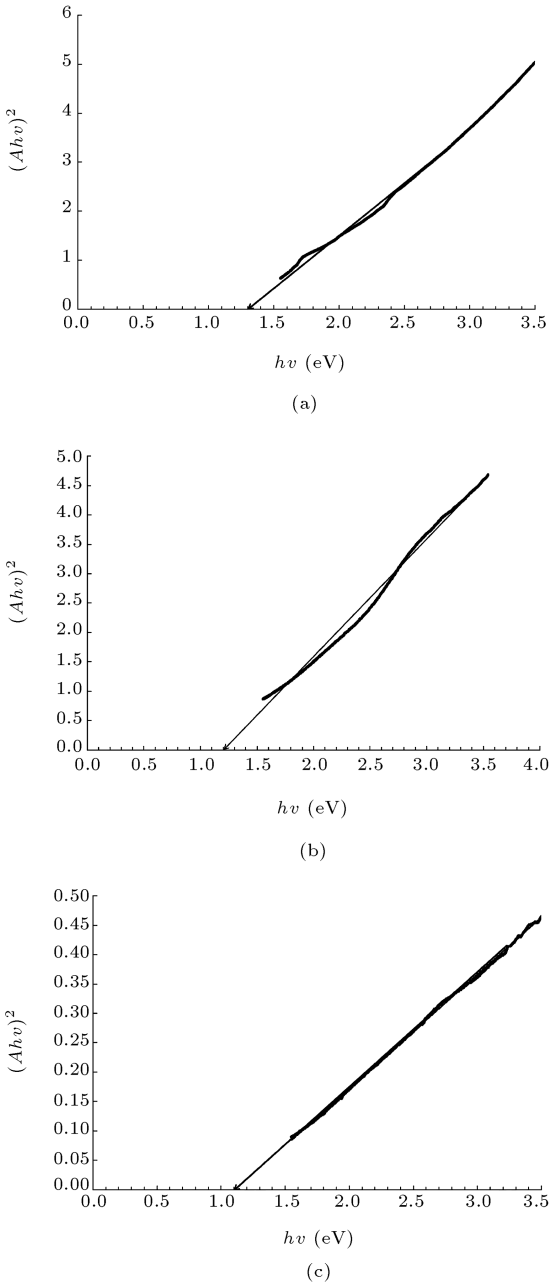

Figure 3. Plot of $(Ahv)^2$ versus hv for the PbSe thin films deposited at various bath temperatures. (a) 40°C, (b) 60°C, and (c) 80°C.

CONCLUSIONS

Lead selenide thin films could be deposited on microscope glass substrates using lead nitrate, sodium selenate and triethanolamine solutions. Based on the X-ray diffraction results, the thin films obtained were found to be polycrystalline in nature with cubic structure. The intensity of the (111) peak showed a significant increase as the bath temperature was increased from 40 to 80°C. The films deposited at 80°C indicated that the crystallinity was improved and more PbSe peaks were observed. On the other hand, the grain size, film thickness and surface roughness were increased while band gap energy decreased, as could be observed in atomic force microscope and UV-Vis optical studies.

EXPERIMENTAL SECTION

Materials and Sample Preparation

Lead selenide thin films were deposited on microscope glass slides using chemical bath deposition method. Prior to deposition, the substrate was degreased in ethanol for 10 min, followed by ultrasonically cleaned with distilled water for another 15 min, and finally dried in air. During deposition process, an aqueous solution of lead nitrate [$Pb(NO_3)_2$] was used as lead source; sodium selenate [Na_2O_4Se] was supplied as selenate source and triethanolamine [$(HOC_2H_4)_3N$] acted as complexing agent. All these chemicals used for the deposition were analytical grade. All the solutions were prepared in deionised water (Alpha-Q Millipore). For deposition, 20 ml of 0.15 M lead nitrate was complexed with 10 ml of triethanolamine agent. To this, 20 mL of 0.15 M sodium selenate was added slowly to the reaction mixture. The pH was adjusted to 6 by addition of hydrochloric acid (0.5 M) with constant stirring. The clean glass substrate was vertically immersed into the chemical bath with the temperatures of 40, 60 and 80°C. After the deposition time of 60 min, the glass substrate was taken out of the bath, washed with distilled water and kept in desiccator for further characterization.

Characterization methods

X-Ray Diffraction (XRD) analysis was carried out using a Philips PM 11730 diffractometer for the 2θ ranging from 20° to 60° with CuKα (λ = 1.5418 Å) radiation. The surface morphology, thickness and roughness were examined by recording Atomic Force Microscopy (AFM) images with a Q-Scope 250 in contact mode with a commercial Si_3N_4 cantilever. Values of Root Mean Square (RMS) roughness were calculated from the height values in the atomic force microscopy images using the commercial software. The optical properties of the thin films were measured with a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer in the wavelength range of 350 to 800 nm. The film-coated indium tin oxide glass was placed across the sample radiation pathway while the uncoated indium tin oxide glass was put across the reference path. From the analyses of absorption spectra, the band gap energy (E_g) was determined.

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