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EFFECT OF BATH TEMPERATURE ON THE CHEMICAL BATH DEPOSITION OF PbSe THIN FILMS

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ABSTRACT
PbSe thin films are prepared by chemical bath deposition technique over microscope glass substrates from an aqueous acidic bath containing lead nitrate and sodium selenate. The influence of bath temperature on the properties of PbSe film is investigated. The X-ray diffraction analysis showed the deposited films were polycrystalline and having the (111) orientation. The surface morphology study revealed that the grains have cubic shape crystal. The band gap energy was decreased from 2.0 to 1.3 eV as the bath temperature was increased from 40 to 80 °C. The films deposited at 80 °C showed good crystallinity and uniformly distributed over the surface of substrate with larger grain sizes. Therefore, the optimum bath temperature is 80 °C.

Keywords: Lead selenide, X-ray diffraction, Band gap energy, Chemical bath deposition, Thin films

INTRODUCTION
Recently, extensive research has been devoted to grow various kinds of binary[3,5] and ternary[1,10] semiconductor thin films. This is due to their potential application in the area of solar cells, optoelectronic devices, photoconductors, sensor and infrared detector devices. The PbSe thin films attract attention of many researchers due to they consist of cheap, abundant and posses semiconducting properties. The preparation of the thin film of PbSe has been explored by number of methods including electrodeposition[14], chemical bath deposition[8], electrochemical atomic layer epitaxy[17], photochemical[18], molecular beam epitaxy[7] and pulsed laser deposition method[15]. Thin films prepared by chemical methods are generally less expensive than those prepared by the capital-intensive physical techniques. We have selected chemical bath deposition method owing to its many advantages like low cost, large area production and simplicity in instrumental operation. Up-to-date, chemical bath deposition method has been successfully used to deposit many different semiconductors thin films including SnS[2], CdSe[6], ZnSe[9], CdS[11], PbS[12], Cu_2S[13], $CuInS_2$[4] and $CuBiS_2$[16].

MATERIALS AND METHODS
Materials and sample preparation
Lead selenide thin films were deposited on microscope glass slides (25 mm x 75 mm x 1mm) 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. An aqueous solution of lead nitrate [$Pb(NO_3)_2$], was used as lead source, sodium selenate [Na_2O_4Se] as sulfide source and triethanolamine [$(HOC_2H_4)_3N$] as complexing agent for depositing PbSe thin films. 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 of resultant mixture was adjusted to 6 by addition of hydrochloric acid with constant stirring. The clean glass slides were vertically immersed into the chemical bath solution with the temperatures of 40, 60 and 80 °C, respectively. After the deposition time of 60 min, the glass slide was taken out of the bath, washed with distilled water and dried in desiccators for further characterization.

Characterization methods

The X-ray diffractogram were recorded using a Philips PM 11730 diffractometer with CuK_α (λ=1.5418 Å) radiation in the different range 2□ angle 20-60°. Surface morphology was studied by JEOL (JSM-6400) scanning electron microscopy operating at an accelerating voltage of 20 kV. The optical absorption measurement was carried out in the wavelength range from 400 to 800 nm by using a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated glass substrate was placed across the sample radiation pathway while the uncoated glass substrate was put across the reference path. The absorption data were manipulated for the determination of the band gap energy.

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction (XRD) patterns of films deposited at various bath temperatures such as 40, 60 and 80 °C. The film prepared at 40 °C shows only two peaks occurred at 2θ=25.5° and 29.0°. However, as the bath temperature was increased to 80 °C, the intensity 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. This means that the grain size of thin film increases with increase in the bath temperature. The number of peaks due to PbSe also increased at this bath temperature. These peaks obtained indicate that PbSe structure with (111), (200), (220) and (311) planes have been deposited. All these peaks corresponding to cubic phase of PbSe were well matched with the standard JCPDS (Reference code: 00-065-1040) data. The lattice parameter values are a=b=c=6.128Å. On the other hand, the presences of the silicone dioxide (JCPDS reference No.: 01-074-0201) peaks in the XRD pattern are due to the glass substrate used in the analysis. Two peaks occurred at 2θ values of 43.3° and 53.8° corresponding to (211) and (213) planes were obtained. 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 oxide.

Scanning electron microscopy (SEM) is a useful technique analysis of the surface morphology of a film. It can give the grain size and structure of samples. Figure 2 shows surface morphologies of the films deposited at various bath temperatures ranging from 40 to 80 °C. All the samples taken at 20 kV with a 250 X magnification. Changes in film morphology with the deposition temperature were observed. The SEM micrograph shows that PbSe thin films prepared at 40 °C are not compact and do not have good coverage of glass substrate (Fig. 2a). These films revealed that grains were very small in size with no well-defined grain boundaries. From the Fig. 2b, well defined grains of 0.5 μm are observed for the film deposited at 60 °C. The cubic shaped PbSe crystal covered the glass substrate

surfaces. As the bath temperature increases, the surface morphology of the PbSe becomes more homogeneous. Also, the grain sizes were noticed to increase gradually. At 80 °C, the small polycrystalline materials agglomerate together to form PbSe grains (Fig. 2c). The grains somehow formed compact morphology structure over the substrate and were densely packed. It is found that the bath temperature plays a vital role on the quality of the PbSe films.

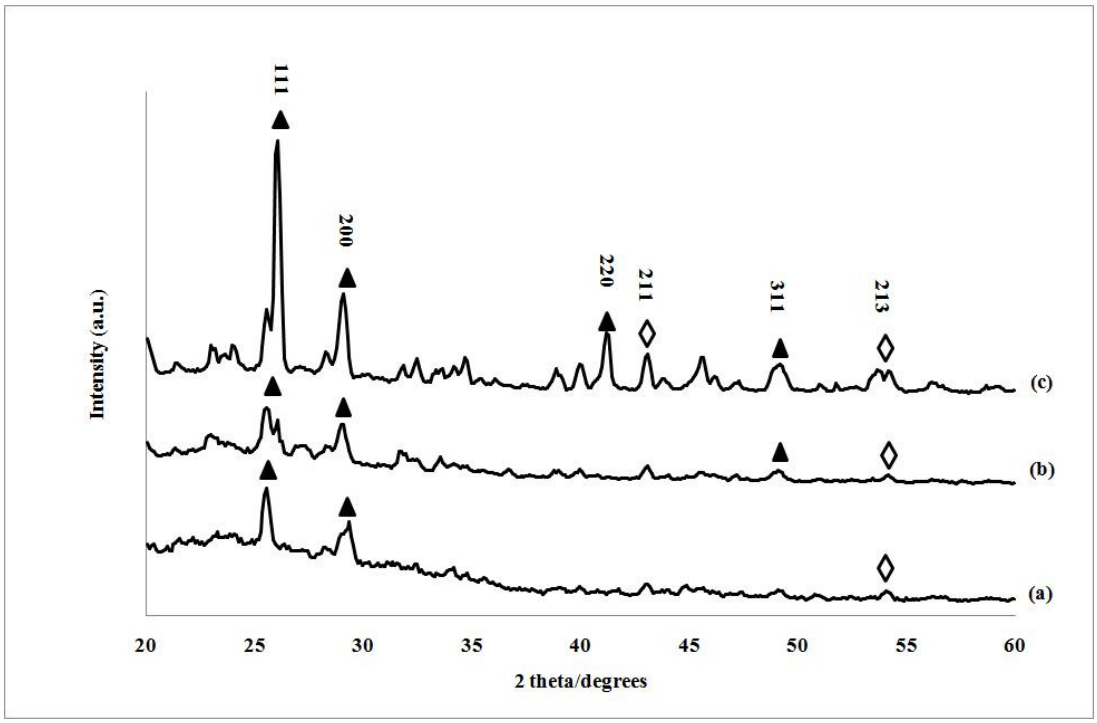


Fig. 1: X-ray diffraction pattern of PbSe thin films deposited at various bath temperatures

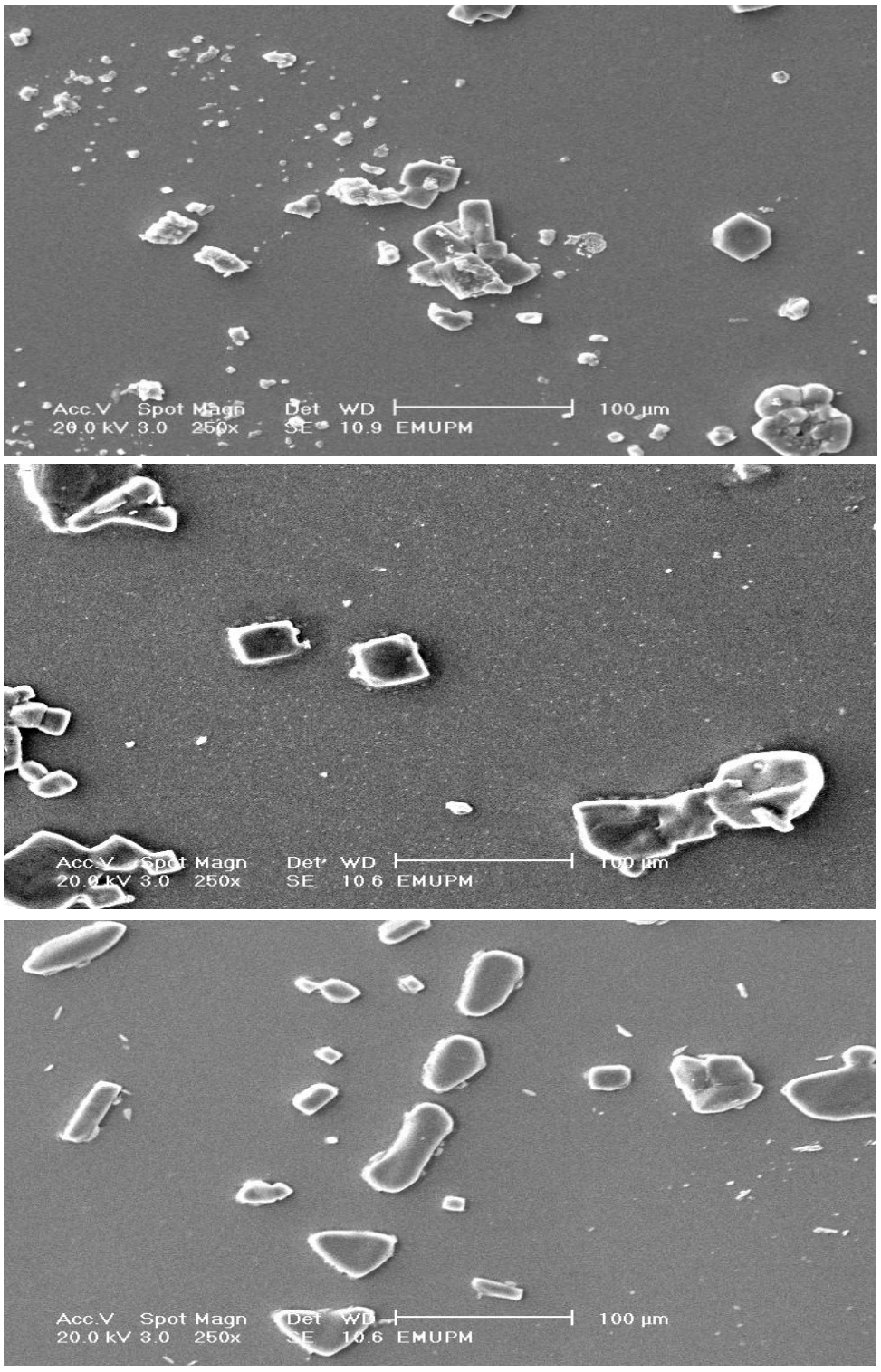
(a) 40 °C (b) 60 °C (c) 80 °C (▲ PbSe, ◊ SiO_2)

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with following relationship for near-edge absorption (Equation 1):

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

where v is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The value of n is 1 and 4 for the direct transition and indirect transition, respectively. Figure 3 shows the plots of $(Ahv)^2$ versus hv of the films deposited under various bath temperatures. The linear nature of the plots indicated the existence of direct transitions. The band gap energy is obtained by extrapolating the linear portion of $(Ahv)^{2/n}$ versus hv to the energy axis at $(Ahv)^{2/n} = 0$. The results reveal that the band gap energy decreases linearly when the bath temperature was increased. The band gap values were found to be 2.0, 1.4 and 1.3 eV as bath temperature was increased from 40, 60 to 80 °C, respectively. The decrease in band gap energy can be attributed to the improvement of

crystallinity at higher bath temperature. This result correlates well with the data obtained from the XRD and SEM analysis.



(a)

(b)

(c)

Fig. 2: The SEM micrograph of PbSe thin films deposited at various bath temperatures (a) 40 °C (b) 60 °C (c) 80 °C

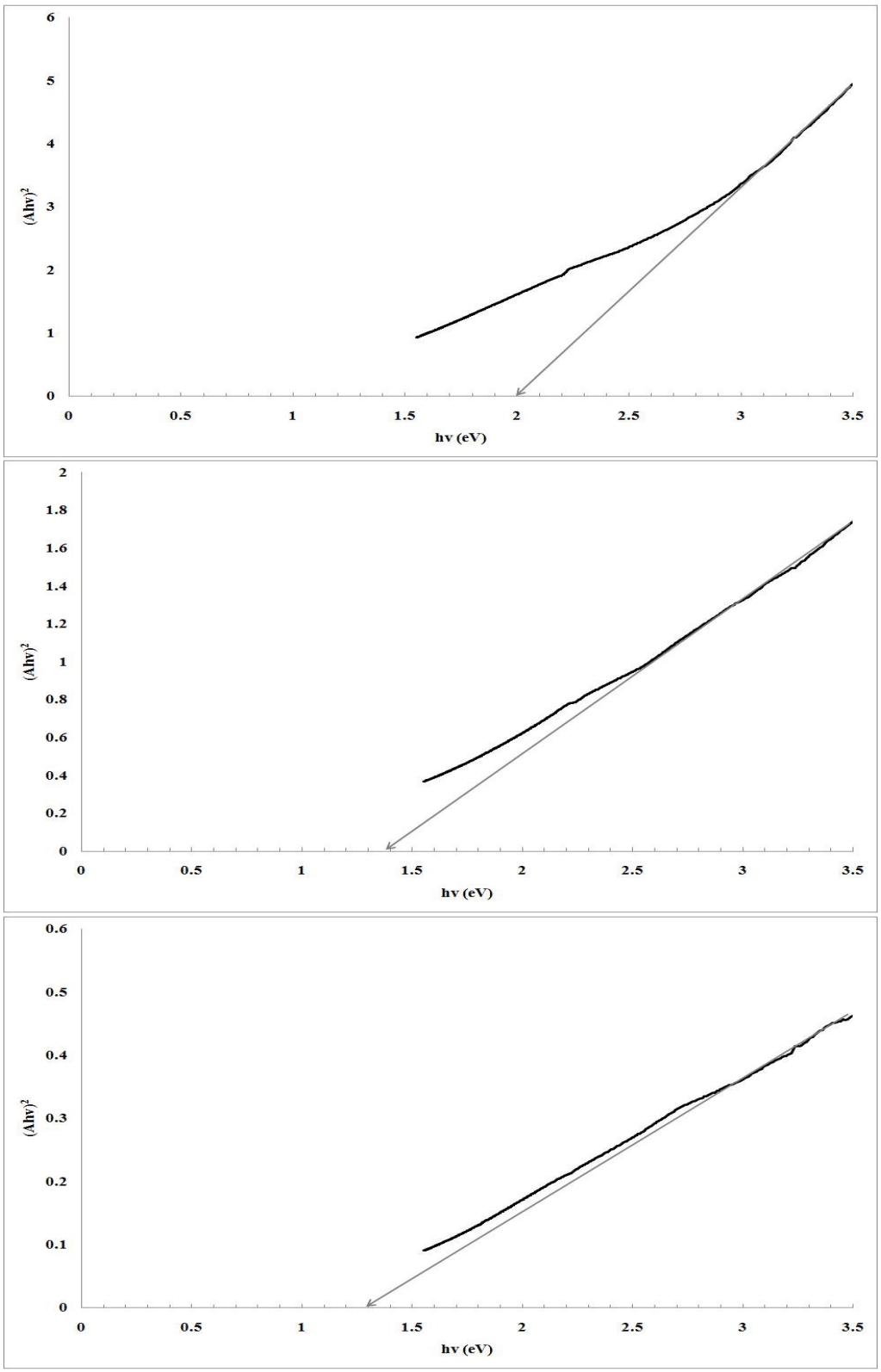


Fig. 3: Plot of $(Ahv)^2$ versus hv for the PbSe thin films deposited at various bath temperatures (a) 40 °C (b) 60 °C (c) 80 °C

CONCLUSIONS

The PbSe thin films can be deposited by using simple and cost-effective chemical bath deposition method. The chemical bath contained lead nitrate and sodium selenate solutions. The TEA was used as complexing agent during deposition process. The XRD pattern reveals that formation of cubic structure, with the strongest peaks attributed to (111) plane of PbSe. The band gap energy was decreased from 2.0 to 1.3 eV as the bath temperature was increased from 40 to 80 °C. The films deposited at 80 °C showed good crystallinity and uniformly distributed over the surface of substrate with larger grain sizes. Therefore, the optimum bath temperature is 80 °C.

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