



Optical, Structural and Surface Morphology Properties of PbSe Thin Film Deposited By Chemical Bath Deposition

Dr. H. K. SADEKAR

Department of Physics, Arts, Commerce and Science College, sonai-414105, M.S., India
E-mail: sadekarhk@gmail.com

Abstract

Lead selenide (PbSe) thin films were deposited on glass slide substrates using the chemical bath deposition (CBD) technique at 60°C temperature for 120 minutes. Surface morphology and structure of the films was studied by scanning electron microscopy (SEM) and XRD respectively. The SEM micrograph shows uniform deposition of PbSe thin film. Optical properties of the thin films were studied by spectrophotometer in the wavelength range of 500–1200 nm. Band gap (E_g), absorbance (A), and absorption coefficients (α) were examined as a function of wavelength and photon energy. Further analysis revealed that PbSe thin films had a band gap of 1.23 eV, optical transmittance below 60% in the near infrared range and high absorbance in the visible range of the spectrum suitable for solar cell applications.

Keywords: PbSe thin film; semiconductor; chemical bath deposition; optical; structural; surface morphology.

Introduction

Lead chalcogenides are one of the basic and potential materials for modern infrared optoelectronics due to narrow band gap and high carrier mobilities [1]. PbSe is a IV-VI group, direct narrow energy band gap (0.27 eV) and large excitation bohr radius (46 nm) [2] semiconductor possessing excellent optoelectronic properties. Optical bandgap of PbSe can be tuned (~ 1.5 eV) by decreasing the crystallite size upon changing the preparation conditions [3]. E_g range of 1-1.5 eV is suitable to achieve high energy conversion efficiency when used as absorber material in optoelectronic devices. In addition, PbSe nanocrystals have major industrial uses such as field effect transistors [4], infrared detectors [5], thermoelectric material [6], etc. due to their unique electronic, optical and physical properties. For these reasons, many research groups have shown a great interest in the development and study of this material by various deposition processes such as electrodeposition [7], RF magnetron sputtering [3], Inert gas condensation [8], electron beam evaporation technique [9], Chemical bath deposition [2,10]. CBD method is presently attracting considerable attention, as it does not require sophisticated instrumentation. It is relatively inexpensive, easy to handle, convenient for large area deposition and capable of yielding good quality thin films. The characteristics of chemically deposited PbSe thin film by CBD strongly depend on the growth conditions.

In this paper, we report optical and surface morphological properties of PbSe thin films obtained by CBD method by optimizing different deposition parameters such as precursor concentration, bath pH and deposition time.



Experimental

Thin film preparation

The PbSe thin films were deposited using mixture of aqueous solutions of lead nitrate, selenium powder, sodium sulphite, trisodium citrate, triethanolamine (TEA), hydrazine hydrate, and sodium hydroxide (NaOH), where TEA was used as the complexing agent and sodium hydroxide for adjusting the pH. CBD enables decomposition of sodium selenosulphate in an alkaline solution containing lead salt and a suitable complexing agent. The deposition process is based on the slow release of Pb^{2+} and Se^{2-} ions in the solution, which then condenses on the glass substrate. The deposition of PbSe occurs when the ionic product of Pb^{2+} and Se^{2-} exceeds the solubility product of PbSe. Control of Pb^{2+} and Se^{2-} ions in the solution ultimately controls the rate of precipitation and hence the rate of film growth.

The substrates used for the deposition of PbSe thin films were commercial microscope glass slides (Blue Star) with the size of 75 x 25 x 1.35 mm. Before deposition, the substrates were degreased in HNO_3 solution for 24 h, cleaned by commercial detergent and finally rinsed with de-ionized water and dried in desiccator. This process was carried to ensure clean surface, essential for formation of nucleation centers, required for thin film deposition. All chemicals used in the present investigations were AR grade. Aqueous solutions of 0.25 M lead nitrate [$\text{Pb}(\text{NO}_3)_2$], 0.25 M sodium selenosulphate (Na_2SeSO_3), 0.2 M trisodium citrate, triethanolamine (TEA), 80 % hydrazine hydrate and 4 M sodium hydroxide (NaOH) were used to prepare thin films. Sodium selenosulphate was prepared by refluxing 0.25 M selenium powder mixed with 1 M sodium sulphite in de-ionized water, which was heated to 80 °C for 8 h [11]. 20 mL lead nitrate solution, was taken in a 50 mL glass beaker. Under continuous stirring 30 drops of TEA, 5 mL NaOH, and 5 drops of hydrazine hydrate solutions were added slowly. Initially the solution was milky and turbid due to the formation of $\text{Pb}(\text{OH})_2$ suspension. Addition of excess NaOH led to the dissolution of turbidity and made the solution clear and transparent. Then 5 mL trisodium citrate and 20 mL freshly obtained sodium selenosulphate solutions were added slowly with constant stirring. pH of the final mixture was adjusted to ~ 10. Pre-cleaned glass substrates were inserted into the reaction mixture standing parallel with the walls of the beaker. The deposition bath and the solution was stirred well with the help of magnetic stirrer to maintain the homogeneous mixture which was kept for 4 h at room temperature.

Thereafter, the substrate coated with PbSe was removed, rinsed with distilled water, and dried in desiccator. It was observed that the film was uniform, well adhered. The as-deposited PbSe film was reflective and brown in appearance when observed under transmitted white light [12]. Adhesion of the film was confirmed by centrifugal method. Thickness of the film was found to be ~ 300 nm by using weight difference method.

Characterization techniques

As-deposited thin film of PbSe was characterized for structural, optical and electrical properties. Glancing incidence angle X-ray diffraction (GIXRD) pattern of the film was recorded on a Bruker AXS, Germany (D8 Advanced) diffractometer. The scanning range of diffractometer used is $20-70^\circ$ (2θ), using $\text{Cu-K}\alpha_1$ radiations with wavelength 1.5405 \AA at 0.5° glancing angle. The surface morphology was studied by scanning electron microscopy (SEM, JOEL-JSM-5600) Transmittance and absorbance spectra were recorded in the range $500-1200 \text{ nm}$ by means of Jasco V630 spectrophotometer.

Results and discussions

Surface morphological and structural Studies

Fig.1 shows SEM image of as-deposited PbSe thin film. It is observed that the film is uniform and covers the entire substrate surface. The fine grains were well defined, spherical with different sizes and were uniformly distributed over a smooth homogeneous background corresponding to the nanocrystalline phase of PbSe. Some of the grains are seen to be united/fused forming agglomerates and the grain size obtained from SEM is about $\sim 200 \pm 20 \text{ nm}$.

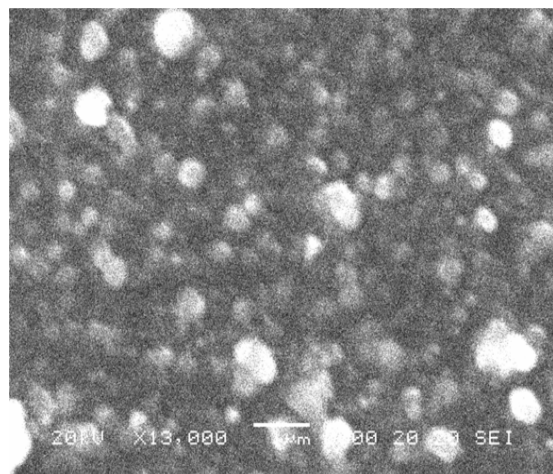


Fig. 1. SEM image of as-deposited PbSe thin film

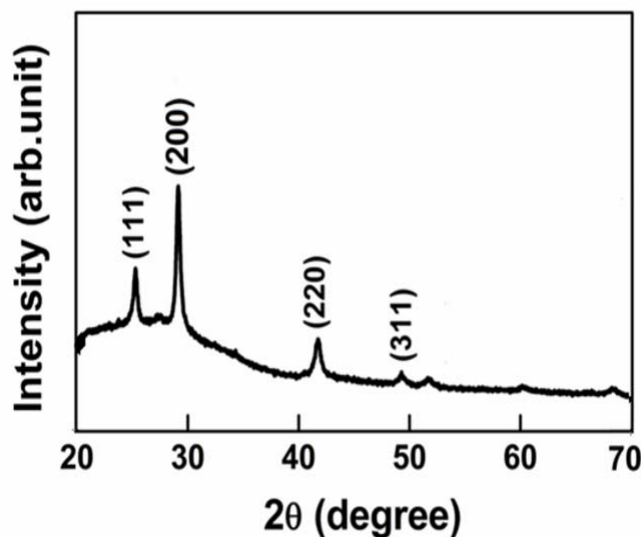


Fig. 2. XRD pattern of as-deposited PbSe thin film

Fig. 2 shows X-ray diffraction pattern of as-deposited PbSe nanoparticles. The XRD peaks indicate that the film is polycrystalline in nature. The 2θ peaks at 25.25° , 29.23° , and 41.81° correspond to reflections from (111), (200), and (220) planes, respectively. The (200) plane is the preferred orientation, and it is the close-packing direction of the zinc-blend structure of cubic PbSe phase (JCPDS Card No.78-1902). Crystallite size (D) of the film was calculated using Scherrer's formula [13] from the full width at half maximum (β) of the peaks expressed in radians,

$$D = \frac{K \lambda}{\beta \cos \theta} \quad (1)$$

where 'K' is constant dependent on crystallite shape (0.89), ' λ ' is wavelength of $\text{CuK}_{\alpha 1}$ radiation, and ' θ ' is angle between the incident and scattered X-ray. The average crystallite size (derived from Fig. 2) is found to be ~20 nm.

Optical studies

Fig.3 shows transmittance and absorbance spectra obtained from as-deposited PbSe thin film. The optical transmittance of over 60% is noted in the visible region. The relation between the absorption coefficient α and the incident photon energy ($h\nu$) can be written as [13],

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where 'A' is constant, $n = \frac{1}{2}$ for direct allowed transition, ' E_g ' is optical band gap of the material. Fig. 4 shows the plot of $(\alpha h\nu)^2$ against ($h\nu$) for PbSe thin film derived from the absorbance spectra. Extrapolating the straight-line portion of the plot of $(\alpha h\nu)^2$ vs ($h\nu$) for zero absorption coefficient value gives the band gap, which is found to be 1.23 eV at room temperature. The energy band gap increases by decreasing crystallite size.

Fig.3. Plot of absorbance and transmittance versus wavelength

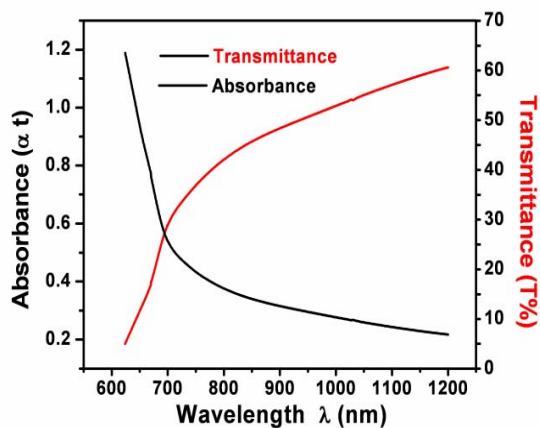
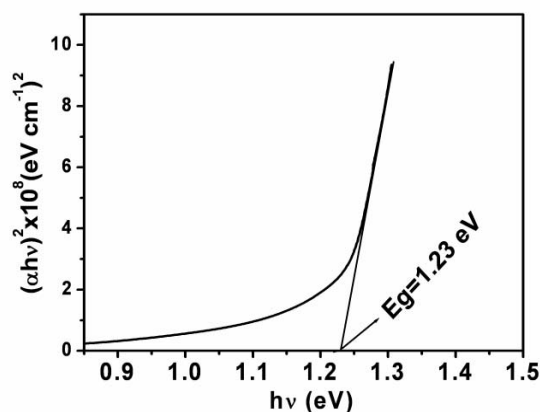


Fig.4. Plot of $(\alpha h\nu)^2$ versus ($h\nu$) obtained from as-deposited PbSe thin film



Conclusion

CBD, a novel and simple method was used to prepare PbSe thin film. The deposition is uncomplicated, environmentally friendly and economical. It increases the utilization efficiency of chemicals, simplifies the experimental process, and reduces cost. Structural, surface morphological and optical properties study reveals that the PbSe thin film can be suitably employed in window layer for solar cell.



Acknowledgement

We are thankful to Dr. Kalhapur G.B., Principal, Arts, Commerce and Science College, Sonai for providing laboratory facilities.

References:

- [1] A.M Samoylov., M.K Sharov., S.A Buchnev., A.M., Khoviev and E.A Dolgoplova., *J. Cryst. Growth*, **240**, 340-346, (2002).
- [2] A. Begum, A. Hussain and A. Rahman, , Beilstein J. Nanotechnol., **3**,438-443, (2012).
- [3] W. Feng, X. Wang, H. Zhou, F. Chen, *Vacuum*, **109**,108-111, (2014).
- [4] F.Hetsch, N. Zhao, S. V. Kershaw, L. A. Rogach, *Materials Today*, **16(9)**, 312-325, (2013).
- [5] E. Theocharous, *Infrared Phys. Technol.* , **50 (1)**, 63-69, (2007).
- [6] M.M. Ibrahim, S.A. Saleh, , E.M.M. Ibrahim, A.M. Abdel Hakeem, *J. Alloys Compd.*, **452(2)**, 200-404, (2008).
- [7] Y.A. Ivanova, D.K. Ivanou, E.A. Streltsov, *Electrochim. Acta.*, **53 (15)**, 5051-5057, (2008).
- [8] M. A. Mahdy, I. A. Mahdy, E.A. Mahmoud, *Physica E*, **59**, 117-123, (2014).
- [9] H.M. Ali, S.A. Saleh, *Thin Solid Films*, **556**, 552-559, (2014).
- [10] E. B. Salgado, M.T.S. Nair, P.K. Nair, R. A. Zingaro, *Thin Solid Films*, **519(21)**, 7432-7437, (2011).
- [11] H. K. Sadekar, A. V. Ghule, R. Sharma, *Composites Part B*, **44**, 553-557, (2013).
- [12] I. Grozdanov, M. Najdoski, S.K. Dey, *Mater. Lett.*, **38,28-32**, (1999).
- [13] H.K. Sadekar, N.G. Deshpande, Y.G. Gudage, A. Ghosh, S.D. Chavhan , S.R. Gosavi, R. Sharma, *J. Alloys Compd.*, **453(1-2)**, 519-524, (2008).