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Temperature Dependence of Optical Properties of Pbse Thin Films

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Abstract: *Lead Selenide (PbSe) thin films have been deposited on glass substrates (25.4mm x 76.2mm x 1.0mm) by Chemical Bath Deposition (CBD) technique. All the chemicals used were of Analytical Grade.Pb $(NO_3)_2$, Na_2SeSo_3, $[C_3H_4\ (OH)\ COONa]_3$. H_2O and NaOH as complexing agents, were used for the deposition and the deposited films were annealed at temperatures of 373K and 473K. The influence of the annealing temperature on the optical properties of the films was investigated. The structure and morphology of the films were obtained by XRD and SEM which revealed that, the films are polycrystalline in nature. UV/VIS spectrophotometer was used for the optical studies and it was found that, the annealed sample films have low transmittance with increasing temperature and wavelength, while, they absorbed higher with increasing temperature and wavelength. Hence, both sample recorded low reflectance. Hence, energy band gap of 0.29eV to 0.27eV was recorded for the films annealed at 373K and 473K respectively. This confirmed the potential of the films for application in fabrication of solar cells, window screens as well as anti-reflection coatings.*
Keywords: *PbSe films, Chemical bath deposition, annealing temperature, optical properties, solar cells.*

I. Introduction

For the past years, the IV-VI Compound Semiconductor thin films [e.gPbSe, PbTe, PbS, etc.] have received an intensive attention due to their applications in IR detectors, Photographic plates, Photo resistors, Photo emitters in IR, Lasers, Photovoltaics and Various Optoelectronic devices. Recently, several techniques have been employed by many researchers to obtain Lead Selenide (PbSe) thin films such as Chemical Bath Deposition (CBD) [1]-[5]; Electrodeposition [6]; Electrochemical Atomic Layer Epitaxy [7]; Photochemical [8]; Molecular Beam Epitaxy [9]; Pulsed Laser Deposition [10]; Vacuum Evaporation [11] and Thermal Evaporation [12-[13]. The Chemical Bath Deposition (CBD) technique has become popular in recent decades especially because of its simplicity, it does not require expensive and sophisticated equipment, it is very easy to handle and it applied to many compounds such as Sulphides, Oxides and Selenides [14]-[17]. In this paper, thin films of Lead Selenide (PbSe) were deposited onto glass substrates by Chemical Bath Deposition (CBD) technique. The films were characterized for their Optical properties and their possible application in solar device technology.

II. Materials and Methods

Lead Selenide (PbSe) thin films were deposited onto cleaned glass substrates using Chemical Bath Deposition (CBD) technique. All the chemicals used were of Analytical Grade. Before the deposition, the substrates were rinsed with distilled water, washed with detergent and then rinsed with distilled water. The substrates were again degreased with ethanol, rinsed with distilled water and then dried in an oven. This process was carried out to ensure clean surface essentially for the formation of nucleation centres that is required for thin film deposition. For the deposition, 10ml (0.5M) Pb $(NO_3)_2$ was dissolved into 6ml (1M) Na_2SeSo_3 followed by the addition of 5ml (1M) $[C_3H_4\ (OH)\ COONa]_3$. H_2O and 5ml (2M) NaOH ascomplexing agents. The resulting solution was made up to 150ml with addition of distilled water and stirred with glass rod stirrer for few seconds. The pH of the reaction mixture was maintained at about 10.5 confirming the alkalinity of the bath. Cleaned glass substrate was inserted into the reaction bath and held vertically in a synthetic foam cover, for 120 minutes. The bath temperature was at 70^{o}C throughout the deposition times. After the deposition, the coated substrates were removed from the bath, rinsed with distilled water, dried in an air, and then annealed in an oven at temperatures of 100^{o}C and 200^{o}C. However, the coated films were characterised for their optical and structural properties using Spectrophotometer, Scanning Electron Microscope and Diffractometer respectively.

III. Theoretical considerations and calculations

Optical:

The transmittance (T) can be calculated from the relationship [18];

$$A = \log\frac{1}{T}(1)$$

Where A is the absorbance and T is given [18]:

$$T = \frac{1}{10^A} \quad (2)$$

The reflectance (R) is calculated from the relation [18];

$$A + R + T = 1 \quad (3)$$

Or

$$R = 1 - (A + T) \quad (4)$$

The absorption coefficient (α) can be calculated from the observed absorbance data using Beer Lanbert'sformular [19] given by;

$$\alpha = 2.303 \left(\frac{A}{d}\right) (5)$$

Where A is the total optical absorbance and d is the thickness of the film.
The photon energy, E, is given [18] by:

$$E = h\nu \quad (6)$$

Where h is the Plank`s Constant and ν is the frequency of the photon.
Similarly,

$$E = \frac{hc}{\lambda} \quad (7)$$

Where c is the speed of light and λ is the wavelength. Substituting for constants in equation (7) gives:

$$E = \frac{12{,}400}{\lambda} eV \quad (8)$$

For semiconductors (where $K^2 << n^2$) there exist a relationship between R and n [20] given by:

$$R = \frac{(n+1)^2}{(n-1)^2} \quad (9)$$

Where R is the reflectance and n is the refractive index.
And the relation between K and α (Pankove, 1971) given by;

$$K = \frac{\alpha\lambda}{4\pi} \quad (10)$$

Also, the relationship existing between R, K and n is given [19] by;

$$n = \left(\frac{1+R}{1-R}\right) = \sqrt{\frac{4R}{(1-R)^2} + K^2} \quad (11)$$

Where n is the refractive index, K is the extinction coefficient and R is the optical reflectance.

Structural:
The crystallite size is calculated using the Debye-Scherer's formular;

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (12)$$

Whereλ is the wavelength of the X-ray = 1.5406Å, β is the half intensity width of the peak (FWHM in radians), 0.9 = K, is the crystallite shape (though varies with (hkl)),θ is the diffraction angle and D is the crystallite size.
The Dislocation density is evaluated using the relation;

$$\delta = \frac{1}{D^2} (13)$$

IV. Results and Discussions

The equation governing the reaction and deposition of PbSe thin films were as follows:

$$Pb(NO)_3 + 2NaOH \xrightarrow{yields} Na_2PbOH^{2+} + 2NO_3 \quad (14)$$

$$Na_2Pb(OH)_2 \xrightarrow{yields} Pb^{2+} + 2NaOH \quad (15)$$

$$Na_2SeSO_3 + OH^- \xrightarrow{yields} HSe^- + Na_2SO_4 \quad (16)$$

$$Pb^{2+} + OH^- + HSe \xrightarrow{yields} PbSe + H_2O \quad (17)$$

The presence of the Pb^{2+} and Se^{2-} ions led to the formation of PbSe

$$Pb^{2+} + Se^{2-} \xrightarrow{yields} PbSe \quad (18)$$

The deposition process is based on the slow release of Pb^{2+} and Se^{2-} ion 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.

Structural:

Fig.1. Shows the X-ray diffraction pattern of the as-deposited sample of the PbSe film in which the pulses (a.u) were plotted against the diffraction angle (2θ). The prominent peaks corresponds to (200), (220) and (111) planes of reflection at different diffraction anglesconfirming clausthalite cubic structure and the presence of large number of peaks indicates the polycrystalline nature of the film [21].

The surface morphology of the as-deposited film is given in Fig.2. From the micrograph, it is seen that the light- grey PbSeadhere very well to the substrate with crystallites scattered randomly on the surface confirming the polycrystalline nature of the film.

Optical:

Fig. 2. Shows the plot of transmittance versus wavelength forPbSe film samples annealed at 373K and 473K. The transmittance of both samples increase with increase in wavelength. The observed transmission spectra showed that, the film samples transmit very low within the UV-VIS regions (2.5μm – 3.35μm) but moderately high in the NIR region for both samples except that the sample annealed at 373K has higher transmittance than the sample annealed at 473K. This indicates that, increase in thermal annealing tends to reduce transmittance in all spectrum of solar light energy as a result of formation of denser films due to water evaporation [22].

The plot of absorbance versus wavelength for the PbSe film samples annealed at 373K and 473K is given in Fig. 3. From the graph, it is observed that the absorbance for both sample films decrease with increasing wavelength and are high within the visible regions. The sample annealed at 473K has the highest absorbance with maximum at 0.67%, 2.5μm wavelength and minimum at 0.35%, 5.0μm wavelength, while the sample annealed at 373K has lowest absorbance with maximum at 0.51%, 2.5μm wavelength and minimum at 0.24%, 5.0μm wavelength. The sample with the highest absorbance has the potential application in fabrication of solar cells.

Fig. 4. Depicts the graph of reflectance versus wavelength of the PbSe thin films annealed at 373K and 473K. Is it observed that the sample film annealed at 473K recorded very low reflectance (0.245%-0.255%) within the wavelength range (2.5 μm-3.25 μm) ,then the reflectance raised sharply to a maximum peak of 0.45% at wavelength of 4.0 μm and then fall to 0.395% at wavelength of 4.95 μm. Whereas, the the sample film annealed at 373K recorded raise in reflectance (0.395%-0.45%) within the wavelength range (2.5 μm-4.0 μm) and then fall to 0.395% at wavelength of 4.95%. Hence, the reflectance increases with annealing temperature.

The absorption coefficient versus the photon energy of the PbSe sample films annealed at 473K and 373K are shown in Fig.5the graph depicts sharp increase in α with increase in energy which characterize the crystalline state of the film. Also, it is observed that, α increases with annealing temperature, which is in agreement with [22].

Fig. 6 shows the optical band gap of PbSe sample films. It is observed that the energy gap decreased from 0.29eV to 0.27eV for the filmsannealed at 373K and 473K respectively. The decrease in the energy band with increase in annealing temperature could possibly be due to the decrease in the number of defects, evaporation of water molecules offthe film, reorganisation of the film (that is, filling the voids in the film which results in denser films and lower energy gaps) and self-oxidation [23].

The plot of refractive index versus photon energy of the PbSe sample films annealed at 373K and 473K is shown in Fig. 7. From the graph it is observed that both sample films exhibited a sharp increase in refractive index within the energy range 0.250eV-0.335eV and the refractive index then, begin to decrease with increase in photon energy to 0.495eV.The highest value of refractive index was recorded by the filmannealed at 473K, that is, 5.48 at 0.31eV.

Fig.8 shows the Extinction coefficient as function of photon energy of the PbSe samples films annealed at 473K and 373K from the plot it is observed that the film annealed at 473K has the highest value of 0.535 at 0.379eV and lowest value of 0.425 at 0.31eV. While the sample annealed at 373K recorded its highest value of 0.395 at energies of 0.335eV to 0.385eV.

V. Conclusion

Thin films of Lead Selenide were deposited successfully using the Chemical Bath Deposition Technique and the effect of annealing temperature on the optical properties of the film was investigated. The XRD pattern and the SEM micrograph of the sample reveals the polycrystalline nature of the film. The annealed sample films were found to have low transmittance with increasing temperature and wavelength, while, they absorb higher with increasing temperature and wavelength. Hence, both sample recorded low reflectance.This confirms the potential of the films for application in fabrication of solar cells, window screens as well as anti-reflection coatings.

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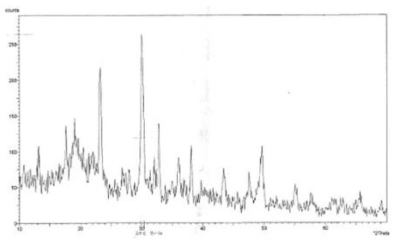

FIG.1. XRD pattern of the as-deposited PbSe film

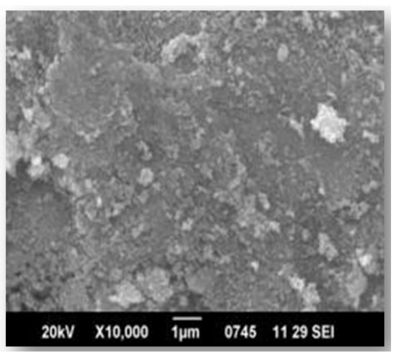

FIG. 2: Scanning Electron Micrograph of as-deposited PbSe film.

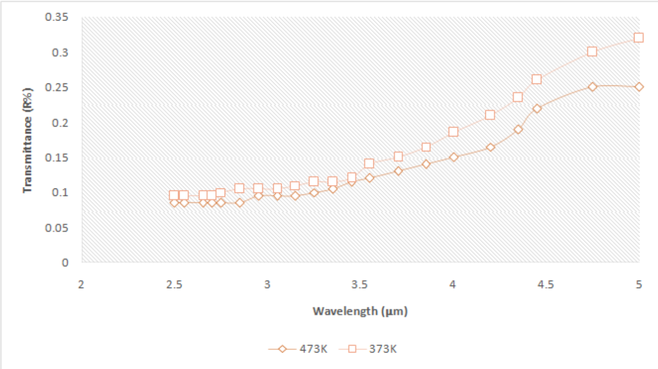

FIG. 3: Transmittance Vs Wavelength of PbSe thin films annealed at temperatures of 473K and 373K.

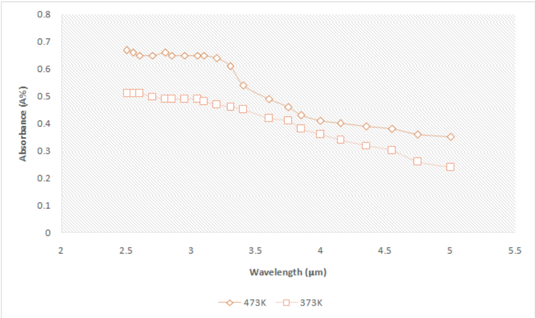

FIG. 4: Absorbance Vs Wavelength of PbSe thin films annealed at temperatures of 473K and 373K.

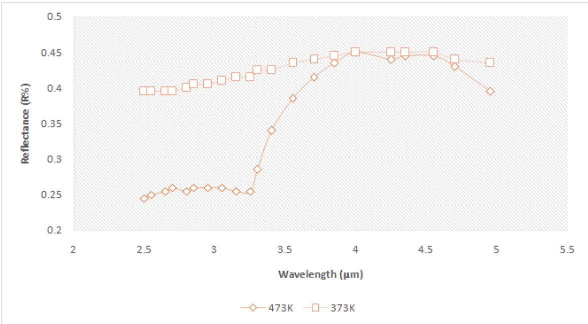

FIG. 5: Reflectance Vs Wavelength of PbSe thin films annealed at temperatures 473K and 373K.

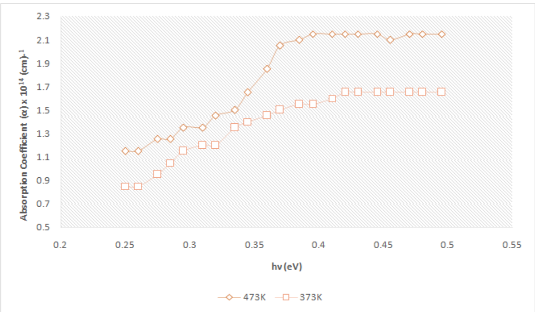

FIG. 6: Absorption Coefficient Vs Energy of PbSe thin films at temperatures of 473K and 373K.

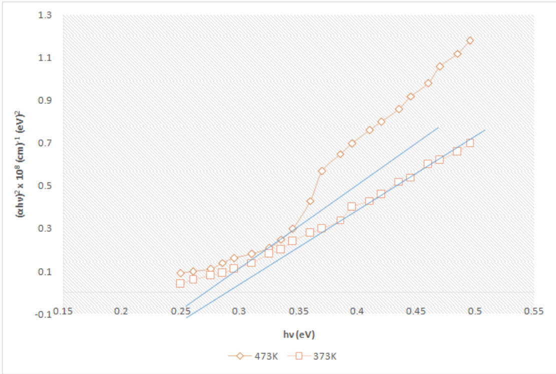

FIG. 7: Band gap (E_g) estimation for PbSe thin films annealed at temperatures of 473K and 373K.

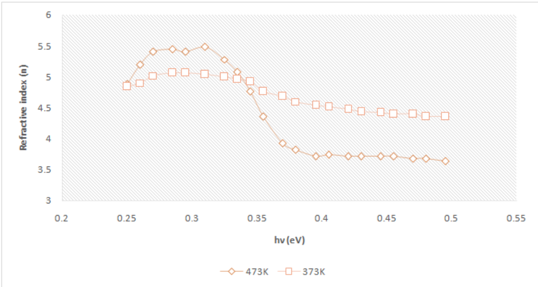

FIG. 8: Refractive index Vs Energy of PbSe thin films annealed at temperatures of 473K and 373K.

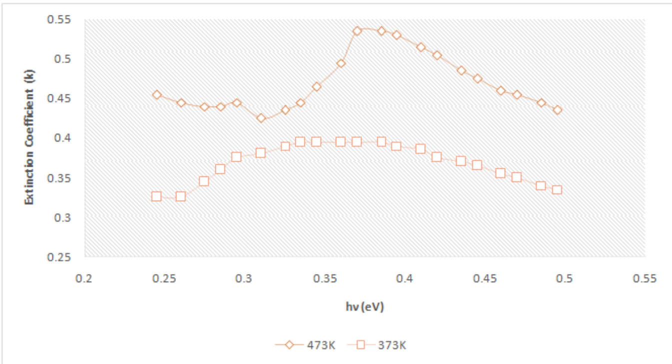

FIG.9: Extinction Coefficient Vs Energy of PbSe thin films annealed at temperatures of 473K and 373K.