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PROPERTIES OF LEAD SELENIDE FILMS DEPOSITED BY CHEMICAL BATH METHOD

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Lead Selenide (PbSe) thin films were deposited on glass substrates by Chemical Bath Deposition (CBD) method within the pores of polyvinyl alcohol (PVA) at 60°C. The bath for the film deposition was composed of lead nitrate, the source of the anion, sodium citrate, the enhancing agent, sodium hydroxide, the complexing agent, sodium selenosulphate, the source of the cation and PVA solution. The deposited films were annealed in the oven at temperatures of between 100°C and 300°C and characterized for the optical, composition, surface morphology and structural properties. These properties were studied by means of x-ray diffraction (XRD), Rutherford backscattering (RBS) and optical absorption measurements. The value of the optical band gap energy, E_g, calculated from the absorption spectra ranged between 2.25 and 2.50 eV. The results shows that high temperature annealing has significant effect on both the optical and solid-state properties of the films.

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1. Introduction

Polymer capped inorganic thin film is the focus of many research groups [1–5] due to their enhanced optical and electronic properties. For example, CdSe-polymer composites can be used to make blue light emitters [1]. Silver nanoparticles have been incorporated in the polyvinyl alcohol matrix in order to improve its properties such as higher glass transition temperature and elastic modulus than only PVA [2]. Pattabi et al [4] prepared PVA capped CdS nanoparticles which showed better photoluminescence property. Nanocrystalline thin films are also polycrystalline in nature but with sizes of crystallites of the order of a few nanometers. Extensive literature on size reduction effect is available [6-9]. Thin film deposition carried out within the pores of PVA is an effective means of modifying the sizes of the crystallites [6,7,10]. PbSe is an important binary IV – VI semiconductor material with a narrow band gap at room temperature. The band gap can be blue shifted from the near infrared to the visible region by forming nanocrystallites.

The CBD method for metal chalcogenide thin film preparation attractied considerable attention, as it is relatively less expensive, simple and convenient for large area deposition. A variety of substrates such as insulators, semiconductors or metals can be used, since it is a low temperature process. The basic principle of CBD method has been already reported [11 – 14]

2. Experimental details

The chemical bath used for the preparation of the thin films in PVA matrix in this work was prepared in the following manner. First the PVA solution was prepared by adding 900 ml of distilled water to 1.8g of solid PVA $(-C_2H_4O)_n$ (where n=1700), and stirred by a magnetic stirrer at

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90^{o}C for 1hour. The temperature of the resulting homogenous solution was allowed to drop down to 25^{o}C. The PbSe films were grown on glass substrate from an alkaline bath at a temperature 60^{o}C. The films were prepared by dipping previously cleaned glass substrates in a mixture of solution of (1M) lead nitrate, (1M) sodium citrate, (2M) sodium hydroxide, (1M) sodium selenosulphate and PVA solution. The substrates were vertically immersed into the solution and supported on the walls of the beaker. The substrates were taken out of the beaker after 6hrs, rinsed with distilled water and allowed to dry. The films were annealed in the oven for 1 hour at temperatures of between 100 and 300^{o}C and labelled A(as-grown), B(annealed at 100^{o}C), C (annealed at 200^{o}C) and D (annealed at 300).

The chemical reaction for the deposition of PbS by CBD is given by

$$Pb(NO_3)_2 + 4NaOH \leftrightarrow Na_2[Pb(OH)_4] + 2NaNO_3$$
$$Na_2[Pb(OH)_4] \leftrightarrow Pb^{2+} + 2NaOH + 2OH^-$$
$$Na_2SeSO_3 + OH^- \leftrightarrow HSe^- + Na_2SO_4$$
$$Hse^- + OH^- \leftrightarrow Se^{2-} + H_2O$$
$$Pb^{2+} + Se^{2-} \leftrightarrow PbSe$$

The structures of the films were studied with optical microscope and Philips PW 1500 XRD. The composition of the films was determined by using Rutherford back scattering. The absorption coefficient (α) and the band gap of the films were determined by using the absorbance and transmittance measurement from Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1000nm.

3. Results and analysis

3.1 X-ray diffraction study

Typical XRD diffractograms of CBD PbSe thin film is presented in fig. 1. The samples were grounded to below 100 mesh in an agate mortar and then loaded into a 2.5cm diameter circular cavity holder and ran on an MD 10 mini diffractometer. CuKα was selected by a diffracted beam monochromator. The thin films were scanned continuously between 0 to 75 at a step size of 0.03 and at a time per step of 0.15s. Phase identification was then made from an analysis of intensity of peak versus 2θ.

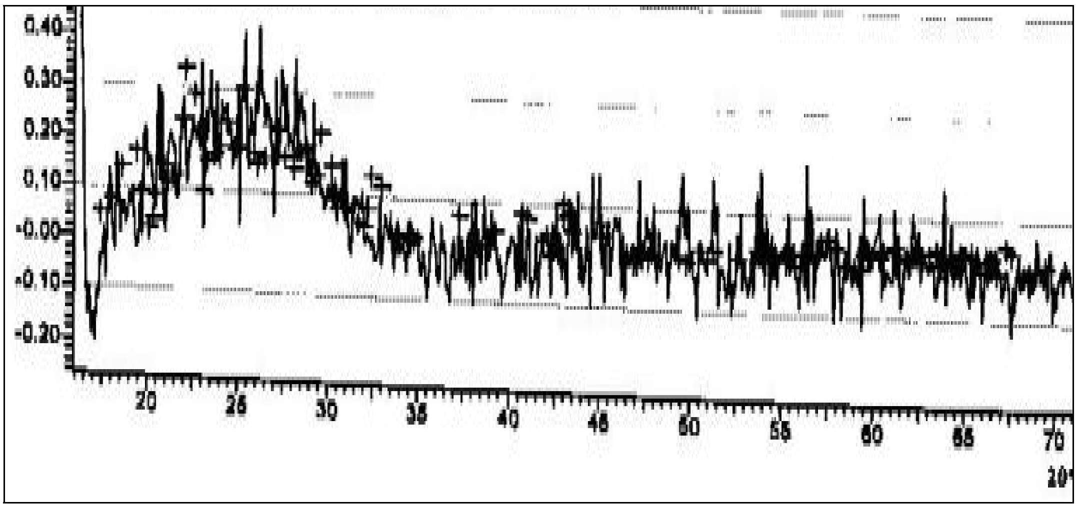
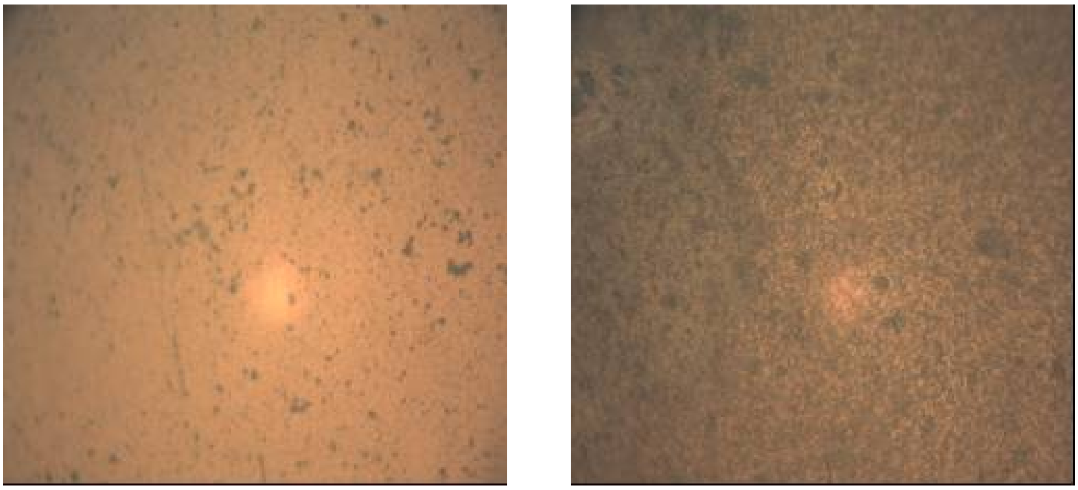


Fig. 1. XRD pattern of PbSe thin film annealed at 200 ^{o}C

The pattern for the thin film of PbSe displayed diffraction peaks at 2θ values of approximately 29.1^{o} and 66.4^{o}, corresponding to (200) and (331) planes respectively.

3.2 Photomicrography study

The surface microstructure of the films were obtained by taking the photomicrographs of the films coated on the glass slides with wide KPL-W10x/ 18 Zeiss Standard 14 photomicroscope with M35 4760+2-9901 camera at a magnification of X200. The photomicrographs of the films are displayed in figures 2a and 2b. A close observation of the optical micrographs of PbSe films shows that homogeneity and crystallinity of the films increased with post deposition annealing.



(a) *(b)*

Fig.2: Photomicrograph of PbSe thin films annealed at (a) 100^{o}C and (b) 300^{o}C

3.3 Composition Study

The elemental composition and chemical state of the films annealed at 200^{o}C was analysed by Rutherford Backscattering (RBS) at Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife. The results are presented in fig. 3. From the film composition presented in fig. 3, we can deduce that PbSe thin film deposited in this work has no impurity content.

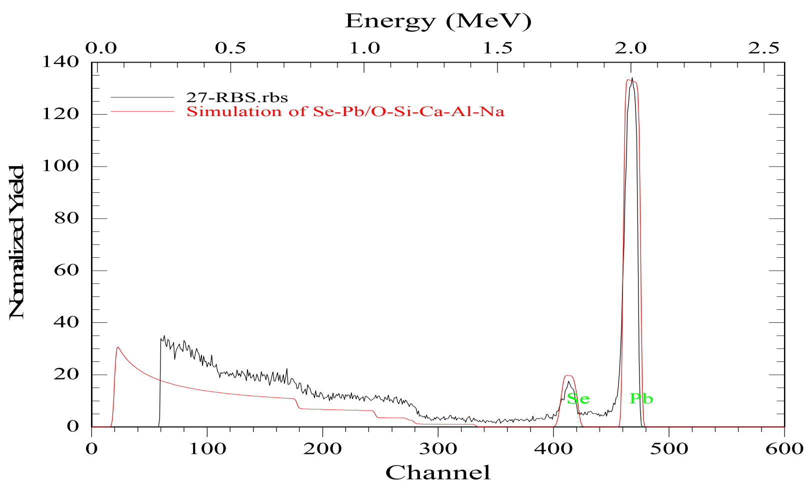


Fig. 3. RBS result for PbSe thin film annealed at 200^{o}C.

3.4 Optical Studies

3.4.1 Variation of the absorbance, transmittance and reflectance of the films with wavelength

Figs. 4 and 5 are plots of absorbance vs. wavelength and transmittance vs. wavelength for PbSe thin films deposited in this work. From fig. 4, we can deduce that thin films of PbSe absorb fairly well in the visible region of the solar spectrum. The figure shows similar trend in the absorbance of the films as wavelength increases, with the unannealed film having lower absorbance at any specific wavelength.

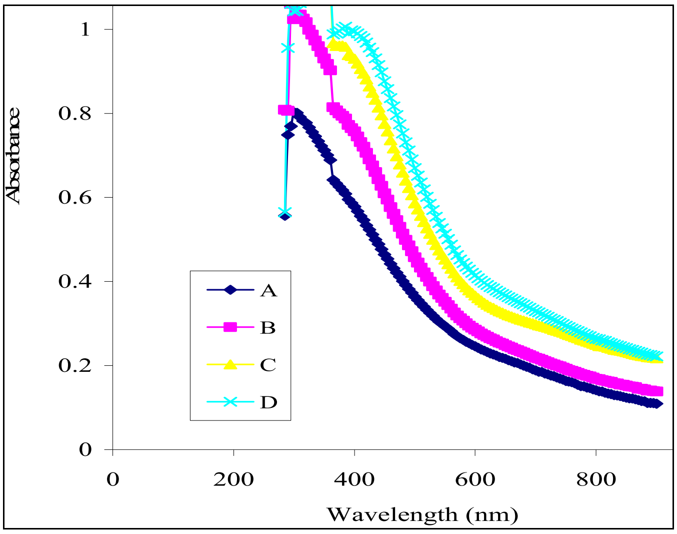


Fig.4. Absorbance vs. wavelength for PbSe thin films annealed at different temperatures.

The spectral dependence of transmittance as a function of wavelength for as-grown and annealed films of PbSe thin films with different annealing temperature were also studied (fig.5). Table 1 gives the values of the transmittance of the films at some specified wavelengths. The table shows that the transparency of PbSe thin films varies from 11.74 – 64.78% in the visible and 54.51 – 77.80% in the NIR region of the solar spectrum. Within each wavelength, the transparency decreases as the annealing temperature increases.

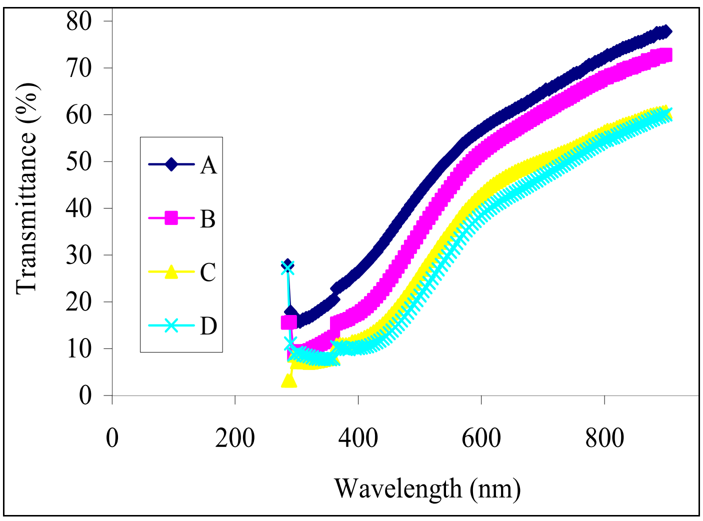


Fig. 5. Transmittance vs. wavelength for PbSe thin films annealed at different temperature.

Table 1. Percentage transmittance of PbSe thin films in the wavelength range of 300-900 nm.

Sample label	300 nm	400 nm	500 nm	600 nm	700 nm	800 nm	900 nm
A(as-deposited)	15.73	26.42	43.30	56.75	64.78	72.19	77.80
B(annealed at 100°C)	9.46	17.49	34.87	51.82	60.46	67.84	72.77
C(annealed at 200°C)	7.12	11.74	25.94	43.00	50.35	56.36	60.60
D(annealed at 300°C)	9.06	10.10	21.37	38.50	46.82	54.51	60.04

Fig. 6 shows the spectral reflectance against wavelength for PbSe thin films deposited in this work. The figure shows that the reflectance of the film increases rapidly with wavelength up till a maximum value in the wavelength range of 450 – 650 nm. However, the reflectance is in general less than 20% and shows a trend, which decreases with annealing temperature.

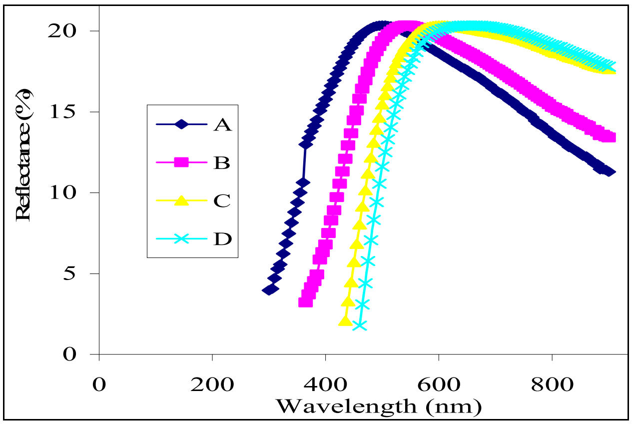


Fig.6. Reflectance vs. wavelength for PbSe thin films annealed at different temperature.

The application of solar energy as a source of heat in chick brooding requires thin films with high transmittance in the NIR with moderate reflectance. The property of high transmittance in the NIR exhibited by the films therefore makes them good materials for the construction of poultry roofs and walls. This has the potential to minimize the cost of energy consumption associated with the use of electric bulbs, heater, stove etc and the hazards associated with them, while at the same time protecting the chicks from UV radiation.

3.4.2 The absorption coefficient and optical band gap energy

The details of the mathematical determination of the absorption coefficient (α) can be found in literature [7, 8] while the plots of absorption coefficient against photon energy is shown in fig.7. These absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap, E_g. The optical band gap E_g was calculated using Tauc's plot ($(\alpha h\nu)^2$ vs. $h\nu$)[9, 10] as shown in fig. 8. The value of α is determined from transmittance spectra. The photon energy at the point where $(\alpha h\nu)^2$ is zero represents E_g, which is determined by extrapolation. The values obtain for PbSe thin film lie in the range of 2.25 - 2.50eV.

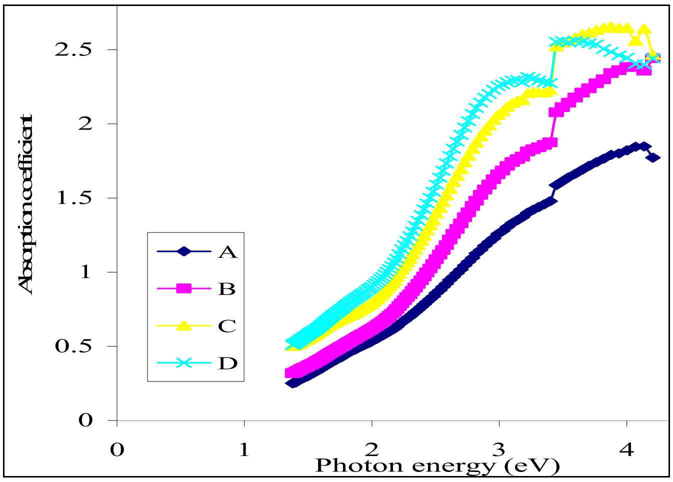


Fig.7. Absorption coefficient vs. photon energy for PbSe thin films annealed at different temperatures.

A close observation of fig. 8 shows that the energy gap decreased from 2.50 to 2.25eV for the samples annealed in the oven for 1 hour. This is possibly due to the decrease in the number of defects, evaporation of water molecules off the film and reorganization of the films. The temperature dependence parameters that affect the band gap are reorganization of the film and self-oxidation [15]. The reorganization of the film should occur at all annealing temperature. By filling the voids in the film one expects denser films and lower energy gaps.

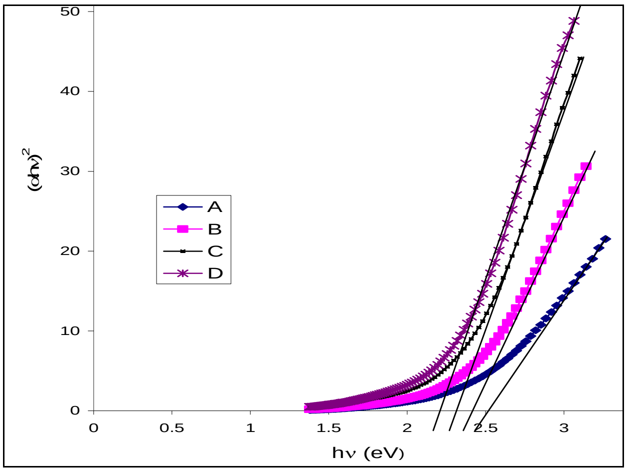


Fig. 8. Direct band gap plot for PbSe thin films annealed at different temperature.

3.4.3 Other properties

The average values of other optical and solid-state properties studied in this work are summarized in table 2. These values were obtained from figures 9, 10, 11 and 12.

Table 2. Average optical properties for PbSe thin film.

Sample label	n	K	ε_r	ε_i
A	1.91	29.57	3.72	113.00
B	1.82	36.66	3.51	126.56
C	1.78	47.79	3.58	155.94
D	1.73	51.78	3.43	163.03

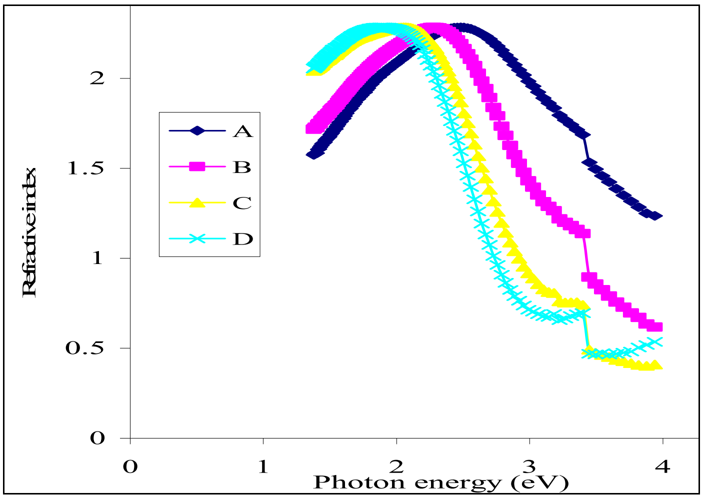


Fig. 9. Refractive index vs. photon energy for PbSe thin films annealed at different temperatures.

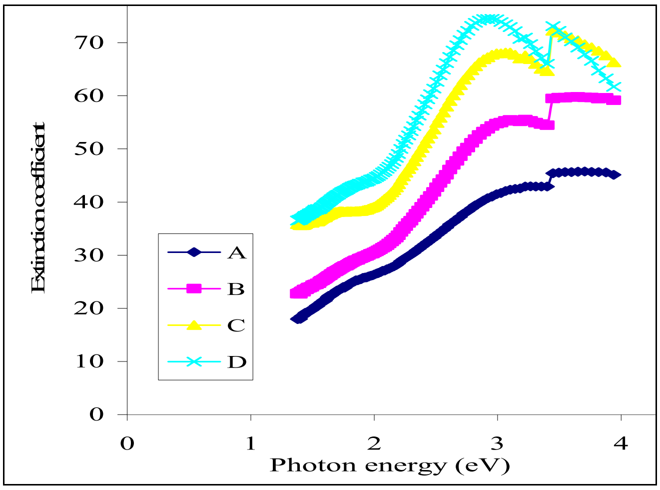


Fig.10. Extinction coefficient vs. photon energy for PbSe thin films annealed at different temperatures

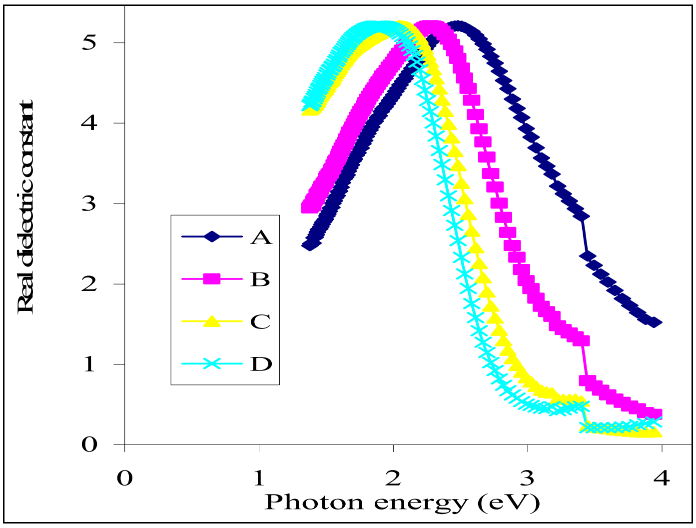


Fig.11. Real dielectric constant vs. photon energy for PbSe thin films annealed at different temperatures.

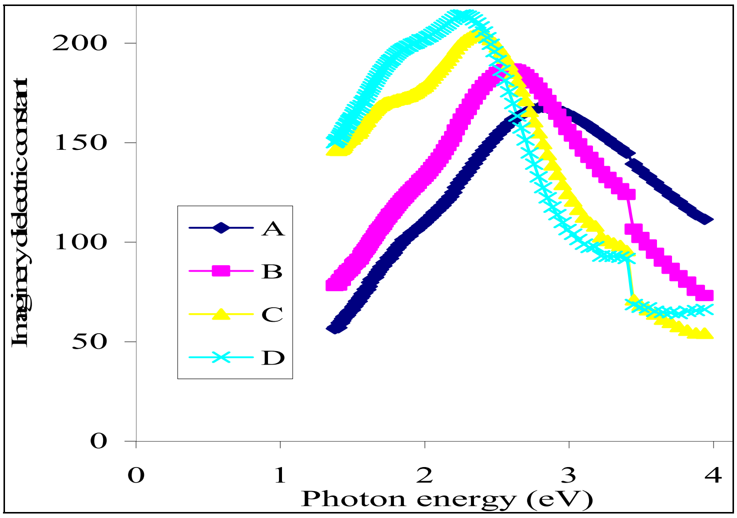


Fig.12. Imaginary dielectric constant vs. photon energy for PbSe thin films annealed at different temperatures.

5. Conclusions

PbSe thin films have been successfully deposited onto glass slide using chemical bath deposition technique. The optical studies showed that the films have good absorption in the visible spectrum of solar radiation. The absorbance decreased with wavelength from 350 nm up to 700 nm. The properties of high absorbance in the VIS and wide band gap energy exhibited by the films make them suitable as window layers for solar cell application.

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