

ORIGINAL ARTICLE

Impurity Effects of Cadmium Ions on the Fundamental Absorption Edge and Structure of Chemically Prepared Binary PbS Films

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ABSTRACT

Thin films of PbS were prepared with varying concentrations of cadmium ion impurities from chemical bath, and annealed at 373K for 1 hour. The presence of nanocrystals was evidenced by broadening of XRD diffraction peaks. Crystallite sizes of the films were observed to change with concentration of cadmium ions, as estimated using Sherrers' formula. Microstructures of the films showed varied polycrystalline structures that depended on the impurity concentrations. The fundamental absorption edges of the films indicated strong blue shifts in both the direct and indirect allowed transition energy band gaps when compared with the band gaps reported earlier for pure PbS thin films. These shifts can be attributed to enhancement of the crystallites by cadmium ions, which resulted in the modifications of the fundamental absorption edges of the films.

Key words: PbS thin films, Cd ions, fundamental absorption edge, band gap and crystallite size.

Introduction

Recently, the preparation of lead sulphide (PbS) thin films has attracted much attention due to their potential applications in photonic systems. Infact the synthesis of binary metal chalcogenides of group II-VI semiconductors in nanocrystalline form has experienced an enormous development in the recent years owing to their interesting size dependent optical and electrical properties (Hodes, 2003; Woggon, 1997). PbS thin film is known to be a narrow direct transition band gap semiconductor. Exploring the behaviour of semiconductors and insulators is of fundamental importance in the study of their band structures. A direct transition occurs when the lowest energy state in the conduction band has the same value of wave vector as the highest energy state in the valence band, otherwise indirect transition results (Kittel, 1966). At room temperature, PbS films are known to exhibit direct energy band gap of approximately 0.37-0.4eV (Pankove, 1971).

The material properties of chemically deposited thin film PbS are known to depend strongly on the deposition conditions (Valenzuela-Jauregui *et al.*, 2003). By chemical bath deposition (CBD) technique, the dimensions of the crystallites can be varied by controlling the deposition parameters such as deposition temperature, pH, reaction time, and presence of impurities in the solution bath (Pentia *et al.*, 2001).

In this paper, we investigated the effects of introducing cadmium ions in PbS thin films deposition bath, on the fundamental absorption edge and structures of the PbS thin films. The studies looked at the energy band gaps, microstructures, and crystallite sizes of the resulting thin films.

Experimental:

The chemicals in the reaction bath for the deposition of PbS thin films consist of lead acetate [Pb(CH₃COO)₂·3H₂O], thiourea [(H₂N)₂CS], sodium hydroxide (NaOH), triethanolamine (TEA) and distilled

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water. The source of cadmium ions was aqueous cadmium chloride ($\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$). All reagents used were of analytical grade. The volumetric composition of the bath was obtained as follows: 1ml of varying concentrations (0.1, 0.5, 1.0M) of $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ were prior mixed with 2.5ml of 0.5M lead acetate, poured into a 50ml beaker and stirred. Then 4.0ml of 2M sodium hydroxide was added to the bath and then stirred to obtain a milky solution. To this was added 3ml of 1M thiourea, followed by 1ml of 1M TEA. The resulting solution was thoroughly mixed and stirred. Finally, 35ml of distilled water was added to make up the bath solution, while stirring continued. Cleansed glass substrate was then inserted vertically into the beaker, and the bath was left undisturbed for 3 hours at room temperature (300K). The resulting films were then annealed in an electric oven at 373K for 1 hour.

The absorption spectra (A) of the deposited thin films were recorded with a double beam (Pye-Unico UV-2102 PC) spectrophotometer. Absorbance of the films was determined in the ultraviolet, visible, and near infrared regions of the electromagnetic spectrum.

Theory: The transmittance is the ratio of the transmitted flux I to the incident flux I_0 .

$$T = I / I_0 \quad (1)$$

But absorbance (A) is defined as:

$$A = \log_{10} I_0 / I \quad (2)$$

Therefore;

$$A = \log_{10} 1/T \quad (3)$$

From equation (3), the transmittance can be written as:

$$T = 10^{-A} \quad (4)$$

The Absorption Coefficient of the thin film is the fractional decrease in intensity per unit increase in distance (Ezekoye, 2003). When a beam of electromagnetic radiation is incident on a thin film surface, then,

$$I_0 / I = e^{at} \quad (5)$$

where t, is the distance traversed by the radiation. From equation 1, equation (5). becomes;

$$1/T = e^{at} \quad (6)$$

Taking the natural logarithm of equation (6) we obtain;

$$\ln 1/T = at \quad (7)$$

For a unit distance, equation (7) becomes;

$$a = \ln (1/T) \quad (8)$$

Equation (8) was used to deduce the absorption coefficient of the thin films.

The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band (Gosh *et al.*, 2005), can be used to determine the nature and value of the optical energy band gap. The relationship between the fundamental absorption coefficient (α) and incident photon energy ($h\nu$) can be written as (Gosh *et al.*, 2006; Ezema *et al.*, 2006).

$$(ah\nu)^{1/n} = A (h\nu - E_g) \quad (9)$$

where A is a constant, h is the planck's constant and n is also a constant, which depends on the type of transition. For direct allowed transition $n = 2$, for indirect allowed transition $n = \frac{1}{2}$.

To determine the possible transitions, $(ah\nu)^{1/n}$ versus $(h\nu)$ was plotted. The corresponding band gap energies were obtained from extrapolating the straight portion of the graphs on the $h\nu$ axis at

$$(ah\nu)^{1/n} = 0; \text{ (Eya, 2006).} \quad (10)$$

XRD technique was used to ascertain a wide variety of structural information including; crystal interatomic spacing, Bragg diffraction angle, and crystallite size of the deposited films. The XRD patterns were obtained using a mini- diffractometer (model MD-10) using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056\text{\AA}$) in the 2θ scanning mode. To determine the crystallite sizes of the films, the well known Sherrers' formula was applied (Valenzuela-Jauregui *et al.*, 2003; Eya, 2006).

$$D = K\lambda / \beta \cos \theta \quad (11)$$

where, D = crystallite size, k = constant = 0.9, λ = wavelength of the X-ray source, θ = Bragg's diffraction angle in degrees, β = Full-Width-at-Half-Maximum (FWHM). The thin film surface microstructure was obtained by the use of optical microscope (Olympics BH) attached to an Olympics digital camera (Model C – 4040 zoom).

Results and Discussions

The X-ray diffraction patterns (diffractographs) of all the samples (figures 1, 2 and 3) showed diffraction peaks corresponding to certain Bragg's diffraction angles 2θ . Some of these peaks exhibited by the samples are broad peaks, but the prominent diffraction peak in the thin film samples is approximately at $2\theta - 28^\circ$. This corresponds to (200) reflections, which is the crystal preferred orientation for PbS (Eya, 2006).

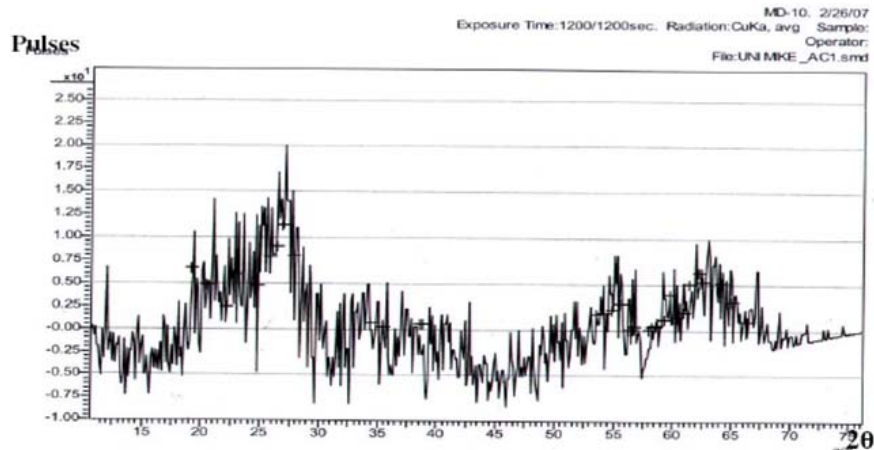


Fig. 1: XRD of PbS films deposited with 0.5M Cadmium ion.

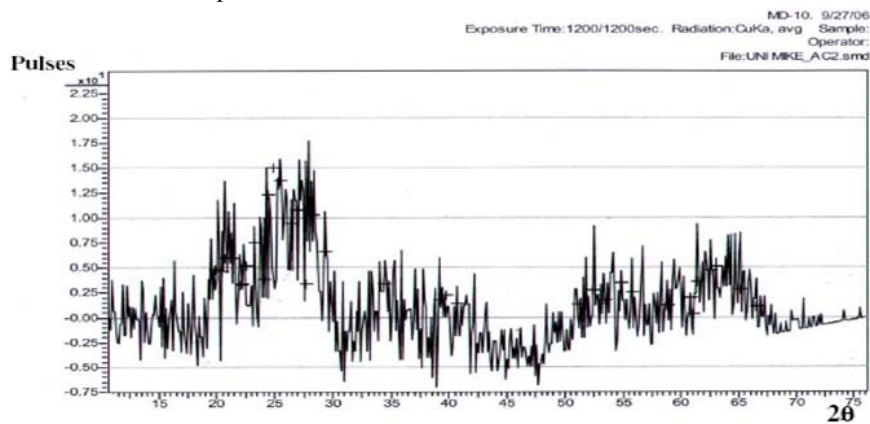


Fig. 2: XRD of PbS films deposited with 0.1M Cadmium ion.

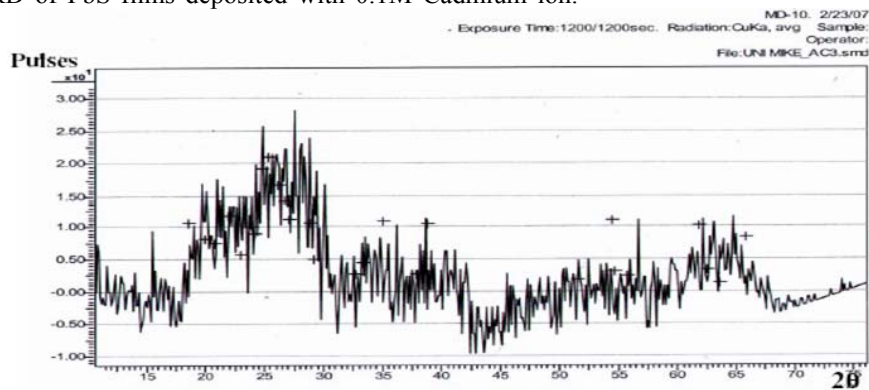


Fig. 3: XRD of PbS films deposited with 0.05M Cadmium ion.

Other observed peaks can be attributed to the contribution of the impurity ions introduced into the PbS deposition bath. The presence of broad crystal diffraction peaks indicate that the thin films deposited on the substrates are of nano-sizes (Gosh *et al.*, 2005; Oladeji and Chow, 2005). Nanocrystalline thin films are of significant interest for a large variety of electronic and optoelectronic devices (Popa *et al.*, 2006; Mehta *et al.*, 2007). The thin film samples exhibited varied polycrystalline and not well defined structural arrangement (figs. 4a, b, and c).

The depositions process of PbS films with varying concentrations (0.5M, 0.1M, 0.05M) of cadmium impurity ions were carried out at room temperatures (about 300K). The influence of cadmium impurity can be observed in the absorption and transmission of the thin films in figs.5 and 6. PbS thin films deposited with 0.5M cadmium ion showed peak absorption 0.84 of incident electromagnetic radiation which corresponds to wavelength of about 497nm. PbS thin films deposited with 0.1M cadmium ion showed peak absorption 0.94 of incident electromagnetic radiation which corresponds to wavelength of about 559nm. With impurity

concentration of 0.01M Cadmium ion, the absorption of incidence radiation was 0.93 at 467nm, all in the visible region of the electromagnetic spectrum. PbS films deposited with 0.5M, 0.1M, and 0.05M cadmium ions exhibited peak transmissions of incident electromagnetic radiations of 54%, 58%, and 56% respectively in the near infrared spectral regime.

Fig.7 represents the plot of absorption coefficient (α) against incident photon energy for PbS films deposited with cadmium ions. This is the fractional decrease in intensity of electromagnetic radiation as it travels on these films.

Table 2 shows the average values of the films absorption coefficient. The value of absorption coefficient was slightly optimal ($1.380 \times 10^6 \text{m}^{-1}$) when the cadmium impurity concentration is minimal (0.05M). The direct transition band gaps (E_g^d) (fig.8) and the indirect transition energy band gaps (E_g^i) (fig.9) were due fundamental absorption between the valence and conduction band. PbS is a semi conductor with band gap of approximately 0.37eV - 0.41eV (Pankove, 1971; Kanazawa *et al.*, 1998) at room temperature, and 0.29eV at liquid nitrogen temperature (Pentia *et al.*, 2001). Direct and indirect allowed transition band gaps of 1.10eV and 2.44eV respectively, were recently reported (Oriaku *et al.*, 2008), for optimized PbS films with similar composition and annealed at 373K. It can be seen from table 2, that the presence of Cadmium impurities resulted in strong blue shifts in the energy band gaps of PbS thin films when compared with our earlier report (Oriaku *et al.*, 2008). The reason for these shifts in energy band gap can be attributed to the enhancement of the crystallites by cadmium ions, which in turn coursed the modifications in the fundamental absorption edge of the films (Pentia *et al.*, 2001).

Table1: Crystallographic properties of PbS films deposited with cadmium ions.

Cd ⁺ ion conc (M)	INTERATOMIC DISTANCE (Å°)	FWHM (β)	CRYSTALLITE SIZE, D (nm)
0.50	1.40974	0.49918	0.4707
0.10	3.82747	0.23007	0.6151
0.05	3.72651	0.10616	1.3250

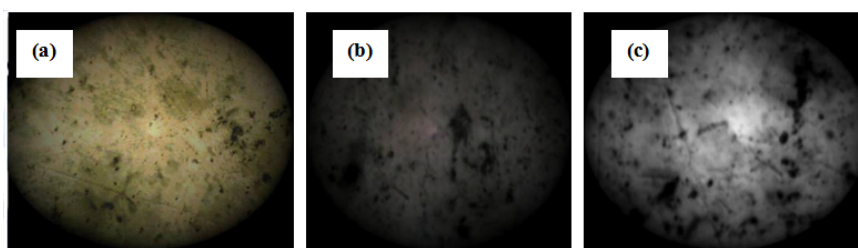


Fig. 4: Micrograph (x400) of PbS deposited with: (a) 0.5M Cd⁺ ions (b) 0.10M Cd⁺ ions (c) 0.05M Cd⁺ ions

Table 2: Average value of absorption coefficient (α) and energy band gaps (E_g) of PbS thin films deposited with varying concentrations of cadmium ions.

Cd ⁺ ion conc (M)	$\alpha(10^6 \text{m}^{-1})$	E_g^d (eV)	E_g^i (eV)
0.50	1.19	0.50	1.60
0.10	1.13	0.91	1.55
0.05	1.38	0.80	1.53

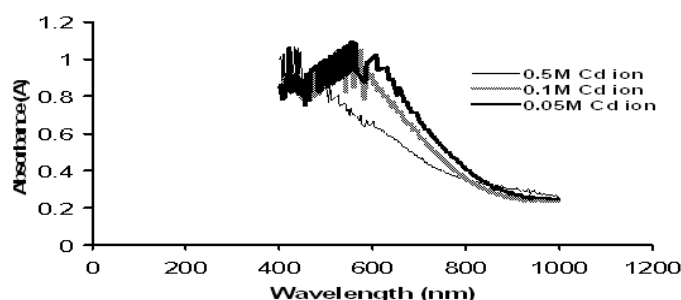


Fig. 5: Absorption spectra of PbS films deposited with Cd ion.

Conclusions:

The addition of cadmium ions as impurity in PbS deposition bath has been carried out at room temperature (300K) by adopting CBD technique, and its effects on the structure and absorption edge investigated as well. It was observed that the presence of cadmium ions on PbS thin films enhanced the crystallites, which in turn modified the absorption edges of the films. This effect was observed in the strong blue shifts in energy band gaps of the resulting films.

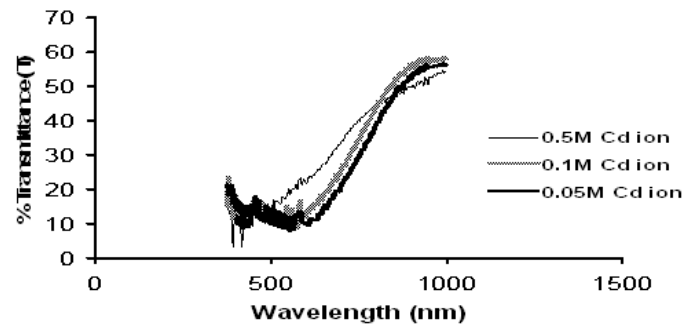


Fig. 6: Transmission spectra of PbS films deposited with Cd ion.

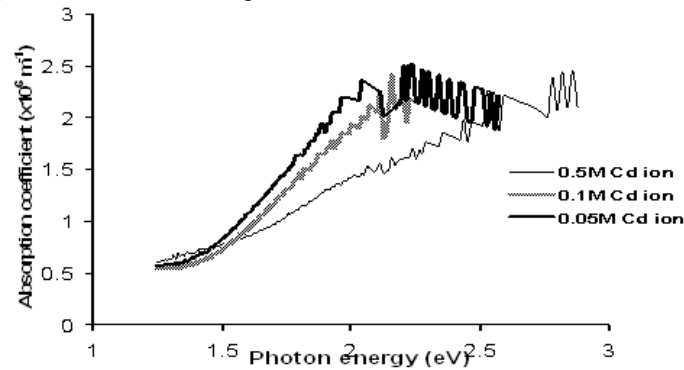


Fig. 7: Plot of absorption coefficient versus photon energy of PbS films deposited with Cd impurity.

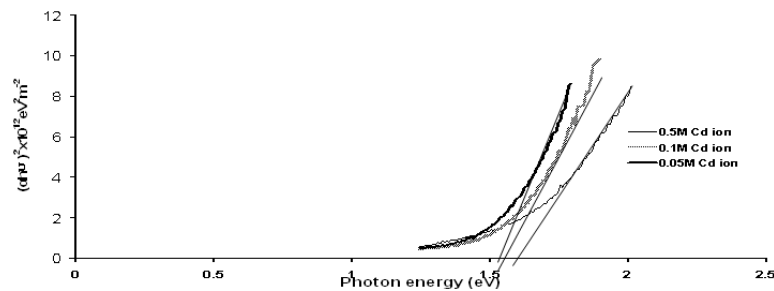


Fig. 8: Plot of $(ahv)^2 \times 10^2 \text{eV}^2 \text{m}^{-2}$ versus photon energy (eV)

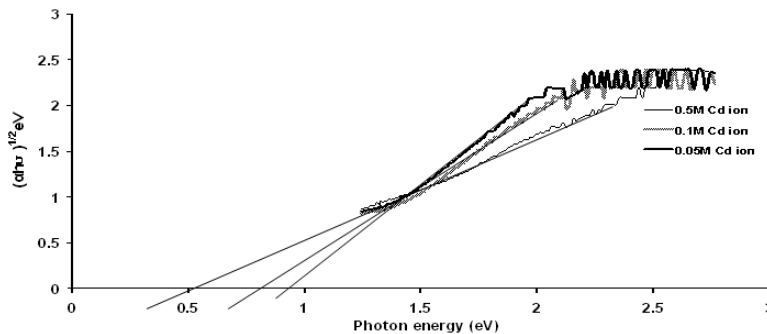


Fig. 9: Plot of $(ahv)^{1/2} \text{eV}$ versus photon energy.

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