Structural and Optical Properties of Nanocrystalline $Pb_{1-x}Cd_xS$ Thin Films Prepared by Chemical Bath Deposition

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Abstract

In this study, nanocrystalline thin films of $Pb_{1-x}Cd_xS$ were prepared by the chemical bath deposition technique on glass slides at 333 K. The structural parameters of these films were studied by XRD. The thin films were polycrystalline in nature and doping with Cd brought about shifts in peak position and changes in peak intensity. The surface morphology of the films was characterized by AFM and SEM, and the spherical crystallite size of the films was found to range from 23 nm to 38 nm. The optical, absorption, and transmission properties of the films were further determined by UV-vis spectrophotometry, and the direct optical energy gap was found to range from 2.1 eV to 3.95 eV depending on the amount of Cd doping. Finally, the extinction coefficient, refractive index, and real and imaginary dielectric constants of the films were investigated.

Keywords: $Pb_{1-x}Cd_xS$ thin films, CBD method, nanocrystalline thin film, structural and optical properties

1. Introduction

Thin films of lead and cadmium sulfate show promise in many physical applications, such as optoelectronics, infrared photo detectors, optical switches, and solar cells Thangavel et al. (2010), Herna´ndez et al. (2011) and Seghaier et al. (2006). Mixed thin film structures of PbS and CdS ($Pb_{1-x}Cd_xS$) have generated significant interest because they offer the advantage of tunable optical and opto-electronic properties of PbS, viz., its band gap, electrical conductivity, and structural properties Thangavel et al. (2010), Modaffer et al. (2009) and Deshmukh et al. (1996). In nanocrystallites, electrons confined within a narrow potential well exhibit extraordinary optical and electrical properties Ubale et al. (2007). Thus, when the width of such a confining potential is very small, that is, in the order of a few hundred angstroms, quantum size effects increase Ubale et al. (2007). Doping of PbS by Cd has been found to influence film growth and result in reductions in crystallite size Thangavel et al. (2010). Increases in the optical energy band gap (Eg) of thin films can be attributed to quantum size effects, as expected from thin films with a nanocrystalline nature Alex et al. (2008). One of the cheaper, simpler and more energy-efficient thin film deposition methods is chemical bath deposition (CBD), which is traditionally used to prepare thin films of chalcogenide semiconductors Diwaker et al. (2009). In the current paper, the structural and optical properties of $Pb_{1-x}Cd_xS$ nanostructure films obtained by the CBD method at various doping concentrations are reported and the results are discussed.

2. Experimental

$Pb_{1-x}Cd_xS$ thin films were deposited on glass slides using the CBD technique. A bath containing 0.05 M solutions of lead acetate, cadmium acetate, and thiourea was developed, and the pH of the solution was adjusted to 10 by addition of NH_4OH. Glass slides were cleaned using liquid detergent in an ultrasonic bath, dipped into a chromic acid bath for 2 h at room temperature, washed with distilled water and acetone, and then dried. The glass substrates were immersed vertically in the reaction vessel, and the bath was set to the desired temperature. Deposition was carried out at 333 K for 30 min, and the slides were left in the bath for 24 h at room temperature. The deposited films were then washed with distilled water and dried in air. Some of the prepared thin films were annealed at 473 K for 1 h, after which Eg was determined. The crystallinity phase and orientation of the $Pb_{1-x}Cd_xS$ films were determined by XRD using a Philips PW 1840 instrument with a Cu-Kα target. The morphology of the films was determined by AFM (AA 3000 Angstrom Advanced Inc.) and SEM (VEGA, S/N: VG6120980CN). A UV-Vis spectrophotometer (Jenway 6800) was used to measure the absorbance and transmittance of the films in the wavelength (λ) range from 300 nm to 1100 nm; optical parameters were

calculated from these measurements.

3. Results and Discussion

3.1 Reaction Mechanism

The CBD is based on sequential reaction at the substrate surface. The formation of $Pb_{1-x}Cd_xS$ may involve the following steps Thangavel et al. (2010), Ubale et al. (2007) and Zahid et al. (2011):

In an aqueous solution with NH_4OH as a complex agent.

$$Pb(CH_3COO)_2 \rightarrow Pb^{2+} + 2CH_3COO^- \tag{1}$$

$$Pb^{2+} + 4NH_3 \rightarrow Pb(NH_3)_4^{2+} \tag{2}$$

And

$$Cd(CH_3COO)_2 \rightarrow Cd^{2+} + 2CH_3COO^- \tag{3}$$

$$Cd^{2+} + 4NH_3 \rightarrow Cd(NH_3)_4^{2+} \tag{4}$$

In alkaline medium dissociation of $CS(NH_3)_2$ takes place

$$CS(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + SH^- \tag{5}$$

$$SH^- + OH^- \rightarrow S^{2-} + H_2O \tag{6}$$

Then the overall chemical reaction is as follows Thangavel et al. (2010):

$$(1-x)[Pb(NH_3)_4]^{2+} + x[Cd(NH_3)_4]^{2+} + CS(NH_2)_2 \xrightarrow{NH_4OH} Pb_{1-x}Cd_xS + 6NH_3 + CO_3^{2-} + H_2O \tag{7}$$

The reaction solution color changed after heating for ten minutes indicating of chemical reaction. At the end of different duration of deposition a homogenous compact $Pb_{1-x}Cd_xS$ nano-films are formed with optimized conditions.

3.2 XRD Studies

Figure 1 shows the XRD spectra of $Pb_{1-x}Cd_xS$ films where $0 \leq x \leq 1$. In the case of PbS films at x=0, peak positions observed are consistent with the fcc structure of PbS and represented by Miller indices of the (111), (200), (220), and (311) crystalline planes. Comparing the d space of the peaks with the appropriate ASTM cards, a small shift (0.6%) towards higher d was observed, as shown in Table 1. These results are similar to those reported by Thangavel et al. (2010) and Diwaker et al. (2009). Comparison of the XRD patterns of PbS and $Pb_{1-x}Cd_xS$ films at $x \leq 0.2$ clearly indicates significant broadening and decrease in peak intensities after doping, a behavior that has been explained by several authors Thangavel et al. (2010), Abbas et al. (2011) and Jana et al. (2008).Two reasons are cited for peak broadening: an increase in the heterogeneity of the films due to host lattice occupation by Cd and a decrease in crystallite size to nanoscale levels. Similar results have been reported for Cd-doped PbS Thangavel et al. (2010) and Pb-doped CdS Deshmukh et al. (1996). When $0.2 < x < 1$, the XRD spectra of the $Pb_{1-x}Cd_xS$ films show one peak indicating the (002) crystalline plane, which is related to hexagonal CdS films. This finding coincides with the results obtained by Herna´ndez et al. (2011) and Seghaier et al. (2006).

Table 1. Values of the structural parameters and optical energy gap of $Pb_{1-x}Cd_xS$ nanocrystalline thin films

X	2θ	hkl	d(A) exp.	d(A) ASTM	Average D(nm)fromXRD	Eg eV	Eg annealing(eV)
0.0	25.930	111	3.436	3.428	19.5	2.1	-
0.01	25.895	111	0.440	-	8.25	2.2	-
0.03	25.975	111	3.449	-	-	2.35	-
0.05	25.909	111	3.438	-	5.7	2.45	2.4
0.2	25.859	111	3.445	-	5	2.8	2.47
0.4	-	-	-	-	-	3.79	-
0.6	26.625	002	3.3523	-	3	3.95	3.7

Figure 1. X-ray diffraction patterns of $Pb_{1-x}Cd_xS$ nano-crystalline thin films deposited at a bath temperature of 333 K

No other peaks were detected in the XRD patterns, confirming the high purity of the $Pb_{1-x}Cd_xS$ thin films obtained. The average diameter (D) of $Pb_{1-x}Cd_xS$ nanocrystallites was calculated using the Debye-Scherrer formula Seghaier et al. (2006):

$$D_{hkl}=A\lambda/\beta cos\theta \tag{8}$$

where A is a constant (0.9) and β is the full width at half maximum of the XRD peak at 2θ recorded at an incident wavelength (λ=1.54 A). Crystallite sizes were found to range from 3 nm to 19.5 nm and are tabulated in Table 1. The D for PbS was equal to 19.5 nm and decreased with doping by Cd. The value of D calculated for $Pb_{1-x}Cd_xS$ films at 0<x<1 was found to range from 3 nm to 8.25 nm, compared with results obtained by Thangavel et al. (2010), which ranged from 9 nm to 11 nm. Smaller grains with increasing x obtained by Deshmukh et al. (1996), are attributed to a mixture of cubic and hexagonal phases.

3.3 AFM and SEM Studies

Figure 2 shows an AFM image of the $Pb_{1-x}Cd_xS$ thin films. Well-defined particle-like features with granular morphologies that indicate the presence of small crystalline grains may be observed. The root mean square surface roughness values at x=0.01 and x=0.6 are 2.15 nm and 4.56 nm respectively. The image also shows that the thin film is homogenous, without any cracks, and continuous with very well connected grains.

Crystal sizes of $Pb_{1-x}Cd_xS$ films were determined from AFM to be about 23.6 nm at x=0.01 and 38.15 at x=0.6; crystal sizes obtained from XRD were 8.25 nm and 3 nm at x = 0.01 and x = 0.6, respectively. Nanocrystallites sizes observed from AFM were greater than average crystallite sizes calculated from XRD peak broadening. Abbas et al. (2011) found that the size of PbS, as observed by AFM, is equal to 37.67 nm, larger than the average crystallite size calculated using the Debye–Scherrer relation. Alex et al. (2008) found that the typical size of PbS particles varies between 40 nm and 60 nm.

The morphology of $Pb_{1-x}Cd_xS$ thin films was examined by SEM and is shown in Figure 3. In these images, the almost spherical shape of crystallites and the average crystallite size deduced from the Scherrer formula are much lower than the grain sizes observed from the SEM images. However, grains with sizes less than 100 nm are also evident in the micrograph in Figure 3 Thangavel et al. (2010) found that the domains of nanocrystalline thin films tend to increase in size near the film surface; thus, SEM images representing the surface features of the film could yield the maximum possible size of grains. Addition of Cd into the deposition solution modifies thin film growth and increases the grain size, as shown in Figure 3.

Figure 2. AFM image for $Pb_{1-x}Cd_xS$ nano-crystalline thin films (**a**) x=0.01 (**b**) x=0.6

Figure 3. SEM surface micrograph of $Pb_{1-x}Cd_xS$ nano-crystalline thin films (a) x=0.01 (b) x=0.6

3.4 Optical Studies

The optical absorption of $Pb_{1-x}Cd_xS$ thin films was studied in the λ range from 300 nm to 1100 nm. The variation in the optical absorption coefficient (α) with λ is shown in Figure 4. All films show higher absorptions (α $\geq 10^4 cm^{-1}$) at the shorter wavelength side, indicating that the films undergo direct optical electronic transitions Chawla et al. (2010). The spectra in Figure 4 show that absorbance edges are blue shifted with respect to the bulk $Pb_{1-x}Cd_xS$ and with increasing x, that is, with doping by Cd. This blue shift in absorption is also a signature of nanostructure formation. Similar behaviors have been reported for CBD, PbS, and CdS films Thangavel et al. (2010) and Chawla et al. (2010). Furthermore, the increase in α with decreasing λ shows a sharp change, which may be related to the increase in crystallinity of the films and the occurrence of direct optical transitions Shaukat

et al. (2007).

Figure 4. The absorption coefficient spectra for prepared $Pb_{1-x}Cd_xS$ nano-crystalline thin films

The optical band gap of the films was obtained using the empirical equation Ben Rabeh et al. (2009):

$$\alpha h\upsilon = C(h\upsilon - Eg)^r \qquad (9)$$

where C is a constant and $r = \frac{1}{2}$ for allowed direct transitions. A value of $r = \frac{1}{2}$ was found to fit the results of the current study best. Figure 5 shows a plot of $(\alpha h\upsilon)^2$ versus photon energy $(h\upsilon)$ of the prepared films. The linearity of the plots indicates that the material has a direct band gap nature Seghaier et al. (2006). Extrapolation of the straight line to $(\alpha h\upsilon)^2=0$ axis yields the energy band gap (Eg) of the film material. Eg varied between 2.1 eV and 3.95 eV for x=0 (PbS) and x=0.6, respectively, which is greater than the Eg of bulk PbS (0.41eV) Alex et al. (2008) and CdS (2.4eV) Shaukat et al. (2007), indicating quantum confinement effects in the nano particles Chawla et al. (2010). Eg values found for the PbS and CdS nanostructures are within the range reported by Ubale et al. (2007), Diwaker et al. (2009) and Thambiduria et al. (2009).

Figure 5. Plot of $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ for prepared $Pb_{1-x}Cd_xS$ nano-crystalline thin films

Variations in Eg with the composition parameter x are shown in Table 1, which clearly shows that direct band gaps increase with increasing x (Cd doping). This result may be attributed to alloying of PbS with CdS, which changes the structure of the films from cubic to hexagonal, as shown in the XRD pattern in Figure 1. This result has also been reported by Deshmukh et al. (1996) and Modaffer et al. (2009). The large modification in the band gap confirms the formation of a ternary $Pb_{1-x}Cd_xS$ alloy and presence of strong quantum confinement in the

system, which could be, attributed to the decrease in effective mass and increase in binding energy in PbS nanocrystals Thangavel et al. (2010),. The properties of nanocrystalline materials change according to their bulk properties because the sizes of the crystallites become comparable with the exciton Bohr radius. The estimated mean crystallite size of the prepared $Pb_{1-x}Cd_xS$ in this work was smaller than or equal to the exciton Bohr radius of PbS (18nm) Diwaker et al. (2009), and CdS (3nm) Chawla et al. (2010) and strong confinement was observed in $Pb_{1-x}Cd_xS$ thin films. Annealing of some samples at 473 K for 1 h increased the Eg, as shown in Table 1, which may be attributed to an increase in crystallite size.

A plot of the extinction coefficient (k) versus λ spectra is shown in Figure 6. Values of k are high in the visible region and decrease sharply with λ to become approximately constant in the NIR region. Furthermore, the edge of k shifted to shorter λ depending on x, which is related to the high absorbance of different films in that region. As seen the behavior of k is similar to the corresponding (α).

Figure 6. The extinction coefficient (k) as a function of wavelength for $Pb_{1-x}Cd_xS$ nano-crystalline thin films

A plot of the refractive index (n) versus λ is shown in Figure 7. The refractive index increases with λ to maximum values ranging from 2.4 to 2.6 in the visible region and then remains constant with further increases in λ. However, the value and region of the maximum n depend on x, an observation that may be related to polarization of the thin films, which affects n. Polarization depends on the crystallinity and grain size of thin films. Similar (n) behaviors and value ranges have been reported by Mahdi et al. (2009) and (Ugwu & Onah, 2007).

Figure 7. Refractive index as function of (hυ) for prepared $Pb_{1-x}Cd_xS$ nano-crystalline thin films

The real and imaginary parts of the dielectric constant (ε_1 and ε_2, respectively) are shown in Figures 8 and 9, respectively. The behavior of ε_1 is similar to that of n because of the smaller value of k^2 compared with n^2. The behavior of ε_2 is also similar to n and is affected by the extinction coefficient, which is related to variations in α.

Figure 8. The real part of the dielectric constant (ε_1) as a function of wavelength for $Pb_{1-x}Cd_xS$ nano-crystalline thin films

Figure 9. The imaginary part of the dielectric constant (ε_2) as a function of wavelength for $Pb_{1-x}Cd_xS$ nano-crystalline thin films

4. Conclusion

Nanocrystalline $Pb_{1-x}Cd_xS$ thin films were prepared by a simple CBD method. XRD, AFM, and SEM results show that the deposited $Pb_{1-x}Cd_xS$ films consist of spherical nanosized crystallites. The grain size, according to XRD studies, decreased with increasing x (Cd amount). AFM studies, however, yielded contradictory results. Optical studies revealed that $Pb_{1-x}Cd_xS$ thin films allow direct transition of the optical band gap, varying from 2.1 eV to 3.95 eV with Cd doping. A higher energy gap indicates quantum confinement effects in nanocrystallites. Since the band gap maybe tuned to cover wide photo-regions, $Pb_{1-X}Cd_XS$ nanocrystalline films are promising candidates for solar cell and photo-detector applications.

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