Pacific Science Review A: Natural Science and Engineering 18 (2016) 72–77

HOSTED BY

Contents lists available at ScienceDirect

Pacific Science Review A: Natural Science and Engineering

journal homepage: www.journals.elsevier.com/pacific-science-review-a-natural-science-and-engineering/

Studies on the structural, morphological and optoelectrical properties of spray deposited CdS:Pb thin films

M. Anbarasi, V.S. Nagarethinam*, R. Baskaran, V. Narasimman

PG and Research Department of Physics, AVVM Sri Pushpam College, Poondi 613503, Tamilnadu, India

ARTICLE INFO

Article history:
Received 20 June 2016
Received in revised form
30 July 2016
Accepted 23 August 2016
Available online 1 September 2016

Keywords:
Crystal structure
Optical transparency
Doping
Band bowing
Thin films

ABSTRACT

Undoped and Pb-doped CdS (CdS:Pb) thin films were prepared on glass substrates by a spray technique using a perfume atomizer. The effects of Pb doping on the structural, morphological and optoelectrical properties of CdS thin films were studied. All of the films are polycrystalline in nature exhibiting hexagonal crystal structure. Crystallite size estimated from the Scherrer formula increased from 18.42 nm to 34.76 nm with increases in Pb doping concentration. The expansion of lattice parameters experienced with Pb doping might be due to the larger ionic radius of Pb^{2+} ions compared to that of the host Cd^{2+} ions. Increased optical transparency is observed for the doped films and the optical band gap experienced band bowing with increase in Pb doping concentration. Electrical resistivity values of the films were found to be on the order of 10^1 Ω cm. From the obtained results, it is observed that the CdS thin film coated with 6 wt.% Pb doping concentration exhibit better structural, morphological, optical and electrical properties.

1. Introduction

Cadmium sulphide (CdS) is a II–VI wide direct band gap semiconductor with such applications as thin film solar cells, photodetectors, transistors, and light emitting diodes [1]. The high transmittance and moderate band gap (2.42 eV) possessed by CdS make it suitable as an ideal material for the fabrication of solar cells especially as an efficient window layer [2]. However, the higher resistivity of as-deposited CdS thin films (of the order of 10^6–10^7 Ω cm) limits its application as an efficient window layer for solar cell fabrication [3]. For this reason, it is very important to control the resistivity of pure CdS, which can be achieved through doping. It has been reported earlier that the optical and electrical properties of CdS thin films can be altered by doping it with metallic ions such as Mg^{2+} [1], Zn^{2+} [4], Cu^{2+} [5], Fe^{2+} [6], Co^{2+} [7], etc. having ionic radii smaller than that of the host ion Cd^{2+}. These dopant ions due to their smaller ionic radii diffuse well into the host CdS lattice enhancing its conductivity due to lattice unit cell compression. However, the effect of incorporation of dopant ions of greater ionic radii than that of Cd^{2+} on the optical, electrical and structural properties of CdS is still under investigation. Pb^{2+} is a heavy metal ion having ionic radius of 1.20 Å, which is slightly higher than that of Cd^{2+} (0.97 Å), and hence it is supposed that the lead ions can alter the physical properties of pure CdS. Therefore, in the present study, Pb-doped CdS (CdS:Pb) thin films with different concentrations of Pb (0, 1, 2, 3 and 4 wt.%) were deposited by a spray technique using a perfume atomizer, the effects of Pb doping on the structural, morphological, optical and electrical properties of CdS thin films were investigated, and the obtained results are reported in detail. The use of a perfume atomizer has several advantages over the conventional spray technique, which uses carrier gas for film deposition, such as: no need for carrier gas, fine atomization, improved wettability between the sprayed micro particles and no loss of the precursor solution to the surroundings [8].

2. Experimental details

Undoped CdS thin films were prepared on glass substrates kept at 400 °C by spraying an aqueous solution (50 ml in volume) containing 0.05 M each of cadmium chloride ($CdCl_2$) and thiourea ($SC(NH)_2$). To achieve Pb doping, lead nitrate $Pb(NO_3)$ with different concentrations (0, 2, 4, 6 and 8 wt.%) was added to the starting solution. When the resultant solution was sprayed over the hot

* Corresponding author.
E-mail address: nagarethinamavvm@gmail.com (V.S. Nagarethinam).

Peer review under responsibility of Far Eastern Federal University, Kangnam University, Dalian University of Technology, Kokushikan University.

http://dx.doi.org/10.1016/j.psra.2016.08.004

glass substrates, pyrolytic decomposition took place, resulting in the formation of Pb-doped CdS (CdS:Pb) thin films. A stylus type profilometer (Surftest SJ–301) was used to measure the thicknesses of the films. Determination of crystal structure and the microstructural parameters were achieved through the use of an X-ray diffractometer (PANalytical X′ Pert–PRO) with CuK_α (λ = 1.5406 Å) as the source. Scanning electron microscope (HITACHI S-3000 H) was used to analyse the surface morphologies of the films. Optical transmission and band gap were determined using a double beam spectrophotometer (LAMBDA 35) in the wavelength region of 300–1100 nm. Electrical studies were performed using a d.c two point probe setup.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the XRD patterns of Pb-doped CdS (CdS:Pb) thin films coated with different concentrations of Pb (0, 2, 4, 6 and 8 wt.%). The XRD patterns confirm the polycrystalline nature of the films.

The diffraction peaks at 2θ values approximately equal to 24.362°, 26.122°, 27.682°, 36.368°, 43.292°, 47.484° and 51.508° correspond to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) planes, which fit fell with the hexagonal crystal structure of pure CdS (JCPDS card No.41–1049). It is observed from the XRD patterns that the undoped film has a strong (0 0 2) preferential orientation that decreased with increase in Pb doping concentration. The preferential orientation factor f(hkl) values of the films were calculated by the way adopted by Suganya et al. [9]. Fig. 2 shows the variation of f(1 0 0), f(0 0 2), and f(1 0 1) of the CdS:Pb films as a function of Pb doping concentration.

It is observed that f(0 0 2) decreases linearly with increase in Pb doping concentration whereas f(1 0 0) and f(1 0 1) increases. The lesser values of f(1 0 0) and f(1 0 1) compared to that of f(0 0 2) confirmed that the films have a strong (0 0 2) preferential orientation. The decrement in the value of f(0 0 2) with increase in Pb doping concentration confirmed that the crystalline quality of pure CdS deteriorated with Pb doping.

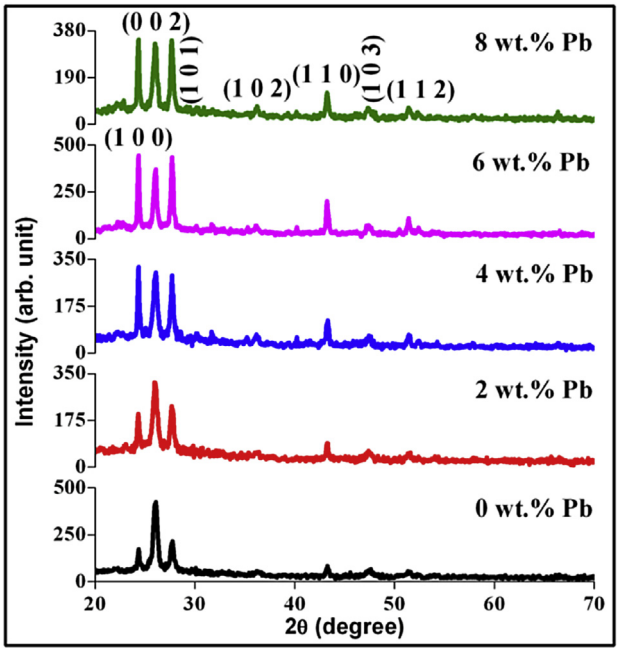

Fig. 1. XRD patterns of CdS:Pb thin films.

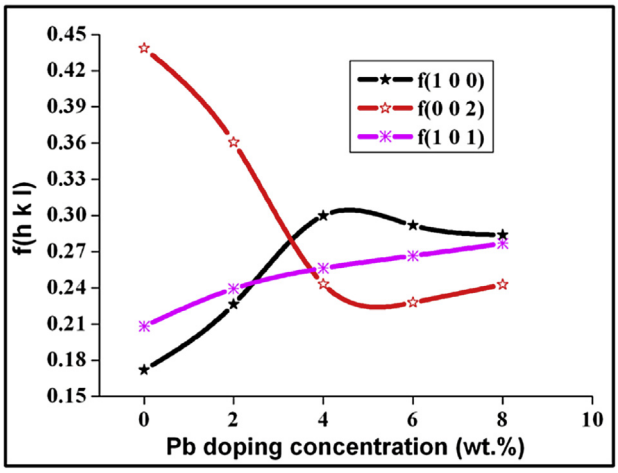

Fig. 2. variation of f(h k l) as a function of CdS:Pb thin films.

It is seen from Fig. 3 that the 2θ values of the (1 0 0) and (0 0 2) peaks shift towards lower 2θ value with increase in Pb concentration, which favours an expansion in lattice volumes of the doped films.

The lattice parameter values were estimated using the equation [10]:

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \quad (1)$$

and the calculated values are compiled in Table 1.

It is observed that the lattice parameter values increase with an increase in Pb doping concentration as expected. The increase in lattice parameter values might be due to the strain induced in the host CdS lattice by the substitution of Pb^{2+}, which have an ionic radius of 1.2 Å that is greater than that of Cd^{2+} (0.97 Å). The c/a values of the films remained constant, which indicates that Pb doping does not affect the fundamental crystal structure.

Microstructural parameters such as crystallite size (D), strain (ε) and dislocation density (δ) were calculated using the formulae [11]:

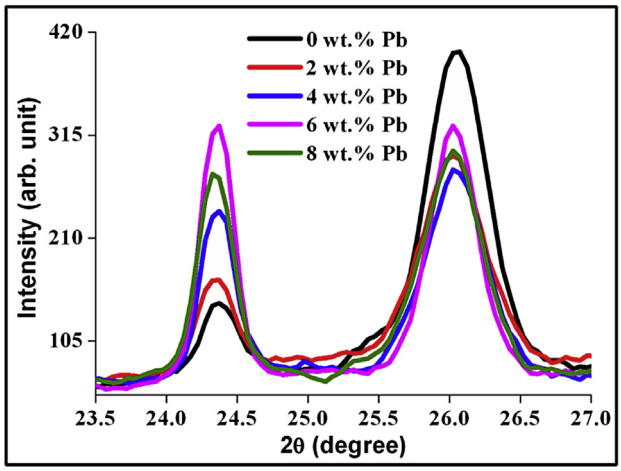

Fig. 3. Angle shift of CdS:Pb thin films.

Table 1
Structural parameters of CdS:Pb thin films.

Pb doping concentration (wt.%)	Thickness, t (nm)	Lattice parameters			Crystallite size, D (nm)	Strain, $\varepsilon \times 10^{-3}$	Dislocation density, $\delta \times 10^{15}$ lines/m^2
		a (Å)	c (Å)	c/a			
0	756	4.1780	6.8228		34.76	0.997	0.828
2	787	4.1881	6.8392		30.96	1.119	1.043
4	762	4.1932	6.8476	1.6330	27.62	1.254	1.311
6	729	4.1884	6.8398		23.68	1.463	1.783
8	740	4.1868	6.8372		18.42	1.881	2.948

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \tag{2}$$

$$\varepsilon = \frac{\beta cos\theta}{4} \tag{3}$$

$$\delta = \frac{1}{D^2} \tag{4}$$

where λ is the wavelength of the X-ray used (1.5406 Å), β is the full-width at half maximum (FWHM) in radians and θ is the angle of diffraction. The calculated microstructural parameters are presented in Table 1. It is observed that the crystallite size value decreases linearly with increase in Pb doping concentration, confirming the fact that the crystalline nature of the CdS film decreases with Pb doping, and the increased strain and dislocation density values obtained strongly favours this supposition.

3.2. SEM and elemental analyses

Fig. 4(a–e) shows the SEM images of the CdS:Pb thin films.

All of the surfaces appear to be densely packed with grains of different sizes and shapes. The undoped film surface is composed of cloudy regions of nanosized grains, along with a few pin holes (Fig. 4(a)). With Pb doping, the surface gets modified with cloudy regions embedded with equally sized nano grains for the film coated with 2 wt.% Pb doping concentration (Fig. 4 (b)). Cloudy regions disappear for the CdS film coated with 4 wt.% Pb doping concentration, and the film morphology gets modified with equally sized nano grains (Fig. 4(c)). Plenty of nanoneedles are evinced for the CdS film coated with 6 wt.% Pb doping concentration (Fig. 4 (d)). The surface gets modified with nanoneedles and nanosized grains tightly packed without any cracks or pinholes for the film coated with 8 wt.% Pb doping concentration (Fig. 4 (e)). Thus the CdS film morphology gets modified from irregular shaped grains to nanoneedled grains with Pb doping.

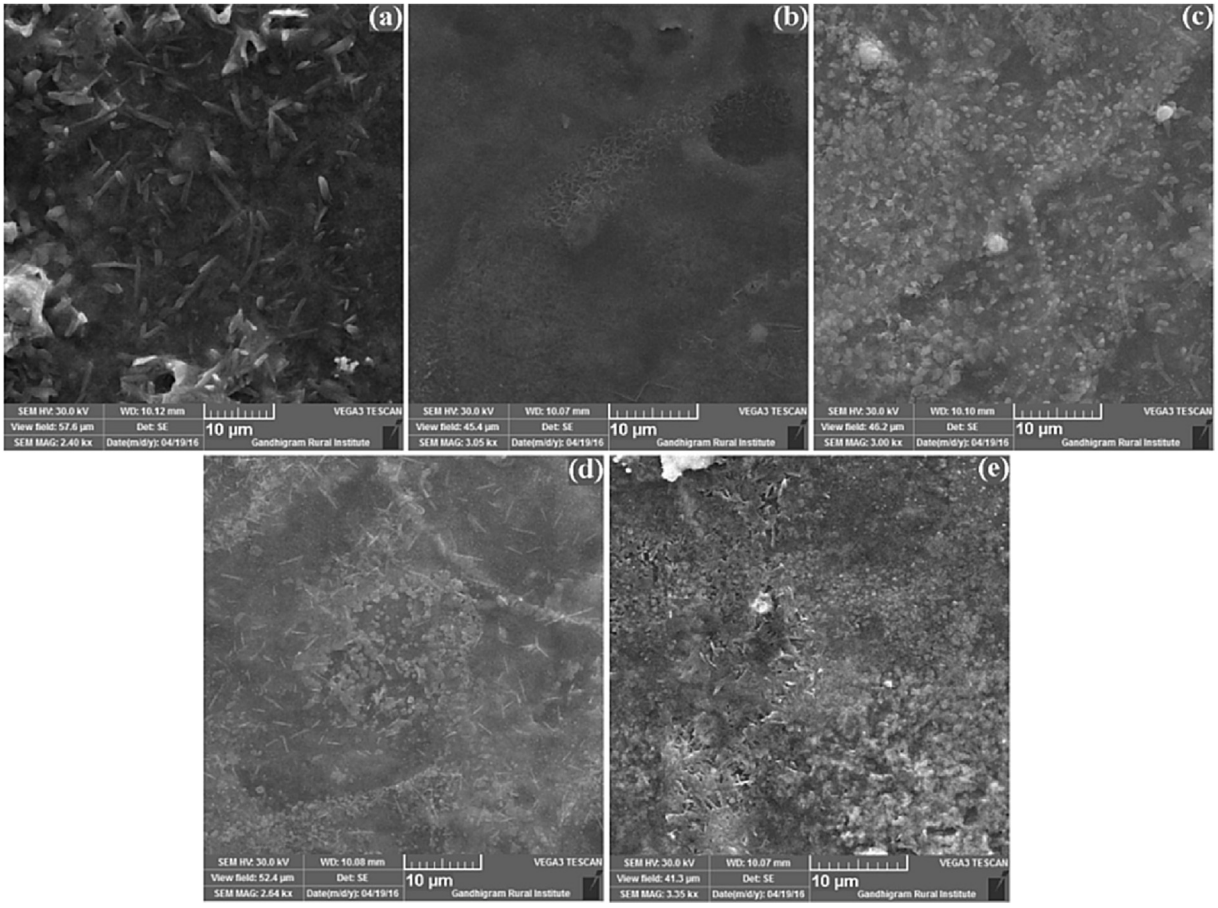

Fig. 4. SEM images of CdS thin films coated with a) 0 wt.%, b) 2 wt.%, c) 4 wt.%, d) 6 wt.% and e) 8 wt.% Pb doping concentrations.

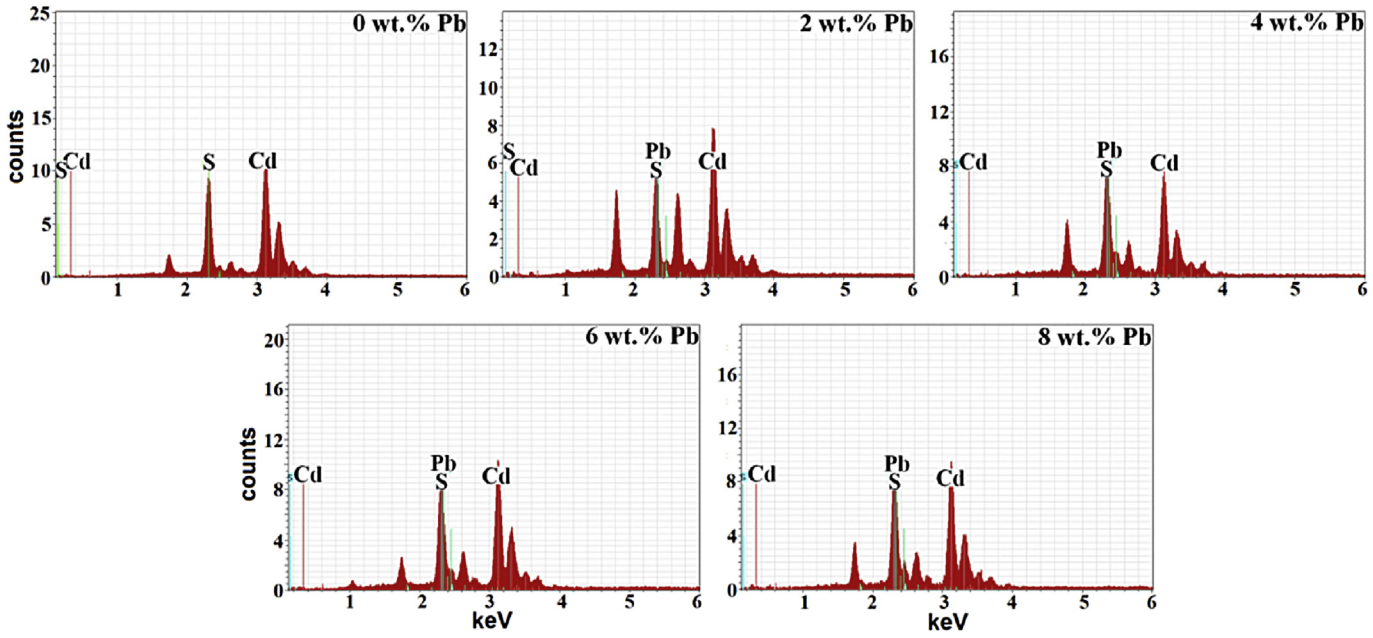

Fig. 5. EDX spectra of CdS:Pb thin films.

The EDX spectra of CdS:Pb thin films are shown in Fig. 5.

The spectra reveal the presence of Pb in the doped films. The atomic percentage composition of the elements Cd, S and Pb are displayed in Table 2.

It is observed that the content of the elements Cd and S show a decreasing trend, whereas the content of Pb shows an increasing trend with increase in Pb doping concentration. It is also observed that the doped films are deficient with sulphur and this might have played a role in decreasing their electrical resistivity values (Section 3.3).

3.3. Electrical studies

The electrical resistivity values of the CdS:Pb thin films are given in Table 2. The undoped CdS film has a resistivity of $0.137 \times 10^1\ \Omega$ cm which exactly matches with the value reported by Anbarasi et al. [12]. The resistivity initially increased with Pb doping and then it started decreasing, attaining a minimum value for the CdS film coated with 6 wt.% Pb doping concentration. The initial increase in resistivity of the CdS films coated with 2 wt.% Pb doping concentration might be due to the increased amount of defects such as structural disorder, dislocation and surface imperfections. The reduction in resistivity observed for the CdS films coated with Pb doping concentration greater than 2 wt.% might be due to the increase in free carriers due to increased sulphur deficiencies as observed in elemental analysis [13].

3.4. Optical studies

Fig. 6 shows the absorbance spectra of the CdS:Pb thin films.

The spectra resembles the same shape for all the films, however differences in absorbency is evinced for the doped films. It is observed that the CdS films coated with 2 and 4 wt.% Pb doping concentrations exhibited increased absorbency compared to that of the undoped film. However, for the CdS films coated with 6 and 8 wt.% Pb doping concentrations the absorbency decreased. The variation in absorbency observed here can be correlated with thickness variation of the films. The increased thickness observed for the CdS films coated with 2 and 4 wt.% Pb doping concentrations might be the reason for their increased absorbency, and the decreased thickness values obtained for the films coated with 6 and 8 wt.% Pb doping concentrations favour their decreased absorbency. It is well known that increased film thickness results in the increase in the number of atoms, and hence more states are present for the photon energy to be absorbed thereby increasing the absorption [14].

The transmittance spectra of the CdS:Pb thin films are shown in the inset of Fig. 7.

All the films have an average transparency of 80% in the visible region. It is observed that the CdS films coated with 2 and 4 wt.% Pb doping concentrations exhibit lower transparency whereas the films coated with 6 and 8 wt.% Pb doping concentrations exhibit better transparency compared to that of the undoped film. The

Table 2
Elemental composition, optical band gap and electrical resistivity values of CdS:Pb thin films.

Pb doping concentration (wt.%)	Elemental composition (at.%)				Optical band gap, E_g (eV)	Electrical resistivity, $\rho \times 10^1\ \Omega$ cm
	Cd	S	Pb	S/(Cd + Pb)		
0	49.63	50.37	–	1.01	2.36	0.137
2	48.43	48.93	2.64	0.96	2.25	0.241
4	48.04	48.74	3.22	0.95	2.3	0.096
6	47.92	47.92	4.16	0.92	2.42	0.068
8	48.14	48.12	3.69	0.93	2.48	0.146

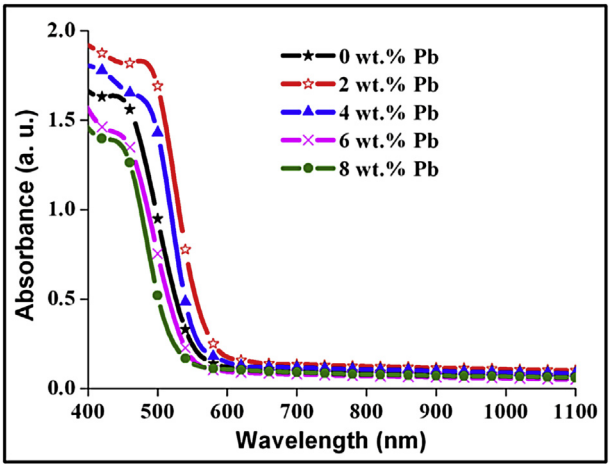

Fig. 6. Absorbance spectra of CdS:Pb thin films.

increased transparency for the CdS films coated with 6 and 8 wt.% Pb doping concentrations might be due to their reduced thickness values which leads to an increase in light scattering losses [15].

To determine the optical band gap (E_g) values of the films it is essential to find the absorption coefficient (α), which is estimated from the transmittance values using the following relation [16]:

$$\alpha = \frac{-\ln(T)}{t} \tag{5}$$

where t is the thickness of the films. The absorption coefficient of the films is found to be on the order of 10^4 cm^{-1}. The absorption coefficient is related to the incident photon energy (hυ) as [17]:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^{\frac{1}{2}} \tag{6}$$

where A is a constant. A plot of $(\alpha h\upsilon)^2$ vs. hυ allows an estimate of the band gap values of the films. From the plots of $(\alpha h\upsilon)^2$ vs. hυ (Fig. 8), the E_g values are estimated by extrapolating the straight line portion of the plots to the energy axis at $\alpha = 0$.

The calculated band gap values are compiled in Table 2. The undoped CdS film has a band gap value of 2.36 eV, which decreased to 2.25 eV for the film coated with 2 wt.% Pb doping concentration, and above this doping concentration it started to increase, attaining a maximum value of 2.48 eV for the CdS film coated with 8 wt.% Pb

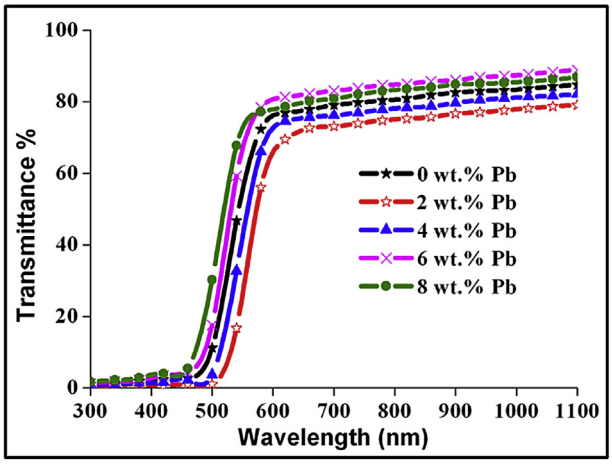

Fig. 7. Transmittance spectra of CdS:Pb thin films.

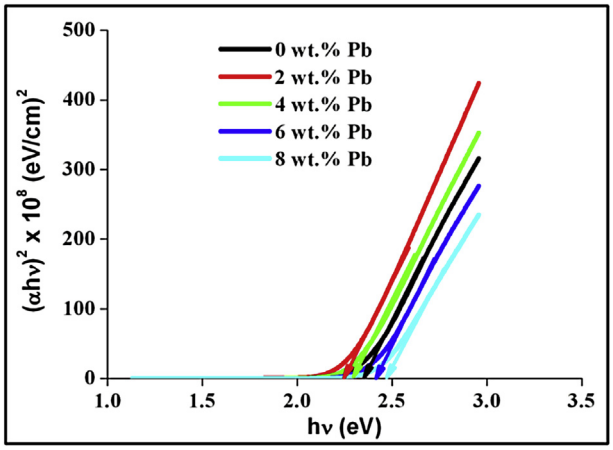

Fig. 8. Plots of $(\alpha h\nu)^2$ vs. hν of CdS:Pb thin films.

doping concentration. Similar results of band bowing have been reported earlier for Mn-doped CdS films prepared by an r.f sputtering technique [18]. The red shift in the optical band gap value observed for the CdS films coated with 2 and 4 wt.% Pb doping concentrations might be due to their increased thickness, the degree of preferred orientation, internal microstrain and stoichiometry [19]. The blue shift in the optical band gap value of the films coated with 6 and 8 wt.% Pb doping concentrations may be attributed to the Burstein–Moss (BM) effect [13], according to which the dopant Pb^{2+} ions cause an increase in free carrier concentration, which lifts the Fermi level up into the conduction band, leading an increase in the optical band gap.

4. Conclusions

CdS:Pb thin films were successfully fabricated on glass substrates by a spray technique using a perfume atomizer with different concentrations of Pb (0, 2, 4, 6 and 8 wt.%). The films were characterized by XRD, SEM, EDX, optical and electrical studies. All the films exhibited hexagonal crystal structure. Undoped films exhibited a strong (0 0 2) preferential orientation which decreased with increase in Pb doping concentration. Decreased crystallite size values were observed for the doped films. The surface morphology was modified from unequally sized grains to equally sized nano grains. EDX spectra confirmed the presence of Pb in the doped films. All the films exhibited an average transmittance nearly equal to 80% in the visible region. The CdS:Pb film coated with 6 wt.% Pb doping concentration exhibited a maximum transparency nearly equal to 90%. The band gap experienced both red and blue shifts with Pb doping concentration. Electrical resistivity decreased with Pb doping concentration, attaining a minimum value of 0.068×10^1 Ω cm for the CdS film coated with 6 wt.% Pb doping concentration. The increased optical transparency, optimum band gap and decreased electrical resistivity values obtained make CdS:Pb thin films suitable for future optoelectronic device applications.

References

[1] T. Sivaraman, A.R. Balu, V.S. Nagarethinam, Effect of magnesium incorporation on the structural, morphological, optical and electrical properties of CdS thin films, Mater. Sci. Semicon. Proc. 27 (2014) 915–923.
[2] R. Mendoza-Perez, J. Sastre-Hernandez, G. Puente, O. Vigil-Galan, CdTe solar cell degradation studies with the use of CdS as the window material, Sol. Energy Mater. Sol. Cells 8 (2009) 79–84.
[3] J. Hiie, T. Dedova, V. Valdna, K. Muska, Comparative study of nano-structured CdS thin films prepared by CBD and spray pyrolysis: annealing effect, Thin Solid Films 511–512 (2006) 443–447.

[4] M. Anbarasi, V.S. Nagarethinam, A.R. Balu, Investigations on the structural, morphological, optical and electrical properties of undoped and nano sized Zn-doped CdS thin films prepared by a simplified spray technique, Mater. Sci. Pol. 32 (2014) 652–660.
[5] N.A. Shah, R.R. Sagar, W. Mahmood, W.A.A. Syed, Cu-doping effects on the physical properties of cadmium sulfide thin films, J. Alloys Compd. 512 (2012) 185–189.
[6] N. Badera, B. Godbole, S.B. Srivastava, P.N. Vishwakarma, L.S. Sharath Chandra, D. Jain, M. Gangrade, T. Shripathi, V.G. Sathe, V. Ganesan, Quenching of photoconductivity in Fe doped CdS thin films prepared by spray pyrolysis technique, Appl. Surf. Sci. 254 (2008) 7042–7048.
[7] S.T. Mane, P.C. Pingale, R.V. Suryawanshi, V.S. Karande, L.P. Desmukh, M. Sharon, On the surface morphology and transport properties of chemical bath deposited $Co_xCd_{1-x}S$ thin films: a correlation, Electrochim. Acta 114 (2013) 494–499.
[8] K. Usharani, A.R. Balu, G. Shanmugavel, M. Suganya, V.S. Nagarethinam, Tansparent conducting CdO thin films fabricated by low cost simplified spray technique using perfume atomizer, Int. J. Sci. Res. Rev. 2 (2013) 53–68.
[9] M. Suganya, A.R. Balu, K. Usharani, Role of substrate temperature on the growth mechanism and physical properties of spray deposited lead oxide thin films, Mater. Sci. Pol. 32 (2014) 448–456.
[10] N. Manjula, K. Usharani, A.R. Balu, V.S. Nagarethinam, Studies on the physical properties of three potentially important TCO thin films fabricated by a simplified spray technique under same deposition conditions, Int. J. Chem-Tech Res. 6 (2014) 705–718.
[11] S. Ravishankar, A.R. Balu, M. Anbarasi, V.S. Nagarethinam, Influence of precursor molar concentration on the structural, morphological, optical and electrical properties of PbS thin films deposited by spray pyrolysis technique using perfume atomizer, Optik 126 (2015) 2550–2555.
[12] M. Anbarasi, T. Sivaraman, V.S. NAgarethinam, A.R. Balu, CdS thin iflms fabricated by a simplified spray technique using cadmium acetate as cationic precursor, Int. J. Chem. Phys. Sci. 3 (2014) 1–9.
[13] T. Sivaramn, V. Narasimman, V.S. Nagarethinam, A.R. Balu, Effect of chlorine doping on the structural, morphological, optical and electrical properties of spray deposited CdS thin films, Prog. Mater. Sci. Mater. Int. 25 (2015) 392–398.
[14] T. Noorunisha, V.S. Nagarethinam, M. Suganya, D. Prabha, S. Ilangovan, K. Usharani, A.R. Balu, Doping concentration and annealing temperature effects on the properties of nanostructured ternary CdZnO thin films towards optoelectronic applications, Optik 127 (2016) 2822–2829.
[15] R. Kumar, R. Dass, M. Gupta, V. Ganesan, Preparation of nanocrystalline Sb doped PbS thin films and their structural, optical and electrical characterization, Superlattices Microstruct. 75 (2014) 601–612.
[16] T. Sivaraman, V.S. Nagarethinam, A.R. Balu, CdS thin films fabricated by a simplified spray technique from different substrate temperatures – structural, morphological, optical and electrical analysis, Res. J. Mater. Sci. 2 (2014) 6–15.
[17] G. Selvan, M.P. Abubacker, K. Usharani, A.R. Balu, Precursor aging effect on the properties of CdZnS films, Surf. Eng. 32 (2015) 212–214.
[18] C.T. Tsai, S.H. Chen, D.S. Chu, W.C. Chu, Fabrication and physical properties of radio frequency sputtered $Cd_{1-x}Mn_{xs}$ thin films, Phys. Rev. B 54 (1996) 11555–11560.
[19] J.P. Enriquez, X. Mathew, Influence of the thickness on structural, optical and electrical properties of chemical bath deposited CdS thin films, Sol. Energy Mater. Sol. Cells 76 (2003) 313–322.