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Preparation and characterization of $Cd_xZn_{1-x}S$ thin films by spray pyrolysis technique for photovoltaic applications

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Abstract

$Cd_xZn_{(1-x)}S$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, and 1) thin films were deposited by the chemical spray pyrolysis technique using a less used combination of chemicals. Depositions were done at 573 K on cleaned glass substrates. The composition, surface morphology and structural properties of deposited films were studied using EDAX, SEM and X-ray diffraction technique. XRD studies reveal that all the films are crystalline with hexagonal (wurtzite) structure and inclusion of Cd into the structure of ZnS improved the crystallinity of the films. In the entire compositions, the (0 0 2) diffraction peak is prominent which gives lattice matching to the chalcogenide semiconductor such as $CuIn_xGa_{1-x}Se_2$ and $CuIn\ (s_{1-x}Se_x)_2$, which are used in photovoltaic devices. The value of lattice constant '*a*' and '*c*' have been observed to vary with composition from 0.382 to 0.415 nm and 0.625 to 0.675 nm, respectively. The band gap of the thin films varied from 3.32 to 2.41 eV as composition varied from $x = 0.0$ to 1.0. It was observed that presence of small amount of cadmium results in marked changes in the optical band gap of ZnS.

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Keywords: Semiconductor thin films; Spray pyrolysis; XRD; SEM; EDAX; UV–VIS spectrophotometer

1. Introduction

$Cd_xZn_{1-x}S$ ternary compounds are promising materials for a variety of optoelectronic device applications, such as electroluminescent, photoluminescent and photoconductor devices (Abrahams and Buiocchi, 1988; Torres and Gordillo, 1992; Gordillo, 1992; Dona and Herrero, 1995) and especially in photovoltaic cells with different polycrystalline absorber materials like Cu_xS (Burton and Hetch, 1976; Kwok, 1983), $CuInSe_2$ (Potter and Sites, 1983; Bowron et al., 1991), CdTe (Hussain et al., 1991; Chu et al., 1991), $CuGaSe_2$ (Reddy and Reddy, 1992). The reason is the possibility of tailoring its semiconductor properties between the values corresponding to the pure binaries. This fact allows us to adapt the material properties to the device requirements. In recent years there have appeared several papers on fabrication of these compounds by different methods such as physical vapour deposition (PVD) (Kumar et al., 2004; Lee et al., 2003), chemical bath deposition (CBD) (Dona and Herrero, 1995; Yamaguchi et al., 1996; Yamaguchi et al., 1999; Oladeji and Chow, 2005; Borse et al., 2007; Chavhan et al., 2008; Lee et al., 2003) and chemical vapour deposition (Razykov, 1985). However, only few papers on preparation of $Cd_xZn_{1-x}S$ thin film by chemical spray pyrolysis (Akyuz et al., 2007; Ilican et al., 2007) can be found, despite being one of the most common methods used for the deposition of II–VI compound semiconductor thin films.

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Table 1
A summary of preparation of $Cd_xZn_{1-x}S$ thin films reported in the literature and corresponding sources of Cd, Zn and S.

	Sources of Cd, Zn & S	Growth technique	$T_{deposition}$ (°C)	Crystal structure	E_g (eV)	Reference
1.	CdS and ZnS powder	PVD	–	–	2.62–3.25	(Kumar et al., 2004)
2.	CdS and ZnS powder	PVD	150	Wutzite and Zinc blende	2.39–3.53	(Lee et al., 2003)
3.	$CdSO_4$, $ZnSO_4$ and thiourea	CBD	70	Wurtzite	2.45–3.2	(Dona and Herrero, 1995)
4.	CdI_2, ZnI_2 and thiourea	CBD	60–80	Wurtzite	2.5–3.6	(Yamaguchi et al., 1996)
5.	CdI_2, ZnI_2 and thiourea	CBD	80	Wurtzite	2.4–3.5	(Yamaguchi et al., 1999)
6.	$CdCl_2$, $ZnCl_2$ and thiourea	CBD	55	–	–	(Oladeji and Chow, 2005)
7.	$CdCl_2$, $ZnCl_2$ and thiourea	CBD	70	Wurtzite	2.34–3.43	(Borse et al., 2007)
8.	$CdCl_2$, $Zn(NO_3)_2$ and thiourea	CBD	80	Wurtzite	2.46–2.62	(Chavhan et al., 2008)
9.	$Cd(CH_3COO)_2$, $Zn(CH_3COO)_2$ and thiourea	CBD	75	Wurtzite	–	(Lee et al., 2003)
10.	$CdCl_2$, $ZnCl_2$ and thiourea	Spray pyrolysis	275	Wurtzite	–	(Ilican et al., 2007)
11.	$CdCl_2$, $ZnCl_2$ and thiourea	Spray pyrolysis	250	Wurtzite	2.486–3.513	(Akyuz et al., 2007)

The spray pyrolysis technique is particularly attractive because of its simplicity in comparison with methods requiring vacuum conditions or complex equipments. It is fast, inexpensive, vacuumless and is suitable for mass production. The spray pyrolysis technique is basically a chemical deposition technique, in which solutions of the desired material are sprayed onto a preheated substrate. Continuous films are formed onto hot substrate by thermal decomposition of the reactants. Films prepared by this technique are generally polycrystalline in structure and their properties are extremely influenced by the deposition process. In particular, spray pyrolysis has proved well suited for producing semiconductor films of the desired stoichiometry on large and non-planar areas. Although the spray deposition technique was employed earlier for the preparation of $Cd_xZn_{1-x}S$ thin films, cadmium chloride and zinc chloride were used as source for the cadmium and zinc in the deposits (Akyuz et al., 2007; Ilican et al., 2007). A summary of preparation of $Cd_xZn_{1-x}S$ thin films reported in the literature and corresponding sources of Cd, Zn and S is given in Table 1.

In this work, cadmium acetate, zinc acetate and thiourea combination has been used as source materials for the first time (to the best of our knowledge) to fabricate thin films of $Cd_xZn_{1-x}S$ with different composition ($x = 0.0$–1.0) using spray pyrolysis technique. The growth, structural and optical properties of these films in relation to composition 'x' are reported and discussed.

2. Experimental details

$Cd_xZn_{1-x}S$ films of 1 μm thickness were deposited on glass substrates with different Cd concentrations (for $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1) using chemical spray pyrolysis technique. Here x represents the Cd concentration in the spraying solution as also in the films. Aqueous solutions of 0.05 M $Cd(CH_3COO)_2{\cdot}2H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$ and $CS(NH_2)_2$ were used as sources for Cd, Zn and S, respectively. Deionised water was used as a solvent. In each run, 100 ml of solution was sprayed at the rate of 2 ml/min on cleaned glass substrates maintained at an optimized temperature of 573 K. The thickness of the films was measured using optical and gravimetric methods. The average thickness of the prepared films was 1000 ± 10 nm. The films were characterized by X-ray diffraction (XRD) with Cu Kα radiation (Bruker axs D8 Advance model) in the 2θ range from 20° to 60°. The surface properties of all the films were investigated using JEOL SEM 5800 LV. The compositions of samples were determined by energy dispersive X-ray spectroscopy (EDAX). The optical data were obtained within the spectral range 350–750 nm using UV–VIS spectrophotometer (GBC Cintra 101).

3. Results and discussion

3.1. Structural study

II–VI Chalcogenide semiconductor materials show the structural duality, and can be formed as either sphalerite (cubic) or wurtzite (hexagonal) type (Bouroushian et al., 1997). To determine the crystal structure of the $Cd_xZn_{1-x}S$ thin film, the X-ray diffraction patterns were studied. The XRD patterns of the $Cd_xZn_{1-x}S$ films are shown in Fig. 1(a–f). The diffractograms indicate the presence of prominent peaks corresponding to (1 0 0), (0 0 2), (1 0 1) and (1 1 0) planes of the material with hexagonal phase. Moreover, the intensity of the (0 0 2) plane increased with the composition of cadmium, showing that the crystallinity of the films increased with 'x'. The standard crystallographic data for the CdS and ZnS metals were taken from JCPDS (card numbers 41-1049, 36-1450, respectively). In these entire compositions, the (0 0 2) diffraction peak was prominent. The plane (0 0 2) gives lattice matching to the

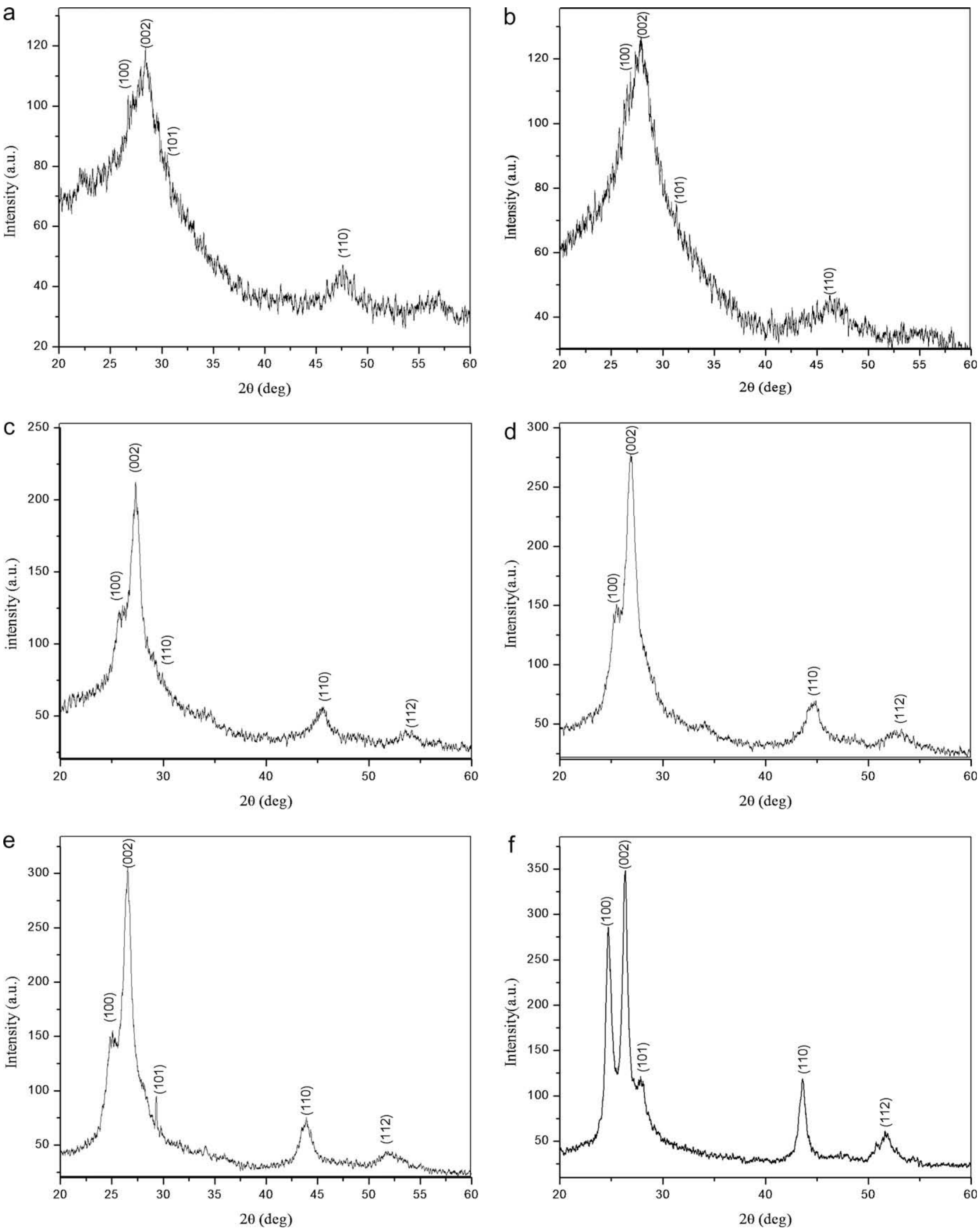

Fig. 1. (a–f) X-ray diffractograms of $Cd_xZn_{1-x}S$ films (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, and (f) $x = 1$.

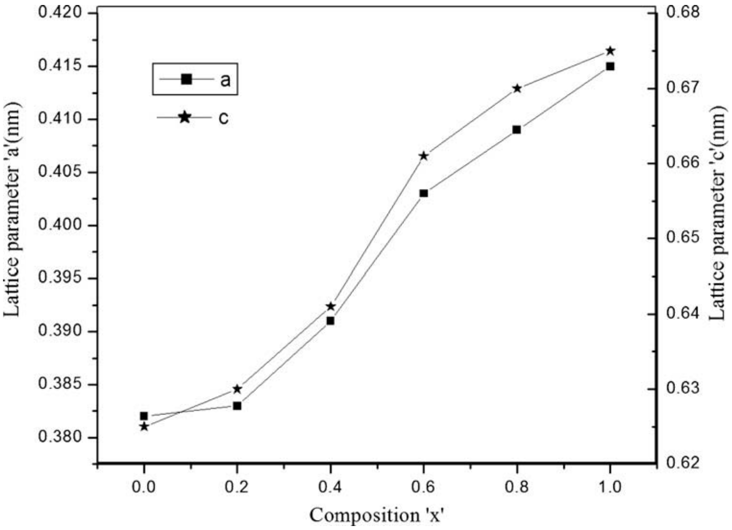

Fig. 2. Plot of lattice parameters versus Cd concentration (x).

chalcogenide semiconductor such as $CuIn_xGa_{1-x}Se_2$ and $CuIn(s_{1-x}Se_x)_2$, which are used in photovoltaic devices. For best solar cell efficiency, the composition of the $Cd_xZn_{1-x}S$ thin film must be in the range $x = 0.9–0.8$ (Jiyon et al., 2006).

The lattice constant a and c for hexagonal phase of CdZnS thin films are calculated using the following equation (Azaroff, 1968)

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

The value of lattice constant 'a' and 'c' varies with composition from 0.382 to 0.415 nm and 0.625 to 0.675 nm, respectively. Fig. 2 shows the variation of lattice parameters with the composition of cadmium (from $x = 0$ to 1) in the films. It is observed that incorporation of Cd leads to an increase in the lattice parameter and hence the unit cell size. This is in agreement with the results obtained earlier (Lee et al., 2003; Yamaguchi et al., 1996; Borse et al., 2007). The grain size 'D' of the samples was estimated by using 'Scherrer's formula (Chatterjee, 2008).

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

where λ is the wavelength of the X-ray used, β is the broadening of the diffraction line measured at half of its maximum intensity (FWHM) and θ is the Bragg angle. The change in the values of lattice constant and the grain sizes with the composition x are given in Table 2. From this table it is observed that the grain size of the $Cd_xZn_{1-x}S$ films increases with increasing cadmium content, attains maximum grain size of about 12 nm for $x = 1$. It is concluded from the structural analysis that the Cd incorporation has a strong effect on the structural properties.

The composition of films was confirmed by energy dispersive X-ray spectroscopy (EDAX). Table 3 shows

Table 2
Summary of the structural parameters and band gap of $Cd_xZn_{1-x}S$ films.

Material	Lattice constants		Average grain size(nm)	Band gap (E_g in eV)
	a (nm)	c (nm)		
ZnS	0.382	0.625	4.5	3.32
$Cd_{0.2}Zn_{0.8}S$	0.383	0.630	5.1	2.98
$Cd_{0.4}Zn_{0.6}S$	0.391	0.641	7.0	2.83
$Cd_{0.6}Zn_{0.4}S$	0.403	0.661	8.3	2.70
$Cd_{0.8}Zn_{0.2}S$	0.409	0.670	9.5	2.55
CdS	0.415	0.675	12	2.41

Table 3
Elemental compositions of $Cd_xZn_{1-x}S$ thin film prepared by spray pyrolysis technique.

Composition 'x'	Film composition	Initial atomic percentage in the spray solution			Final atomic percentage in the film by EDAX analysis		
		Cd	Zn	S	Cd	Zn	S
0.0	$Cd_{0.0}Zn_{1.0}S$	00	50	50	00.00	51.84	48.16
0.2	$Cd_{0.2}Zn_{0.8}S$	10	40	50	10.44	40.81	48.75
0.4	$Cd_{0.4}Zn_{0.6}S$	20	30	50	21.44	30.46	48.10
0.6	$Cd_{0.6}Zn_{0.4}S$	30	20	50	31.63	20.59	47.79
0.8	$Cd_{0.8}Zn_{0.2}S$	40	10	50	41.5	10.36	48.14
1.0	$Cd_{1.0}Zn_{0.0}S$	50	00	50	51.91	00.00	48.09

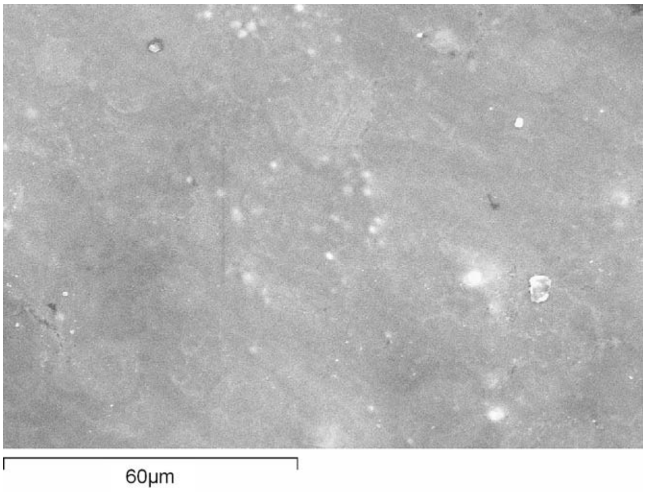

Fig. 3. A representative scanning electron micrograph of ZnS thin film.

the composition of elements in film and initial composition of elements in the sprayed solution. It is concluded that doping can be done very easily and effectively using spray pyrolysis technique. However, sulphur deficiency was observed in all the films. This may be due to the fact that sulphur has great affinity towards oxygen, so it might have converted to SO_2 and then evaporated.

Surface morphological study has been carried out on deposited films using scanning electron microscopy. Fig. 3 is a representative micrograph of ZnS film deposited onto glass substrate at a deposition temperature of 573 K. The film is observed to be uniform in thickness and composition, and is characteristic of deposits obtained by chemical deposition technique. The films with other chemical composition were also similar in their surface features.

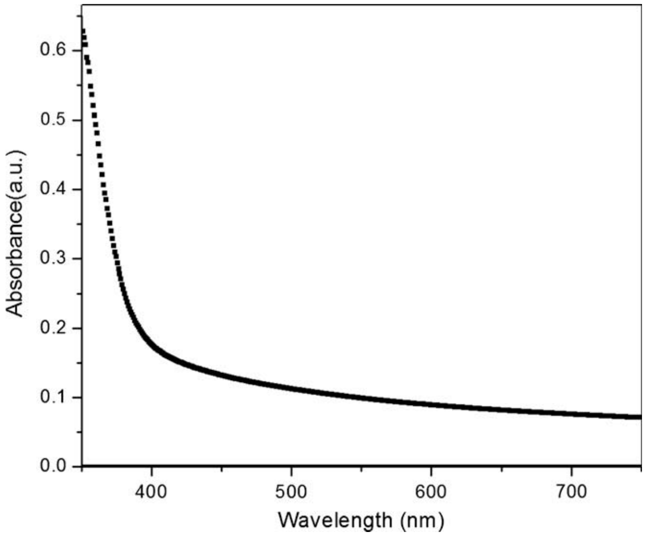

Fig. 4. A representative graph of absorbance versus wavelength of ZnS thin film.

3.2. Optical study

The absorption spectra of the $Cd_xZn_{1-x}S$ thin films for $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 were recorded in the wavelength range 350–750 nm. A representative plot of optical absorbance of film versus wavelength of light is shown in the Fig. 4. The optical studies revealed that the films were highly absorptive with a direct type of transition, which allowed the optical band gap (E_g) to be determined using the following relationship

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

where 'A' is a constant and '$h\nu$' is the radiation energy. The experimentally observed values of $(\alpha h\nu)^2$ plotted against $h\nu$ is shown in Fig. 5 for different composition. The linear nature of the plots at the absorption edge confirmed that $Cd_xZn_{1-x}S$ is a semiconductor with a direct band gap (Wu, 2004). The optical band gap is varied from 3.32 to 2.41 eV. The variation of band gap with the composition of x is shown in Table 2 and Fig. 6. It is observed that small amount of Cd present in the films greatly affects the optical band gap of ZnS. In the initial stages of Cd incorporation, the change in the band gap energy is large. At higher concentrations of Cd, the variation of band gap energy with composition is more or less linear. It becomes necessary to investigate whether the added Cd goes into the lattice at small concentration or remains as interstitials, etc. to explain this observation, which was beyond the scope of this work. The band gap was observed to increase with an increase in the concentration of zinc in the deposits. The nature of this variation in the band gap energy may be useful to design a suitable window material in fabrication of solar cells.

4. Conclusion

$Cd_xZn_{1-x}S$ thin films have been synthesized for the first time by the chemical spray pyrolysis technique using aqueous solutions of $Cd(CH_3COO)_2{\cdot}2H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$ and CH_4N_2S. The XRD study showed the compounds to have hexagonal phase. It was observed that crystallinity of film increased with the composition. In the entire compositions, the (0 0 2) diffraction peak was prominent which gives lattice matching to the chalcogenide semiconductor such as $CuIn_xGa_{1-x}Se_2$ and $CuIn(s_{1-x}Se_x)_2$, Which are used in photovoltaic devices. The lattice parameters are modified with the composition and optical band gap varies from 3.32 to 2.41 eV. It is easy to dope and get required composition and hence the optical band gap using spray pyrolysis technique. Presence of very small amount of cadmium greatly affects the band gap of ZnS films. The range of band gap energy for the mixed films may be helpful in designing a suitable window material in fabrication of solar cells.

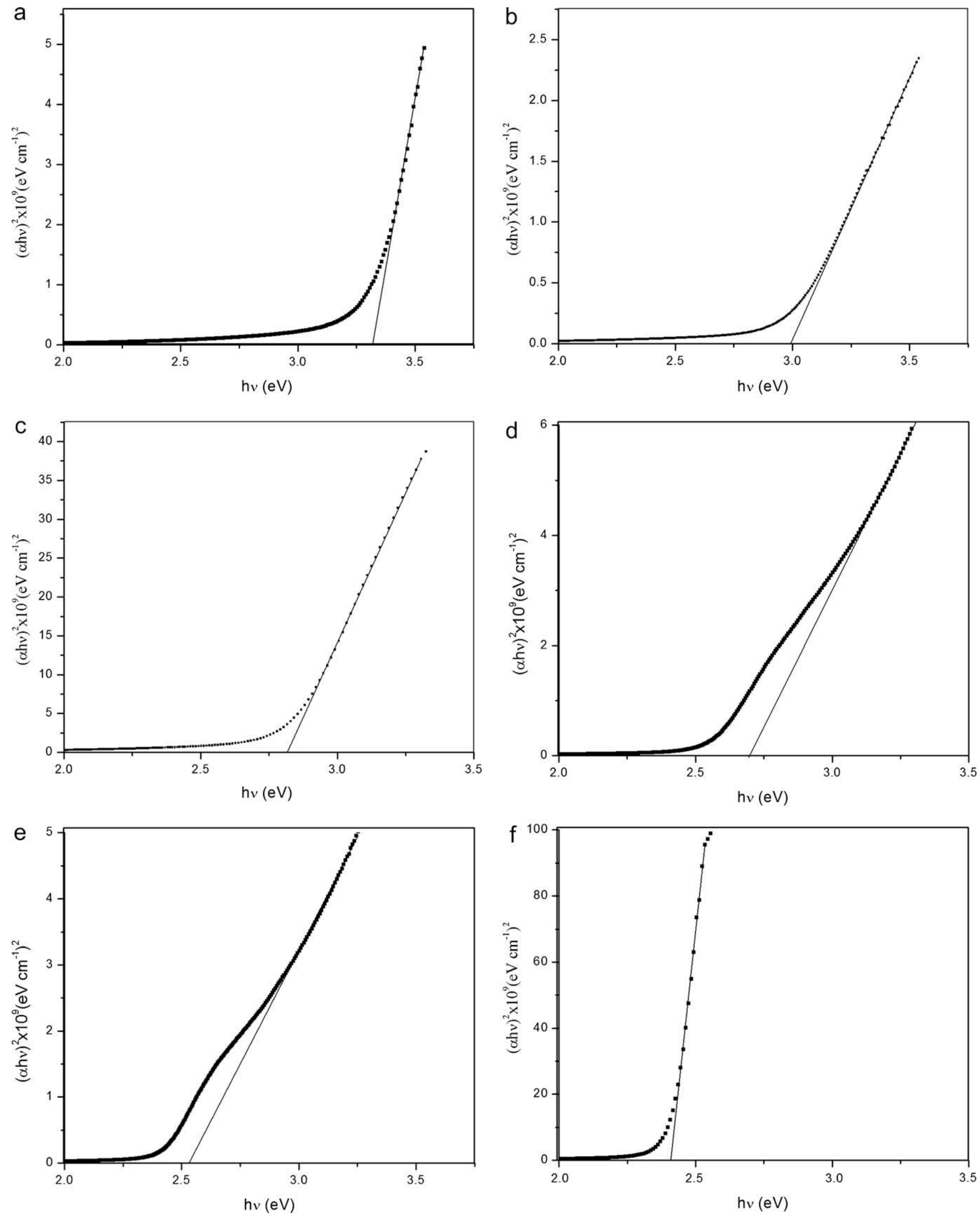

Fig. 5. $(\alpha h\nu)^2$ versus $h\nu$ graph of $Cd_xZn_{1-x}S$ films with $x = 0$, 0.2, 0.4, 0.6, 0.8, 1.

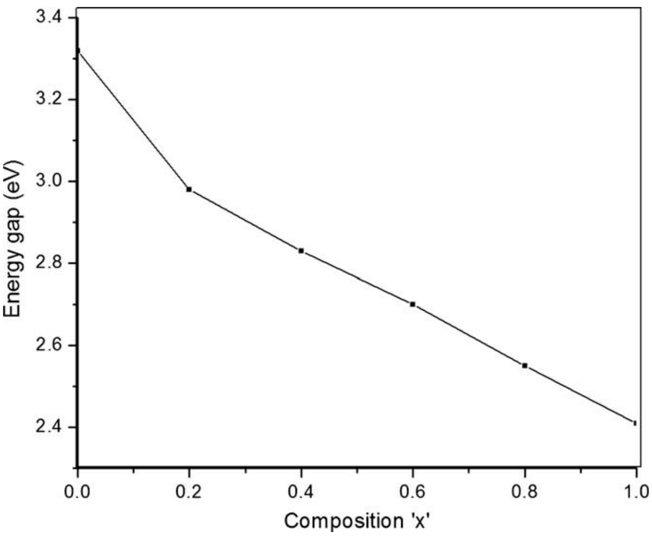

Fig. 6. Dependence of the optical band gap of $Cd_xZn_{1-x}S$ films on composition parameter x.

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