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Structural, optical and electrical properties of Cl-doped ternary CdZnS thin films towards optoelectronic applications

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ABSTRACT

This paper reports the effect of chlorine doping on the structural, morphological, optical and electrical properties of spray deposited ternary CdZnS thin films. Cadmium chloride ($CdCl_2{\cdot}2H_2O$), thiourea ($SC(NH_2)_2$) and $ZnCl_2{\cdot}6H_2O$ were used as precursors to prepare CdZnS thin films. Cl doping is achieved by adding NaCl with concentrations 0, 2, 4, 6 and 8 at.%. XRD analysis showed that the CdZnS and Cl-doped CdZnS films exhibit hexagonal crystal structure with a (0 0 2) preferential orientation. Film transparency increased with Cl doping and the band gap values exhibit a blue shift from 2.55 eV to 2.78 eV. Electrical studies showed that the CdZnS film resistivity decreased from 4.96×10^{-3} ohm-cm to 0.614×10^{-3} ohm-cm with Cl doping. The Raman studies confirmed the presence of defects in samples. Improved transparency, widened band gap and decreased resistivity values observed for the Cl-doped CdZnS films confirm that chlorine might be a suitable anionic dopant which can enhance the physical properties of CdZnS thin films.

1. Introduction

Cadmium sulfide (CdS) is an extensively investigated II–VI metal chalcogenide thin film due to its application in solar cells, optical detectors and optoelectronic devices [1]. CdS thin film is used as window layer in heterojunction solar cells due to its high transparency, wide and direct band gap transition, high electron affinity and n-type conductivity [2]. However, polycrystalline CdS when used in solar cells have some adverse properties due to the creation of high defect density arising from its low band gap, thickness and lattice mismatch [3]. In order to decrease the defect density, the optical and electrical properties of CdS must be improved which can be achieved through doping. It has been reported earlier that when CdS is doped with certain cationic impurities such as Al, Ga, Mn, Zn, Cu, In and with certain anionic impurities such as F, Cl, B etc., its optoelectronic properties may be improved. In our previous work, we reported that Zn doping can improve the optical and electrical properties of pure CdS [4]. Improved optical and electrical properties in CdS through Mg incorporation have been reported earlier by Sivaraman et al. [5]. Besides these cationic impurities, there are earlier reports on anionic impurities influencing the electrical and optical properties of pure CdS. Novruzov et al. [6] reported that boron doping reduces the electrical resistivity of pure CdS. Improved optical transparency, widened optical band gap and decreased electrical resistivity was reported for Cl-doped CdS thin films by Sivaraman et al. [7]. From their results, it is evident that Cl (an anionic dopant) can enhance the physical properties of CdS very much than the cationic dopants. So in the present work, ternary CdZnS thin film was prepared by spray technique using perfume atomizer with fixed concentration of zinc. Cl-doping has been performed by adding NaCl with 0, 2, 4, 6 and 8 at.% Cl concentrations and the effects of Cl doping on the structural, morphological, optical and electrical properties of the as deposited CdZnS thin films were investigated and the results are reported here. The use of perfume atomizer has some specific advantages over the conventional spray technique such as: low cost, non requirement of carrier gas, capable of forming powdered layers through fine atomization and no loss of the precursor to the surroundings [8].

2. Experimental details

Spray pyrolysis technique using perfume atomizer is used to fabricate CdZnS thin films on glass substrates maintained at 400 °C. Cadmium chloride, [$CdCl_2{\cdot}2H_2O$] (0.05 M), thiourea, [$SC(NH_2)_2$] (0.05 M) and zinc chloride [$ZnCl_2{\cdot}6H_2O$] 6 at.% were used as precursor salts to prepare CdZnS thin films. Zinc chloride concentration

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Table 1
Structural parameters of Cl-doped CdZnS thin films.

Cl doping concentration (at.%)	$2\theta_{(002)}$ (°)	Thickness, t (nm)	$f_{(002)}$	Lattice parameters (Å)	
				a	c
0	26.458	429	0.5867	4.122	6.731
2	26.469	437	0.5837	4.116	6.721
4	26.478	448	0.5739	4.114	6.718
6	26.482	459	0.5689	4.108	6.700
8	26.489	465	0.5492	4.111	6.713

is fixed as 6 at.% as it has been optimized as the better concentration to prepare CdZnS thin films in our earlier work [5]. The precursor salts were dissolved in de-ionized water (50 ml in volume) and sprayed on preheated cleaned glass substrates to form CdZnS thin films. Cl doping in CdZnS films was achieved by adding sodium chloride, (NaCl) with concentration 0, 2, 4, 6 and 8 at.% to the starting solution. A PANalytical–PW 340/60 X'pert PRO X-ray diffractometer is used to determine the crystal structure of the films. The thicknesses of the films calculated using Profilometer (Surftest SJ–301) was given in Table 1. Scanning electron microscope (HITACHI S–3000H) is used to analyse the surface morphologies of the films. A Perkin Elmer double beam UV–vis–NIR spectrophotometer is used to find the band gap values of the films. Resistivity values of the films were measured using two point probe setup.

3. Results and discussion

3.1. XRD analysis

XRD patterns of the CdZnS and Cl-doped CdZnS thin films shown in Fig. 1(a–e) confirmed their polycrystalline nature. Five diffraction peaks were observed for all the films at 2θ values approximately equal to 24.828°, 26.458°, 28.140°, 43.640° and 47.830° indexed to (1 0 0), (0 0 2), (1 0 1), (1 1 0) and (1 0 3) planes of hexagonal crystal structure of pure CdS (JCPDS Card No. 06–0314). A (0 0 2) preferential orientation is observed for all the films which exactly matches with the results reported by Sivaraman et al. [9] and Selvan et al. [10] for Mg, Cl co-doped CdS and CdZnS thin films prepared by spray pyrolysis technique using perfume atomizer. The occurrence of preferential orientation might have existed owing to the

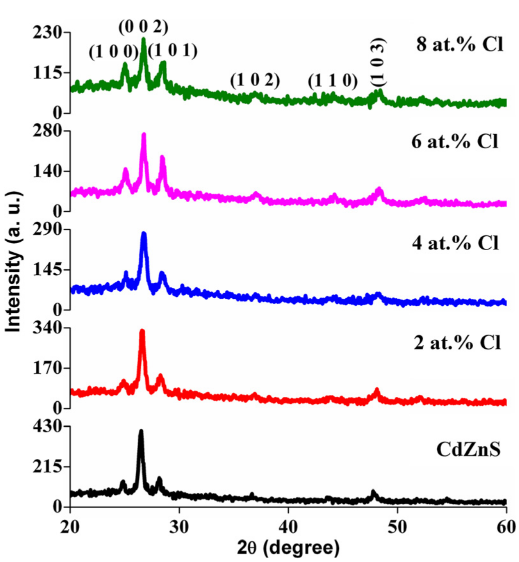

Fig. 1. XRD patterns of Cl-doped CdZnS thin films.

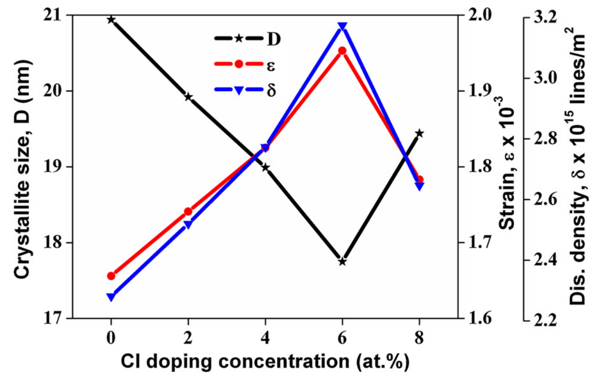

Fig. 2. Variation of microstructural parameters of Cl-doped CdZnS thin films.

minimization of surface energy and internal stress [11]. The preferential orientation factor $f(0\,0\,2)$ values of the films estimated by the way adopted by Suganya et al. [12] are compiled in Table 1. A linear decrement is observed in the $f(0\,0\,2)$ values for the doped CdZnS films confirming that crystalline quality of CdZnS deteriorates with Cl doping. A close examination of the XRD patterns showed that the width of the (0 0 2) peak of the CdZnS film gets broadened with Cl doping indicating the formation of smaller crystallites in the doped films. Presence of large number of defects might also be another reason for the peak broadening effect observed here [13]. It can be observed from the XRD patterns, that the 2θ values of the (0 0 2) peak shift towards higher Bragg angles for the doped films inferring a contraction in their lattice parameter values. The lattice parameter values were calculated using the formula [4]:

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

and the obtained values are compiled in Table 1[1].

The microstructural parameters such as crystallite size (D), strain (ε) and dislocation density (δ) values of the films were estimated using formulae [14]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (3)$$

$$\delta = \frac{1}{D^2} \quad (4)$$

where λ is the wavelength of the X-rays used (1.5406 Å), β is the full-width at half maximum of the strongest peak ((0 0 2) in this case) and θ is the Bragg's angle. Fig. 2 shows the variation of micro structural parameters of the Cl-doped CdZnS thin films. From this figure, it is observed that the crystallite size decreased from 20.94 nm for the CdZnS film to 17.55 nm for 6 at.% Cl-doped CdZnS film and then it slightly increased to 19.44 nm for the CdZnS film coated with 8 at.% Cl doping concentration. Correspondingly, the lattice defects like strain and dislocation density showed an increasing trend with Cl doping up to 6 at.% concentration and above this concentration it slightly decreases. A possible explanation for the decreased crystallite size values obtained for the Cl-doped CdZnS films can be given as follows: When CdZnS film is doped with Cl, Cl^- ions uniformly substitute S^{2-} ions in the host

[1] It is observed that the lattice parameter values decreases with doping which might be due to the ionic size difference between the dopant Cl^- (1.81 Å) and host S^{2-} (1.84 Å) ions.