ZnS ASSISTED Zn DOPING IN CdZnS ELECTRODEPOSITION

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ABSTRACT

Many reports have been published elsewhere on making thin films of cadmium zinc sulphide (CdZnS) using different techniques. This article summarizes a method developed to form CdZnS by incorporating electrodeposited Cd and S atoms simultaneously to the chemically formed ZnS material in the electrolytic bath at the conducting surface of fluorine doped tin oxide (FTO) coated glass substrate. Moreover, the mechanism of formation of CdZnS is proposed as a solid state reaction between electrodeposited Cd and S atoms on the glass/FTO substrate with adsorbed ZnS particles from the electrolytic bath. The precursors used for Cd, S and ZnS in the electrolyte were aqueous solutions of CdCl₂, ZnCl₂ and Na₂S₂O₃. Two different methods were tested to form ZnS within the electrolyte bath where one forming ZnS in the bath at the beginning of electrodeposition of Cd and S and in the other one, ZnS is formed before the electrodeposition of Cd and S. The results of the band gap measurements show an undulation which is closer to the band gap energy of CdS (2.42 eV), ZnS (3.7 eV), CdO (2.2 eV), and ZnO (3.2 eV) along with CdZnS.

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The Tauc plot resulted by the material produced in method 1 has shown an undulation at the onset of Tauc plot which is near the band gap energy of CdS indicating the codeposition of CdS with CdZnS, but the Tauc plot of CdZnS electrodeposited from method 2 has shown clear separation in band gaps from 2.44 – 2.52 eV, when the annealing temperature, the Zn^{2+} ion concentration in bath and the electrodeposition pH were varied. These thin films were also characterized by photoelectrochemical (PEC) cell analysis, x-ray diffraction (XRD), energy dispersive x-ray analysis (EDXA) and scanning electron microscopy (SEM) techniques.

Keywords: electrodeposition, CdZnS, Tauc plot, undulation, doping

INTRODUCTION

The cadmium zinc sulphide (CdZnS) thin films have been studied as a potential wide band gap semiconductor to be used in solar cells, detectors and other optoelectronic devices (Panbude et al., 2018). The CdZnS is an n-type semiconductor which is basically produced by doping the CdS lattice with Zn atoms. The CdZnS is mostly deposited by chemical bath deposition and vapour deposition techniques (Sanap and Pawar 2011; Lee *et al.*, 2003), while electrodeposition technique is used infrequently though it is a simple and low cost technique. The CdZnS has been electrodeposited by Jayachandran *et al.*, (1990), at high deposition voltages (-0.9 V to -1.1 V) and mostly the electrodeposition of CdZnS were carried out under room temperature conditions (Lokhande *et al.*, 1988; Jayachandran *et al.*, 1990; Nagalingam *et al.*, 2011). Morris and Vanderveen (1992) have electrodeposited CdZnS at high temperatures with the assistance of ZnS formation reaction in which $\text{ZnCl}_2(\text{aq})$ and $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ were reacted to form ZnS. Further, the same reaction has also been followed by some other researchers (Clark 1974; John 1935). Kassim *et al.*, (2011)

have carried out the chemical bath deposition of ZnS by reacting Zn^{2+} ions and $\text{Na}_2\text{S}_2\text{O}_3$. The reaction between Cd^{2+} and $\text{Na}_2\text{S}_2\text{O}_3$ was reported to be feasible only under UV radiation according to works of photochemical deposition technique (Kumar *et al.*, 2013; Pushpalatha and Ganesha 2015) while no such condition was required for ZnS formation in the reaction between Zn^{2+} ions and $\text{Na}_2\text{S}_2\text{O}_3$.

In Tauc plots of CdZnS thin films, undulations were observed in studies carried out elsewhere (Sanap and Pawar 2011; Kumar 2007) and these undulations revealed to be more pronounced when the materials were deposited at low temperature than at high temperatures (Sanap and Pawar 2011; Lee *et al.*, 2003). Similar undulation was also encountered in the present study, but a method has been developed to eliminate the formation of undulation near the band gap of CdZnS and hence to minimize the codeposition of other materials such as CdS (2.42 eV), ZnS (3.7 eV), CdO (2.2 eV), and ZnO (3.2 eV) with CdZnS.

METHODOLOGY

Prior to electrodeposition, glass/FTO substrates (Sigma Aldrich, $13 \Omega/\text{sq}$, $3 \times 1 \text{ cm}^2$) were thoroughly cleaned with detergent soaked cotton buds and washed with deionized water followed by sonication at 40°C for 10 minutes. Then glass/FTO substrate was chemically cleaned with acetone, methanol and isopropanol by heating the glass/FTO substrate at 80°C in each solvent for 5 minutes separately.

A three electrode system was employed in the electrodeposition process that consisted of a working electrode (glass/FTO substrate), a reference electrode [saturated calomel electrode (SCE)] and a counter electrode (99.5% purity graphite rod). The deposition potentials of precursor ions were selected based on cyclic voltammogram studies of each precursor solution performed using the potentiostat/galvanostat (Gamry “300” series).

In the method-1, CdZnS thin films were potentiostatically deposited using an electrolytic bath consisted of 0.1 mol/L CdCl₂ (Sigma Aldrich, 99%), 0.01 mol/L ZnCl₂ (Sigma Aldrich, 99%) and 0.01 mol/L Na₂S₂O₃ (Sigma Aldrich, 99%). The CdZnS thin films were produced at a deposition voltage of -0.71 V, pH of 2.5, and deposition temperature of 50 °C for 60 minutes under a 65 rpm stirring rate. Then the thin films were annealed at 400 °C for 10 minutes in air (Lenton WHT 6/30). Further studies were performed by varying the Zn²⁺ ion concentration of the electrolyte (0, 0.01, 0.03 and 0.05 mol/L) to see the effect of the dopant on the properties of the resultant CdZnS.

In method-2, the electrolyte bath consisted of CdCl₂ (0.2 mol/L), ZnCl₂ (0.02, 0.04 & 0.06 mol/L) and Na₂S₂O₃ (0.01 mol/L) underwent a pretreatment process before starting the electrodeposition, in which, the bath was stirred at a high rate (350 rpm) at pH of 3.0 and temperature of 65 °C for 60 minutes. The CdZnS thin films were electrodeposited using the same deposition parameters discussed above in method 1, at pHs of 2.8, 2.7, 2.6, 2.5 & 2.4. The resultant CdZnS thin films were annealed at 350 °C in air for 10 minutes. The variation of band gap at two annealing temperatures were also obtained at 350 °C and 400 °C. The electrodeposited materials were characterized using a photoelectrochemical (PEC) cell, UV-visible spectrometer (Cintra 202), X-ray diffractometer (Rigaku-Ultima IV), scanning electron microscopy (FEI-SEM NOVA NANO) and energy dispersive x-ray analysis (ZESIS EVO LS 15 SEM & INCAx-act 51-ADD0048 x-ray detector).

The PEC cell was constructed with the above mentioned 3 electrode system in 0.1 mol/L Na₂S₂O₃ electrolyte. I-V curves were obtained by chopping the light beam that was used to illuminate the thin film/electrolyte junction, at a rate of 30 cycles/minute. The PEC signals were obtained at zero bias condition under dark and illumination using the same setup. The Tauc plot was used to determine band gap of semiconductor using Equation 1.

Where, A is absorption h is the Plank constant, ν is frequency and E_g is the band gap of the semiconductor.

$$(Ah\nu)^2 \propto (h\nu - E_g) \quad (1)$$

RESULTS AND DISCUSSION

CdZnS electro-deposition by method-1

The visual appearance of the of CdZnS thin films electro-deposited in method-1 is shown in Figure 1. The Tauc plots of these samples have shown an undulation near the band gap energy corresponding to CdS. When Zn^{2+} ion concentration in the electrodeposition bath was changed as 0.01 mol/L, 0.03 mol/L and 0.05 mol/L, the variation of the band gap energies of CdZnS thin films were shown in Figure 2 that is increased from 2.48 eV to 2.85 eV. The undulation encountered in the plot in advance to the band gap energy of CdZnS could be due to multi-reflections occurring inside the spectrophotometer by CdZnS thin film while taking the measurements (Milosevic & King, 2012) and/or due to existence of mixed phase/s which absorb energy in different wavelength regions. The undulation occurred in this work was considered as mainly due to the codeposition of CdS and CdZnS, since it appear at the onset of each Tauc plot in Figure 2. The band gap of CdS around 2.35 - 2.40 eV hindered the determination of band gap corresponding to the CdZnS thin film. The band gap of mixed phases of CdS and CdZnS are shown in Table 1. The undulation was less pronounced in Tauc plot of CdZnS thin film electrodeposited from 0.05 mol/L Zn^{2+} ion bath.

(a) As-deposited samples

(b) Annealed samples

Figure 1: The images of (a) as deposited and (b) annealed CdS and CdZnS samples.

The Cd:Zn ratios of electrodeposition baths were denoted with each image.

Figure 2: Tauc plots of CdS (a) and CdZnS thin films electrodeposited from 0.01 mol/L (b), 0.03 mol/L (c), and 0.05 mol/L (d) Zn^{2+} ion in the electrodeposition baths in method-1.

Table 1: Band gap values of different phases in CdZnS thin films according to**Figure 2.**

[Zn ²⁺] in electrodeposition bath (mol/L)	band gaps of mixed phases (eV)
0.00 (deposition of pure CdS)	2.38 (a)
0.01	2.35 and 2.48 (b)
0.03	2.38 and 2.64 (c)
0.05	onset of the undulation at 2.4 and 2.85 (d)

The photoelectrochemical cell results have shown that CdZnS is an n-type semiconductor (the effective area $\sim 0.8 \text{ cm}^2$). When semiconductor is in equilibrium with the electrolyte, the energy bands of semiconductor are bent near the interface. Therefore, I-V curve of n-type semiconductor which is obtained from PEC cell has negative open circuit voltage (V_{oc}) while that is positive in p-type semiconductor. The V_{oc} values of CdZnS thin films electrodeposited from 0.01 mol/L, 0.03 mol/L and 0.05 mol/L Zn^{2+} ion in the baths in method-1 are shown in Table 2.

Table 2: The open circuit voltages (V_{oc}) of I-V curves obtained by PEC cell studies of CdZnS thin films electrodeposited by varying Zn^{2+} ion concentration.

[Zn ²⁺] in electro-deposition bath (mol/L)	Open circuit voltage (mV)
0.01	-353
0.03	-471
0.05	-298

A CdZnS thin film grown using CdCl_2 (1 mol/L), ZnCl_2 (0.01 mol/L) and $\text{Na}_2\text{S}_2\text{O}_3$ (0.01 mol/L) under the deposition voltage of -0.71 V, pH of 2.5, and deposition temperature of 50 °C for 60 minutes at 65 rpm stirring rate followed by annealing at 400 °C for 10 minutes, was subjected to XRD analysis. The x-ray diffractogram of CdZnS thin film shown in Figure 3, indicates the wurtzite hexagonal crystal structure of the material. The XRD of glass/FTO/CdZnS was compared with greenockite (00-041-1049), sphalerite (00-001-0792) and cassiterite (00-046-1088) in PDF-2 ICDD database to identify CdS, ZnS and SnO_2

respectively (Figure 3 and Table 3). In the diffractogram, peaks analogous to CdS and ZnS phases were not present due to amorphous or weakly crystalline nature of these materials. But the undulation in the Tauc plot provides evidence to the presence of CdS phase, and hence support this argument. The d-spacing of XRD peaks were used to calculate crystal parameters of hexagonal crystal structure by using Equation 2. The Table 4 gives the calculated a, b and c crystal parameters from d-spacing of (1 0 0), (1 0 1), (1 1 0), (1 0 3) and (0 0 4) miller indexed peaks of CdZnS. According to calculations, lattice parameter ‘a’ of CdZnS was lower than that of pure CdS and the change in lattice parameter ‘c’ is negligible. The ionic radii of Cd^{2+} and Zn^{2+} are 74 pm and 95 pm respectively. Therefore, a possible replacement of Cd^{2+} by Zn^{2+} in CdS, likely to result in the observed reduction in the lattice parameters.

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

Figure 3: X-ray diffractogram of CdZnS thin film electrodeposited in method-1.

Table 3: XRD peak positions and relative intensities of CdZnS peaks. The standard CdS peaks were used to identify the crystal system of CdZnS.

d spacing of CdS standard peak	CdZnS XRD peaks			
	Peak position (2 θ)	d spacing	Assign miller index for CdZnS	Relative intensity (cps)
3.5823	24.8661	3.5764	(1 0 0)	22
3.1608	28.3156	3.1481	(1 0 1)	21
2.0682	43.8077	2.0641	(1 1 0)	10
1.8977	47.9543	1.8948	(1 0 3)	9
1.6783	54.6012	1.6788	(0 0 4)	10

Table 4: The calculated crystal parameters from Equation 2 of a hexagonal lattice.

Unit cell parameter	Miller index of CdZnS peak	Unit cell parameter of CdZnS (Å)	Unit cell parameter of CdS (Å)
a	(1 0 0)	4.1297	4.1365
a	(1 1 0)	4.1282	4.1364
c	(0 0 4)	7.7540	7.7517

Energy dispersive x-ray analysis (EDXA) is used for the determination of element ratio in the thin film and the results shows the presence of Zn in thin film analyzed (Figure 4). Table 5 gives the percentages of Cd and Zn in five different positions of CdZnS thin film. The Cd : Zn was about 9:1 in CdZnS thin film which was fabricated from electrodeposition bath consisted of Cd : Zn = 10:1. The peaks of Sn and O elements in EDXA represent the FTO substrate.

Figure 4: EDXA of CdZnS thin film electro-deposited from method-1.

Table 5: The Cd and Zn atomic percentages at five random positions of CdZnS thin film.

Measurement position	Atomic percentage of Cd and Zn in CdZnS thin film	
	Cd%	Zn%
1	94.44	5.56
2	93.59	6.41
3	90.77	9.23
4	90.77	9.23
5	95.02	4.98

Since the presence of CdS phase was observed in Tauc plot (Figure 2) the method-1 was modified to eliminate codeposition of CdS and described as method-2.

CdZnS electro-deposition by method-2

ZnS particles were induced to form in the electro-deposition bath before starting the electrodeposition (deposition potential = -0.71 V) in this method. Undulation in the Tauc plots of thin films that fabricated were observed to be not so pronounced due to minimal codeposition of CdS. Variation of the band gap by changing the annealing temperature (300 °C & 400 °C), concentration of Zn^{2+} (0.02, 0.04 & 0.06 mol/L), and pH of the bath (2.4, 2.5, 2.6, 2.7 & 2.8) were also studied. Tauc plots of thin films subjected to above annealing temperatures were compared with that of as-deposited CdZnS thin film as shown in Figure 5. In here the band gaps tend to decrease with lowering the annealing temperature from 400 °C to 350 °C. When Zn^{2+} concentration in the bath was increased from 0.02 mol/L to 0.06 mol/L, the band gap was increased from 2.44 – 2.50 eV (Figure 6). That reveals, the concentration of dopant Zn^{2+} ions in the thin film produced has increased. According to the reports elsewhere bath pH around 3 have been used for electrodeposition of ZnS while pH around 2 have been used for electrodeposition of CdS (Echendu *et al.*, 2014). Figure 7 has shown that with the gradual change of pH value from 2.4 to 2.8, the increase of band gap

from 2.44 to 2.52 eV occurs. Therefore, Zn doping to CdS can be induced by increasing electrodeposition within this pH range.

Figure 5: Variation in band gap as a function of annealing temperature of CdZnS thin film electrodeposited from method-2.

Figure 6: Variation in band gap of CdZnS thin film as a function of the concentration of Zn²⁺ ion in the electrodeposition bath of method-2.

Figure 7: Variation in band gap of CdZnS thin film with pH of the electrodeposition bath in method-2.

ZnS can be formed by reacting ZnCl_2 with $\text{Na}_2\text{S}_2\text{O}_3$. ZnS was formed at the beginning of electrodeposition in method-1 while in the method-2, ZnS was formed in the electrodeposition bath before starting the electrodeposition process by setting up favorable condition for it [i.e., stirring the bath at a higher rate (350 rpm) at pH of 3.0 and at temperature of 65°C for 60 minutes]. When the electrodeposition bath was adjusted to required acidic pH (3.0), sulfur tend to form due to the reaction between H^+ and $\text{Na}_2\text{S}_2\text{O}_3$. There was not enough ZnS at the beginning of electrodeposition in method-1, but ZnS was present in the bath to occur solid state reaction with CdS at the beginning of electrodeposition in method-2. Therefore, codeposition of CdS with CdZnS phase was minimized. The following chemical and electro-chemical reactions occurred in the CdZnS electro-deposition process.

However, Zn^{2+} can be reduced to Zn at the corresponding potential and can react with CdS to form CdZnS as well.

According to SEM analysis, the CdZnS thin films produced in method-2 consisted of uniform grain sized distribution (Figure 8). The CdZnS thin film had grains around 150 – 200 nm sizes with no aggregated grains and pin holes.

Figure 8: SEM image of CdZnS thin film electrodeposited from method -2.

CONCLUSION

The main problem encountered in CdZnS thin film deposition was the formation of mixed phases which is evident in the Tauc plots. This affect the purity of the material formed and hence its properties. A pretreatment step was tested and described as method-2 to eliminate the undulation occurred due to codeposition of CdS with CdZnS through the formation of ZnS before starting the electrodeposition process.

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