

DEPOSITION OF $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ FILMS BY BRUSH ELECTRODEPOSITION AND THEIR CHARACTERISTICS

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$\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ films ($0 \leq x \leq 1$) were deposited for the first time by the brush plating technique at room temperature from an aqueous bath containing zinc sulphate, cadmium sulphate and selenium oxide. The deposition current density was varied in the range of 50 – 250 mA cm^{-2} . The as deposited films exhibited cubic structure. Composition of the films was estimated by EDAX studies. Optical band gap of the films varied from 1.72 eV to 2.70 eV as the composition varied from CdSe to ZnSe side. Electrical properties of the films were determined at room temperature. The room temperature resistivity, carrier density and mobility varied in the range of 9.0 ohm cm – 200 ohm cm, $10 - 2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $6.94 \times 10^{16} - 1.56 \times 10^{16} \text{ cm}^{-3}$ respectively as the composition changed from CdSe to ZnSe side.

(Received January 11, 2008; accepted January 15, 2009)

Keywords: Semiconductor, II-VI, Thin films, Electrodeposition

1. Introduction

Several semiconducting films have been deposited for optoelectronic device applications. Amongst them, CdSe is a very promising candidate for photoelectrochemical cells and photoconductive cells. ZnSe is a very important material for luminescent and light emitting devices. However, CdSe is found to undergo photocorrosion when used in photoelectrochemical cells, whereas, ZnSe is found to be more stable though less photoactive due to its wide band gap [1,2]. Coupling of cadmium selenide and zinc selenide would provide materials with different band gaps depending upon the composition, which in principle may be suitable for accomplishing the twin tasks of increased absorption of solar spectrum and enhanced resistance towards photocorrosion [3 -5]. $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ films were deposited by different physical and chemical methods. To our knowledge, the brush plating technique has been used for the first time to deposit $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ (CZS) films.

2. Experimental Methods

Thin films of CZS have been deposited by the brush plating technique at room temperature using AR grade (99.99% pure) ZnSO_4 , CdSO_4 and SeO_2 at room temperature and at deposition current densities in the range of 50 – 250 mA cm^{-2} . In order to obtain CZS films of different compositions, the concentration of ZnSO_4 and CdSO_4 were varied in the range of 0.45 – 0.05M and 0.05 – 0.45M respectively. In all cases 3 ml of CdSO_4 and 3 ml of ZnSO_4 of each concentration was taken and to this mixture, 1 ml of 0.001M SeO_2 was added. Titanium and conducting glass substrates were used for the deposition of the films. Thickness of the films estimated by Mitutoyo surface profile meter was found to be in the range of 1.5 – 2.8 micrometres as the composition changed from $x=0$ to 1 in $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ films. The thickness of the films deposited at low current densities is low, the thickness increases as the deposition current density

increases irrespective of composition. The films were characterized by x-ray diffraction to determine the structure of the films. Optical absorption measurements were made on the films to determine the band gap of the films. Composition of the films was estimated by EDAX studies. Hall measurements were made on the films adopting the procedure reported earlier [6]. In this method the CdZnSe layer is mechanically transferred from the conducting substrate onto a non-conductive epoxy resin without the formation of cracks [7]. The electrical properties of the CdZnSe layers were examined at room temperature by resistivity and Hall measurements using Van der Pauw method. Vacuum evaporated Indium served as the ohmic contact.

3.Results and discussion

X-ray diffraction studies indicate the formation of cubic structure. As the deposition current density increased, the width as well as the intensity of the peaks decreased. Fig.1 indicates the XRD patterns of the as deposited films of different composition deposited at different current densities. The peaks corresponding to cubic structure was observed in all cases. The peaks corresponding to (111),(220) and (311) were observed in all cases. As the CdSe content in the mixture increases, the above peaks are found to shift towards CdSe side. In all the cases, the peaks were broad for the films deposited at lower current densities and the peaks became sharper as the current density increased. The 'd' values are observed to shift from ZnSe to CdSe values as the concentration of CdSe increases in the ternary. Composition of the films was studied by Energy dispersive analysis of X-rays. Table-I indicates the composition of the films. It is observed from the table that the composition of the as-deposited films were nearly equal to the starting composition of the precursors taken for deposition. The EDAX spectrum of the CZS films deposited at a current density of 250 mA cm^{-2} is shown in Fig.2, the peaks corresponding to Cd increase in height as the cadmium selenide content in the film increases.

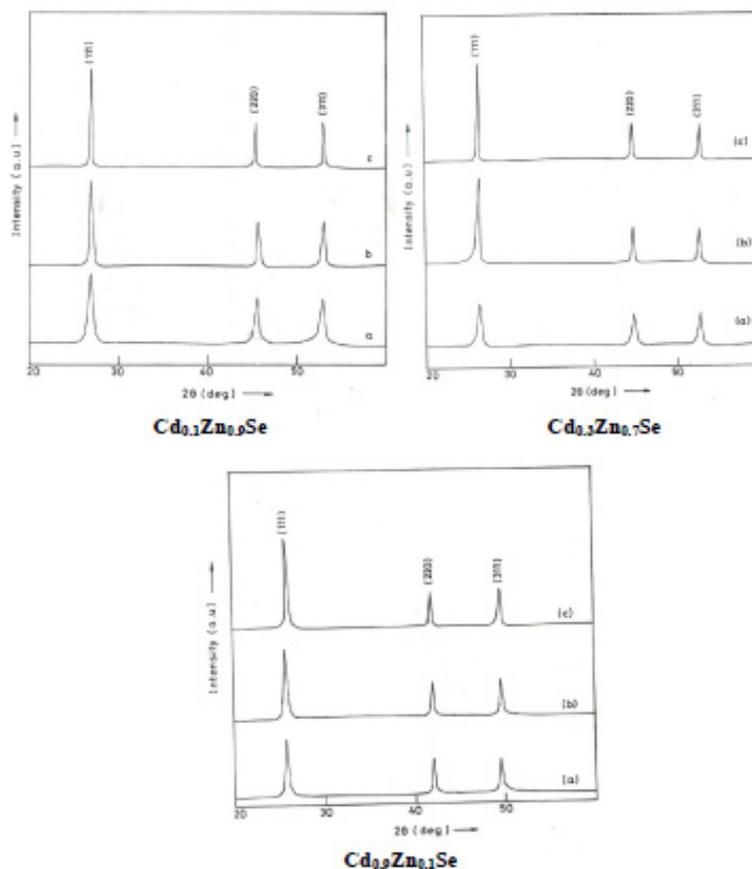


Fig.1. X-ray diffraction pattern of $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ films of different composition deposited at a different current densities (a) 50 mA cm^{-2} (b) 150 mA cm^{-2} (c) 250 mA cm^{-2} .

Table 1. Composition of the Films

Precursor Composition	EDAX Composition
$Cd_{0.1}Zn_{0.9}Se$	$Cd_{0.11}Zn_{0.89}Se$
$Cd_{0.2}Zn_{0.8}Se$	$Cd_{0.21}Zn_{0.79}Se$
$Cd_{0.3}Zn_{0.6}Se$	$Cd_{0.30}Zn_{0.70}Se$
$Cd_{0.5}Zn_{0.5}Se$	$Cd_{0.50}Zn_{0.50}Se$
$Cd_{0.7}Zn_{0.3}Se$	$Cd_{0.70}Zn_{0.30}Se$
$Cd_{0.9}Zn_{0.1}Se$	$Cd_{0.90}Zn_{0.10}Se$

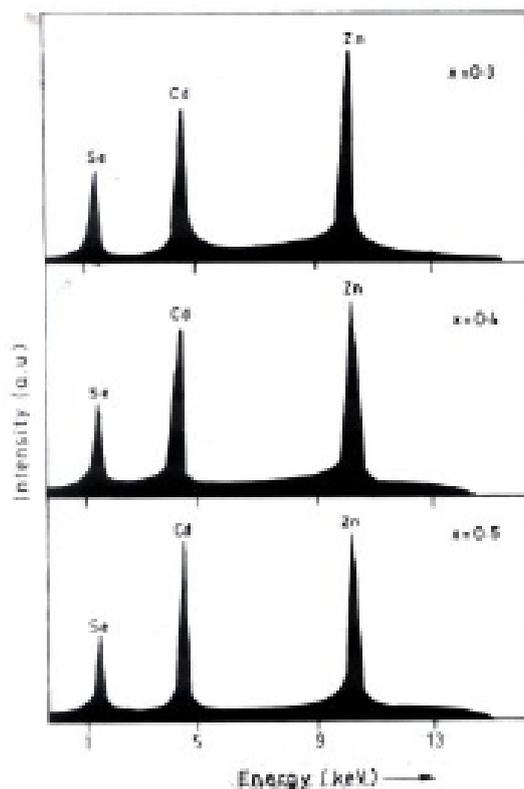


Fig. 2. EDAX spectrum of $Cd_xZn_{1-x}Se$ films of different composition deposited at a deposition current density of 250 mA cm^{-2} .

The absorbance spectra of the CZS films of different compositions was determined in the wavelength range 300 – 800 nm at room temperature. Substrate absorption, if any was corrected by keeping an identical uncoated conducting glass substrate in the reference beam. Fig.3 indicates the absorbance spectrum of the CZS films of different composition deposited at a current density of 250 mA cm^{-2} . In order to estimate the band gap of the films, a plot of $(\alpha h\nu)^2$ vs $h\nu$ was plotted for the films of different composition (Fig.5). The variation of band gap with composition is linear, the band gap increases from 1.72 eV for CdSe films to 2.70 eV for ZnSe films. These values are in good agreement with the earlier report[8].

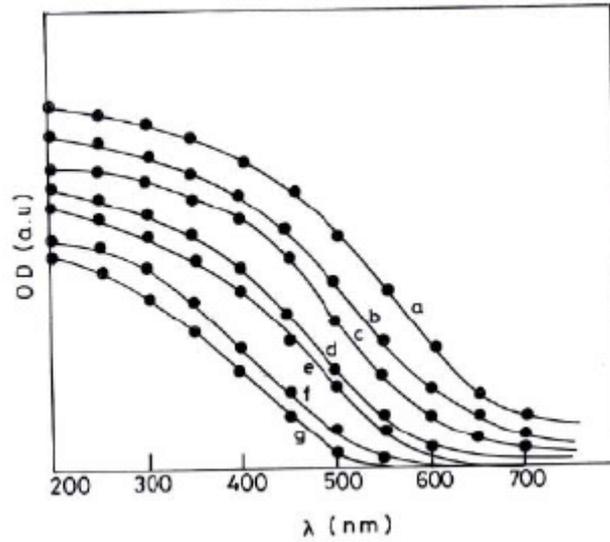


Fig. 3. Absorbance spectrum of the $Cd_xZn_{1-x}Se$ films of different composition (x) deposited at a deposition current density of 250 mA cm^{-2} (a) 0.1 (b) 0.3 (c) 0.4 (d) 0.5 (e) 0.7 (f) 0.8 (g) 0.9.

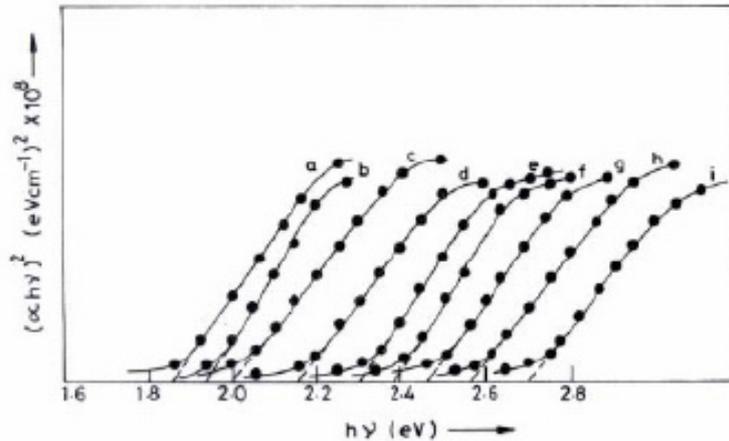


Fig. 5. $(ahv)^2$ vs hv plot of the $Cd_xZn_{1-x}Se$ films of different composition (x) deposited at a deposition current density of 250 mA cm^{-2} (a) 0.1 (b) 0.2 (c) 0.3 (d) 0.4 (e) 0.5 (f) 0.6 (g) 0.7 (h) 0.8 (i) 0.9.

The value of the resistivity determined from Van der Pauw method varied from 10^4 to 10^2 ohm cm as the substrate temperature increased (CdSe concentration in the CdZnSe films increased). Hall measurements also indicated the films to be n-type. The carrier density, mobility and resistivity of the films of different composition deposited at a deposition current density of 250 mA cm^{-2} are shown in Table-II.

Table 2. Variation of resistivity, carrier density and mobility of $Cd_xZn_{1-x}Se$ films with composition

Composition (x)	Resistivity (ohm cm)	Carrier density (cm^{-3})	Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
0.1	200	1.56×10^{16}	2.0
0.3	100	1.90×10^{16}	3.3
0.5	60	2.23×10^{16}	4.8
0.7	28	3.38×10^{16}	6.7
0.9	9	6.94×10^{16}	10.0

Photoluminescence(PL) spectra were recorded at room temperature using an excitation wavelength of 450 nm for the films of different composition deposited at a duty cycle of 50%. The samples rich in CdSe did not exhibit any photoluminescence. As the composition of the films is decreased below $x = 0.7$ in $Cd_xZn_{1-x}Se$ films, the photoluminescence emission spectrum increased in intensity with increase in ZnSe concentration. The spectra peaks at 678 nm for the films of composition $Cd_{0.7}Zn_{0.3}Se$, the peak is observed to shift towards blue side as the x -value decreases and for a film of composition $Cd_{0.1}Zn_{0.9}Se$, the PL emission peaks at 675nm (Fig.6). The PL

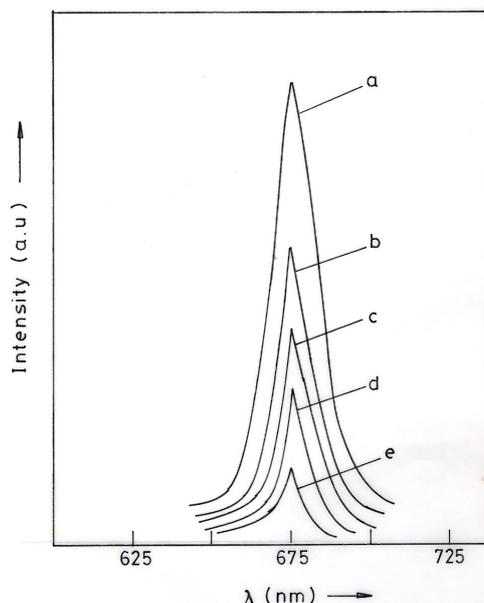


Fig.6. PL spectra of $Cd_xZn_{1-x}Se$ films of different composition deposited at a current density of $250 mA cm^{-2}$ (a) $x = 0.1$ (b) $x = 0.2$ (c) $x = 0.3$ (d) $x = 0.5$ (e) $x = 0.7$

emission from pure ZnSe has been attributed to the presence of native defects like zinc and selenium vacancies or interstitial, which are likely to be introduced during the growth process[9]. Self activated centers arising from the complexes of zinc vacancies and shallow donors (selenium interstitials) would occur around 2.0 eV[10]. The emission band observed in the present case at 675 nm may be attributed to the above complex.

4. Conclusions

All the results indicate that $Cd_xZn_{1-x}Se$ films of different composition could be deposited by the brush plating technique. Films with resistivities in the range of 9 – 200 ohm cm can be prepared with change in composition from CdSe to ZnSe side. Films with photoluminescence emission at 675 nm can be obtained by this technique. Further work is in progress for doping the films with Cu and Mn to obtain different colours of emission and also to increase the PL intensity.

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