PROPERTIES OF ZnSe FILMS PULSE PLATED ON HIGH TEMPERATURE SUBSTRATES

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ZnSe films were deposited on titanium and conducting glass substrates at 50 % duty cycle and at different deposition temperatures in the range of 30 - 80°C. The deposition current density was maintained constant at 100 mAcm^{-2}. The prominent peaks corresponding to the cubic phase are observed in all cases. Optical measurements indicated yields band gap in the range of 2.64 – 2.68 eV for the films deposited at different deposition temperatures. Atomic force microscopy studies showed that the crystallite size increased from 43 – 76 nm as the deposition temperature increases. The cross plane resistivity of the films was found to decrease with increase of substrate temperature. The films were doped with copper and the resistivity was found to decrease by three orders.

1.Introduction

Zinc selenide is an n-type semiconducting material with wide band gap (2.7 eV). It is a suitable material for red, blue and green light emitting diodes, photovoltaic, laser screens, thin film transistors, photoelectrochemical cells, etc. [1- 5]. ZnSe thin film has been used as n-type window layer for thin film heterojunction solar cells. Also, interest in ZnSe–GaAs heterojunction has greatly increased in recent years because of possible applications in a number of high speed and optoelectronic devices [6]. The buffer layer determines properties of thin film solar cells such as intensity of the electric field in the absorber interfacial states and electronic bands alignment. It is also involved in the long-term stability of the cells and light soaking effect [5]. A requirement of best buffer layer is the wider band gap, smaller lattice mismatch and good conduction band with respect to the absorber layer. High efficiency values in Cu(In,Ga)(S,Se)$_2$ based solar cells have been achieved by the use of interfacial CdS buffer layer. However, for industrial production and for environmental protection, it is necessary to replace CdS by non-toxic alternative buffer material, which in addition more transparent in blue spectral range [7]. ZnSe is a promising candidate for the replacement of the toxic CdS in the buffer layer, due to its wide band gap (2.7 eV) than that of CdS (2.4 eV) and good lattice match with Cu(In,Ga)(S,Se)$_2$ [8].There are several techniques for the growth of ZnSe thin films, but the deposition from aqueous solution is attractive due to the low cast, suitable for the commercial solar cell devices[9]. There are several reports available on the aqueous solution deposition technique such as chemical bath deposition[10,11] and electrodeposition[12–14] of ZnSe. In an earlier work, the pulse electrodeposition technique was used for the deposition of ZnSe films at different duty cycles and at room temperature[15].In this work, the pulse electrodeposition technique has been employed to deposit ZnSe films at different deposition temperatures and at 50 % duty cycle.

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2. Experimental

Thin films of ZnSe were deposited by the pulse plating technique at a current density of 100 mA cm^{-2} on titanium and conducting glass substrates at room temperature. The precursors used were 20 ml of 0.25M ZnSO$_4$ and 2 ml of 0.01M selenium di-oxide. The duty cycle was varied in the range 6- 50%. The duration of deposition was 60 min. To dope the films with copper, 0.01M concentration copper nitrate solution was added in different quantities (1ml – 5 ml)during the last 15 min of pulse deposition for the films deposited at 50% duty cycle. Thickness of the films estimated by the weighing method was in the range of 1.0 to 2.5μm. The films were characterized by x-ray diffraction technique using Philips X-ray diffraction unit and CuK$_α$ radiation. Optical absorption measurements were made using U3400 UV-Vis-NIR spectrophotometer. XPS studies were made on the films using ESCALAB. Photoluminescence studies were made at room temperature with an excitation wavelength of 450nm. Surface morphology of the films was measured using a Hitachi 35CF SEM. The composition of the films was estimated using EDAX. Laser Raman studies were carried out on the films using Renishaw laser Raman microscope with a 633 nm He-Ne laser. To estimate the amount of copper doped in ZnSe, the films were dissolved in aqua regia and used in Perkin Elmer Atomic absorption spectrometer.

3. Results and discussion

X-ray diffraction(XRD) studies were made on the films deposited at 50% duty cycle and at different deposition temperatures.XRD pattern of the films deposited at different deposition temperatures is shown in Fig.1. It is observed that the films exhibit cubic structure with peaks corresponding to the (111), (220) and (311) reflections. As the duty cycle increases the intensity of the peak corresponding to the (111) reflection increased, indicating the preferential orientation in this direction, the peaks corresponding to the Ti substrate are absent. The thickness of the films increases from 1.5 to 2.5 μm as the deposition temperature increases. Broad peaks are observed for the films deposited at lower deposition temperatures. As the deposition temperature increases, the peaks become sharper due to improved crystallinity.
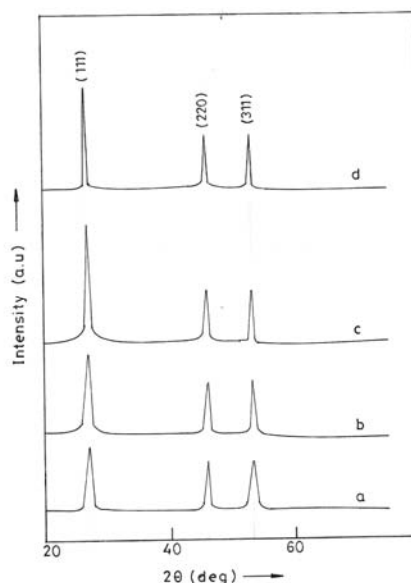

Fig.1. X-ray diffraction pattern of ZnSe films deposited at different deposition temperatures (a) 30°C (b) 50°C (c) 70°C (d) 80°C.

To examine the chemical composition of the films, the XPS spectra of the ZnSe films grown at different deposition temperatures were measured and is shown in Fig.2 for the films deposited at a deposition temperature of 80°C. The XPS spectrum exhibit the binding energies of the Zn(2p$_{3/2}$) and Se(3d$_{5/2}$ and 3d$_{3/2}$)

level. As shown in the Fig.2a, the peak energy levels associated with $Zn(2p_{3/2})$ appeared at about 1022 eV, which is in good agreement with the literature value(8). Fig.2b shows the peak energy associated with the $Se(3d_{5/2}$ and $3d_{3/2})$ level, which appeared at 53.9 and 59.2 eV, respectively.
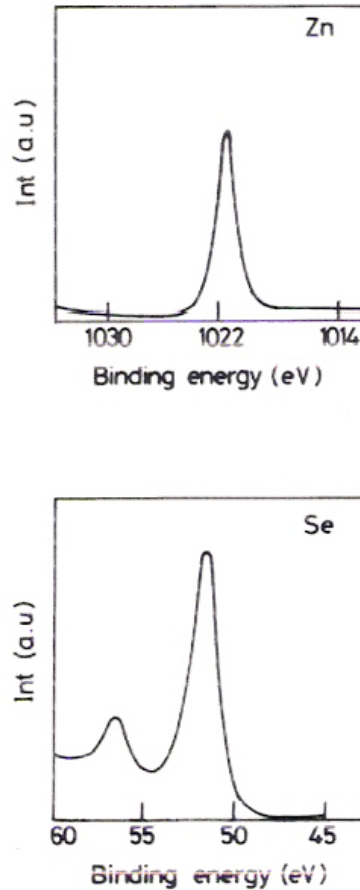

Fig. 2. XPS spectra of ZnSe films deposited at 50 % duty cycle and at 80°C.

Optical absorbance measurements were made on the films deposited on conducting glass substrates in the wavelength range 300 – 900 nm at room temperature to ascertain the nature of the band gap. Substrate absorption, if any was corrected by placing an identical uncoated tin oxide substrate in the reference beam. The absorption co-efficient(α) at various wavelengths has been calculated using the equation[16]

$$\alpha = 2.303A/t \tag{1}$$

where A is the absorbance value at a particular wavelength and t is the thickness of the film. The band gap of the films were determined by plotting a graph between $(\alpha h\nu)^2$ vs $h\nu$. Extrapolation of the linear region to the $h\nu$ axis gives the band gap of the material. Fig.3 shows the $(\alpha h\nu)^2$ vs $h\nu$ graph for the films deposited at different duty cycle. An absorption coefficient of 10^4 cm^{-1} was observed. The plots are linear, extrapolation of the plot to the $h\nu$ axis yields the band gap in the range of 2.64 – 2.68 eV for the films deposited at different deposition temperatures.
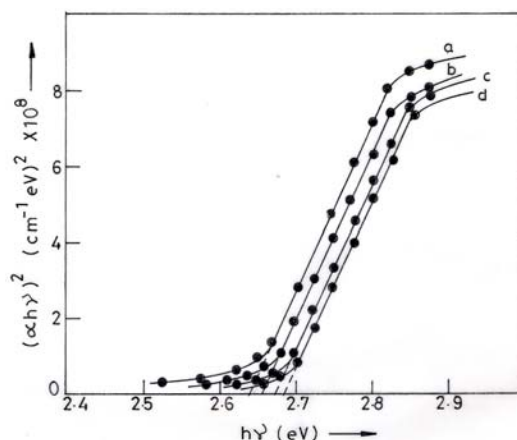
Fig.3. (αhv)^2 vs hv plot of ZnSe films deposited at different deposition temperatures and with 50 % duty cycle(a) 80°C (b) 60°C (c) 50°C (d) 30°C.

Laser Raman studies were made using 633 nm laser radiation. The films deposited at lower duty cycles, indicated a broad and small peak at 252 cm^{-1}. Fig. 4 shows the spectra for the films deposited at different duty cycle. This peak corresponds to the longitudinal optical (LO) phonon in ZnSe. As the duty cycle increases, the peak becomes sharper and increase in intensity, this is due to the improved crystallinity of the films deposited at higher duty cycles supported by the XRD and AFM results. This is similar to the results obtained with photochemically deposited ZnSe films[17].
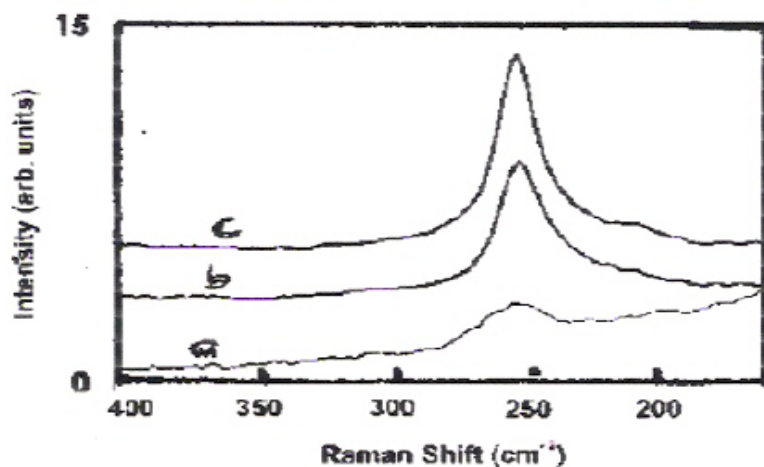

Fig. 4. Raman spectrum of ZnSe films deposited at different deposition temperature and with 50 % duty cycle(a) 30°C (b) 60 (c) 80°C.

Surface morphology of the films deposited at different deposition temperatures and with 50 % duty cycle is shown in Fig.5. The grain size is observed to increase from 43 nm – 76 nm as the deposition temperature increases. The films are uniform. The increase in grain size with increase of deposition temperature is due to the increase in thickness as well as the improved crystallinity as observed from the XRD results.
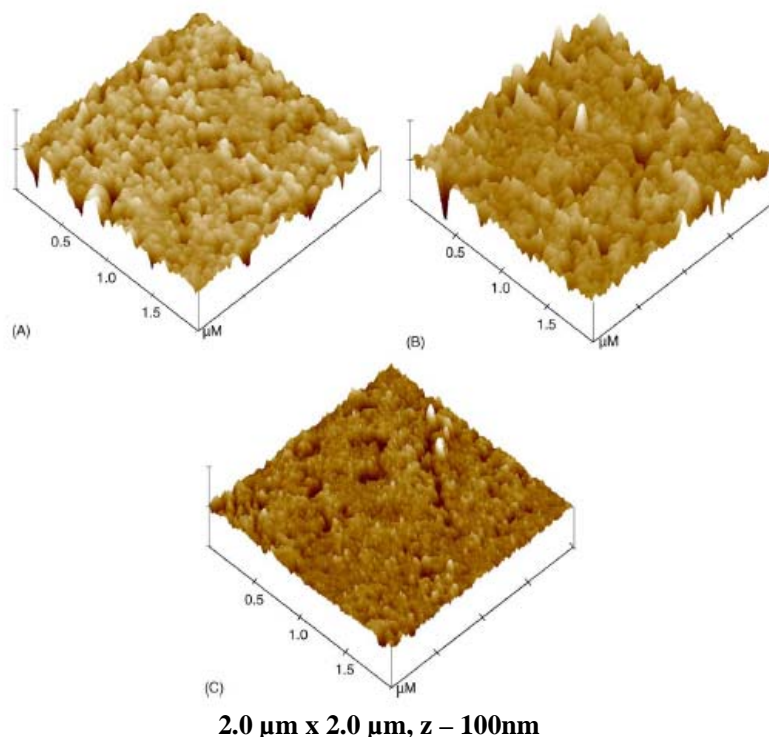
2.0 µm x 2.0 µm, z – 100nm

Fig. 5. Atomic force micrographs of ZnSe films deposited at different deposition temperatures (A) 80°C (B) 60°C (C) 50°C.

Table 1. Variation of Resistivity with copper doping.

Conc of Cu(ppm)	Resistivity(ohm cm)
0	2.5×10^5
0.001	7.8×10^4
0.002	1.4×10^4
0.003	6.6×10^3
0.005	1.2×10^3
0.007	8.8×10^2
0.009	1.0×10^2

Room temperature resistivity studies were carried out on the undoped and copper doped ZnSe films deposited at 50 % duty cycle. Gold (0.5 cm^2 area) was vacuum evaporated on the top surface of the film surface to serve as the ohmic contact, the ohmicity of the contacts were cross checked by the forward and reverse current- voltage characteristics(linear characteristics were observed). The amount of copper doped in the films varied from 0.001 ppm – 0.009 ppm. The resitivity of the undoped films was 2.5 x 10^5 ohm cm. After doping with copper, the resistivity decreased by three orders. The resistivity values of the doped ZnSe films are indicated in Table-I. The values of the resistivity are higher than the values reported on copper doped two source evaporated ZnSe films[18], but in this case the copper doping was achieved without any post heat treatment.

4. Conclusion

The results of this study clearly indicate that single phase cubic ZnSe films with 100 ohm cm resistivity after doping with copper can be obtained at a deposition temperature of 80˚C. The crystallite size can be varied in the range of 43 – 76 nm with change of the deposition temperature.

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