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STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF BRUSH PLATED ZnSe FILMS

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ZnSe films were brush plated on conducting glass substrates from a solution containing $ZnSO_4$ and SeO_2 .The substrate temperature was varied in the range of 30 - 85°C. 3 ml of $ZnSO_4$(0.25M) and 3ml of SeO_2(0.05M) were taken as the precursors. X-ray diffraction studies indicated cubic structure. Direct band gap of 2.51 eV was obtained from absorption measurement for the films deposited at 85°C. Electrical measurements were made on the films by providing Indium contact at the centre of the top surface of the films. The films possessed a conductivity in the range of 1000 ohm cm - 100 ohm cm as the deposition temperature increases.

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1.Introduction

The wide band gap candidates are ubiquitous component of modern technology with considerable interest in the electronic and optical devices. Zinc selenide (ZnSe) is one of the important materials as a buffer layer in copper indium selenide (CIS)-based solar cells, compare to CdS buffer layer because of better conformity of lattice parameter and non-toxicity. Also, it has potential applications in red-, blue- and green-light-emitting diodes, photovoltaic, laser screens, thin-film transistor, photoelectrochemical cells[1 – 5]. Thin films of ZnSe have been deposited using molecular beam epitaxy, electron beam evaporation, chemical deposition, electrodeposition, vacuum evaporation, successive ionic layer adsorption and reaction (SILAR) technique[6 – 11]. In this work, the brush plating technique has been employed for the deposition of thin ZnSe films on conducting glass substrates maintained at different temperatures in the range 30 - 85°C and the results are discussed in terms of the literature available on ZnSe thin films.

2.Experimental

ZnSe thin films were deposed by the brush plating technique using 3ml of AR grade $ZnSO_4$(0.25M) and 3 ml of SeO_2 (0.05M). A deposition current density of 80 mA cm^{-2} was employed. The total deposition time was 20 min. An electroplating process performed with hand held portable tool rather than a tank of solution is known as brush plating. The brush plating processes are also called as contact plating, selective plating or swab platting. This is essentially a plating method, deposition of a material on the surface by electrochemical means, where the work is connected cathodically to the current source. The plating is then applied by means of a brush or swab, soaked with solution and connected to a flexible anode cable. A direct current power pack drives the electrochemical reaction, depositing the desired metal on the surface of the substrate. In practice, movement between the anode and cathode is required for optimum results when plating, stripping, activating and so on. In this case, graphite wound with cotton was used as the swab. The graphite swab was dipped in the electrolyte solution and brushed on the cathode surface by applying a deposition current density of 80 mA cm^{-2}. Thickness of the films were measured by Mitutoyo surface profilometer. The films were characterized by x-ray diffraction technique using Xpert PANanlaytical x-ray diffractometer, optical absorption measurements were made using an Hitachi UV-VIS-NIR spectrophoiometer.

3.Results and discussion

Thickness of the films obtained from surface profilometer was in the range of 500 nm. X-ray diffraction studies on the films deposited at different substrate temperatures is shown in Fig.1. The diffractograms indicated the presence of all the prominent peaks of ZnSe are arising from (111), (220) and (311) reflections having f.c.c cubic zinc blende structure. The full width at half maximum (FWHM) values of the (111) and (220) peaks of this film are calculated to be 0.409 and 1.230, respectively. As the deposition temperature increased, it is seen that the FWHM of the (111) peaks is higher than that of the films deposited at room temperature. But, in the case of the (220) peak, the FWHM is found to decrease with the increase of deposition temperature. This may be due to lattice damage resulting in the decrease of the fraction of (111) orientation and the increase of the degree of orientation along the (220) plane. An additional peak with (311) orientation appeared for the films deposited at higher temperatures.

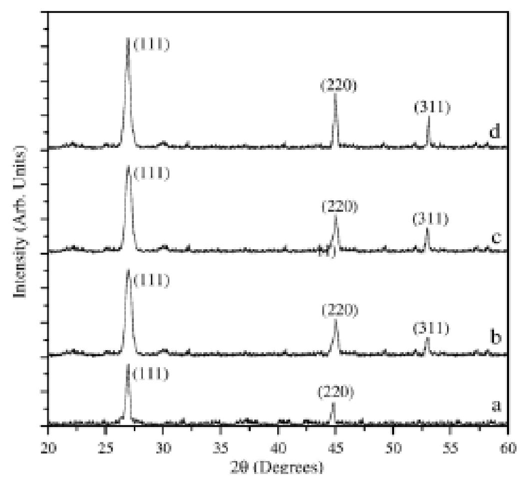

Fig.1. X-ray diffraction pattern of ZnSe films deposited at different temperatures (a) 30°C (b) 50°C (c) 70°C (d) 85°C

The grain size was calculated using Scherrer's equation:

$$D = 0.9\ \lambda/\beta\cos\theta \tag{1}$$

where D is the grain size, λ is the wavelength of CuKα radiation, θ is the diffraction angle and β is the full width at half maximum. It is observed that the grain size increases with increase of substrate temperature.

Lattice parameters ‘a’ and ‘c’ were calculated using the relation,

$$1/d^2 = 1/a^2(h^2 + k^2 + l^2) \tag{2}$$

The lattice strain(ε) is calculated using the relation,

$$\varepsilon = (\beta\cos\theta)/4 \tag{3}$$

It is observed that the strain values decrease as the substrate temperature increases, indicating better crystallinity for the films deposited at higher temperatures.

The dislocation density was calculated from the relation[12],

$$\delta = 15\varepsilon/aD \tag{3}$$

The dislocation density varies in the range of 2.5 x 10^{-15} to 0.5 x 10^{-15} lines/m as the deposition temperature increases.

The transmission spectra exhibited interference fringes. The fringes observed are a result of the interference between two interfaces of the air-film and film-substrate. The low value of transmission observed for the films deposited at lower substrate temperature may be due to the scattering related to surface roughness.

It is well known that the optical constants such as refractive index (n) and the extinction coefficient (k) can be determined from the transmittance spectrum by the envelope method. The refractive index can be obtained as follows

$$n = [N + (N^2 - n_s^2)]^2 \tag{4}$$

$$N = (n_s^2 + 1)/2 + 2n_s(T_{max} - T_{min})/ T_{max} T_{min} \tag{5}$$

where n_s is the refractive index of the substrate, T_{max} and T_{min} are the maximum and minimum transmittances at the same wavelength in the fitted envelope curve on a transmittance spectrum. The extinction coefficient was calculated by trhe following equation,

$$k = \alpha\lambda/ 4\pi \tag{7}$$

$$\alpha = 1/d \ln \{ (n-1)(n-n_s)/(n + !)(n - n_s)\} [(T_{max}/T_{min})^2 + 1]/[(T_{max}/T_{min})^2 - 1] \tag{8}$$

$$d = (\lambda_1\lambda_2)/ 2n(\lambda_2 - \lambda_1) \tag{9}$$

where 'α' is the absorption coefficient and 'd' is the film thickness, λ_1 and λ_2 are the wavelengths at the two adjacent maxima or minima.

From the envelope method[13], the refractive index was calculated for the films deposited at different deposition temperatures. The refractive index decreases from 2.56 – 2.51 as the deposition temperature decreases from 85°C. These values agree well with the literature.

The band gap of the films were determined from the transmission spectrum and by plotting a graph between $(\alpha h\nu)^2$ vs hν(Fig.2). An absorption coefficient of 10^4 cm^{-1} was observed. The plots were linear, extrapolation of the plot to the hν axis yields the band gap in the range of 2.64 – 2.68 eV for the films deposited at different deposition temperatures in the range of 85 - 30°C.

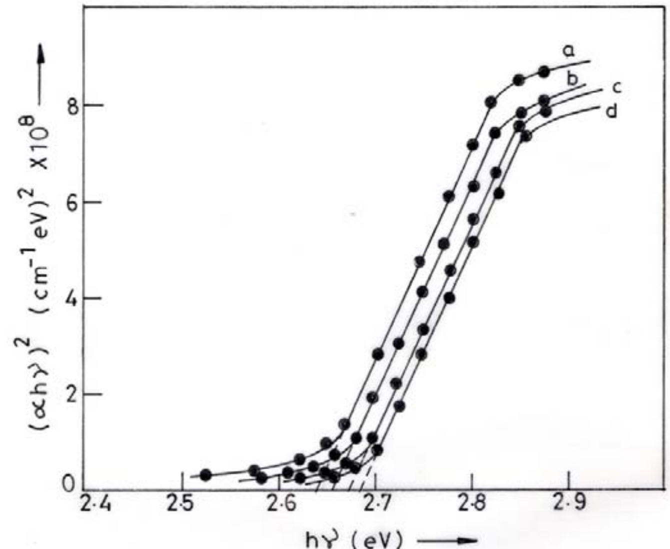

Fig.2 - $(\alpha h\nu)^2$ vs hν plot of ZnSe films deposited at different temperatures (a) 85°C (b) 70°C (c) 50°C (d) 30°C

Cross plane resistivity of the films was measured by providing an Indium contact at the centre of the top surface of the film and the conducting glass substrate served as the other contact. The resistivity decreased with increase of deposition temperature. It decreased from 1000 ohm cm – 100 ohm cm. This may be due to the increase of grain size with increase of deposition temperature, wherein the scattering by grains decrease.

4.Conclusion

ZnSe thin films with grain size in the range of 20 – 50 nm can easily be obtained by the brush plating technique. Films with band gap in the range of 2.64 – 2.68eV can be obtained by this technique. Films with refractive index values of 2.56 can be obtained. Films with resistivity in the range of 100 – 1000 ohm cm can be obtained.

References

[1] R.B. Kale, C.D. Lokhande, Appl. Surf. Sci, **252**,929 (2005).
[2] O. Akira, S. Noriyoshi, S. Zembutsu, J. Appl. Phys, **64**,654 (1988).
[3] A. Ennaoui, S. Siebntritt, M.Ch. Lux-Steiner, W. Riedl, F. Karg, Sol. Energy Mater. Sol. Cells, **67**,31(2001).
[4] R.R. Alfano, O.Z. Wang, J. Jumbo, B. Bhargava, J. Phys. Rev., **A 35,**459(1987).
[5] S.T. Lakshmikumar, A.C. Rastogi, Thin Solid Films, **259**,150 (1995).
[6] N. Katsumura, K. Maemura, T. Mori, J. Saraie, J. Crystal Growth,**159**,85(1996).
[7] R. Islam, D.R. Rao, J. Mater. Sci. Lett., **13**, 1637 (1994).
[8] A. M. Chaparro, M. T. Gutierez, J. Herero, Electrochim. Acta, **47**,977(2001).
[9] A. Chandramohan, T. Mahalingam, J.P. Chu, P.J. Sebastian, Sol.Energy Mater. Sol. Cells, **81**,371 (2004).
[10] P. K. R. Kalita, B. K. Sarma, H. L. Das, Bull. Mater. Sci, **23**,313 (2000).
[11] R. B. Kale, C.D. Lokhande, Mater. Res. Bull, **39**, 1829 (2004).
[12] S. Venkatachalam, R.T. Rajendrakumar, D. Mangalaraj, Sa.K. Narayandass, K. Kim, J. Yi, Solid State Electron, **48**,2219 (2004).
[13] H. Y. Joo, H.J.Kim, J.Vac.Sci and Technol, **A17,**862(1999).