

Structural and optical properties of CdSe films brush plated on low temperature substrates

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Abstract

CdSe thin films were brush plated on conducting glass and titanium substrates maintained at temperatures in the range 5–30 °C from the precursors. The films exhibited hexagonal structure. Optical band gap was found to vary in the range of 1.65–2.1 eV as the substrate temperature is decreased from 30 °C. XPS measurements indicated the formation of CdSe. Atomic force microscopy studies indicated fine grains of the order of 10 nm for the films deposited at 5 °C. Luminescence measurement indicated emission at 520 nm for an excitation of 570 nm.

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CdSe is a direct band gap semiconductor belonging to the II–VI groups and possessing excellent optoelectronic properties. Several physical and chemical techniques are available for the growth of thin films of CdSe [1–5]. Though results on brush plated CdSe films have been reported earlier [6], the films were deposited on room temperature substrates. To our knowledge, this is the first report on CdSe films grown by the brush plating technique on substrates maintained at low temperatures.

CdSe films were brush plated on to titanium and conducting glass substrates maintained at different temperatures in the range 5–30 °C. The precursors used were 0.5 M CdSO₄ and 0.1 M SeO₂. A current density of 100 mA cm² was employed and the plating time was 10 min. Thickness of the films was measured by the weight difference method. The thickness was found to vary in the range of 3.0–5.0 μm, as the substrate temperature increased. The films were characterized by X-ray diffraction technique using Philips X-ray diffractometer with Cu Kα radiation. Optical absorption measurements were made on the films using

Hitachi UV–vis–NIR spectrophotometer. XPS studies were made on the films using ESCALAB. EDAX measurements were also made. AFM investigations were also made on the films.

XRD patterns of the films deposited at different substrate temperatures is shown in Fig. 1. The prominent peaks corresponding to (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3), (1 1 2) and (0 0 3) of the hexagonal phase are observed in all cases. It is observed that as the substrate temperature increases, the width of the peak decreases due to improved crystallinity. The lattice constants ‘a’ and ‘c’ calculated using the XRD data are 4.304 and 7.044 Å, which are in close agreement with the ASTM data. The crystallite size calculated using the Debye Scherrer equation is found to increase with increase of substrate temperature (Table 1).

To examine the chemical composition of the films, the XPS spectra of the CdSe films grown at different bath temperatures were measured and are indicated in Fig. 2. Fig. 2a exhibits the detailed spectra of Cd3d and Se3d regions, respectively. The two strong peaks at 411.8 and 405.1 eV correspond to Cd3d_{3/2} and Cd3d_{5/2} binding energies. Fig. 2b shows the binding energies of the Se (3d_{5/2} and

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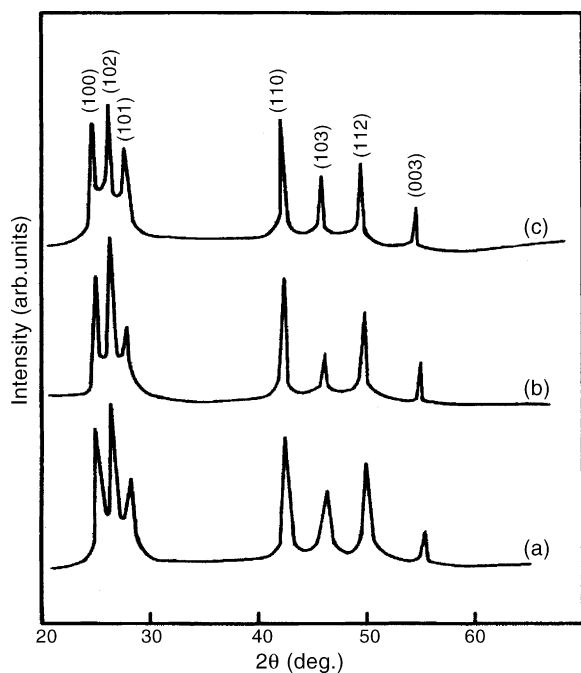


Fig. 1. X-ray diffraction pattern of CdSe films plated at different substrate temperatures (a) 5 °C, (b) 15 °C and (c) 30 °C.

3d_{3/2}) levels at 53.9 and 59.2 eV, respectively. These values are similar to the earlier values [7,8]. There is no evidence of shifting of the energy levels to higher binding energies corresponding to SeO₂ formation [9]. No significant variation was observed in the XPS spectra with temperature of deposition, hence only the spectrum corresponding to one temperature is indicated. Depth profiling was done to find out the uniformity of composition throughout the thickness and it was observed that the films had a slight excess of Cd throughout. EDAX measurements indicated Cd (50.2%) and Se (49.8%). Hot probe measurements indicated n-type behaviour.

Optical absorption measurements were made at room temperature by placing an uncoated identical conducting glass substrate in the reference beam. A plot of $(\alpha h\nu)^2$ versus $h\nu$ for the films deposited at different substrate temperatures is shown in Fig. 3. The plot is linear indicating the direct band gap nature of the films. Extrapolation of the line to the $h\nu$ axis indicated a direct band gap in the range 1.65–2.0 eV as the substrate temperature is decreased. This is due to the decrease in particle size with decrease of temperature. The variation of band gap at various substrate temperature is due to the variation of crystallite size with

Table 1
Variation of crystallite size with bath temperature

Bath temperature (°C)	Crystallite size (nm)
10	10
40	40
30	100

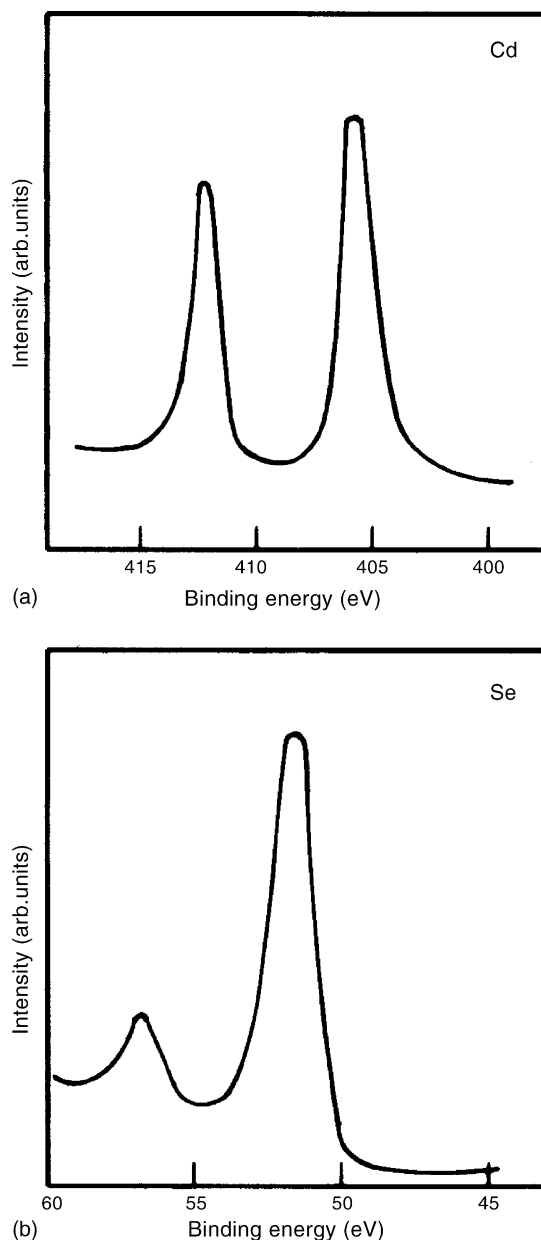


Fig. 2. XPS spectra of CdSe films deposited at a substrate temperature of 5 °C: (a) Cd and (b) Se.

substrate temperature. Hodes et al. [10] found that the band gap varied from 1.725 to 2.40 eV on varying the electro-deposition parameters. Strong and weak confinements were noticed for the films. The effective Bohr radius for CdSe is 27 Å. For strong confinement, the exciton energy is given by,

$$E_s = E_g + \frac{h^2\pi^2}{2\mu^2} - \frac{1.786e^2}{4\pi\epsilon_0\epsilon R} - 0.248E_{Ry}^*$$

where E_g is the band gap of bulk CdSe, the first term is related to the quantum localization energy, the second term represents the Coloumb energy and the third term represents

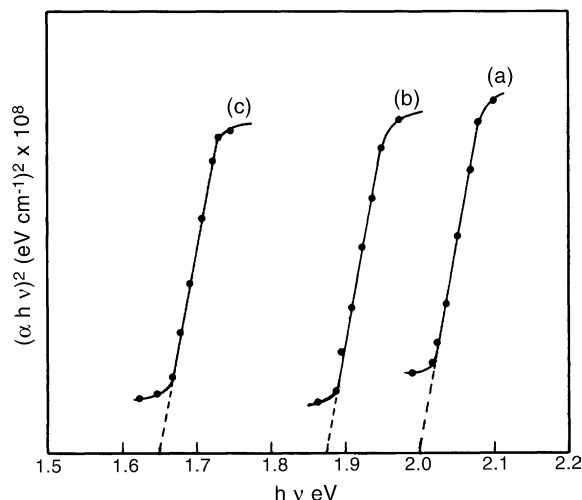


Fig. 3. $(\alpha h\nu)^2$ vs. $h\nu$ plot of CdSe films deposited at different substrate temperatures (a) 5 °C, (b) 15 °C and (c) 30 °C.

the correlation energy in which E_{Ry}^* is the effective Rydberg energy and can be written as

$$\left\{ \frac{\mu e^4}{2(4\pi\epsilon_0\epsilon)^2 h^2} \right\}$$

where μ is the reduced effective mass, ϵ the dielectric constant for CdSe and ϵ_0 is the permittivity of free space. The estimated band gap of 2.0 eV due to strong confinement matches with the band gap value obtained from absorption measurements for the films deposited at 5 °C.

Atomic force micrographs of the films deposited at different temperatures is indicated in Fig. 4. An increase of grain size from 20 to 130 nm is observed as the substrate temperature increases from 5 to 30 °C. Moreover, the surface of the films has a uniform coverage at 5 °C compared to 30 °C.

Cross plane resistivity measurements were made on the films by evaporating Indium contacts on the surface of the film. The cross plane resistivity was found to be in the range of 50 Ω cm. Room temperature photoluminescence studies indicated that the emission band occurred at 520 nm for an excitation wavelength of 570 nm. Subbu Ramaiah et al. [10] observed PL peaks at 1.725 and 2.132 eV and these were explained as due to donor acceptor pair recombination, and the other one was due to bound excitonic recombination in the small crystallites. The emission observed in the present case can also be explained in terms of bound excitonic recombination in the crystallites. The results of this investigation clearly point to the possibility of depositing nano meter sized films of CdSe by this technique. Steps to further decrease the particle size is in progress.

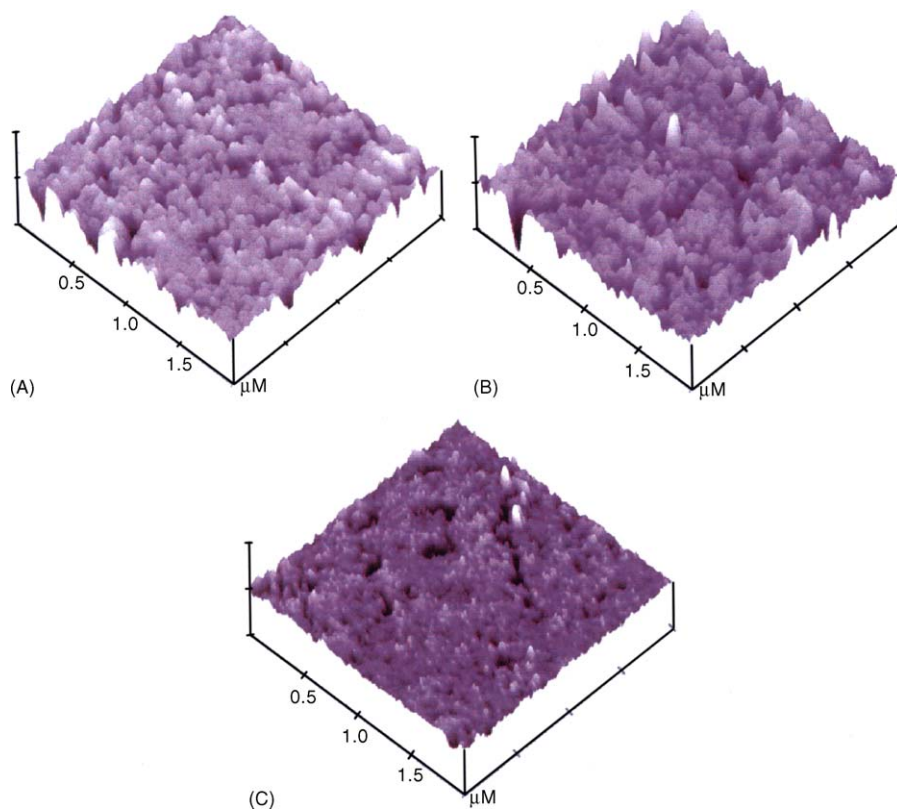


Fig. 4. AFM image of CdSe films deposited at (A) 30 °C, (B) 15 °C and (C) 5 °C.

References

- [1] T. Elango, V. Subramanian, K.R. Murali, *Surf. Coat. Technol.* 123 (2000) 8.
- [2] H.P. Sarma, N. Rangarajan, K.R. Murali, *Phys. Stat. Solidi A* 148 (1993) 209.
- [3] K.R. Murali, V. Subramanian, N. Rangarajan, A.S. Lakshmanan, S.K. Rangarajan, *Bull. Electrochem.* 9 (1993) 209.
- [4] O. Savadago, K.C. Mandal, *Mater. Chem. Phys.* 31 (1992) 301.
- [5] G. Hodes, *Nature* 285 (1980) 29.
- [6] K.R. Murali, V. Subramanian, N. Rangarajan, A.S. Lakshmanan, S.K. Rangarajan, *J. Electroanal. Chem.* 368 (1994) 95.
- [7] R.N. Noufi, P.A. Kohl, J.W. Riggers, J.M. Whiteand, A.J. Bard, *J. Electrochem. Soc.* 126 (1979) 949.
- [8] K.T. de Silva, D. Hanemann, *J. Electrochem. Soc.* 127 (1980) 1554.
- [9] K.C. Mandal, O. Savadago, *J. Mater. Sci.* 15 (1993) 340.
- [10] K. Subbu Ramaiah, Y.K. Su, S.J. Chang, F.S. Jung, K. Ohdaira, Y. Shiraki, H.P. Liu, I.G. Chen, A.K. Bhatnagar.