

Preparation of $\text{CdS}_x\text{Se}_{1-x}$ films by brush plating technique and their characteristics

K. R. Murali · P. Elango · P. Andavan ·
K. Venkatachalam

Received: 17 March 2007 / Accepted: 1 May 2007 / Published online: 31 May 2007
© Springer Science+Business Media, LLC 2007

Abstract $\text{CdS}_x\text{Se}_{1-x}$ films were deposited for the first time by the brush plating technique from aqueous precursors. X-ray diffraction patterns of the films indicated polycrystalline structure with peaks corresponding to the hexagonal phase. Optical absorption measurements indicated the band gap to shift from 1.68 to 2.39 eV as the value of x is increased. XPS spectra indicated the peaks corresponding to Cd ($3d_{5/2}$ and $3d_{3/2}$), Se ($3d_{5/2}$ and $3d_{3/2}$) and S ($3d_{5/2}$ and $3d_{3/2}$) levels. Surface morphology studies indicated the grain size to increase with increase of selenium concentration. The resistivity of the films changed from 20 ohm cm to 250 ohm cm as the sulphur content increased.

1 Introduction

Synthesis and characterization of II-VI semiconducting materials have gained importance by virtue of their proven potential capabilities in a variety of electronic and optoelectronic devices. It is worth mentioning that cadmium sulphide and selenide have an important place in this respect and it is already documented and established that CdS and CdSe form a solid solution throughout the entire composition range. The addition of CdSe to CdS has

resulted in very interesting properties related to photoelectrochemistry and optoelectronics. Several techniques like flash evaporation [1–3], molecular beam evaporation [4], spray pyrolysis [5], electrodeposition [6] and chemical bath deposition [7] have been employed for the deposition of $\text{CdS}_x\text{Se}_{1-x}$ films. In the present study, $\text{CdS}_x\text{Se}_{1-x}$ films have been deposited by the brush plating technique on conducting glass and titanium substrates. The novel feature of this work is the employment of the simple brush plating technique for the deposition of the films. To our knowledge, this is the first report on the use of brush plating technique for deposition of $\text{CdS}_x\text{Se}_{1-x}$ films.

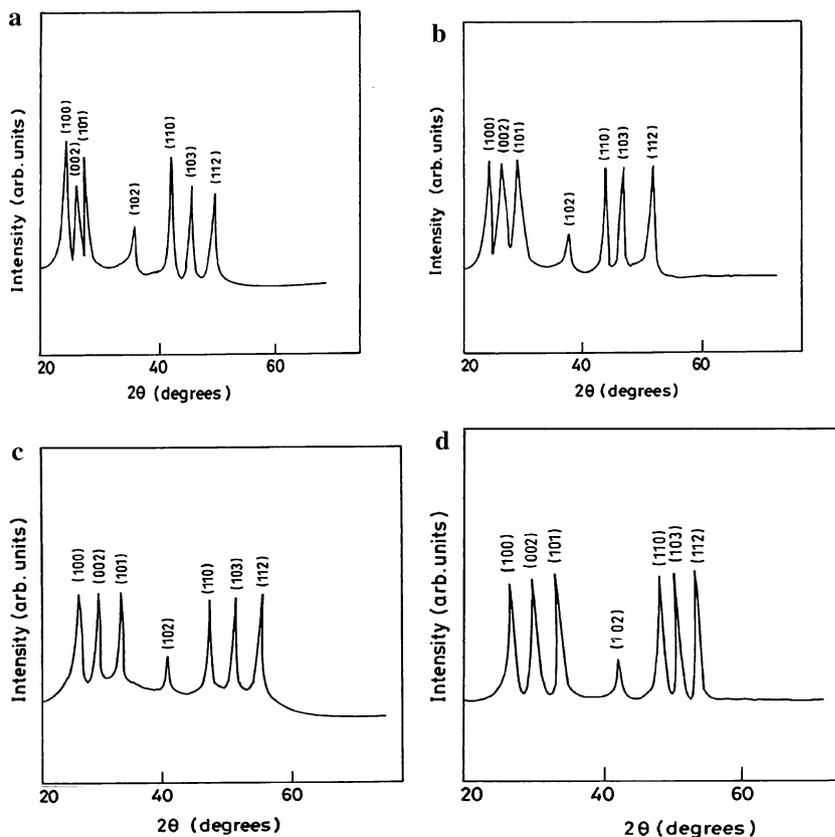
2 Experimental methods

Thin films of $\text{CdS}_x\text{Se}_{1-x}$ were deposited by the brush plating technique on titanium and conducting glass substrates using Analar grade CdSO_4 , SeO_2 and sodium thiosulphate. The concentration of CdSO_4 was kept constant at 0.25 M and the concentrations of sodium thiosulphate and SeO_2 were varied from 5 mM to 50 mM. The films were deposited at a current density of 80 mAcm^{-2} at room temperature. The precursors used for deposition, deposition time and deposition current densities were optimized and fixed. Thicknesses of the films were found to be in the range of $3.0 \mu\text{m}$ (estimated by gravimetry). The details of the brush plating technique are described in an earlier paper [8]. The films were characterized by X-ray diffraction technique using Philips PANalytical X-ray diffractometer with $\text{CuK}\alpha$ radiation. Optical absorption studies were made on the films deposited on conducting glass substrates using Hitachi U3400 UV-VIS-NIR spectrophotometer. Composition of the films was studied using $\text{MgK}\alpha$ radiation from a MK III VG scientific X-ray photoelectron spectrometer.

K. R. Murali (✉)
Electrochemical Materials Science Division, Central
Electrochemical Research Institute, Karaikudi 630 006, India
e-mail: muraliramkrish@gmail.com

P. Elango · P. Andavan · K. Venkatachalam
Department of Physics, Government Arts College, Coimbatore
641 018, India

Fig. 1 X-ray diffraction patterns of CdS_xSe_{1-x} films of different compositions (a) $x = 0.1$ (b) $x = 0.3$ (c) $x = 0.5$ (d) $x = 0.8$



Surface morphology of the films were studied by Atomic force microscopy.

3 Results and discussion

The XRD patterns of the films of different composition deposited at room temperature are shown in the Fig. 1. The peaks corresponding to (100), (002), (101), (102), (110), (103) and (112) reflections were observed in all cases. The diffraction peak shifts towards higher angles with increasing x , indicating that the lattice constant decreases with S concentration. This is demonstrated in Fig. 2 as a shift in the (002) orientation of the films. All the samples exhibited single phase hexagonal structure and the lattice parameters ' a ' and ' c ' were calculated using the standard relation,

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

The calculated values of ' a ' and ' c ' for CdSe and CdS are in good agreement with the ASTM data. The variation of lattice constants of cadmium sulpho selenide solid solutions with composition is shown in Fig. 3. A linear variation of the lattice constants with composition indicates that Vegard's

law is obeyed [9]. Similar variation has been observed for sintered pellets [10], flash evaporated layers [11], single crystals [12] and sprayed layers [13]. Earlier reports have indicated either cubic or mixed crystal structures.

Optical absorption measurements were made at room temperature by placing an uncoated identical conducting glass substrate in the reference beam. A plot of $(\alpha hv)^2$ versus $h\nu$ for the films of different compositions indicates

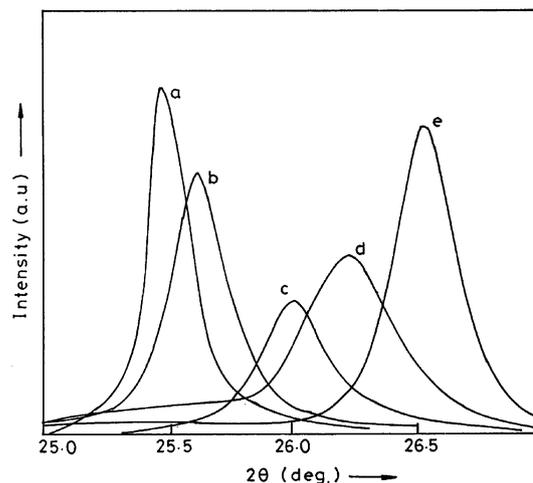


Fig. 2 Shift of the (002) peak with change of composition (a) $x = 0$ (b) $x = 0.2$ (c) $x = 0.4$ (d) $x = 0.6$ (e) $x = 1.0$

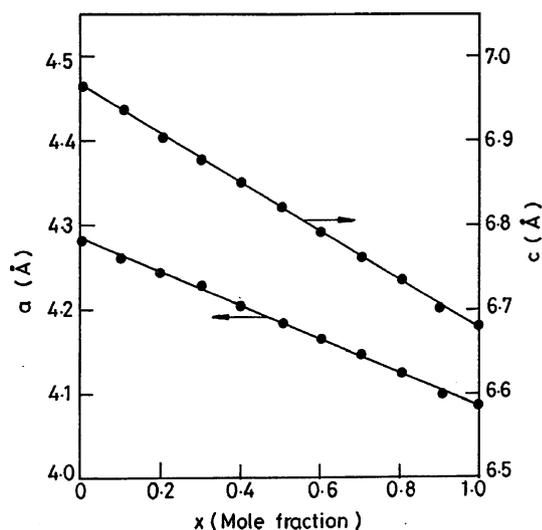


Fig. 3 Variation of lattice constants with composition

the direct band nature of the films. Extrapolating the linear region to the $h\nu$ axis indicates that the band gap is in the range 1.68–2.39 eV as the value of x is increased. The band gap is found to shift towards the red region as the selenium content in the films increased (Figs. 4 and 5). The variation of band gap with composition is shown in Fig. 6. These values are in good agreement with earlier reports [14, 15]. The slope of the linear region in all the cases is related to the transition probability matrix element.

Figure 7 show the XPS spectra of Cd ($3d_{5/2}$ and $3d_{3/2}$), Se ($3d_{5/2}$ and $3d_{3/2}$) and S ($3d_{5/2}$ and $3d_{3/2}$) levels for the films of $CdS_{0.5}Se_{0.5}$ composition as a representative. As observed from the figures, the $Cd3d_{5/2}$ and $Cd3d_{3/2}$ appeared in the range 405.7–406 eV and 411.7–412.4 eV respectively, the $Se3d_{5/2}$ and $Se3d_{3/2}$ appeared in the range 56–60.1 eV and 60.5–67 eV respectively and the $S3d_{5/2}$

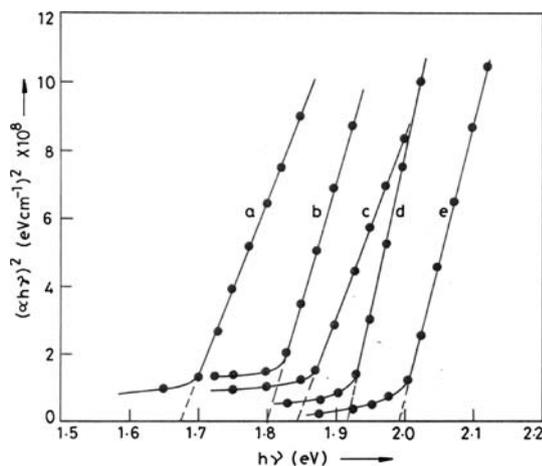


Fig. 4 $(\alpha h\nu)^2$ versus $h\nu$ for the CdS_xSe_{1-x} films of different composition (a) $x = 0.1$ (b) $x = 0.2$ (c) $x = 0.3$ (d) $x = 0.4$ (e) $x = 0.5$

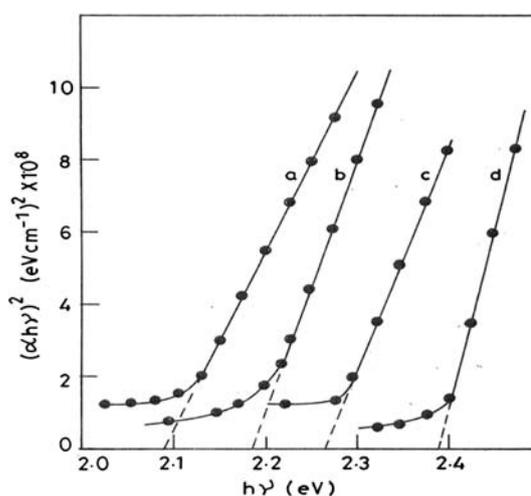


Fig. 5 $(\alpha h\nu)^2$ versus $h\nu$ for the CdS_xSe_{1-x} films of different composition (a) $x = 0.6$ (b) $x = 0.7$ (c) $x = 0.8$ (d) $x = 0.9$

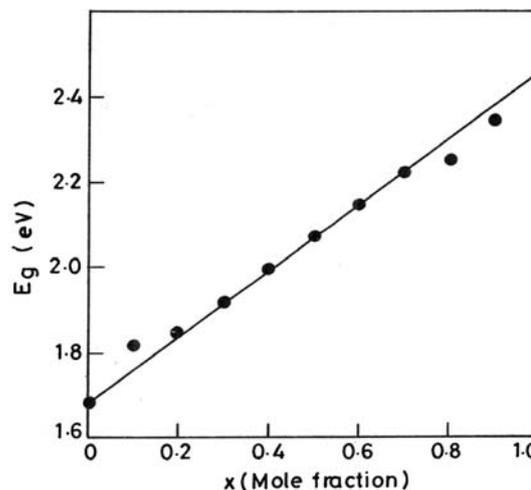


Fig. 6 Variation of band gap with composition

and $S3d_{3/2}$ appeared in the range 146.5–153 eV and 153–159.3 eV respectively as the x value changes from 0 to 1. Atomic concentration measurements were made on the films of different composition selecting suitable sensitivity factors for Cd, S and Se. It was observed that these concentrations agreed well with the concentration values estimated from EDAX measurements. Further, as the ‘ x ’ value increased, the area under the peak for S ($3d_{5/2}$) also increased and the area under the Se ($3d_{5/2}$) decreased. The values of binding energies obtained for the Cd, S and Se levels are in very good agreement with that reported in the literature [16]. The values of the binding energy are observed to shift from CdSe side to CdS side as the concentration of CdS in the films increases.

Figure 8 indicates the scanning electron micrographs of the CdS_xSe_{1-x} films of different compositions deposited at

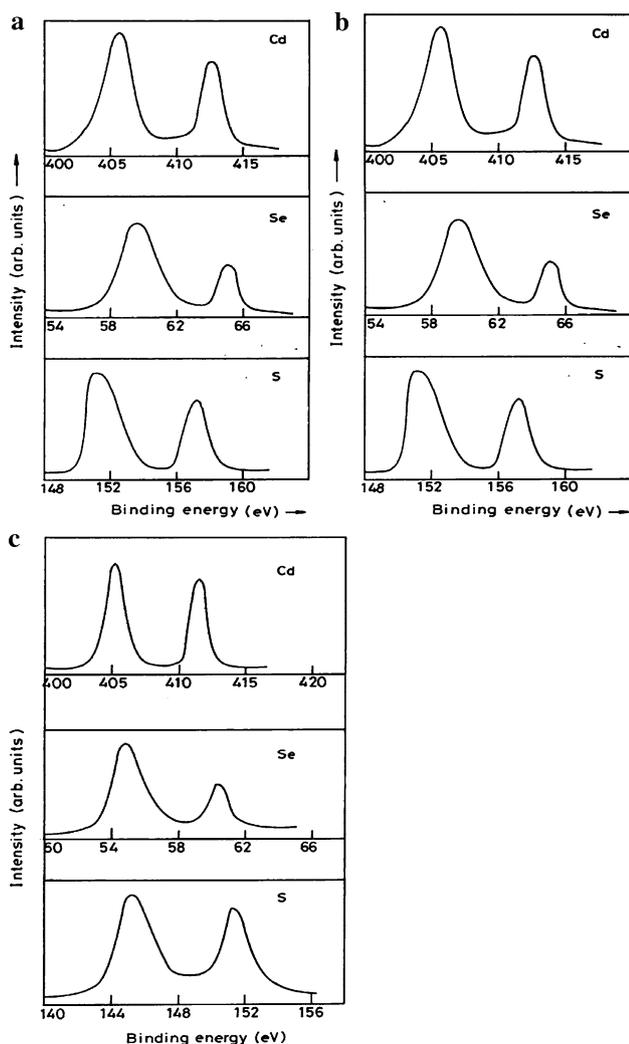
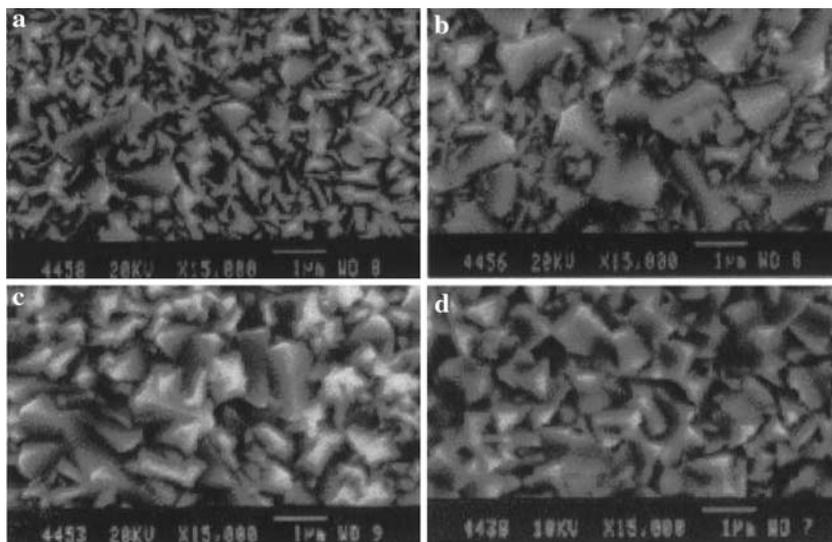


Fig. 7 XPS spectrum of CdS_xSe_{1-x} films deposited at room temperature (a) $x = 0.8$ (b) $x = 0.5$ (c) $x = 0.1$

Fig. 8 Scanning Electron Micrograph of CdS_xSe_{1-x} films of different compositions (a) $x = 0.9$ (b) $x = 0.7$ (c) $x = 0.5$ (d) $x = 0.3$



room temperature. It is observed that the surface contained small crystallites of size 250 nm for the sulphur rich films and as the selenium concentration in the films increase, the grain size increases. Grains of size around 1300 nm are observed in the films with composition CdS_{0.1}Se_{0.9}. The grain size of CdS_{0.1}Se_{0.9} is higher since under the same conditions of brush plating, CdSe possesses larger grains compared to CdS films, hence as the composition tends towards CdSe the grain size is found to be higher.

Cross plane resistivity of the films were measured by two probe resistivity method at room temperature by applying an indium dot on the top surface of the film and the titanium substrate served as the other contact. The resistivity of the films changed from 20 ohm cm to 250 ohm cm as the sulphur content increased. This may be due to the fact that the grain size is relatively small for the sulphur rich films, hence the scattering of carriers should be more in these cases.

Photoelectrochemical measurements were made on the films using 1 M polysulphide electrolyte (1 M Na₂S, 1 M NaOH, 1 M S) and a 250 W tungsten halogen lamp. The intensity of the light falling on the films was adjusted to 60 mW cm⁻². The as-deposited films exhibited photoactivity, films with composition CdS_{0.1}Se_{0.9} exhibited maximum photo output. An open circuit voltage of 0.45 V and short circuit current density of 1.2 mA cm⁻² was observed. These values are higher than the previous reports [17, 18]. The higher output obtained with this composition is due to the fact that these electrodes have exhibited maximum value of flat band potential (V_{fb}) (-1.35 V versus SCE) from the capacitance voltage studies ($1/C^2$ versus Voltage plot). V_{oc} is the difference of V_{fb} and V_{redox} , V_{redox} being a constant value for a particular redox electrolyte, increase in V_{fb} would result in an increase of V_{oc} . In the present study,

the films were not post heat treated to induce photoactivity, in all the previous reports, the films were post heated in air/argon at 450–550°C for different durations to obtain photo response. Hence, the present study clearly demonstrates that films with good photo response can be deposited by this technique.

4 Conclusions

The present study indicates that films with low resistivity can easily be obtained by the brush plating technique. The as-deposited films exhibit good photoactivity. The as-deposited films exhibit single phase hexagonal structure. Further work is in progress to study the photoelectrochemical properties of the films after post heat treatment.

References

1. H.J. Yu, T.H. Weng, *Solid State Electron.* **13**, 93 (1970)
2. H. Weng Tung, *Proc. IEEE* **59**, 1503 (1971)
3. H. Weng Tung, *J. Electrochem. Soc.* **126**, 1820 (1979)
4. N.V. Gavrilenko, V.P. Kolchikov, S.V. Svechnikov, N.M. Torchun, *Izv.Akad.Nauk. SSSR, Neorg. Mater.* **6**, 1787 (1970)
5. A.K. Rathuri, R. Thangaraj, A.K. Sharma, O.P. Agnihotri, *J. Phys. C.* **15**, 4933 (1982)
6. A.S. Baranski, W.R. Fawcett, K. Gatner, A.C. McDonald, J.R. McDonald, S. Matselen, *J. Electrochem. Soc.* **130**, 579 (1983)
7. R.C. Kainthla, D.K. Pandya, K.L. Chopra, *J. Electrochem. Soc.* **129**, 99 (1982)
8. K.R. Murali, M. Ziaudeen, N. Jayaprakash, *Solid State Electron.* **11**, 1692 (2006)
9. H. Leweranz, *An Introduction to Luminescence of Solids*, (Wiley, 1950), p. 93
10. R.H. Bube, *J. Appl. Phys.* **32**, 1707 (1961)
11. F.L. Chan, D.A. Brooks, *Advan. X-ray Anal.* **8**, 420 (1965)
12. R.H. Bube, *J. Phys. Chem. Solids* **1**, 234 (1957)
13. L.D. Budenya, I.B. Mizetskaya, E.V. Sharkina, *Tekh. Mikroelektron.* **23**, 539 (1976)
14. (a) M.A. Kenaway, H.A. Zayed, A.M. Ibrahim, *Ind. J. Pure Appl. Phys.* **29**, 624 (1994); (b) B. Champagnon, M. Ferrari, B. Androsolo, S. Durak, *J. Phys. IV*, 1991 1(CZ, Int Conf. Laser M 2P, 2nd 1991) 263
15. P.K. Mahapatra, A.R. Dubey, *Solar Energy Mater.* **32**, 29 (1994)
16. J. Lee, M. Silvestri, R. Markus, K. Hwang, L. Wen, P.D. Parsons, *Mater. Res. Symp. Proc.*, 1997, p.452
17. G. Rokakha, S.V. Stelsyura, *Inorg. Mater.* **35**, 452 (1999)
18. L.P. Deshmukh, G.S. Shahane, R.M. garadkar, *Ind. J. Pure Appl. Phys.* **35**, 560 (1997)