J Mater Sci: Mater Electron (2009) 20:92–97
DOI 10.1007/s10854-008-9618-0

Photoelectrochemical properties of brush plated $Cd_xZn_{1-x}Se$ films

K. R. Murali · A. Austine

Received: 13 December 2007 / Accepted: 29 January 2008 / Published online: 19 February 2008

Abstract $Cd_xZn_{1-x}Se$ films ($0 \leq x \leq 1$) were deposited for the first time by the brushplating technique at room temperature from an aqueous bath containing zincsulphate, cadmium sulphate and selenium oxide. The deposition current densitywas varied in the range of 50–250 mA cm^{-2}. The as deposited films exhibitedcubic structure. Composition of the films was estimated by EDAX studies. XPSstudies indicated the binding energies corresponding to $Zn(2p_{3/2})$, $Cd(3d_{5/2}$ and $3d_{3/2})$ and $Se(3d_{5/2}$ and $3d_{3/2})$. Optical band gap of the films varied from 1.72 to 2.70 eV as the composition varied from CdSe to ZnSe side. Atomic forcestudies indicated grain size in the range of 20–150 nm. Photoelectrochemical cells were made with polysulphide as the redox electrolyte. The output was maximum for the photoelectrodes of composition $Cd_{0.9}Zn_{0.1}Se$.

1 Introduction

Several semiconducting films have been deposited for optoelectronic device applications. Amongst the, 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 if 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]. In this work $Cd_xZn_{1-x}Se$(CZS) films have been deposited for the first time using the brush plating technique. In this paper, the results obtained on the films are presented and discussed.

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 0.45–0.05 M and 0.05–0.45 M 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 0.001 M SeO_2 was added. Titanium and conducting glass substrates were used for the deposition of the films. Thickness of the films stimated by Mitutoyo surface profile meter was found to be in the range of 1.5–2.8 μm as the composition changed from $x = 0$ to 1 in $Cd_xZn_{1-x}Se$ films. The thickness of the films deposited at low current

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

A. Austine
Department of Physics,
JJ. College of Engineering and Technology,
Trichy, India

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. Atomic force microscopy was used for the study of the surface morphology 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 XPS and EDAX studies. Density of the films of different composition was determined by specific gravity method. The as deposited films of different composition were scrapped from the substrate. The scraped material was dropped in Dioxane.

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. Figure 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 1 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

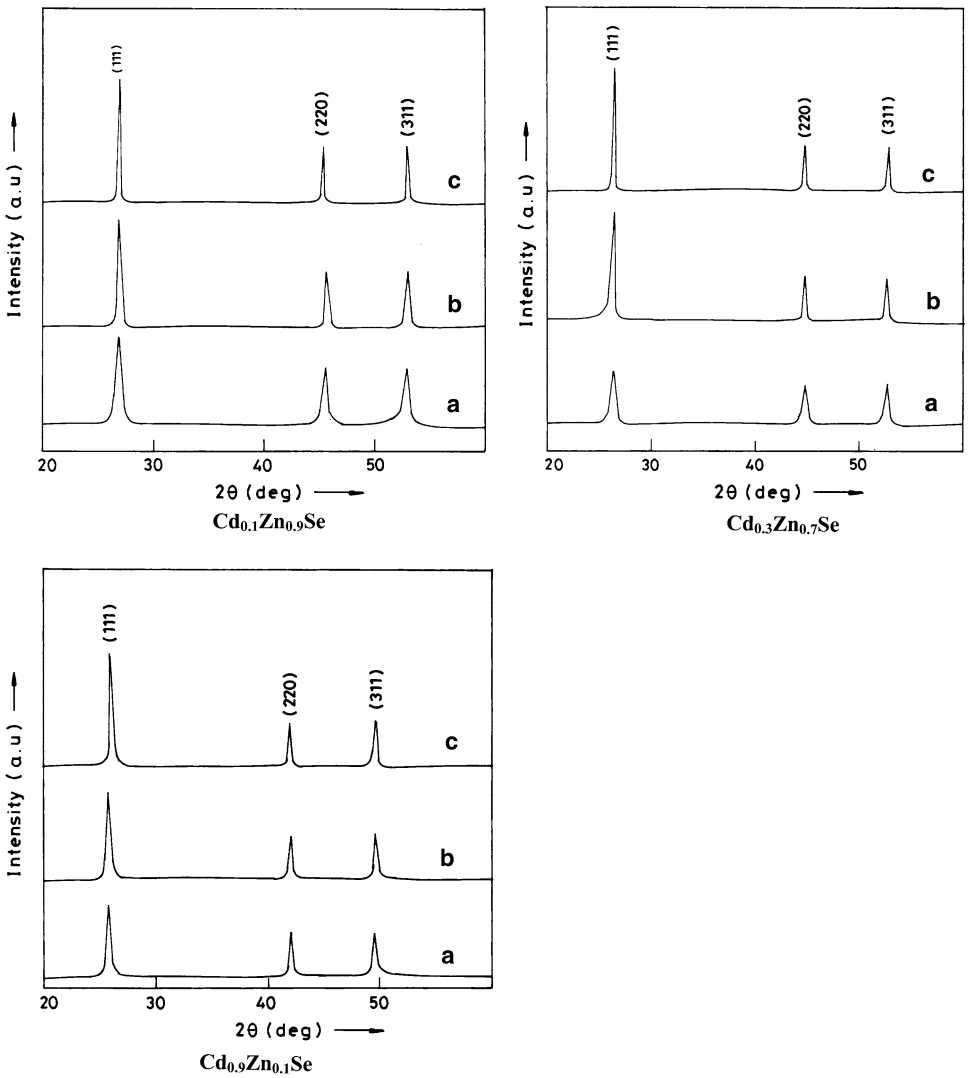

Fig. 1 X-ray diffraction pattern of $Cd_xZn_{1-x}Se$ films of different composition deposited at a different current densities (**a**) 50 mA cm^{-2} (**b**) 150 mA cm^{-2} (**c**) 250 mA cm^{-2}

Table 1 Composition of the films

Precursor composition	EDAX composition
$Cd_{0.1}Zn_{0.9}Se$	$Cd_{0.11}Zn_{0.89}Se$
$Cd_{0.2}Zn_{0.8}Se$	$Cd_{0.21}Zn_{0.79}Se$
$Cd_{0.3}Zn_{0.6}Se$	$Cd_{030}Zn_{0.70}Se$
$Cd_{0.5}Zn_{0.5}Se$	$Cd_{0.50}Zn_{0.50}Se$
$Cd_{0.7}Zn_{0.3}Se$	$Cd_{0.70}Zn_{0.30}Se$
$Cd_{0.9}Zn_{0.1}Se$	$Cd_{0.90}Zn_{0.10}Se$

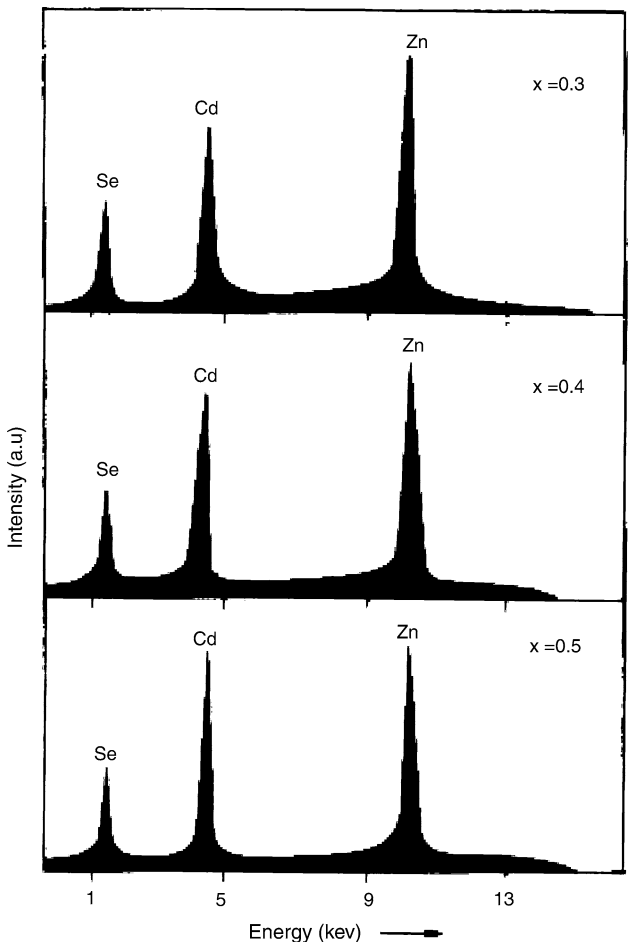

Fig. 2 EDAX spectrum of $Cd_xZn_{1-x}Se$ films of different composition deposited at a deposition current density of 250 mA cm^{-2}

the 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. The XPS spectra of the CZS films deposited at different current densities, were measured and is shown in Fig. 3. The XPS spectrum exhibit the binding energies of the Zn($2p_{3/2}$) and Cd($3d_{5/2}$ and $3d_{3/2}$) and Se($3d_{5/2}$ and $3d_{3/2}$) level. In all the figures, the peak energy levels associated with Zn($2p_{3/2}$) appeared in the range of 1022 eV, which is in good agreement with the literature value [6]. It is also observed that the area under the curve increases as the deposition current density increases. 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, the peak energy associated with Cd($3d_{5/2}$ and $3d_{3/2}$) occurred in the range of 405 and 411.7 eV respectively, which are in good agreement with the literature [7]. The peak values of Zn and Cd are found to shift towards Cd binding energy value in CdSe, as the CdSe content increased. Experimentally estimated density values of the films with varying composition were in close agreement with the theoretically calculated values (Table 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. Figure 4 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 $(\alpha h\nu)^2$ versus $h\nu$ 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].

Atomic force microscopic images of the films of $Cd_{0.5}Zn_{0.5}Se$ composition deposited at a different current densities are shown in Fig. 6. Fine grained structure is observed for the films with lower current densities, as the deposition current density increases, the grain size also increases from 20 to 40 nm, the surface roughness increases from 1.04 to 5.45 nm. The higher surface roughness is due to the larger grain size and higher thickness obtained for the films deposited at higher current densities. The as deposited CdZnSe films of different composition were used as photoelectrodes in photoelectrochemical solar cells. 1 M polysulphide(1 M Na_2S, 1 M NaOH, 1 M S) was used as the redox electrolyte. Figure 7 shows the load characteristics of the as deposited films of different composition deposited at 250 mA cm^{-2}. It is observed that the as deposited films have exhibited low photoactivity. The photo output is maximum for the films of composition $Cd_{0.9}Zn_{0.1}Se$. To increase the photooutput, the $Cd_{0.9}Zn_{0.1}Se$ films were heat treated in argon

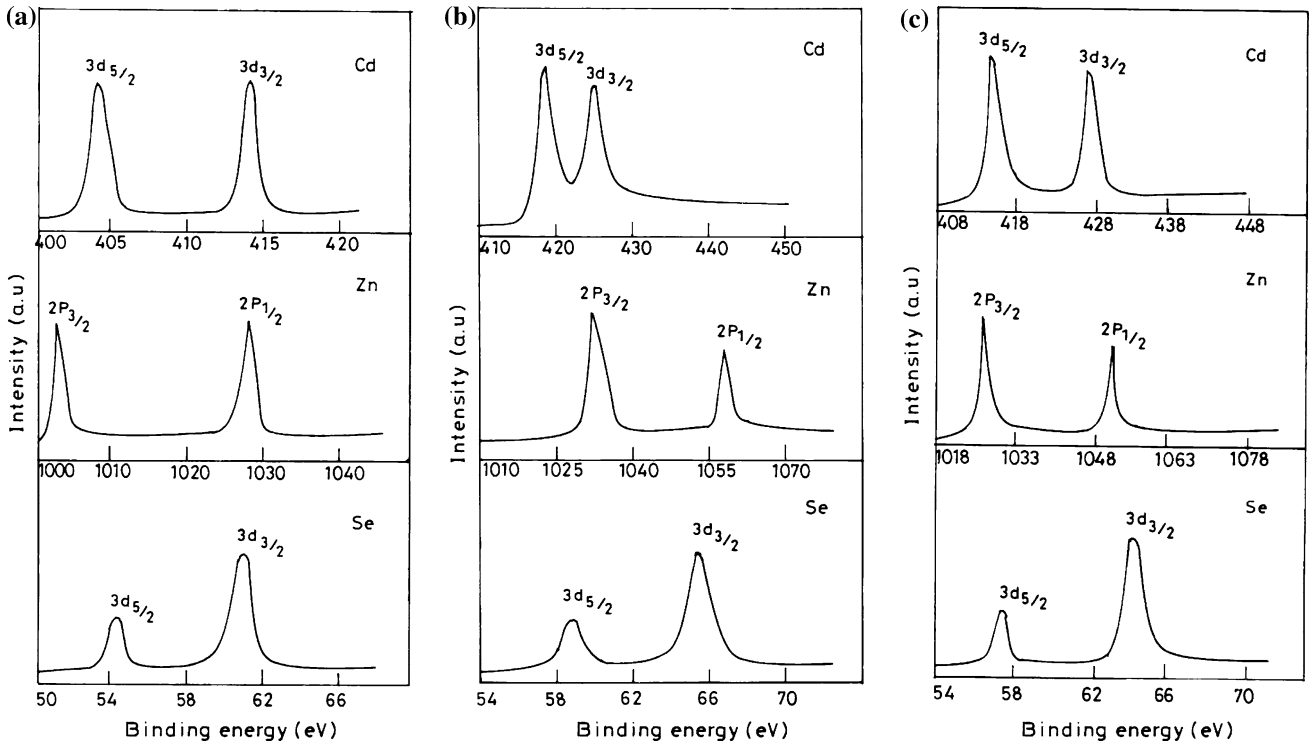

Fig. 3 XPS spectrum of $Cd_xZn_{1-x}Se$ films of different composition deposited at a deposition current density of 250 mA cm^{-2} (**a**) $x = 0.9$ (**b**) $x = 0.3$ (**c**) $x = 0.1$

Table 2 Density of $Cd_xZn_{1-x}Se$ films

Composition (x)	Theoretical density (g/cm^2)	Experimental density (g/cm^2)
0.1	5.317	5.314
0.2	5.364	5.361
0.3	5.411	5.410
0.4	5.458	5.457
0.5	5.505	5.502
0.6	5.552	5.550
0.7	5.599	5.598
0.8	5.646	5.643
0.9	5.693	5.691

atmosphere at different temperatures in the range of 450–550 °C. Figure 8 shows the load characteristics of the films post heat treated in argon. For the sake of comparision, the load characteristics of CdSe and ZnSe post heat treated in argon at 525 °C is shown in Fig. 9. It is observed that the photo output of the $Cd_{0.9}Zn_{0.1}Se$ is higher than those obtained with the end components CdSe and ZnSe. This is similar to the earlier observation [9, 10].

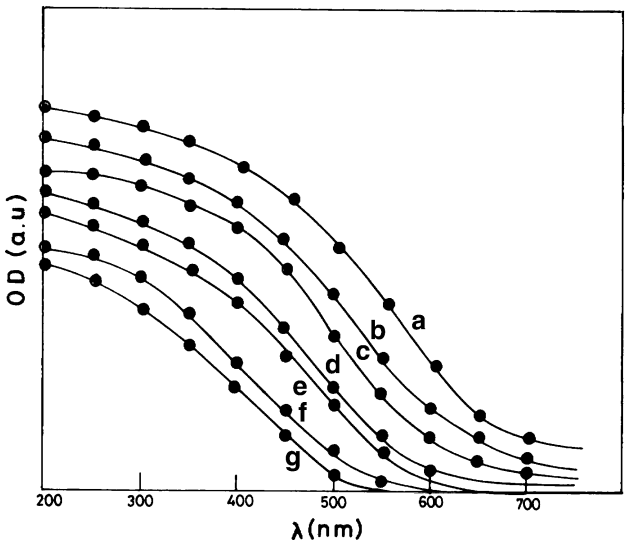

Fig. 4 Absorbance spectrum of the $Cd_xZn_{1-x}Se$ films of different composition(x) deposited at a deposition current density of 250 mA cm^{-2} (a) 0.1 (b) 0.3 (c) 0.4 (d) 0.5 (e) 0.7 (f) 0.8 (g) 0.9

4 Conclusions

All the results indicate that $Cd_xZn_{1-x}Se$ films of different composition could be deposited by the brush plating

technique. Nanocrystalline films could be obtained by this technique. Moreover the as deposited photoelectrodes prepared by this technique have exhibited photo output higher than the earlier reports.

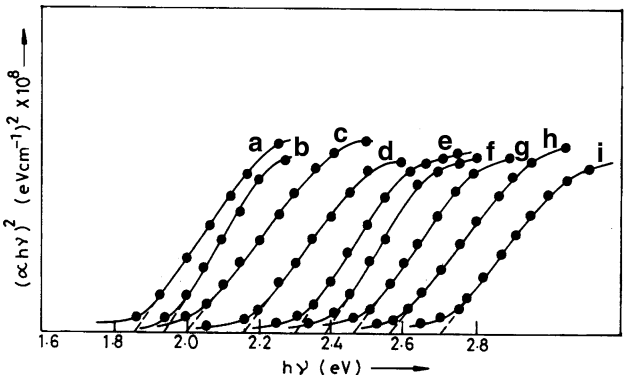

Fig. 5 $(\alpha h\nu)^2$ versus $h\nu$ plot of the $Cd_xZn_{1-x}Se$ films of different composition(x) deposited at a deposition current density of 250 mA cm^{-2} (a) 0.1 (b) 0.2 (c) 0.3 (d) 0.4 (e) 0.5 (f) 0.6 (g) 0.7 (h) 0.8 (i) 0.9

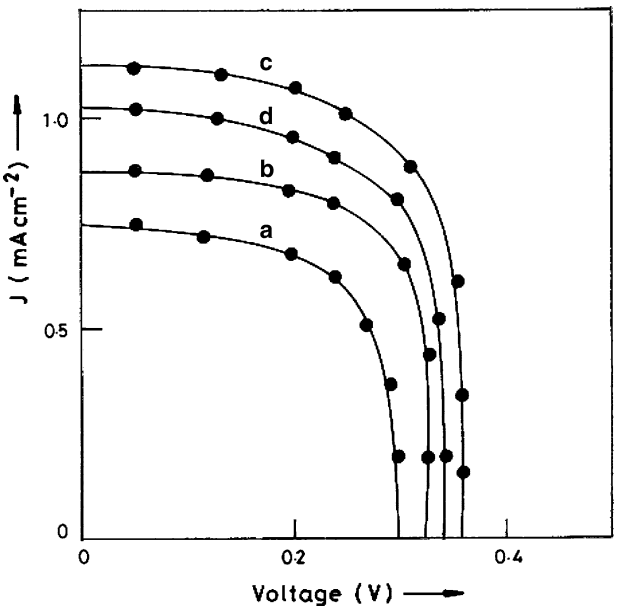

Fig. 7 Load characteristics of $Cd_xZn_{1-x}Se$ films of different composition(x) deposited at a current density of 250 mA cm^{-2}(a) 0.2 (b) 0.5 (c) 0.9 (d) 0.8

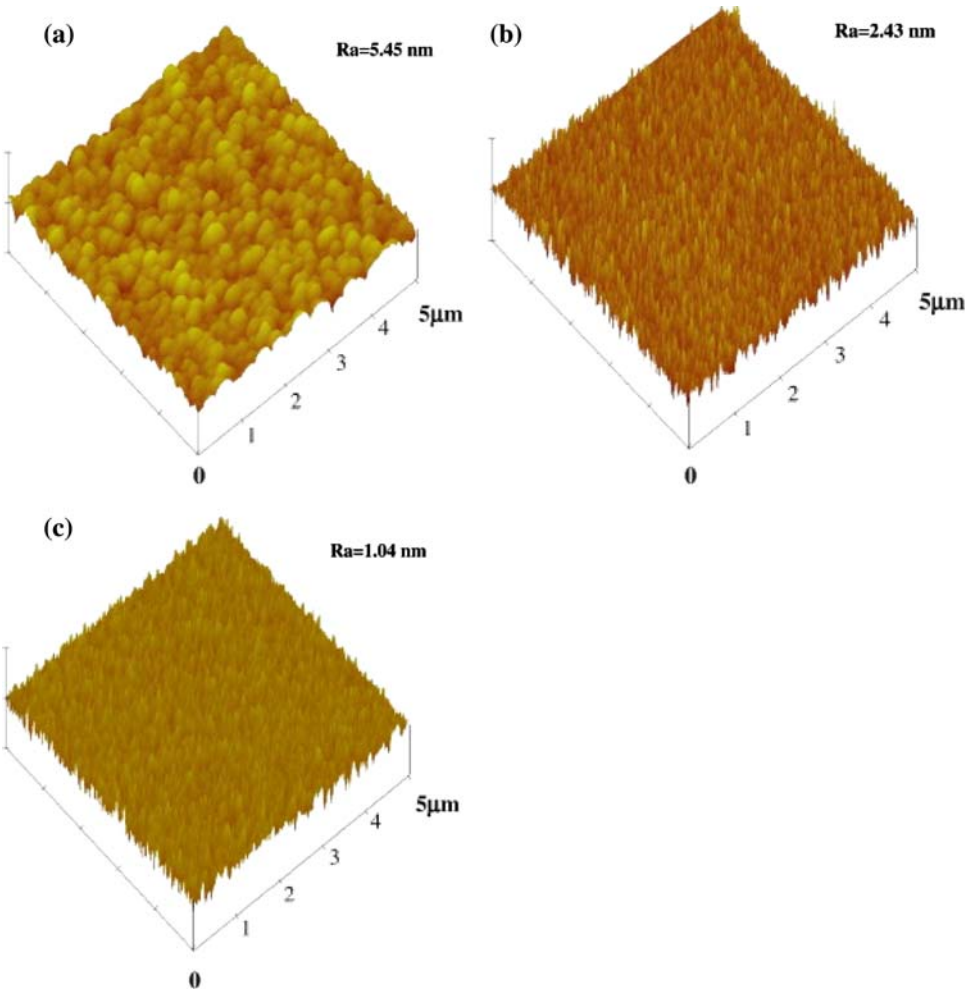

Fig. 6 AFM images of $Cd_{0.5}Zn_{0.5}Se$ films deposited at different current densities (**a**) 250 mA cm^{-2} (**b**) 150 mA cm^{-2} (**c**) 50 mA cm^{-2}

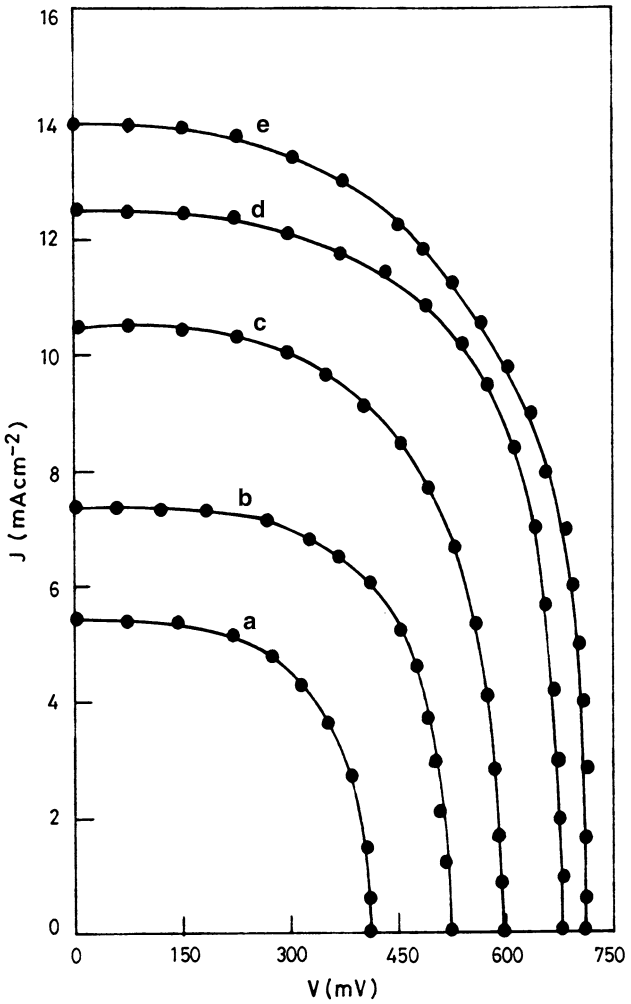

Fig. 8 Load characteristics of $Cd_{0.9}Zn_{0.1}Se$ films post heated at different temperatures (a) 450 °C (b) 475 °C (c) 500 °C (d) 525 °C (e) 550 °C

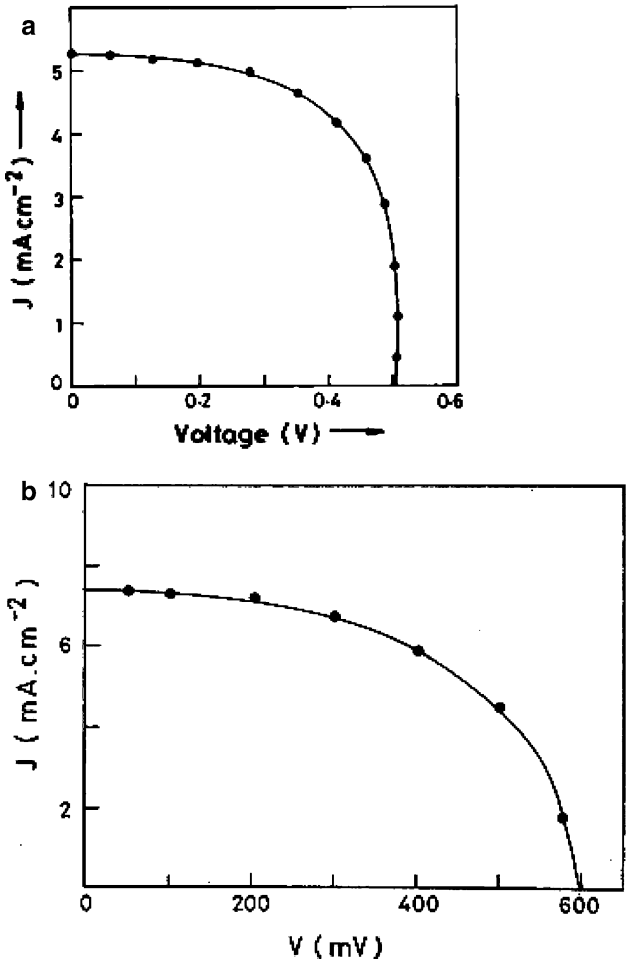

Fig. 9 Load characteristics of brush plated CdSe and ZnSe films post heated at 525 °C (**a**) ZnSe (**b**) CdSe

References

1. G.H. Schoemaker, E.P.A.M. Bakkers, J.J. Kelly, J. Electrochem. Soc. **144**, 2329 (1997)
2. K. Singh, R.K. Pathak, Electrochim. Acta. **39**, 2693 (1994)
3. S. Licht, Electrochem. Soc.(Interface) **6**, 37 (1993)
4. H.C. Choi, A. Rohatgi, E.W. Thomas, S. Kamira, A.K. Bhat, J. Electrochem. Soc. **142**, 254 (1995)
5. T. Yoshida, J. Electrochem. Soc. **142**, 3232 (1995)
6. R. Kumaresan, M. Ichimura, E. Arai, Thin Solid Films **414**, 25 (2002)
7. O. Savadago, K.C. Mandal, Mater. Chem. Phys. **31**, 301 (1992)
8. M. Kumar, M. Sharon, Thin Solid films **312**, 139 (1998)
9. C. Natarajan, G. Nogami, M. Sharon, Thin Solid Films **261**, 44 (1995)
10. A. Darkowski, A. Grabowski, Solar Energy Mater. **23**, 75 (1991)