Brush plated CdSe films on high temperature substrates

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CdSe is a direct band gap semiconductor belonging to the II–VI group and possessing excellent optoelectronic properties. Thin film transistors and image intensifier tubes have been fabricated with this material. It is also a very stable photo anode in wet photovoltaic cells. 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 higher temperatures.

CdSe films were brush plated on to titanium and conducting glass substrates maintained at different temperatures in the range 30–90 °C. The precursors used were 0.5 M $CdSO_4$ and 0.1 M SeO_2. A current density of 100 mA cm^{-2} 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 a Philips X-ray diffractometer with Cu K_α radiation. Optical absorption measurements were made on the films using a Hitachi UV-VIS-NIR spectrophotometer. XPS studies were made on the films using ESCALAB. EDAX measurements were also made. Preliminary studies on the photoelectrochemical properties of the films were made in 1 M polysulphide electrolyte (1 M NaOH, 1 M Na_2S and 1 MS) under illumination from an ORIEL tungsten halogen lamp.

XRD patterns of the films deposited at different substrate temperatures are shown in Fig. 1. The prominent

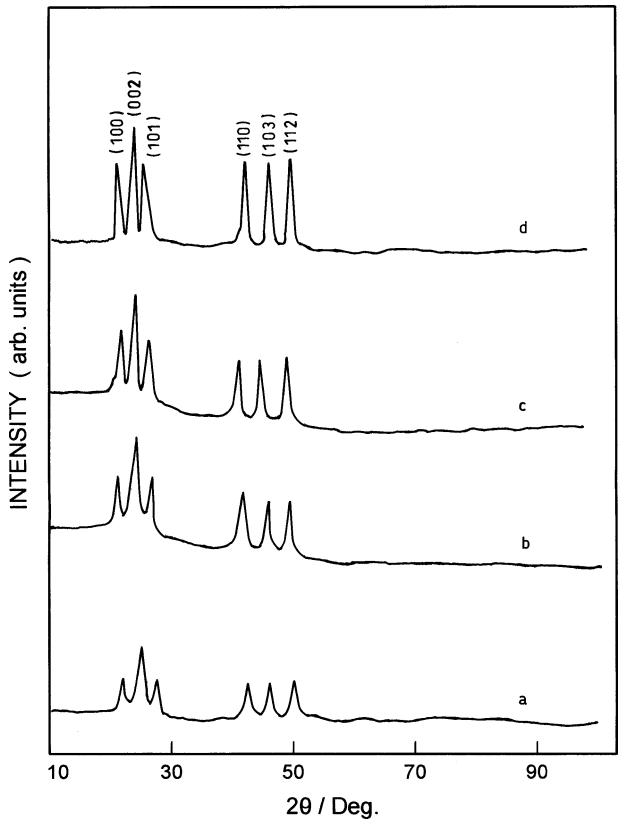

Figure 1 X-ray diffraction pattern of CdSe films plated at different substrate temperatures: (a) 30 °C, (b) 70 °C, (c) 80 °C and (d) 90 °C.

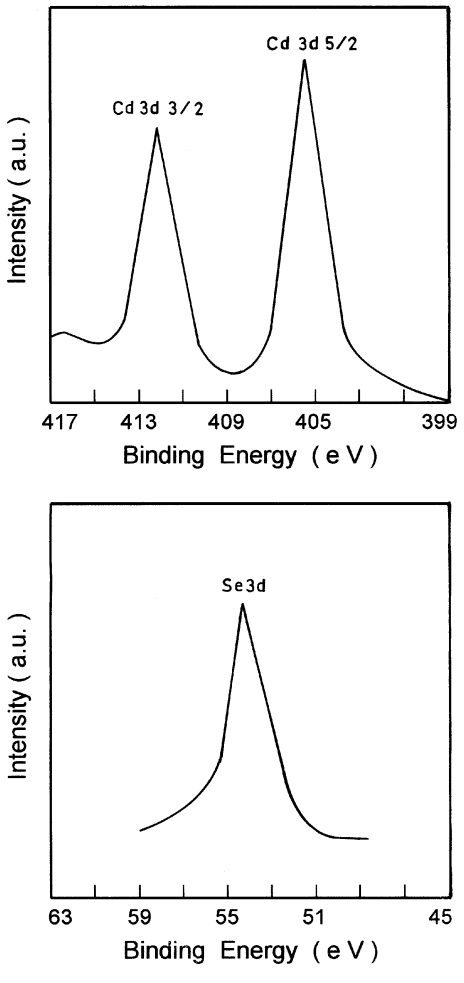

Figure 2 XPS spectra of CdSe films deposited at a substrate temperature of 90 °C.

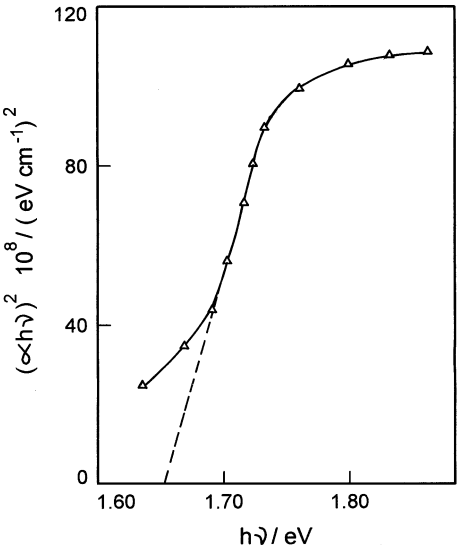

Figure 3 $(\alpha h\nu)^2$ vs. $h\nu$ plot of CdSe films deposited at a substrate temperature of 90 °C.

peaks corresponding to (100), (002), (101), (110), (103) and (112) are observed in all cases. It is observed that as the substrate temperature increases, the intensity of the peaks also increase and 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 I).

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. The peak at 54.3 eV (Fig. 2b), measured in the Se energy region is attributed to the Se3d transition. The energies for Cd and Se are in good agreement with the literature [7]. EDAX measurements indicated Cd(50.2%) and Se(49.8%), and as the substrate temperature increased the selenium concentration increased slightly (Cd–49.2% and Se–50.8%). Hot probe measurements indicated *n*-type behaviour.

TABLE I Variation of crystallite size with bath temperature

Bath temperature (°C)	Crystallite size (nm)
30	100
50	150
70	230
80	340
90	450

Optical absorption measurements were made at room temperature by placing an uncoated identical conducting glass substrate in the reference beam. A plot of $(\alpha h\nu)^2$ vs. $h\nu$ for the films deposited at a substrate temperature of 90 °C 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 of 1.65 eV.

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 increase from 50 to 120 ohm cm with increase of substrate temperature. This may be due to the increase in selenium concentration and decrease in cadmium concentration for the high temperature deposited films. Capacitance–voltage measurements were made on the films in 1 M sodium sulphate electrolyte. The nature of the plot (Fig. 4) indicates *n*-type behaviour, agreeing well with hot probe measurements. The value of the carrier density calculated from the slope of the plot was found to be in the range of 10^{17} cm^{-3}. Photoelectrochemical cell studies were made on the films deposited at high temperatures, while the low temperature grown films did not exhibit any photoresponse, those deposited at 90 °C exhibited a weak photoactivity. A photovoltage of 250 mV and photocurrent of 100 μA

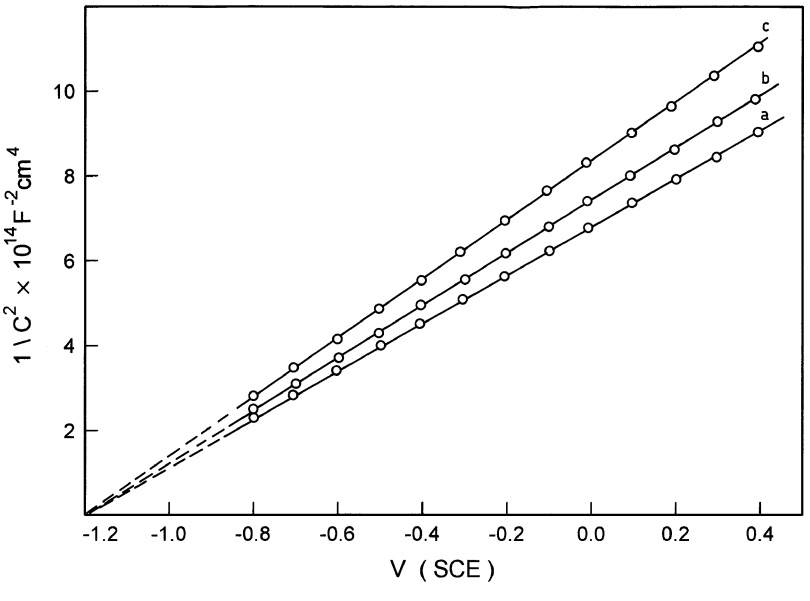

Figure 4 Capacitance—Voltage plot of CdSe film deposited at: (a) 30 °C, (b) 80 °C and (c) 90 °C.

were obtained. Earlier work on brush plated films [6] did not report any photoactivity for the room temperature as deposited films. Further work is in progress for studying the photoelectrochemical properties of the above films after heat treatment at high temperatures in argon atmosphere at high temperatures.

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