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Growth of cadmium selenide layers by electrodeposition

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Cadmium selenide (CdSe) films have been electrodeposited from a bath containing $CdSO_4$ and SeO_2. The pH of the bath was around 2. The deposition was done by short circuiting different substrates like Indium Tin Oxide ITO, molybdenum, sodium selenosulphite etc. to an easily oxidizable electrode (such as Al/Cd) in an electrolytic bath. The temperature of the deposition bath was varied in the range 60 to 85° C. The as-grown films were characterized by X-ray diffraction and scanning electron microscopy. Electrical characterization of the ITO/CdSe/In structure was made by studying the current–voltage characteristics. Optical absorption measurements yielded a direct band gap around 1.65 eV.

1. Introduction

The study of electrodeposited thin semiconducting films on transparent electrodes like SnO_2- and ITO-coated glass substrates presents several advantages as compared with the study of such films on opaque substrates. First, the optical properties of electrodeposited films can be easily analysed. Second, a number of low-cost devices like solar cells and photoelectrochemical (PEC) cells can be developed, offering a choice of either front-wall or back-wall illumination. So far, CdSe films have been electrodeposited using an aqueous solution of electrolytes containing cadmium, chloride, sodium selenosulphite (SS), etc. [1, 2] and non-aqueous solutions of electrolytes [3]. In the present work CdSe films are deposited on ITO substrates by short-circuiting the substrates to an easily oxidizable electrode (aluminium or cadmium). Here some of the results on the structural, electrical and optical properties of CdSe films, prepared by short circuiting ITO substrates to aluminium foil, are presented and discussed.

2. Experimental methods

Thin films of ITO were deposited on glass substrates by adopting a procedure described elsewhere [4]. The deposition bath normally contained $CdSO_4$ and SeO_2. The pH of the bath was adjusted to a value of ~ 2 by adding 10% H_2SO_4. In a typical deposition run, the bath was first thermostatted at the required temperature, and the temperature of the bath was varied in the range 60 to 85° C. After the desired temperature was attained the substrates were suspended in solution and shorted to an aluminium sheet. Film formation was easy and visible to the naked eye. Deposition was carried out for 5 h to achieve a good film. The deposited films were characterized by X-ray diffraction and the morphology of the surface was studied by scanning electron microscope (SEM). Electrical characterization of the ITO/CdSe/In configuration was made by studying the current–voltage characteristics. Optical absorption measurements were made at room temperature using a Hitachi spectrophotometer. The thickness of the films was measured by weighing.

3. Results and discussion

Films of varying thickness in the range 0.5 to 2 μm were routinely grown on ITO substrates. The X-ray diffraction patterns of the as-deposited CdSe films (Fig. 1) exhibited broad peaks corresponding to (1 1 1), (2 2 0) and (3 1 1) orientations. Films deposited at a bath temperature of 80° C exhibited sharper diffractograms compared with the films deposited at

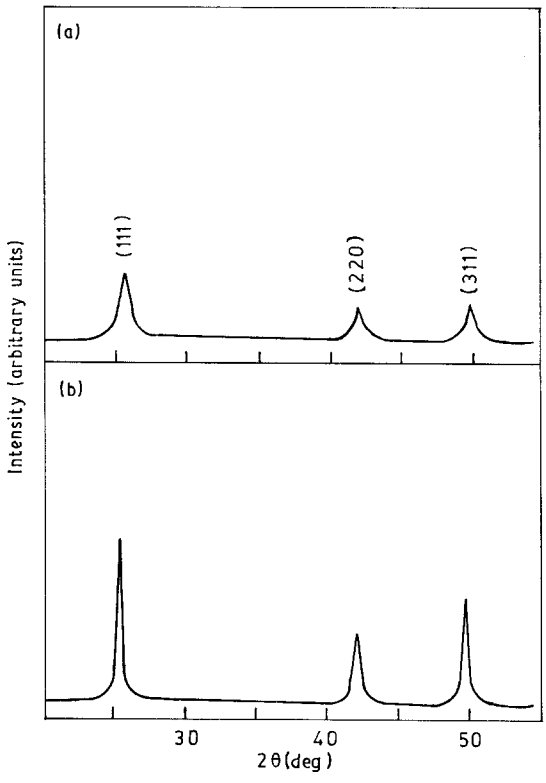

Figure 1 X-ray diffractograms of CdSe films grown at different bath temperatures. (a) 70° C; (b) 80° C.

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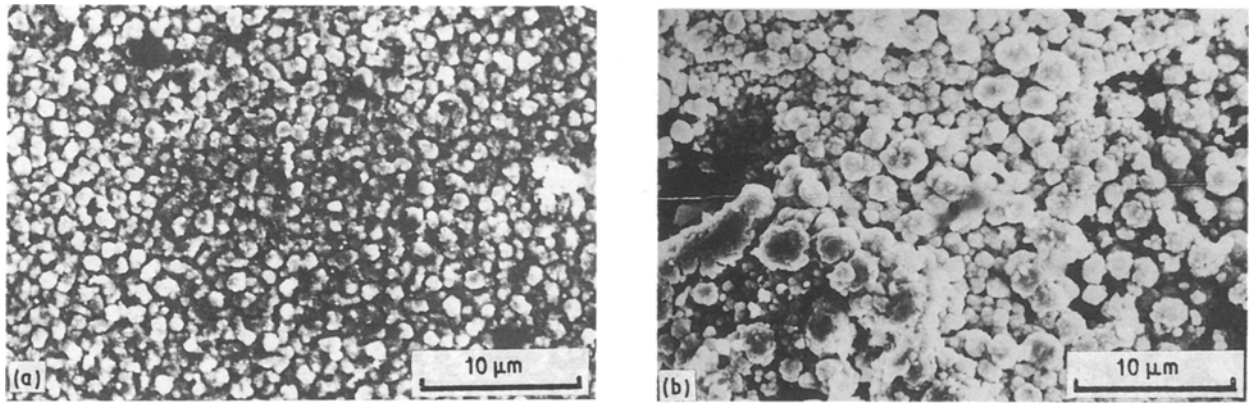

Figure 2 Scanning electron micrographs of CdSe films on (a) ITO; (b) stainless steel.

temperatures around 70° C. The surface morphology of the films examined by JEOL 35CF model SEM is shown in Fig. 2. While films deposited on ITO substrates have exhibited small grains ($< 0.8\,\mu$m), those deposited on SS substrates exhibited larger grains ($> 1.5\,\mu$m). This can be easily understood from the fact that the films deposited on ITO substrates are a replica of the metallic oxide microtexture. EPMA analysis of the films indicated the presence of cadmium and selenium in stoichiometric quantities.

In the electrical characterization of as-deposited CdSe film on ITO substrate, ITO was used as one electrode and the other was formed by vacuum evaporating an indium film on the electrodeposited CdSe layer. The current–voltage characteristic was measured using the above metal/semiconductor/metal configuration. For low voltages the current–voltage plot was a straight line, the slope of which was unaffected on changing the polarity. This shows that the contact is ohmic. The resistivity of the deposited material is around 200 Ω cm.

The conduction mechanism in semiconductors can be understood by analysing the current–voltage plots. For single carrier injection at low voltages, the plot is generally a straight line showing the validity of Ohm's law. However, at higher voltages some deviation is expected. In most cases, beyond a certain voltage the current increases steeply. This is explained by noting that the current transport in the semiconductor is controlled by the space charge and the current is referred to as being space charge limited. In Fig. 3 the plot of log current against voltage is shown for a film deposited with a bath temperature of 80° C. The ohmic behaviour observed at lower voltages is attributed to the filling of a discrete set of traps lying at or below the Fermi level E_F. Further, it is observed that for a small increase in voltage after a critical voltage (V_{TFL}), the current suddenly shoots up. This could be explained by arguing that the traps are filled directly by the charge carriers up to V_{TFL}. When the voltage reaches V_{TFL} all the traps are filled and any further increase in voltage causes a rapid increase in current. Lampert *et al.* [5] have shown that the value of V_{TFL} is related to the trap density, N_t by

$$N_t = 1.1 \times 10^6 \varepsilon_s V_{TFL}/l^2 \qquad (1)$$

where l is the film thickness and ε_s is the relative dielectric constant of the material. Using the film thickness $l = 2\,\mu$m, the trap density is found to be $2.0 \times 10^{14}\,\text{cm}^{-3}$.

Optical absorption measurements were made using an UV–VIS–IR Hitachi spectrophotometer at room temperature using unpolarized radiation. Transmission spectra of the films were recorded as a function of the wavelength in the range 400 to 1200 nm. Substrate absorption, if any, was corrected for by introducing an uncoated ITO substrate in the reference beam. The transmittance, T, was converted into optical density (OD) according to the relation

$$\text{OD} = \log_{10}(1/T) \qquad (2)$$

The absorption coefficient, α, rises sharply owing to the band-to-band transitions, and levels off later. An analysis of the absorption spectrum in the region $1.7\,\text{eV} < h\nu < 2.1\,\text{eV}$ indicated that α follows the

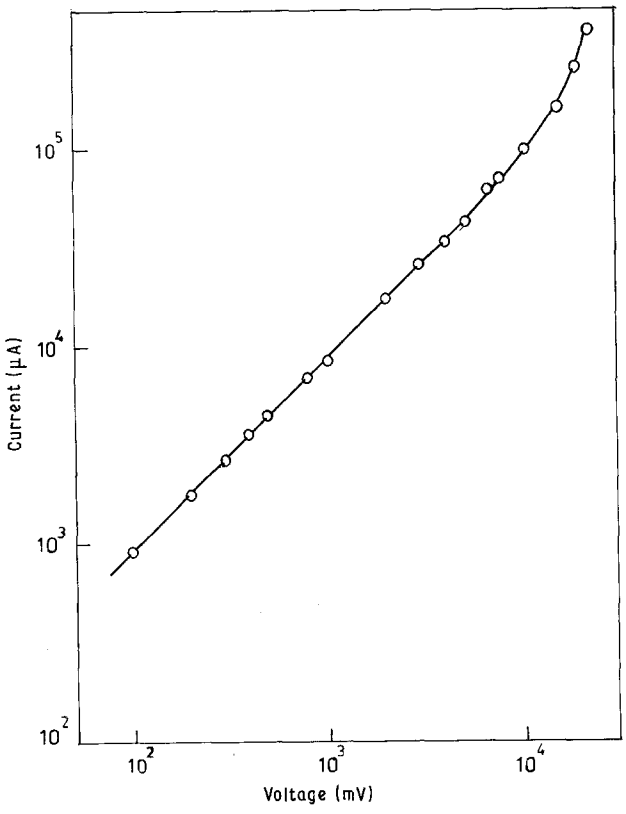

Figure 3 Log current against log voltage plot for electrodeposited CdSe film.

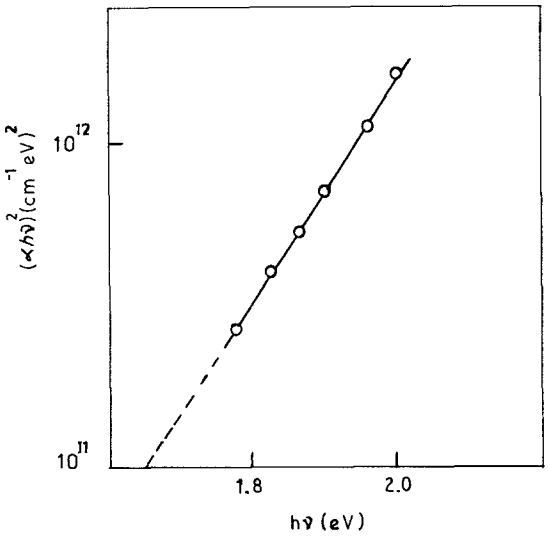

Figure 4 Plot of $(\alpha hv)^2$ against photon energy near the absorption edge.

relation

$$\alpha = \frac{A}{hv}(hv - E_g)^{1/2} \quad (3)$$

where A is a constant and E_g is the energy gap. A plot of $(\alpha hv)^2$ against hv should give a straight line whose intercept on the hv axis is $E_g (\sim 1.65\,eV)$ and the slope is A. Such a plot is shown in Fig. 4. This value is comparable to those reported for CdSe films deposited by other techniques.

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