FURTHER STUDIES ON THE TEMPERATURE DEPENDENCE OF THE ELECTRIC AND PHOTOVOLTAIC PROPERTIES OF CdSe THIN FILMS FOR SOLAR CELLS

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ABSTRACT

CdSe thin films were prepared under vacuum at different glass substrate temperatures. The effects of substrate temperature, temperature on the X-ray diffraction patterns, electrical (DC-current–voltage characteristics), and photovoltaic properties have been investigated in detail. The results obtained were mathematically interpreted leading to a hopping conduction mechanism. Valuable semiconducting parameters were evaluated for the thin films investigated, comprising surface charge density (4.8×10^{12} cm^{-2}), thickness of depletion layer (7.4×10^{-7} cm) and donor concentration (6.5×10^{18} cm^{-3}), for useful application in the photovoltaic or solar-cell industries.

INTRODUCTION

Thin films of CdSe are of great interest for their useful application in photoelectric devices. It has been shown that the conditions of preparation have a marked influence on their structural properties and photosensitivity. The influence of substrate temperature, in the range 25–200°C, on the electrical properties of CdSe thin films has been studied [1–3]. Results indicated that the resistivity increases with increasing substrate temperature.

The number of ionized impurities decreases with increasing substrate temperature and consequently the effective mobility increases slightly. Impurity scattering predominates up to a substrate temperature of approximately 70°C. Above this temperature, the intergrain height increases and therefore the intergrain barrier scattering begins to predominate, thus decreasing the absolute value of mobility. The carrier concentration also decreases with increasing substrate temperature. Three energy donor levels exist in the CdSe films studied. The first has a ΔE value of 0.025 eV the second, 0.14 eV, and the third, 0.4 eV. The first energy level corresponds to

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the monovalent impurity atoms, the second and third correspond to the divalent selenium vacancies [1–3].

In the present work, nonlinear I–V behaviour is noticed, with hopping conduction also taking place at low temperatures. The density of ionizable impurities is estimated, and the surface density of the depletion layer depths are calculated. Moreover, the effect of mercury light (265 nm) on the thin films is studied to evaluate their photovoltaic properties for the solar-cell industries.

EXPERIMENTAL PROCEDURES

Material preparation

CdSe thin films were prepared by evaporation of CdSe under a vacuum of 10^{-5} Torr. They were evaporated onto glass substrates, at definite temperatures, provided with silver electrodes. The dimensions of each thin film prepared are 0.3 cm^2 area and 0.01 μm thickness. The CdSe films were of cubic structure.

X-ray diffraction measurements

In order to detect if any structural changes were present a Shimadzu X-ray diffractometer (Kyoto, Japan) was utilized.

Cu K_α radiation and Ni-filter were used at room temperature (25°C). During all measurements, all X-ray experimental conditions (time = 5 min, width = 5 nm, range = CPS, gain = 4 and CHS = 10) were kept constant.

Electrical measurements

These were performed with DC bias voltage, provided by a power supply (No. 168105 0062) and the current was recorded by an electronic Avometer (model 820).

The voltage across the sample was monitored by a DC microvoltmeter (type TM10).

Sample temperatures were monitored with a small chromel–alumel thermocouple attached to the substrate.

RESULTS AND DISCUSSION

The effects of substrate temperatures on the X-ray diffraction patterns for thin films of CdSe are shown in Fig. 1. It is clearly shown that the peak intensity of the reflected beam decreases as the substrate temperature
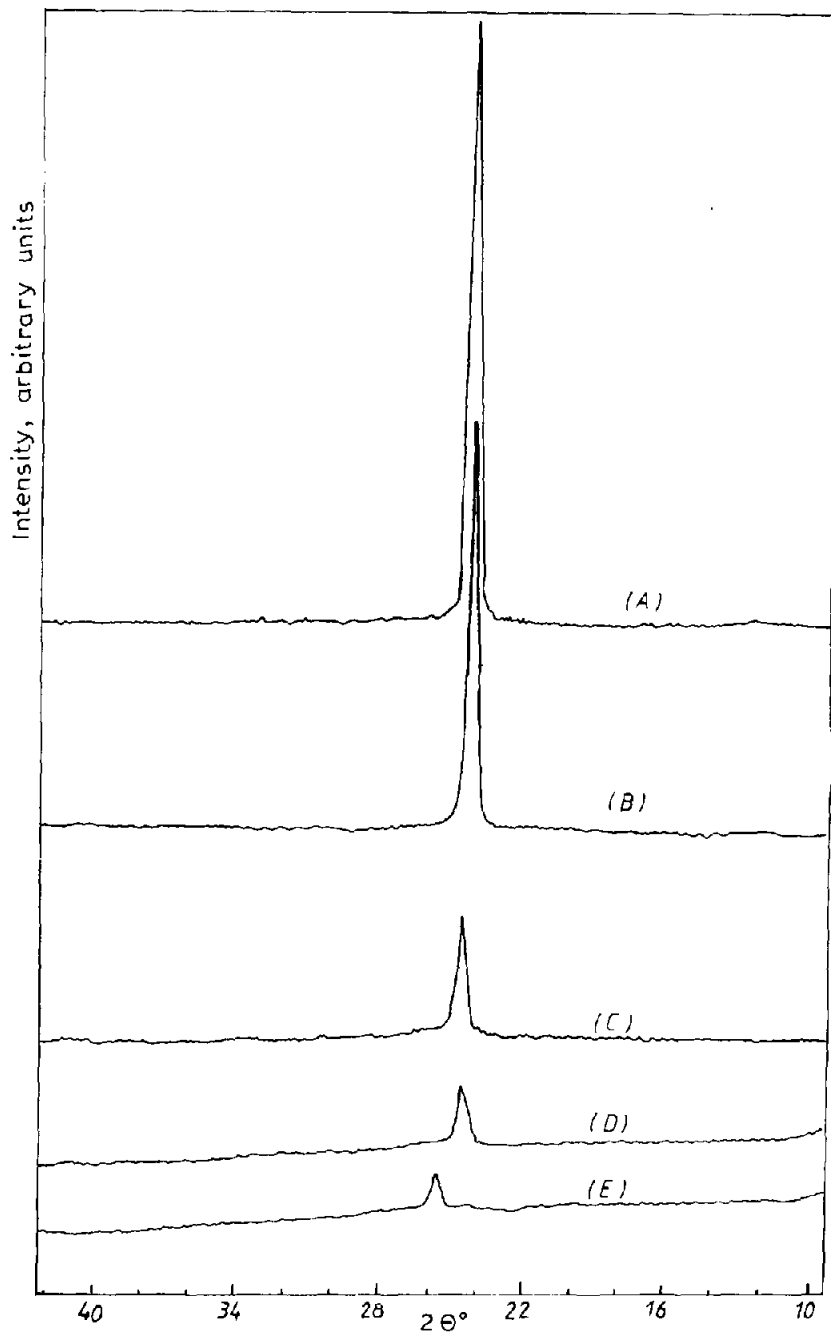
Fig. 1. The room-temperature Cu K_α X-ray diffraction patterns obtained for the different CdSe thin films: (A) substrate temperature $(t_s) = 25°C$; (B) specimen pre-heated at 160°C; (C) $t_s = 110°C$; (D) $t_s = 150°C$; (E) $t_s = 200°C$.

increases. It should be noted that the effect of the substrate temperature on crystal orientation is predominant. The diffraction of these thin films is dependent mainly on the conditions of crystallization, the decrease in intensity of reflected beam being due to the decrease in the degree of crystallinity. Consequently, at lower substrate temperatures, the orientation of the crystals is greater; on the other hand, at higher substrate temperatures or after heating the sample at 160°C (annealing), the grain size increases and the degree of orientation deteriorates (see Fig. 1). This is further explained on the basis that the crystallite size and cubic [4] centered phase increase with increasing substrate temperature and/or with heat treatment (160°C Fig. 1B).

As has been described, the structure of CdSe thin films strongly depends on the substrate temperatures. A temperature rise during the deposition of the films leads to an increase in grain size and a reduced degree of orientation.

Current–voltage characteristics

The nonlinear dependencies of current on voltage at different temperatures are shown in Fig. 2. This can be explained by the formation of space charges in a depletion region due to the difference in the work functions of the metal and the material of thin film. This depletion layer will give rise to an electric field in the region investigated.

The depletion layer, λ, could be determined from the equation [4–7]

$$\lambda = \left(\frac{2\epsilon_0 \epsilon_r V}{q N_d} \right)^{1/2} \approx 1052 \left(\frac{\epsilon_r V}{N_d} \right)^{1/2} \tag{1}$$

where V is the effective potential across the electrodes; ϵ_r is the relative dielectric constant; N_d is the density of ionizable impurities; λ is calculated and is found to be 7.4×10^{-7} cm.

The dielectric field (E) at the electrodes is given by

$$E = \left(\frac{2q N_d V}{\epsilon_0 \epsilon_r} \right)^{1/2} \approx 1.9 \times 10^{-3} \left(\frac{N_d V}{\epsilon_r} \right)^{1/2} \tag{2}$$

$$I = A A^* T^2 \exp\left[-\frac{\phi - 8.26 \times 10^{-6} q (N_d V / \epsilon_r^3)}{KT} \right]^{1/4} \tag{3}$$

where A is the effective area; A^* is the effective Richardson–Dushman constant; T is the absolute temperature; K is the Boltzmann constant (8.62×10^{-5} eV k^{-1}); ϕ is the contact-barrier height; and V is the applied voltage.

Equations (2) and (3) and the slope of the plot of log I against $V^{1/4}$ (Fig. 3) would give the value of the donor density (N_d) to be 6.5×10^{18} cm^{-3}.
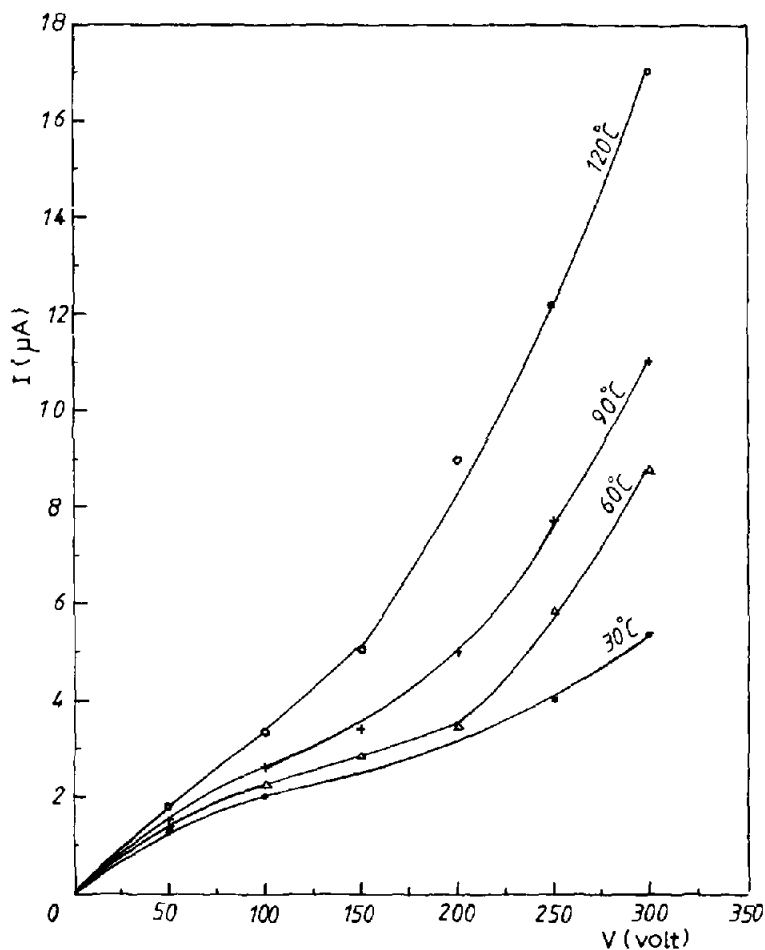
Fig. 2. Current–voltage characteristics at various temperatures.

The surface density of charges (N_s) per unit area which is required to screen the internal field (E), is given by

$$N_s = \lambda N_d \tag{4}$$

Taking $\lambda = 7.4 \times 10^{-7}$ cm and $N_d = 6.5 \times 10^{18}$ cm^{-3}, thus, $N_s = 4.8 \times 10^{12}$ cm^{-2}.

The temperature dependence of current of CdSe thin films

The logarithm of current is plotted against the reciprocal of absolute temperature at different applied voltages as shown in Fig. 4. The current varies with temperature in accordance with the equation
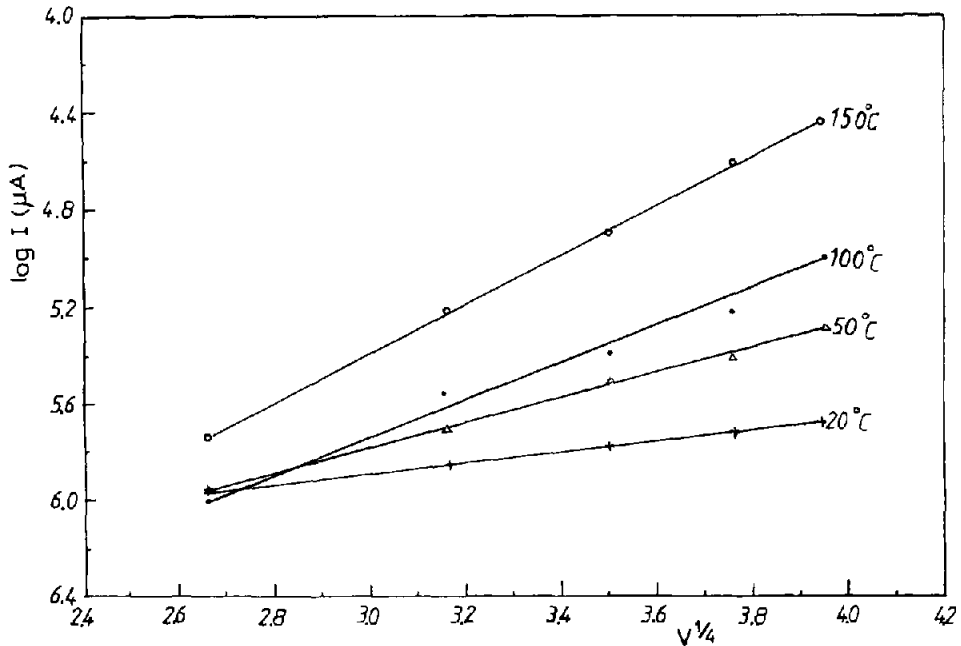
$$I = I_0 e^{-\Delta E / KT} \tag{5}$$

Fig. 3. Variation of $\log I$ (μA) as a function of $V^{1/4}$ at various working temperatures.

where ΔE is the activation energy for donors. According to eqn. (5) the gradients for these slopes yield a consistent value of activation energy, $\Delta E = 0.047-0.126$ eV at low temperature (20–70°C) and at different voltages (Table 1). For temperatures between 70 and 120°C, $\Delta E \approx 0.12-0.19$ eV, above 120°C, $\Delta E \approx 0.236-0.378$ eV.

The breakthrough current or a transition from a straight line with low gradient to one with a higher gradient, as the temperature is increased, suggests that more than one conduction mechanism is involved. The low-temperature activation energy may be attributed to the hopping conduction mechanism which is expected at such a low temperature range (20–70°C).

Alternatively, it was proposed that in the films studied three donor

TABLE 1

Values of the activation energies obtained for conduction corresponding to different temperature ranges at various applied voltages

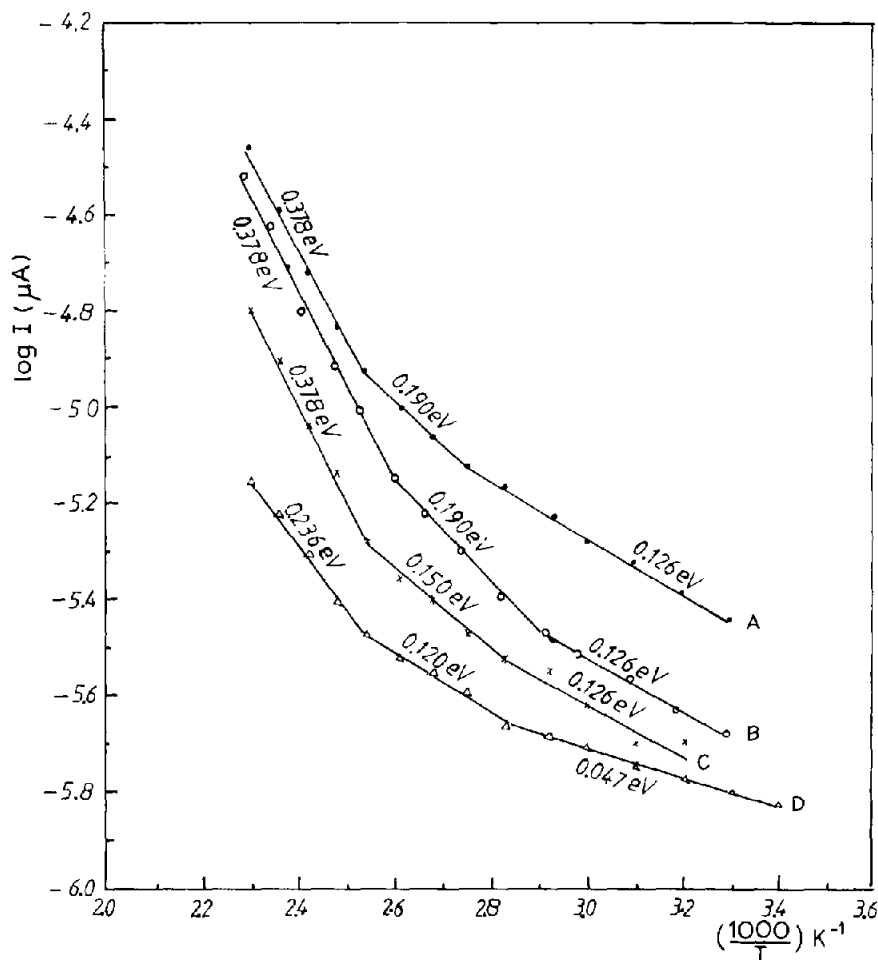| Applied voltage (V)	ΔE (eV) low temp. (20–70°C)	ΔE (eV) medium temp.	ΔE (eV) high temp.
20	0.126	0.19	0.378
100	0.047	0.12	0.236
150	0.126	0.15	0.378
200	0.126	0.19	0.378

Fig. 4. Variation of $\log I$ (μA) as a function of the reciprocal of absolute temperature at various applied voltages: (A) 250 V; (B) 200 V; (C) 150 V; (D) 100 V.

excitation levels exist, the first one ($\Delta E \approx 0.12$ eV) corresponding to the impurity atoms, and the second ($\Delta E \approx 0.19$ eV) and third ($\Delta E \approx 0.378$ eV) corresponding to divalent selenium vacancies. This gives useful information about the carrier excitation mechanism involved.

Effect of distance from the mercury light source on the photoelectric current

The effect of the distance between the mercury light and the CdSe thin film at different fields on the photoelectric current generated is shown in Fig. 5. The decrease in photoelectric current with increasing distance may be attributed to the incident photons of energy, $h\nu$, exciting charge carriers. It is proposed that in the films [3] studied three donor excitation levels exist, the first one corresponding to the impurity atoms, and the second to the
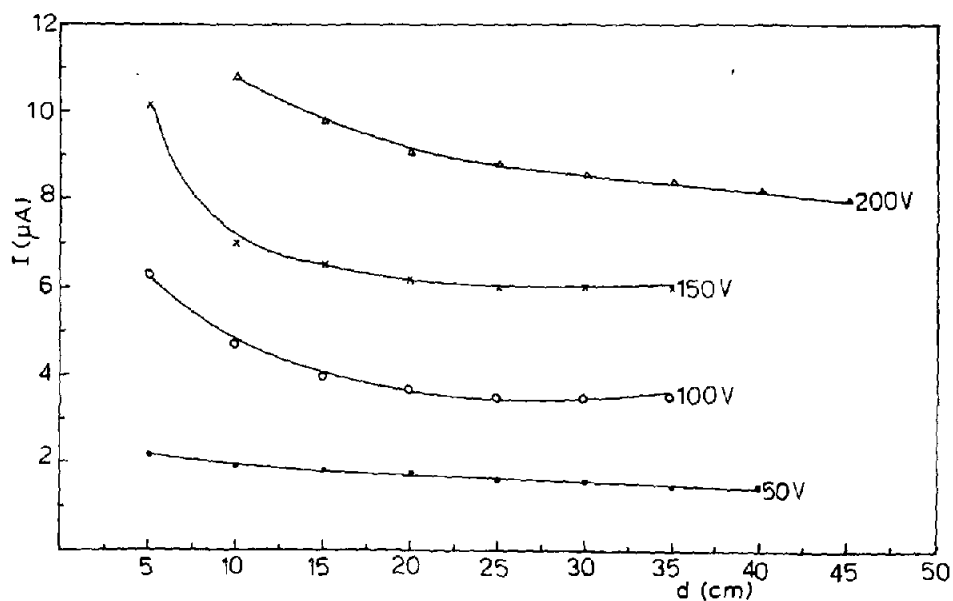
Fig. 5. Variation of the photoelectric current generated as a function of distance (d) from the light source at various applied voltages.
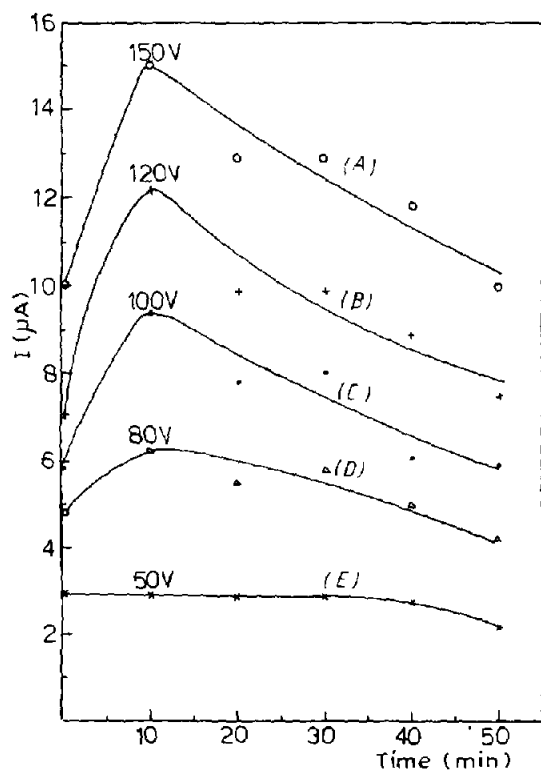

Fig. 6. Variation of the photoelectric current generated as a function of time of exposure at various applied voltages.

divalent selenium vacancies. As the distance increases, the photoelectric current decreases due to the decrease in photo-intensity. The film resistance increases giving rise to a decrease in photoelectric current.

Figure 6 shows the variation of photoelectric current generated (μA) as a function of exposure time (min) at various applied voltages. From this Figure it can easily be seen that:

(a) increasing the applied voltage resulted in an increase in the photoelectric current generated;

(b) with the exception of curve (E), all curves have a common trend, namely, they are characterized by an initial rise in the photoelectric current generated with increasing time of exposure reaching a maximum value, followed by a subsequent gradual decrease. This could be explained by various scattering mechanisms of free carriers [8]. The number of ionized impurities increases at longer exposure times beyond 10 min and consequently the effective mobility increases slightly (Fig. 6). The impurity scattering begins to predominate and, thus, the absolute value of the effective mobility decreases. All of these factors may contribute to the decreased photoelectric current generated at longer light exposure times (Fig. 6).

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