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

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Thin CdSe films were prepared under vacuum at different glass substrate temperatures. The effects of substrate heating and temperature on the X-ray diffraction patterns, electrical, DC current-voltage characteristics and photovoltaic properties were investigated in detail. the results obtained were interpreted mathematically, which led to a hopping conduction mechanism. Valuable semiconducting parameters were evaluated for the thin films investigated, for their useful application in photovoltaic or solar cell industries: 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}).

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 the substrate temperature, in the range 25–200°, on the electrical properties of thin CdSe films has been studied [1–3]. The 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 slightly increases. The impurity scattering predominates up to a substrate temperature of approximately 70°. Above this temperature, the intergrain height increases and therefore the intergrain barrier scattering begins to predominate, decreasing the absolute mobility value. The carrier concentration also decreases with increasing substrate temperature. Three energy donor levels exist in the CdSe films studied. The first has $\Delta E = 0.025$ eV, the second has $\Delta E = 0.14$ eV and the third has $\Delta E = 0.4$ eV. The first energy level corresponds to the monovalent impurity atoms, and the second and third to the divalent selenium vacancies [1–3].

In the present work, nonlinear I–V behaviour is observed with hopping conduction, also taking place at low temperatures. The density of ionizable

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impurities is estimated, and the surface density of the depletion layer depths is also calculated. Moreover, the effect of mercury light (265 nm) on the thin films is studied to evaluate their photovoltaic properties for the solar cell industry.

Experimental

A) Material preparation:

Thin CdSe films were prepared by evaporation of CdSe under 10^{-5} torr. They were evaporated onto glass substrates provided with silver electrodes at definite temperatures. The dimensions of each thin film prepared were 0.3 cm^2 (area) and 0.01 μ (thick). the CdSe films had a cubic structure.

B) X-ray diffraction measurements:

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

Cu—K_α radiation and a Ni filter were used at room temperature (25°). During every measurement, all X-ray experimental conditions (time = 5 min, width = 5, range = C.P.S., gain = 4 and C.H.S. = 10) were maintained constant.

C) Electrical measurements:

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

The voltage across the sample was monitored with a TM10 DC-microvoltmeter.

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

Results and discussion

The effects of the substrate temperature on the X-ray diffraction patterns of the thin films of CdSe are shown in Fig. 1. It is clearly seen that the peak intensity of the reflected beam decreases as the substrate temperature increases. It should be noted that the effect of the substrate temperature on the crystal orientation predominates. The diffraction of these thin films depends mainly on the conditions of crystallization; the decrease in intensity of the reflected beam is due to a 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 the sample is heated at 160° (annealing), the grain size increases and the degree of orientation deteriorates (see Fig. 1). This is further explained in that the crystallite size and cubic (4) face-centred structure increase with increasing substrate temperature and/or with heat treatment (160°, Fig. 1, curve B).

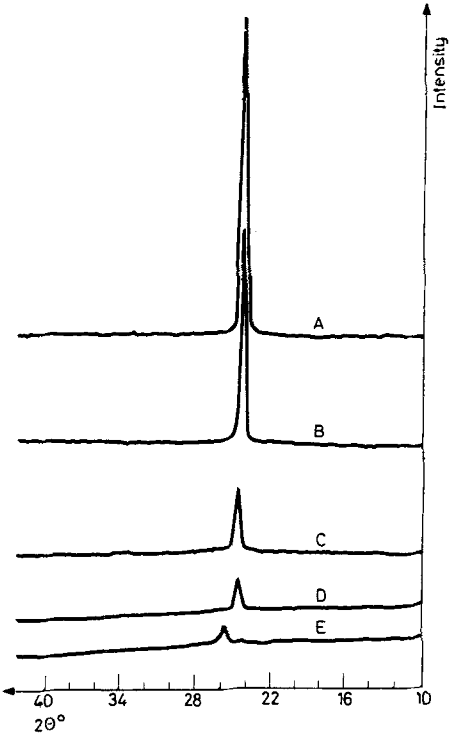

Fig. 1 The obtained room temperature Cu—K_α X-ray diffraction patterns of the different CdSe thin films: (A) Substrate temperature (t_s) = 25°C. (B) Specimen pre-neated at 160°C. (C) t_s = 110°C. (D) t_s = 150°C. (E) t_s = 200°C.

The structure of thin CdSe films depends strongly on the substrate temperature. 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 dependence of current on voltage at different temperatures is 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

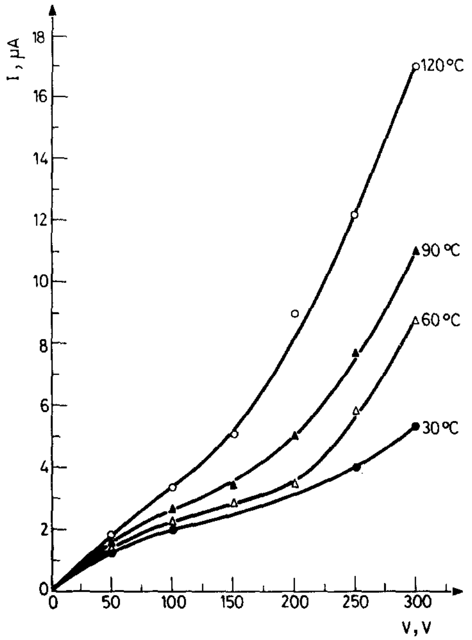

Fig. 2 A representation showing the current-voltage characteristics at various temperatures

material of the 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):

$$\lambda = \left(\frac{2\epsilon_0\epsilon_r V}{qN_d}\right)^{1/2} \simeq 1052\left(\frac{\epsilon_r V}{N_d}\right)^{1/2} \qquad (1)$$

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 has been calculated to be 7.4×10^{-7} cm.

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

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

$$I = A\acute{A}\,T^2 \times \exp\left[-\frac{\varnothing - 8.26 \times 10^{-6} q(N_d V/E_r^3)}{KT}\right)^{1/4} \qquad (3)$$

where: A is the effective area,
$\acute{A}$ is the effective Richardson–Dushman constant,
T is the absolute temperature,
K is the Boltzmann constant (8.62×10^{-5} eVK^{-1}),
$\varnothing$ is the contact-barrier height,
and V is the applied voltage.

Equations (2) and (3) and the slope of the relation log I vs. $V^{1/4}$ (Fig. 3) give the value of donor density (N_d) as 6.5×10^{18} cm^3.

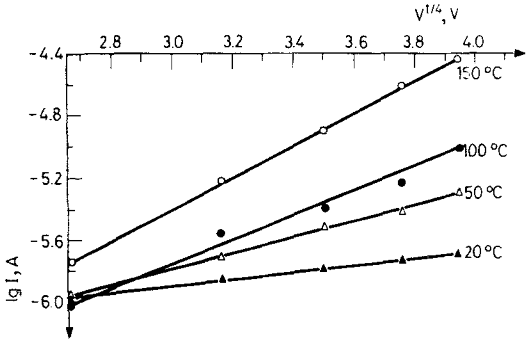

Fig. 3 An illustration showing the variation of log. I (A) as a function of $V^{1/4}$ at various working temperatures

The surface density of charges (N_s) per unit area 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}, we have $N_s = 4.8 \times 10^{12}$ cm^{-2}.

Temperature-dependence of current of thin CdSe film

The log 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:

$$I = I_0 e^{-\Delta E/KT} \tag{5}$$

where ΔE is the activation energy for donors. According to Eq. (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°) and at different voltages. For the temperature range 70–120°, $\Delta E \simeq 0.12$–0.19 eV; above 120°, $\Delta E \simeq 0.236$–0.378 eV.

The breakthrough current, or a transition from a straight line with a 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 a hopping conduction mechanism, which is expected in such a low temperature range (20–70°).

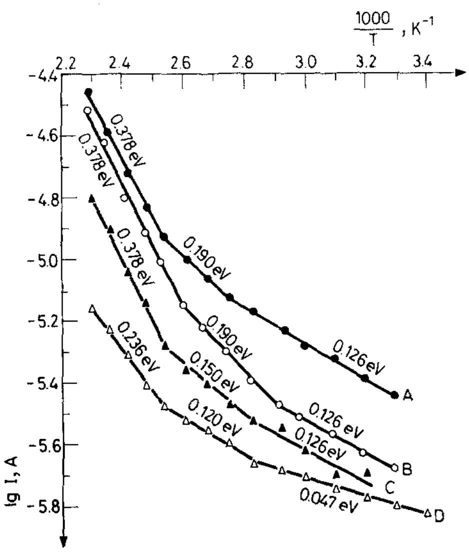

Fig. 4 A schematical representation for the variation of log *I* (A) as a function of reciprocal of absolute temperature at various applied voltages (A) 250 V, (B) = 200 V, (C) = 150 V, (D) = 100 V

Table 1 Activation energies for conduction corresponding to different temperature ranges at various applied voltages

Applied voltage *V*	*ΔE*, eV low temp. (20–70°)	*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

Alternatively, it was proposed that in the films studied, three donor excitation levels exist: $\Delta E \simeq 0.12$ eV corresponding to the impurity atoms, $\Delta E \simeq 0.19$ eV and $\Delta E \simeq 0.378$ eV corresponding to the divalent selenium vacancies. This gives useful information about the carrier excitation mechanism involved.

Effect of distance from mercury light source on photoelectric current

The effect of the distance between the mercury light and the thin CdSe film at different fields on the generated photoelectric current during light exposure for 5 min are shown in Fig. 5. The decrease of photoelectric current with increasing distance may be attributed to the incident photons of energy *hv* exciting charge carriers. It is proposed that in the films [3] studied three donor excitation levels exist, the first corresponding to the impurity atoms, and the second to the divalent selenium vacancies.

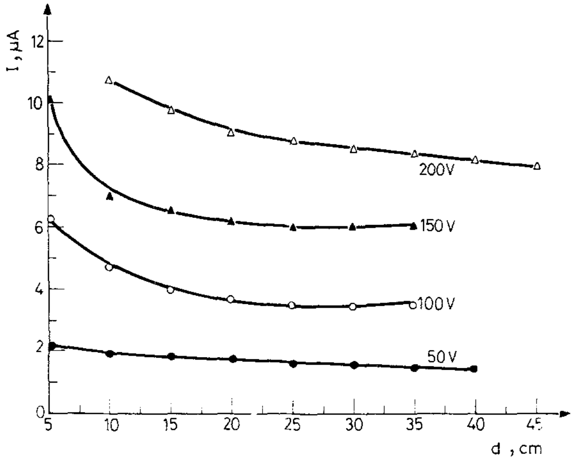

Fig. 5 A diagrammatical representation showing the variation of the generated photo-electric current as a function of distant (d) apart from the light source at various applied voltages, light irradiated for two minutes

As the distance increases, the photoelectric current decreases due to the decrease in photointensity, while the film resistance increases, giving rise to a decrease in photoelectric current.

Figure 6 shows the variation of the generated photoelectric current (μA) as a function of exposure time (min) at various applied voltages taken 1 cm from the light source. It can readily seen that:

(a) Increase of the applied voltage results in an increase in the generated photoelectric current.

(b) With the exception of curve *E*, all curves have a general trend in common, characterized by an initial rise of the generated photoelectric current with increasing time of exposure; this continues up to a maximum value, followed by a gradual decrease back again. This could be explained by various scattering mechanisms of free carriers [8]. The number of ionized impurities increases at exposure times beyond 10 min, and consequently the effective mobility slightly increases (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 generated photoelectric current on longer exposure to light (Fig. 6).

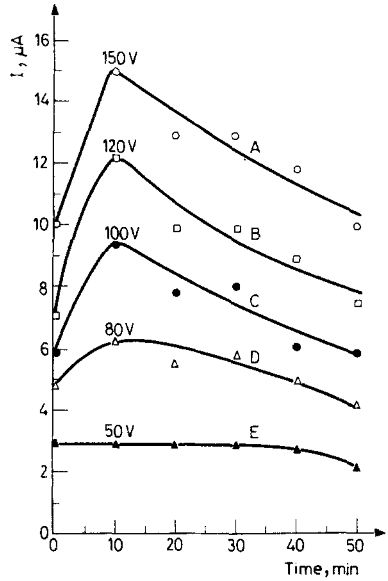

Fig. 6 A diagram showing the variation of the generated photo-electric current as a function of time of exposure at various applied voltages, at one cm distance apart from the light source

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Zusammenfassung — Dünne Cd-Se-Filme wurden unter Vakuum bei verschiedenen Glassubstrattemperaturen hergestellt. Die Auswirkung der Substraterhitzung und -temperatur auf die röntgendiffraktogramme, die elektrische und Gleichstromspannungscharakteristik und die Sperrschichtphotoeigenschaften wurden detailliert untersucht. Die erhaltenen Ergebnisse wurden mathematisch interpretiert, was zu einem Sprungleitungsmechanismus führte. Halbleiter-Parameter der Untersuchten dünnen Filme wurden für den Gebrauch in der Sperrschicht- und Solarzellen herstellenden Industrie ermittelt: Dichte der Oberflächenladung ($4{,}8 \cdot 10^{12}$ cm^{-2}), Dicke der trägerverarmten Schicht ($7{,}4 \cdot 10^{-7}$ cm) und Donorkonzentration ($6{,}5 \cdot 10^{18}$ cm^{-3}).

Резюме — Тонкие пленки CdSe были получены при различных температурах подложки из стекла. Подробно исследовано влияние нагрева и температуры подложки на их рентгенограммы, на электрические, вольтамперные характеристики и фотоэлектрические свойства. Проведена математическая интерпретация полученных результатов, что способствовало установлению прижкового механизма проводимости. С целью использования этих пленок в фотоэлектрических и солнечных батареях, определены их полупро водниковые характеристики: поверхностная плотность заряда равная $4{,}8 \cdot 10^{12}$ см$^{-2}$, толщина обедненного слоя равная $7{,}4 \cdot 10^{-7}$ см и концентрация доноров равная $6{,}5 \cdot 10^{18}$ см$^{-3}$.