JOURNAL OF MATERIALS SCIENCE **28** (1993) 2183-2186

Thin and superthin photoconductive CdSe films deposited at room substrate temperature

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Low conductive and photosensitive CdSe films were deposited on substrates at room temperature. X-ray diffraction spectra showed a microcrystalline cubic structure for film thicknesses greater than 20 nm and an amorphous structure for film thicknesses below 10 nm. An optical band gap, E_g^0, of 1.6 eV was determined using the Tauc-dependence usually employed for amorphous semiconductors. The dark conductivity, σ, of $10^{-9}\,\Omega^{-1}\,\text{cm}^{-1}$ was measured in the as-deposited state, but an increase of five orders of magnitude was observed after heating the layer above 450 K. High photosensitivity was observed under illumination with white light as well as with monochromatic light over a wide spectral region (400–750 nm). A conclusion is reached concerning the existence of compensated donor and acceptor defects in the as-deposited state.

1. Introduction

Cadmium selenide is an appropriate material for preparing thin-film field-effect transistors [1], vidicones [2], electrophotographic photoreceptors [3, 4], etc. Many authors have investigated the influence of substrate and source temperature, type of substrate, chemical composition of the evaporated material, etc., on the growth and structure of the cadmium chalcogenides, as well as on their electrophysical properties. A detailed review of these investigations has been published by Kalinkin *et al.* [5]. However, deposition of amorphous CdSe layers has only been reported in a few papers. Such layers have been obtained with room temperature substrates [1–3], and their properties have not been the subject of more detailed studies. Furthermore, the amorphous CdSe layers reported elsewhere [2, 3] were not stoichiometric but selenium-rich ($Cd_{0.2}Se_{0.8}$).

In this paper, the possibility of depositing thin and superthin (down to 2.5 nm) low-conductive and photosensitive CdSe layers is reported. The changes in their structure and electrical properties with decreasing film thickness are described. The superthin CdSe layers were used to build amorphous CdSe/Se and CdSe/Se-Te superlattices and some peculiarities in their optical and photoelectrical properties connected with quantum-size effects were observed [6, 7].

2. Experimental procedure

CdSe layers were deposited from powdered CdSe (Merck–Suprapure) loaded into tantalum boat in a vacuum of 2–4 × 10^{-4} Pa. The source temperature measured using a Pt/Pt–Rd thermocouple was about 750 K, and the substrate temperature was 295 K. Corning glass and mica "Muscovit" substrates were used placed on a rotating (8 rev. min^{-1}) disc. During the evaporation, CdSe vapour was confined to a vertical Jena-glass cylindrical screen (10 cm diameter). Its temperature was not especially monitored. On the rotating disc, material deposition on the substrates occurred only when they were above the screen aperture. The ratio of the duration time above this aperture to the entire period of rotation was 1:13 (step-by-step method). The film thickness and the evaporation rate were measured during evaporation using a calibrated quartz monitor; they varied between 2 and 1000 nm, and 0.4 and 8 nm s^{-1}, respectively.

X-ray diffraction spectroscopy performed with an automated "Siemens D500" diffractometer (λ = 0.154 nm), was used to investigate the layer structure. Optical band gap, E_g^0, and refraction coefficient, n, were determined solely from the optical transmission, T, using the method proposed by Swanepoel [8]. The transmission was measured with spectrophotometers Specord UV–VIS and Specord 61 NIR. Electrical measurements were carried out with a Keithley 61OC electrometer using ohmic In–Ga and evaporated aluminium contacts. Spectral dependences of the photoconductivity were measured under light illumination varying between 0.1 and 1 W m^{-2} in the spectral region 400–900 nm. The spectral dependence of the photocurrent presented here was obtained at equal light illumination using the intensity dependences of the photocurrent at different wavelengths.

3. Results and discussion

3.1. Structure

The X-ray diffraction pattern of 200 nm thick CdSe film is shown in Fig. 1a. A single sharp peak having

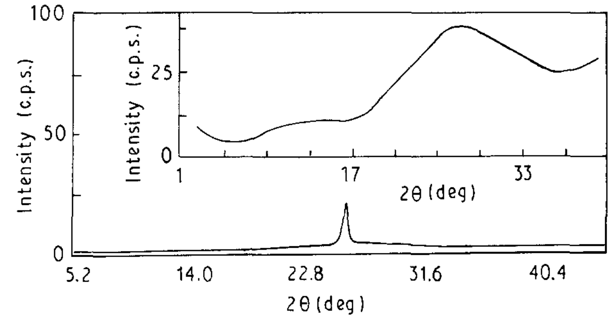

Figure 1 X-ray diffraction spectrum of (a) a 200 nm thick CdSe monolayer and (b) a CdSe (5 nm)/Se(5 nm) superlattice with a total thickness of 200 nm.

wide tails in its base appears at $2\theta = 25.5^\circ$. Because there are no other peaks up to $2\theta = 40^\circ$ one can conclude that the layers studied consist of microcrystallites with presumably cubic structure. The peak observed is due to X-ray diffraction from the [1 1 1] plane. This result differs from those obtained by Shallcross [1] and Schottmiller *et al.* [2] where mixed and pure hexagonal structures were reported, respectively. A zinc-blende structure of CdSe layers deposited on a glass substrate has been reported [9, 10]. An electron micrograph [11] has shown that the CdSe films retain their microcrystalline structure down to a layer thickness of 20 nm with a crystalline size of about 20 nm. However, if the film thickness is continued to be reduced, an amorphization of the layer occurs.

An X-ray diffraction pattern of a CdSe(5 nm)/a-Se(5 nm) multilayer is shown in Fig. 1b. Sharp peaks typical of a crystalline structure do not appear. A vanishing of the characteristic peak of the cubic CdSe layers with decrease of their thickness below 32 nm has also been observed [22], but the reason for this has not been discussed. The wide peak observed in Fig. 1b is typical of amorphous materials. Thus one can infer that both layers (Se and CdSe) building the multilayers are amorphous. Furthermore, the superlattices CdSe/a-Se have shown clearly defined small-angle X-ray diffraction patterns [12]. All these results prove that smooth amorphous superthin CdSe films (2.5–10 nm thick) can be deposited under the deposition conditions described here (step-by-step method).

3.2. Optical properties

The results from the complex investigation of the optical, electrical and photoelectrical properties of our CdSe layers differ essentially from those reported so far for polycrystalline CdSe layers [1–3, 5, 13]. A behaviour similar to that of amorphous semiconductors is observed and a discussion in terms of non-crystalline materials [14] is presented. Firstly, our results for the absorption coefficient, α, do not obey the dependence $\alpha E \sim (E - E_g^0)^{\frac{1}{2}}$ (Fig. 2a, curve 1) valid for absorption connected with direct allowed transitions. Such a dependence has been observed in the polycrystalline layers investigated by El-Naha *et al.* [13]. The Tauc law $\alpha E = B(E - E_g^0)^2$ is appropriate for E_g^0 determination (Fig. 2a, curve 2). It is known [14] that this law characterizes indirect phononless transitions in amorphous semiconductors. Values of $E_g^0 = 1.6\,\text{eV}$ and $B = 1.6 \times 10^5\,\text{eV}^{-1}\,\text{cm}^{-1}$ were evaluated by an extrapolation of the linear part of the dependence $(\alpha E)^{\frac{1}{2}}$ versus E. The E_g^0 value obtained is smaller than those reported by other authors [4, 13, 15] for thin polycrystalline CdSe films. The Tauc law has also been used by Shirai *et al.* [16] to determine E_g^0 of a-Se/Cd$_x$Se$_{1-x}$ ($x < 0.5$) multilayers, which is practically identical to E_g^0 of the Cd$_x$Se$_{1-x}$ layers. Hence, the absorption mechanism observed in the CdSe polycrystalline films investigated here is different from that reported so far by other authors.

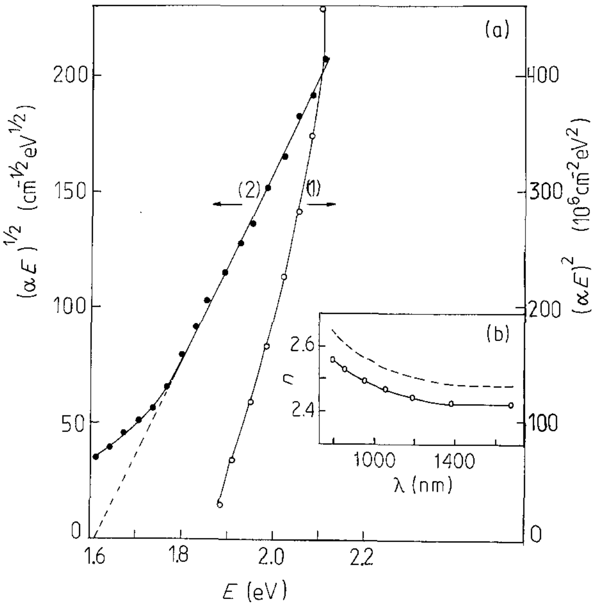

Figure 2 (a) Absorption coefficient, α, of a 0.85 μm thick CdSe monolayer versus the energy of the incident light according to (1) $\alpha E = A(E - E_g^0)^{\frac{1}{2}}$ and (2) $\alpha E = B(E - E_g^0)^2$ dependences. (b) Dispersion curves of the refractive coefficient *n*: (——) present work; (– – –) [13].

Dispersion of the refraction coefficient was also studied in the weak absorption region (λ > 700 nm). A curve similar to that reported by El-Naha *et al.* [13] was obtained (Fig. 2b), but the *n*-values are lower by 0.06–0.09 than those given by El-Maha *et al.* [13] and vary between 2.4 and 2.6. These lower values of *n* and E_g^0, as well as the Tauc law, show that the polycrystalline CdSe layers studied here behave like an amorphous semiconductor.

3.3. Electrical properties

Fig. 3 shows the temperature dependence of the dark conductivity, σ, of the films with different thicknesses. A region of conductivity decrease appears at about room temperature, when the specimen is heated. This peculiarity also appears in the cooling direction. Similar results with different explanations have been reported earlier [5, 17].

(i) A parallel decrease of both drift mobility, μ, and free electron concentration, *N*, has been found for selenium rich CdSe layers in the same temperature region [5]. The change in μ has been explained assuming that the film consists of crystallites of different size and crystal structures (different μ and *N*) and that a

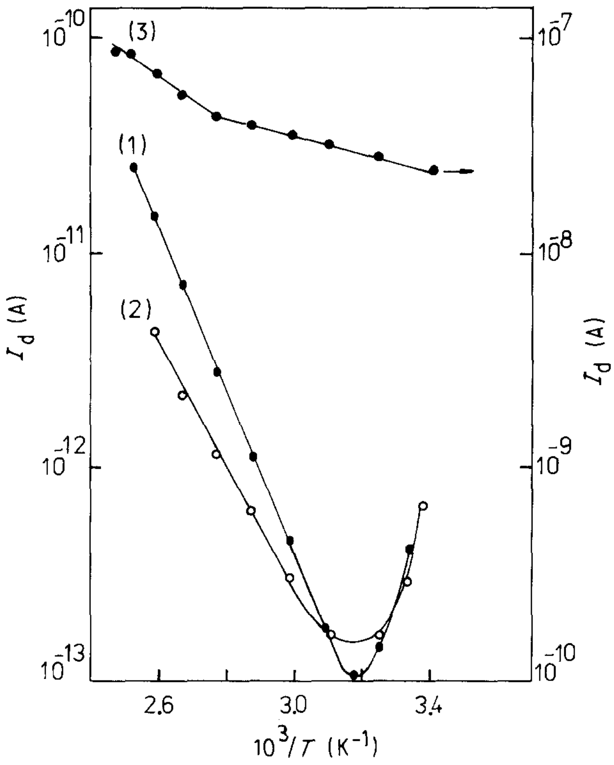

Figure 3 Temperature dependences of the dark current, I_d, in as-deposited CdSe layers (1) 200 nm thick and (2) 55 nm thick, and (3) after heating the layer up to 450 K.

change in the free-carrier dispersion mechanism occurs at about room temperature. However, the μ changes measured there were rather weak and they could not account for the strong σ changes observed. The results reported [5] and obtained here show that the changes in σ are mainly due to strong changes of *N*. But the reason for the decrease in *N* with decreasing of temperature has not been discussed.

(ii) Such a peculiarity in the temperature dependence of the dark conductivity has been observed [17] but only in the heating direction. For this reason, the explanation which is based on irreversible structure changes [17] is not appropriate in our case.

In our opinion other possible reasons for the above temperature dependence of σ could be:

(i) the so-called "high voltaic polarization" investigated in detail in chalcogenide glass materials [18]. However, polarization could explain the discussed peculiarity only in the case of film heating, but not in the case of cooling;

(ii) creation of new defects. Some experimental data supporting such an hypothesis have been obtained: (a) the amplitude of the conductivity decrease on cooling, depends on the rate of thermal treatment; (b) the layer shows lower conductivity without any peculiarity if the layer is heated immediately after a fast cooling ($30\,°C\,s^{-1}$). This result could mean that the defects created are frozen. But this hypothesis requires further experimental evidence.

Owing to the peculiarity of σ (*t*) discussed above, the dark conductivity of the different specimens reported here was determined at 357 K. The film thicknesses between 50 and 850 nm evaporated at rates $v = 0.5$–$2\,nm\,s^{-1}$ have a conductivity, σ, of $3 \times 10^{-9}\,\Omega^{-1}\,cm^{-1}$, while the specimens evaporated at $v = 7\,nm\,s^{-1}$ show $\sigma = 10^{-5}\,\Omega^{-1}\,cm^{-1}$. It is known [1, 5, 19] that the CdSe films deposited at a substrate temperature of about 295 K, are highly conductive ($\sigma = 10^{-3}$–$10^{-2}\,\Omega^{-1}cm^{-1}$) due to excess cadmium. Contrary to that, our layers deposited at lower rates (0.5–$2\,nm\,s^{-1}$) are among the lowest conductive CdSe films [4, 5, 15, 20]. Furthermore, the data reported by Curtis *et al.* [4] are related to monocrystalline stoichiometric CdSe, deposited at substrate temperature $T_S = 940\,K$, while the other references are related to selenium-rich CdSe films. Therefore, the evaporation conditions described here make it possible to obtain low conductive CdSe films at low substrate temperature using only one source.

Activation energies $\Delta E = E_C - E_F$ and "extrapolated prefactors" σ_0^* in the expression $\sigma = \sigma_0^* \exp(-\Delta E/kT)$, were calculated from the temperature dependence of the dark conductivity (Fig. 3). It was established that ΔE depends on the layer thickness. It changes from 0.75 eV at $d = 200\,nm$ to 0.52–0.55 eV at $d = 50\,nm$. A decrease of σ_0^* from $2 \times 10^2\,\Omega^{-1}cm^{-1}$ at $d = 200\,nm$ to $10^{-1}\,\Omega^{-1}\,cm^{-1}$ at $d = 50\,nm$ was also observed. The Meyer–Neldel rule $\sigma_0^* = \sigma_{00}^* \exp(G\Delta E)$ was fulfilled for layers with thicknesses of 200, 100, 74 and 50 nm. This indicates that there are no discrete donor levels, but a donor distribution over a large region of the forbidden band gap takes place [17]. Therefore, the behaviour of our layers is similar to that observed in the amorphous materials. However, the calculated values of the *G* constant of $33\,eV^{-1}$ is an indication [21] of the relatively small concentration of states in the forbidden gap.

If the layers are heated to above 450 K for a period longer than 30 min, two modifications in the σ(*T*) dependence take place: (i) the dark conductivity rises by several orders of magnitude (Fig. 3, curve 3); (ii) two regions with different slopes ($\Delta E_1 = 0.08\,eV$ and $\Delta E_2 = 0.25\,eV$) smaller than the initial one ($\Delta E = 0.75\,eV$) appear. These changes are probably related to a partial recrystallization of the layers. The strong conductivity increase on heating is probably due to the overstoichiometric cadmium donors available in the layers. Therefore, one can conclude that in the as-deposited state these cadmium donors are probably compensated by other internal defects (for instance cadmium vacancies and/or interstitial selenium) playing the role of acceptors. This compensation makes the layers slightly conductive. The recrystallization reduces the internal defect concentration but a portion of the cadmium donors remains uncompensated causing a conductivity increase. So, the defect compensation in as-deposited layers could be the reason for the high resistivity measured.

3.4. Photoelectric properties

It is known [1, 22] that the CdSe films deposited at substrate temperatures $T_s = 390$–$420\,K$ are either not photosensitive [22] or they have weak photosensitivity [1] ($P = I_p/I_d \approx 10$ at white light illumination intensity $\phi \approx 5\,W\,m^{-2}$). Even when T_s is high enough ($T_s > 600\,K$) the photosensitivity does not exceed $P = 100$. A long treatment at high temperatures and

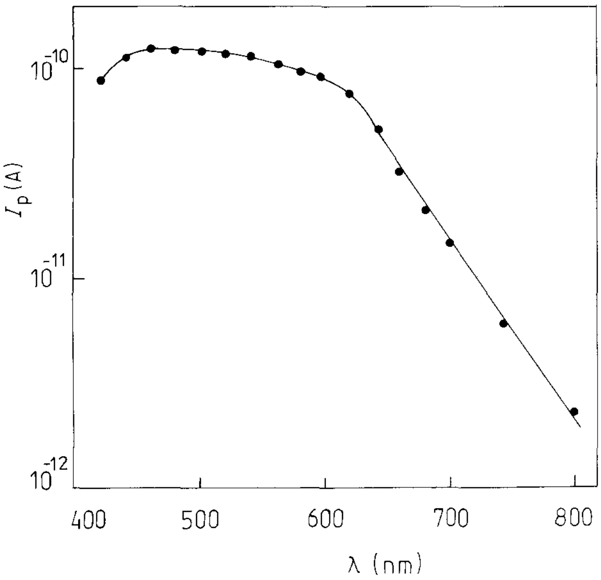

Figure 4 Photocurrent, I_p, spectral dependence of a 200 nm thick CdSe layer obtained at an illumination intensity of $\phi = 0.1\ \mathrm{W\,m^{-2}}$.

appropriate ambient is necessary [23, 24] to ensure high photosensitivity of the CdSe layers.

Our CdSe layers showed a high photosensitivity. At light illumination $\phi = 25\ \mathrm{W\,m^{-2}}$, values of $P = 10^3$ and 5×10^2 were obtained in layers evaporated at $v = 7$ and 0.5–2 nm $\mathrm{s^{-1}}$, respectively. Therefore, these layers are not only very slightly conductive but they have a high photosensitivity as well. Both these properties are important for electrophotographic applications.

The intensity dependence of the photocurrent, $I_p \sim \phi\gamma$, was also measured. It is sublinear ($\gamma = 0.5$–0.7) and differs from the corresponding dependence obtained by Burogohain and Barna [22] for polycrystalline layers. Such a result is usually observed in amorphous semiconductors [14] at $I_d \ll I_p$. Owing to the sublinearity obtained, a high photosensitivity at low illumination intensities was observed, i.e. at $\phi = 0.2\ \mathrm{W\,m^{-2}}$, values of $P = 50$–100 were measured. We suppose that the high photosensitivity observed might be due to acceptor defects compensated by overstoichiometric cadmium atoms playing the role of slow recombination centres.

Fig. 4 shows a typical spectral dependence of the photocurrent. It is seen that the photosensitivity of the layers remains high up to wavelengths $\lambda = 400$ nm. The last result is essentially different from those obtained by other authors [23, 24]. In the intrinsic absorption region, these authors have observed a photocurrent decay typical for a crystalline semiconductor. This decay is caused by the enhanced role of the surface recombination. The photocurrent spectral dependence shown in Fig. 4 does not have such a decay. It is similar to the results obtained in amorphous semiconductors. In this case the influence of the surface states on the recombination processes is weak because of the existence of a large defect concentration in the whole volume. The shape of the measured I_p spectral dependence is evidence supporting the assumption for existence of a high concentration of compensated donor and acceptor internal defects in the as-deposited layers.

In conclusion, the method of CdSe film deposition described here enables us to obtain thin and superthin ($2.5 \leqslant d \leqslant 10$ nm) low conductive and photosensitive CdSe layers. They show a good reproducibility and stability of their properties. The low substrate temperature used facilitates the CdSe layer application in building of multilayer structures including a-Se or a-Se-Te. These structures are sensitive in the red and near infrared region and they are suitable for preparation of xerographic and laser printer photoreceptors [6].

Acknowledgements

The authors thank Dr Malina Baeva for help with the discussion of X-ray diffraction patterns. This work was supported by the contract F-122 with Ministry of Culture, Science and Education.

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Received 12 December 1991
and accepted 11 August 1992