YU ISSN 0015—3206
FZKAAA 22 (4) 605 (1990)

MICROSTRUCTURE AND OPTO-ELECTRICAL STUDIES OF CADMIUM SELENIDE THIN FILMS

SIHAM MAHMOUD and ABDEL-HAMID EID

Electron Microscope and Thin Films Department, National Research Centre, Dokki, Cairo, Egypt

Received 26 January 1990

UDC 538.95

Original scientific paper

Nucleation and growth of cadmium selenide thin films are of considerable interest because of their direct effect on the optical and electrical properties of the material. Vacuum deposited layers on amorphous and crystalline substrates showed a polycrystalline structure. The layers were deposited at a pressure of 10^{-4} Pa, with two deposition rates of 12 nm/s and 15 nm/s. The electrical resistivity and the optical absorption were studied for a group of layers on quartz substrate. As well the morphology and the microstructure were investigated by X-ray and electron microscopy. Few activation energies were estimated from the optical absorbance and thermo-resistance relationship. Their values are consistent with the published data.

1. Introduction

Evaporated layers of CdSe are widely used in the fabrication of thin film field effect transistors and solar cells$^{1)}$. The cadmium selenide films contain the hexagonal structure and grain growth occurs during anneal. The electrical properties of these films depend largely on their structure and composition, and consequently on the deposition environments. The resistivity and carrier concentration, as well the energy gap had been followed by many authors$^{2-5)}$. Some complex changes of the resistivity due to duration and temperature of annealing in air or under vacuum is then due to recrystallization and re-ordering of the CdSe lattice$^{6,7)}$. The electronic properties of thin CdSe films prepared through physical vapour transport were investigated using photoluminescence and electronic measurements$^{8)}$.

The films were studied at each of the main preparation steps, i. e., evaporation, annealing, etching, and finally photo-etching. At 3 K two distinct donor-acceptor transitions at 1.75 and 1.7 eV were found in the photoluminescence spectra in addition to deep states at about 1.55 eV at 20 K.

Lot of differences still exist among the published data dealing with the electro-optical behaviour of the thermally evaporated CdSe films especially of those prepared under normal vacuum of 10^{-4}—10^{-5} Pa. Since this range of vacuum is mainly of the order employed in any mass-production technology, more work is now needed to furnish a clear background about the electro-optical characteristics of thermodeposited CdSe layers.

2. *Experimental technique*

Groups of CdSe layers of different thicknesses were thermally deposited by vacuum sublimation, on carefully cleaned optically flat quartz slids, very thin layers of evaporated amorphous carbon and freshly cleaved surfaces of mica and rock-salt. The substrates were maintained at room temperature during the deposition. Two different deposition rates of 12 nm/s and 15 nm/s were selected. Electron microscope copper grids which were previously covered with a thin film or carbon were used for fishing the layers for transmission electron microscopy investigations. The microstructure was studied by X-ray and electron diffraction. The optical density was recorded in visible and UV regions using a Beckmann 5260 double beam spectrophotometer. The electrical resistivity was measured as a function of temperature. The specimen holder in contact with a calibrated thermocouple were placed inside a temperature regulated oven. Thick vacuum deposited gold layers served as electrodes of ohmic contacts. Film thicknesses were measured interferometrically[9)].

3. *Results and discussion*

Since CdSe can have both wurtzite and zinc blende structure[10)], an X-ray run was carried on the powder employed in the present work. The corresponding difffraction is shown in Fig. 1 with the analysis listed in Table 1 compared with the ASTM Card. The calculated data is in good agreement with a matrix of wurtzite plus traces of zinc blende. Figs. 2 and 3 show X-ray diffractograms of CdSe films of different thicknesses deposited with different rates on quartz slides and freshly cleaved plane of mica, respectively. At a rate of 12 nm/s, the preffered orientation of (002) plane normal to the substrate is clear especially for layers of 200 nm and 300 nm. Besides, the intensity of the planes increased with thickness employing that some coalescence took place leading to the formation of bigger crystals. As the rate of deposition increases (15 nm/s) more planes started to appear indicating secondary nucleation of polycrystalline CdSe nuclei. For film thickness 800 nm, the (101) plane of metallic cadmium appears. This may be due to the more prolonged time of heating due to the evaporation filament and the high flux of deposition.

TABLE 1.

$d_{calc.}$	$(I/I_0)_{calc.}$ %	d_{X-ray}	hkl	$(I/I_0)_{X-ray}$%
3.7198	100	3.72	100	100
3.517	56	3.51	002	70
3.2873	72	3.29	101	75
3.0074	8.6	3.01	200 (cubic)	100
2.5543	34.4	2.554	102	35
2.1493	90	2.151	110	85
1.9794	82.8	1.98	103	70
1.861	20	1.863	200	12
1.8294	59	1.834	112	50
1.7957	15.6	1.8	201	12
1.646	9.7	1.645	202	8
1.4555	23.6	1.456	203	20
1.4104	12.4	1.407	210	8
1.3792	11.8	1.38	211	8
1.3152	17.2	1.312	105	14
1.312	14.5	1.3059	212	6
1.2442	12.4	1.2411	300	10
1.2428	8.6	1.2218	310	1
1.2084	25.8	1.2056	213	18
1.1729	9.7	1.17	302	8
1.1231	8.6	1.1201	205	8
1.119	5.4	1.144	106	2

X-ray diffraction of wurtzite CdSe powder.

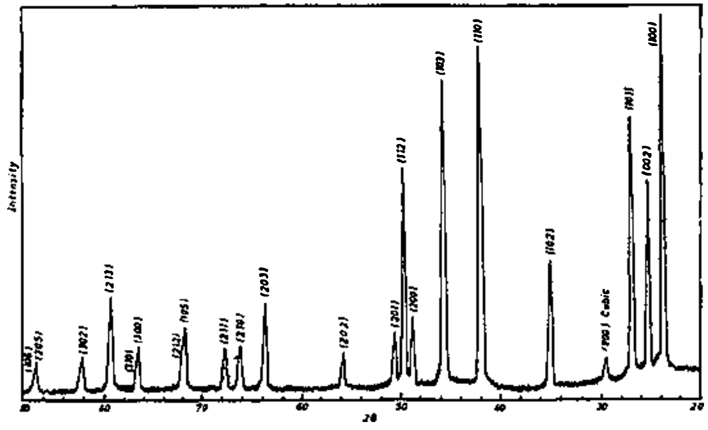

Fig. 1. X-ray diffractogram of CdSe powder.

Keeping in mind that the nucleation and growth as well as the possibility of epitaxy on crystalline substrates critically depend upon the physico-chemical state of the substrate surface whose cleanless up to the molecular level is essential. At a vacuum close to 10^{-4} Pa enough molecules of residuals impinge on the surface of the substrates every second to furnish a complete layer of condensed molecules. Most of them are re-evaporated, but the available time for working on a clean

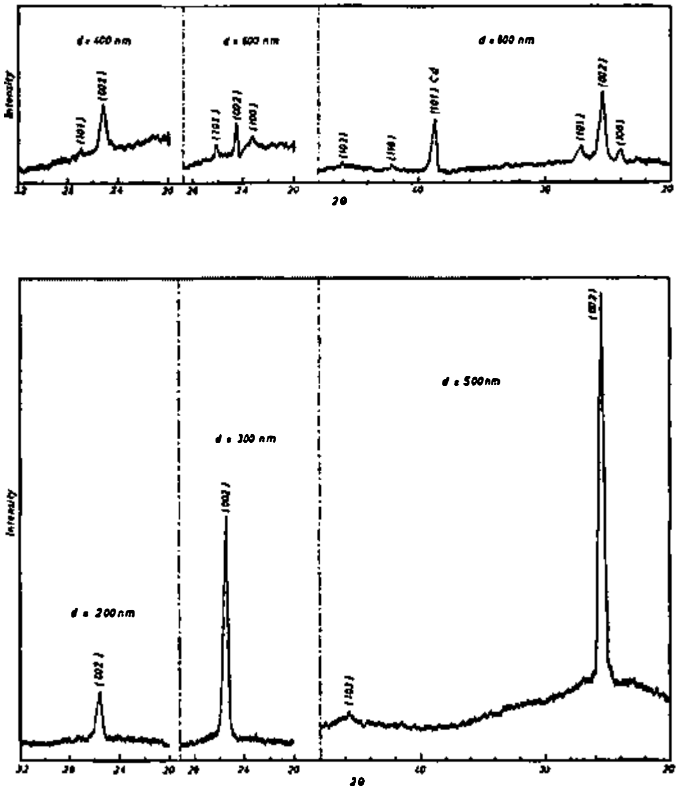

Fig. 2. X-ray diffractogram of a freshly deposited CdSe films on quartz slides of different thicknesses and rates. (a) 15 nm/s, (b) 12 nm/s.

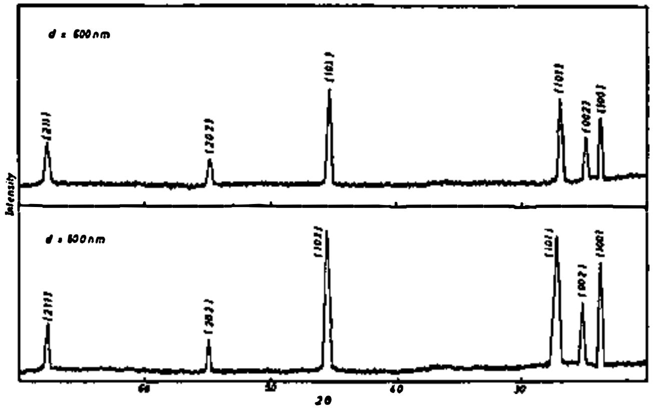

Fig. 3. X-ray diffraction pattern of CdSe films deposited on a mica cleavage plane of different thicknesses with a rate of 15 nm/s.

surface remains very short. Accordingly, using high rates of deposition is now essential to increase the flux of the deposited molecules such that the contaminated molecules are diluted in the deposits. In the light of this result, using high rates of deposition during the preparation of thin CdSe layers at normal high vacuum, is needed now for releasing the discrepancies between the experimental results. This conclusion is confirmed by the theoretical approach of Hirth and Pound[11] for the nucleation and overgrowth. They assumed that the substrate surface contains a number of mobile adsorbed atoms and/or molecules plus a number of clusters in the form of spherical caps. The first stage of nucleation is then influenced by the presence of these impurities, besides some other parameters; deposition rate, substrate temperature, contamination, type of substrates and state of vacuum.

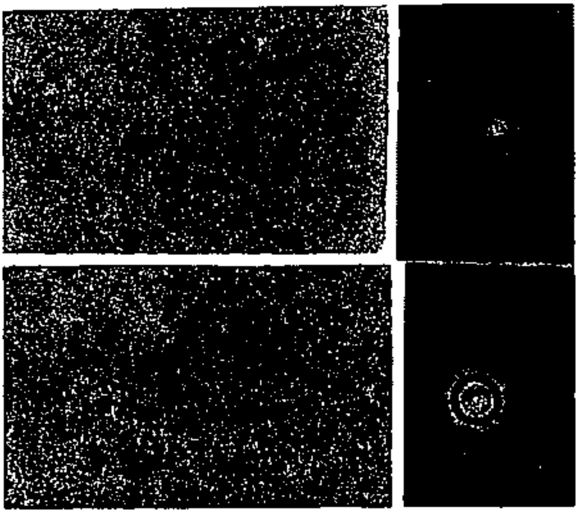

Fig. 4. Transmission electron micrographs and electron diffraction patterns of CdSe deposited on carbon substrate at a rate of 15 nm/s.

Figs. 4, 5 and 6 are typical transmission electron micrographs of thin CdSe film deposited on carbon and freshly cleaved surfaces of rock-salt and mica, respectively; no preferred orientation could be noticed. The ring electron diffraction pattern with the corresponding micrographs indicate that, in the early stages of nucleation and growth, the film is mainly composed of ultra small nuclei which at some places quickly coalesce and form aggregates of small crystallites randomly oriented irrespect of the substrate type. These results are consistent with the previously published work[12]. The electron diffraction patterns were indexed according to the wurtzite structure.

Accordingly, one may conclude that the deposited thick layers were polycrystalline at high rates of deposition. As the rate decreases, some preferred orientation with (002) plane normal to the substrate started to take place for films of thickness greater than 200 nm which were investigated by X-ray, on the other hand, films of thickness less than 100 nm, the transmission electron micrographs showed small nuclei in between large aggregates of polycrystalline structure randomly oriented on the substrates.

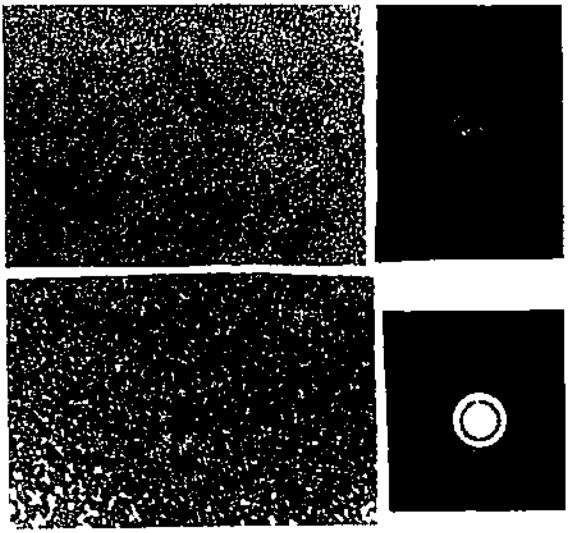

Fig. 5. Transmission electron micrographs and diffraction patterns of CdSe deposits on a cleaved surface of rock-salt at a rate of 15 nm/s.

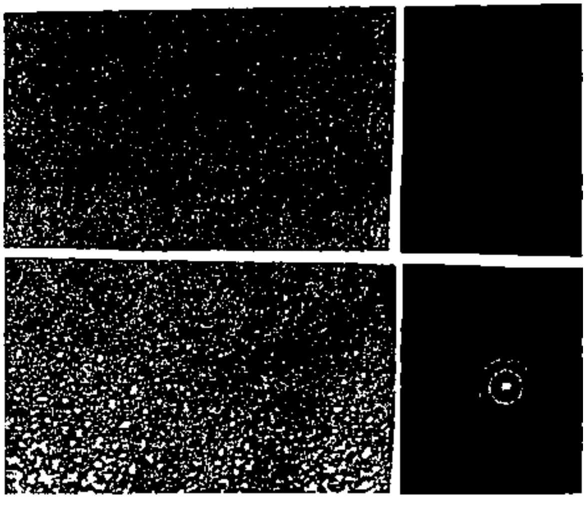

Fig. 6. Transmission electron micrographs and electron diffraction patterns of CdSe film deposited on a freshly cleaved surface of mica at a rate of 15 nm/s.

Fig. 7 shows the optical density of various CdSe layers over the spectral range from 200 nm to 900 nm. The absorption edge depends on the thickness of the sample and shifts towards higher photon energies as the film thickness decreases. The estimated values for the optical energy gaps are 1.65 eV, 1.58 eV and 1.55 eV for layers of 200 nm, 300 nm and 500 nm, respectively. These values are consistent with the value of 1.55 eV obtained by Jaeger-Waldau et al.[8].This indicates that beside the intrinsic activation energy, there is an energy activated mechanism which may exist in thin films. A similar phenomena was observed in thermo-resistance relationship and was attributed to the effect of film surface and scattering of the charge carrieres at the grain surfaces[13].

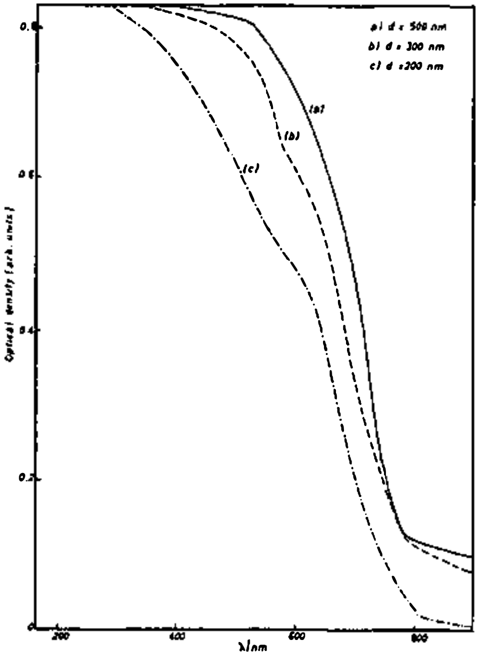

Fig. 7. Dependence of optical density of vacuum-deposited CdSe films on wavelength.

For an electrically active impurity[14] the absorption spectrum may be observed only in the very low temperature range when the free charge carriers are still bound to their impurity atoms. While, as the impurity atoms get ionized with the rise in temperature their absorption spectrum vanishes. Accordingly, one might expect that the activation energies estimated from the resistance-temperature relationship can have values with no correspondence in the absorption spectrum which is recorded at room temperature and above. Besides, the temperature may indirectly affect the value of the intrinsic gap width. If the density of states in the conduction band is small, they will be rapidly filled with electrons of donors and unable to accommodate new electrons with the result that the value of intrinsic activation energy estimated from resistance-temperature relationship could be greater than the real value calculated for impurity free sample.

Since the X-ray showed excess cadmium in the deposited CdSe film (Fig. 2a), accordingly one might expect the occurence of cadmium donor levels into the energy gap. These levels have a fundamental rule in the activation process. Fig. 8 is a representative example for log R versus $1/T$ for a layer of about 800 nm thick. This relation is divided into three linear sections with different slopes. The first one covers the range from room temperature up to 353 K with an activation energy of 0.4 eV. It can be due to the ionization of excess cadmium levels into the conduction band. The second sections which covers the range from 353 K to 493 K with activation energy of 1.12 eV, may be due to raising electrons from the valence band into the empty states of the cadmium level till it get filled once more. The last section of activation energy of 1.73 eV is an intrinsic activated process. It represents a transition of electrons from the valence band to the partially empty states into the conduction band. These states, then are expected to be about few hundreds of meV above the bottom of the conduction band; it depends on the concentration of donors »cadmium« in the matrix layer. One might then expect that the measured intrinsic gap width of 1.73 eV could be greater than the sum of the activation energies of the first and second section.

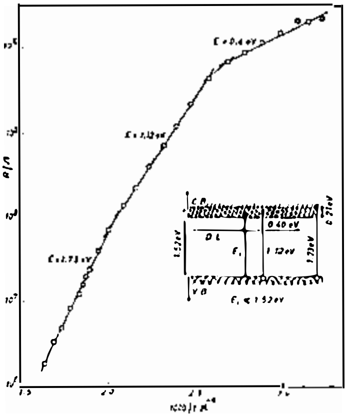

Fig. 8. log R vs. $1/T$ for a layer of about 800 nm thick with a model of expected transitions.

Since the depth of the donor level »0.4 eV« is not certain to be measured from the bottom of the conduction band, then, the sum of the transitions donor -> conduction band plus valence band -> donor level can be greater than the intrinsic gap width E_i of the impurity-free layer (Fig. 8). The effect of impurity concentration was noticed in indium antimonide; as the electron concentration changes from 10^{17} to 5×10^{18} cm^{-3}, the available allowed energy states into the conduction band shift up by about 0.3 eV[14)].

Referencse

1) M. J. Lee, S. W. Wright and C. P. Judge, Solid State Electron. **23** (1980) 671;
2) S. R. Jawalekar and M. K. Rao, Indian J. Phys. **54** (1980) 223;
3) A. Van Calster, A. Vervaet, I. de Rycke and J. de Baets, J. Cryst. Growth **86** (1988) 924;
4) P. Singh and B. Baishya, Indian J. Phys. **61** (1987) 230;
5) N. S. Alvi and I. Kaufman, Solid State Electron. **31** (1988) 45;
6) V. V. Serdyuk and V. A. Smyntyna, Poluprovodn. Tekh. and Mikroelektron. (USSR) **22** (1976) 5;

7) I. Spanulescu, I. Secareanu, N. Baltateanu, I. Z. Abdi and T. Khalass, Thin Solid Films **143** (1986) 1;
8) R. Jaeger-Waldau, N. Stuecheli, M. Braun, M. Lux-Steiner, E. Bucher, R. Tenne, H. Flaisher, W. Kerfin, R. Braun and W. Koschel, J. Appl. Phys. **64** (1988) 2601;
9) S. Tolansky, *Introduction to Interferometry*, Longmans Green and Co., London, 2nd Edition (1973) 157;
10) R. W. C. Wyckoff, *Crystal Structures*, Interscience, New York (1963);
11) J. P. Hirth and G. M. Pound, *Progress in Materials Science*, Vol. II, Macmillan New York (1963);
12) B. D. Chas, G. C. S. Collins, F. A. Huntley and J. W. Steeds, Thin Solid Films **67** (1980) 207;
13) V. K. Miloslavskii, E. N. Naboikina, V. A. Lebedev and V. I. Khramtsova, UKV, Fiz. Zh. **14** (1969) 819;
14) P. S. Kireev, *Semiconductor Physics*, Mir Publishers, Moscow (1975) 568.

STUDIJA MIKROSTRUKTURNIH I OPTOELEKTRIČNIH SVOJSTAVA TANKIH SLOJEVA CdSe

SIAM MAHMOUD i ABDEL HAMID EID

Electron Microscope and Thin Films Department, National Research Centre, Dokki, Cairo, Egypt

UDK 538.95

Originalni znanstveni rad

Tanki slojevi CdSe vakuumski su deponirani na amorfnim i kristalnim podlogama, a pokazali su polikristalnu strukturu. Slojevi su deponirani na 10^{-4} Pa pritiska sa dvije brzine depozicije, od 12 nm/s i 15 nm/s. Električni otpor i optička apsorpcija proučavani su za grupu slojeva na kvarcnoj podlozi. Mikrostruktura i morfologija istraživana je pomoću difrakcije X-zraka i pomoću elektronskog mikroskopa. Iz mjerenja optičke apsorpcije i ovisnosti otpora o temperaturi određeno je nekoliko energija aktivacije za različite nivoe. Također, dana je i odgovarajuća interpretacija.