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## Phase transformation on CdSe thin films under annealing in Ar + Se<sub>2</sub> atmosphere

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### Abstract

Cubic CdSe thin films of approximately 2000 Å thickness have been prepared onto glass substrates by chemical bath deposition. The samples were annealed in an Ar + Se<sub>2</sub> atmosphere at normal pressure for 30 h at different temperatures in the range of 50–500°C, in order to perform the crystalline phase transformation from cubic zincblende (ZB) to the hexagonal wurtzite (W) structure. The characterization of samples included both optical absorption and X-ray diffraction analyses. The optical absorption spectra allowed to calculate the energy band-gap ( $E_g$ ) values and, hence, the evolution of  $E_g$  in the thermally treated samples through the transformation from the cubic crystalline phase to the hexagonal phase. The X-ray diffraction spectra also showed the complete microstructural transformation from as-grown cubic samples up to the entire hexagonal lattice for samples with higher annealing. The critical point of the ZB → W transformation is proposed to occur at  $355 \pm 25^\circ\text{C}$ . © 2000 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

The physical properties of CdSe thin films are continuously being studied for their important applications in photovoltaic cells and in the fabrication of electronic devices [1,2]. This material in thin-film form has been grown by employing several techniques: thermal evaporation [3], molecular beam epitaxy (MBE) [4], sputtering [5], chemical bath deposition (CBD) [6], laser ablation [7], among others, both in zincblende (ZB) or wurtzite (W) structures, or in a ZB–W mixture [6,8].

In this work the CBD method was used to grow ZB–CdSe thin films on glass substrates. CBD is a low-cost technique and can be used to deposit several II–VI semiconductor compounds on a variety of substrates, provided the pH

does not affect their original properties. CdSe thin films in metastable ZB-structure have been obtained by CBD and other deposition techniques, at present and in the past [4,9–11]; however, it is not so common to obtain this phase in a pure form. For this reason, the material in W-structure has been more widely studied. On the other hand, there are few studies on the evolution of structural changes from the metastable cubic modification toward the stable hexagonal structure [12]. There are only few works dealing with the changes of its physical properties through this structural transition, such as energy band gap ( $E_g$ ), electrical conductivity, reflectivity, which can be meaningful for an overall understanding of the material [13]. Similar structural changes promoted in other binary semiconductor compounds and in ternary solid solutions either by critical concentration of constituents or by thermal treatment into appropriated atmospheres, respectively, have been reported [14,15]. Previous works [12] on CdSe crystalline phase transformation do not agree about the ZB → W phase

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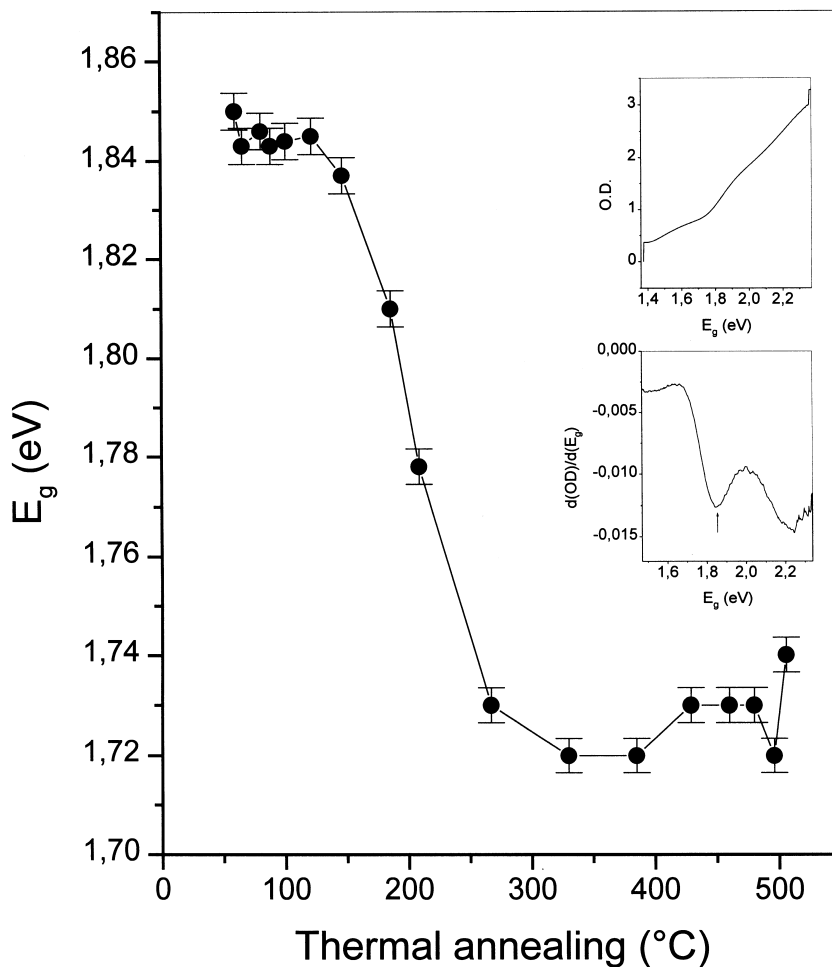


Fig. 1.  $E_g$  versus thermal annealing temperature (TAT) in an Ar + Se<sub>2</sub> atmosphere. The upper inset shows the optical density (OD) versus photon energy.  $OD = (\log e)\alpha d$ , where  $\alpha$  is the absorption coefficient,  $d$  the thickness of the film (constant) and  $e$  the base of natural logarithm. The lower inset depicts the first derivative of OD as a function of the photon energy. The arrow below the minimum indicates the  $E_g$  value.

transition temperature. In some cases the transition temperature is reported to occur at around 80°C, and, in other cases, in the range 350–400°C. Thermodynamically, the ZB → W transition is an irreversible process, however by milling processes it is possible to be provoked. The ZB–CdSe obtained in this manner has been recently tested to be stable at least up to 225°C [16].

## 2. Experimental

The studied CdSe polycrystalline thin films were grown by the CBD technique on glass substrates. Experimental details about the process have been described elsewhere [17]. The samples thickness obtained by using a Decktak II profilometer was in the interval  $2000 \pm 100 \text{ \AA}$ . The chemical agents were the same as those used to grow CdS in cubic phase [17], except for using selenourea

(CSe(NH<sub>2</sub>)<sub>2</sub>) instead of thiourea (CS(NH<sub>2</sub>)<sub>2</sub>), and a growth temperature of  $65 \pm 3^\circ\text{C}$  instead of  $80 \pm 3^\circ\text{C}$ . The post-deposition thermal annealings were carried out in a quartz tubular furnace with Se<sub>2</sub>-vapors transported by Ar gas, at normal pressure, along a  $50\text{--}506 \pm 3^\circ\text{C}$  temperature gradient existing in the furnace. The samples were placed in appropriate positions in this temperature gradient during 30 h. X-ray diffractograms were obtained employing a Siemens D5000 diffractometer. The optical absorption (OA) spectra were measured utilizing a UNICAM 8700 spectrophotometer over the 190–900 nm wavelength range, with a line resolution of  $\pm 0.3 \text{ nm}$ . These spectra allowed us to calculate approximately the  $E_g$  values. A typical optical absorption versus photon energy ( $h\nu$ ) spectrum of CdSe films is shown in the upper inset of Fig. 1. In this figure, the optical density (OD) was plotted against the energy, since the OD is directly proportional to the absorption coefficient ( $\alpha$ ), therefore, for  $E_g$  calculation one can use

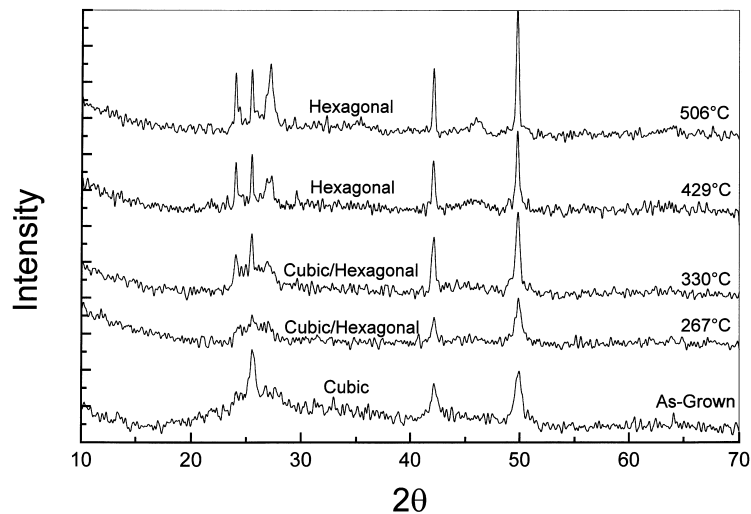


Fig. 2. X-ray diffractograms of CdSe as-grown and thermally annealed samples. Numbers next to peaks indicate the  $2\theta$  positions.

either  $\alpha$  or OD. The minimum in the first derivative of the OD versus photon energy curve corresponds to the absorption edge [18]. The lower inset illustrates the  $d(\text{OD})/dE$  plot with a minimum at about 1.83 eV, the  $E_g$  value, indicated by the upward arrow.

### 3. Results and discussion

The  $E_g$  values as a function of thermal annealing temperature (TAT) plotted in the range 50–506°C evidence a shift of the absorption edge toward lower values as TAT increases. A minimum in the  $E_g$  versus TAT curve around  $355 \pm 25^\circ\text{C}$  can be observed in Fig. 1. The initial  $E_g$  value is not recovered after the last TAT, it slightly rises its value at 506°C TAT. The maximum  $\Delta E_g$  reached from the initial  $E_g$  value to the minimum  $E_g$  is 0.13 eV, and the difference between the initial  $E_g$  and the last value for 506°C is 0.11 eV. The recovery of  $E_g$  after passing the minimum is only 0.02 eV.

The experimental results for the above-mentioned CdSe layers are similar to CdS layers results reporting a ZB  $\rightarrow$  W phase transformation, found previously by two of us using a TAT of 30 h in Ar + S<sub>2</sub> [14]. These cubic CdS thin films were also prepared by the CBD method. There, the minimum value for  $E_g$  versus TAT was related with the structural transition ZB  $\rightarrow$  W. The position of the minimum was well defined, i.e. the transition temperature from a material dominated by the cubic phase to a material dominated by the hexagonal phase was clearly observed to occur at  $300 \pm 5^\circ\text{C}$ . In the present case, the  $E_g$  versus TAT lineshape does not evidence an abrupt transition, as could be seen in Fig. 1. The minimum of the  $E_g$  value in the CdS case has been associated till date with the disorder provoked in the transition, when the crystalline lattice is not dominated by any of the two structural phases [14–16,19]. In those works, the

initial  $E_g$  value for as-grown CdS and the last thermally annealed layer were almost the same. With these arguments in mind, we can associate a CdSe phase transition to occur at  $355 \pm 25^\circ\text{C}$ , according to Fig. 1; however, the  $E_g$  value for W–CdSe does not go back nearer to the initial value for ZB–CdSe. Some authors have reported theoretical results, supported by experimental measurements, showing  $E_g$  for ZB–CdSe to be higher by about 0.11 eV than the corresponding  $E_g$  for W–CdSe [9,20]. In our case the difference is 0.13 eV. Nevertheless, other authors have reported the contrary:  $E_g(\text{W–CdSe}) = 1.75 \text{ eV}$  and  $E_g(\text{ZB–CdSe}) = 1.67 \text{ eV}$ , based on experimental results from epitaxial MBE–CdSe/GaAs films [4]. We suppose that our study is so similar to the CdS transformation to assume that in CdSe a ZB to W phase transition occurs at  $355 \pm 25^\circ\text{C}$ , in agreement with previous reports of other authors using different experimental techniques [16,21–23]. The similarity in optical properties between CdS and CdSe is usually claimed in band structure analyses of both compounds. An important comment deserves to be added here: similar to CdS the phase change phenomenon is a thermally activated process where ions have to surmount an energy barrier to pass from a minimum to the next one in the periodical potential. Consequently, the movement from ZB to W structure occurs, according to Fig. 1, at any TAT between 120 and 330°C with an activation energy of 0.11 eV as calculated from data of Fig. 1, thus obtaining a lower critical temperature, but, of course, at much longer times than 30 h of thermal treatment as employed in this work. At room temperature the metastable CdSe is, for any practical purpose, a stable material.

In order to support the precedent conclusions, X-ray diffraction measurements were carried out in all samples. Fig. 2 shows the angular position, of five representative films, of the signal intensities at  $2\theta =$

{25.52, 42.15, 49.94}, which indicates a ZB structure for the as-grown samples according to JCPDS data files. When TAT is 267°C the diffractogram indicates that the peak at  $2\vartheta = 25.52$  decreases, and two other peaks move slightly to lower values, because the ZB structure is in transition toward the W structure. When TAT is 330°C, intensities belonging to hexagonal symmetry begin to appear at  $2\vartheta = \{24.02, 26.91\}$ , the other three peaks shift to lower  $2\vartheta$  values. Finally when the temperature of TAT is 506°C the samples are entirely in the hexagonal phase, whose peaks are at  $2\vartheta = \{24.00, 25.47, 27.19, 42.08, 45.93, 49.73\}$ . Both  $2\vartheta$  sets of ZB and W angular positions aforementioned are sufficiently very close to the main peaks of ZB and of W in JCPDS file cards for CdSe (ZB: 19-0191, and W: 08-0459): {25.375, 42.044, 49.741} and {23.901, 25.354, 27.080, 41.968, 45.788, 49.669}, respectively.

#### 4. Conclusions

In summary, we have characterized the phase transformation from the metastable ZB structure of CdSe to the more stable W structure caused by a thermal annealing during 30 h in the range 50–500°C in an Ar + Se<sub>2</sub> atmosphere on the cubic as-grown samples. X-ray diffraction measurements allowed to observe that the structural phase transformation from cubic to hexagonal crystalline lattice occurs in the range of temperatures  $355 \pm 25^\circ\text{C}$ . From optical absorption data the band gap energy was well approximately calculated by using the first derivative of the absorbance versus  $h\nu$ . The  $E_g$  versus thermal annealing temperature plot evidences a minimum in the region of  $355 \pm 25^\circ\text{C}$ , where we have considered the real phase transformation to occur. According to our measurements  $E_g(\text{ZB}) = 1.85 \text{ eV} > E_g(\text{W}) = 1.74 \text{ eV}$ .

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