

Properties of CdSe Polycrystalline Thin Films Grown by Chemical Bath

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CdSe polycrystalline thin films were grown onto glass substrates by chemical bath deposition at 65°C. Structural, optical, and electrical properties of samples were characterized. The layers grew in the cubic phase as evidenced by X-ray diffractograms. Using the first derivative of the optical absorption vs. phonon energy curves, two transitions were found, the fundamental at 1.8 eV and a second one at 2.2 eV, respectively. It is worthwhile to mention that the second transition has been reported only for the hexagonal CdSe modification. From the dark conductivity vs. $1/KT$ behavior on the 100-500 K range, it could be determined an activation energy of 0.3 eV at higher temperatures (>350 K) and a behavior following the variable range hopping model of Mott was satisfied at lower temperature. Electron dispersion spectroscopy measurements indicated stoichiometric CdSe material within the 1% error bar.

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Semiconducting CdSe films have been continuously studied as a photoconductive material^{1,2} for their importance in photovoltaic energy conversion,^{3,4} and lately, for their noticeable quantum confinement effect properties.⁵⁻⁸ Wurtzite is the stable phase of CdSe, and the sphalerite CdSe modification is a metastable structural phase. In spite of the relatively abundant works published in CdSe thin films, this material is the least studied II-VI compound in thin-film format, especially for cubic CdSe. Many physical properties of cubic CdSe remain as uncompleted studies, for instance, band structure and phonon dispersion, among others. By using new deposition techniques like molecular beam epitaxy,⁹ laser ablation,¹⁰ electrochemical atomic layer,¹¹ etc., it has been possible to grow CdSe in cubic phase with a wide variety of changing growth conditions. In this way, a lot of information has been gained recently for a better understanding of the physical properties of thin films of this material.

In this work the chemical bath deposition (CBD) technique was used to prepare polycrystalline CdSe thin films on glass substrates having about 200 nm thickness. Although this technique has been already used to grow this material,^{1,2,12} the optical and electrical properties usually depend upon the growing parameters such as temperature, stirring, chemical agents, and concentrations during the grown process. Thus, stoichiometric thin films of CdSe in cubic phase were obtained similar to CdS with the same structural symmetry using the CBD technique.¹³ Band structure analysis from optical absorption data evidenced two critical points at 1.84 and 2.2 eV, respectively. Theoretical calculations of band structure of cubic modification of CdSe do not predict the existence of this last electronic transition;^{14,15} however, the recent experimental data of dielectric function in cubic CdSe reveal a spin-orbit split of 0.41 eV in accordance with our results.¹⁶ Dark conductivity (DC) measurements in the 100-500 K range showed the presence of a high density of deep levels that promotes the carrier conduction described by the Mott's variable range hopping (VRH) model. After this first round of DC measurements, two consecutive rounds, in the same range of temperature, were carried out. Then the high density of deep levels disappeared and the conductivity was dominated by a thermally activated process following Arrhenius behavior. The crystalline quality of the films improved already after the first cycle of measurements, as this acted like a thermal annealing.

Experimental

The CBD method to grow II-VI semiconducting materials has been described elsewhere.^{12,13} The substrate cleaning was carried out by immersing them into an acid-chromium mixture for 24 h and then rinsing them in deionized water. The polycrystalline CdSe thin films were grown using deionized water solutions: 0.1 M potassium hydroxide (KOH), 0.01 M cadmium chloride (CdCl₂), 0.5 M ammonium nitrate (NH₄NO₃), and 0.01 M selenourea [CSe(NH₂)₂]. The solutions were mixed and the final solution heated at 65°C for 15 min, with the substrates remaining inside the solution. This process was repeated until the desired thickness was reached.

The X-ray diffraction (XRD) spectra were obtained by using a Siemens D5000 diffractometer. The optical absorption spectra were measured with a UNICAM 8700 system over the 190-900 nm wavelength range with an accuracy of $\Delta\lambda = \pm 0.3$ nm. Dark conductivity measurements as a function of absolute temperature over the 100-500 K range were achieved by using a closed cavity coupled to a vacuum system with a pressure of 10^{-2} mbar. A Keithley 617 programmable electrometer with an accuracy of $\Delta I = \pm 0.005$ pA, $\Delta V = \pm 0.0025$ V, and a DL4600 deep level transient spectrometer with an accuracy of $\Delta T = \pm 0.05$ K were employed for sheet resistivity measurements. Stoichiometry data were obtained by employing a Noran Instruments electron dispersion spectroscopy (EDS) system.

Results and Discussion

In XRD data of Fig. 1, the angular position of the signal intensities at $2\theta = \{25.35, 42.01, 49.69\}$ indicates a cubic system according to standard X-ray data files. In these samples a hexagonal phase contribution does not appear. We believe that the cubic symmetry could be favored by the slow stirring applied during the growth process. The proportion of constitutive elements measured by means of EDS was Cd = 50.83% \pm 0.90%, Se = 49.17% \pm 0.90%. This result indicates good stoichiometry of samples.

From optical absorption vs. photon energy ($h\nu$) plots, shown in Fig. 2, it can be observed that this material begins to absorb at ca. 1.7 eV until becoming saturated at 3 eV. By means of the first derivative of optical absorption vs. $h\nu$ graphs, as shown in the inset, two transitions were found, one of them at 1.84 eV and the next at 2.20 eV. The first of them is close to the value found by Hodes et al.⁷ (1.915 eV) for thin films with the same cubic symmetry and grown by CBD technique at 60°C but utilizing other chemical agents. In relation to the second transition at 2.20 eV, in band structure calcu-

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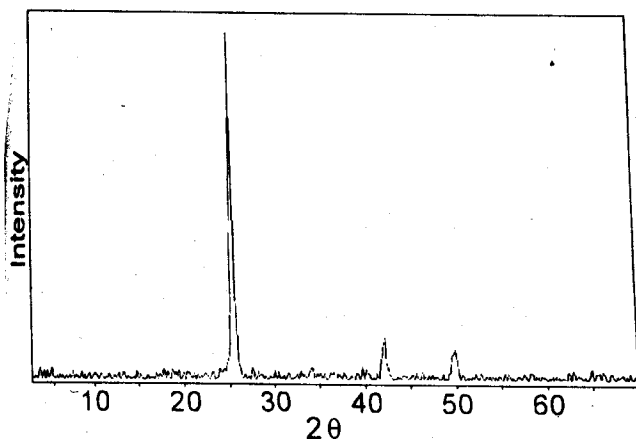


Figure 1. X-ray diffractogram of as-grown CdSe layers. Peaks correspond to (111), (220), and (311) directions of the cubic CdSe crystalline phase as 2θ increases.

lations of CdSe in zinc-blende phase this bandgap shift has not been reported, but in experimental measurement of dielectric function in cubic CdSe modification, a spin-orbit split of 0.41 eV for the fundamental 1.8 eV transition is reported.¹⁶ We think that our transition at 2.20 eV is due to the spin-orbit splitting.

Figure 3 illustrates the electric conductivity (DC) vs. inverse absolute temperature of measurements carried out by heating in vacuum. A level at $E_a = 0.29$ eV was calculated at higher temperature for as-grown samples. Trapping and donor levels in the 0.27-0.43 eV energy range have been reported by Robinson and Bube for Se-annealed samples in single crystals.⁴ Levels allocated in the range 0.27-0.32 eV have been reported for thin films prepared at different growth conditions and post-grown treatments.¹⁷⁻²⁰ In a second stage, the behavior for the same data vs. $T^{-1/4}$, as seen in the inset of Fig. 3, indicated that conduction is dominated by hopping through deep levels into the energy bandgap, and the variable range hopping model of Mott was satisfied for the as-grown samples at lower temperatures. Electrical conductivity by hopping in thermal evaporated

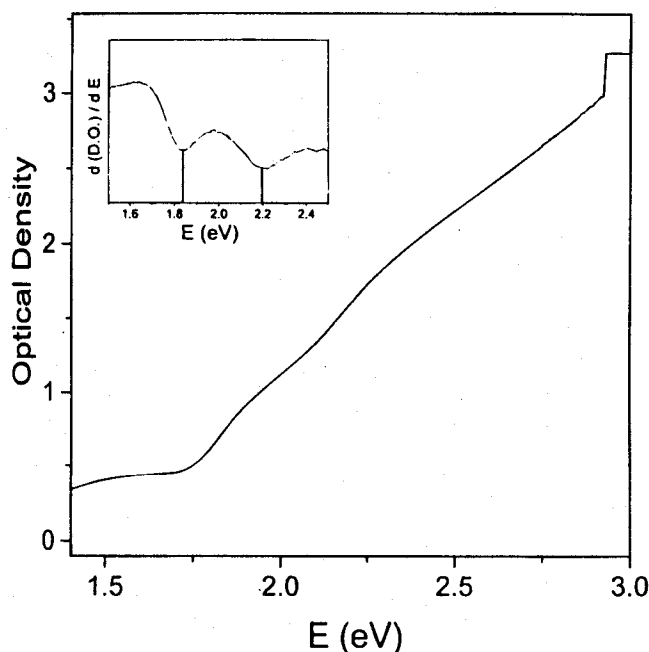


Figure 2. Optical absorption spectrum of CdSe as-grown layers as a function of the photon energy. The inset shows the first derivative of the optical absorption as a function of the photon energy.

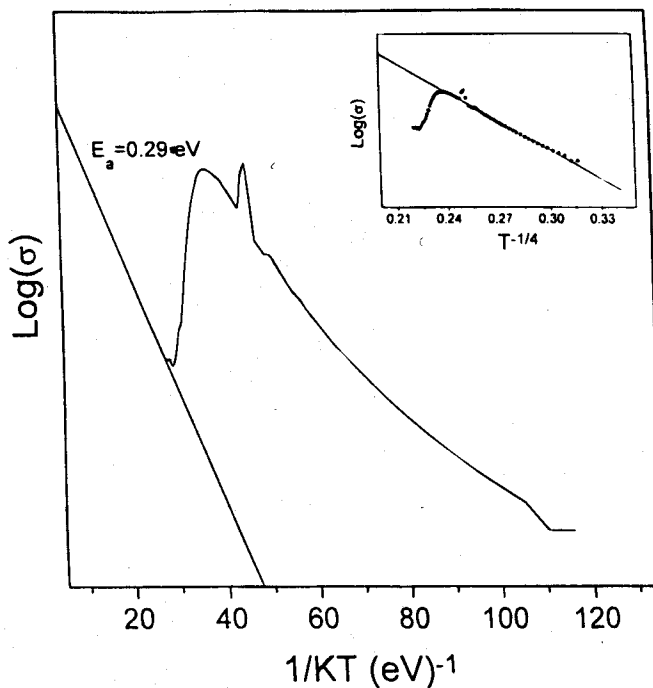


Figure 3. Logarithm of dark conductivity (σ) vs. $1/KT$ for the as-grown layer in both cases. The part of the curve at higher temperatures has an energy activation of 0.29 eV. Inset shows the fitting of the logarithm of σ with $T^{-1/4}$.

CdSe layers at high and low temperatures has been already reported by other authors.²¹ In the middle, the DC line shape has a wide band with a maximum centered at ~ 335 K, probably as a consequence of an intracrystalline disorder on the as-grown samples. For CdSe films, these type of bands have been observed in DC vs. $1/KT$ curves.^{18,22} The transport mechanism has been explained through a Cd excess¹⁸ or thermal intrinsic disorder of lattice atoms and irreversible changes in the crystalline structure.²² In our case, the carrier conduction process can be explained to be similar to the second mechanism. This assumption is supported by the fact that for cubic CdSe, stabilizing effects are provided by the substrate-deposit lattice match and the presence of stacking disorder.²³ Since we employed amorphous glass substrates, the metastable CdSe lattice of as-grown cubic samples can be affected by a large density of stacking faults, which after the first DC vs. $1/KT$ measurement, decreases sensitively in an irreversible manner, such as in an improvement of the crystalline quality of thin films after thermal annealing.

Afterward, i.e., in a second run of DC vs. T measurement, the transport mechanism is merely that of normal semiconductor materials. The high density of stacking faults in as-grown samples could be the origin of deep levels causing the VRH carriers conduction. The quasi-abrupt drop of the carrier at a $\bar{T} \approx 80^\circ\text{C}$ ($1/KT \approx 33$) can be the consequence of overcoming a temperature critical point for the stability of the stacking faults. Moreover, the DC vs. $1/KT$ line shape of Fig. 3 evidences a small peak at around $1/KT = 46 \text{ eV}^{-1}$ ($\bar{T} \approx -21^\circ\text{C}$) which could be related to another critical point in the temperature of the lattice. When these samples were heated again up to 500 K under 10^{-3} Torr pressure in a second measurement process, the wide band vanished as a consequence of the first DC vs. T measurement as seen in curve H1 of Fig. 4. By heating it once more, the DC does not have a strong change, as it can be observed in H2 curve of the same figure. The band vanishes after heating. H1 and H2 show a different behavior as compared with the heating of the as-grown sample. However, the peak at $1/KT = 46 \text{ eV}^{-1}$ was always present. The DC vs. $1/KT$ line shape of the as-grown sample evidences the superposition of two conduction mechanisms in the low-temperature region: the VRH through deep levels added to a thermal-activated process having a 0.7 eV energy barrier, indicating a carriers conduc-

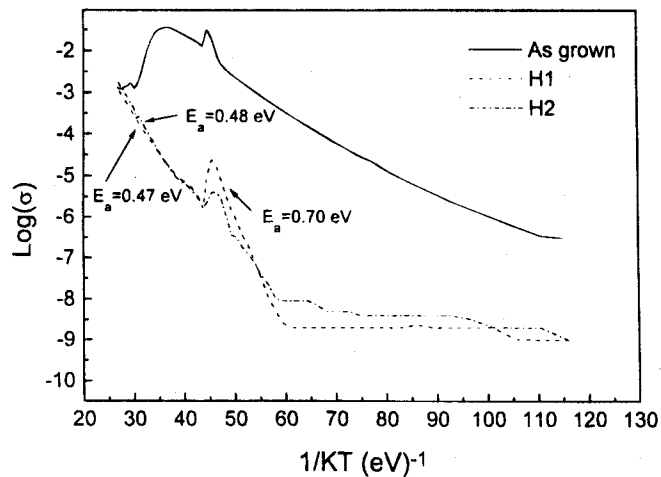


Figure 4. Logarithm of dark conductivity σ vs. $1/KT$ for the as-grown and annealed samples.

tion dominated by this deep level, in the vicinity of $1/KT = 46 \text{ eV}^{-1}$. A trapping level at 0.7 eV has been reported for electrodeposited CdSe thin films on In/ITO/glass substrates; similar to our results, they observed a peak in the carrier mobility vs. inverse temperature at low temperatures.¹⁹ The sharp drop in the carriers conduction immediately after the peak at $1/KT = 46$ suggests another irreversible structural change in the crystalline phase of the film. H2 line shape denotes small changes with respect to the H1 one. Moreover, the peak is not observed if the measurement is performed from higher to lower temperatures.²² This, on the other hand, suggests a sudden filling of traps when a critical temperature point is reached. We believe that the behavior of the peak at $1/KT = 46 \text{ eV}^{-1}$ could be originated by desorption effects. Trapping at surface states in CdSe due to adsorption of impurities from the ambient has been reported.²⁴ Desorption depends strongly upon the critical temperature being reached in thermal annealings. In our case, the annealing process can free an important density of carriers at a given temperature, which are rapidly trapped again by new surface states generated immediately after the desorption process. Desorption processes have been reported in CdS thin films grown by CBD subjected to thermal annealing in vacuum.²⁵

Conclusions

Optical and electrical properties of CdSe thin films in cubic modification grown by chemical bath have been characterized. As-prepared samples show two electronic transitions at 1.8 and 2.2 eV, respectively, by employing optical absorption. The transition at 1.8 eV corresponds to fundamental absorption of CdSe. The transition at 2.2 eV has been reported only for hexagonal modification of

CdSe. We think that this transition can be originated by a degeneration breakdown at the 1.8 eV level due to a high density of stacking faults presence in as-grown samples. Dark conductivity measurements indicate a conduction mechanism dominated by VRH in as-grown samples due to the presence of a high density of deep levels that appears by the stacking faults present in cubic samples. Under thermal annealing in vacuum, DC vs. $1/KT$ curves denote drastic changes, indicating a carriers conduction mechanism dominated by thermally activated carriers from deep levels, and desorption effects

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