Phase transition on CdSe thin films by changing the volume concentration of Se

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Abstract: - In this work CdSe thin films were grown by chemical bath deposition (CBD)[6] onto glass substrate with approximately 2000 Å thickness. The samples have been prepared by changing the volume concentration of the solution in the range of 5-45 ml. of Se, the other growth parameter such as reactive concentration an stirring remained constant during the growth process. The volume of the solution of Se was varied in order to perform the crystalline phase transformation from cubic zincblende (ZB) to the hexagonal wurtzite (W) structure. The change in the crystalline structure and electrical properties were noticeable, whereas the growth volume concentration was increased. The characterization of the samples included optical absorption, X ray diffraction, reflectivity electronic dispersive spectroscopy and dark electrical conductivity analyses. The optical absorption spectra allowed to calculate the energy band-gap (Eg) value and, hence, the evolution of Eg through the transformation from the cubic crystalline phase to the hexagonal phase. The X ray diffraction spectra also showed the complete microstructural transformation from cubic samples up to the entire hexagonal lattice for samples with higher volume of the solution of Se.

Key-Words: - Chemical bath, CdSe, thin films, phase transitions, semiconductors

1 Introduction

Semiconducting CdSe films have been continuously studied as a photoconductive material [1,2] for their importance in photovoltaic energy conversion [3], detection of visible and near-infrared radiation [4], and lately, for their noticeable quantum confinement effect properties [5]. In spite of the relatively abundant work 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 unconcluded studies, for instance, band structure and phonon dispersion, among others.

The CdSe, is a semiconductor of direct band and this material in thin films is obtained in cubic or hexagonal phase crystalline, or in a cubic-hexagonal mixture [1,6], depending on the conditions of growth. There are many techniques used to grow this material in thin-film: thermal evaporation [7], molecular beam epitaxy (MBE) [8], sputtering [9], chemical bath deposition (CBD) [1], laser ablation [10], among others.

In this work the CBD method was used to grow 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. Wurtzite (W) is the stable phase of CdSe, and the zincblende (ZB) CdSe modification is a metastable structural phase and have been obtained by CBD and other deposition techniques, at present and in the past [8,11]; 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. There are only few works dealing with the changes of its physical properties though structural transition, such as energy band gap (Eg), electrical conductivity, reflectivity, which can be meaningful for an overall understanding of the material [12]. 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 [13,14].

Previous works [15] on CdSe crystalline phase transformation reported the ZB $\rightarrow$ W phase transition temperature.

The samples was obtained by changing the volume concentration of the solution in the range of 5-45 ml. of Se, the other growth parameter such as reactive concentration an stirring remained constant during

the growth process. Thin films to perform the crystalline phase transformation from cubic to hexagonal due to the increment in the volume of Se during the growth process. These crystalline phase transformation were determined by X ray diffractograms, in those that a good crystalline quality is shown.

2 Experimental

The CBD method to grow II-VI semiconducting materials has been described by L. Chopra and L. Martínez [16, 17]. The substrate cleaning was carried by immersing them into an acid chromium mixture for 24 h and then rinsing in deionized water. The polycrystalline CdSe thin films were grown [18] 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 of selenourea [CSe(NH2)2]. The solutions were mixed and the final solution heated at 65 ^{o}C for 15 min, with the substrates remaining inside the solution. The properties of thin films depend in general to the conditions of growth. Polycrystalline CdSe thin films were grown on a glass substrate changing the volume concentration of Se, which was added during the growth in the range from 5 to 45 ml, maintaining the other parameters (concentration of reagents and agitation) constant during the growth process.

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 wave length range with an accuracy of $\Delta\lambda$ = 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 pressure of 10^{-2} mbar. A Keithley 617 programmable electrometer with an accuracy of ΔI = 0.005pA, ΔV = 0.0025 V, and a DL4600 deep level transient spectrometer with an accuracy of ΔT = 0.05 K were employed for sheet resistivity measurements.

3 Results and discussion

The Eg values as a function of volume concentration of the solution in the range from 5 to 45 ml. of Se evidence a shift of the absorption edge toward higher values as concentration of Se increases. The sample with 5 ml volume concentration of Se is CdSe as-grown.

Some authors have reported theoretical results, supported by experimental measurements, showing Eg for ZB –CdSe to be higher by about 0.11 eV than the corresponding Eg for W –CdSe [11, 19]. Nevertheless, other authors have reported the contrary: Eg(W –CdSe)=1.75 eV and Eg(ZB –CdSe)=1.67 eV, based on experimental results from epitaxial MBE-CdSe/GaAs films [8].

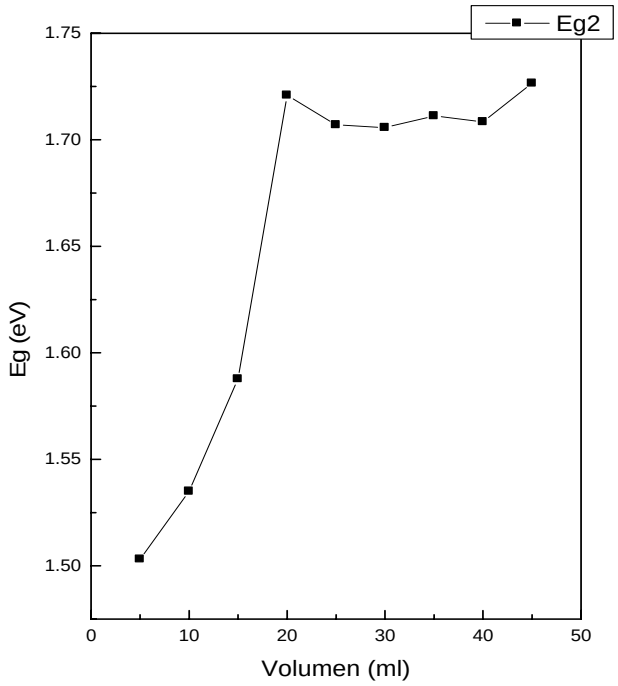

Fig.1. Eg versus the volume concentration of the solution in the range from 5 to 45 ml. of Se.

In our case, according to Fig.1, the values of the gap energy were obtained for the samples of CdSe with different volumes concentration of Se. Can be observed that the gap energy is increased from 1.50 eV to 1.721 eV with volume concentration from 5 to 20 ml of Se and with volume concentration from 20 to 45 ml of Se the Eg values remains almost constant, to assume that in CdSe a ZB to W phase transition occurs with 20 ml volume concentration of Se.

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 2θ={25.52, 42.15, 49.94}, which indicates a ZB structure for the as-grown samples according to JCPDS data files. In the hexagonal phase, whose peaks are at 2θ ={24.00, 25.47, 27.19, 42.08, 45.93, 49.73}. Both 2θ sets of ZB and W angular positions

aforementioned are sufficiently very close to the main peaks of ZB an of W in JCPDS file cards for CdSe (ZB: 19-0191, and W: 08-0459): {25.52, 42.15, 49.94} and {24.00, 25.47, 27.19, 42.08, 45.93, 49.73}, respectively.

In XRD data of Fig.2, the angular position of the signal intensities show that the crystalline structure in the samples from 5ml (sd1) to 20 ml (sd4), it is a cubic structure, and conform the volume of Selenium increased a phase transition from cubic to hexagonal to occur in the sample sd4-20ml. and sd5-25 ml, for the samples with a higher volume of Se to 20 ml, the structure is hexagonal, as the samples of the sd5-25ml. to the sd9-45ml.

The dark conductivity show in Fig.3, it can be observed that samples that presented a higher conductivity to ambient temperature (300 K), they are those that were grown with a volume of Selenium higher than 25 ml., sd5-25ml. to the sd7-35ml. For the samples with an excess of Se as the sd8-40ml. and sd9-45ml. the conductivity diminished due to the concentration of Se accumulated in the samples, since this increment of it is caused the formation of chains or heaps [20] that impede a good carrier conduction. The samples with higher Selenium increased the electric conductivity that the CdSe as-grown (sd1-5ml).

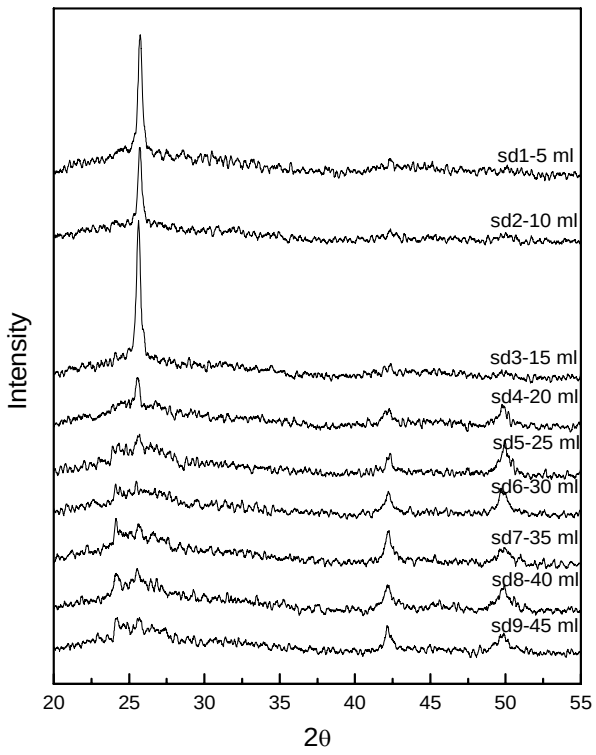

Fig.2. X ray diffractograms of CdSe as-grown and the phase transition ZB → W samples. Number next to peaks indicate the 2θ positions.

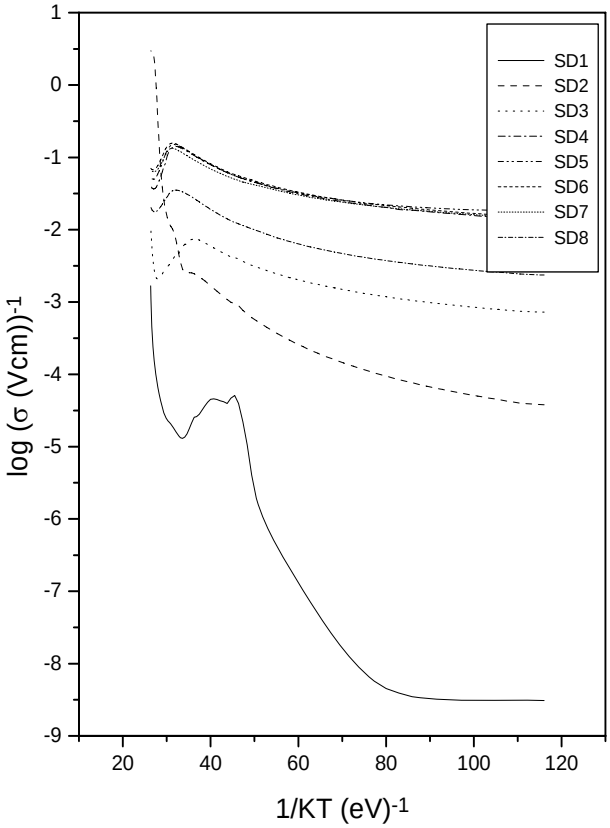

Fig.3. Logarithm of dark conductivity σ vs. 1/KT for the as-grown and in the CdSe thin films with the volume concentration increased from 5 to 45 ml of Se.

4 Conclusions

The changes in the crystalline structure and the electric properties were remarkable, due to the changes in the volume of the concentration of Se which was increased during the growth process. The conductivity, the volume of the unitary cell, the mobility and the density of the carriers were also increased.

It is known that there are two forms of increasing the conductivity, one of them is the increment in the

density of the carriers and the other one is the increment in the grain size and the net parameter. Taking into account that the density of carriers remains constant, we conclude that the electric properties improve for the first form.

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