

Effects of indium doping on the structural and optical properties of CdSe thin films deposited by chemical bath

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Thin films of n-type CdSe have been grown on Corning glass substrate by chemical bath deposition, prepared with Sodium Seleno-Sulphate (Na_2SSeO_3), Cadmium Chloride (CdCl_2) and Indium Tri-Chloride (InCl_3), mixed in an aqueous environment. The effects of different In doping concentrations have been investigated. X-ray diffraction spectra show that at low In concentration only the CdSe lattice is present in the deposited film, whereas CdIn_2Se_4 and InSe compounds are obtained at higher In concentrations. Optical properties have been calculated from transmission spectra and photoluminescence measurements. From transmission spectra, the absorption coefficient and optical gap were obtained; photoluminescence spectra show band-band recombination from 10 K to room temperature.

Keywords: Indium doping; CdSe; thin films; optical properties; structural properties.

Películas delgadas de CdSe tipo-n han sido crecidas sobre vidrios Corning utilizando la técnica de baño químico. El baño fue preparado en solución acuosa de Sulfato de Selenio (Na_2SSeO_3), Cloruro de Cadmio (CdCl_2) y Tricloruro de Indio (InCl_3). Los efectos producidos por diferentes concentraciones de Indio (In) en las propiedades estructurales de las películas fueron analizados por medio de la técnica de difracción de rayos X, donde se evidencia la presencia exclusiva del CdSe para concentraciones del 1% de In, mientras que para concentraciones mayores aparecen los compuestos de CdIn_2Se_4 e InSe. Las propiedades ópticas han sido determinadas a partir de los espectros de transmisión y de mediciones de fotoluminiscencia. A partir de los espectros de transmisión se obtuvieron el coeficiente de absorción y el ancho de banda óptico. Las mediciones de fotoluminiscencia muestran recombinaciones banda-banda para el intervalo de temperaturas desde los 10 K hasta los 300 K.

Descriptores: dopaje con Indio; CdSe; películas delgadas; propiedades ópticas; propiedades estructurales.

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1. Introduction

The II–VI semiconductor compounds, particularly CdS, CdSe, CdTe, are of great interest because they are potential candidates in many practical applications like solar cells, optical detectors, dosimeters of ionized radiation, field effect transistors, and optoelectronic devices. Its suitable band gap, optical properties, and very good stability, recommend cadmium selenide as a very promising semiconducting material for optoelectronic applications, especially for solar cell structures. The performance of the devices based on CdSe thin films depends on the structural and electronic properties of the layers obtained under various experimental conditions [1–4]. The electronic and optical properties of semiconductors are strongly influenced by the doping process, which provides the basis for tailoring the desired carrier concentration and, consequently, the absorption, emission and transport properties. When the density of n-type or p-type doping becomes sufficiently high, the impurity band merges with the

conduction or valence band and causes the formation of a band tail [5] and band gap shrinkage [6].

In this work, we shall discuss experimental data obtained for n-doped CdSe. The dopant used to obtain n-type CdSe is indium (In), which, in substituting for Cd in CdSe, acts as a donor. There are different methods for obtaining In doped CdSe thin films: solution growth, co-evaporation, chemical bath, electrodeposition and laser ablation [7–9]. We deposited In doped CdSe thin films at different concentrations, by means of the chemical bath technique. These films show a crystalline quality, as deduced from X-ray diffraction (XRD) measurements. Optical characterization was carried out using transmission spectra (TS) and photoluminescence (PL) measurements. Red shifts of the absorption edge and band-band luminescence are observed when the indium concentration increases; this effect is consistent with a merging of the donor band with the conduction band when the indium concentration becomes sufficiently high.

2. Experimental

Indium doped CdSe thin films were deposited using the chemical bath technique; Sodium Seleno-Sulphate (Na_2SSeO_3) and Cadmium Chloride (CdCl_2) were mixed together in a stoichiometric solution. Indium Tri-Chloride (InCl_3) was used as the source material for doping. Sodium hydroxide and aqueous ammonia were used to adjust the pH to 10 ± 0.1 , and to increase the film adherence, respectively. The deposition was carried out at a temperature of 60°C over a period of 90 min with a substrate speed of rotation of 80 rpm. The films were deposited on Corning 1737 glass substrate.

The indium liquid phase composition was varied from 0 to 20%.

The film thickness was measured by a contact profilometer (Tencor Instrument 200) with an experimental error of $\pm 2\%$, and five measurements were taken for samples. The film was found to be about 520 nm for the CdSe undoped, 470 nm for the In concentration equal to 1%, 415 nm for 5% of In, 386 nm for In = 10% and 358 for 20% of In.

The X-ray diffraction patterns of the films were recorded with a JEOL 60 PA X-ray diffractometer operating with a 0.15418 nm monochromatized Cu k_α radiation at 40 kV and 30 mA with a Ni filter.

TS were obtained using a Spectra Unicam UV-visible double beam spectrophotometer, at room temperature. Again, several spectra were measured for each sample, confirming identical results for each measurement.

PL measurements were carried out using the line 458 nm of an Ar ion laser for excitation. The PL light emitted from the sample surface was analyzed and detected by a GaAs:Cs photomultiplier, which was cooled to 250 K.

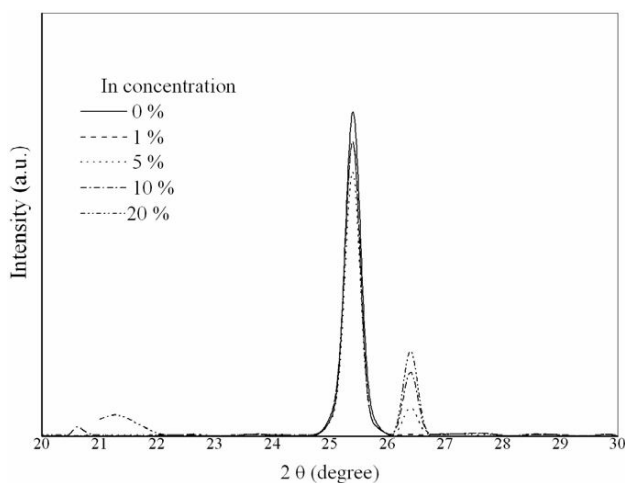


FIGURE 1. XRD spectra of CdSe films deposited with different In doping concentrations.

3. Results and discussion

3.1. XRD measurements

The XRD spectra at room temperature of the five CdSe:In deposited films are shown in Fig. 1. A peak at 25.4° appears in all curves, referring to the (002) reflection of the CdSe lattice; this suggests that the films grow according to a preferential orientation of the hexagonal phase. For 1 % of In concentration, no difference is observed respect undoped CdSe. For films with 5 and 10 % of In, referring a peak at 26.4° refers to the (111) orientation of the tetragonal phase of the CdIn_2Se_4 . In XRD spectra of films with 20 % of In there appears a small peak centered at 21.3° , which is characteristic of the (400) orientation of the hexagonal phase of InSe.

In conclusion, the XRD spectra indicate that at low In concentration only the CdSe compound is present, whereas the increase in the In concentration also causes the formation of the CdIn_2Se_4 and InSe compounds. The chemical bath technique is only suitable for growing CdSe:In thin films when the In concentration is lower than ten percent; other authors have reported the growing of CdSe:In when the In concentrations is lower than five percent using laser ablation [9].

3.2. Transmission spectrum measurements

A large amount of dopants induces a large free carrier density in the bands and a high density of ionized dopant ions: these facts cause a variation in the density of states with respect to the undoped case and the formation of band tails. Several experimental methods have been used to estimate the energy gap value for these materials. The most common methods are based on absorption measurements or transmission spectrum measurement. From the transmission spectra we calculated the absorption spectra using the Swanepoel method [10]; the results are shown in Fig. 2; discrete excitonic features are absent in both the doped and undoped films. This is due to

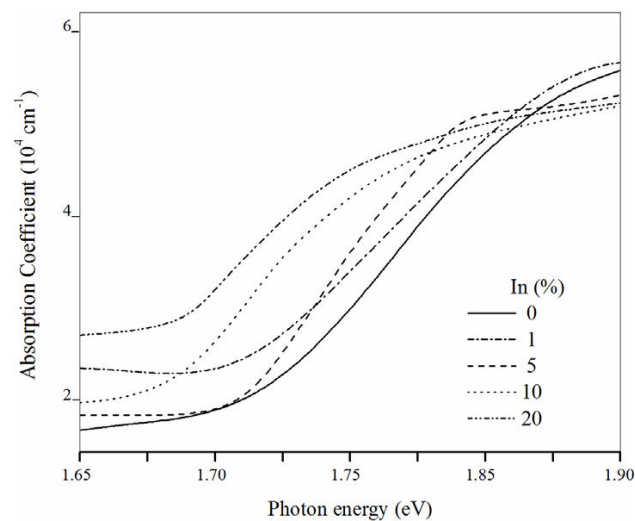


FIGURE 2. Absorption spectra from studied samples.

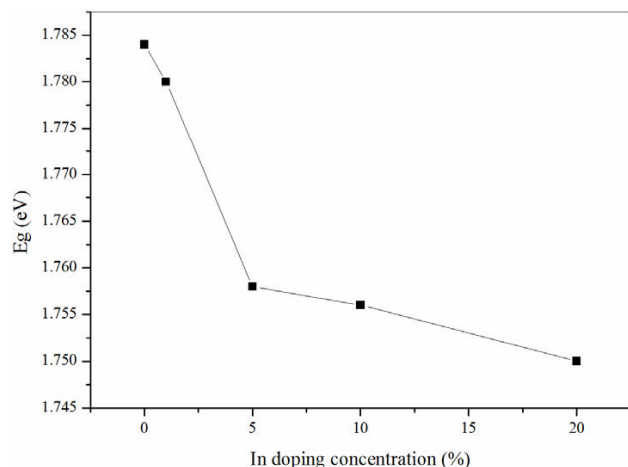


FIGURE 3. Optical gap as In doping function.

the increase in free carriers with doping density, it which reduces the intensity of the oscillator strength of the discrete exciton states. A broadening of the absorption edge results when In doping concentration increases.

The standard empirical method to obtain the optical gap value is the Tauc method [11]; in this model, the optical gap E_g value in the strong absorption region, where the absorption coefficient α is major to 10^4 cm^{-1} , is defined as:

$$(\alpha h\nu)^n = A(h\nu - E_g), \quad (1)$$

where h is the Planck constant, ν is the photon frequency, A is a constant and n is equal to $1/2$ for materials with an indirect gap and 2 for materials with a direct gap. As the absorption edge of the CdSe films is characterized by continuum state transitions, n is evaluated on 2. From a linear extrapolation to the energy axis of the $(\alpha h\nu)^2$ versus $h\nu$, we obtain the optical gap values, as a function of In doping concentration, which are tabulated in Fig. 3. A decrease in the optical gap occurs when In doping increases. The optical gap and absorption coefficient variation, which is due to the increase in the free carriers with doping, enhances the electric screening between holes and electrons and reduces the intensity of the oscillator strength of the discrete exciton state. Similar optical gap values which are obtained from other methods [12, 13], are reported in the literature.

3.3. Photoluminescence measurements

The In doping influence the PL properties of a semiconductor; this technique is a direct way to measure the band gap energy. However, a large amount of impurities induces a large free carrier density in the bands and a high density of ionized dopant atoms. As a consequence, different carrier interactions cause modifications of the line shape and spectral energy of the PL features. When the doping density is high, the disorder due to stoichiometric fluctuations generates strong local fields which dissociate the exciton bound states: therefore, only electron-hole recombination characterizes the PL

spectrum in the band edge region. In addition, strains due to lattice mismatch and thermal expansion differences between substrate and films contribute to the structural disorder and cause a broadening of the emission band and the decrease in luminescence intensity because of the introduction of non radiative recombination centers. Furthermore, renormalization of the band gap occurs when impurity tails merge into the conduction or valence band, thus causing a red-shift and broadening of the PL features.

The PL spectra are shown in Fig. 4. No excitonic emission is evident, but the spectra are characterized by three PL bands. The total PL intensity decreases as the In concentration increases, because of the increase in non radiative traps and defect centers produced by structural disorder. The PL bands are centered at 1.78, 1.62 and 1.43 eV for undoped CdSe and In = 1%. For In = 5, 10 and 20 %, the PL bands are centered at 1.77, 1.63 and 1.45 eV. The energy shifts in the PL bands are due to the different gap values. These peaks for undoped film are similar to those reported in [14], where the films were obtained by a similar technique.

PL spectra as a function of temperature are reported in Fig. 5 for samples with In = 1%; similar behavior is observed in all doped samples. The higher energy band, persisting from low to high temperature values, is due to band-band emission. This band presents a red-shift with increasing temperature, due to thermal shrinkage of the energy gap. The energy of this band maximum is higher than the energy of the optical gap as deduced from absorption measurements. This possibly is due to the fact that the Tauc method underestimates the absorption edge value [9].

The PL band at medium energy corresponds to radiative recombinations involving shallow levels in the band gap due to native impurities. It disappears at high temperatures (100 K) due to thermal ionization of the impurity levels involved.

The low energy band is due to radiative recombinations involving deep impurity levels, these levels cannot be thermally ionized and the radiative recombinations persist up to room temperature.

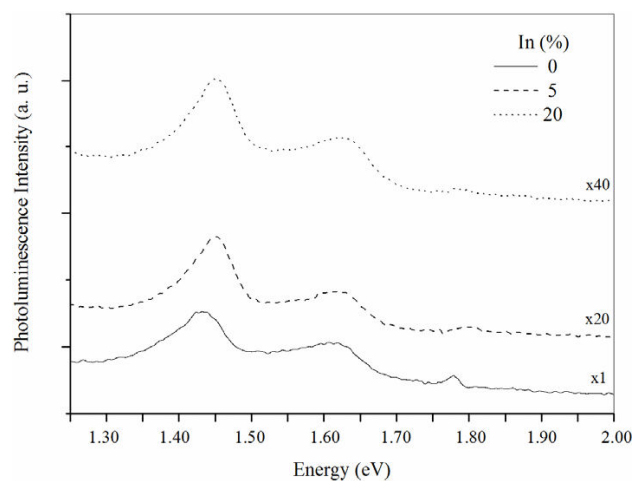


FIGURE 4. Photoluminescence spectra for studied samples at 50 K.

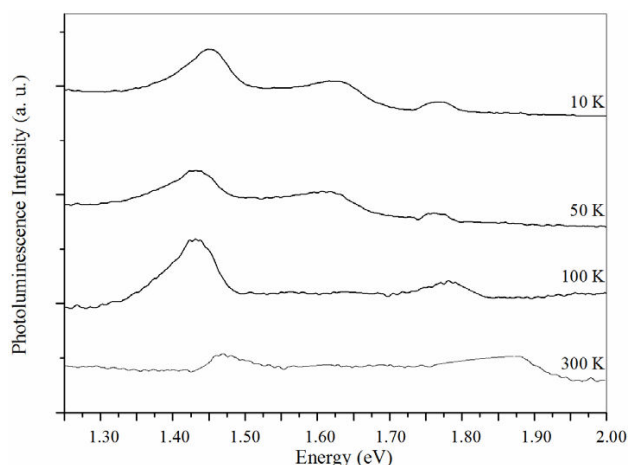


FIGURE 5. Photoluminescence spectra as function of temperature, for sample with Indium concentration of 1 %.

4. Conclusion

In doped CdSe, thin films have been deposited using the chemical bath technique. The results obtained in structural and optical characterization can be summarized as:

1. XRD spectra indicate that for a low In concentration, only the CdSe compound is present; when In concentration increases, CdIn₂Se₄ and InSe compounds appear.

2. The chemical bath technique is only suitable for growing CdSe:In thin films when the In concentration is lower than ten percent.
3. A broadening of the absorption edge results when In doping concentration increases.
4. A decrease of optical gap occurs when In doping increases, due to the increase in free carriers.
5. The total PL intensity decreases as the In concentration increases, because of the increase in non radiative traps and defect centers produced by structural disorder; similar results are reported by Perna *et al.* in Ref. 9.
6. A shift of the center of PL bands appears as a consequence of the optical gap variation.
7. Band-band recombinations are observed from 10 to 300 K.
8. Radiative recombinations due to native impurities disappear for temperatures over 100 K.
9. Radiative recombinations involving deep impurity levels persist up to room temperature.

Acknowledgments

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