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The effect of Er^{3+} doping on the physical properties of CdSe thin films deposited by chemical bath

R.B. López-Flores[a], O. Portillo-Moreno[b], R. Lozada-Morales[c], R. Palomino-Merino[c], and M.A. Hernández Espinosa[d]
[a]Facultad de Cs. de la Electrónica, [b]Facultad de Ciencias Químicas,
[c]Facultad de Ciencias Físico-Matemáticas, Depto de Inv en Zeolitas,
Benemérita Universidad Autónoma de Puebla,
72570, 18 Sur y Av. Sn Claudio, Col. Sn. Manuel, Puebla, Pue. México.

N. Korneev Zabello and A.G. Rojas Hernández
Instituto Nacional de Astrofísica, Óptica y Electrónica,
Apartado Postal 51 y 216, c.p. 72000, Puebla, Puebla, México.

S.A. Tomas and O. Zelaya-Angel
Departamento de Física, Centro de Investigación y de Estudios Avanzados del IPN,
Apartado Postal 14- 740, 07360 México D.F., México.

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CdSe thin films were prepared by a chemical bath on glass substrates and doped with erbium during the growing process at 70°C. Eight impurity levels were obtained by changing the relative volume of the salt solution containing Er in the total CdSe growing solution. The relative volume of the Er-salt solution had the values: 2, 5, 8, 10, 15, 18, 25 and 30%. The electrical, structural, optical and photoconductive properties were characterized. Important changes in the energy band gap, in the photoconductance, and in the refractive index were observed in the CdSe layers as a result of the concentration level of Er in the semiconductor.

Keywords: II-VI semiconductor; Chemical Bath Deposition (CB); rare earths; thin films.

Peliculas delgadas de CdSe fueron depositadas por baño químico sobre substratos de vidrio e impurificadas con erbio durante el proceso de crecimiento a 70°C. Ocho niveles de impurezas fueron obtenidos variando el volumen relativo de la solución de la sal conteniendo Er en la solución total de crecimiento del CdSe. El volumen relativo de la sal de Erbio tuvo los siguientes valores: 2, 5, 8, 10, 15, 18, 25 y 30%. Las propiedades eléctricas, estructurales, ópticas y fotoconductivas fueron caracterizadas. Cambios importantes en la brecha de energía, en la fotoconductividad y en el índice de refracción fueron observados.

Descriptores: Semiconductores II-VI; Baño químico; tierras raras; películas delgadas.

PACS: 61.72.Vv; 73.61.Ga; 81.15.Lm

1. Introduction

CdSe is a semiconductor of the II-VI compound family which has a great potential application such as solar cells [1,2], transistors [3], quantum dots [4,5], photoconductors [6,7], electro-optic devices [8, 9]. On the other hand, Er is a rare earth element used as impurity in optical amplifiers because of its high capacity to supply both high gain and high saturation output. Er^{3+} is also an active lasing element. The aim of this work is to obtain CdSe: Er^{3+} thin films using the chemical bath deposition method (CBD) technique and to investigate the effect of Er doping at different concentrations on electrical, structural, morphological and elemental properties of CdSe. Preliminary results are discussed at this point.

2. Experimental

Polycrystalline CdSe thin film preparation on glass substrates at 70 ± 1°C by the CBD method has been previously reported by us [10]. The following solutions were used in the CdSe:Er layer growth: $CdCl_2$ (0.01 M), KOH (0.01 M), KOH (0.01 M), NH_4NO_5 (0.5 M), $SC(NH_2)_2$ (0.021 M), and $Er(NO_3)_3$ $3H_2O$ (0.5M). The total solution (100 ml) for growing CdSe was completed with relative volumes (V_r) of Er-chemical agent solution from 2 ml (2%) to 30 ml (30%), in order to obtain eight different doping levels. Growing time was 45 min for the all film depositions. The samples were named using the respective V_r value; thus V_r = 0 means the undoped sample whereas V_r = 5 means the sample grown by employing 5% of the relative volume of the Er-solution in the total growing solution. Measurements of the atomic concentration of the elements were achieved by means of the atomic absorption technique. Layer thickness was in the range 140-230 nm, as determined by utilizing a Dektak II profilometer. Structural characterization was carried out by means of a Siemens D5000 diffractometer, using the CuK_α line. Optical absorption spectra allowed us to calculate the forbidden energy band gap (E_g), by using the $(\alpha h\nu)^2$ versus $h\nu$ plot; here α is the optical absorption coefficient and hν the photon energy. For the photo-conductance (PC) measurements, a Con-Optics He–Ne laser ($h\nu = 1.96$ eV or $\lambda = 633$ nm and power = 35 mw) was employed. With this laser-line, the excitation of electrons to the conduction band of CdSe is guaranteed, as its E_g equals 1.72 eV. For the power dissipation experiments, an argon laser (Laser Physics) of five different wavelengths (514 nm to 55mw, 488 nm to 55mw, 476 nm to 7mw, 465 nm to 7mw, 457 nm to 5mw) and a thorlabs FDS 100 photo detector was used.

3. Results and Discussion

Atomic absorption measurements on each sample were useful for determining that Er-atom concentration in the material is of the order of 1% at ($\sim 1 \times 10^{20}$ cm^{-3}). Diffractograms of the CdSe:Er samples display the cubic zincblende (ZB) crystalline structure for all the different CdS:Er layers studied. Fig. 1 shows the x-ray diffraction patterns of five samples. The main reflection corresponds to the (111) planes of the cubic ZB structure at around $2\theta = 25.3°$. The stable crystalline phase of CdSe is the hexagonal Wurtzite; however, for CdSe prepared by CBD, the as-grown structural phase is ZB [10]. The band gap energy (E_g) was calculated from the optical absorption spectra, by employing the relation $(\alpha h\nu)^2 \propto (E_g - h\nu)$, where α is the absorption coefficient and $\nabla\nu$ the photon energy. Fig. 2 illustrates the E_g versus V_r plot, where it is evident that the variation of E_g with V_r has a minimum value for V_r = 18; however, the change in E_g is only 4.5% with respect to the sample with V_r = 0%. In Fig. 3 it can be appreciated how the photo-conductance increases if the beam power increases. The response is different in each sample and has a non-linear form. Even though these are preliminary results, we think the doping level, the refractive index and the configurational disorder introduced into the lattice by the Er^{3+} ions play important roles for the PC-response, and probably for V_r = 5% the optimal conditions are present for the highest PC signal. As E_g does not vary sensitively for all the V_r, this parameter does not seem important for the PC response. The dissipated power (DP = V $\times$ I) versus wavelength of the excitation source for four representative V_r values is observed in Fig. 4. The samples were illuminated using a constant intensity of 2.6 mw/cm^2. We can appreciate how Er contributes to reducing the dissipated power in the CdSe films in the entire range of wavelengths studied. In order to understand the actual influence of Er on this phenomenon, more experimental work is in progress.

The optical absorption coefficient in the mean infrared is displayed in Fig. 5 for all the V_r values. CdSe is transparent in the region from 4×10^3 to 12×10^3 cm^{-1}; the features observed in all the spectra can be due only to interference effects. In this way, the refractive index (n) can be calculated by using the formula $n = 1/[4d(k_1 - k_2)]$, where $k = 1/\lambda$, is the wavenumber in cm^{-1} and d the thickness in cm^{-1}. The procedure for calculating the refractive index is based on the observation of interference minima and maxima values. In our case, as only one minimum and one maximum were ob-

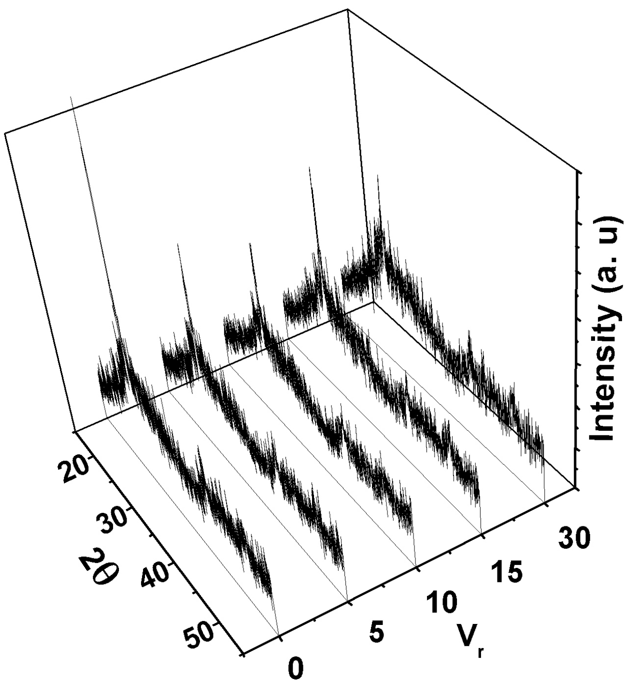

FIGURE 1. Diffractograms of the CdSe:Er samples with Vr = 0, 5, 10, 15 and 30%.

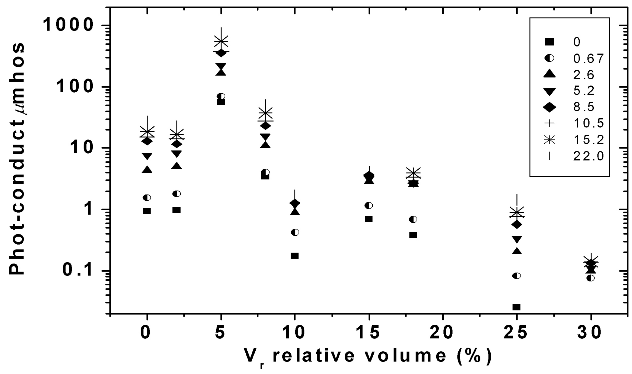

FIGURE 2. Photo-conductance versus Vr for different excitation power values of laser He-Ne (in the inset), which were obtained by using neutral filters.

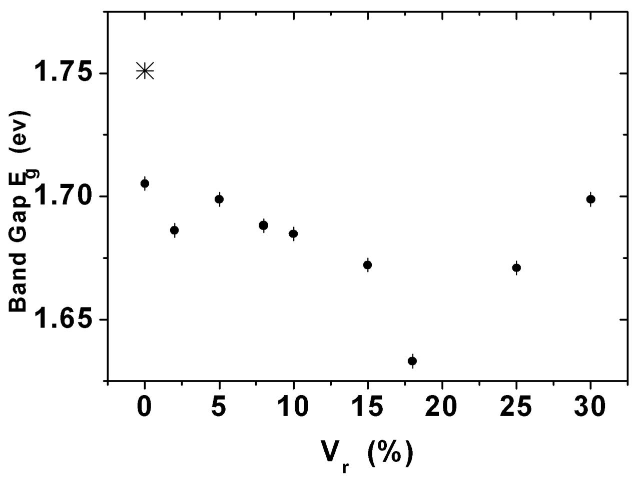

FIGURE 3. Band gap energy as a function of Vr. The asterisk (*) indicates the E_g value for CdSe single crystal.

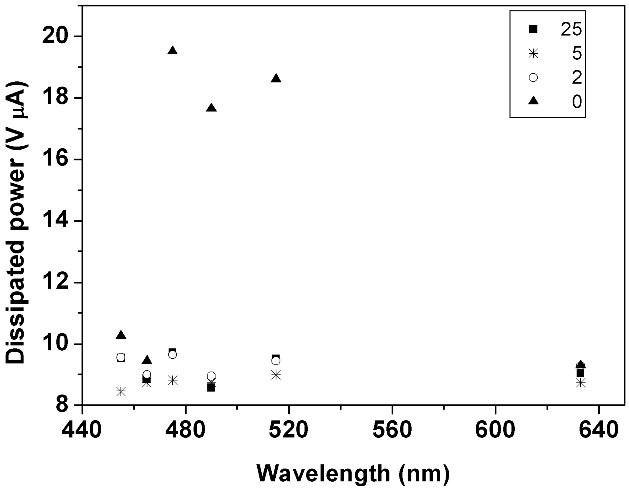

FIGURE 4. Dissipated power versus wavelength for samples with V_r = 0, 2, 5 and 25 (see inset).

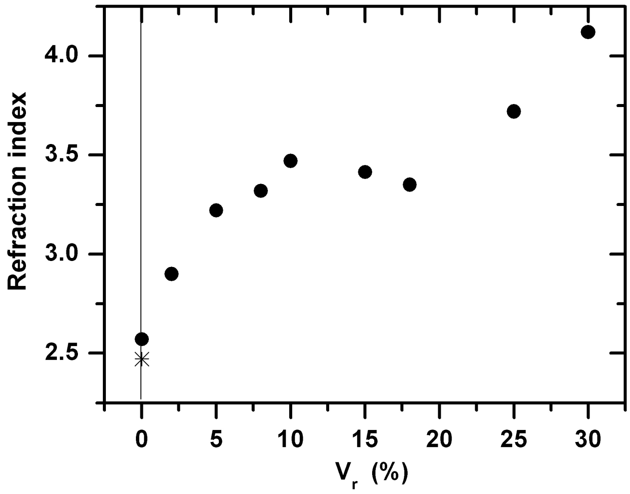

FIGURE 6. Refraction index (n) versus V_r. The asterisk indicates the value 2.47 reported for crystalline CdSe.

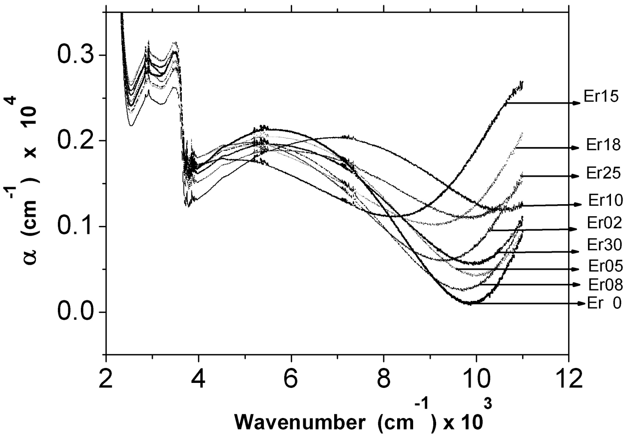

FIGURE 5. Absorption coefficient (α). In all graphics of infrared absorption we are using an infrared lamp, wave number $(1/\lambda)$ in $cm^{-1} \times 10^3$.

served, the aforementioned formula is $1/2$ times the actual formula. To check the validity of this step, we can see in Fig. 6 that the refraction index n = 2.54 for V_r = 0 % is very close to the value n = 2.47 reported for CdSe single crystal. Rare earths introduced in orthophosphates noticeably increase the refractive index of the material [11], which could be the same effect observed in CdSe prepared by CBD. However, we think more work should be developed in this direction in order to reach a good understanding of the actual influence of the Er^{3+}impurities in the semiconductor .

4. Conclusions

Important changes take place in the physical properties of CdSe thin films grown by chemical bath because of the doping with Er^{3+} ions at concentrations of $\sim$ 1%. The Photoconductance is increased up to three orders of magnitude, power dissipation is reduced by 50%, and the refractive index appears to reach values of up to 60% of the non-doped sample.

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