

Optoelectronic properties of polycrystalline CdInTe films

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(Received 9 December 1998; accepted 13 August 1999)

Close-spaced vapor transport combined with free evaporation was used for the growth of polycrystalline CdInTe films on glass substrates. The optoelectronic properties of the films were investigated by absorption at 77 and 300 K, and photoluminescence at 77 K with the indium concentration ranged from 0 to 22 at. %. The band-gap energy was found to vary linearly, and the band-gap temperature coefficient increases as the indium concentration increases. It was found that the ionization energy of indium displaced from the cationic sites of the CdTe lattice corresponds to a donor level at $E_D > 32$ meV ($E_D \approx 36$ meV) below the conduction-band bottom. This level and the acceptor level associated with Cd vacancies stay at the same energy distance of their corresponding bands for all the indium concentrations studied. The relation between E_g and the lattice parameter is also shown. © 1999 American Vacuum Society. [S0734-2101(99)04706-5]

I. INTRODUCTION

In recent years, thin films of semiconductor compounds have been of interest due to their application in optoelectronics, integrated optics, and the photovoltaic industry.¹ The II–VI compounds are attractive candidates. CdTe is one of the II–VI semiconductors with a good outlook because, among other characteristics, it has an optimum band gap (near 1.5 eV) for solar-energy conversion.

Many binary and ternary semiconductor compounds have been studied in the last decades. Considerable attention has been devoted to II–III₂–VI₄ compounds as CdIn₂Te₄, which crystallize in the tetragonal system, but are defect structures.^{2,3} In many cases, the nature of the optical properties of such materials is still under discussion. Recently, many efforts have been made toward growing high-quality CdIn₂Te₄. All the techniques used for obtaining this compound had been limited to the bulk materials. The successful growth of pseudoternary CdInTe films on glass substrates using close-space vapor transport combined with the free-evaporation (CSV-T-FE) technique⁴ has opened possibilities for applications that require large-area coverage. It is known that for large-area applications the growth of high-quality II–VI films on foreign substrates has become a critical technological issue.⁵

On the other hand, it is well known that as-grown CdTe films by the CSV-T-FE technique are normally rich in Cd vacancies (V_{Cd}), which leads to p -type conductivity.^{2,6} This is one of the reasons for its limited introduction.⁷ When atoms of indium are introduced into the lattice of CdTe, the indium atoms could fill Cd vacancies and substitute the Cd atoms of CdTe crystallites. Therefore, this would result in

the compensation of such the vacancies⁸ and the conductivity would turn into n type.

The indium atoms can also be displaced from the Cd vacancy sites of the CdTe lattice. In this case, a donor energy level deeper than a hydrogenic donor level can appear.⁹ The growth of CdTe films with high indium concentration leads to the formation of a compound based on the solid-solution CdTe–In₂Te₃ (Ref. 6) with a wider energy range of absorption.

In this article, the optoelectronic characterization of polycrystalline CdInTe films grown by the CSV-T-FE technique on glass substrates is described.

II. EXPERIMENT

The samples were prepared using the CSV-T-FE technique at a base pressure of 10^{-6} Torr.⁴ The raw materials were CdTe powder 99.99 at. % and indium 99.999 at. % purity from Balzers. Corning 7059 glass slides were used as the substrates. The CdTe source was maintained at 600 °C during the growth procedure, while the In source temperature was varied between 600 and 765 °C to achieve different concentrations (between 0 and 22 at. %). The temperature of the substrate was fixed at 500 °C. The control gas used during the film growth was Matheson argon 99.999 at. % pure. The deposition time of the growth was 5 min. The graphite wall used as the container (5 mm high) and the heater blocks were made from high-density graphite. The temperature was sensed with a Cr–Al thermocouple. A ceramic ring of 6 mm diam was introduced into the graphite block of the CdTe source in order to guide the atoms of the evaporated In and to introduce them into the container. The distance between the In source to the substrate was 8 mm.

The elemental concentration of each sample was determined by x-ray photoelectron spectroscopy (XPS) using a

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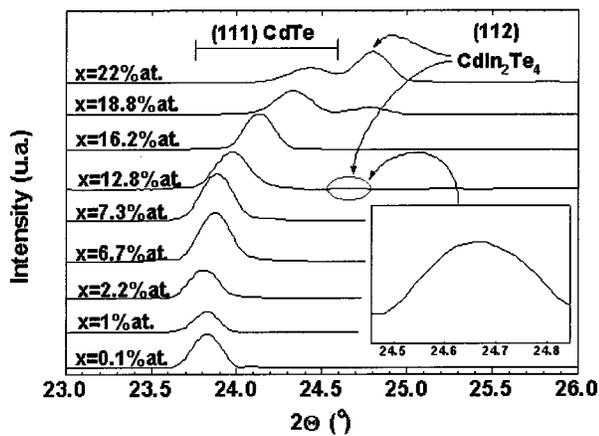


FIG. 1. X-ray diffraction measurements of CdInTe with different indium concentrations.

Perkin-Elmer PHI-560 ESCA-SAM. The anode was aluminum (1486.6 eV). Before analysis, samples were cleaned by immersion for 30 s in a 3% methanol bromine solution. XPS measurements of the elemental composition were obtained after 30 min of argon ion sputtering on an area of $5 \times 5 \text{ mm}^2$. For this work we used an x-ray source power of 300 W, and detection of the photoelectrons was carried out with a double-pass cylindrical-mirror analyzer. X-ray diffraction measurements were performed with a Siemens D5000 diffractometer fitted with a Cu $K\alpha$ radiation anode operating at 40 kV and 35 mA.

The thickness was of about $30 \mu\text{m}$ for CdTe and the lower-indium-concentration films. For those with higher-indium concentrations the thickness was about $10 \mu\text{m}$.

We performed photoluminescence (PL) at 77 K and absorption experiments at 77 and 300 K. The absorption experiment was done with chopped white light focused on the monochromator entrance slit using a lens system. On the other hand, PL spectra at 77 K were recorded employing a 15 mW He-Ne laser as the exciting light and a cold-finger cryostat. The luminescence response signal was equally focused in the monochromator. The detection system consisted of a Lomo MDR-23 monochromator equipped with a FEU-62 photomultiplier in its outlet slit. A SR-510 lock-in amplifier connected to a computer received and recorded the electrical response.

III. RESULTS AND DISCUSSION

The x-ray measurements shown in Fig. 1 indicate that a single phase with a cubic structure (α phase) is found for the samples with lower-indium concentration. At low-indium concentration the strain and distortion of the lattices cause structural disorder in the material. This is because of the indium in the cation sites of the cubic structure, which brings about the peak shift as observed in Fig. 1. Such a shift toward higher angles is a result of the lattice contraction.

For the samples with indium concentrations equal to and greater than 12.8 at. %, a peak corresponding to the β phase, which is a solid solution based on CdIn_2Te_4 with a tetragonal

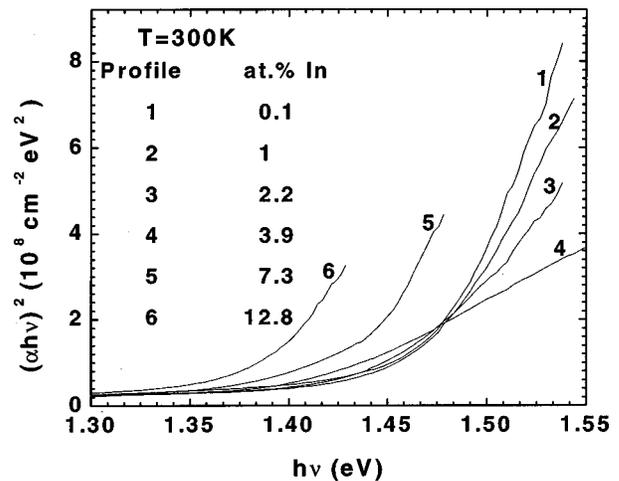


FIG. 2. Absorption profiles of CdInTe samples at 300 K.

structure, begins to be appreciable, and therefore, a mixture of both the α and β phases with different types of lattices takes place.² Thereinafter, the β phase becomes dominant with indium increase as shown in Fig. 1.

Figure 2 shows a plot of the absorption profiles at $T = 300 \text{ K}$. The edge shape varies for low indium concentration, and afterward the edges shift toward low energies. The profiles were corrected by subtraction of the attenuation due to scattering.¹⁰ The edge behavior was observed to be linear in a plotting of $(\alpha h\nu)^2$ vs $h\nu$, where α is the absorption coefficient and $h\nu$ the photon energy. This indicates, as expected in CdTe-like compounds, that the transitions are direct. In spite of the high-indium concentration, the films also contain the CdIn_2Te_4 tetragonal phase with indirect-band-gap energy.³

The variation of E_g for CdInTe films with indium concentrations up to 22 at. % at 77 and 300 K is presented in Fig. 3. The obtained E_g corresponding to CdTe agrees with previous reports^{11,12} for both temperatures. Introducing indium leads to a linear decrease of E_g . The fitting of the dependence of E_g on indium concentration obeys the following expressions:

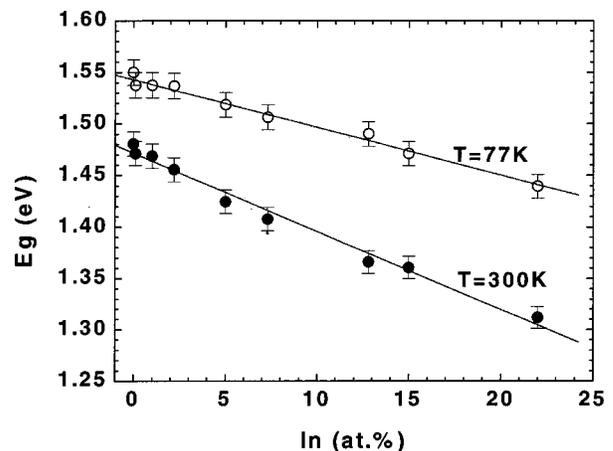


FIG. 3. Behavior of the band-gap energy of CdInTe at 77 and 300 K with the variation of the indium concentration.

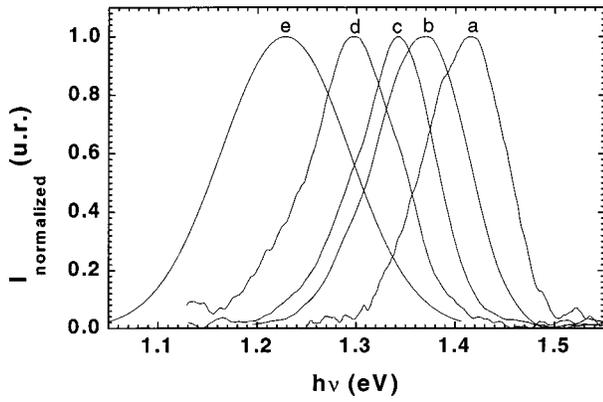


FIG. 4. Normalized 77 K PL spectra corresponding to CdTe (a), and CdInTe with 0.1 (b), 7.3 (c), 12.8 (d), and 22 at. % In (e). Spectrum (e) was smoothed.

$$E_g = 1.472 - 0.00752x, \quad (1)$$

for 300 K, and

$$E_g = 1.549 - 0.00463x, \quad (2)$$

for 77 K, where E_g is given in eV, and x is the indium concentration in the films in at. %.

The difference between E_g at 77 and 300 K indicates that the band-gap temperature coefficient increases as the In concentration increases from $\Delta E_g / \Delta T = -3.5 \times 10^{-4} \text{ eV K}^{-1}$ for CdTe to $-6.2 \times 10^{-4} \text{ eV K}^{-1}$ for films with 22 at. % In, which agrees very well with other values previously reported.^{11,13}

The photoluminescence spectra were constituted of the typical defect band.¹⁴ The energy value of the photoluminescence peaks $E_{\text{PL,max}}$ shifts to lower energies as the indium concentration increases, as shown in Fig. 4. From the difference between the E_g values and the PL peak energy position $E_{\text{PL,max}}$, it is possible to estimate the energy levels that participate in the transition. In Fig. 5 it can be appreciated that the difference is 150 meV for CdTe, which agrees with an acceptor level related to Cd vacancies.^{11,15,16} When indium is

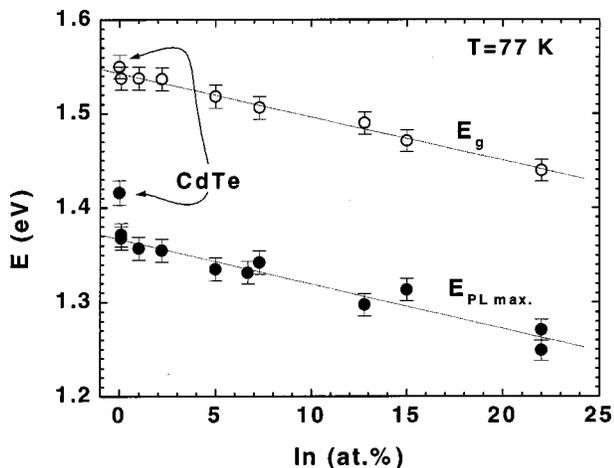


FIG. 5. Behavior of band-gap energy and PL peak energy position as functions of the indium concentration.

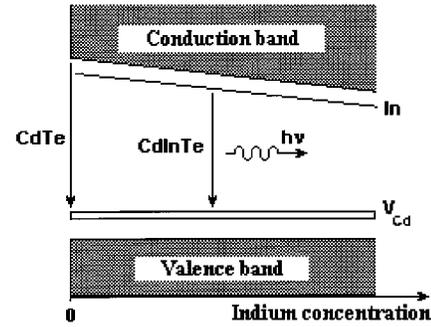


FIG. 6. Schematic behavior of the donor and acceptor energy levels with the variation of the indium concentration.

present the difference sharply increases and reaches a value of about 180 meV. That difference is maintained practically constant from low-indium concentrations until a concentration of 22 at. %, as verified by the behavior of $E_{\text{PL,max}}$ given by

$$E_{\text{PL,max}} = 1.367 - 0.00473x, \quad (3)$$

in which the slope is approximately equal to that of E_g in expression (2). In this fitting CdTe was excluded.

That behavior is attributed to the appearance of a donor level. The presence of this level leading to the PL band could be due to the recombination of donor-acceptor pairs (DAP). The maximum of the DAP band is known to be¹⁷

$$E_{\text{PL,max}} = E_g - (E_D + E_A) + \frac{e^2}{\epsilon_s R}, \quad (4)$$

where E_A is the acceptor ionization energy, ϵ_s the static dielectric constant, and R the mean donor-to-acceptor pair distance. From this expression we estimated that $E_D > 32 \text{ meV}$ below the conduction band, assuming the Coulomb interaction term to be zero. Considering an ionized impurity concentration $N_D \approx 10^{16} \text{ cm}^{-3}$, the Coulomb interaction term is about 4 meV, and $E_D \approx 36 \text{ meV}$. This value of E_D suggests that it is associated with In displaced from the cation vacancy sites of the CdTe lattice. E_D is higher, but consistent with 22 meV reported for this impurity level in Ref. 11, and with 26.4 meV in Ref. 9. Hence, the transitions take place between such a level and the deep acceptor level previously mentioned.¹⁴ The results indicate that the position of both the levels remains constant with respect to their corresponding bands, as is schematically represented in Fig. 6.

A linear dependence of the lattice constant with the indium concentration increase in these samples was previously reported.¹⁸ Combining this result with that of E_g at 300 K in the present work, the relation between the band-gap energy and the lattice parameter of CdInTe for $x \leq 22 \text{ at. %}$ was found, and is presented in Fig. 7. From low-indium concentration it is possible to observe that the E_g variation is monotonically decreasing, but mildly different from the reported linear behavior between CdTe and CdIn₂Te₄ obtained in the CdTe-In₂Te₃ stoichiometric solid solution.^{20,21} That difference is explained from the lack of stoichiometry given by the film growth characteristics. The maximum difference be-

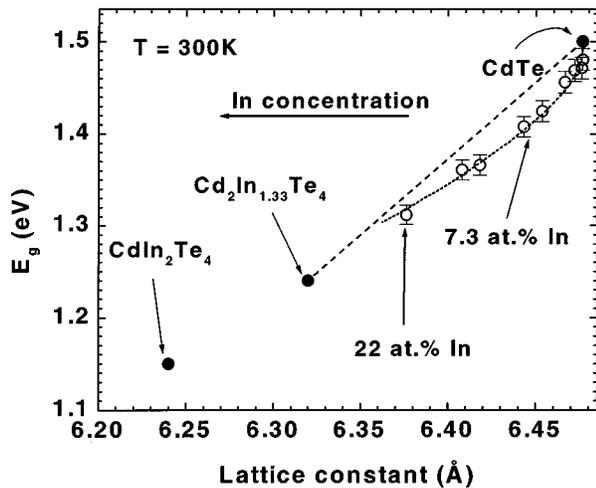


FIG. 7. Relation between the band-gap energy and the lattice constant of CdInTe with different indium concentration.

tween the behavior of our films and the reported one is found for an indium concentration of about 7 at.%, however, for a higher-indium concentration of around and greater than 22 at. % the curve approaches the stoichiometric line indicating a tendency to the stoichiometry of the compound.

IV. CONCLUSIONS

We have measured the indium concentration dependence of band-gap energy and PL of CdInTe thin films grown by CSVT-FE. It was found that E_g diminishes linearly and the band-gap temperature coefficient increases as the indium concentration increases. The acceptor-level position over the top of the valence band is 150 meV for CdTe, but a donor impurity level appears at $E_D > 32$ meV ($E_D \approx 36$ meV) below the bottom of the conduction band associated with the ionization of indium atoms displaced from the Cd vacancy sites in the CdTe lattice, as obtained from comparing E_g and $E_{PL, \max}$ at 77 K. Both levels remain at the same energy distance of the corresponding bands in all the studied ranges of indium concentration. A departure from the line of the CdTe–In₂Te₃ stoichiometric solid solution was found in the relation between E_g and the lattice parameter, but above 22 at. % indium the curve approaches the stoichiometry line as a result of improvement of the compound stoichiometry.

ACKNOWLEDGMENTS

The authors would like to acknowledge R. Sánchez, W. Cauch, and O. Gómez for technical support. Secretarial assistance from C. Simón and L. Pinelo is acknowledged too. One of the authors (A.I.) also thanks CICATA–IPN for the financial support for visiting the Laboratory of Preparation and Characterization of New Materials at CINVESTAV–IPN, Merida Unit.

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