

SEM, EDS, PL and absorbance study of CdTe thin films grown by CSS method

M.E. Hernández-Torres^a, R. Silva-González^a,
G. Casarrubias-Segura^b, J.M. Gracia-Jiménez^{a,*}

^a*Instituto de Física, BUAP, Apdo. Postal J-48, San Manuel, 72570 Puebla, Pue., Mexico*

^b*CIE- UNAM, 62580 Temixco, Morelos, Mexico*

Available online 18 April 2006

Abstract

Oxygen-doped CdTe films were grown on conducting glass substrates by the close spaced sublimation (CSS) method and characterized using SEM, EDS, photoluminescence (PL) and absorbance. A significant change in the polycrystalline morphology is observed when the oxygen proportion is increased in the deposition atmosphere. The EDS analysis showed that all samples are nonstoichiometric with excess Te. The PL spectra show emission bands associated with Te vacancies (V_{Te}), whose intensities decrease as the oxygen proportion in the CSS chamber is increased. The oxygen impurities occupy Te vacancies and modify the surfaces states, improving the nonradiative process.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Cdte; CSS; Morphology; Photoluminescence

1. Introduction

CdTe in the form of thin film is important due to its technological applications; in particular as the absorber layer in solar cells [1–10]. However, the optical properties of CdTe can be modified due to the presence of impurities in the material. For instance, it has been observed that a small quantity of oxygen decreases the resistivity of CdTe films, whereas high concentrations of oxygen increase the resistivity of the films up to 6 orders of magnitude [11]. Diverse growth methods have been used to obtain CdTe thin films,

*Corresponding author.

E-mail address: gracia@sirio.ifuap.buap.mx (J.M. Gracia-Jiménez).

nevertheless, the CdTe solar cells with higher efficiency have been produced using the close spaced sublimation (CSS) method [12–14]. Besides that, this technique allows the introduction of oxygen in the material in a very simple and controllable way [15]. In this work, we study a set of oxygen-doped CdTe thin films grown by the CSS method and characterized by the techniques: scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), photoluminescence (PL) and absorbance.

2. Experimental

CdTe films were prepared by CSS on conducting glass substrates with the following deposition conditions: pressure (5 mbar), source temperature (600 °C), substrate temperature (550 °C), and with different proportions of the carrier gas (O₂:He): 0:5, 1:4, 2:3 and 3:2. The SEM and EDS characterizations were performed with a JEOL (JSM-5400LV) system coupled with a Noran spectrometer. For the PL analysis, the samples were placed in a cryogenic refrigerator and the spectra were recorded in the temperature range 6.5–160 K. The sample was excited with the 488 nm line of an Ar laser. A SPEX 1000 M monochromator with ± 1 meV resolution was used for the spectral analysis. A GaAs photomultiplier was used for signal detection and the data were processed using a DATA-SCAN computer-controlled system. The absorption spectra were measured at room temperature using an IR interferometer BRUKER-EQUINOX 55.

3. Results and discussion

The SEM images of the films deposited with different O₂:He ratios are shown in Fig. 1. It is very clear that the grain size has a significant dependence on O₂, as the O₂ partial pressure increases the grain size decreases. The films grown in the absence of O₂ show a terraced morphology for the grains [16,17]. This type of morphology disappears when the oxygen concentration is increased in the deposition chamber. Grain sizes in the range from 0.8 to 7 μ m were measured. The smaller grain sizes were observed in the sample grown with the highest oxygen proportion in the CSS chamber.

The EDS analysis showed that all samples are nearly nonstoichiometric with excess Te (see Table 1). The stoichiometry changes presented by all CdTe films are due to the nature of the CSS growth process, since the sublimation is nonhomogeneous [18]. Due to the resolution of the EDS system, O₂ could not be detected in the films when the oxygen proportion was higher in the deposition system, which is indicative of the very low O₂ concentrations present in the films. However, as it will be observed in the next paragraphs, O₂ manifests itself in the PL results.

Fig. 2 shows the PL spectra of the samples at 6.5 K with maximum excitation intensity. Two lines (A and A') at 1.583 and 1.573 eV, respectively, and a PL band (B) in the low-energy region are observed in the spectra. As can be seen, the line A exhibits shoulders in the low-energy region for the samples with no oxygen and with the lowest oxygen proportion in the chamber, which correspond to the line A' in the films with higher oxygen concentrations. For the samples in which the oxygen proportion in the chamber was 2:3 and 3:2, the line A disappears and only line A' is observed. As the oxygen concentration is increased, the full-width at half-maximum (FWHM) of the band B decreases since the emission of its shoulder disappears. Besides that, an abrupt reduction of the emission intensity of all lines is observed and the relative intensity of the lines reverses. With the

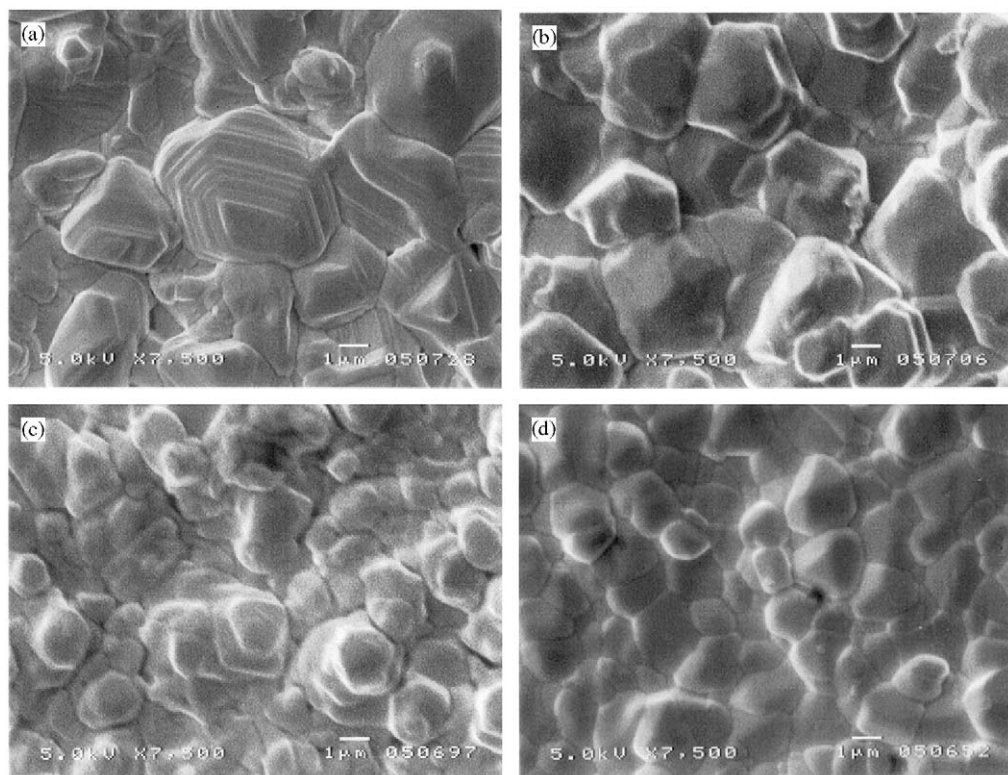


Fig. 1. Characteristic surface morphology of the CdTe films grown by the CSS technique by increasing the oxygen proportion in the carrier gas ($O_2:He_2$): (a) 0:5, (b) 1:4, (c) 2:3 and (d) 3:2.

Table 1

EDS atomic percentages of Cd and Te of the CdTe films grown with different oxygen proportions in the carrier gas

Sample	$O_2:He_2$	Cd (at%)	Te (at%)
GC0	0:5	47.53	52.47
GC1	1:4	47.56	52.44
GC2	2:3	46.63	53.37
GC3	3:2	46.30	53.70

purpose to define the lines associated with the shoulders observed in the line A and in the band B, a PL study by varying the temperature and excitation intensity was carried out.

The evolution of the peak positions of A and A' lines, as well as for the B band for all samples upon varying the measurement temperatures (keeping excitation constant) is shown in Fig. 3. The energy values corresponding to the peak positions of the A and A' lines diminish smoothly as the temperature is increased. However, the band B presents an irregular behavior characteristic of the overlapping of several lines competing for the dominance. Furthermore, it is observed that the presence of the lines is strongly influenced

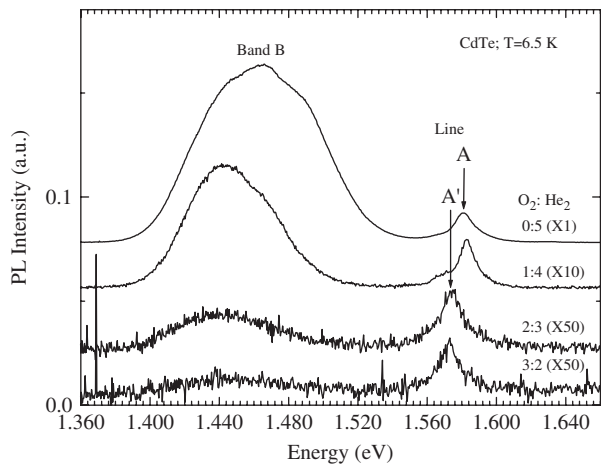


Fig. 2. Photoluminescence spectra of CdTe films at 6.5 K and maximum excitation intensity.

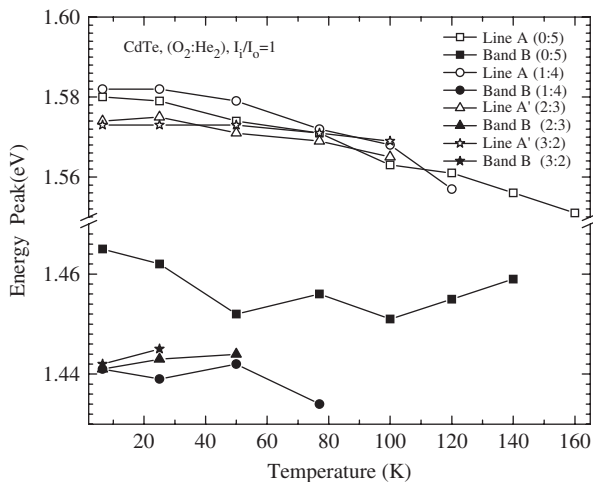


Fig. 3. Evolution of the peaks by varying the measurement temperatures. The continuum lines are for visual purpose.

by the oxygen concentration: as the oxygen concentration is increased, the temperature range for the observation of the lines gets reduced. This effect is stronger for the band B.

Fig. 4 presents the evolution of the peak intensities versus T^{-1} ($1000/T$). For the samples without oxygen and with the lowest oxygen proportion, the relative intensity between the line A and the band B reverses as the temperature is increased. At low temperatures, the band B dominates, whereas at high temperatures the line A dominates. For the other two samples, the line A' dominates for all temperatures values. As can be observed, the O₂ concentration has greater influence on the line A and on the band B than on the line A'.

PL spectra at 6.5 K with varying excitation intensity for the samples with an oxygen proportion of 0:5 and 1:4 are shown in Fig. 5. A slight shift to high-energy side

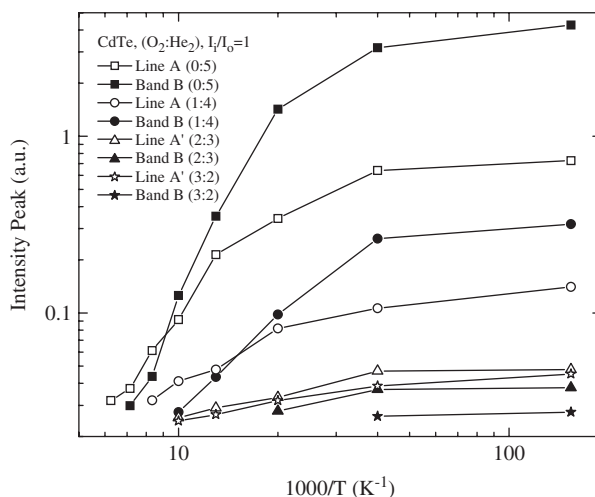


Fig. 4. Evolution of the peaks intensities versus T^{-1} . The continuum lines are for visual purpose.

for the peak positions of the lines A and A' and the subsequent vanishing can be clearly observed as the excitation intensity is decreased. This shifting is due to the overlapping of the A and A' lines and to the saturation effect of the radiative centers as the excitation intensity is increased. The more noticeable feature in Fig. 5a is not only the shifting of the band B to high energy but also its structure conformed by three peaks, while for the sample with the lowest oxygen concentration it is not the case (see Fig. 5b). This observation discards the possibility to associate the A, A' lines and band B with a donor–acceptor transition because it is well known that in this type of transitions, the energetic peaks positions shift to higher energies when the excitation intensity is increased. However, the band B in the sample with an oxygen proportion 1:4 in the chamber (see Fig. 5b) has a behavior that could be associated to a donor–acceptor transition.

According to the behavior shown by the A and A' lines and their position with respect to the energy band gap (1.601 eV at 0 K), we can infer that both lines correspond to impurity-band (IB) or band-impurity (BI) transitions. Considering the peak position of the line A (23 meV) from the energy band gap, this can be assigned to a donor–valence band transition, where the donor is associated to a Te vacancy (V_{Te}^+) [19–21]. Then, as the oxygen concentration is increased, the V_{Te}^+ are gradually occupied by O_2 and consequently the line associated to the IB transition decreases. The position of the A' line is in good agreement with the energy value of 1.575 eV for the transition IB or BI reported by Espinosa et al. [22]. However, the impurity has not been identified. The increment of the oxygen concentration does not have a direct effect on this line (like it does to the A line); nevertheless, a decrease in its intensity is associated to the deterioration of the surface morphology when the oxygen concentration is increased as it is observed by SEM.

The B band conformed by the lines at 1.400, 1.473 and 1.491 eV is associated to a band due to surface defects. This indicates that impurities and defects dominate the CdTe surface and generate donor–acceptor pairs, IB and BI transitions as well as their respective

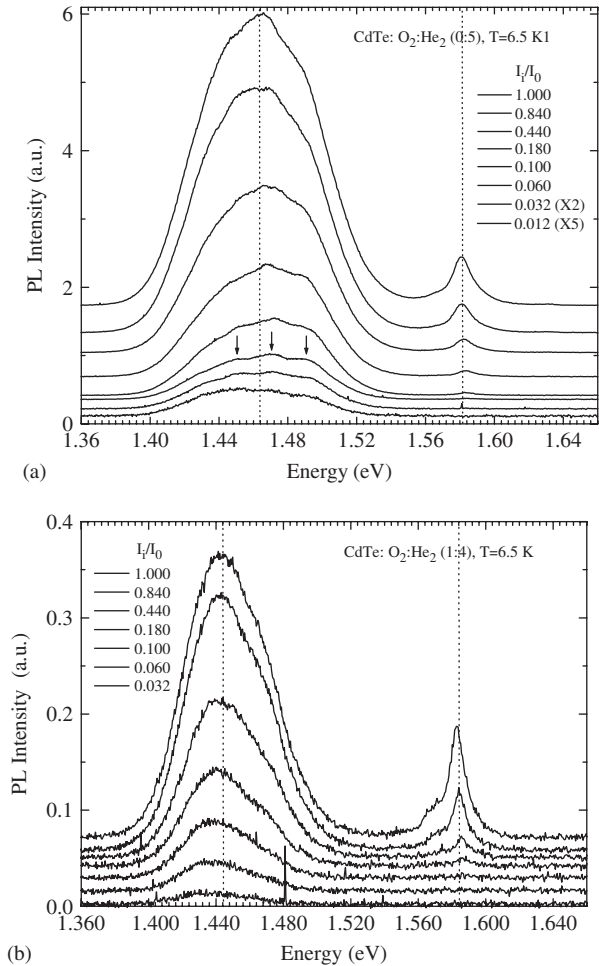


Fig. 5. Deconvolution of spectra for samples in the chamber with an oxygen proportion of (a) 0:5 and (b) 1:4.

phonon transitions [23]. We infer that the increment in oxygen concentration not only modifies the surface morphology but also disturbs the emission intensity of the surface defects. This effect is probably due to the generation of nonradiative defects produced by the oxygen concentration, which are competing for the dominance with more efficiency than the radiative processes.

The optical energy band gap values determined from the absorption spectra are 1.483, 1.484, 1.482 and 1.485 eV for the O₂:He proportions 0:5, 1:4, 2:3 and 3:2, respectively. These E_g values are greater than 1.450 eV of the CdTe bulk, however comparable with the values reported for electrodeposited CdTe thin films [24]. These differences can be explained by considering that the bottom of the conduction band is partially filled with electrons that belong to impurity atoms, which have been thermally excited. As can be seen, there is not a clear relationship between the optical energy band gap and the oxygen concentration.

Conclusion

The CdTe films were grown by the CSS method by varying the O₂ partial pressure in the CSS chamber. The oxygen impurities in the CdTe films produce changes in the surface morphology and in the photoluminescence. The oxygen impurities occupy Te sites and modify the surface states improving the nonradiative processes.

Acknowledgements

This work was partially supported by VIEP-BUAP (Project II59-04/EXC/G and I0/G/EXC/05) and CONACyT: No. 36047-E. The work carried out at CIE-UNAM was supported by the CONACyT projects SEP-2004-C01-47587, 38542-U and G38618-U. One of the authors (M.E. Hernández-Torres) acknowledges CONACyT and VIEP-BUAP (I0/G/EXC/05) for scholarship.

References

- [1] X. Wu, J.C. Keane, R.H. Dhere, C. DeHart, D.S. Albin, A. Duda, T.A. Gessert, S. Asher, D.H. Levi, P. Sheldon, in: *Proceedings of the 17th European PVSEC*, Munich, Germany, 2001, pp. 995–1000.
- [2] L. Feng, J. Zhang, B. Li, W. Cai, Y. Cai, L. Wu, W. Li, J. Zheng, Q. Yan, G. Xia and D. Cai, *Thin Solid Films* (2005).
- [3] X. Mathew, G.W. Thompson, V.P. Singh, J.C. McClure, S. Velumani, N.R. Mathews, P.J. Sebastián, *Sol. Energy Mater. Sol. Cells* 76 (2003) 293.
- [4] X. Mathew, J.P. Enriquez, A. Romeo, A.N. Tiwari, *Sol. Energy* 77 (2004) 831.
- [5] J.P. Enriquez, X. Mathew, G.P. Hernandez, U. Pal, C. Magaña, D.R. Acosta, R. Guardian, J.A. Toledo, G.C. Puente, J.A.C. Carvayar, *Sol. Energy Mater. Sol. Cells* 82 (2004) 307.
- [6] X. Mathew, J.P. Enriquez, G. Casarrubias Segura, A. Sanchez-Juarez, U. Pal, G.C. Puente, D.R. Acosta, C.R. Magaña, in: *Proceedings of the 31st IEEE Photovoltaic Specialist Conference*, 3–7 January 2005, Orlando, Florida.
- [7] X. Mathew, *Semicond. Sci. Technol.* 18 (2003) 1.
- [8] D.L. Linam, V.P. Singh, J.C. McClure, G.B. Lush, X. Mathew, P.J. Sebastian, *Sol. Energy Mater. Sol. Cells* 70 (2001) 335.
- [9] X. Mathew, J.P. Enriquez, *Sol. Energy Mater. Sol. Cells* 63 (2000) 347.
- [10] X. Mathew, *J. Phys. D: Appl. Phys.* 33 (2000) 1565.
- [11] V. Valdna, *Sol. Energy Mater. Sol. Cells* 87 (2005) 369.
- [12] T.L. Chu, S.S. Chu, *Solid State Electron.* 38 (1995) 533.
- [13] R.W. Birkmire, in: *Proceedings of 26th IEEE PVSC*, Anaheim, CA, USA, September 29–October 3, 1997, p. 295.
- [14] H.R. Moutinho, F.S. Hasoon, F. Abulfotuh, L.L. Kazmerski, *J. Vac. Sci. Technol. A Vac. Surf. Films* 13 (1995) 2877.
- [15] G.P. Hernandez, X. Mathew, J.P. Enriquez, B.E. Morales, M.M. Lira, J.A. Toledo, A.S. Juarez, J. Campos, *J. Mater. Sci.* 39 (2004) 1515.
- [16] X. Mathew, J.R. Arizmendi, J. Campos, P.J. Sebastián, N.R. Mathews, C.R. Jiménez, M.G. Jiménez, R. Silva-González, M.E. Hernández Torres, R. Dhere, *Sol. Energy Mater. Sol. Cells* 70 (2001) 379.
- [17] C. Ricárdez-Jiménez, *Characterization of CdTe thin films electrodeposited and sublimed over metallic layers*. Master Thesis, Physics Institute, University of Puebla, 2002, p. 37.
- [18] R. Loebel, *Handbook of Chemistry and Physics*, 66th ed., CRC Press, Boca Raton, FL, 1985–1986, pp. 230–233.
- [19] K. Zanio, *Semiconductors and Semimetals*, vol. 13, Academic Press, 1978, p. 135.
- [20] X. Mathew, *Sol. Energy Mater. Sol. Cells* 76 (2003) 225.
- [21] X. Mathew, N.R. Mathews, P.J. Sebastian, C.O. Flores, *Sol. Energy Mater. Sol. Cells* 81 (2004) 397.
- [22] J.E. Espinosa, J.M. Gracia, H. Navarro, A. Zehe, *J. Lumin.* 28 (1983) 163.
- [23] T.H. Myers, J.F. Schetzina, S.T. Edwards, A.F. Schreiner, *J. Appl. Phys.* 54 (1983) 4232.
- [24] X. Mathew, *J. Mater. Sci. Lett.* 21 (2002) 529.