

Compounds of the CdTe–In₂Te₃ system in CdTe–In film grown by the close-spaced vapor transport technique combined with free evaporation

M. P. Hernández^{a)} and A. Iribarren
IMRE, University of Havana, 10400 Vedado, La Habana, Cuba

M. Zapata Torres
CICATA-IPN, Legaria 294 Col. Irrigación, 11500 México, D. F.

P. Bartolo,^{b)} V. Sosa, and J. L. Peña
Applied Physics Department, CINVESTAV-IPN, Unidad Mérida, 97310, Mérida, Yuc., México

(Received 20 January 1999; accepted 19 November 1999)

Polycrystalline thin films of CdTe–In were grown by the close-spaced vapor transport technique combined with free evaporation of In. The indium concentration in the samples increased according to the rise in temperature of the In source. X-ray diffraction analysis allowed us to identify the CdTe (α) phase in all samples, together with the CdIn₂Te₄ (β) phase in the samples grown at the highest temperatures of the In source. Auger electron spectroscopy was used to quantify the chemical composition of the films. The sensitivity factors were calculated assuming that the solid solution (CdTe)_{1-x}(In₂Te₃)_x was formed. For samples of low In concentration, the lattice parameter decreased linearly with the molar percent of In₂Te₃ in CdTe. This behavior corroborated the presence of the solid solution. © 2000 American Vacuum Society. [S0734-2101(00)01902-3]

I. INTRODUCTION

The pseudobinary system CdTe–In₂Te₃ is of interest since all compounds formed by mixing CdTe and In₂Te₃ are semiconductors.¹ O’Kane *et al.*² report semiconducting properties of these compounds which were verified by electrical conductivity measurements. Particularly, the ternary compound CdIn₂Te₄, which is a *p*-type semiconductor² with indirect band gap^{3,4} has recently been regarded as a potential electro-optical material for applications in the infrared region.⁴

The phase diagram of the CdTe–In₂Te₃ system has been described by Thomassen *et al.*⁵ In this system, the α and β phases are the compounds CdTe and CdIn₂Te₄, respectively. The CdTe has a zincblende structure with lattice parameter $a = 6.481$ Å,⁶ or $a = 6.488$ Å.⁵ As In₂Te₃ is added to the solid solution, the lattice parameter is decreased.⁵ The ternary compound CdIn₂Te₄ has tetragonal structure with $a = c/2 = 6.23$ Å (Ref. 3) and it has been found by Riedel *et al.*⁷ that it belongs to the $I\bar{4}2m$ space group.

Single crystals of the α -CdTe and β -CdIn₂Te₄ phases have been obtained from high-purity elements, Cd, In and Te by different methods. Iwamura⁸ has produced them by the Bridgman method. β -CdIn₂Te₄ has been grown by Jean *et al.*^{3,4} using the Bridgman–Stockbarger method. Thomassen *et al.*⁵ described a method where stoichiometric amounts of the elements were weighed and sealed into clear fused silica ampoules evacuated to a pressure below 10^{-4} Torr. Thereafter, the fusions were carried out through a programmed nonlinear heating cycle over a period of several

hours. In all cases these compounds were fabricated in the form of ingots.

The close-spaced vapor transport technique combined with free evaporation (CSVTE-FE) was used for doping semiconductor thin films.^{9,10} This technique is an auxiliary evaporation source of dopant in conjunction with CSVTE. The atoms of the evaporated dopant into the CSVTE deposition chamber are introduced by a threaded hole in the center of the graphite source block. A source boat for dopant evaporation is below this smaller hole. Castro *et al.*^{9,10} applied it to grow indium doped CdTe films. However a high In content did not meaningfully improve the electrical properties, therefore it was necessary to study the formation of compounds as a possible cause of this behavior.

The aim of this work is to show the formation of the solid solution (CdTe)_{1-x}(In₂Te₃)_x and the ternary compound CdIn₂Te₄ in the CdTe–In polycrystalline films obtained by CSVTE-FE developed by Castro *et al.*^{9,10}

II. EXPERIMENT

The samples were prepared by CSVTE-FE at a base pressure of 10^{-5} Torr. The raw materials were CdTe powder 99.99 at. % and In 99.999 at. % purity from Balzers. Corning 7059 glass slides were used as substrates. The CdTe source temperature T_{CdTe} was maintained at 600 °C during the growth procedure, while the In source temperature T_{In} was varied between 500 and 750 °C to achieve different In concentrations in the films.⁹ The temperature of the substrate T_{sub} was fixed at 400 °C.

X-ray diffraction (XRD) analysis was used to recognize the structural phases, and obtain the lattice parameters. X-ray diffractograms were made with a Siemens D5000 diffractometer, using the $\text{CuK}\alpha$, radiation with $\lambda = 1.5405$ Å.

^{a)} Author to whom correspondence should be addressed; electronic mail: led@ff.oc.uh.cu

^{b)} In postdoctoral stay in CCMC-UNAM.

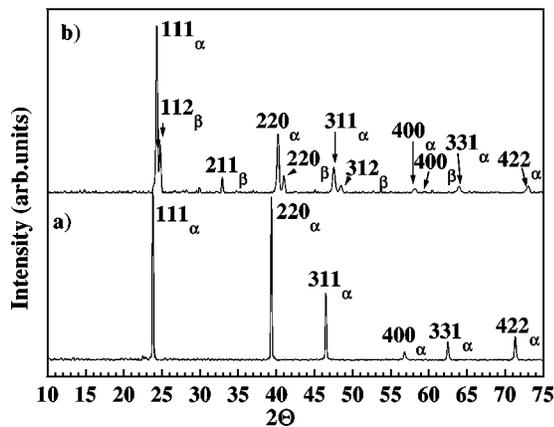


FIG. 1. XRD measurements of the films of the CdTe-In: (a) $T_{In}=500\text{ }^{\circ}\text{C}$, (b) $T_{In}=750\text{ }^{\circ}\text{C}$.

Auger electron spectroscopy (AES) analysis was performed in a Perkin-Elmer PHI 560/ESCA-SAM system equipped with a double-pass cylindrical mirror analyzer, with a base pressure of approximately 2×10^{-9} Torr. A 3 keV electron beam with a typical $0.2\text{ }\mu\text{A}$ current incident at 45° to the surface normal was used. Prior cleaning of the surface was done with Ar^+ sputtering with a beam energy of 4 keV and beam current of $0.36\text{ }\mu\text{A}/\text{cm}^2$, yielding a sputtering rate of about 8–10 nm/min.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of two polycrystalline films corresponding to different In contents, whose T_{In} were 500 and 750 $^{\circ}\text{C}$, respectively. Figure 1(a) represents the XRD spectrum of the α phase. Figure 1(b) shows the corresponding peaks of α phase, which are accompanied by a precipitate recognized as β phase. The α -phase peaks of Fig. 1(b) have a shift toward greater Bragg angles with respect to the α -phase peaks of Fig. 1(a).

As a result, the XRD patterns allowed us to demonstrate the existence of CdTe and CdIn₂Te₄ compounds. The latter appears together with the α phase at In source temperatures of 750 $^{\circ}\text{C}$. In addition, a shift of peak for the α phase toward greater Bragg angles was observed, which indicated that the lattice parameter changes with In content.

The behavior observed in the diffractograms establishes that the current phases in these films can be described by the system CdTe–In₂Te₃. For this reason, the variation of the lattice parameter with the mol % In₂Te₃ in CdTe of these films and Vegard's law of the solid solution of In₂Te₃ in CdTe were necessary to compare them. The relationship between the lattice parameter and the mol % In₂Te₃ in CdTe was found through Vegard's law of the solid solution of In₂Te₃ in Cd₃Te₃ reported by Thomassen *et al.*^{5,8} Consequently, the dependence of the lattice parameter as a function of the mol % In₂Te₃ in CdTe was obtained. The analysis of this curve led us to conclude that the lattice parameter varies in a linear manner according to Vegard's law for values lower than 5 mol % In₂Te₃ in CdTe. This result confirms that

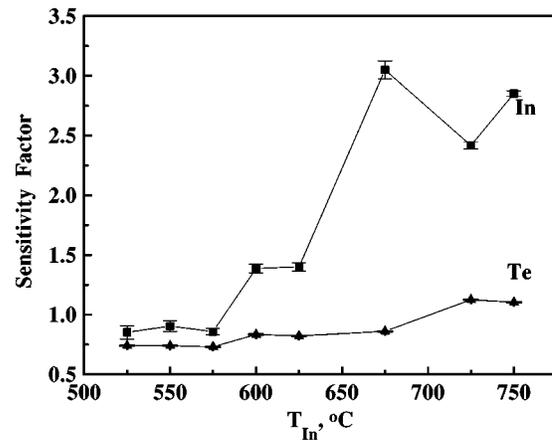


FIG. 2. Sensitivity factors of In and Te from each film.

a solid solution of $(\text{CdTe})_{1-x}(\text{In}_2\text{Te}_3)_x$ exists as reported by Thomassen *et al.*⁵ The resultant linear fit is as follows:

$$M_{\text{calc}} = 647.5 - 99.89a; \quad M_{\text{calc}} < 5, \quad (1)$$

where M_{calc} is the mol % In₂Te₃ in CdTe in the solid solution. M_{calc} for each sample was calculated by inserting the lattice parameter value for each one in expression (1). The lattice parameter was obtained from the XRD patterns considering a zincblende structure for CdTe.

The atomic concentration of Cd, In, and Te for each sample was calculated from M_{calc} . These values, thus achieved, together with the Auger spectra, allowed us to obtain the sensitivity factor of the In and Te, presuming that the sensitivity factor for Cd was equal to the unit.

If we take into account that there is no change in the chemical environment, that the analyzers used for all spectra have the same resolution, and that for all cases the same modulation is used, then the sensitivity factors for each element must have the same value in the different samples.¹¹ The first restriction is perfectly valid because the peak shapes in the Auger spectra are the same for all films.¹² The second and third restrictions are satisfied because the Auger spectra were obtained in the same experimental setup. Consequently, the sensitivity factor of In and Te made it possible to distinguish the film where the solid solution was present as a single phase.

The sensitivity factors of In and Te with respect to the In source temperature for each film are represented in Fig. 2. In it, it can be verified that the sensitivity factor for both compounds remains constant in the grown films with a T_{In} of 525–575 $^{\circ}\text{C}$, meaning that the calculated atomic concentration is correct and, the chemical composition of the films is the solid solution of the $(\text{CdTe})_{1-x}(\text{In}_2\text{Te}_3)_x$ type. On the other hand, it can be observed that the rest of the samples have different values of the sensitivity factor for both elements. This behavior indicates that the calculated atomic concentration is not appropriate and therefore it couldn't be confirmed that the solid solution is an only phase in those films.

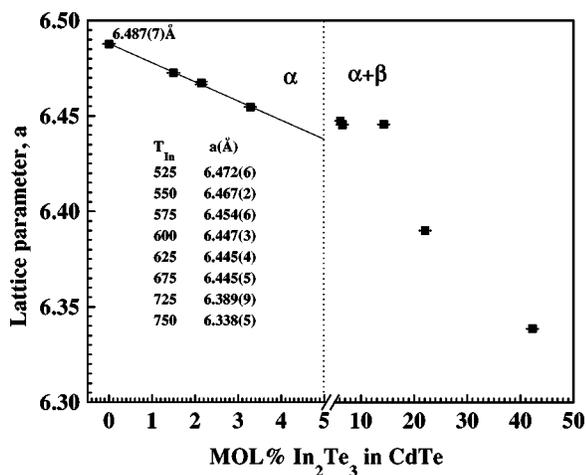


FIG. 3. mol % In₂Te₃ in CdTe dependence of the lattice parameter.

The appropriated value of the atomic concentration of Cd, In, and Te as well as the mol % In₂Te₃ in CdTe for each sample was found using the sensitivity factors of In and Te corresponding to the films of the solid solution. Figure 3 shows the lattice parameter for each film associated with the corresponding mol % In₂Te₃ in CdTe and a point for a pure CdTe films whose $a = 6.487$ Å. Linear behavior can be observed for the region below 5 mol %, which establishes that the samples whose T_{In} are between 525 and 575 °C (1.50–3.29 mol % In₂Te₃ in CdTe) is a solid solution of the (CdTe)_{1-x}(In₂Te₃)_x type. The expression of the linear relation obtained here and Eq. (1) are the same. This result was expected because the sensitivity factors were found from the atomic concentration of Eq. (1). From the rest of the data, higher values of molar percent and of the lattice parameter can be seen, which do not correspond to the relationship between both parameters established for the solid solution.

The behavior observed in the films whose T_{In} meets between 600 and 725 °C (6.09–22.08 mol % In₂Te₃ in CdTe) is caused by the formation of the β phase, which is not distinguished in the diffractograms. The explanation given to this behavior is that there is a region of transition between α and β phases, where the content of the α phase decreases as that of the β phase increases according to the rise in content of In. This can be concluded since it has been previously proven that a solid solution exists for low In content, and a precipitate CdIn₂Te₄ together with the solid solution exists for high In content, particularly for $T_{In} = 750$ °C (42.27 mol % In₂Te₃ in CdTe) which is attained in the diffractograms where the peaks for α and β phases are separated.

IV. CONCLUSIONS

The use of both techniques, XRD measurements and AES, allowed us to demonstrate that in polycrystalline films of CdTe–In grown by CSVT-FE there are compounds of the pseudobinary diagram CdTe–In₂Te₃.

With the help of XRD measurements it was possible to determine the current phases present in the films and to obtain the lattice parameter dependence on the In content. The behavior sensitivity factor for each film made it possible to determinate the presence of a (CdTe)_{1-x}(In₂Te₃)_x type solid solution. The relationship between the lattice parameter and the mol % is linear for values between 1.50% and 3.29% mol In₂Te₃ in CdTe. The behavior for more than 5 mol % In₂Te₃ in CdTe is different due to the formation of the CdIn₂Te₄ precipitates.

The technique CSVT-FE must be used carefully for doping semiconductor thin films because In is consumed by formation of the compounds of the CdTe–In₂Te₃ system.

ACKNOWLEDGMENTS

The authors would like to thank Ing. Wilian Cauich and Ing. F. Caballero for help with the AES and XRD measurements, respectively. They also wish to thank A. Martel, C. F. Alonso, and A. Gutiérrez for useful discussions and for proofreading the manuscript. P.B. acknowledges the financial support of CONACYT.

¹D. R. Mason and D. F. O’Kane, *Proceedings of the International Conference on Semiconductor Physics*, Prague, 1960 (Czechoslovak Academy of Science, Prague, 1961), p. 1025.

²D. F. O’Kane and D. R. Mason, *J. Electrochem. Soc.* **110**, 1132 (1963).

³G. Couturier, B. Jean, J. F. Lambert, J. C. Launay, and P. Joffre, *J. Appl. Phys.* **73**, 1813 (1993).

⁴G. Couturier, B. Jean, J. F. Lambert, and P. Joffre, *Mater. Sci. Eng., B* **21**, 333 (1993).

⁵L. Thomassen, D. R. Mason, G. D. Rose, J. C. Sarace, and G. A. Schmitt, *J. Electrochem. Soc.* **110**, 1127 (1963).

⁶International Center for Diffraction Data, ICDD, JCPDS (1997).

⁷V. Riedel, H. Neumann, V. Krämer, and M. Kittel, *Solid State Commun.* **78**, 211 (1991).

⁸Y. Iwamura, *Jpn. J. Appl. Phys.* **16**, 1489 (1977).

⁹R. Castro-Rodríguez and J. L. Peña, *J. Vac. Sci. Technol. A* **11**, 730 (1993).

¹⁰R. Castro-Rodríguez, M. Zapata-Torres, A. Zapata-Navarro, A. I. Oliva, and J. L. Peña, *J. Appl. Phys.* **79**, 184 (1996).

¹¹*Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, edited by D. Biggs and M. P. Seah Jhon (Wiley, New York, 1983), p. 193.

¹²M. Zapata-Torres, Doctoral thesis, CINVESTAV-Mérida, 1995.