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$(CdTe)_{1-x}(In_2Te_3)_x$ pseudo-binary in polycrystalline CdTe–In films

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Abstract

Polycrystalline CdTe–In films were prepared using close-spaced vapor transport technique combined with free evaporation (CSVT-FE), and the stoichiometry and structural properties were investigated. Auger electron spectroscopy (AES) was used to quantify the stoichiometry of the indium concentration in the films which increased according to the rise of temperature of the In source. X-Ray diffraction analysis allowed to identify the CdTe (α-phase) in all films, together with the $CdIn_2Te_4$ (β-phase) in the films grown at the highest temperatures of the In source. For low In concentration films, the lattice parameter decreased linearly with the molar percent of In_2Te_3 in CdTe (below 5 mol%). This behavior corroborated the presence of the solid solution. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The solid solution system $(CdTe)_{1-x}(In_2Te_3)_x$ is of interest since all compounds formed by mixing CdTe and In_2Te_3 are semiconductors [1]. O'Kane et al. [2] report semiconducting properties of these compounds which were verified by electrical conductivity measurements. Several ternary compounds from this solid solution system have been reported from the In_2Te_3 added in solid solution into the CdTe structure [3]: β-phase with a chalcopyrite-like structure and $x = 0.42–0.72$ is a very wide phase field to call it CIT, $CdIn_8Te_{13}$ (δ-phase) with a cubic structure at $x = 0.8$, and $CdIn_{30}Te_{46}$ (γ-phase) with a cubic structure at approximately $x = 0.94$. Particularly, the ternary compound $CdIn_2Te_4$ ($x = 0.5$) which is a p-type semiconductor with an indirect band gap [4,5], has recently been regarded as a potential electro-optical material for application in the infrared region. Recently, many efforts have been made on growing the solid solution $(CdTe)_{1-x}$ $(In_2Te_3)_x$ and the CIT compound. All the techniques used for obtaining these compounds have been limited to the bulk materials [6–9], and only a few theoretical and experimental studies on these materials have been performed due to problems encountered in the growth techniques [9]. The close-spaced vapor transport technique combined with free evaporation (CSVT-FE) has been employed to grow *n*-type In-doped CdTe films [10–12]. This technique is a convenient method for growing solid solution and ternary compounds because it is possible to control the temperatures of different materials separately. It is also cost-effective as it can operate at atmospheric pressure under inert gas and uses moderate temperatures; its operation is simple, and the

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films are compact with few voids and nearly theoretical density. Our goal in this work is to show the formation of the solid solution $(CdTe)_{1-x}(In_2Te_3)_x$ and its structural transition at the CIT compound during the growth of polycrystalline CdTe–In films from this technique. In order to identify these compounds, we used as a reference the relationship between the lattice parameter and the mol% of In_2Te_3 into CdTe in the solid solution of CdTe–In_2Te_3 reported by Thomassen et al. [3] and Iwamura [13].

2. Experimental details

All the films were prepared in a conventional vacuum evaporation system evacuated by an oil-diffusion pump with a liquid nitrogen trap, capable of obtaining a background pressure of 10^{-6} torr. The pressure during evaporation was below 10^{-5} torr. To obtain the pseudo-binary films we used the technique previously reported by Castro et al. [10] consisting of CSVT combined with free evaporation (CSVT-FE), using In metallic as an evaporation source. Fig. 1 shows a schematic view of the system. In our experiments we used high-purity In (Cerac 99.999 at.%) and CdTe (Balzers 99.999 at.%). The substrates used were 7059 Corning glass slides. The substrate temperature (T_1) was kept at 400°C; the CdTe source temperature (T_2) was maintained at 600°C and the In source temperature (T_3) ranged between 500 and 775°C to achieve different In concentrations in the films. The deposition time and temperatures were controlled by a high performance control system [14]. The growing time of the films was 5 min. The boats used as CdTe and In containers and the block that held the substrate was made from high-density graphite. A 6-mm diameter ceramic ring was introduced into the graphite block of the CdTe source. The function of the ceramic ring was to guide the atoms of the evaporated metallic In and to introduce them into the container. The distance between the In source and the substrate was 8 mm. X-Ray diffraction analysis was used to recognize the structural phase and obtain the lattice parameters. The measurements were performed with a Siemens D5000 diffractometer with a CuKα radiation anode ($\lambda = 1.5405$ Å) operating at 40 kV and 35 mA. Elemental composition was determined by X-ray photoelectron spectroscopy (XPS) using a Perkin-Elmer PHI-560 ESCA-SAM with an Al anode (1486.6 eV) and a double pass cylindrical mirror analyzer, with a base pressure of $\sim 2 \times 10^{-9}$ torr. A 3-keV electron with a typical 0.2-μA current incident at 45° to the surface normal was used. Before analysis, samples were cleaned by immersion for 30 s in 3% methanol bromine solution, and the measurements of elemental composition were obtained after 2 min. of Ar^+ sputtering on an area of 5×5 mm².

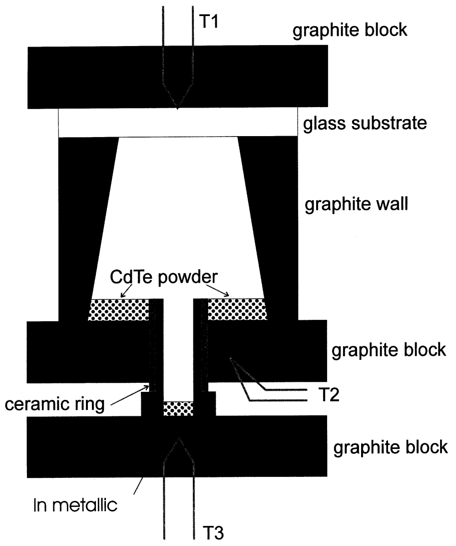

Fig. 1. Schematic view of the system chamber used for CSVT technique combined with free evaporation.

3. Results and discussion

The entire surface of the films was smooth, and adhered firmly to the substrate. Fig. 2a,b shows the X-ray diffraction patterns of two polycrystalline films corresponding to different In contents, where In source temperature was 500 and 775°C, respectively. Fig. 2b represents the X-ray diffraction spectrum of the α-phase, and Fig. 2a shows the corresponding peak of the α-phase accompanied by a precipitate recognized as β-phase. The α-phase peaks of Fig. 2a have a shift towards greater Bragg angles respective to the α-phase peaks of Fig. 2b. Fig. 3 corresponds to the overlapping diffractograms of different samples in the (111) CdTe reflection-peaks. Peaks for α-CdTe undergo a shift towards greater Bragg angle with the In content increasing. For those films with the highest In content, numerated 1 and 2, corresponded to In source temperature of 725 and 775°C, respectively. The smooth shift seen in peaks *a* through *f* suggest the presence of a solid solution. Under this assumption, the relationship between the lattice parameter (obtained from the X-ray diffraction patterns considering a zinc-blende structure for the CdTe) and the mol% of In_2Te_3 in CdTe was found through the Vegard's law of the solid solution of In_2Te_3 in CdTe reported by Thomassen et al. [3] and Iwamura [13]. The resultant linear fit was as follow;

$$M = 647.5 - 99.88a \tag{1}$$

where M is the mol% In_2Te_3 in CdTe and a is the lattice parameter in Å.

On the other hand, in order to obtain the relative sensitivity factor (RSF) of the In and Te (presuming that the RSF of the Cd equal to unit), we combined the values of the atomic concentration of Cd, In and Te

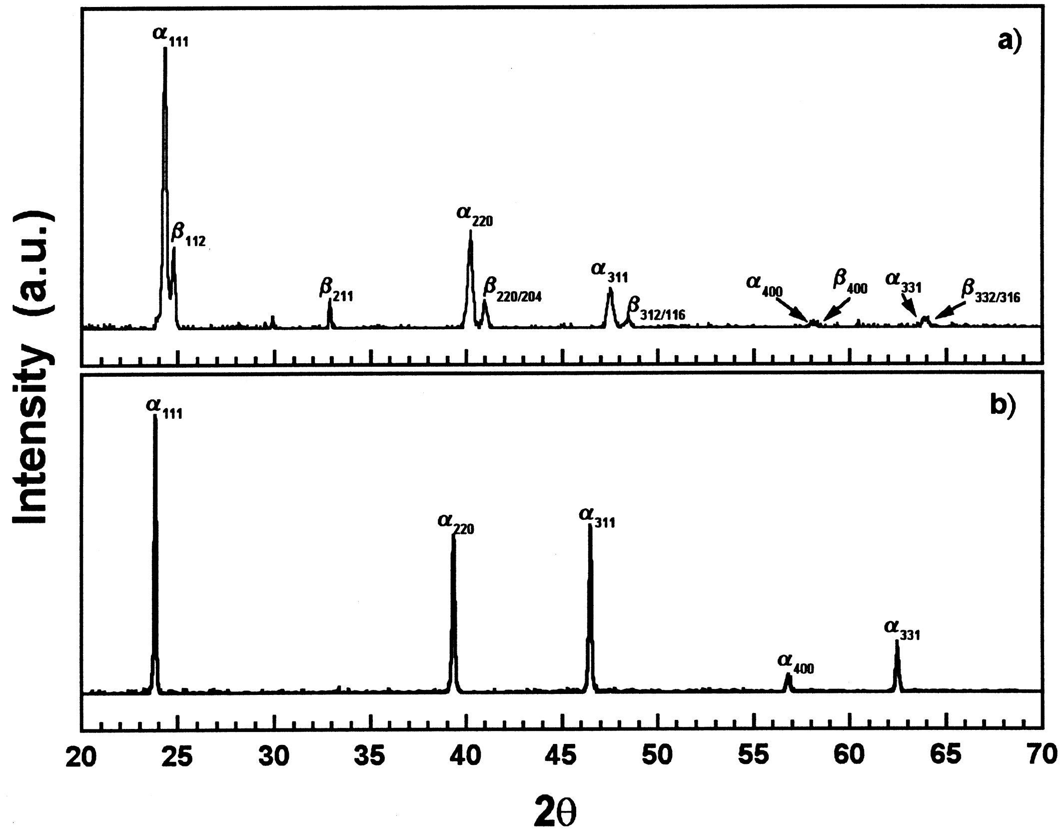

Fig. 2. X-Ray diffraction measurements of the CdTe–In films with In source temperature of: (a) 750°C, and (b) 500°C, respectively.

[obtained from Eq. (1)] with the experimental intensity AES spectra using the relationship:

$$C_x = [I_x/(\mathrm{RSF})_x]/\Sigma_i[I_i/(\mathrm{RSF})_i] \qquad (2)$$

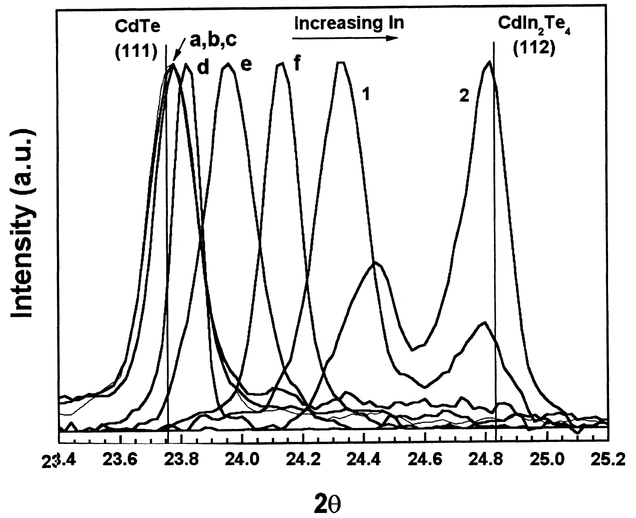

Fig. 3. Overlapping of diffractograms of different films in the region of the plane (111) where 1 and 2 correspond to films with In source temperature of 750 and 775°C, respectively.

where C_x, I_x and $(\mathrm{RSF})_x$ are the atomic concentration, peak-to-peak intensity Auger differentiated spectrum of the element x and the relative sensitivity factor of the transition being considered in element x, respectively [15]. In Fig. 4 the RSF of In and Te with respect to the In source temperature is represented. We can see that the RSF for both compounds remains constant in the grown films with an In source temperature of 525–575°C. This means that the chemical composition of these films correspond to the solid solution of the $(\mathrm{CdTe})_{1-x}(\mathrm{In}_2\mathrm{Te}_3)x$ type. On the other hand, it can be observed that the rest of the films have different values of the RSF for both elements. This behavior indicates that the calculated atomic concentration is not appropriated and therefore it could not be confirmed that the solid solution is an only phase in those films. In order to confirm this phase, we used the mean value of RSF of In and Te corresponding to the solid solution $(\mathrm{CdTe})_{1-x}(\mathrm{In}_2\mathrm{Te}_3)_x$ (films with an In source temperature between 525 and 575°C) to quantify the atomic concentration of Cd, In and Te as well as the mol% $\mathrm{In}_2\mathrm{Te}_3$ in CdTe in all the remaining films. In this sense the lattice parameter for each film could be associated with the correspondence mol% $\mathrm{In}_2\mathrm{Te}_3$ in CdTe. Fig. 5

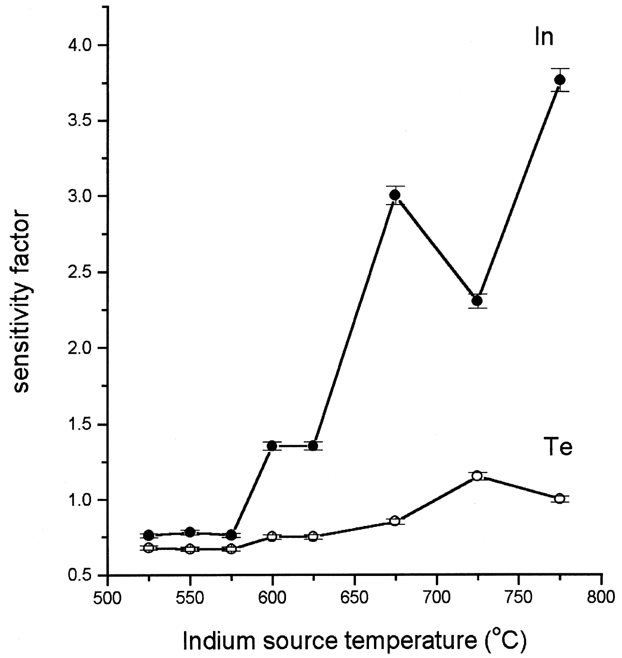

Fig. 4. Relative sensitivity factors of In and Te vs. In source temperature.

shows the lattice parameter as a function of the mol% In_2Te_3 in CdTe. A linear behavior for the region below 5 mol% can be observed which establishes that the samples with In source temperature between 525 and 575°C (1.5–3.29 mol% In_2Te_3 in CdTe) are a solid solution of the $(CdTe)_{1-x}(In_2Te_3)_x$ type as reported by Thomassen et al. [3]. For the remaining films, 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 with In source temperature between 600 and 725°C (6.09–22.08 mol% In_2Te_3 in CdTe) is caused by the formation of the β-phase which increases according to the rise in content of In. This can be concluded as it has been previously proven that a solid solution exists for low In content, and a precipitate $CdIn_2Te_4$ together with CdTe exists for high In content, particularly for In source temperature of 750°C (42.27 mol% In_2Te_3 in CdTe) which is attained in the diffractograms where the peaks for α- and β-phases are separated.

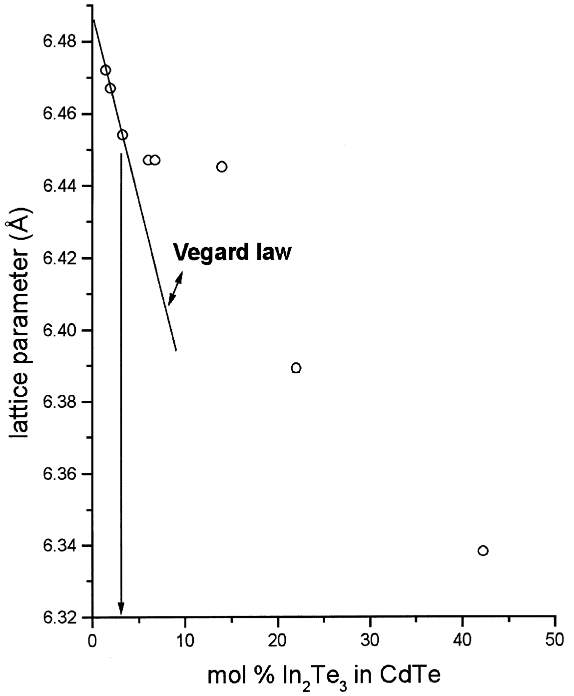

Fig. 5. The mol% In_2Te_3 in CdTe dependence with the lattice parameter.

4. Conclusions

In summary, polycrystalline CdTe–In films were prepared using the close-spaced vapor transport technique combined with free evaporation. In_2Te_3 was incorporated into CdTe during film preparation from In evaporation. Using both techniques, XRD measurements and AES spectra, we demonstrate that in polycrystalline CdTe–In films there are compounds of the pseudo-binary diagram CdTe–In_2Te_3.

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