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Structural transition from $CdTe$ to $CdIn_2Te_4$ in films grown by close paced vapor transport combined with free evaporation

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Abstract

In order to obtain $CdIn_2Te_4$ thin films, $(CdTe)_{1-x}(In_2Te_3)_x$ thin films were grown on glass substrates by the close spaced vapor transport combined with free evaporation technique (CSVT-FE) using coevaporation of CdTe and In_2Te_3. When the saturation limit of In in the CdTe structure is achieved, a $CdIn_2Te_4$ thin film is obtained. Indium incorporation is controlled by the temperature of the In_2Te_3 source. The composition of the films was investigated by Auger electron spectroscopy and X-ray diffraction was used to evaluate the structural transition of the films from CdTe (zincblend) to $CdIn_2Te_4$ (tetragonal). Optical characterization by Raman, transmission and photoreflectance spectroscopies gave us further evidence of the success in the production of $CdIn_2Te_4$ thin films.

Keywords: Cadmium telluride; Deposition process; Semiconductors; X-ray diffraction; Raman; Photoreflectance

1. Introduction

The pseudo-binary system CdTe-In_2Te_3 is of interest since all compounds formed by mixing CdTe and In_2Te_3 are semiconductors [1]. O'Kane et al. [2] reported semiconducting properties of these compounds, which were verified for electrical conductivity measurements. Particularly, the ternary compound $CdIn_2Te_4$, which naturally grows as a p-type semiconductor [2–4] has recently been regarded as a potential electro-optical material for applications in the infrared region.

The phase diagram of the system CdTe-In_2Te_3 has been described by Thomassen et al. [5]. In this diagram, the α and β phases are the CdTe and $CdIn_2Te_4$ compounds respectively. As In_2Te_3 is added in solid solution to the CdTe, the lattice parameter of the compound decreased. The CdTe has a zincblend structure with lattice constant $a = 6.481$ Å [6] while the ternary compound $CdIn_2Te_4$ has a tetragonal structure with $a = c/2 = 6.23$ Å [3] and it has been found by Riedel et al. [7] that it belongs to the I-42 m space group. Only a few theoretical and experimental studies on $CdIn_2Te_4$ have been performed due to problems encountered during its growing [8]. Furthermore, to the best of our knowledge, the growth of $CdIn_2Te_4$ films, by any method, has only been reported by Kim et al. [9]. The preparation of $CdIn_2Te_4$ had been limited to bulk material [1–4] and all the electrical and optical measurements had been also carried out on only single crystal or polycrystalline bulk materials [7,8,10,11].

Close-spaced vapor transport combined with free evaporation is a convenient method for growing ternary materials because it is possible to control the temperatures of different compounds separately [12,13]. It is also cost-effective as it operates at atmospheric pressure under inert gas and uses moderate temperatures; its operation is simple, and films are compact with few voids. In this work the structural transition from CdTe to $CdIn_2Te_4$ in films grown by close-spaced vapor transport combined with free evaporation is reported. Also, we characterized the $CdIn_2Te_4$ film by X-ray diffraction, Auger, Raman, transmission, and photoreflectance spectroscopies. All the results give irrefutable evidence of the production of polycrystalline $CdIn_2Te_4$ films.

2. Experimental details

All films were prepared in a conventional vacuum

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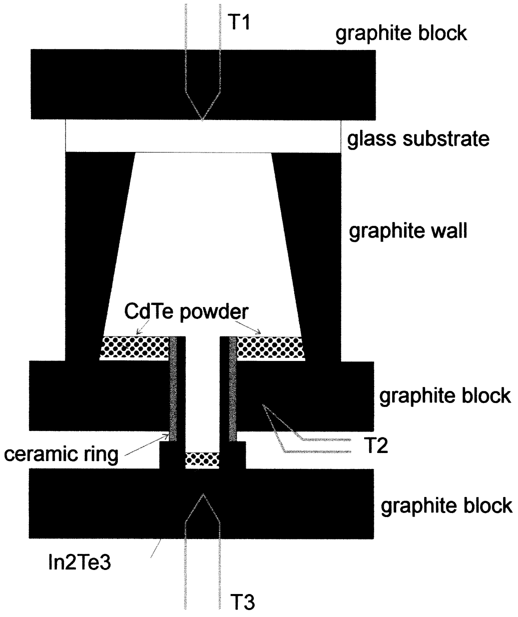

Fig. 1. Schematic of the chamber used for CSVT combined with free evaporation.

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. A schematic figure of the system of growth is seen in Fig. 1. The raw materials were CdTe powder 99.99 at.% and In_2Te_3 99.999 at.% from Balzers. Corning 7059 glass slides were used as substrates. The CdTe source was maintained at 500°C during the growth process, while In_2Te_3 source was varied between 500 and 750°C, in increments of 50°C, to achieve different concentrations. We kept the substrate temperature fixed at 400°C, and the deposition time for 10 min. Additionally, we have grown one film of pure CdTe in order to compare the transition phase between CdTe to $CdIn_2Te_4$. Elemental concentrations were determined by Auger electron spectroscopy (AES) using a Perkin-Elmer PHI-560 ESCA-SAM, all the Auger spectra were obtained after 7 min of Ar^+ sputtering using a beam energy of 4 keV. X-ray diffraction measurements were performed with a Siemens D5000 diffractometer fitted with a Cu anode. Room temperature Raman experiments were carried out in a Labram Dilor micro Raman system using an He–Ne laser. For room temperature photoreflectance measurements, a standard experimental setup was used. A He–Ne laser was also used to modulate the reflectivity of the sample. Room temperature transmission measurements were carried out in a Fourier transform infrared spectrometer.

3. Results and discussion

The surfaces of the films were smooth and slightly grayish. All the films were firmly adhered to the substrate. The films are polycrystalline, with uniform thickness (around 25). The relative atomic concentration values for all films were determined by AES and we found that the indium concentration increases monotonically with the In_2Te_3 source temperature.

The X-ray diffraction patterns of the films showed that the crystalline structure of the sample depends of indium concentration. We did not find peaks related to metallic indium. The films had the cubic phase from 0 to 22 at.% indium, the only effect observed was a decrease of the lattice parameter, as reported previously [13,14]. For indium concentration greater than 22 at.% the presence of cubic and tetragonal phases was observed. Finally the $CdIn_2Te_4$ compound was obtained when a In_2Te_3 source temperature of 750°C was used.

In order to examine the structural phases presented in our samples in Fig. 2 we present the X-ray diffraction patterns of the peaks (111), corresponding to the $CdIn_2Te_4$ structure for the different samples. Fig. 2a corresponds to the pure CdTe film, and Fig. 2b–e corresponds to the samples M600, M650, M700 and M750, produced employing an In_2Te_3 source temperature of 600, 650, 700 and 750°C, respectively. In Fig. 2a we observe the peak related to the (111) plane for pure CdTe; while in Fig. 2b a shift to higher value of 2θ is present as a consequence of the decrease of the lattice parameter, in this sample we only had the cubic phase. In Fig. 2c a new peak, related with the $CdTeIn_2Te_4$ compound, shows up. We explain these features considering that this sample has two phases, one related with the cubic

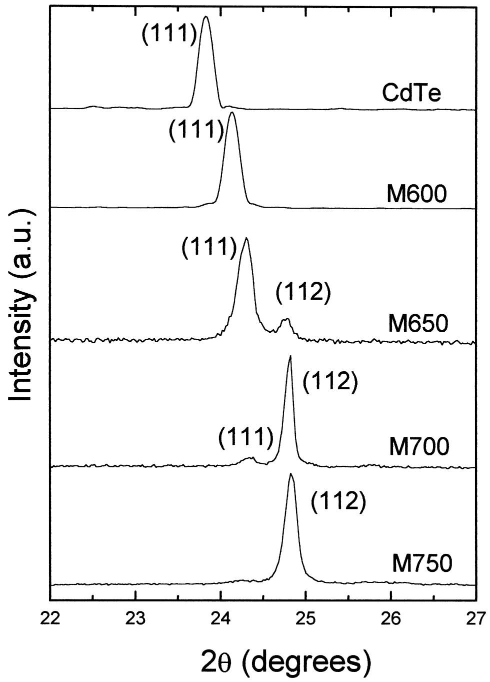

Fig. 2. X-ray diffraction patterns for samples (a) CdTe, (b) M600, (c) M650, (d) M700 and (e) M750. Shift of the (111) cubic peak to higher 2θ and the appearence of the (112) hexagonal peak consistent with the formation of $CdIn_2Te_4$.

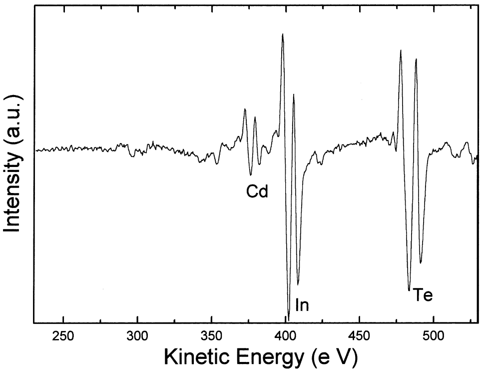

Fig. 3. Auger electron spectroscopy results obtained from sample M750. The intensity ratios are approximately consistent with $CdIn_2Te_4$.

structure and the other with the $CdIn_2Te_4$ structure. As expected in the pattern in Fig. 2d shows an increase of the intensity of the peak related with the $CdIn_2Te_4$ indicating that a pure $CdIn_2Te_4$ film is obtained. The X-ray diffraction pattern for the film grown with an In_2Te_3 source temperature of 750°C (M750), corresponds to a pure $CdIn_2Te_4$ film, and is in full agreement with the one reported in the powder diffraction file (PDF) number 28-190 for $CdIn_2Te_4$ bulk material.

The lattice parameters of a tetragonal structure obtained from the above mentioned X-ray pattern are $a = 6.221$ Å and $c = 12.457$ Å, which are in good agreement with reported data for $CdIn_2Te_4$ [15,16].

Fig. 3 shows the Auger spectrum for the sample M750, it clearly shows that the film consisted only of cadmium, indium and telluride. The ratio of the peak-to-peak intensities among the cadmium, indium, and telluride peaks taking into account the sensitivity factor of $S_{Cd} = 1$, $S_{Te} = 1$ and $S_{In} = 2.5$; indicated roughly that the film has the right composition of $CdIn_2Te_4$.

Raman spectroscopy is a well established technique very sensitive to the microscopic atomic arrangement. Then, Raman results will give us a definitive test about the structural arrangement of the Cd, In and Te atoms present in our film. Fig. 4 shows the Raman spectrum obtained for the sample M750. It revealed five structures, with peaks around 61, 98, 120, 139 and 187 cm^{-1}, in agreement with previous Raman measurements reported for $CdIn_2Te_4$ polycrystalline bulk material [7].

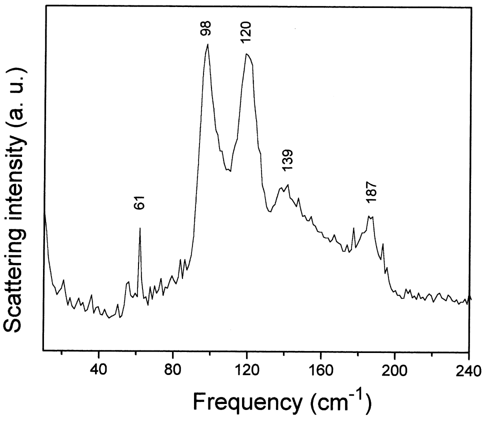

Fig. 4. Raman spectrum of sample M750. The Raman shifts are in agreement with whose reported for bulk $CdIn_2Te_4$.

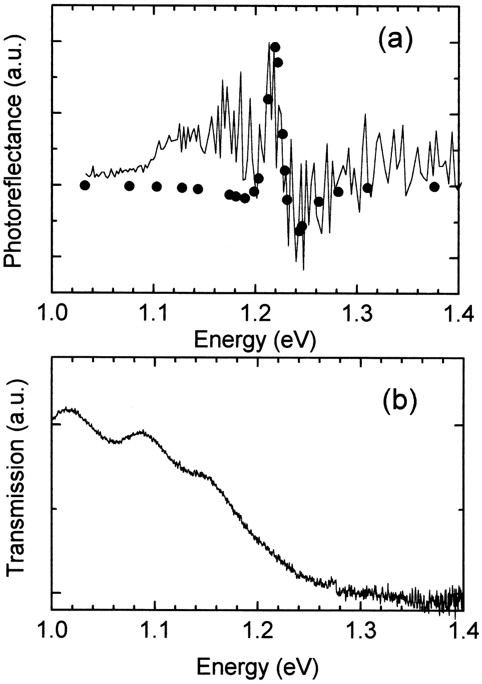

Fig. 5. (a) Photoreflectance spectrum of sample M750, solid dots represent the fitting employing a third derivative line form. (b) Transmission spectrum of sample M750.

While the earlier reports showed the $CdIn_2Te_4$ is an indirect band gap material [3,4] our photoreflectance results indicate that it is a direct band gap material. Photoreflectance spectroscopy is a very sensitive technique and allows important energy values to be measured with much better resolution than from transmission measurements. It is well known that band gap energies obtained from transmission measurements could be dependent on how the transmission spectrum is analyzed. This is a very strong problem for polycrystalline thin films where numerous effects could change the slope of the absorption edge. Fig. 5a,b presents the results of photoreflectance and transmission spectroscopies. Fig. 5b shows the transmission spectrum of sample M750. The start of the absorption is clearly appreciated, however this can not be associated with the band gap value because the presence of states below the band gap associated with disorder is very probable. The oscillations on the top of transmission spectrum are associated with an interference process because of the film thickness. Even though the photoreflectance spectrum shown in Fig. 5a is noisy, a photoreflectance signal can be assigned, the features observed between 1.0 and 1.1 eV are associated with the interference process. Employing a fitting to a third derivative signal, associated with a three dimensional critical point

[17] we obtained a band gap value of 1.22 eV, this value agrees quite well with the reported value for bulk $CdIn_2Te_4$ [7]. The theoretical fitting is shown as solid dots in Fig. 5a, note the close resemblance to the higher energy portion of the experimental photoreflectance spectrum.

Further work is under development in order to carry out an exhaustive characterization of the electronic properties of the $CdIn_2Te_4$ compound.

4. Conclusions

In summary, all the results obtained from the characterization techniques employed indicated that starting with the compounds CdTe and In_2Te_3 we produced pure $CdIn_2Te_4$ films. By increasing the temperature of the In_2Te_3 source the amount of indium in the CdTe lattice was increased as a result of a higher amount of In_2Te_3 present in the growth chamber. During the process to achieve the $CdIn_2Te_4$ films, a clear transition from CdTe to $CdIn_2Te_4$ was observed. Employing the technique of close-spaced vapor transport of CdTe combined with free evaporation of In_2Te_3 the production of pure $CdIn_2Te_4$ films is possible.

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