

## Electronic properties of $(CdTe)_x(In_2Te_3)_{1-x}$ thin films grown by close spaced vapor transport combined with free evaporation

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The electronic properties of  $(CdTe)_x(In_2Te_3)_{1-x}$  thin films as a function of substrate temperature were studied employing transmission, modulated transmission, and Raman spectroscopies. Structural information was obtained from X-ray diffraction studies. The  $(CdTe)_x(In_2Te_3)_{1-x}$  thin films were grown on glass substrates by the close spaced vapor transport technique combined with free evaporation (CSVT-FE);  $CdTe$  and  $In_2Te_3$  were employed as sources. The temperature of evaporation of the  $CdTe$  and  $In_2Te_3$  sources determines the final composition of the films, we set their values at 575 °C and 775 °C, respectively. The temperature of the substrate was varied between 100 °C and 400 °C. Raman spectroscopy showed compositional changes in the films as reflected in the change of intensity of the different Raman modes. Transmission spectroscopy shows that, as we change the substrate temperature, it could be possible to change the band gap energy from a value as low as 0.6 eV up to 1.5 eV, the band gap of  $CdTe$ . It has been reported, from measurements in bulk material, that the band gap of  $CdIn_2Te_4$  is of indirect type. We present evidence that it is of direct type. Our analysis of transmission and modulated transmission measurements allowed us to assign the band gap of  $CdIn_2Te_4$ , between 1.1 and 1.2 eV.

PACS#: 78.30.Fs, 78.40.Fy, 81.15.Ef

### I. INTRODUCTION

The ternary compound  $CdIn_2Te_4$  is of interest since all compounds formed by mixing  $CdTe$  and  $In_2Te_3$  are semiconductors. O’Kane *et al.* reported semiconductor properties for these compounds obtained by electrical conductivity measurements.[1,2] The ternary compound  $CdIn_2Te_4$  has been regarded as a potential electro-optical material for applications in the infrared region and there is recent theoretical work suggesting the possibility to implement electronic devices stable under high levels of ionizing radiation based on intrinsic  $In_2Te_3$ . [3,4] Only few experimental studies on  $CdIn_2Te_4$  have been performed due to problems encountered during its growth.[5] Furthermore, to the best of our knowledge, the deposition of  $CdIn_2Te_4$  films, by any method, was only reported by Kim *et al.*[6] Until now, the whole production of  $CdIn_2Te_4$  has been limited to bulk materials and all electrical and optical measurements had been carried out only on single crystal or polycrystalline bulk materials.

Close spaced vapor transport is a convenient method for growing ternary compounds because it is possible to control the temperatures of different compounds

separately.[8,9] It is also cost effective as it can operate at atmospheric pressure under inert gas and uses moderate temperatures; its operation is simple and produces good quality films. Here we report the electronic properties of  $(CdTe)_x(In_2Te_3)_{1-x}$  films grown by close spaced vapor transport combined with free evaporation as a function of the substrate temperature. Such properties were obtained from room temperature optical transmission and modulated transmission, and Raman spectroscopy. Structural characteristics were obtained from X-ray diffraction measurements.

### II. EXPERIMENTAL DETAILS

All films were prepared in a conventional vacuum evaporation system evacuated by an oil-diffusion pump capable of obtaining a background pressure of  $10^{-6}$  Torr. The pressure during evaporation was better than  $10^{-5}$  Torr. Starting 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  $CdTe$  and  $In_2Te_3$  source temperatures were maintained at 575°C and 775°C respectively, while the substrate temperature was varied between 100°C and 400°C, in steps of 50°C. The deposition time was 5 min. 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 employing a HeNe laser at room temperature. The room temperature transmission spectra of the samples were obtained with a Nicolet Magna IR spectrometer in the near infrared region. Room temperature modulated transmission was made with a standard experimental setup, employing a HeNe laser as modulating source.

### III. RESULTS AND DISCUSSION

The X-ray diffraction patterns obtained for the samples grown with substrate temperatures in the range between 100 and 200 °C showed a peculiar variation. Even when they showed well defined structure the positions of the peaks do not correspond to those reported for *CdIn<sub>2</sub>Te<sub>4</sub>*, *CdTe* or *In<sub>2</sub>Te<sub>3</sub>*, [10,11,12] which is an indication that we have a mixture of non-identified phases. This issue will be addressed in the future. On the other hand, for the samples grown at 250 °C and above, the X-ray diffraction patterns correspond to *CdIn<sub>2</sub>Te<sub>4</sub>*, when compared with the peaks reported in ref. [12]. This corresponds to a tetragonal structure with lattice parameters  $a=c/2=6.23$  Å. The X-ray diffraction patterns for the whole set of samples are shown in figure 1.

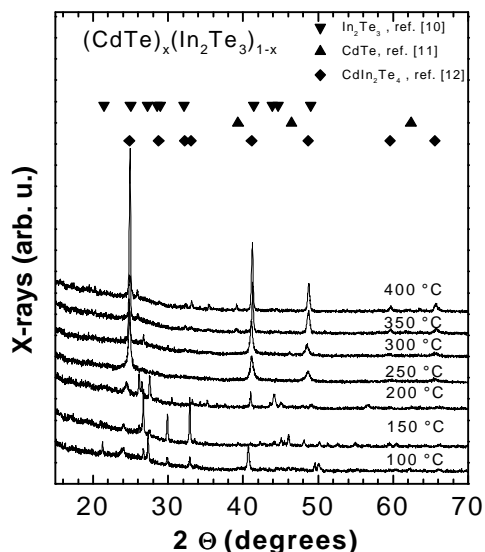


Fig. 1: X-ray diffractograms as function of deposition temperature for the set of studied samples.

These results show that, for substrate temperatures above 250 °C, we have obtained *CdIn<sub>2</sub>Te<sub>4</sub>* thin films.

Figure 2 shows the Raman spectra of the whole set of samples. The Raman modes for the samples grown at 250 °C and above is quite similar; we can notice changes in the intensity of the Raman peaks in the different sample spectra, suggesting changes at the level of the microscopic environment. The peak positions

agrees fairly well with the peaks reported for *CdIn<sub>2</sub>Te<sub>4</sub>*, by J.F. Lambert *et al.*<sup>16</sup> When we compare with the X-ray diffraction results obtained for these samples, it could be suggested that there is some kind of microscopic disorder affecting the Raman results but a macroscopic order as reflected in the complete similitude of the X-ray patterns obtained for these samples. For the samples grown at substrate temperature below 200 °C we detected the presence of Raman modes different to those aforementioned. These changes could be due to differences in composition, what in fact is suggested by the X-ray diffraction patterns. In comparing Raman spectra for samples grown in the range of 250 to 400 °C with the respective X-ray diffraction patterns, we can see the high sensitivity of Raman spectroscopy to the atomic environment.

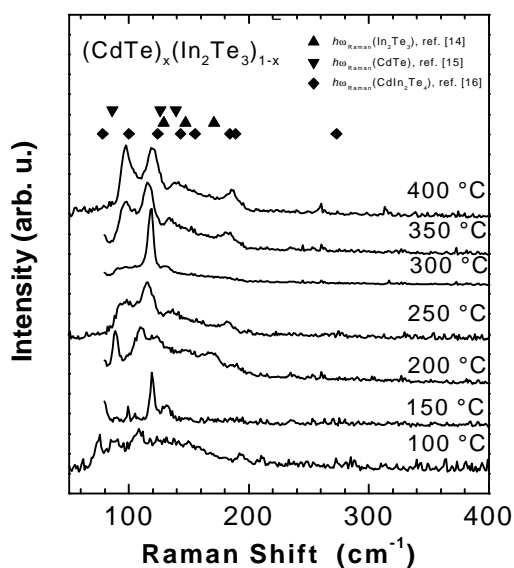
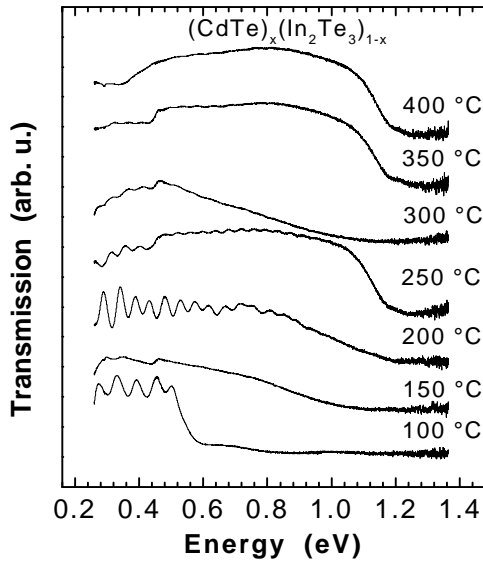


Fig. 2: Raman spectra as function of deposition temperature for the set of samples studied.

Figure 3 presents spectra corresponding to room temperature optical transmission spectroscopy for the whole set of samples. In spite that from X-ray diffraction and Raman spectroscopy it appears that the samples have a very similar structure for temperatures of 250 °C and above, transmission measurements show the presence of differences for the sample grown at 300 °C, this sample has an extended spectral region of absorption. From Raman measurements it could be established the presence of a big difference between the sample grown at 300 °C and all the other samples. So, for some reason this sample was deposited under conditions producing very similar structural characteristics, see figure 1, but its electronic properties change drastically. The slow transition between full absorption and complete transparence in the sample grown at 300 °C could be due to the presence of

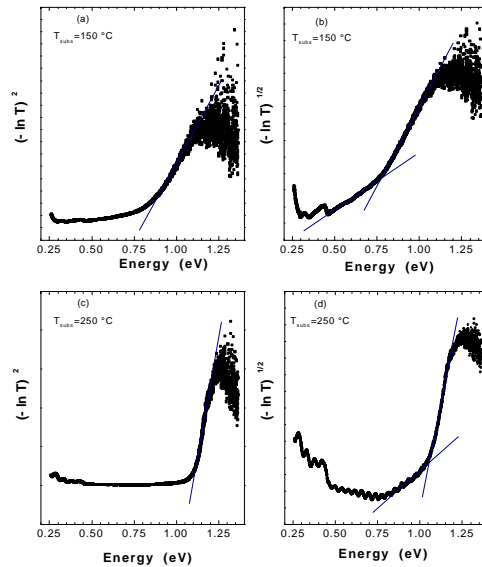
small amounts of phases of  $(CdTe)_x(In_2Te_3)_{1-x}$  with a band gap smaller than 1.2 eV along with important amounts of  $CdIn_2Te_4$ . These small amounts would be undetectable by X-ray diffraction but enough to change the transmission profile. Another explanation for this odd behavior is the possibility of having a sudden change in the type of electronic transition, *i.e.* a change from direct to indirect transition. This possibility will be explored below. The transmission spectra corresponding to samples produced at 150 and 200 °C is associated to unidentified phases of  $(CdTe)_x(In_2Te_3)_{1-x}$ . A very interesting feature can be found in the spectrum corresponding to the sample grown at 100 °C, see figure 3. Even when we do not know the  $(CdTe)_x(In_2Te_3)_{1-x}$  phase obtained for this particular growth condition, this spectrum suggest the possibility of modulating of the band gap of a semiconductor based in  $In_2Te_3$  and  $CdTe$  between 0.6 and 1.5 eV.



**Fig. 3:** Transmission spectra as function of deposition temperature for the set of samples studied. Notice the change in absorption between the sample grown at 100 and 250 °C.

As seen from figure 3, the transmission spectra can be sorted in two groups. We take as representative of each group those corresponding to 150 and 250 °C. In order to check the type of electronic transition associated with them we have adjusted, as a rough approximation, a simple model of direct and indirect band gap transitions[13]; we show this adjust for the selected transmission spectra in figure 4. The values obtained for the entire set of samples are shown in Table I. Even when the fitting to the indirect transition model for the sample grown at 150 °C is reasonably good, figure 4.(b), in the sense that there is a good fitting in the region below and above of the possible band gap transition, the obtained band gap value (0.26 eV) is well within the region of complete transparency for this sample.

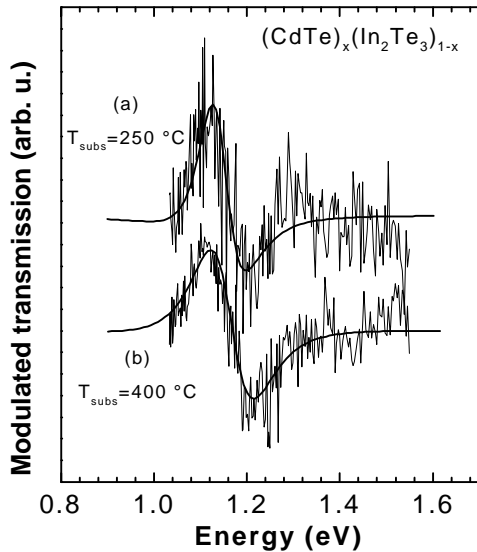
Moreover, the subtraction between the values of the ordinate to the origin from these two lines gave one value higher than the expected for the phonon energies corresponding to this material. The application of the model of indirect transitions to the sample grown at 250 °C gave a value for the bang gap again within the region of complete transparency and as seen from figure 4.(d) interference oscillations are present even in the region where a complete absorption should exist. So we came to the conclusion that the model of indirect transitions is inadequate to explain the transmission process for  $(CdTe)_x(In_2Te_3)_{1-x}$  thin films .



**Figure 4:** (a) and (c), fitting to the model of direct optical transitions ( $\alpha=M(h\omega-E_g)^{1/2}$ ) and (b) and (d) to the model of indirect optical transitions ( $\alpha=M(h\omega-E_g-h\omega_p)^2$ ) for representative samples.

As shown in figures 4.(a) and 4.(c), the fitting to the direct transition model is good for both cases but in the case of the sample grown at 150 °C the transition is not as sharp as for the sample grown at 250 °C. This difference could be associated with the presence of a higher amount of defects for the sample grown at low temperature. These results provide evidence in the direction that the band gap of the material is direct. The above affirmation is reinforced by the results obtained by modulated transmission, see figure 5. Modulated spectroscopies are very sensitive to direct transitions. Modulated transmission spectra for  $CdIn_2Te_4$  samples grown at 250 °C and 400 °C, figures 5.(a) and 5.(b), showed a clear signal associated to the band gap. A third derivative signal was fitted to the experimental spectra. The band gap values obtained from it are around 1.15 eV, notice the good fit to the trend of the experimental spectra. These results are a strong evidence to assure that the optical transition in these samples are of direct type. For those samples that did not present a sharp change in

their transmission spectrum we did not observe any modulated transmission signal, this could be due to the presence of an important amount of defects.



**Figure 5:** Modulated transmission spectra for (a) sample grown at 250 °C, and (b) sample grown at 400 °C.

**TABLE I.** Band gap and phonon energy values as obtained from the fitting to the direct and indirect optical transition model. The last column shows the band gap as obtained from the fitting to the modulated transmission spectra.

| $T_{\text{subs}}$<br>(°C) | $E_g^D$<br>(eV) | $E_g^I$<br>(eV) | $(\hbar\omega)_{\text{ph}}$<br>(eV) | $E_0^{MT}$<br>(eV) |
|---------------------------|-----------------|-----------------|-------------------------------------|--------------------|
| 100                       | 0.52            | -               | -                                   | -                  |
| 150                       | 0.79            | 0.26            | 0.48                                | -                  |
| 200                       | 0.89            | 0.13            | 0.25                                | -                  |
| 250                       | 1.09            | 0.78            | 0.18                                | 1.14               |
| 300                       | 0.73            | 0.12            | 0.04                                | -                  |
| 350                       | 1.11            | 0.76            | 0.20                                | -                  |
| 400                       | 1.11            | 0.74            | 0.21                                | 1.16               |

$T_{\text{subs}}$ : substrate temperature.  $E_g^D$ : direct band gap from transmission.  $E_g^I$ : indirect band gap from transmission.  $(\hbar\omega)_{\text{ph}}$ : phonon energy from transmission.  $E_0^{MT}$ : direct band gap from modulated transmission.

**IV. CONCLUSIONS**

We have obtained  $CdIn_2Te_4$  thin films by a relatively simple method for the substrate temperature range of 250 to 400 °C; as observed from X-ray diffraction and Raman spectroscopy results. Transmission results suggest the fact that this material has a direct band. Modulated transmission give us additional support about the direct character of the band gap. It was also evident the possibility that the band gap may be tuned, depending upon film composition, between 0.6 and 1.5 eV.

From transmission measurements there is not a clear trend of the band gap energy with substrate temperature, in fact it can be seen from X-ray diffraction patterns that there were not strong changes in the structure of the films through the 250 to 400 °C substrate temperature range, while the transmission spectra in this range presented clear differences. These differences could be due to the presence of compositional and structural inhomogeneities as can be inferred from the broadening and changes in intensity of the several peaks associated with  $CdIn_2Te_4$  in Raman spectroscopy and/or to the presence of structural defects.

**ACKNOWLEDGEMENTS**

We want thank Eng. Marcela Guerrero for her helpful technical assistance. This work was partially supported by CONACyT-México..

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