Electronic properties of \((\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}\) thin films grown by close spaced vapor transport combined with free evaporation

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The electronic properties of \((\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}\) 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 \((\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}\) thin films were grown on glass substrates by the close spaced vapor transport technique combined with free evaporation (CSVTFE); \text{CdTe} and \text{In}_2\text{Te}_3 were employed as sources. The temperature of evaporation of the \text{CdTe} and \text{In}_2\text{Te}_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 \text{CdTe}. It has been reported, from measurements in bulk material, that the band gap of \text{CdIn}_2\text{Te}_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 \text{CdIn}_2\text{Te}_4, between 1.1 and 1.2 eV.

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I. INTRODUCTION

The ternary compound \text{CdIn}_2\text{Te}_4 is of interest since all compounds formed by mixing \text{CdTe} and \text{In}_2\text{Te}_3 are semiconductors. O’Kane \textit{et al.} reported semiconductor properties for these compounds obtained by electrical conductivity measurements.[1,2] The ternary compound \text{CdIn}_2\text{Te}_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 \text{In}_2\text{Te}_3.[3,4] Only few experimental studies on \text{CdIn}_2\text{Te}_4 have been performed due to problems encountered during its growth.[5] Furthermore, to the best of our knowledge, the deposition of \text{CdIn}_2\text{Te}_4 films, by any method, was only reported by Kim \textit{et al.}[6] Until now, the whole production of \text{CdIn}_2\text{Te}_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 \((\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}, \text{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 \text{CdTe} powder 99.99 at.% and \text{In}_2\text{Te}_3 99.999 at.% from Balzers. Corning 7059 glass slides were used as substrates. The \text{CdTe} and \text{In}_2\text{Te}_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
A 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$_2$Te$_4$, CdTe or In$_2$Te$_3$,[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$_2$Te$_4$, 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.

These results show that, for substrate temperatures above 250 °C, we have obtained CdIn$_2$Te$_4$ thin films. Figure 2 shows the Raman spectra 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 transparency 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.

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 transparence 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.

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

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

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

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 CdIn₂Te₄ in Raman spectroscopy and/or to the presence of structural defects.

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REFERENCES