

## Near-IR bandgap engineering employing the alloy $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$

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Bandgap variation in the near infrared employing CdTe-based alloys has potential applications in the optoelectronic industry. Pursuing it we have deposited thin films of the alloy  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  employing the closed space vapor transport technique combined with free evaporation. As sources we employed CdTe and  $\text{In}_2\text{Te}_3$  powders. The temperature of the sources and the substrate controlled sample composition. Structural characterization was carried out employing x-ray diffraction and scanning electron microscopy. Chemical composition was determined by energy dispersive x-ray analysis. Room temperature transmission and modulated transmission spectroscopies were employed for optical characterization. The results shown a sharp band edge in the transmission spectrum. From it a potential bandgap variation depending on the indium content in the range from 0.5 to 1.5 eV is inferred. Modulated transmission results clearly showed that the band edge is of the direct type.

**Keywords:** IR materials, ordered vacancies compounds, semiconductor thin films

### 1. Introduction

CdTe and its alloys are versatile optoelectronic materials, some of their applications are in photovoltaics devices and as substrate material for IR detectors[1,2]. The alloy CdZnTe is employed in gamma and x-ray detectors and as substrate of HgCdTe IR detectors [3,4]. By alloying with sulfur a bandgap variation from 1.5 eV up to 2.4 eV could be achieved, with potential applications in the production of visible light emitting quantum devices. The possibility to extend the modulation of the bandgap of CdTe-related alloys toward the near infrared is very exciting and has potential applications in photovoltaics, near-IR detection, near-IR quantum lasers, etc. In the case of a binary alloy the modification of the bandgap can be described employing the virtual crystal approximation. According to it, the bandgap of the alloy  $A_xB_{1-x}$  is simply the weighted bandgap of the individual bandgaps of the semiconductors A and B. Then, the bandgap of the alloy  $A_xB_{1-x}$  would change linearly between the bandgap values of the semiconductors A and B. The existence of the semiconductors  $\text{In}_2\text{Te}_3$ , and  $\text{CdIn}_2\text{Te}_4$ , for which direct bandgap values of 1.19 eV and 1.15 eV have been reported [5, 6], suggest the use of the compounds  $\text{In}_2\text{Te}_3$  and CdTe to produce the alloy  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  in which we could expect a bandgap variation between 1.19 and 1.5 eV. In fact A. Iribarren et al.[7] added indium to CdTe up to nominal concentrations of 30 % producing a change in the CdTe bandgap of 200 meV. However, the fact that  $\text{In}_2\text{Te}_3$  and  $\text{CdIn}_2\text{Te}_4$  are materials with ordered vacancies is an additional parameter worth to be considered. The presence of ordered vacancies give to these materials very particular properties; it had been proposed to produce electronic

devices capable to sustain high radiation doses employing  $\text{In}_2\text{Te}_3$ [8, 9]. It has been reported that in  $\text{In}_2\text{Te}_3$  the proportion of ordered vacancies is 16.6% of the total number of lattice sites[10]. The ordered vacancies in the crystallographic structure of  $\text{In}_2\text{Te}_3$  can be described as surrounded tetragonally by Te atoms in a similar way to the Cd atoms in a CdTe crystal. The above characteristic and the existence of the  $\text{CdIn}_2\text{Te}_4$  compound could be taken as evidence of the affinity of the incorporation of Cd in the lattice of  $\text{In}_2\text{Te}_3$  making plausible the formation of the alloy  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  in the whole range of x values. Calculations *ab-initio* of the electronic properties of  $\text{CdIn}_2\text{Te}_4$  had been carried out recently by M. Fuentes-Cabrera et al.[11] and other ordered vacancies compounds are subject of intense study[12].

In this work we present results of the structural, chemical and optical characterization by x-ray diffraction(XRD) , scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and transmission and modulated transmission spectroscopies of  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  films produced by closed space vapor transport assisted with free evaporation (CSVTFE). CSVTFE deposition is a very interesting technique that allows the modification of three important parameters during the deposition: substrate temperature, free evaporation material source temperature and closed space vapor transport material source temperature. Our results shown clearly that single-phase samples with different amounts of indium were obtained by changing the parameters of deposition, allowing the variation of the direct bandgap from a value of 0.5 to 1.5 eV.

**Table 1:** Growth parameters, lattice parameters, composition and bandgap values for the studied samples.

| Sample | T <sub>s</sub><br>(°C) | T <sub>In<sub>2</sub>Te<sub>3</sub></sub><br>(°C) | a<br>(Å) | b<br>(Å)  | c<br>(Å)  | System     | Cd<br>(at. %)* | In<br>(at. %)* | Te<br>(at. %)* | E <sub>g</sub><br>(eV) |
|--------|------------------------|---|----------|-----------|-----------|------------|----------------|----------------|----------------|------------------------|
| M0     | 400                    | -   | 6.477(1) |           |           | Cubic      | 49             | 0              | 51             | 1.51(1)                |
| MA600  | 400                    | 600   | 6.475(1) |           |           | Cubic      | 45             | 3              | 52             | 1.42(8)                |
| MA550  | 400                    | 550   | 6.44(2)  |           |           | Cubic      | 42             | 6              | 52             | 1.34(5)                |
| MA650  | 400                    | 650   | 6.42(0)  |           |           | Cubic      | 39             | 8              | 53             | 1.36(5)                |
| M400   | 400                    | 775   | 6.194(3) | 6.194(3)  | 12.387(3) | Tetragonal | 12             | 30             | 58             | 1.17(6)                |
| M250   | 250                    | 775   | 6.184(2) | 6.184(2)  | 12.504(2) | Tetragonal | 11             | 32             | 57             | 1.23(5)                |
| M100   | 100                    | 775   | 4.282(1) | 13.238(1) | 16.504(2) | Triclinic  | 13             | 39             | 48             | 0.52(2)&               |

\*: Effective compositions obtained from EDX analysis.

E<sub>g</sub>: Bandgap from modulated transmission spectroscopy.

T<sub>s</sub>: Substrate temperature.

T<sub>In<sub>2</sub>Te<sub>3</sub></sub>: Temperature of the In<sub>2</sub>Te<sub>3</sub> source.

&: taken from ref. [14].

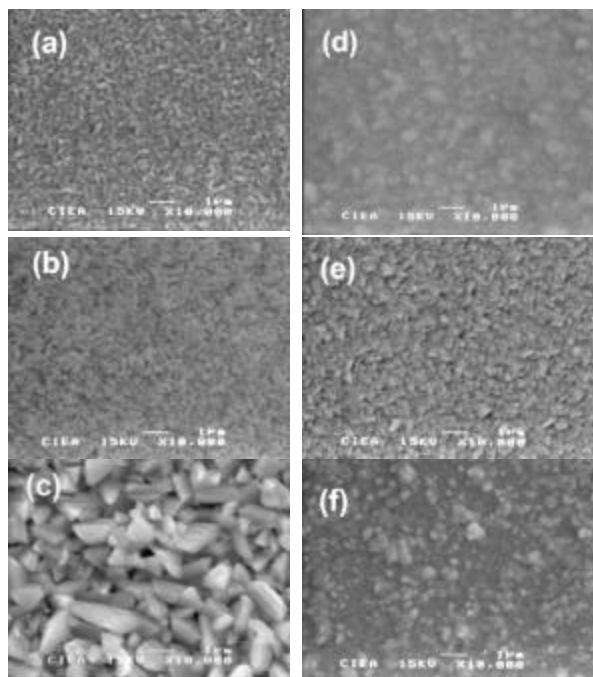
## 2. Experimental Details

The films were prepared in a conventional closed space vapor transport evaporation system modified to allow simultaneous free evaporation, details of the system have been published elsewhere[6]. The CSVT-FE system was evacuated by an oil-diffusion pump capable of obtaining a background pressure of 10<sup>-6</sup> Torr. The pressure during evaporation was better than 10<sup>-5</sup> Torr. The starting materials were CdTe 99.99 at.% and In<sub>2</sub>Te<sub>3</sub> 99.999 at.% powders from Balzers. In<sub>2</sub>Te<sub>3</sub> is the free evaporation and CdTe the closed space vapor transport material sources. Corning 7059 glass slides were used as substrates. The CdTe source temperatures was maintained for all the samples at 575°C. The studied samples were obtained employing the In<sub>2</sub>Te<sub>3</sub> source and substrate temperatures shown in Table 1. For all the samples the deposition time was 5 min, producing films with thickness around 1µm. X-ray diffraction measurements were performed with a Rigaku Geigerflex diffractometer fitted with a Cu anode. 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 measurements were made employing light from a 250 W tungsten-halogen lamp passing through a 0.25 m focal length monochromator. Detection was carried out with a silicon PIN detector. A HeNe laser was the modulating source. The monochromator and data acquisition were controlled by a personal computer. Elemental concentrations were determined by energy dispersive x-ray analysis (EDX) using a JEOL 6300 scanning electron microscope. EDX compositional measurements from different regions of each sample indicated the same composition within 1 at. %. Optical measurements showed a complete reproducibility in the spectra obtained from different regions of each sample.

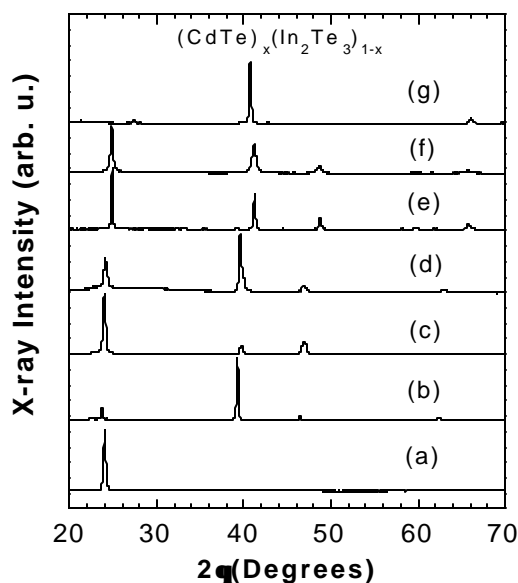
## 3. Results and discussion

SEM micrographs showed uniformity in the grain size of each sample with a strong change in grain morphology and size depending on the growth parameters. Figure 1 presents the SEM micrographs only for the

samples of the alloy (CdTe)<sub>x</sub>(In<sub>2</sub>Te<sub>3</sub>)<sub>1-x</sub>. The micrograph for the CdTe sample was not included. The grain size for the CdTe sample is of the order of microns and the grain morphology is irregular. Elemental effective concentrations obtained by EDX are reported in Table 1. Indium content depends on the growth parameters. However we did not find a clear trend of it with any of them, mainly because the characteristics of the growth method. The growth mechanism of the films is influenced by the interaction of the clouds of CdTe and In<sub>2</sub>Te<sub>3</sub> near and on the substrate, the substrate temperature and by the temperature of the walls in the deposition system. The above mentioned characteristics make difficult to have a fine control of the film characteristics with the deposition parameters. Figure 2 shows x-ray diffractograms of the studied



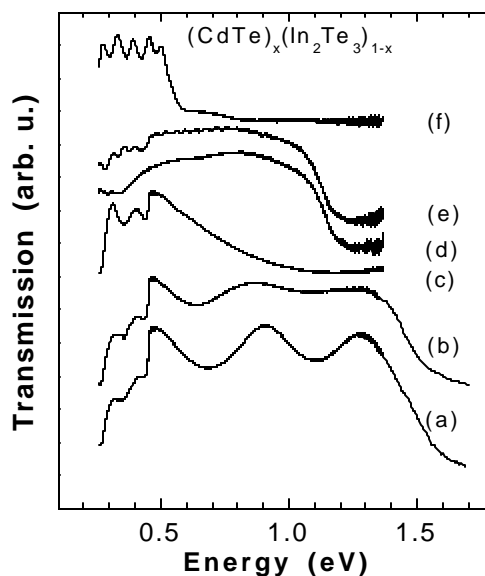
**Figure 1.** SEM micrographs for the studied samples, (a) MA600, (b) MA550, (c) MA650, (d) M400, (e) M250, (f) M100. Grain morphology is very dependent on the growth parameters and consequently on indium composition, however there is not a clear trend.



**Figure 2.** Diffractograms for the studied samples, (a) M0, (b) MA600, (c) MA550, (d) MA650, (e) M400, (f) M250, (g) M100. All diffractograms correspond to single phase material. The shift in peak position is associated to the different indium composition in each sample.

samples; indium content increases as we go from diffractogram 2.(a) to 2.(g). All of them were normalized to the peak of higher intensity. The change in the position of the different diffraction peaks is clearly seen. This is taken as an indication of the increase in the amount of indium atoms occupying lattice sites. A fitting of the x-ray diffractograms by the Rietveld method allowed us to obtain the crystallographic structure and the lattice parameter of each of the studied samples [13]. The results are reported in Table 1. As the amount of indium increases the zincblende lattice of CdTe suffers structural changes. The structure goes from cubic, to tetragonal and then triclinic for sample M100 (Fig. 2.(g)), the sample with the higher amount of indium. X-ray analysis indicated that samples were single phase in all cases. As reported by M. Zapata-Torres *et al.* this is crucial to obtain good optical properties in  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  films [14]. It is worth to mention that EDX afford a global evaluation of the atomic composition. Then, it is still necessary to quantify the real amount of indium occupying lattice sites. However, we observe a clear trend in the bandgap of the samples with the increase of it.

Figure 3 shows the room temperature transmission spectra for the samples here discussed. Spectra are arranged in the same order as in the previous figure but the CdTe transmission spectrum was not included. Spectrum 3. (a) corresponds to the sample with the lowest amount of indium while spectrum 3.(f) corresponds to the sample with the highest amount of indium. Except for the sample grown employing a substrate temperature of 400 °C and 650 °C for  $\text{In}_2\text{Te}_3$  source (sample MA650), all the samples exhibited a sharp absorption edge characteristic of direct optical transitions. The odd behavior of the transmission spectrum of sample MA650 is probably due to a random internal scattering process of the light on the grain facets

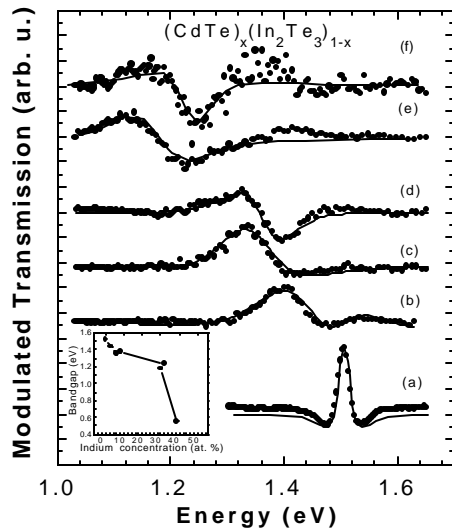


**Figure 3.** Room temperature transmission spectra, (a) MA600, (b) MA550, (c) MA650, (d) M400, (e) M250, (f) M100. Note the energy absorption edge for sample M100.

because its morphology, figure 1.(c). From the transmission spectra, we clearly observe a change in the bandgap with the indium content. The behavior from figure 3.(a) to 3.(e) could be taken as the one expected from the virtual crystal approximation as we go from CdTe to  $\text{CdIn}_2\text{Te}_4$ : a continuous bandgap variation from 1.5 eV to 1.12 eV. The spectrum 3.(f), corresponding to the sample M100 with the highest amount of indium: 13 at. % of Cd, 39 at % of In and 48 at% of Te; is very interesting. In this case it is clear that an absorption edge and consequently a bandgap of around 0.5 eV is obtained for this sample. An evaluation of the absorption coefficient for the samples studied gave values greater than  $10^4 \text{ cm}^{-1}$  at energies above the bandgap [15], in agreement with a direct bandgap behavior for the  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  alloy. The above results make very promising to pursue the production of the alloy  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  under tighten growth conditions in order to achieve a controlled incorporation of indium. This will allow to evaluate the possibility to produce a continuous bandgap variation between 0.5 and 1.5 eV.

A detailed study of samples with indium compositions in the range of 30 to 40 % is necessary in order to evaluate the role that the change in structure has in the abrupt change in the bandgap value. In fact, it is possible that as the indium incorporation increases the structure changes toward a metal-like  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  compound. Theoretical studies stated that  $\text{CdIn}_2\text{Te}_4$  changes its properties from semiconductor to metal as its structure changes from tetragonal to spinel [11].

Another very interesting characteristic of the alloy  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  is inferred from modulated transmission spectroscopy. Figures 4.(a) to 4.(f) present the modulated transmission spectra obtained at room temperature. Modulated spectroscopies are very sensitive to direct bandgap transitions. So, the obtaining of clear modulated transmission signals for the studied samples allow us to said



**Figure 4.** Modulated transmission spectra for samples: (a) M0, (b) MA600, (c) MA550, (d) MA650, (e) M400, (f) M250. Continuous curves represent the fittings to the third derivative theory of electroreflectance, see text. The inset presents the bandgap values obtained from the fitting, the continuous line is just a guide to the eye.

that the alloy  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  has a direct bandgap, at least up to an indium content of around 32 at. %. The above stated fact is quite important for the production of light emitting devices and gives an additional interest to the study of this material. Depending on the band offset associated with the heterostructure CdTe/CdInTe it could be possible to obtain quantum confinement of carriers in a CdTe/CdInTe/CdTe heterostructure making feasible the production of opto-electronic near-IR quantum devices. Of course the production of such heterostructures would demand the use of very controlled deposition techniques such as molecular beam epitaxy. Another interesting application, in which CSVT-FE could be easily employed, would be the production of polycrystalline solar cells based in the heterostructure CdTe/ $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$ . In figure 4 the experimental spectra of modulated transmission are presented along with the fittings obtained employing the third derivative theory of electroreflectance for a tridimensional critical point developed by Aspnes[16]. The

obtained values for the bandgap are reported in Table 1 and plotted as function of the indium content in the inset of figure 4. The continuous line in the inset is just a guide to the eye, however from it could be inferred that in order to produce a bandgap reduction beyond 1.2 eV in the  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  alloy a very controlled incorporation of indium is needed.

#### 4. Conclusions

A continuous bandgap variation from 0.5 to 1.5 eV could be obtained through the production of  $(\text{CdTe})_x(\text{In}_2\text{Te}_3)_{1-x}$  alloys employing CdTe and  $\text{In}_2\text{Te}_3$  as sources. From the results of modulated transmission spectroscopy it is clear that the bandgap is of the direct type at least up to 1.17 eV. The characteristics of the transmission spectrum for the sample with the higher

indium content let us expect that the bandgap in the whole range of compositions will be of the direct type.

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