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Evidence of scattering effects on the thermal transport in indium-doped CdTe films

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Abstract. Photoacoustic (PA) heat transmission measurements were used to study thermal transport in *n*-type polycrystalline CdTe films doped with metallic indium. Thermal diffusivity (TD) at room temperature was determined using an open cell PA technique. The TD obtained for each sample was correlated with x-ray diffraction measurements. It can be shown that the TD of the undoped films under investigation is significantly reduced compared with corresponding doped films. This reduction is a result of the high concentration of indium atoms and defects depending on the deposition parameters. It is shown that the effects of CdTe lattice shrink produced by indium doping, induces an increase in phonon scattering reflected in the large TD decrease even with moderated indium concentration. We have calculated the relation between the TD and the lattice parameter as a polynomial function $\alpha(\mathrm{cm}^2\ \mathrm{s}^{-1}) = -35225.2 + 14259a - 1532.7a^2 - 27.9a^3 + 8.4a^4$.

1. Introduction

Photoacoustic (PA) and photothermal effects are terms used to describe the generation of acoustic waves and other thermoelastic effects in materials under light excitation. The material is usually irradiated by a modulated light beam, which is then absorbed by the sample and converted into heat. The heat diffuses to the sample surface and then into the surrounding gas atmosphere of the PA cell. Finally, thermal expansion of the gas generates a PA signal. Thus, the absorption of a modulated light beam at any point in the sample results in periodic localized heating of the medium. The heat energy is transmitted to the surrounding matter by conduction and diffusion. Thermal property data are, therefore, important for every material exposed to thermal loading. The thermal diffusivity (TD) and the heat capacity are the thermophysical parameters which determine the distribution of temperatures in systems where heat may flow. During the past few years various properties of semiconductors have been intensively investigated, using PA signal measurements [1–3]. The TD of semiconductors is normally measured [4], using PA signal amplitude measurements as a function of the modulation frequency. The TD in semiconductor films can exhibit strong deviations from the corresponding value of the bulk material [5]. Heat transport is carried out by phonons in semiconductors and their mobility and determines the thermal transport properties. The phonon mobility is affected by scattering processes due to the defects and boundaries, which can be more important in films than in bulk materials. On the other hand, indium-doped CdTe is a good candidate for the observation of lattice relaxations created by the introduction of In. Experimental observation is the rapid decrease of the unit cell parameter as a function of dopant concentration [6]. Thermal diffusivity is strongly dependant and sensitive to these structural properties. Therefore this thermal property can be used as a means to identify the presence of lattice relaxations in semiconductors and, as a consequence, the effect of scattering on thermal transport.

In this paper, we apply the PA technique in heat transmission configurations to investigate the thermal properties of polycrystalline indium-doped CdTe films. The observed dependence of thermal properties on the crystalline quality of the sample was further supported by x-ray diffraction, in order to associate the observed variation with crystalline imperfections and the role played by this imperfection on the thermal transport properties in films.

2. Experimental details

The samples were prepared using close-spaced vapour transport combined with free evaporation at a base pressure of 10^{-5} Torr [7]. The raw materials were CdTe powder 99.99 at% and indium 99.999 at% purity from Balzers. Corning 7059 glass slides were used as substrates. The CdTe source was maintained at 600 °C during the growth procedure, while the In source temperature was varied between 550 °C and 750 °C to achieve different concentrations. The temperature of the substrate was fixed at

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500 °C [8]. All film surfaces were smooth and adhered firmly to the substrate. The colour of the film surface co-evaporate at a low-temperature In source was dark brown and that co-evaporated at a high-temperature In source was dark grey. The stoichiometry of the films was analysed by AES using an ESCA-SAM system of Perkin-Elmer PHI-560. Before analysis, the samples were cleaned by immersion for 30 s. in a methanol-3% bromine solution. Auger measurements of elemental composition were obtained for several points on the film after 2 min of argon ion sputtering. For this work we used a 3 keV electron beam and the detection of Auger electrons was carried out with a double pass cylindrical mirror analyser. X-ray diffraction measurements were performed with a Siemens D5000 diffractometer fitted with a Cu anode.

The experiments of the PA measurements were performed using a similar configuration to the so-called open photoacoustic cell (OPC). In the OPC configuration the samples were mounted and fixed with vacuum grease on the sound inlet, which was a hole of $d = 2$ mm. The construction of the cell was very similar to that presented by Pinto Neto *et al* [9]. The inner diameter of the cell was 10 mm and the distance between the back sample surface and the metallized membrane was ∼1.5 mm. The OPC experimental arrangement for the PA measurements consists of a 250 W halogen lamp whose polychromatic beam mechanically chopped (Par, model 192) and focused onto the sample which plays the role of a second window closing the PA cell. A Brüel and Kjear condenser microphone (model 4166) mounted in one of the cell walls was in contact with the air inside the PA chamber by means of a 1 mm diameter duct. The signal from the microphone was connected to a lock-in amplifier (Par model 5210) in which the signal amplitude and phase were both recorded as functions of the modulation frequency.

The arrangement corresponds to a heat transmission configuration. That is, the heat deposited at the rear-side face of the sample which first diffuses through the sample before reaching the PA air chamber, where it causes the pressure fluctuations to be detected by the microphone. The thermal wave attenuation in the sample is basically determined by the sample thermal diffusivity. The samples were 7×7 mm^2 and the surface was sprayed with black paint. In this way, we ensure not only a good light-absorbing surface, but also the same heat-transfer coefficient for each surface. The average sample thickness was 218 μm.

3. Results and discussion

To understand the PA signal and to be able to monitor the homogeneity of our undoped and doped CdTe samples we examined the modulation frequency dependence of the detected signal. As is well known, the modulation frequency dependence of the PA signal is the usual method for extracting information about the TD of samples [10]. For rear-side illumination the TD model of Rosencwaig and Gersho [11] predicts that, for an opaque sample of thickness l_s and TD α, the PA signal is

$$S = (\text{Constant}/f)\exp(-af^{1/2}) \qquad (1)$$

for a thermal thick sample ($l_s a_s \gg 1$), where $a_s = (\pi f/\alpha)^{1/2}$, $a = l_s(\pi/\alpha)^{1/2}$ and f is the frequency of the modulated light beam. Knowing the coefficient a from the fitting procedure, the thermal diffusivity α is readily obtained.

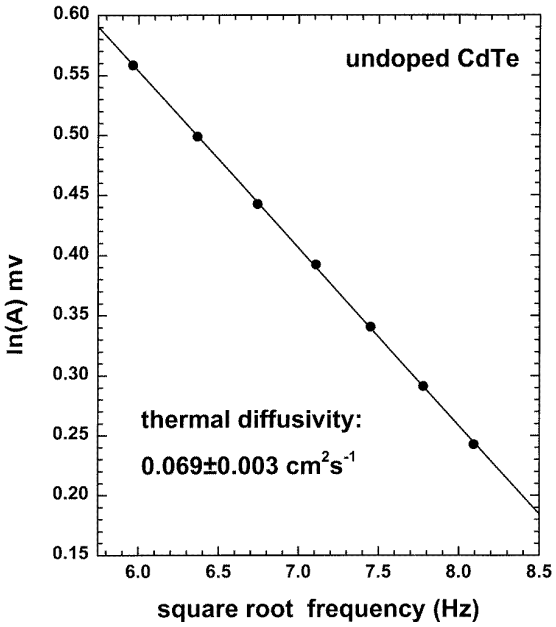

Figure 1. PA signal amplitude as a function of the square root of the modulation frequency for an undoped CdTe sample. The full curve represents the data fitted to equation (1).

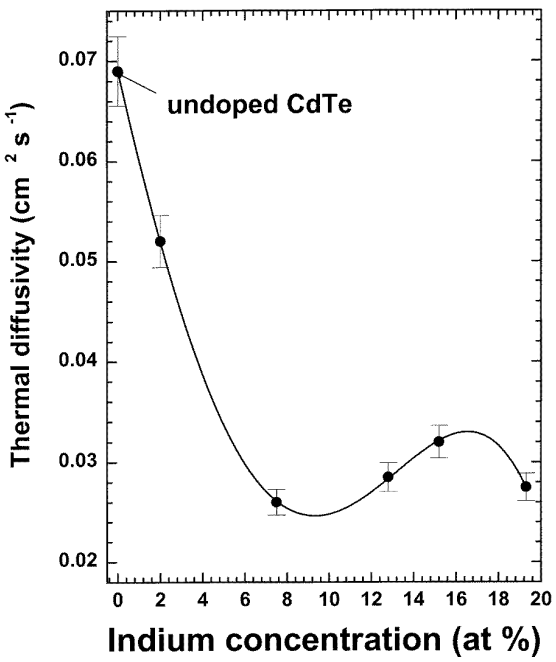

Figure 2. Effective thermal-diffusivity data as obtained by the OPC technique for the In-doped CdTe samples as a function of In at% concentration. The full curve represents the fit to the data.

In figure 1 we show the PA signal amplitude as a function of the modulation square root of the frequency for an undoped CdTe sample (the PA signal of the In-doped CdTe samples, was similar). The full curve in this figure represents the fit of the experimental data to equation (1). The resultant value of α from the fitted data was $\alpha = 0.069 \pm 0.003$ cm^2 s^{-1}. The room temperature measured values of the diffusivity of

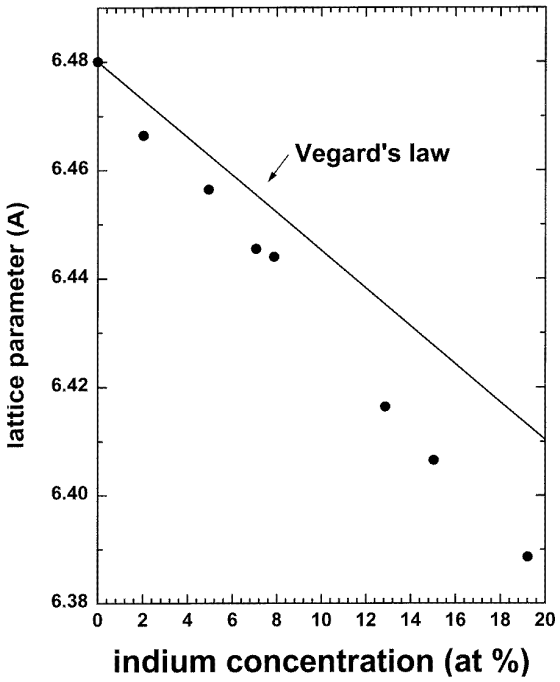

Figure 3. Lattice parameter as a function of In at% concentration, calculated as explained in the text (full curve), XRD measurements (full circles).

the undoped and doped CdTe samples are shown in figure 2. The TD first decreased monotonically with In concentration before reaching a minimum point. Afterwards, TD increased and reached a maximum point. Then, the TD showed a saturation tendency. In order to explain the characteristics observed in figure 2, we analysed the film structure in detail using x-ray analysis. The structure of the deposited films was of zinc blende (ZB) type with a preferential orientation of the (111) planes parallel to the substrate. These measurements showed a linear decrease in the unit cell parameter with In concentration (see figure 3). We note that the observed decrease is larger than the expected decrease obtained assuming a single substitutional model, with a Cd to Te distance of 2.806 Å and In to Te distance of 2.730 Å (the shortest reported In to Te distance for a compound containing both In and Te [12]) (see figure 3). Such a rapid decrease in the unit cell parameter with dopant concentration has been reported in other II–VI doped semiconductors [6] and has been related to the presence of native defects [6]. The decrease in the TD of the films is thought to be due to this effect. In other words, the lattice becomes greatly distorted because the radius of the In ion is smaller than the Cd ion radius, the distorted lattice may then enhance the phonon scattering and decrease the TD. Therefore, a CdTe lattice doped with substitutional In atoms may shrink and become distorted. When the Cd vacancies in CdTe evaporated films are completely compensated by In atoms, they can be doped interstitially into the films. Therefore, the spacing of principal lattice planes corresponding to the (111) plane can become larger upon further doping [13]. This effect decreases the phonon scattering. Then, the thermal diffusivity increases towards saturation.

X-ray absorption fine structure (XAFS) has been used to identify the presence of lattice relaxations in semiconductors.

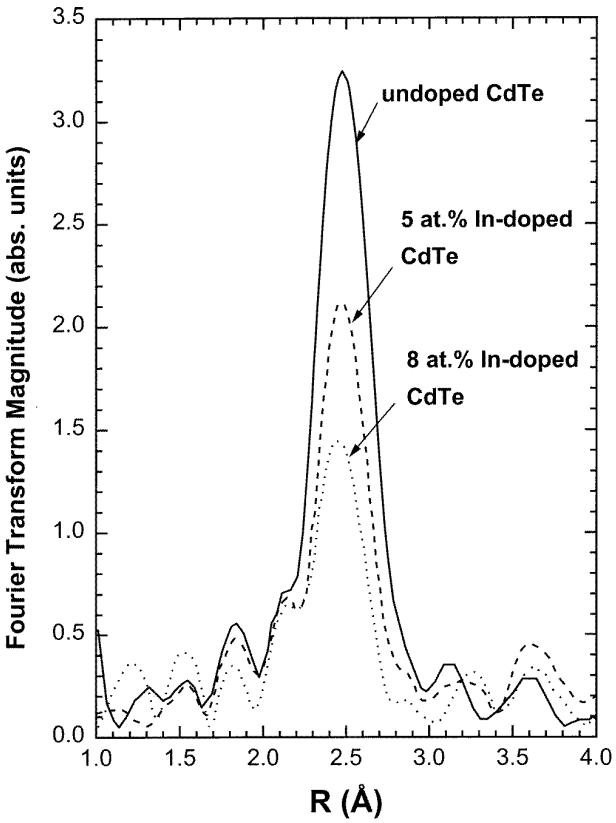

Figure 4. Fourier transform magnitude of $k2\chi(k)$ for undoped CdTe, 5 at% In doped CdTe and 8 at% In doped CdTe, respectively (reproduced by permission of the authors [16]).

This technique can provide quantitative information about the near-neighbour environment of a particular absorbing atom, for example, pair distance differing slightly from those derived from the ideal crystal structure, appearing in substitutional impurities [14], or additional nearest-neighbour distance appearing in complex formation [15]. In order to confirm our interpretation of experimental results, we used the direct observation of lattice instability in our samples from XAFS measured by Espinosa *et al* [16]. The details of the experimental set-up can be seen in this reference. The magnitude of the Fourier transform of the XAFS spectra shows qualitative changes as the In concentration of the samples increases. The main peak associated with the nearest-neighbour environment around the Cd absorber shows a decrease and shift towards a low bondlength R (see figure 4). This shows that the addition of In modifies the nearest-neighbour environment of the Cd atoms, which in the case of the undoped material, consists of four Te atoms located at a distance of $R = 2.806$ Å. We note that In enters in the place of Cd vacancies, but it does not enter in the Te site [17]. Hence, this result is unexpected and indicates that the introduction of In leads to a lattice relaxation, which affects the Cd nearest-neighbour environment. Furthermore, the phonon mobility is affected by scattering processes due to these lattice relaxations.

The TD data combined with the lattice parameter (figures 2 and 3) can be plotted, as can be seen in figure 5. The TD of indium-doped CdTe over the lattice parameter ranged

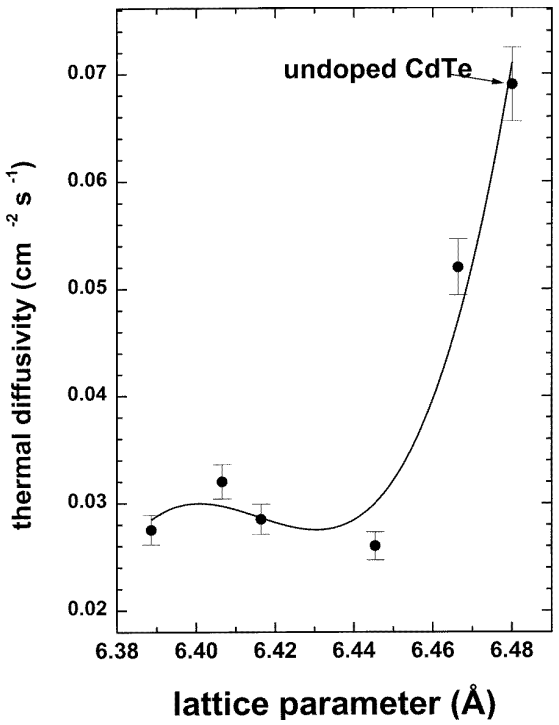

Figure 5. Thermal diffusivity as a function of lattice parameter. The full curve represents the fit to the data.

between 0–20 In at% and can be given by an appropriate polynomial approximation

$$\alpha(\mathrm{cm}^2\ \mathrm{s}^{-1}) = -35225.2 + 14259a - 1532.7a^2 - 27.9a^3 + 8.4a^4 \quad (2)$$

where a is in Å and, as can be seen in figure 5, the TD is not strongly affected when the lattice parameter is below 6.447 Å, at higher values the TD increases monotonically with the lattice parameter.

4. Conclusions

We have shown, by x-ray diffraction and XAFS measurements, using the OPC technique, that In-doped CdTe films have a lattice distortion and relaxation around Cd generated by the introduction of In in CdTe. This effect produces phonon scattering in TD. We have calculated the relation between the TD and the lattice parameter as a polynomial function.

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