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High resistivity In-doped ZnTe: electrical and optical properties

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Abstract. **Semi-insulating <111> ZnTe prepared by In doping during Bridgman growth was found to have a resistivity of $5{\cdot}74 \times 10^7$ ohm-cm, the highest reported so far in ZnTe, with hole concentration of $2{\cdot}4 \times 10^9$/cm^3 and hole mobility of 46 cm^2/V·s at 300 K. The optical band gap was 2·06 eV at 293 K compared with 2·26 eV for undoped semiconducting ZnTe. Thermally stimulated current (TSC) studies revealed 2 trap levels at depths of 202–222 meV and 412–419 meV, respectively. Photoluminescence (PL) studies at 10 K showed strong peaks at 1·37 eV and 1·03 eV with a weak shoulder at 1·43 eV. Short anneal for 3 min at 250°C led to conversion to a *p*-type material with resistivity, 14·5 ohm-cm, indicating metastable behaviour. Raman studies carried out on undoped and In-doped samples showed small but significant differences. Possible models for semi-insulating behaviour and meta-stability are proposed.**

Keywords. **II–VI compound; ZnTe.**

1. Introduction

ZnTe is a II–VI compound semiconductor whose properties have not been studied as extensively as those of ZnSe and CdTe. It has a direct band-gap of 2·26 eV at 300 K with zinc-blende structure having lattice constant of 6·1037 Å. It is well known that while ZnS and ZnSe are difficult to dope *p*-type, ZnTe shows opposite behaviour and is difficult to dope *n*-type (Chadi 1994). Attempts to introduce donor impurities such as Ga and Al in ZnTe result in high resistivity material due to compensation. Park and Chadi (1995) suggested that this involves the formation of DX centres by the substitutional donors. DX centres have also been reported with In doping in alloys such as $Zn_xCd_{1-x}Te$ (Khachaturyan *et al* 1989) and $Cd_xMn_{1-x}Te$ (Terry *et al* 1992). Recently, pure green light emitting diodes (LEDs) based on ZnTe have been realized by various techniques (Asahi and Oda 2000). It is also of interest in applications for particle detectors and as a substrate for the growth of lattice-matched InAs ($a = 6{\cdot}058$ Å) and GaSb ($a = 6{\cdot}096$ Å).

ZnTe(In) with resistivity, $\sim 3 \times 10^5$ ohm-cm was grown by Nahory and Fan (1967) in graphite reinforced quartz crucibles. Jordan and Derich (1969) reported growth of ZnTe(In) with resistivity of $7{\cdot}4 \times 10^5$ ohm-cm by a static vapour transport method.

In the present work, ZnTe was intentionally doped with $\sim 10^{19}$/cm^3 In during slow Bridgman growth. The material was found to have a high resistivity of $5{\cdot}74 \times 10^7$ ohm-cm but on slight annealing for 3 min at 250°C, it reverted to a low resistivity state. The possible reasons for this behaviour are investigated with the help of electrical and optical measurements.

2. Experimental

ZnTe was synthesized as reported earlier from 6Ns purity Zn and Te in a microwave oven (Bhunia and Bose 1998). The polycrystalline material was used as the starting material for slow Bridgman growth in a sealed quartz crucible at 6 mm/day using a vertical silicon carbide furnace. For doping, In (6Ns) at $\sim 10^{19}$/cm^3 was added to the starting material and the growth procedure described before was followed. ZnTe(In) ingots of about 1 cm diameter and 3–4 cm in length were thus obtained from which 0·5–1 mm thick samples were sliced. Laue back-reflection studies revealed the growth direction which was <111>. Etch-pit studies revealed triangular pits in agreement with the Laue observation. Impurity analysis by inductively-coupled plasma (ICP) technique on undoped ZnTe gave the following impurity concentrations: Si, 1·2 ppm; In, 0·28 ppm; Cu, 0·04 ppm and Au, 0·017 ppm. It is known that due to ores and extraction processes, Au, Cu, In and S are impurities in Zn while Au and Se are the usual impurities in Te.

3. Results

ZnTe(In) differed visually from undoped ZnTe being a darker shade of orange. Optical absorption measurements

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shown in figure 1 revealed a direct optical band gap of 2·06 eV at 293 K compared with 2·26 eV for undoped ZnTe. Photoluminescence (PL) studies were carried out using an Argon ion laser (488 nm) with the sample kept in a closed cycle He cryostat. The output signal was detected using a cooled InGaAs detector followed by an E.G. & G 520 lock-in amplifier. The PL spectrum at 10 K showed in figure 2 differed considerably from undoped ZnTe in that there was no evidence of the prominent peak at 2·06 eV due to O_{Te} (Bhunia *et al* 1998). Strong PL peaks were obtained at 1·37 eV and 1·03 eV with a shoulder at 1·43 eV. Undoped ZnTe gave PL peaks at 1·05 eV and 1·47 eV attributed to Cu I and Cu II, while the 1·33 eV peak was considered to be due to Au. The same assignments can be made here, the small differences being induced due to strain.

Hall-resistivity studies were carried out using a high-impedance Keithley set up. The resistivity was thus found to be $5{\cdot}74 \times 10^7$ ohm-cm with hole concentration, $2{\cdot}4 \times 10^9/\text{cm}^3$ and hole mobility, 45 $\text{cm}^2/\text{V}\cdot\text{s}$ at 300 K. This may be compared with the properties of undoped ZnTe: resistivity 8·5 ohm-cm, $p = 1{\cdot}6 \times 10^{16}/\text{cm}^3$ and $\mu_p = 46\ \text{cm}^2/\text{V}\cdot\text{s}$. Thus the resistivity of ZnTe(In) was found to be higher than that reported by earlier workers while the hole mobility was comparable with that of low resistivity material, the latter being indicative of absence of additional scattering centres.

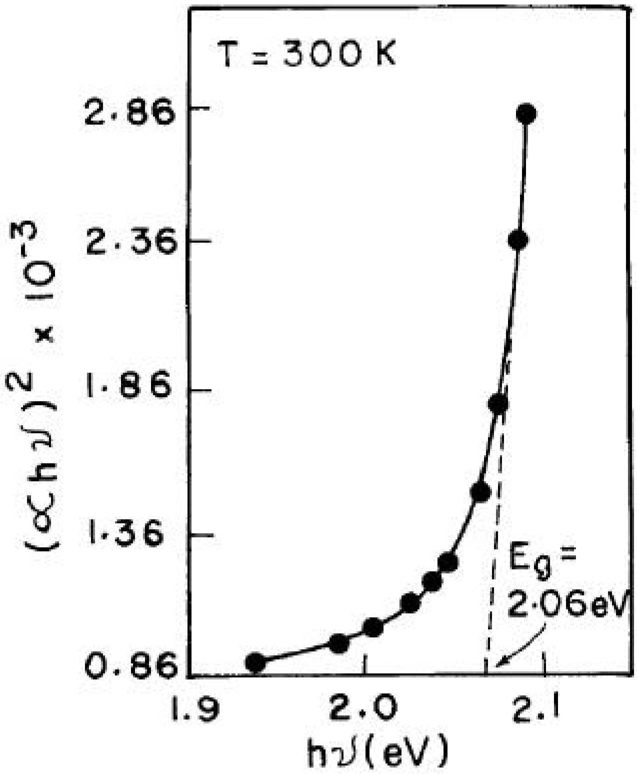

Figure 1. Optical absorption of ZnTe(In) at 300 K.

Time-resolved photoconductivity measurements on as-grown semiconducting, Zn-annealed as well as SI–ZnTe have already been reported (Bose *et al* 1999). It is significant that whereas for as-grown ZnTe the minority carrier life-time was found to be $4{\cdot}6 \times 10^{-8}$ s, the values for Zn-annealed and SI–ZnTe were much larger and almost equal, being $3{\cdot}2 \times 10^{-7}$ s and $3{\cdot}1 \times 10^{-7}$ s, respectively. Thus while Zn annealing reduces the V_{Zn} concentration, the In dopants also interact with V_{Zn} as discussed later.

Thermally stimulated current (TSC) measurements were carried out to determine the defect energy levels. Au contacts were used on samples 0·4 × 0·4 × 0·07 cm in size, the separation between the contacts being ~ 0·1 cm. After cooling the sample in a liquid nitrogen cryostat, the sample was illuminated by a tungsten lamp. A bias of 8 V was applied across the sample and the temperature raised at 0·26 K/s. The current was measured by a Keithley digital picoammeter. The TSC spectra (figure 3) showed 2 prominent peaks at 128 K and 211 K. From these peak temperatures the trap energies could be estimated as discussed below. From the area of the peaks and the heating rate the total number of carriers in the traps was estimated to be ~ $10^{17}/\text{cm}^3$ compared with ~ $10^{19}/\text{cm}^3$ In atoms introduced into the melt. This appears reasonable since the hole concentration in undoped ZnTe was $1{\cdot}6 \times 10^{16}/\text{cm}^3$ and was reduced to $2{\cdot}4 \times 10^9/\text{cm}^3$ due to In doping.

Raman scattering studies were carried out on undoped ZnTe and ZnTe(In) for comparison. A micro-Raman set up with an Argon ion laser was used with results shown in figure 4. For undoped ZnTe the strongest peaks were at

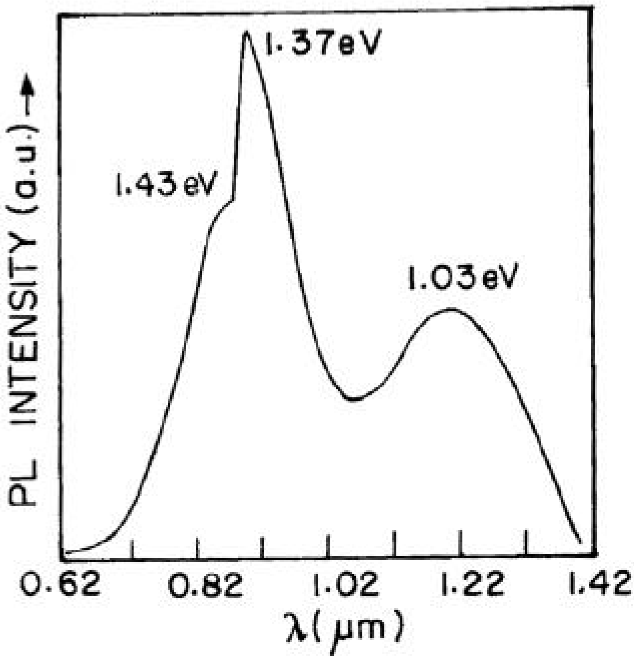

Figure 2. Photoluminescence (PL) spectrum of ZnTe(In) at 10 K.

177·77 cm^{-1} and 207·31 cm^{-1} while for ZnTe(In) the corresponding peaks occurred at 177·19 cm^{-1} and 205·01 cm^{-1}. These represent the TO and LO phonon peaks for ZnTe which are reported to occur at 176·5 cm^{-1} and 205·02 cm^{-1}, respectively (Camacho *et al* 2002). The selection rules indicate that both phonons can be observed for the <111> surface as verified above. In addition, weak peaks are observed for both samples as given in table 1.

It is seen that the LO and TO phonon lines for ZnTe(In) are shifted towards each other, the separation decreasing from 35 cm^{-1} to 29·54 cm^{-1}. This is indicative of internal strain due to the presence of In^{3+} with $r = 0{\cdot}92$ Å substituting for Zn^{2+} with $r = 0{\cdot}83$ Å. There is also a change in relative intensities, the TO phonon peak being stronger for undoped ZnTe and the LO phonon peak stronger for ZnTe(In).

A gap mode due to S^{2-} ion in ZnTe was reported by Dean Sciacca *et al* (1995) at 144·6 cm^{-1}. This corresponds fairly closely to the line observed at 145·55 cm^{-1} in undoped ZnTe. Thus this low frequency mode can be attributed to S^{2-} which is known to be an impurity occurring in Zn. The mode between 123 and 126 cm^{-1} has not been observed earlier in ZnTe. However, Amrithraj and Pollak (1984) had observed a mode at 120 cm^{-1} in CdTe which they attributed to crystalline Te precipitates. Since ZnTe crystals as grown had a Zn : Te ratio of 48·5 : 51·5 indicating excess Te, the mode between 123 and 126 cm^{-1} could very likely be due to small Te precipitates.

ICP analysis showed that In at 0·28 ppm level was also present in nominally undoped ZnTe compared with ~ 2·5 ppm for ZnTe(In). In being a heavier element substituting for Zn, a gap mode is not expected. Thus there is qualitative agreement between the spectra from the 2 samples.

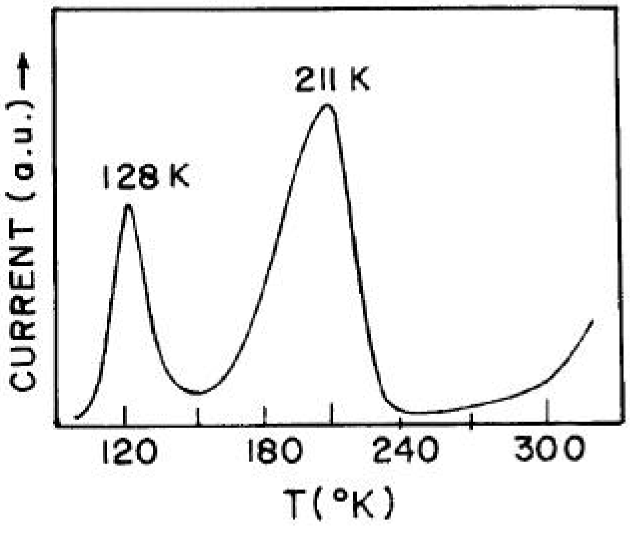

Figure 3. Thermally stimulated current (TSC) of ZnTe(In) vs temperature.

4. Discussion

A variety of techniques have been used to determine trap depths from TSC curves. If the temperature of a TSC peak is T_M, Look (1983) has shown that the trap depth, E_T, is given by

$$E_T/kT_M = \ln(T_M^4/b),$$

where b = heating rate. This relation gives the two trap depths as 222 meV and 419 meV, respectively. Another

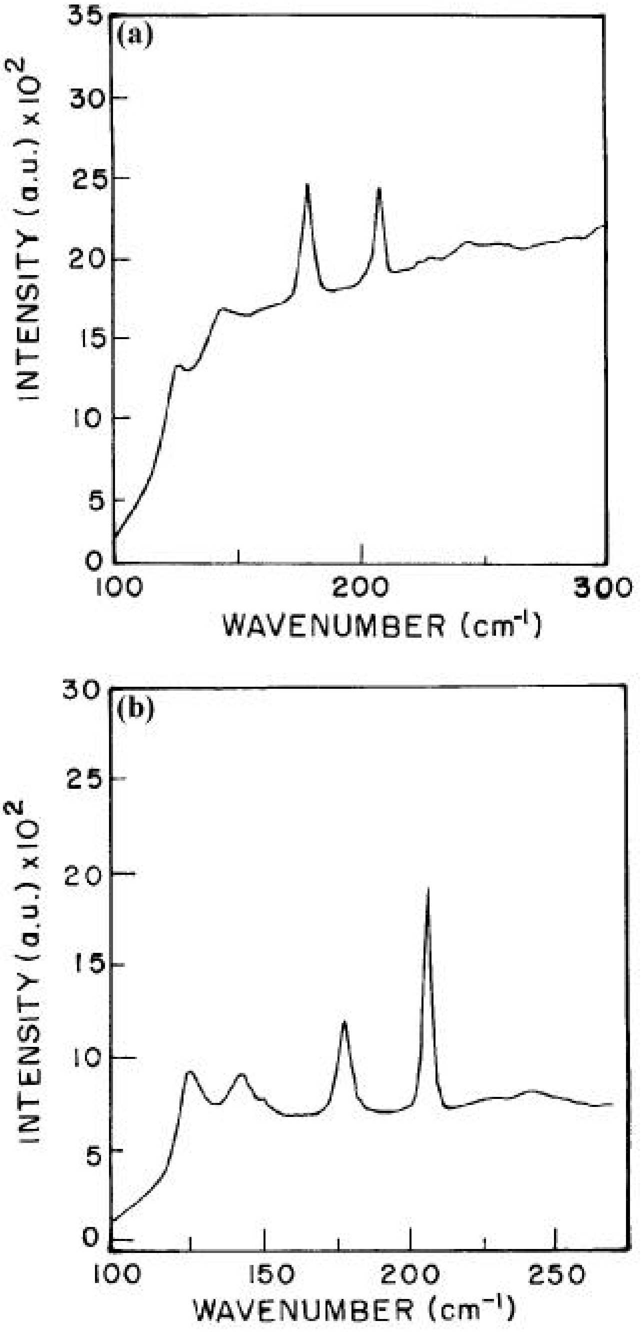

Figure 4. Raman scattering spectra for (**a**) undoped ZnTe and (**b**) ZnTe(In).

Table 1. Raman spectra of undoped ZnTe and ZnTe(In).

ZnTe (undoped)		ZnTe(In)	
Peak position (cm^{-1})	Peak intensity (arbitrary)	Peak position (cm^{-1})	Peak intensity (arbitrary)
126·60	206·9	123·51	250
145·55	137·9	141·83	216
177·77	706·9	177·19	500
207·31	603·5	205·01	1243

method devised by Iida (1972) uses the semi-logarithmic plot of intensity vs $1/T$ on the low temperature side of the curves. This method gives the trap depths as 202 meV and 419 meV in reasonable agreement with the first method.

The lower energy trap corresponds to the ionization of the In impurity which was reported to be 180–200 meV by Nahory and Fan (1967). The shift of the band gap by 0·20 eV could be due to excitation from the valence band to this level. The level at 412–419 meV can be attributed to the complex defect V_{Zn}^{2-}–In_{Zn}^{+} which is known as an A centre. This centre having a net negative charge (–) can capture a free hole and thus may give rise to the observed high resistivity. The In donor is bonded to the same Te atom as the Zn vacancy, V_{Zn}. Such an arrangement can have 12 possible orientations, 3 of them lying in a (110) plane. The hole trapped at the A centre is not centred at the V_{Zn} because the In^{3+} having an extra +ve charge over the Zn^{2+} it substitutes, repels the hole. On annealing the trapped hole is presumably captured by the V_{Zn}^{2-} to become V_{Zn}^{-}. The In atom then takes an off-centre position and a deep-shallow level transition takes place thus lowering the resistivity. The observed change in the Raman spectra indicates a change in the local bonding.

Chadi (1994) on the other hand has suggested that the formation energies of native defects such as vacancies, interstitials and anti-site defects in wide band gap semiconductors are too large to explain compensation in ZnSe and ZnTe along classical lines. He invoked the formation of *DX* centres with displacement of the Al or Ga donor by 1·85 Å along the anti-bonding [111] direction. The formation of a *DX* centre involves the following reaction:

$$2d^0 \rightarrow d^+ + DX^-.$$

Thus one donor releases an electron to become positively charged while a second donor captures an electron to form a DX^- centre. This reaction was found to be exothermic by 0·40 eV for Ga and 0·20 eV for Al and 0·34 eV for In in ZnTe (Park and Chadi 1995). For comparison the values for CdTe are 0·08 eV for Ga, – 0·42 eV for Al and – 0·04 eV for In.

A configuration coordinate diagram was used to explain *DX* centre formation. The optical excitation energy required to excite an electron from an ZnTe: In *DX* centre was found to be 2·06 eV from optical absorption studies. The thermal ionization energy, E_0, as found from TSC studies is 0·419 eV. The thermal activation energy for reverting to the semiconducting state is $kT \sim 0{\cdot}05$ eV corresponding to a temperature of 300°C. The effect of annealing is thus to reverse the above reaction. This results in neutral In donors which do not compensate the background hole concentration any more, thus reverting to the carrier concentration of undoped ZnTe. Further studies will be carried out to distinguish between the 2 models.

5. Conclusions

ZnTe single crystal doped with In was found to have semi-insulating properties with a reduced optical gap of 2·06 eV. Strong photoluminescence (PL) peaks were found at 1·37 eV and 1·03 eV with a weak shoulder at 1·43 eV. Two defect levels in the band gap were evident through thermally stimulated current studies. On annealing above 250°C, the material reverted to a low-resistivity state indicating metastable behaviour. Two models for this are discussed.

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