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Microwave synthesis, single crystal growth and characterization of ZnTe

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Abstract

ZnTe has been synthesized for the first time by microwave heating from high purity Zn and Te and the minimum reaction time determined to be 30 min. Single crystals were grown by modified vertical Bridgman technique from 4% rich Te melt, the growth direction being found to be $\langle 111 \rangle$. XRD showed formation of the zincblende phase with lattice constant 6.106 Å. Inductively coupled plasma (ICP) analysis showed Si, In, Cu, Au and Fe to be the main impurities present at ppm level. Crystals were p-type with resistivity 8.5 Ω cm, hole concentration $1.6 \times 10^{16} \text{ cm}^{-3}$ and mobility 46 cm²/V s at 300 K. Mobility was found to vary with temperature as $\mu_p \propto T^{-2.7}$ in the range 120–300 K. Photoluminescence (PL) at 10 K showed emission peaks at 2.06, 1.47, 1.33 and 1.05 eV. Thermal quenching of the PL bands has been studied. The samples showed weak photoconductivity due to small minority carrier lifetime. From the temperature dependence of the photoconductive gain, the minority carrier lifetime (τ_n) has been determined in the temperature range of 80–300 K. τ_n was thus found to go through a maximum of 4.5×10^{-7} s at 220 K and its variation with temperature is also discussed. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Among the wide gap II–VI semiconductors ZnTe, with its direct gap of 2.26 eV at 300 K is a promising material for a variety of optoelectronic devices such as green emitting diodes, solar cells,

waveguides and modulators. Triboulet et al. [1] have grown ZnTe by the cold travelling heater method. The growth of ZnTe crystals from vapour phase in closed or open tubes has been reported by several authors [2,3]. ZnTe crystals have been grown at 800°C by sublimation travelling heater method by Taguchi et al. [4]. ZnTe crystals doped with group III impurities are generally high resistive p-type due to self compensation [5]. Title et al. [6] have prepared Al-doped solution grown ZnTe

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by the addition of Al to the Te-rich liquid. Tubota [7] and Nahory and Fan [8] have grown In-doped ZnTe crystals in graphite reinforced quartz capsules using a modified Bridgman technique originated by Fischer [9].

All these growth techniques have used conventional thermal synthesis of ZnTe from the elements Zn and Te or synthesised powder of ZnTe for vapor growth. One of the most important and attractive developments in the context of synthesis of various inorganic compounds is the use of microwave heating. Microwaves are coherent and polarized and couple effectively with lossy materials, its primary action being very rapid heating. However, both physical and chemical characteristics of species (e.g. particle size and reaction enthalpy) seem to affect microwave coupling and hence microwave heating. The free energy of formation for ZnTe (-24.9 kcal/mole) may help the rate of the reaction to escalate rapidly. One important characteristic of microwave heating is that the entire volume of particles is heated up internally.

In this study, microwave heating has been used for the first time to synthesize ZnTe. It has the following advantages over conventional thermal synthesis: (i) for thermal synthesis, the system has to be kept above 900°C for 24–48 h. Zn and Te are viscous liquids at their respective melting points with viscosity decreasing with increase in temperature. Thus in order to have homogeneous mixing and complete reaction of the two components, the system is kept at a temperature much higher than their melting points for a long duration. (ii) The possibility of contamination of the high purity elements by the quartz ampoule itself is reduced in microwave heating since unlike in conventional heating, heat is generated within the material itself, instead of being supplied from external sources. As a result of this internal and volumetric heating, the reaction takes place very rapidly thus synthesizing ZnTe within 30–40 min. The various advantages of the microwave process over conventional heating have been discussed in great depth by Sutton [10].

In this paper, we first present the microwave synthesis of ZnTe followed by crystal growth by the vertical Bridgman technique. The crystals have then been fully characterised by electrical and

optical methods including resistivity, Hall effect, optical absorption, photoluminescence (PL) and photoconductivity (PC).

2. Synthesis and crystal growth

2.1. Microwave synthesis

In our study, 7Ns purity Zn and Te were used and 15 g of materials were prepared at a time using 48 and 52 at% of Zn and Te, respectively. Silica ampoules with 1.2 cm inner diameter and 2 mm wall thickness having a conical tip were first cleaned in acetone, dipped in chromic acid for 24 h and then washed thoroughly several times in de-ionized water. Zn was etched in a solution of $\text{HNO}_3 : \text{H}_2\text{O} : \text{HF} = 1 : 10 : 0.2$ while Te was etched in 20% aqueous solution of HCl. Zn was

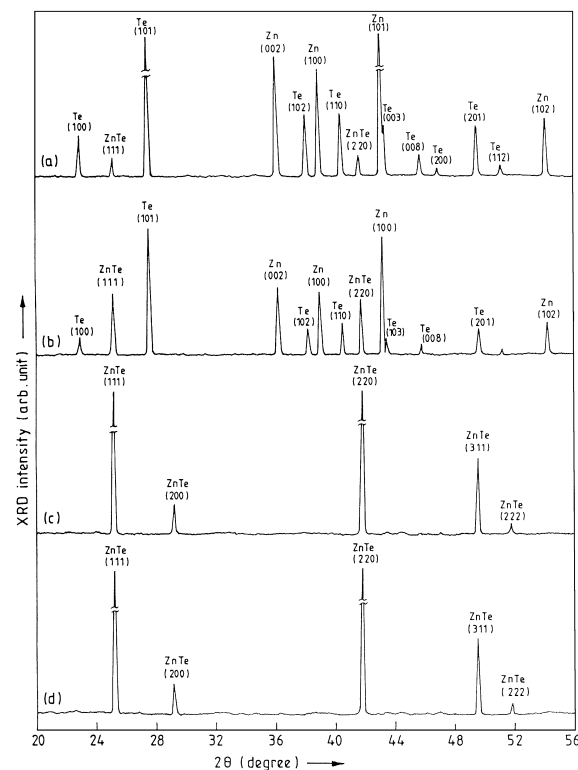


Fig. 1. X-ray diffraction spectra after (a) 10, (b) 20, (c) 30 and (d) 40 min of microwave synthesis of ZnTe.

taken in the form of small lumps of dimensions 1 mm^3 while Te was crushed to fine powder of approximate particle size $20\text{--}40\text{ }\mu\text{m}$. The silica tube containing the materials in powder form was evacuated to a pressure of 10^{-6} Torr and sealed. The ampoule was placed in a conventional microwave oven having a power rating of 900 W operating at 2.45 GHz with the sample being subject to slow revolution on the base plate. The ampoule content was rocked for proper redistribution twice in-between by interrupting the heating. Coloured flashes were seen emerging from the ampoule during the first few minutes of microwave exposure associated with rapid reaction between Zn and Te powder. The content of the ampoule became red hot indicating that quite high temperatures (around 900°C) were reached within a short time without explosion or breaking of the ampoule. The durations of microwave heating were 10, 20, 30 and 40 min. Fig. 1 shows the XRD of these synthesized ZnTe powders. Peaks corresponding to elemental Zn and Te were found in addition to ZnTe peaks after 10 and 20 min reaction time, thus showing incomplete reaction. After 30 and 40 min of synthesis, the material was in spongy form. There were

no peaks due to Zn, Te or any other phase except zincblende ZnTe. Thus a minimum reaction time of 30 min was determined for 15 g of material and the given aspect ratio of the ampoule. After 30 min the reaction stopped and the material turned red. This material was subsequently used for crystal growth.

2.2. Growth from Te rich melt

ZnTe crystals were then grown from the melt by the vertical Bridgman method. It is evident from the T - x diagram that for Te rich solutions a sharp decrease of melting point occurs with 4% deviation from the stoichiometry, its value being 1150°C at this composition [11]. This indicates a tendency of the liquid phase to separate into two phases, one with a composition close to $\text{Zn}:\text{Te} = 1:1$ and other which consists mainly of pure Te.

The furnace used for crystal growth had four SiC rods as heating elements. The temperature was controlled to better than $\pm 2^\circ\text{C}$ by using an 'Indotherm' programmable temperature controller providing approximately 5 cm long uniform temperature zone ($\pm 1^\circ\text{C}$) (Fig. 2). Keeping the synthesised ampoule in this zone, the temperature was

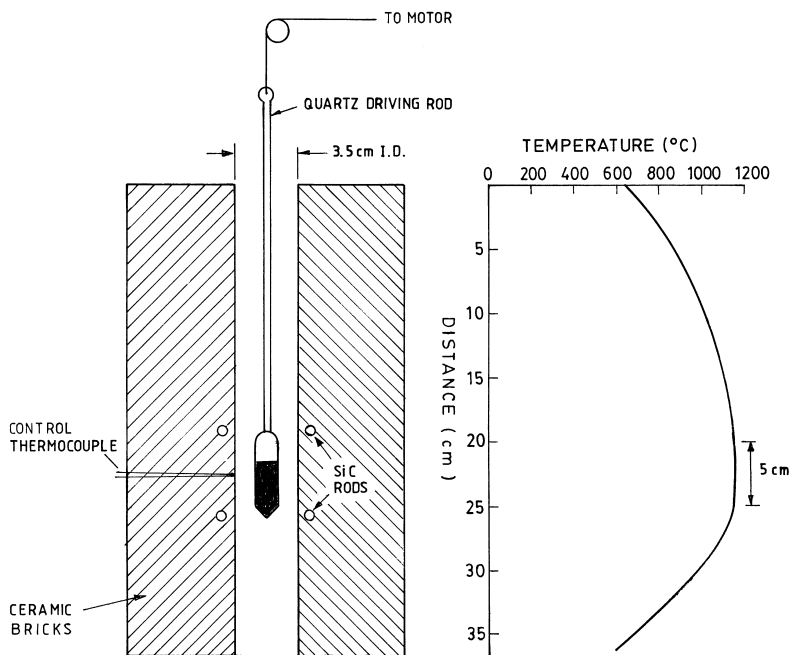


Fig. 2. Sketch of the furnace and a typical temperature profile used for vertical Bridgman growth of ZnTe.

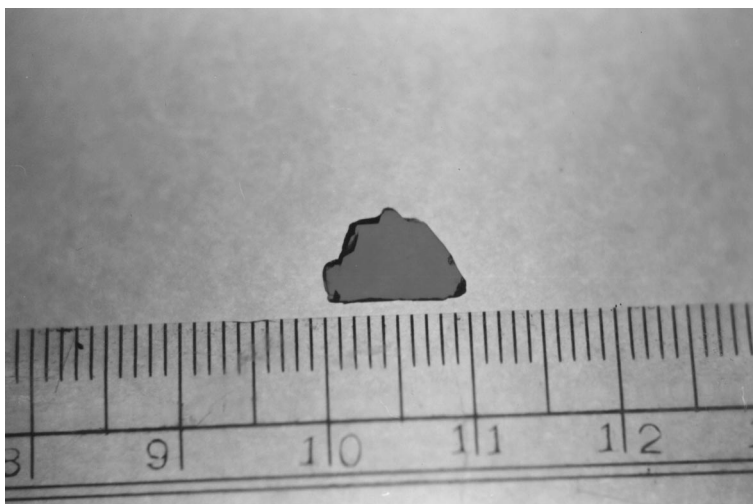


Fig. 3. Photograph of a single crystal of ZnTe.

raised at a rate of $\sim 30^\circ\text{C/h}$ to 1150°C . After holding the ampoule at this temperature for 1 h, it was given a downward motion at a rate of 6 mm/day to grow ZnTe single crystals. After 4 days of growth, the temperature of the furnace was lowered at a rate of 10°C/h down to 900°C and then power was switched off to allow natural cooling to room temperature in 12 h. Photograph of a typical single crystal of 1 cm diameter is shown in Fig. 3. Sometimes large grain polycrystalline ZnTe with 6–8 mm grain size were found.

3. Characterization

Inductively couple plasma (ICP) analysis of the sample showed Si to be the main impurity having concentration of $2.2 \times 10^{16} \text{ cm}^{-3}$. Larsen et al. [12] used the same method of crystal growth and found that a relatively high concentration of Si ($2\text{--}6 \times 10^{17} \text{ cm}^{-3}$) was not electrically active. In the present case the Si concentration was found to be one order of magnitude less than that reported by Larsen et al. [12]. Other impurities were In ($5 \times 10^{15} \text{ cm}^{-3}$), Fe ($2 \times 10^{15} \text{ cm}^{-3}$), Cu ($7 \times 10^{14} \text{ cm}^{-3}$) and Au ($3 \times 10^{14} \text{ cm}^{-3}$). The crystal structure and lattice constant were determined by X-ray powder diffraction method. The position and intensities of X-ray diffraction peaks of powder

ZnTe corresponded to the ASTM standard X-ray pattern of ZnTe with zinc-blende structure and lattice constant 6.106 \AA . The strongest diffraction peaks corresponding to (1 1 1) and (2 2 0) planes. Laue pattern of single crystal slice cut perpendicular to the growth direction gave a pattern with three fold symmetry characteristic of the $\langle 111 \rangle$ direction. This is the preferential growth orientation of the II–VI compounds since the (1 1 1) plane has the largest number of Zn–Te bonds/area which lowers the energy of the system.

Hot probe measurement showed that the samples were p-type. The Van der Pauw technique was used to determine the resistivity and Hall mobility of the crystals in the temperature range of 120–300 K using a Keithley Hall effect system. Ohmic contacts for undoped p-type crystals were prepared by thermal evaporation of Au followed by annealing at 400°C for 3 min in Ar atmosphere. Luqman et al. [13] have found good ohmic contacts with Au after annealing at 150°C for 2 h. However we have found that annealing at 400°C for 3 min gave best ohmic behavior with lowest contact resistance. This did not affect the electronic properties of the crystals significantly. The results are summarized in Table 1.

The carrier concentration derived from Hall measurements shows a linear $\ln p$ versus $1/T$ behaviour for $T < 200 \text{ K}$ and saturation for

Table 1

Temperature T (K)	Hole conc. p (cm $^{-3}$)	Mobility μ_p (cm 2 /V s)	Resistivity ρ (Ω cm)
300	1.6×10^{16}	46	8.5
120	4.5×10^{13}	537	258

$T > 200$ K. This suggests that carriers originated from one energy level. The temperature dependence of the hole concentration can thus be described by one-centre-one-level statistics [14] associated with the four fold degenerate valence band edge and is given by

$$p(p + N_D)/(N_A - N_D - p) = N_v/g \exp(-E_A/kT), \quad (1)$$

where $N_v = 2(2\pi m_h^* kT/h^2)^{3/2}$, E_A is the acceptor ionization energy, g the degeneracy factor, N_A and N_D are the total acceptor and donor concentrations, respectively, m_h^* is the average density-of-states effective mass of holes. The solid line in Fig. 4 shows the theoretical curve for $N_A = 4.8 \times 10^{16}$ cm $^{-3}$, $N_D = 2 \times 10^{15}$ cm $^{-3}$ and $E_A = 134$ meV. Deviation from the theoretical curve of Eq. (1) was observed for $T > 200$ K due to saturation of the acceptor level at 134 meV. A more rigorous two-centre-two-level model has to be employed in this range of temperature as discussed by Larsen et al. [12]. The compensation was found to be small ($N_D/N_A = 0.04$). Fig. 5 shows the temperature dependence of hole mobility. The mobility was found to vary with temperature according to $\mu \propto T^{-n}$ with $n = 2.7$ in the temperature range of 120–300 K.

The high quality of the crystals was demonstrated by their high transparency. Optical absorption of single crystals ($(\alpha h\nu)^2$ versus $h\nu$) shown in Fig. 6 gave a direct band gap of 2.26 eV at 300 K. The photoluminescence (PL) spectrum was measured with a conventional lock-in (EG and G 5209) technique using the 488 nm line of Ar $^+$ laser at a power of 50 mW and approximately 2 mm spot diameter as the excitation source. The sample temperature was varied between 10 and 300 K using an APD closed cycle cryostat. The emission spectrum was analyzed by a 0.67 m McPherson grating

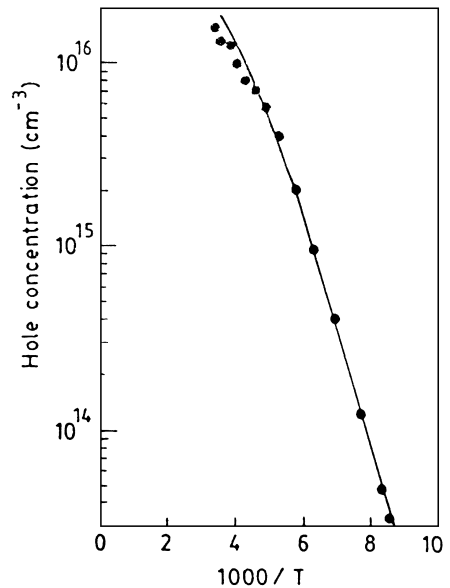


Fig. 4. Temperature dependence of hole concentration of ZnTe.

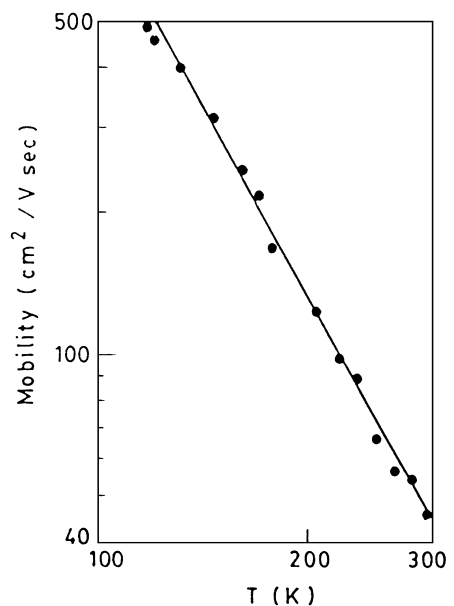


Fig. 5. Temperature dependence of hole mobility of ZnTe.

monochromator and detected by a liquid nitrogen cooled InGaAs detector. The detailed PL spectrum at 10 K is shown in Fig. 7. The PL consists of three emission bands. The first band had a peak at

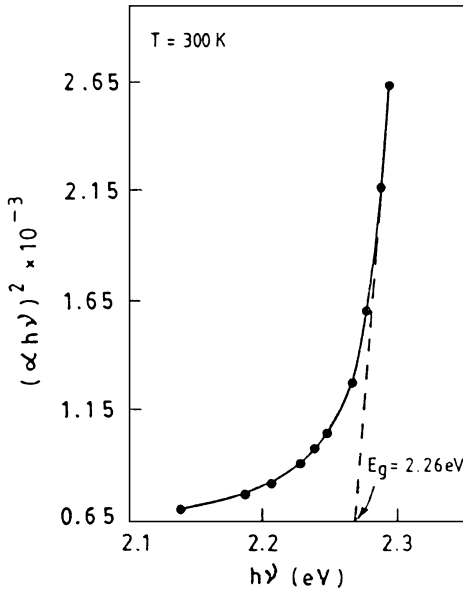


Fig. 6. $(\alpha hv)^2$ versus $h\nu$ plot obtained from optical absorption spectrum of ZnTe at 300 K.

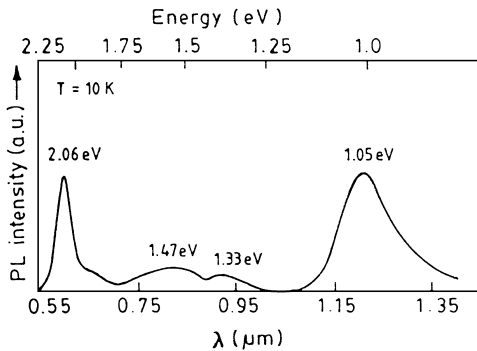


Fig. 7. Photoluminescence spectrum of ZnTe at 10 K.

2.06 eV. This may be due to a transition associated with the point defect O_{Te} which is located ~ 0.4 eV above the valence band edge [15]. The second band consisted of two peaks at 1.47 and 1.33 eV and are due to Cu and Au respectively [16]. The third band peaking at 1.05 eV has also been reported in undoped crystals [17] but its origin is not known. Temperature variation did not show any shift in the energy of the PL bands. Thermal quenching of the PL intensities of the three bands were studied and are shown in Fig. 8. The three bands had

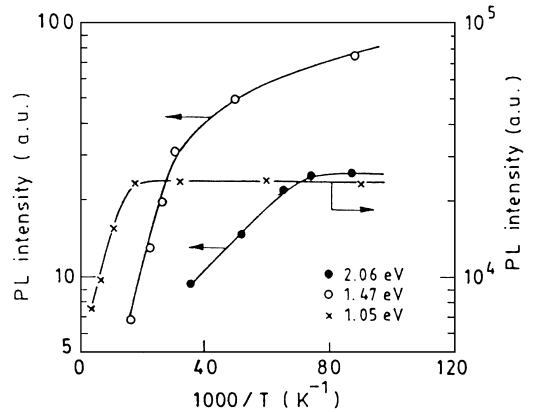


Fig. 8. Thermal quenching of the PL intensities of the three bands at 2.06, 1.47 and 1.05 eV.

quenching activation energies of 37.1, 85.8 and 95.3 meV respectively.

For photoconductivity (PC) studies, a planar geometry was taken with Au ohmic contacts. The ZnTe surface exposed to radiation being typically 0.1×0.4 cm². Samples were kept in a closed cycle He cryostat and illuminated with a tungsten–halogen source. A Jarrel-Ash monochromator with chopper and lock-in amplifier was used for the study of photoconductivity spectral response. In the dark, $\ln I_d$ versus $1/T$ plot showed two activation energies viz. 120 and 24 meV. The photocurrent increased with decrease in temperature and showed a maximum at 220 K and then decreased. From the variation of photocurrent, the temperature dependence of the mobility–lifetime product (or photocurrent gain $G = \mu_n \tau_n + \mu_p \tau_p$) was calculated using the expression

$$\Delta\sigma_{ph} = fe(\mu_n \tau_n + \mu_p \tau_p), \quad (2)$$

where f is the generation rate and is given by $f = \eta \alpha I / h\nu$ where η = quantum efficiency, α = absorption coefficient of ZnTe at the incident wavelength of light, I = intensity of light and $h\nu$ = incident photon energy which was chosen to be 2.5 eV which is above the band gap of ZnTe. $\Delta\sigma_{ph}$ is related to I_{ph} by the relation $I_{ph} = \Delta\sigma_{ph} E$ where E is the applied electric field. $\Delta\sigma_{ph}$ was calculated from the geometry and applied bias. The photocurrent gain had a maximum at 220 K. It is possible to simplify Eq. (2) since electron (minority

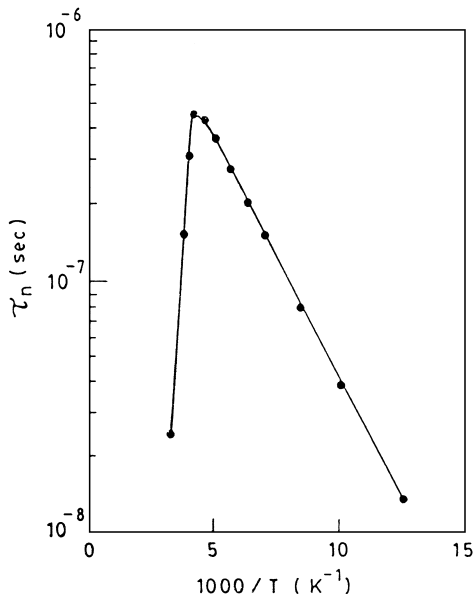


Fig. 9. Temperature dependence of the minority carrier (electron) lifetime of ZnTe.

carrier) contribution to the photoconductivity was much larger than that of holes i.e. $\Delta n/n_0 \gg \Delta p/p_0$ and also the electron mobility is considerably much larger than hole mobility ($\mu_n > \mu_p$). Thus the expression for gain can be written as

$$G = \mu_n \tau_n, \quad (3)$$

where τ_n is the free minority carrier lifetime rather than the recombination lifetime. Assuming theoretical variation of electron mobility with temperature as $\mu_n \propto T^{-1.5}$ and taking $\mu_n = 220 \text{ cm}^2/\text{V s}$ at 300 K as reported recently by Ogawa et al. [18] in low-resistivity n-type ZnTe (since experimental data on electron mobility of ZnTe at low temperature is not available), the electron lifetime was calculated at different temperatures from the PC gain. The Arrhenius plot of $\ln \tau_n$ versus $1000/T$ is shown in Fig. 9. The activation energies in the two regions viz. below and above 220 K were determined to be 40.2 and 404.1 meV, respectively. The first may be attributed to the donor level due to In impurity found by ICP analysis. The activation energy of 404.1 meV can be attributed to an acceptor level due to the point defect O_{Te} as determined from PL (Fig. 7). Thus for $T > 220 \text{ K}$, the minority

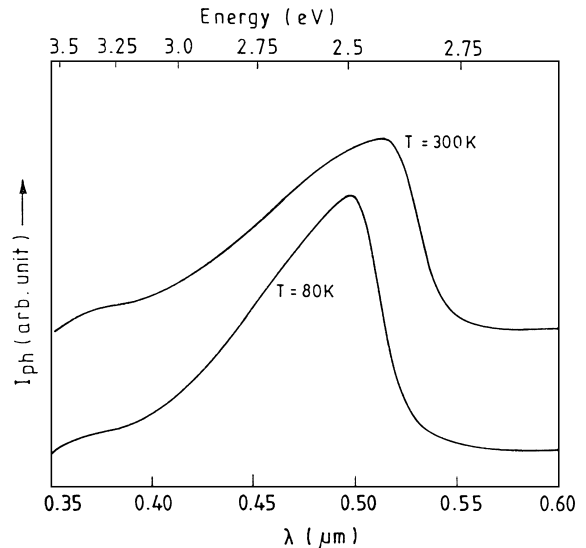


Fig. 10. Photoconductivity spectral response of ZnTe.

carrier (electron) lifetime decreases due to thermal generation of holes from the deep acceptor level. For $T < 220 \text{ K}$, the decrease in τ_n is due to trapping of minority carriers by the donor level 40.2 meV below E_c . Fig. 10 shows the photoconductivity spectral response of ZnTe at different temperatures. The spectra had a peak at 2.41 eV at 300 K and was found to shift towards higher energy with decrease in temperature. The rate of shift of the peak with temperature was the same as that of the band gap of ZnTe which is 0.5 meV/K.

4. Conclusions

Microwave synthesis of ZnTe has been successfully carried out from 7Ns purity Zn and Te. High quality crystals of ZnTe were grown by the vertical Bridgman technique and fully characterized by electrical and optical methods. The PL spectrum was dominated by impurity related transitions. Detailed study of photoconductivity spectral response and temperature dependence is reported. The temperature dependence of minority carrier lifetime is shown to be controlled by shallow donors (40 meV) at low temperature and by a deep hole trap (404 meV) at higher temperatures.

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