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The energy profile of polymorphous PbTe films: II. Recombination in heterophase PbTe films at high levels of optical excitation

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Abstract. Picosecond photoconductivity measurements of polymorphous PbTe films have been performed. Excess carriers were excited in the films by means of a picosecond YAG:Nd laser with pulse duration $t = 12$ ps. The instantaneous relaxation times of photoconductivity were obtained as a function of the excess carrier concentration ΔN from the kinetic analysis. The heterophase junction nature of the comparatively thin ($d \simeq 1$ μm) films was confirmed by their high photosensitivity. The junction thickness was evaluated from the interpretation of the instantaneous lifetime dependence on the excess carrier concentrations.

1. Introduction

It has been shown in part I (Baleva *et al* 1992) that PbTe films grown on KCl substrates by laser-assisted deposition (LAD) are heterophase junctions. The thickness of the heterophase transition is expected to be comparatively small as a result of the sharp phase transition from the high-pressure (HP) BCC CsCl-type or orthorhombic GeS-type to the FCC NaCl-type PbTe crystal phase. Our experiments also showed that the thickness of the region with HP phases is about 0.7 μm, thick enough to form a heterophase junction whose properties can be investigated.

The purpose of the present work was to confirm by other means, i.e. recombination at high levels of optical excitation, the heterophase junction nature of the PbTe films. With that end in view we have studied both thick films (in which the thickness d_r of the relaxed sublayer is much greater than the thickness d_s of the strained sublayer) and thin films (in which the thicknesses of the two sublayers are comparable).

2. Samples and experiment

2.1. Samples

The recombination at high levels of optical excitation was investigated only in undoped PbTe films, grown as in part I by LAD on (100)-oriented KCl substrates. It follows

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from the results reported in part I that the thicknesses of the strained sublayers, the carrier concentrations and Hall mobilities, as well as the energies of the junction transitions, depend strongly on the technological conditions and vary from film to film. Thus the interpretation of the photoconductivity relaxation requires each film to be characterized separately by optical and electrical measurements (as has been done in part I).

The thicknesses of the strained sublayers of the thick films were estimated from the modulated transmittance spectra to make sure that they are many times smaller than those of the relaxed sublayers. In sample K2609T, the results for which will be presented, $d_s = 3.6$ μm and $d_r = 0.6$ μm.

The types of the prevailing phase as well as the energies of the junction transitions have to be evaluated for each film under investigation from the dispersion of the refractive index $n(E)$. Figure 1 gives $n(E)$ for thick ($d = 4.2$ μm) sample K2609T and thin ($d = 0.9$ μm) sample K2709T. As is expected, the maximum at 0.32 eV, corresponding to the interband transition in the FCC phase, appears in the $n(E)$ dependences of both groups of samples. Three additional lower-energy maxima are clearly resolved only in the $n(E)$ dependence of sample K2709T. As was shown in part I the maximum at 0.23 eV corresponds to the interband transitions in the BCC phase. The other two maxima at 0.155 and 0.265 eV can obviously be assigned to transitions across the junction between the orthorhombic and the FCC phase (see part I, figure 9). However, if the junction between the FCC and orthorhombic phases governs the film properties, an activation energy ΔE of about 0.055 eV has to be determined from the temperature dependence of the Hall mobility $\mu(T)$. The $\mu(T)$ dependences for samples K2609T and K2709T are shown in figure 2. Sample K2609T demonstrates the behaviour typical of bulk PbTe, while the $\mu(T)$ dependence of sample K2709T indicates the presence of a potential barrier with energy $\Delta E = 0.09$ eV. The value of this activation energy (0.09 eV) together with the value of the BCC phase energy gap (0.23 eV) gives exactly the value of the FCC phase energy gap (0.32 eV). Thus, it is reasonable to assume that the junction between the BCC and the FCC phases is the junction that governs the film properties. The latter is supported by the clearly pronounced maximum at 0.23 eV (E_g of the BCC phase) in the dispersion of the refractive index (figure 1). Therefore, the potential energy profile of sample K2709T, whose conductivity is p type, must be the same as that in figure 3(*b*). The energy profile of sample K2609T must also be the same, as they are deposited under the same technological conditions. The only difference between the two samples is the different thicknesses of the relaxed sublayer, which is schematically shown in figures 3(*a*) and 3(*b*). The Fermi levels E_F in figures 3(*a*) and 3(*b*) were calculated numerically using Fermi integrals in the framework of the modified Kane model applied to FCC PbTe with a standard density-of-states effective mass. The Fermi level for sample K2609T calculated in this way lies 0.092 eV above the valence band (VB) top, and for sample K2709T 0.105 eV above the VB band top at room temperature.

2.2. Experiment and experimental results

Picosecond photoconductivity measurements have been performed. On appropriately prepared films, half-open aluminium stripes 0.5 mm wide with a gap for optical excitation were deposited. A coplanar system of contacts ensured matching to a 50 Ω microstrip line. Excess (non-equilibrium) carriers were excited in the films by means of a picosecond YAG:Nd laser ($\lambda = 1.08$ μm; the duration of a single pulse was $t = 12$ ps). The kinetics of the photoconductivity were taken directly from the

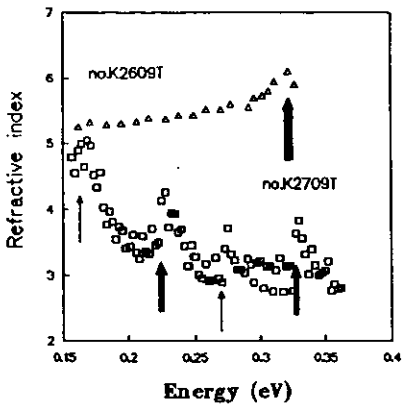

Figure 1. The refractive index dispersions of a thick sample (K2609T; $d = 4.2$ μm; $d_s \simeq 0.6$ μm; $d_r \simeq 3.6$ μm) and a thin sample (K2709T; $d = 0.9$ μm; $d_r \simeq d_s$). The bold arrows indicate the interband transitions at 0.32 and 0.23 eV. The thin arrows correspond to the transitions across the junction between the FCC and orthorhombic phases: $E_p^{FCC} - E_n^{orth} = 0.265$ eV and $E_p^{orth} - E_p^{FCC} = 0.155$ eV in sample K2709T.

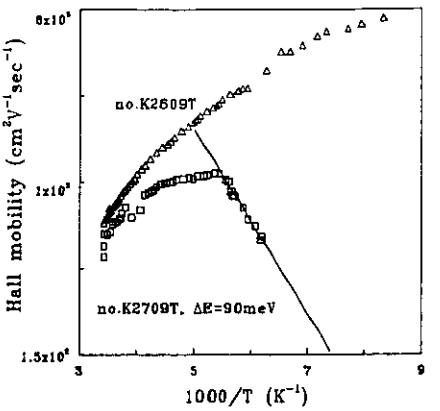

Figure 2. The temperature dependence of the Hall mobility of thick sample K2609T and thin sample K2709T.

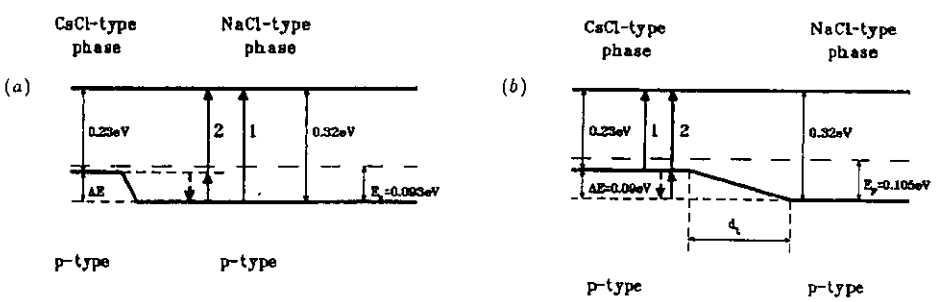

Figure 3. Schematic diagram of the potential energy profile of (*a*) sample K2609T and (*b*) sample K2709T. Arrows 1 indicate band-to-band Auger recombination, and arrows 2 recombination through 'recombination centres'.

recording oscillograph. From the kinetic analysis we have obtained the instantaneous photoconductivity relaxation times τ (defined as $1/\tau = -\mathrm{d}\{\ln[\Delta N(t)]\}/\mathrm{d}t$) as a function of the excess carrier concentration ΔN. Details of the experimental set-up have been given by Vaitkus *et al* (1990). The dependences of τ (ΔN) for samples K2609T and K2709T are shown in figure 4, by open triangles and open squares, respectively. It is evident that they differ considerably from one another.

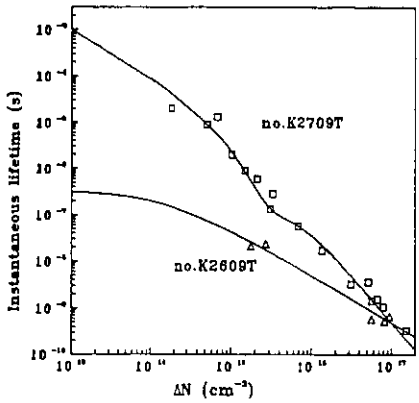

Figure 4. The dependence of the instantaneous lifetime of photoconductivity τ on the excess carrier concentration ΔN for thick sample K2609T and thin sample K2709T.

3. Discussion

Recombination investigations show that the Auger mechanism governs the recombination behaviour in PbTe, and, this being so, the dependences of the excess carrier lifetimes τ on their concentrations ΔN must be determined by a linear term due to the presence of recombination centres and a term describing band-to-band Auger recombination:

$$1/\tau = (\gamma_L M)\Delta N + \gamma_A(\Delta N)^2 \tag{1}$$

where γ_L is the coefficient of the centre-assisted recombination, M is the recombination centre density and γ_A is the interband Auger recombination coefficient.

We succeeded in interpreting the experimental dependences of τ on ΔN on the following assumptions.

(i) The term describing the process of radiative recombination was neglected, which is quite reasonable in the case of films grown by non-equilibrium techniques, such as ours.

(ii) The equilibrium concentration p_0 is homogeneously distributed in the samples.

(iii) The recombination processes that govern the relaxation of the photoconductivity in the thick films are those in the FCC phase (arrow 1 in figure 3(*a*)), as the quantity of the BCC phase is about six times smaller. In the thin films, where the quantities of the BCC and FCC phases are comparable, the photoconductivity relaxation of the samples is determined by the recombination processes in the BCC phase (arrow 1 in figure 3(*b*)), the energy gap of this phase (0.23 eV) being smaller than the energy gap of the FCC PbTe phase (0.32 eV). The coefficient of the interband Auger recombination depends on the energy gap E_g according to the relation (Herrmann 1978)

$$\gamma_A = 7.2 \times 10^{-32}(T/E_g)^{1/2}(1/E_g^5)\exp(-E_g/1.72 \times 10^{-3}T)\,(36/\epsilon_\infty) \tag{2}$$

where ϵ_∞ is the optical dielectric constant and $T = 300$ K. The values for the band-to-band Auger coefficients calculated from this relation are $\gamma_A = 4.5 \times 10^{-28}$ cm^6 s^{-1}

for the FCC phase ($E_g = 0.32$ eV and $\epsilon_\infty = 36$) and $\gamma_A = 3.2 \times 10^{-27}$ cm^6 s^{-1} for the BCC phase ($E_g = 0.23$ eV and $\epsilon_\infty = 44$).

(iv) At a lower level of excitation the empty states in the VB top of the BCC phase, which is in fact the equilibrium concentration $p_0(M = p_0)$, play the part of recombination centres in the case of the thick samples.

It is known that, when the Fermi level is situated between the middle of the energy gap and the recombination centres level with energy ΔE, the term for the centre-assisted recombination (arrow 2 in figure 3(*a*)) is (Rivkin 1963, 1965)

$$1/\tau = \gamma_L p_0 \exp(\Delta E/kT)\Delta N \tag{3}$$

where k is Boltzmann's constant.

In the case of the thin samples the energy ΔE is of the opposite sign and depends on the non-equilibrium concentration ΔN as well. It is well known that the transition potential $\Phi(x)$ across the junction is written in the form

$$\Phi(x) = (ed_t^2/\epsilon_\infty \epsilon_0)\,\Delta N + \Phi_0 = \Phi_N \Delta N + \Delta E/e \tag{4}$$

where

$$\Phi_N = ed_t^2/\epsilon_\infty \epsilon_0 \qquad \Phi_0 = \Delta E/e$$

and e is the electron charge. Here x is the coordinate perpendicular to the samples surface, d_t is the junction thickness (see figure 3(*b*)), ϵ_0 is the static dielectric constant and ϵ_∞ is the optical dielectric constant.

Thus in the case of the thin samples the term for the centre-assisted recombination (arrow 2 in figure 3(*b*)) has to be written in the form

$$1/\tau = \gamma_L p_0 \exp[\Phi(x)e/kT]\,\Delta N. \tag{5}$$

Hence for the dependence of $1/\tau$ on ΔN which describes the recombination in the thick samples we have

$$1/\tau = \gamma_L p_0 \exp(\Delta E/kT)\,\Delta N + \gamma_A(\Delta N)^2 \tag{6}$$

and for the thin samples

$$1/\tau = \gamma_L p_0 \exp(-\Delta E/kT) \exp[(\Phi_N e/kT)\Delta N]\Delta N + \gamma_A(\Delta N)^2. \tag{7}$$

The curves in figure 4 are calculated according to equations (6) and (7), where $\Delta E = 0.09$ eV is the activation energy determined from the temperature dependence of the Hall mobility, $\gamma_A = 4.5 \times 10^{-28}$ cm^6 s^{-1} and $\gamma_L p_0 = 5.5 \times 10^{-10}$ cm^3 s^{-1} in equation (6), and $\gamma_A = 9.8 \times 10^{-27}$ cm^6 s^{-1}, $\gamma_L p_0 = 1.5 \times 10^{-10}$ cm^3 s^{-1} and $d_t = 300$ nm in equation (7). In the case of the thick samples the interband recombination Auger coefficient is identical with the value theoretically calculated from equation (2), while in the case of the thin samples a better fit was obtained with γ_A larger than the theoretically calculated value. It is seen from figure 4 that the agreement between theoretically calculated curves and experimental data is very good.

It is worth mentioning that the dependence of $1/\tau$ on ΔN is sensitive to the parameter d_t which means that the junction thickness can be evaluated from the fitting.

From equations (3) and (7) at equilibrium, i.e. $\Delta N \ll p, (\exp[(\Phi_N e/kT)\Delta N] = 1)$, we obtain the ratio of the stationary lifetime τ_{st}^{thin} of a thin sample to the stationary lifetime τ_{st}^{thick} of a thick sample to be

$$(\tau_{st}^{thick}/\tau_{st}^{thin})_{expected} = \exp(-2\Delta E/kT) = 2.7 \times 10^{-4}.$$

The value experimentally detected for this ratio (as seen from figure 4) is

$$(\tau_{st}^{thick}/\tau_{st}^{thin})_{experimental} = 3.2 \times 10^{-4}.$$

This good agreement between the experimentally obtained ratio and the expected ratio of the stationary lifetimes confirms that the assumptions on which we have attempted to explain the recombination behaviour of both groups of PbTe films are reasonable. As the photoconductivity $\sigma = e^2 \Delta N \tau_{st}/m$ (m is the effective mass) depends on τ_{st}, its value has to be approximately four orders of magnitude higher in the thin samples than in the thick samples. This has been observed in the experiment.

4. Conclusions

On the grounds of the investigations of the recombination at high levels of optical excitation we can draw the following conclusions.

(i) The PbTe films deposited on KCl substrates are indeed heterophase junction structures.

(ii) The thin PbTe layers, the properties of which are governed by the heterophase junction, demonstrate high photosensitivity.

(iii) The junction thickness d_t, which is a fitting parameter in equation (7), can be evaluated from the investigation of the dependence of the instantaneous lifetimes on the excess carrier concentrations.

Acknowledgments

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