Impurity-induced photoconductivity in gallium-doped Pb$_{1-x}$Ge$_x$Te alloys

Evgeniy Skipetrov$^{a,*}$, Elena Zvereva$^a$, Lyudmila Skipetrova$^a$, Evgeniy Slyn’ko$^b$

$^a$Low Temperature Physics Department, Faculty of Physics, Moscow State University, 119899 Moscow, Russia
$^b$Institute of Material Science Problems, Chernivtsy Department, 274001 Chernivtsy, Ukraine

Abstract

Photoelectric properties of Pb$_{1-x}$Ge$_x$Te(Ga) (0.04$\leq$$x$$\leq$0.08) alloys were investigated under controlled infrared illumination. At least two types of relaxation processes of the photoconductivity after removing the illumination at $T$$<$$T_c$$\approx$ 60 K and an anomalous peak of negative photoconductivity followed by characteristic delay time on the front of kinetic curves were observed. Results were explained assuming the photoexcitation of the electrons from gallium-induced defect states to the conduction band and existing energy barrier separating localized and band states in configuration space. Appearance of a negative photoconductivity peak was attributed to the phase transition of the alloys from the rhombohedral phase to the cubic one due to the reconstruction of defect centers surroundings induced by illumination. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is known that doping of lead telluride with gallium leads to the emergence of deep impurity-induced level in the gap and an appearance of long-term relaxation processes under infrared (IR) illumination of the samples at temperatures below critical one $T_c$$\approx$ 70 K [1,2]. According to existing conceptions [3–5] it is attributed to the Jahn–Teller nature of the gallium-induced defect centers. It implies that capturing electron in the defect center under an external excitation and hence changing in a charge state of the defect center leads to the reconstruction of the defect center lattice surrounding and the formation of energy barrier between localized and band states in configuration space. So the rate of carrier transitions between the centers and the band is drastically reduced and the characteristic relaxation time $\tau$ increases up to about $10^5$ s at $T$ = 4.2 K. Such a high value of $\tau$ coupled with low close to intrinsic carrier concentration leads to high photosensitivity and makes PbTe(Ga) to be very attractive for the purposes of optoelectronics as a material for the fabrication of photonic devices.

One can expect that the alloys based on the PbTe(Ga) also might turn out the perspective materials for the purposes mentioned. However, lead telluride-based alloys doped with gallium have been investigated much worse than...
PbTe(Ga) [6,7]. In particular, no reliable data regarding the photoelectrical properties of the alloys are obtained up to the present moment. In order to investigate photoelectric properties and to determine the main parameters of relaxation processes in Pb$_{1-x}$Ge$_x$Te(Ga) under IR illumination in the present work the temperature dependence of resistivity and photoconductivity kinetics are investigated.

2. Experimental details

The n-type Pb$_{1-x}$Ge$_x$Te (0.04 ≤ x ≤ 0.08) single crystals doped with gallium (C$_{Ga}$ = 1.5–2 mol%) were synthesized by the sublimation from the vapor phase. Main parameters of the samples to be studied at helium temperatures are presented in Table 1. For each sample the temperature dependencies of resistivity (4.2 ≤ T ≤ 300 K) in the shielded from the external illumination chamber or under controlled illumination from IR heat source and kinetics of photoconductivity under IR illumination (T ≤ 60 K) were investigated. As a source of IR illumination we used a carbon resister, passing a various current $I$ through it.

3. Results and discussion

It was established that the alloys possess high infrared photosensitivity at temperatures below the critical one and the photoconductivity kinetics has a complicated long-duration character (Figs. 1 and 2). Switching on the IR illumination at low temperatures results at first in only a weak positive photoresponse on the front of kinetic curve, which after a certain delay time $\Delta t$, depending on the intensity of the illumination transmutes into an anomalous peak of negative photoconductivity (Fig. 1). Then a considerable long-term positive photoresponse with following saturation is observed that is typical of PbTe(Ga) [2]. The value of photoresponse achieves about two order of the magnitude in the range of highest intensity of the illumination.

As the temperature increases a peak of negative photoconductivity is smoothed out gradually (Fig. 2). Its amplitude monotonously decreases while the width increases. It is also interesting to note that a characteristic delay time $\Delta t$ rapidly decreases with increasing intensity of IR-illumination and practically disappears in the range of

<table>
<thead>
<tr>
<th>Samples</th>
<th>x</th>
<th>C$_{Ga}$ (mol%)</th>
<th>Type</th>
<th>$R_H$ (cm$^2$/C)</th>
<th>$\rho$ (Ωcm)</th>
<th>$n$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-4-7</td>
<td>0.04</td>
<td>1.5</td>
<td>n</td>
<td>&lt;1 × 10$^5$</td>
<td>9.1 × 10$^2$</td>
<td>&lt;3 × 10$^{14}$</td>
</tr>
<tr>
<td>Ge-6-4</td>
<td>0.06</td>
<td>1.5</td>
<td>n</td>
<td>&lt;1 × 10$^5$</td>
<td>3.4 × 10$^3$</td>
<td>&lt;4 × 10$^{14}$</td>
</tr>
<tr>
<td>Ge-8-5</td>
<td>0.08</td>
<td>2</td>
<td>n</td>
<td>&lt;4 × 10$^5$</td>
<td>1.4 × 10$^3$</td>
<td>&lt;4 × 10$^{14}$</td>
</tr>
</tbody>
</table>

Fig. 1. Kinetics of the photoconductivity in Pb$_{0.94}$Ge$_{0.06}$Te(Ga) (C$_{Ga}$ ≈ 1.5 at.%) at $T = 25$ K under variation of the IR illumination intensity from heat source.
maximal intensities. On the contrary a decrease in the illumination intensity leads to increasing \( D_t \) up to the values exceeding the characteristic time of the experiment (more than 50 s).

By comparing the temperature dependencies of resistivity \( \rho(T/I) \) measured in the darkness and under IR illumination the critical temperature of the appearance of photoconductivity \( T_c \) was determined as high as \( T_c = 50-60 \) K that practically attains the values \( T_c \) typical of PbTe doped with gallium \( (T_c \approx 70 \text{ K}) \) [2].

After removing the illumination the relaxation of photoconductivity appear to be rather complicated and the character of the photoconductivity decay to be non-exponential (Fig. 2). There observe at least two distinct regions in the \( \Delta \sigma(t) \) curves: a fast process occurring immediately after switching off the illumination and a following long-duration tail. One can suppose that two exponential parts with different arguments can fit the experimental dependence \( \Delta \sigma(t) \). At \( T = 4.2 \) K the characteristic time corresponding to the fast process was estimated as \( \tau_1 \approx 0.1 \) s while the relaxation time \( \tau_2 \) characterizing the long-term process exceeds \( 10^3 \) s and effect of the persistent photoconductivity takes place. So the full relaxation of conductivity to its initial dark value becomes possible only after heating the samples up to the temperatures higher than critical one \( T_c \).

Upon an increase in the temperature, an amplitude of the fast initial conductivity dropping after switching off the illumination increases, while the relaxation time \( \tau_2 \) obtained from the slopes of the exponential regions of the relaxation curves (straight lines in Fig. 2) decreases according to the nearly exponential law \( \tau_2 \sim \exp(W/kT) \) (Fig. 3).

To explain the experimental results we can assume that, just as in PbTe\( \langle \text{Ga} \rangle \), gallium-induced defect states in Pb\( _{1-x} \)Ge\( _x \)Te alloys have the Jahn–Teller nature [3–5] and IR illumination induces the photoexcitation of the free electrons from the gallium-induced defect states, located within the gap [6,7], to the conduction band. Due to capturing of the electrons from the defect center under the IR illumination and therefore changing in charge state of the center a reconstruction of the defect center lattice surrounding takes place, that
leads to the formation of an autolocalization barrier $W$ between localized and band states. In this case the temperature dependence of the characteristic relaxation time may be described by the equation $\tau_2 = \tau_2(0) \exp(W/kT)$ (Fig.3). Estimation of the barrier $W$ for the alloy with $x = 0.06$ gives us its value as about $23 \pm 2$ meV.

In order to explain the appearance of a negative photoconductivity peak the model was proposed assuming the structure phase transition of at least part of the sample bulk from the rhombohedral phase to the cubic one under the action of IR illumination. We suppose that such a situation can be put into effect due to the devastation of the defect centers under the action of IR illumination as a result of the electrons pass from the impurity to the band states, and the distortion of the crystalline lattice surrounding of the defects. In the frame of this model a character of resistivity changing under the illumination can be illustrated as follows (Fig.4). A weak initial positive photoresponse can probably be attributed to the photoresponse in the rhombohedral phase (process is illustrated by arrow 1 in Fig.4). Then after a certain delay time $\Delta t$ a transition of the sample to the cubic phase due to IR illumination accompanied with a sharp increase of the resistivity (arrow 2) takes place. At last, the continuos illumination of the sample in the cubic phase induces a long-term relaxation process of decreasing the resistivity (large positive photoresponse), which is typical of gallium-doped lead telluride (arrow 3).

In the frame of this approach, a delay time $\Delta t$ can be interpreted as a characteristic time of the distortion accumulation in the crystalline surrounding of the gallium-induced defect centers under illumination. Obviously this time has to be decreased by increasing the intensity of the illumination just as it was observed from the experiments (see Fig.1).

4. Conclusions

(1) High photosensitivity of $\text{Pb}_{1-x}\text{Ge}_x\text{Te} \langle \text{Ga} \rangle$ alloys, an effect of persistent photoconductivity at $T = 4.2$ K and a long-term relaxation processes at $T < T_c \approx 60$ K were revealed. Photoconductivity kinetics is characterized by at least two types of relaxation processes with drastically different characteristic times: a fast one with $\tau_1 \approx 0.1$ s and a long-duration one with $\tau_2 > 10^3$ s at $T = 4.2$ K. In the terms of the model assuming the existence of an energy barrier separating the localized and band states in the configuration space at low temperatures a height of the barrier was estimated for the $\text{Pb}_{0.94}\text{Ge}_{0.06}\text{Te} \langle \text{Ga} \rangle$ alloy as high as $W = 23 \pm 2$ meV.

(2) An anomalous peak of negative photoconductivity following a characteristic delay time, depending on intensity of IR illumination, was revealed on the front of kinetic curves. To explain the observed peculiarities a model was proposed, according to which a transition of at least part of the sample volume to the cubic phase under illumination occurs. We suppose that it might be connected with the devastation of the defect centers under illumination as a result of electron activation from impurity to the band states and...
the reconstruction of the crystalline surrounding of the defects.

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References