TENSORESISTIVE EFFECT IN SINGLE CRYSTAL MICROWIRES OF PbTe DOPED WITH Tl

E.A. Zasavitsky

Institute of Electronic Engineering and Industrial Technologies, Academy of Sciences of Moldova, 3/3, Academiei str., MD-2028, Chisinau, Republic of Moldova
E-mail: efim@lises.asm.md, efim@iieti.asm.md
(Received 28 November 2006)

Abstract

Results of room temperature measurements of tensoresistive effect in thin single crystal microwires of Pb$_{1-x}$Tl$_x$Te (x=0.0000 ÷ 0.0025, d = 5 ÷ 20 μm) obtained of the melted compound of corresponding composition by the filling of quartz capillary followed by the material crystallization are presented. For the samples corresponding to chemical composition with thallium concentration x ~0.0025 an essential increase of the tensoresistive effect in comparison with nondoped samples is observed; i.e., resistance changes for elastic elongations per unit length of a crystal. Various mechanisms which can lead to observed anomalies, including resonance scattering are discussed. Obtained experimental results allow us to suppose that the observed peculiarities can be interpreted on the basis of a model of Tl impurity band in PbTe.

1. Introduction

Interest to narrow-gap to semiconductor compounds A$_4$B$_6$ is caused by a lot of unique physical properties and an opportunity of their practical application in various technical devices: infrared detectors, lasers, tensometers, etc. In some aspects compounds A$_4$B$_6$ are unique physical objects: in system PbTe <Tl> superconductivity with superconducting transition temperature being extraordinarily high for semiconductor compounds [1] is observed; in systems PbTe <In> and PbTe <Ga> long-term relaxation processes are observed [2], etc.

The common characteristic property for all these compounds is formation of deep impurity levels and stabilization of the Fermi level. It is necessary to add that the impurities stabilizing the Fermi level are also transition elements Cr, Mo and rare-earth elements Yb, Gd [2]. Unique consequence of stabilization of the Fermi level in alloys on the basis of lead telluride is a high homogeneity of electrophysical properties, in spite of strong doping and high concentration of defects [3].

Presence of an impurity band of thallium against the background of the permitted band states of the valence band of PbTe can lead to essential changes of its electrophysical properties. In particular, a change of relative position of the impurity band and hole extreme of the valence band under external influence, e.g. under deformation, will lead to redistribution of carriers. Change of concentration of carriers in the impurity band, i.e. resonant scattering, will be essential to affect electrophysical properties of PbTe doped with thallium. Convenient objects for such research are single crystal wires.

Thin single crystal microwires of pure materials possess a number of the peculiar properties making them different from bulk crystals, e.g. elastic properties [4, 5]. Wire crystals of micron thickness admit elastic elongation per unit length up to 2÷5%. Research of uniaxial
deformation influence on electrophysical properties of microwire crystals has been carried out for a lot of materials [4–6].

The scale effect, i.e. substantial increase of mechanical strength of wire crystals at reduction of the sample diameter is explained by reduction of probability of defect occurrence both inside a crystal and on its surface. First of all, dislocations sharply decreasing with reduction of the crystal diameter and non-uniform inclusions of impurity pertain to volumetric defects. It is known that the mechanical strength is influenced only by the impurity mechanically captured during growth. The mechanism of reduction of strengthening actions of impurity in wire crystals can be connected with the fact that aggregations of impurity atoms can be a source of nucleation of dislocations.

2. Experimental results and discussion

Single crystal microwires of Pb$_{1-x}$Tl$_x$Te (diameter d = 5 ÷ 100 μm, length l ~ 20 cm) with thallium average concentration x = 0.00 ÷ 0.02 were grown in the following way [7]. The initial material of corresponding chemical composition was placed into a quartz tube of diameter 15 mm. The bulk material was prepared in the following way. Since pure Tl oxidizes in the air quickly and greatly, for preparation of initial mixtures it is necessary to use compounds of thallium, in our case TlTe. Syntheses of polycrystalline materials (PbTe)$_{1-x}$(TlTe)$_x$ of corresponding compounds were made in the quartz tube in the hydrogen atmosphere. Over the material a bunch of quartz capillaries is situated. The choice of quartz as the material for capillaries is limited by the high temperature of its softening, what must be higher than the melting temperature of the material. The tube was evacuated up to residual pressure $10^{-2}$ ÷ $10^{-3}$ Pa and placed in vertical zone furnace, in which the temperature along the full length of the capillary is the same and higher than the melting temperature of the material ($T_{\text{melt}} < T < T_{\text{soft}}$). After the material melting the capillaries with open lower ends were put down in the melted material. Afterwards in the tube pressure under which capillaries were filled with the melted material increased. Crystallization of melted material was realized directly beginning from soldered ends to the open ones due to move of the furnace; rate of the move may be changed and makes up several centimeters per hour. The given method of obtaining of single crystal microwires allows producing samples with different diameters under the same growth conditions with high structural perfection. The structural quality was tested by X-ray diffraction and Laser Microprobe Mass Analyzer (LAMMA).

The samples for measurements were prepared in the following mode. The sample of the corresponding diameter was chosen from the set of crystals prepared for measurements. As the initial sample has glass isolation, it was preliminarily subjected to selective etching in a solution of acid HF. Measurements were carried out on installation developed in our laboratory.

Figure 1 shows the resistivity dependence on value of uniaxial deformation applied to wire crystal PbTe in a direction similar to the crystallographic direction [100]. The analysis of the dependence shows that the maximal elastic elongations per unit length of a crystal for all samples achieve the order of 1%. The resistance changes slightly and makes up several percent.

Dependence of resistance on a degree of deformation of doped wire crystal Pb$_{1-x}$Tl$_x$Te ($x=0.0025$) also is presented in Fig. 1. One can see that in the case of the doped wire crystals, other things being equal, this dependence is stronger by an order of magnitude.

Uniaxial deformation essentially influences band structure of the material. For films of PbSe and PbTe such researches have been carried out earlier [8]. Deformation had elastic
character of elongations per unit length to 6 %. It has been shown that uniaxial deformation allows realizing semimetal state, which cannot be obtained either by means of isotropic deformation or in solid state solutions of type PbTe-SnTe. For all this, generally, occurrence of semimetal state is connected with various displacements of valleys under action of deformation. In particular, uniaxial deformation applied along the direction [111] leads to a removal of degeneration of four ellipsoids of constant energy of the valence band and of the conduction band in L-point of the Brillouin zone; that is, the so-called valley splitting occurs. Thus, one valley along the direction [111] is picked out and the other three remain equivalent. It leads to redistribution of charge carriers between the valleys that should affect kinetic factors, in particular resistivity of microwire crystals; for example, those based on PbTe.

The effect of valley splitting is absent in the case of deformation application along the direction [100]. In this case influence of uniaxial deformations on a zone spectrum is reduced only to the change of the bandgap value and, therefore, to the change of the effective mass value. According to this, the piesoresistance effect should be weaker than in case of deformation along other directions when there is a redistribution of the carriers between the valleys. Thus, the obtained results on research of uniaxial deformation influence on resistance of pure microwire crystals of PbTe can be well explained within the limits of such approach.

It is considered established that doping of lead telluride with thallium leads to formation of an impurity band against the background of the permitted band states of the valence band of PbTe [1] (Fig. 2).
Energetic position of a maximum of density of states of thallium impurity band $\varepsilon_i$ at $T=77$ K makes $\varepsilon_i \approx (0.26 \pm 0.02)$ eV. Thus, the width of thallium impurity band $\Gamma$ strongly depends on concentration of impurity: $\Gamma = 0.053$ eV at $N_{\text{Tl}} = 1.2$ at%; $\Gamma = 0.023$ eV at $N_{\text{Tl}} = 0.5$ at%. As the temperature grows the impurity band is displaced towards edges of the valence band $\frac{d\varepsilon_i}{dT} \approx -(1/2) \times 10^{-4}$ eV / K.

Considering as the gap between extremes of the valence band submits to approximately the same empirical relations

$$\frac{d\varepsilon_{\text{v}}}{dT} \approx -4 \times 10^{-4} \text{ eV} / \text{K}.$$ 

It is possible to state that in a wide temperature region the influence of thallium impurity band on the transport phenomena of lead telluride is actual. Application of pressure leads to change of the gap between extremes of the valence band according to the empirical expression [1],

$$\frac{d\varepsilon_{\text{v}}}{dP} \approx 8 \times 10^{-4} \text{ eV} / \text{bar},$$

that is, the application of pressure leads to an increase of the gap between heavy-hole band $\Sigma$ and light-hole band $L$. Thus, the pressure dependence of position of the impurity band level is described by the formulas [1]

$$\frac{d\varepsilon_i}{dP} \approx (1/2) \text{meV} / \text{kbar}.$$ 

Considering a sign and weak dependence of the impurity level position on pressure, it is possible to draw a conclusion that the basic contribution to change of electrophysical parameters will be made by movement of the valence band extremes: heavy-hole band $\Sigma$ and light-hole band $L$.

It is known [1] that density of impurity states $g_i(\varepsilon)$ is described by the Lorenz curve

$$g_i(\varepsilon) = \frac{N_{\text{Tl}} \Gamma}{\pi (\varepsilon - \varepsilon_i)^2 + (\Gamma/2)^2}.$$ 

The analysis of this expression allows drawing the following conclusion:
• the strongest dependence of electrophysical parameters will be observed in region of the charge carrier concentration when the Fermi level only starts entering the impurity band;
• in the region of greater charge carrier concentration, in process of the Fermi level approaching to the middle of the impurity band, this dependence will become weaker.

Thus, in the case of wire crystals Pb$_{1-x}$Tl$_x$Te the unique reason of the sharp increase in degree of the resistivity dependence on applied uniaxial deformations, alongside with the stated reasons of the resistivity change for wire crystals PbTe, is presence of the impurity band of thallium. In the field of small concentration of thallium impurity when the Fermi level only enters the impurity band, small changes in the concentration of carriers caused by deformation lead to an essential change of the mechanism of the carrier dispersion. Thus, the observed features on the resistance dependence on the applied deformation are caused by features of the band of structures PbTe doped with Tl: by the relative energetic position of edges of bands (light-hole band L and heavy-hole band Σ) and impurity band ε$_i$.

Investigation of wire crystals Pb$_{1-x}$Tl$_x$Te at small impurity concentration is caused by the following reasons. Introduction of an impurity influenced strongly and nonmonotonously the material dislocation structure. A decrease in density of dislocations begins at the certain impurity concentration corresponding to formation of sufficiently powerful impurity atmospheres on dispositions. Experimentally such dependences were observed on many materials: Si, Ge, and GaAs [9]. In our case formation of structural complexes on the basis of Tl$_n$Te$_n$ in the field of small impurity concentration possibly leads to a decrease in density of dislocations. It will explain that the doped crystals withstand a load of applied deformations comparable with pure crystals. However, at an increase in the impurity concentration a partial decay of supersaturated solution PbTe - TlTe is observed. It leads to additional generation of dislocations. It follows from measurements of dependence of the wire crystal microhardness that such boundary concentration of the impurity is equal to 1.125 at%. Crystals with the charge carrier concentration when the Fermi level only starts entering the impurity band are of interest.

3. Conclusions

In the present work the results on research of tensoresistive properties of thin single crystal microwires of Pb$_{1-x}$Tl$_x$Te (x=0.0000 ÷ 0.0025, d = 5 ÷ 20 μm) at the room temperature for uniaxial deformation to 1% are presented. The main task of the given research was determination of thallium impurity influence on electrophysical properties of lead telluride. It was revealed that for the samples of PbTe<Tl> corresponding to chemical composition with concentration of thallium x ~0.0025 an essential increase of tensoresistive effect in comparison with nondoped samples is observed. It is qualitatively shown that this dependence is a function of charge carrier concentration and should be observed most strongly in the region of concentration where the Fermi level only starts entering the impurity band.

Thus, at presence of the impurity band it is possible to obtain stronger dependences of the resistance on deformation connected with both redistribution of carriers between a zone and an impurity band and with resonant dispersion.

This work was supported by the Supreme Council for Research and Technological Development of Moldova under the State Program “Nanotechnologies, New Multifunctional Materials, and Electronic Microsystems".
References

[8] M.P. Volotskoi and V.I. Kaidanov, Thermoelectric materials and films, 101-107, Lenin-
grad, (1976).
[9] M.G. Milvidskii and V.B. Osvenskii, Structural defects in monocystals of semiconduc-