

## Highly resistive *p*-PbTe films with carrier concentration as low as $10^{14} \text{ cm}^{-3}$

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We propose here a model according to which a high density of semiconductor–insulator interface states can deplete practically the whole film volume, provided that the film thickness is of the order of Debye screening length. We demonstrated this experimentally by showing that thin *p*-PbTe films, thermally deposited on mica substrate, have an unusually low concentration of free holes, as low as  $10^{14} \text{ cm}^{-3}$  at 100 K, resulting in a very high value of resistance, Hall constant, and Seebeck coefficient, respectively. Such low concentration of free carriers allows an investigation of a whole series of phenomena in  $A^{IV}B^{VI}$  semiconductors, such as injection currents, injection electroluminescence, electronic memory phenomena, electric field effect control of thermopower, and more. © 2004 American Institute of Physics. [DOI: 10.1063/1.1728319]

In a series of articles<sup>1</sup> we have analyzed the potential of electric field effect (EFE) control of various transport and galvanomagnetic properties in thin films of Bi and PbTe. The feasibility of this method is based on the basic requirement of low intrinsic concentration of charge carriers and a large enough Debye screening length.

Trying to apply this method to narrow-gap semiconductors (e.g., PbTe) encounters the difficulty of relatively high carrier concentrations, of the order of  $10^{17}$ – $10^{18} \text{ cm}^{-3}$ , which makes the EFE method practically inefficient in these cases. On the other hand we are interested in thin PbTe films because of their relatively high thermoelectric power,<sup>2</sup> and their IR photoelectric properties.<sup>3</sup> Thus, the question is: is there a way to reduce significantly the concentration of the charge carriers in these films?

We suggest here that such situation can be realized when the interface between the semiconductor film and the substrate has a high concentration of trapping sites. Such interface will drain the film of its charge carriers over a layer of the thickness of the Debye screening length  $L_D$ . Thus, if the film thickness is of the same order of magnitude, the concentration of free-charge carriers can be reduced down to  $10^{14}$ – $10^{15} \text{ cm}^{-3}$ , i.e., the film will be practically intrinsic over its whole thickness. Such low carrier concentration PbTe films have not been realized or studied so far.<sup>4–6</sup> Under such conditions one could expect a considerably large EFE. On the other hand, however, it is well known that surface states screen an external electric field, thus weakening the EFE. Nevertheless, we argue that under suitable conditions one can achieve, at the same time, both a very low carrier concentration as well as significantly large EFE. In the following we present experimental results and quantitative analysis that support our assertion.

The *p*-PbTe films have been thermally deposited in vacuum on 10–20  $\mu\text{m}$  mica substrate by standard procedure. The films were polycrystalline, with a crystallite characteristic size of about 1–10  $\mu\text{m}$ . The insert to Fig. 1 shows the MDS structure: “Metal gate–Dielectric (mica)–Semiconductor PbTe film” of the sample. The free surface of the PbTe film was protected from the atmospheric oxygen by an EuS layer. Gold contact pads were sputtered on the sample to measure the resistance  $R$ , the Hall constant  $R_H$ , the Seebeck coefficient  $S$ , and EFE. The measurements were carried out in the temperature interval of 15–310 K, in the range of gate voltage  $V_g$  of  $\pm 1000$  V, and in a vacuum better than  $10^{-7}$  torr.

We present here the results of measurements on one of

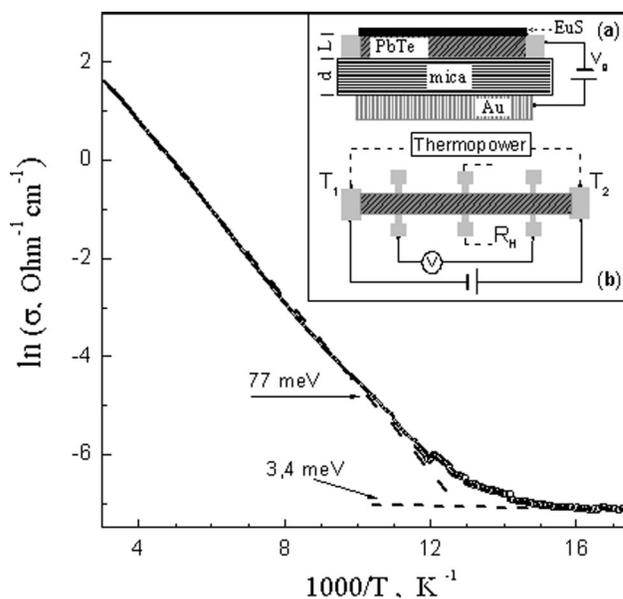


FIG. 1. The temperature dependence of the resistance. The high-temperature activation energy is  $E_a = 77$  meV. The inset shows: (a) the experimental MDS structure of the sample and (b) the connections for the various measurements.

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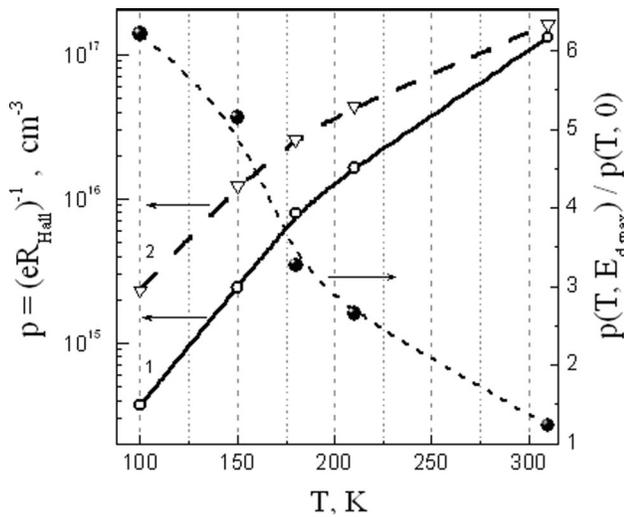


FIG. 2. On the left: the temperature dependence of the Hall concentration of holes at (1)  $E_d=0$  and (2)  $E_d=-0.875 \times 10^8$  V/m. On the right: the temperature dependence of the relative Hall hole concentration.

the sample films with the thickness of 533 Å. Preliminary characterization of the type of electroconductivity of as-grown films was established by the method of thermoelectric probe.

Figure 1 shows the temperature dependence of  $R(T)$ . The high-temperature activation energy derived from these results,  $E_a=77$  meV, is close to the PbTe half-gap at  $T=0$  K,  $E_g(0)/2=95$  meV. This activation energy being close to  $E_g(0)/2$  over such a wide temperature interval is consistent with the observed high resistance of the film. The specific resistivity,  $\rho(T)$ , varies from  $\rho=0.24$  Ω cm at room temperature (310 K), to  $\rho=120$  Ω cm at 100 K.

The smaller, low-temperature activation energy, of about 3.4 meV, corresponds apparently to some acceptor-like levels.

Figure 2 presents the average Hall concentration of holes in the absence of EFE, and at the maximal negative  $E_d$ . The hole concentration varies from  $\approx 10^{17}$  cm $^{-3}$  at room temperature to  $\approx 10^{14}$  cm $^{-3}$  at 100 K, i.e., the film is practically intrinsic.

It should be noticed that the Seebeck coefficient,  $S(T)$ , varies from  $S=60$  μV/K at 310 K up to an unusually high value of  $S=4500$  μV/K at 100 K. This extraordinarily high thermopower is also an evidence of the extremely low carrier concentration in the film.

According to Fig. 2, the average concentration of the thermally generated holes is  $\langle p \rangle \approx 1.5 \times 10^{17}$  cm $^{-3}$  at room temperature. At lower temperatures, the hole concentration becomes as low as  $10^{14}$  cm $^{-3}$  or less. At room temperature all the acceptors, which in PbTe have a very small activation energy,<sup>4–6</sup> must be ionized, so that their concentration in the film is  $N_a \approx 10^{17}$  cm $^{-3}$ . Due to their small activation energy, the fraction of ionized acceptors varies only weakly within the temperature range of the experiment, and cannot account for the 3 orders of magnitude decrease of  $\langle p \rangle$ . Thus, it is plausible that practically all the thermally generated holes will be captured and localized on the mica–PbTe interface. For PbTe with  $N_a \approx 10^{17}$  cm $^{-3}$  and a dielectric constant  $\epsilon(300 \text{ K}) \approx 400$ , we obtain  $L_S \approx 500$  Å, i.e., the thickness of

our films. Thus, practically, the whole film volume becomes almost completely depleted.

Using the experimental results, one can derive some quantitative estimates. First, let us estimate the maximal charge induced into the film at  $|E_{d,max}|=0.875 \times 10^8$  V/m. For mica, with a dielectric constant  $\epsilon_d=7$

$$|Q_{is}^{max}| = \frac{\epsilon_0 \epsilon_d |E_{d,max}|}{e} \approx 3.4 \times 10^{12} [e]/\text{cm}^2,$$

and the average induced charge concentration in the 533 Å film is

$$\langle p_i \rangle = \frac{|Q_{is}^{max}|}{L} = 6.4 \times 10^{17} [e]/\text{cm}^3.$$

Figure 2 shows that, at decreased temperatures, most of the induced positive charge is trapped. The same results are observed for the maximal negative induced charge. Despite the strong trapping of the induced charge, the relative change of free carriers reaches a value as high as about 10 at low temperatures. This is a direct result of the extremely low intrinsic carrier concentration in the film. It follows then that the mica/PbTe interface has a high concentration  $N_S$  of surface states of acceptor and donor type. One can estimate a lower limit of  $N_S^{\min} \geq |Q_{is}^{max}| = 3.4 \times 10^{12}$  cm $^{-2}$ . Since, ordinarily the relative occupation of the surface states constitutes  $10^{-1}–10^{-2}$  of the total, it follows that  $N_S \approx 10^{13}–10^{14}$  cm $^{-2}$ . This value is obviously higher than the total number of the acceptor states in the film:  $N_{at} \approx 10^{17}$  cm $^{-3} \times L = 10^{11}$  cm $^{-2}$ .

The carriers trapped on the intergrain surfaces consist of only a small fraction, 0.01–0.001, of the total trapped charge, as can be easily estimated from the crystallite size and film thickness. However, these charged barriers can be an impeding factor, limiting the carrier mobility.

One can now derive consistently the energy-band scheme of the film at the mica–PbTe interface. The simplest assumption one can make is that  $N_{Sa}=N_{Sd} \approx 10^{13}–10^{14}$  cm $^{-2}$ , and that these states are distributed uniformly over the PbTe forbidden gap  $E_g$  at the interface. It is well known that when the concentration of surface states is very high, the surface becomes quasidelectronneutral by itself, practically independent on the bulk. Thus, the film bulk is charged negatively due to the ionized acceptors, while the interface is charged positively, as the bulk holes are trapped by the interface states. The Fermi level  $E_F$  at the interface is located just below the middle of the forbidden gap, so as to provide a positive surface charge equal to the total number of the bulk acceptors. In fact, if  $N_S \approx 10^{13}–10^{14}$  cm $^{-2}$ , then the energy density of states at the interface surface is  $D_S \approx N_S/E_g \approx (10^{13}–10^{14})$  cm $^{-2}/0.3$  eV  $\approx 3 \times (10^{13}–10^{14})$  cm $^{-2}$  eV $^{-1}$ . As the total number of the bulk acceptors is  $N_{at} \approx 10^{11}$  cm $^{-2}$ , even a maximally possible number of bulk holes will occupy an energy interval of  $\Delta E_S \approx 1–10$  meV. Thus, the  $E_F$  at the interface adjusts itself somewhat below, but close to, the middle of  $E_g$  within  $\approx \Delta E_S$ . On the other hand,  $E_F$  inside the film must be located near the acceptor levels, i.e., close to the valence band. Hence, the bands bend down at the interface, the magnitude of this bend being the difference between the position of the Fermi level at the

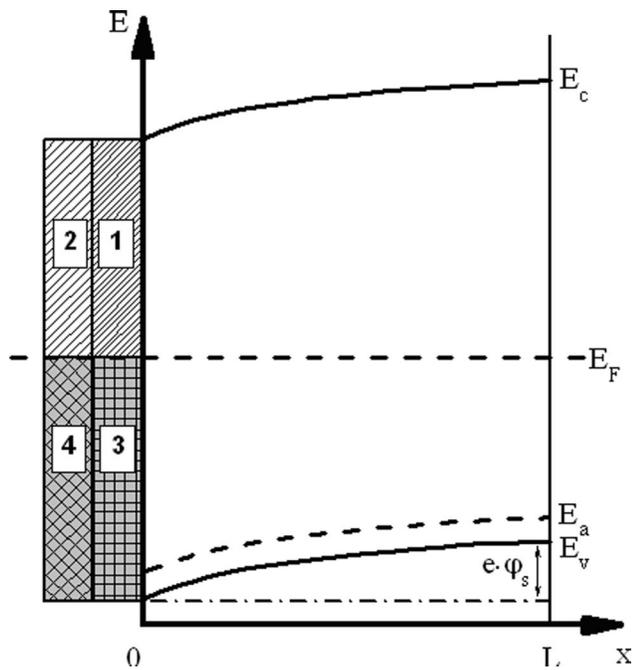


FIG. 3. The energy band diagram of the mica-*p*-PbTe film interface: (1) Empty positively charged IF donors; (2) Empty neutral IF acceptors; (3) Occupied neutral IF donors; (4) Occupied negatively charged IF acceptors;  $L$  is the film thickness;  $E_V$  is the top of the valence band;  $E_a$  is the acceptor level;  $E_F$  is the Fermi level, and  $e\varphi_s$  is the magnitude of the band bending at the interface.

interface and its position in the bulk, as shown schematically in Fig. 3. The bend cannot be large, as  $\epsilon \gg 1$  and  $L \sim L_S$ , and the carrier concentration is close to intrinsic.

In conclusion, we have proven that high density of interface states can deplete practically the whole film bulk, provided that the film thickness is of the order of  $L_S$ . Under

these conditions the *EFE* control may be rather strong at low temperature. We demonstrated this by showing that thin *p*-PbTe films, thermally deposited on mica substrate, have an unusually low free-hole concentration, resulting in a very high value of resistance, Hall constant, and Seebeck coefficient. Such low concentration of free carriers allows us to investigate now a whole series of phenomena in  $A^{IV}B^{VI}$  semiconductors, such as the Fermi glass behavior of the films (due to a random potential of the charged interface states), injection currents, injection electroluminescence, electronic memory phenomena (the dependence of properties on the  $E_d$  and  $T$  history), and control of various thermogalvanomagnetic and optical characteristics including thermopower.

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<sup>1</sup>V. Sandomirsky, Y. Schlesinger, A. V. Butenko, I. G. Kolobov, and A. Ronen, *Physica B* **329–333**, 1521 (2003); V. Sandomirsky, A. V. Butenko, R. Levin, and Y. Schlesinger, *J. Appl. Phys.* **90**, 2370 (2001), and references therein.

<sup>2</sup>G. D. Mahan, *Solid State Phys.* **51**, 81 (1998).

<sup>3</sup>D. Khokhlov, "Infrared Photodetectors Based on Doped Lead Tellurides," in *Lead Chalcogenides: Physics & Applications*, Vol. 18, edited by M. O. Manasreh (Taylor and Francis, London, 2003), p. 617.

<sup>4</sup>G. Nimtz and B. Schlicht, "Narrow-Gap Lead Salts," in *Narrow-Gap Semiconductors*, Springer Tracts in Modern Physics, Vol. 98 (Springer, Berlin, 1983), p. 1.

<sup>5</sup>Yu. I. Ravich, "Lead Chalcogenides: Basic Physical Features," in Ref. 3, p. 3.

<sup>6</sup>L. Ryabova and B. Akimov, "Doped Lead Chalcogenides," in Ref. 3, p. 427.