Stabilization of the donor action of gallium in electron-irradiated $Pb_{1-x}Sn_xTe$ alloys

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The effect of fast-electron irradiation ($T \approx 300$ K, $E = 6$ MeV, $\Phi \leq 8.1 \times 10^{17}$ cm^{-2}) and subsequent hydrostatic compression ($P \leq 16$ kbar) on the electrical properties of gallium-doped $Pb_{1-x}Sn_xTe$ alloys ($x = 0.19$, 0.23) has been studied. It is established that fast-electron irradiation results in virtually linear variation of the charge-carrier concentration, which is apparently associated with generation during the irradiation of quasi-local, donor-type levels in the conduction band of the alloys. As the flux of bombarding electrons increases, the breakdown of the donor action of gallium under pressure gradually disappears and the donor action of gallium stabilizes. The results are explained in terms of a model that assumes that a radiative donor level E_d appears in the conduction band during irradiation, and that the density of the quasi-local gallium levels E_{Ga} varies because of transitions of the gallium atoms between neutral and electrically active states under the action of electron bombardment and pressure. © *1995 American Institute of Physics.*

INTRODUCTION

Doping with group-III elements results in the appearance in the energy spectrum of IV–VI semiconductors of deep, quasi-local levels whose position relative to the energy-band edges depends upon the sort of impurity, the alloy composition, the temperature, the pressure, and the magnetic field. The existence of such levels currently makes it possible to satisfactorily explain a large part of the experimental data obtained in the study of the electrical and optical properties of doped materials based on a IV–VI compound.[1-3]

One of the few exceptions is PbTe and $Pb_{1-x}Sn_xTe$ alloys doped with gallium. It is well known that gallium in these materials is a donor.[4-6] Thus, as the gallium content C_{Ga} in PbTe increases, the hole concentration in p-type samples decreases, and $p-n$ conversion occurs. In this case, in a wide region of impurity concentrations in the neighborhood of the $p-n$ conversion point, the Fermi level is stabilized within the band gap, and the charge-carrier concentration is anomalously low ($n, p \leq 10^{13}$ cm^{-3} at $T = 78$ K). When the samples are doped further, the Fermi level drops into the conduction band, while the electron concentration increases and tends to saturation ($C_{Ga} > 1$ at. %). The electron-concentration saturation level at $T \sim 80$ K in PbTe amounts to $n_{sat} \approx 5 \times 10^{19}$ cm^{-3} and gradually decreases with increasing tin concentration in $Pb_{1-x}Sn_xTe$ alloys, reaching $n_{sat} \approx 2 \times 10^{18}$ cm^{-3} in an alloy with[7,8] $x = 0.3$.

It has also been established that hydrostatic compression of gallium-doped $Pb_{1-x}Sn_xTe$ alloys ($0 \leq x \leq 0.3$) causes a decrease of the electron concentration and $n-p$ conversion in degenerate n-type samples and an increase of hole concentration in p-type samples.[9-11] Moreover, at $T = 4.2$ K in gallium-doped $Pb_{1-x}Sn_xTe$ ($x = 0.19$, 0.20) alloys, a basically abrupt transition of the Fermi level from the conduction band into the valence band was detected in the $n-p$-conversion region, indicating that local levels are absent in the band gap.[11]

Such unusual behavior of the charge-carrier concentration for doped semiconductors under pressure allowed Akimov *et al.*[11] to hypothesize that the doping action of gallium was unstable in $Pb_{1-x}Sn_xTe$ alloys: as a result of lattice deformation under the action of pressure and possibly during the increase of the tin concentration in the alloy, the gallium atoms go from an electrically active state to a neutral state. As a result, the concentration of electrons introduced by the gallium decreases. The existence of such adjustable centers can be attributed to the possibility for the existence of nonequivalent positions for gallium in the $Pb_{1-x}Sn_xTe$ crystal lattice,[12-14] and their concentration apparently substantially depends on the method of producing the crystals. It can therefore be assumed that by varying the equilibrium defect concentrations in the metal and chalcogenide sublattices, bombardment with fast electrons makes it possible to efficiently control the electrical properties of $Pb_{1-x}Sn_xTe\langle Ga\rangle$.

In this paper we present the results of an experimental study of how electron bombardment and subsequent hydrostatic compression affects the electrical properties of $Pb_{1-x}Sn_xTe\langle Ga\rangle$ alloys ($x = 0.19$, 0.23), in order to determine whether the properties of the alloys can be controlled by means of irradiation and to determine how irradiation affects the energy spectrum of the alloys under consideration.

1. SAMPLES AND MEASUREMENT PROCEDURE

This paper describes a study of single-crystal samples of $Pb_{1-x}Sn_xTe$ ($x = 0.19$, 0.23) alloys grown by the Czochralski method and doped with gallium ($C_{Ga} = 0.2$–0.3 at. %) by isothermally annealing them in GaTe vapor. The parameters of these samples at $T = 4.2$ K are given in Table I.

The starting samples were bombarded with fast electrons ($T \approx 300$ K, $E = 6$ MeV, $\Phi \leq 8.1 \times 10^{17}$ cm^{-2}) on the ÉLU-6 pulsed linear accelerator. In each sample, the temperature dependences of the resistivity ρ and the Hall coefficient R_H ($4.2 \leq T \leq 300$ K, $B \leq 0.04$ T) were measured before bombardment and after bombardment with several electron

TABLE I. Parameters of $Pb_{1-x}Sn_xTe\langle Ga\rangle$ samples at $T=4.2$ K

Sample	x	Type	N, cm^{-3}	ρ, $\Omega\cdot\mathrm{cm}$	μ_H, $\mathrm{cm}^2/\mathrm{V\cdot sec}$	$\Phi_{\max}\cdot 10^{-17}$, cm^{-2}
Ga-1	0.19	n	2.1×10^{17}	8.4×10^{-5}	2.9×10^{5}	8.1
Ga-2	0.19	n	1.3×10^{17}	7.9×10^{-5}	4.9×10^{5}	2.0
Ga-3	0.19	n	1.5×10^{16}	2.1×10^{-3}	1.7×10^{5}	0.6
Ga-4	0.23	p	5.2×10^{17}	5.9×10^{-3}	1.7×10^{3}	2.1

fluxes, along with the Shubnikov–de Haas oscillations at $T=4.2$ K ($B\leq7$ T, $\mathbf{B}\|\langle100\rangle$).

Similar measurements were made in samples Ga-2, Ga-3, and Ga-4 under conditions of hydrostatic compression ($P\leq16$ kbar). Sample Ga-4 was studied under pressure before irradiation, sample Ga-3 was studied under pressure before irradiation and after irradiation by an electron flux of $\Phi=0.6\times10^{17}$ cm^{-2}, and sample Ga-2 was studied under pressure after irradiation by an electron flux of $\Phi=2\times10^{17}$ cm^{-2}.

2. THE EFFECT OF ELECTRON IRRADIATION ON THE ELECTROPHYSICAL PROPERTIES OF $Pb_{1-x}Sn_xTe\langle Ga\rangle$ ALLOYS

The starting samples of $Pb_{1-x}Sn_xTe\langle Ga\rangle$ alloys studied in this project had not only n- but also p-type conductivity (see Table I). Under the action of electron irradiation, monotonic and coordinated variation of the electrical parameters is observed in all the samples. In the n-type samples, the resistivity slowly decreases at $T=4.2$ K. The Hall coefficient has a negative sign in the entire temperature range of interest and decreases by about an order of magnitude during electron bombardment. The opposite variations are observed in the p-type sample—the resistivity and the Hall coefficient at 4.2 K increase with increasing irradiation flux. For all the irradiation fluxes, the temperature dependences of the resistivity and the Hall coefficient of the investigated samples had a metallic character typical of undoped and unirradiated $Pb_{1-x}Sn_xTe$ alloys.

The indicated variations of ρ and R_H in the irradiated samples are evidence that the electron concentration increases in the n-type samples and the hole concentration decreases in the p-type samples during irradiation (Figs. 1 and 2). The variation rate of charge-carrier concentration with increasing irradiation flux differs significantly in these samples and amounts to $dN/d\Phi=0.2-4$ cm^{-1}. The charge-carrier mobility in the irradiated samples varies severalfold, which is evidently associated with the variation of the effective mass at the Fermi level and of the charged-defect concentration in the samples during irradiation.

High electron mobilities ($\mu_H\leq5\times10^4$ $\mathrm{cm}^2/\mathrm{V\cdot sec}$) are maintained in the n-type samples up to the maximum irradiation fluxes, which makes it possible to observe distinct Shubnikov–de Haas oscillations over the entire investigated range of irradiation fluxes. The decrease of the oscillation period, $\Delta_{100}(1/D)$, also indicates that the electron concentration increases during the irradiation. The electron concentration calculated from the oscillation period coincides within $\sim10\%$ with the data obtained from Hall measurements.

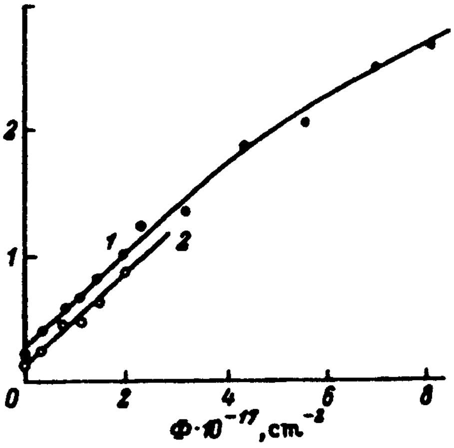

FIG. 1. Electron concentration at $T=4.2$ K vs irradiation flux for $Pb_{1-x}Sn_xTe\langle Ga\rangle$ samples. 1—Ga-1, 2—Ga-2.

The variations of the electrical parameters of the investigated samples satisfactorily coordinate with each other and are evidently determined by the concentration increase of donor-type defects during irradiation. In principle, such variations of the parameters qualitatively agree with currently known data on the low- and high-temperature electron irradiation of undoped $Pb_{1-x}Sn_xTe$ alloys and do not contradict the energy-spectrum model of the electron-irradiated $Pb_{1-x}Sn_xTe$ ($x=0.2$) alloy.[15] However, when the results are considered in greater detail, two characteristic features become evident.

First, the dependences of the charge-carrier concentration on the irradiation flux are virtually linear in all the investigated samples. In Ga-1, which was the sample studied in greatest detail, the linearity of the $n(\Phi)$ dependence is maintained up to an irradiation flux of $\Phi\approx5\times10^{17}$ cm^{-2}, at which the electron concentration has increased by more than an order of magnitude. Second, a very high variation rate of the charge-carrier concentration is observed in several gallium-doped samples during irradiation, $dn/d\Phi\approx4$ cm^{-2}, about an order of magnitude higher than the analogous value for the undoped alloys.[15]

Both of these circumstances are evidence that irradiation can be accompanied by the appearance of defects of donor character, whose generation rate can, in contrast with that in undoped alloys, substantially exceed the generation rate of acceptor-type defects.[15] There apparently are two factors responsible for the variation in charge-carrier concentration in these samples as a result of electron bombardment.

1. Fast-electron irradiation can result in the appearance of a radiative donor level E_d associated with the simplest point defects and located in the conduction band above the Fermi level in the investigated crystals. The flow of electrons from the E_d level into the allowed bands can cause a linear decrease of the hole concentration in the p-type sample and a linear increase of the electron concentration in the n-type samples, but taking into account only this possibility makes it impossible to satisfactorily explain the experimental results, since the variation rate of charge-carrier concentration during irradiation is significantly less in undoped n- and p-type $Pb_{1-x}Sn_xTe$ crystals than in $Pb_{1-x}Sn_xTe\langle Ga\rangle$ crystals.

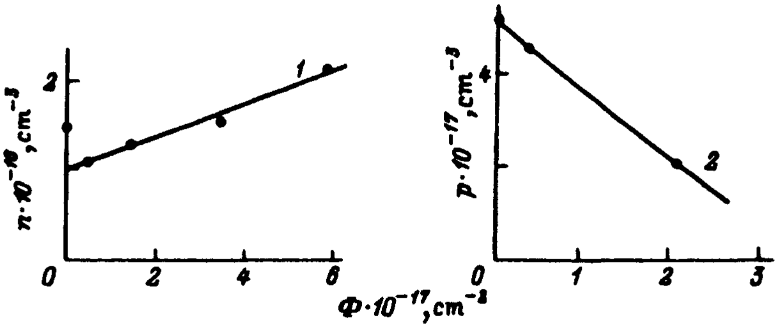

FIG. 2. Charge-carrier concentration at $T=4.2$ K vs radiation flux for $Pb_{1-x}Sn_xTe\langle Ga\rangle$ samples. 1—Ga-3, 2—Ga-4.

2. On the other hand, several experimental observations indicate that gallium atoms can occupy nonequivalent positions in the $Pb_{1-x}Sn_xTe$ lattice and can thus possess different charge activity.[12-14] Moreover, they are not distributed singly in the $Pb_{1-x}Sn_xTe$ lattice, but form electrically inactive clusters (segregations and second-phase microinclusions). The simplest defects are generated in the metal and chalcogenide sublattices during electron irradiation. It is therefore quite possible that electron irradiation increases the uniformity of the gallium distribution in the lattice, causing transitions of gallium atoms from the neutral state into an electrically active state. In this case, the density of quasi-local gallium impurity levels E_{Ga} in the conduction band can increase,[7,8] and the charge-carrier concentration in the irradiated samples can change as a result of the flow of electrons from the gallium levels into the allowed bands.

Depending on how the samples are fabricated, the amount of gallium impurity introduced, and the initial defect structure of the sample, one of the indicated mechanisms, or a combination of them, can dominate. However, the Fermi level and the electron concentration in any case, should stabilize as the irradiation flux increases if the Fermi level coincides with one of the quasi-local levels. In sample Ga-1, a departure from linearity and a tendency for the $n(\Phi)$ dependence to saturate is observed at the maximum irradiation fluxes ($\Phi>5\times10^{17}$ cm^{-2}) (Fig. 1). Calculations in terms of Cane's two-band model[16] show that the Fermi level in the sample reaches an energy of $E_F>E_c+50$ meV in this region of the irradiation fluxes. It is therefore quite possible that the departure of the $n(\Phi)$ dependence from linearity is associated with the approach of the Fermi level to a local gallium level, which, according to the data of Ref. 8, should have an energy of $E_{Ga}\approx E_c+75$ meV in the $Pb_{1-x}Sn_xTe$ $(x=0.19)$ alloy.

3. STABILIZATION OF THE DONOR ACTION OF GALLIUM IN ELECTRON-IRRADIATED $Pb_{1-x}Sn_xTe$ ALLOYS UNDER PRESSURE

The $Pb_{1-x}Sn_xTe\langle Ga\rangle$ samples were also studied under conditions of hydrostatic compression to a pressure of $P\leq16$ kbar. It was established that, in unirradiated n-$Pb_{1-x}Sn_xTe\langle Ga\rangle$ crystals, in accordance with the data of Ref. 11, a sharp increase is observed in the resistivity and the absolute value of the Hall coefficient under the action of pressure. At a pressure $P\approx0.3$ kbar, the resistivity passes through a maximum, and $n-p$ conversion occurs at $T=4.2$ K. A further pressure increase results in a decrease of ρ and R_H at 4.2 K. In the unirradiated p-$Pb_{1-x}Sn_xTe\langle Ga\rangle$ sample, the variations of the electrical parameters are similar to the variations in an n-type sample after $n-p$ conversion.

The indicated variations of the parameters of the starting samples under pressure are evidence of an increase of hole concentration in the n- and p-type samples, as well as of $n-p$ conversion (Fig. 3). At the maximum pressures, the variation rate of the hole concentration decreases, and the $p(P)$ dependence saturates.

The behavior of the electrical parameters of the irradiated samples does not differ qualitatively from that of the parameters of the starting crystals (Figs. 3–5). However, as the irradiation flux increases, the maximum in the $\rho(P)$ dependences and the inversion point of the sign of R_H at $T=4.2$ K shift toward higher pressures, while only insignificant variations of the electrical parameters occur under the action of pressure in sample Ga-2, irradiated by the maximum electron flux of $\Phi=2\times10^{17}$ cm^{-2}. The resistivity at

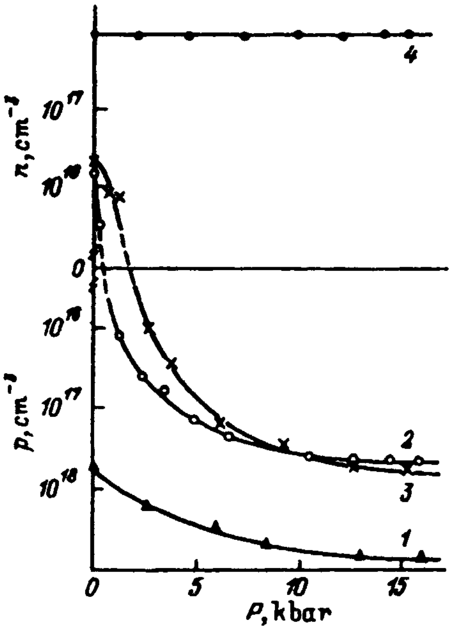

FIG. 3. Electron concentration at $T=4.2$ K vs pressure in electron-irradiated $Pb_{1-x}Sn_xTe\langle Ga\rangle$ samples. $\Phi\cdot10^{-17}$, cm^{-2}: 1—0 (Ga-4), 2—0 (Ga-3), 3—0.6 (Ga-3), 4—2.0 (Ga-2).

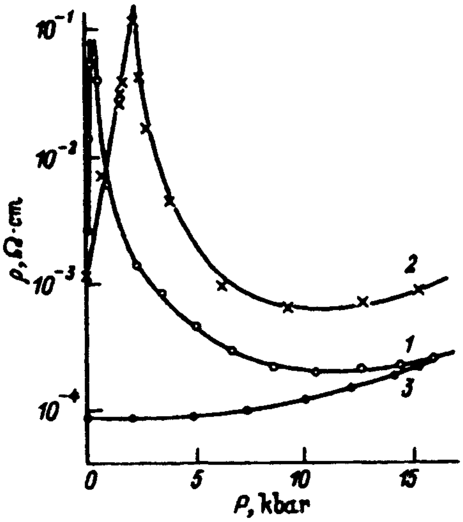

FIG. 4. Resistivity at $T = 4.2$ K vs pressure in electron-irradiated $Pb_{1-x}Sn_xTe\langle Ga\rangle$ samples. $\Phi \cdot 10^{-17}$, cm^{-2}: 1—0 (Ga-3), 2—0.6 (Ga-3), 3—2.0 (Ga-2).

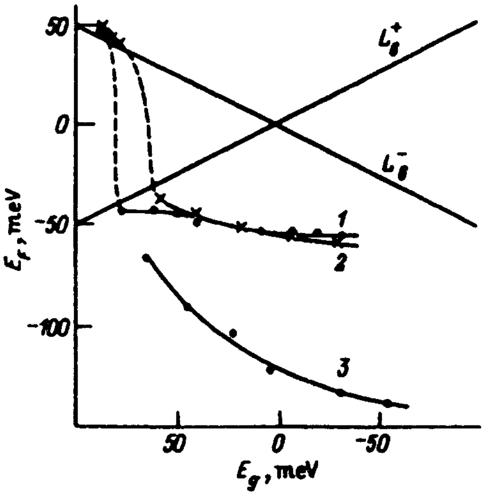

FIG. 6. Position of the Fermi level relative to the L terms vs band gap in electron-irradiated $Pb_{1-x}Sn_xTe\langle Ga\rangle$ samples. 1—Ga-3 ($\Phi = 0$), 2—Ga-3 ($\Phi = 0.6 \times 10^{17}$ cm^{-2}), 3—Ga-4 ($\Phi = 0$).

4.2 K monotonically increases by about a factor of 2, while the electron concentration remains constant with an accuracy of $\approx 2\%$ in the pressure interval $P \leqslant 16$ kbar.

One can construct dependences of the position of the Fermi level on pressure in the investigated samples from the results of measurements of the charge-carrier concentration in the starting and the irradiated samples in terms of Cane's dispersion law[16] (Fig. 6). It has been established that, in the n-type samples acted on by pressure, the Fermi level moves essentially discontinuously from the conduction band into the valence band, while the $E_F(P)$ dependences, in contrast with the case of $Pb_{1-x}Sn_xTe\langle In\rangle$ alloys,[16] differ from linear. It can therefore be asserted that no local levels appear in the band gap in the investigated $Pb_{1-x}Sn_xTe\langle Ga\rangle$ alloys, and that stabilization of the Fermi level by a gallium impurity level does not occur. This confirms the model of the energy spectrum of $Pb_{1-x}Sn_xTe\langle Ga\rangle$ alloys proposed in Ref. 8, according to which, in the investigated alloys, the quasi-local gallium level should be located substantially above the Fermi level in all the investigated samples.

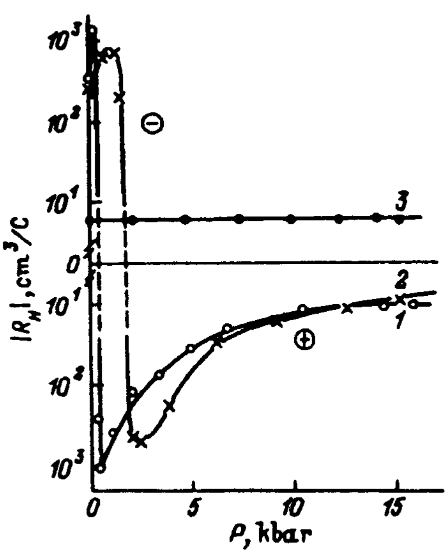

FIG. 5. Hall coefficient at $T = 4.2$ K vs pressure in electron-irradiated $Pb_{1-x}Sn_xTe\langle Ga\rangle$ samples. $\Phi \cdot 10^{-17}$, cm^{-2}: 1—0 (Ga-3), 2—0.6 (Ga-3), 3—2.0 (Ga-2).

CONCLUSION

Thus, the experimental results obtained in this paper support the following conclusions:

1. Bombardment of $Pb_{1-x}Sn_xTe\langle Ga\rangle$ alloys with fast electrons results in a linear decrease in the hole concentration in a p-type sample and a virtually linear increase of the electron concentration in n-type samples. This behavior apparently associated with the generation of quasi-local, donor-type levels in the conduction band of the alloys. In most of the test samples, the rate of change of the charge-carrier concentration during irradiation substantially exceeds the value that characterizes undoped $Pb_{1-x}Sn_xTe$ alloys. The results are satisfactorily explained in terms of a model which assumes that a radiative donor level E_d located above the Fermi level appears during irradiation in the crystals under consideration, and that the density of quasi-local gallium levels E_{Ga}, associated with transitions of gallium atoms from a neutral state to an electrically active state, increase during irradiation.

2. In the electron-irradiated n-$Pb_{1-x}Sn_xTe\langle Ga\rangle$ samples, the point where the sign of the Hall coefficient inverts under the action of pressure shifts toward higher pressures. Thus, electron irradiation causes the breakdown of the donor action of a gallium impurity under pressure to disappear and causes the donor action of gallium to stabilize in the investigated samples. It can be hypothesized that electron irradiation, by generating point defects in the metal and chalcogenide sublattices and by breaking up electrically inactive clusters of

gallium atoms, increases the concentration of electrically active gallium atoms and promotes a more uniform gallium distribution in the $Pb_{1-x}Sn_xTe$ lattice.

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