Dislocation microwave conductivity of germanium

Yu. A. Osip'yan, V. I. Tal'yanskiĭ, and S. A. Shevchenko

Institute of Solid State Physics, USSR Academy of Sciences
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The dc conductivity and Hall effect and the microwave conductivity of deformed p-germanium were measured in the temperature interval 60–4.2 K. The dependence of the microwave conductivity on the temperature, on the concentration of the chemical acceptors, and on the density and orientation of the dislocations was investigated. The microwave conductivity is compared with the dc measurements. It is concluded that the microwave conductivity is due to conduction, along the dislocation, of holes produced as a result of the transfer of electrons from the dislocations to chemical acceptors.

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Investigations of the electric and optical properties of plastically deformed germanium lead to the conclusion that states determined by the presence of dislocations exist in the forbidden band and lie approximately 0.1 eV above the top of the valence band.[1–3] These states determine both the magnitude and the temperature dependence of the electric conductivity of plastically deformed germanium. It has turned out that the dislocations can act both as donors and as acceptors, either capturing or delivering conduction-band carriers. The dislocations charged in this manner exert also a substantial influence on the scattering of the carriers. As a result of all these factors, the electric properties of plastically deformed germanium differ substantially from the analogous properties of the initial undeformed germanium. Another interesting aspect of the effect of dislocations on the electric properties was the observation of dc conductivity along the dislocations in deformed p-germanium.[4] The main feature of this conductivity was the absence of the Hall effect, a feature typical of one-dimensional conductivity.[5] All these data make it possible to proceed to a development of model representations of the microscopic mechanisms whereby the dislocations influence the electric conductivity. This, however, raises immediately a number of questions that are quite important for the dislocation model of conductivity. Some of these questions are: 1) Do the dislocation states form a separate level or an energy band? 2) If this is a band, what are its parameters (width, occupation)? 3) Is there an energy gap between occupied and empty states in the dislocation band?

It can be assumed that a number of data on the dislocation-conductivity mechanism can be extracted from the frequency dependence of the conductivity.

To this end, we have undertaken an experimental investigation of the electric properties of deformed p-germanium in the microwave band (9.5 GHz). The measurements have shown that at low temperatures the high-frequency conductivity (σ_{micro}) of deformed samples is larger by many orders of magnitude than the dc conductivity (σ_0). It was therefore possible to measure the conductivity in samples with a low dislocation density ($N_D > 10^5$ cm^{-2}), in which it was possible to produce a more or less ordered anisotropic dislocation structure.

SAMPLES AND PROCEDURE

The investigations were performed on two series of p-Ge single crystals with a differential acceptor concentration $N_A = 2\times10^{12}$ cm^{-3} and 7×10^{13} cm^{-3}. The deformation was produced in air at $T = 430$ °C by four-point bending. The edges of the initial samples, in the form of parallelepipeds measuring 22×12×3.5 mm, were oriented respectively along the directions $\langle100\rangle$, $\langle011\rangle$, and $\langle0\bar{1}1\rangle$. The bending axis was directed along $\langle0\bar{1}1\rangle$. This orientation contributes to a predominant introduction of sixty degree dislocations. The dislocation density was determined from the etch pits on the (011) and $(0\bar{1}1)$ faces. After the deformation, the samples were gold-coated by sputtering in vacuum and were annealed for 10 minutes at $T = 700$ °C in an atmosphere of ultrapure argon. Two samples were cut from each of the crystals prepared in this manner, along and across the bending axis. After grinding and chemical polishing, the dc electric conductivity and Hall effect of samples measuring 9.0×8.0×0.8 mm were measured by a standard procedure[2] in the temperature range 300–4.2 K, and microwave measurements of the conductivity were carried out in the temperature interval 60–4.2 K by the resonator method.1) The sample was placed in a reentrant resonator operating in the E_{010} mode. We measured the width of the resonance curve and calculated the conductivity from the formula[3]:

$$\sigma^{-1} = \frac{5\cdot10^{11}}{\eta(\Delta f_1 - \Delta f_0)}\ [\Omega\text{-cm}]\ . \qquad (1)$$

Here $\eta = V_{res}/V_{sample}$, V_{res} is the volume of the resonator, V_{sample} is the volume of the sample, Δf_1 is the band width of the resonator with the sample, and Δf_0 is the band width of the empty resonator.

MEASUREMENT RESULTS

Figure 1 shows data on the temperature dependence of the electric conductivity at low temperatures (4.2–60 K) for plastically deformed samples of highly purified p-type germanium with different dislocation densities. The initial concentration of the chemical acceptors was 2×10^{12} cm^{-3}. It is seen from the data of Fig. 1 that all temperatures the electric conductivity de-

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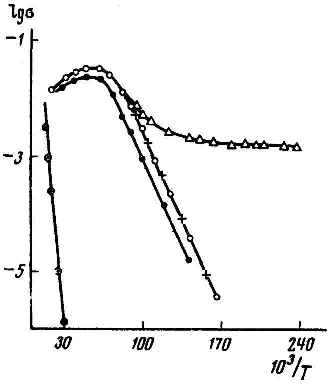

FIG. 1. Temperature dependence of the dc and microwave conductances in control and deformed samples at $N_A = 2\times 10^{12}$ cm^{-3}. For dc (σ_0) the symbols are: o—control samples, ● and ⊙ —deformed samples with dislocation densities 5×10^5 and 1×10^7 cm^{-2} respectively. The symbols for σ_{micro} are: ×—control sample, Δ—deformed sample with dislocation density 5×10^5 cm^{-2}.

creases with increasing dislocation density. This is caused both by the compensation of the acceptor centers by the electrons from the dislocations (and consequently by the decrease of the concentration of the free holes in the valence band), and by the decrease of the mobility of the free holes as a result of their additional scattering by their electrically charged dislocations.

Data on the decrease of the concentration of the free holes, obtained by Hall-effect measurements in the same temperature region, are shown in Fig. 2. This action of plastic deformation on the conductivity of p-germanium was also observed by us earlier,[2] as well as by Schröter,[1] and was explained with the aid of the model of the donor-acceptor action of the dislocations.

Figure 3 shows the temperature dependence of σ_{micro} for deformed samples with different dislocation densities at $N_A = 2\times10^{12}$ cm^{-3}. For all samples it is possible to separate on the $\sigma_{\text{micro}}(T)$ curves two sections. At first, with decreasing temperature, a sharp nearly exponential decrease of the microwave conductivity is observed, followed by a region with a weaker dependence. For samples with dislocations density on the order of

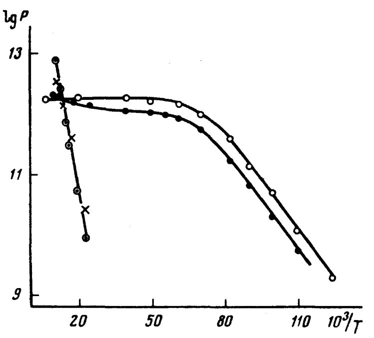

FIG. 2. Temperature dependence of the free-hole density in a control sample (o) and deformed samples with dislocation density 5×10^5 cm^{-2} (●), 5×10^6 cm^{-2} (×), and 1×10^7 cm^{-2} (⊙) at $N_A = 2\times10^{12}$ cm^{-3}.

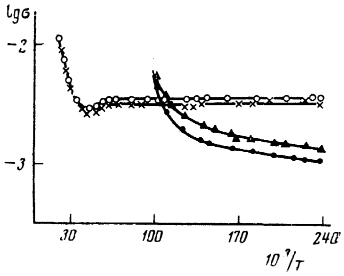

FIG. 3. Temperature dependence of the microwave conductance for deformed samples with dislocation density 3×10^5 cm^{-2} (●), 5×10^5 cm^{-2} (▲), 1×10^7 cm^{-2} (o), and 5×10^6 cm^{-2} (×) at $N_A = 2\times10^{12}$ cm^{-2}.

10^5 cm^{-2}, this is a weak decrease, and for densities on the order of 10^6 cm^{-2}—a very weak growth.

Figure 4 shows the dependence of σ_{micro} at 4.2 K on the dislocation density. This dependence turns out to be different for $N_A = 2\times10^{12}$ cm^{-3} and $N_A = 7\times10^{13}$ cm^{-3}. A distinguishing feature in the first case is the presence of a saturation region at $N_D > 2\times10^6$ cm^{-2}, which follows the linear growth of σ_{micro} with increasing dislocation density up to $N_D = 2\times10^6$ cm^{-2}. In the second case, σ_{micro} increases linearly with increasing dislocation density, up to $N_D = 1\times10^7$ cm^{-2}.

It is also seen from Fig. 1 that in the investigated temperature interval, at all temperatures, the microwave conductivity of the samples with dislocations is much higher than the dc conductivity (σ_0). Similar data were obtained also for silicon.[7] The temperature dependences of σ_{micro} and σ_0 in the investigated temperature interval are significantly different. Whereas σ_0 decreases exponentially with decreasing temperature, σ_{micro} is practically independent of temperature between 10 and 4.2 K (Fig. 1). Consequently, the difference between σ_{micro} and σ_0 increases with decreasing temperature. At a temperature near 6 K it amounts to about three orders of magnitude, and at 4.2 K about six orders, since σ_0 drops to a value 10^{-9} Ω-cm whereas σ_{micro} remains practically unchanged at about 10^{-3} Ω-cm.

The data obtained in the investigation of the forms of p-germanium samples with initial chemical-acceptor concentration $N_A = 7\times10^{13}$ cm^{-3} are qualitatively analogous. As to the electric conductivity of the initial and control samples, into which no dislocations were introduced, at all temperatures σ_0 and σ_{micro} coincide for both investigated chemical-acceptor concentrations.

Investigations of the anisotropy of σ_{micro} of samples

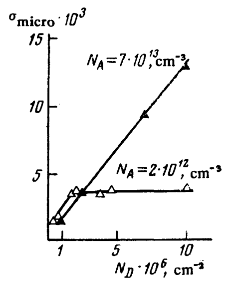

FIG. 4. Dependence of the microwave conductance on the dislocation density at $T = 4.2$ K for deformed samples with initial acceptor concentration 2×10^{12} cm^{-2} (Δ) and 7×10^{13} cm^{-3} (▲).

cut along and across the bending axis yielded the following results:

$\sigma_{\parallel}/\sigma_{\perp} = 3.6$ for the sample with $N_D = 1 \cdot 10^6$ cm^{-2} and $N_A = 7 \cdot 10^{13}$ cm^{-3},

$\sigma_{\parallel}/\sigma_{\perp} = 3$ for the sample with $N_D = 2.5 \cdot 10^6$ cm^{-2} and $N_A = 7 \cdot 10^{13}$ cm^{-3},

$\sigma_{\parallel}/\sigma_{\perp} = 2.7$ for the sample with $N_D = 1.8 \cdot 10^6$ cm^{-2} and $N_A = 2.10^{12}$ cm^{-3}.

A count of the etch pits on two mutually perpendicular faces of the $\{110\}$ type has shown that the ratio of the dislocation numbers on these faces is also close to three.

DISCUSSION OF RESULTS

The principal result that calls for discussion is, in our opinion, the anomalous dispersion of the conductivity in samples with dislocations introduced by the plastic deformation. As seen from Fig. 1, σ_{micro} in deformed samples exceeds σ_0 by many orders of magnitude. A similar anomalously high σ_{micro} appears also in strongly doped compensated semiconductors in the case of hopping conduction over the impurities. In our case no bulk hopping conductivity was observed at all in the initial state, and it would be different to expect it in samples of so high a purity. It is not excluded, however, that in cylindrical regions adjacent to the dislocations in the crystal, where the impurities can concentrate, hopping conduction can occur even at relatively low initial impurity concentrations. Finally, the most probable mechanism is conduction along the dislocation line itself—along the dislocation core.

Let us examine the electron distribution among the different states for different dislocation densities in the investigated samples.

It follows from Fig. 2 that at $T < 80$ K the dislocations in deformed p-germanium exhibit donor action[2] that manifests itself in the fact that the dislocation gives up part of its electrons to the dislocations that surround it. The latter are charged negatively and form Read cylinders, while the dislocation itself is positively charged. So long as the dislocation density is low, the dc conduction is due to the free holes produced when the electrons are excited from the valence band to the acceptors that remain unoccupied (at $T \lesssim 30$ K) and to the dislocation (at $T \gtrsim 30$ K). The samples with $N_D \lesssim 2\times10^6$ cm^{-2} correspond to this case (Fig. 2). With increasing dislocation density, the electrons from the dislocations can fill up all the existing acceptors, the Read cylinders overlap, and with further increase of N_D the cylinders vanish completely, and the crystal contains positively charged dislocations and more or less uniformly distributed acceptors. The electrons from the valence band can now be excited only by dislocations. This case corresponds to samples with $N_D = 4.5\times10^6$ and 1×10^7 cm^{-2}. In the sample with $N_D = 1\times10^7$ cm^{-2} the filling coefficient is $f = 0.01$, so that the Coulomb interaction of the carriers on the dislocations can be neglected, and from the temperature dependence of the hole density we can determine the position of the dislocation level (or the end point of the band). We obtained a value 0.07 eV, which differs little from the value 0.09 eV obtained by us earlier.[2]

Thus, so long as the dislocation density is low, the cylinders do not overlap and the electric properties of the germanium outside the cylinders remain unchanged. We note once more in this connection that in deformed p-germanium there is no volume hopping conduction, since it is not observed in the control samples. The same conclusion can be drawn from an analysis of the experimental data on the anisotropy of σ_{micro}. Indeed, the very presence of microwave-conductivity anisotropy is the strong argument in favor of conduction along the dislocations. However, volume hopping conductivity can in principle also have an anisotropy as a result of the effect of the bending of the cylinders, but then the anisotropy should depend on the radius of the Read cylinder and on the dislocation density. Measurements show, on the other hand, that the anisotropy of σ_{micro} is determined only by the anisotropy of the dislocation structure and does not depend on the dislocation density or on the degree of doping of the initial germanium, i.e., on the radius of the Read cylinder.

One can assume on the basis of the foregoing that hopping conduction (if indeed it does play any role in our measurements) can take place only near the dislocations. But for this purpose it is necessary that the donor and acceptor concentrations near the dislocations be much larger than in the volume. An important argument against the model of hopping conduction near the dislocations, in our opinion, is the dependence of the microwave conductivity on the dislocation density, shown in Fig. 4. Indeed, until the Read cylinders begin to overlap, the microwave conductivity should increase with increasing dislocation density, regardless of the conduction mechanism. This situation is realized for samples with initial acceptor concentration $N_A = 7\times10^{13}$ cm^{-3}. The good satisfaction of the linear law for these samples offers evidence that the "quality" of the dislocation structure remains unchanged in the investigated range of dislocation densities ($N_D \lesssim 10^7$ cm^{-2}).

We consider now the dependence of the microwave conductivity on the dislocation density for samples with acceptor concentration $N_A = 2\times10^{12}$ cm^{-3}. So long as $N_D < 2\times10^6$ cm^{-2}, a linear growth of the microwave conductivity is observed. At $N_D > 2\times10^6$ cm^{-2} the Read cylinders overlap and all the acceptors in the volume of the sample are occupied by electrons coming from the dislocations. For hopping conduction it is necessary that both occupied and "empty" (uncharged) acceptors be present. Therefore, if the observed conduction were of the hopping and impurity type, then the microwave conductivity would decrease abruptly at $N_D > 2\times10^6$ cm^{-2}. What is observed in experiment, however, is saturation of the microwave conductivity. This fact can be easily explained by assuming that the conduction is realized by holes produced on dislocations as a result of the transfer of the electrons to the acceptors. At $N_D > 2\times10^6$ cm^{-2} the number of all the holes on all the dislocations is equal to the number of acceptors in the sample, and consequently, remains unchanged with increasing dislocation density. It is also obvious that the number of holes on an individual dislocation decreases with increasing dislocation density. If we assume that at $N_D > 2\times10^6$ cm^{-2} the mobility of the holes on the dislocations depends little on their number on the given dislocation, then the microwave conductivity remains unchanged when the dislocation density is increased.

Thus, the dependence of $\sigma_{\rm micro}$ at $T = 4.2$ K on the concentration of the doping impurity and on the dislocation density makes it possible to conclude that $\sigma_{\rm micro}$ is due to holes produced on dislocations as a result of the departure of electrons from the dislocations to acceptors. Knowing $\sigma_{\rm micro}$ and the total number of holes on the dislocations for samples with $N_A = 2\times10^{12}$ cm^{-3} and $N_D > 2\times10^6$ cm^{-2}, we can estimate the hole mobility along the dislocations. Calculation yields a value 10^4 cm^2/V-sec, which is smaller by only one order of magnitude than the hole mobility in the valence band of germanium at $T = 4.2$ K.

Insofar as $\sigma_{\rm micro}$ is due to holes on dislocations, it follows that the dislocation states form an energy band separated by a gap. At low temperatures the motion of the holes takes place in the lower subband, and at higher temperatures the dislocation electrons themselves can be excited from the lower subband to the upper one. An exponential increase of $\sigma_{\rm micro}$ with temperature should then be expected. This increase is in fact observed in the temperature interval 25–50 K (Fig. 3) with an activation energy 0.01 eV, and is not connected with the excitation of the electrons from the valence band to the dislocations, for in the latter case, as noted above, the activation energy is equal to 0.07 eV. The activation energy 0.01 eV might be identified with the width of the gap between the two subbands, all the more since it coincides with our preliminary results of the dc measurements of the Hall emf in strongly deformed *n*- and *p*-germanium, from which it follows that if a gap does exist, it does not exceed 0.01 eV. However, the fact that $\sigma_{\rm micro}$ is independent of the dislocation density in the temperature interval 25–50 K does not make it possible as yet to identify unequivocally the growth of $\sigma_{\rm micro}$ with a thermal bridging of the gap between the two subbands. To be sure, the dependence of $\sigma_{\rm micro}$ on the dislocation density in this temperature interval can be attributed in principle to the formation of an exciton that binds the excited electron with a hole. This assumption has presently no experimental corroboration and can be regarded only as a hypothesis in subsequent studies of $\sigma_{\rm micro}$.

The facts and arguments presented above show quite convincingly, in our opinion, that $\sigma_{\rm micro}$ is due to conduction along the dislocations. It is much more difficult, however, to say anything final concerning the mechanism of this conduction. Useful information in this respect can be obtained from the temperature and frequency dependences of $\sigma_{\rm micro}$. The frequency dependence in germanium has not yet been investigated by us, and the temperature dependence has the following singularities (Fig. 3): at small N_D ($<2\times10^6$ cm^{-2}), so long as the Read cylinders do not overlap, $\sigma_{\rm micro}$ decreases with decreasing temperature, with a small activation energy. At large N_D ($>2\times10^6$ cm^{-2}), when there are no cylinders and all the acceptors are occupied by electrons from the dislocations, $\sigma_{\rm micro}$ increases with decreasing temperature. It seems natural to assume that this difference between the temperature dependences is due to a difference between the interaction energies of the electrons on the dislocations, since the filling coefficient at small and large dislocation densities differs by almost one order of magnitude. The increase of the conductivity with decreasing temperature is a characteristic of metallic conduction. It is not clear as yet, however, what causes the dispersion of the conductivity, which in principle can be attributed to breaks on the dislocation lines, but one cannot exclude the possibility of a more profound cause inherent in the very mechanism of conduction along dislocations, in analogy with the situation in organic one-dimensional conductors.[8] To ascertain the mechanism of dislocation conduction, further research is therefore necessary, which should serve as the basis for a theoretical model of dislocation conduction.

[1)] The direction of the electric field coincided with the predominant direction of the dislocations.

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