Effect of Dislocations on the Electrical Properties of Germanium

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In n-type germanium single crystals with a resistivity 49 ohm-cm at room temperature the effect of dislocations on the concentration and mobility of the carriers is studied at temperatures between 77 and 300°K. An acceptor effect of the dislocations and a decrease of electron mobility were observed for carriers moving perpendicular to the bending axis. The experimental results were treated with the aid of the Read theory. The acceptor level ascribed to dislocations is 0.175 eV below the bottom of the conduction band and corresponds to minimal dislocation filling. The effect of dislocations on electron mobility is less than that predicted by the Read theory.

1. INTRODUCTION

NUMEROUS experimental results demonstrating the interaction of dislocations in n-type semiconductors[1-4] are treated within the concepts of Read's theory[5-7]. This theory is based on the model wherein the dislocation line is represented as a chain of atoms with one broken chemical bond per atom. Each such atom can combine with an electron from the conduction band, and as a result of such an acceptor action the dislocation line turns out to be charged. This charge is screened in a certain cylindrical volume (Read cylinder).

By virtue of the Coulomb repulsion between the electrons that settle on neighboring bonds, a situation arises wherein not all the broken bonds are filled with electrons, but only a certain fraction determined by the occupation coefficient f, which should be much smaller than unity. The purpose of the Read theory was indeed to calculate this coefficient under different assumptions concerning the energies of the electrons on the dislocations. An important fact is that in all the approximations of the Read theory the value of f should not exceed 0.1.

At the same time, practically all the available experimental data indicate that this quantity, determined by direct experiment, is actually always larger than 0.3, and in some cases even larger than unity,[2,8-11]. It can be assumed that this is due to two factors. First, after the deformation, point defects could remain and exercise their acceptor action. The second possible cause is that in the actually investigated insufficiently-pure semiconducting crystals the initial number of impurities was of the order of the number of broken bonds on the dislocations or might even have exceeded it[1,2,10]. This could hinder a quantitative estimate of the pure dislocation contribution against the background of the other process of redistribution of the impurities during the course of plastic deformation.

For a quantitative verification of the concepts concerning the influence of dislocations on the concentration and mobility of carriers in semiconductors, it was therefore deemed expedient to perform experiments on the purest possible crystals with controlled dislocation structure, and also to eliminate as much as possible the influence of point defects by using suitable heat treatment.

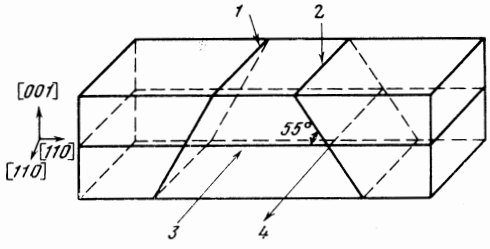

FIG. 1. Orientation of sample for flexure about the [110] axis: 1–2) glide planes ($\bar{1}11$) and ($1\bar{1}1$), 3) neutral plane, 4) flexure axis [110]. The long edge of the sample is parallel to the [110] direction.

2. PROCEDURE

We investigate single crystals of very pure n-germanium with resistivity 49 ohm-cm at room temperature. The concentration of the donors (phosphorus), determined from measurements of the Hall emf from room to helium temperature, was 3.2×10^{12} cm^{-3}. The initial density of the growth dislocations, determined from the etch pits, did not exceed 1×10^4 cm^{-2}. The excess dislocations were introduced by plastic flexural deformation.

The samples were initially cut in the form of bars measuring $30 \times 3 \times 2$ mm or $30 \times 5 \times 2$ mm. The orientation of the samples is shown in Fig. 1.

After mechanical grinding, chemical polishing, and thorough washing, the samples were covered prior to deformation with a protective layer of gold (sputtered in vacuum) or tin (deposited electrolytically). The deformation was by four-point flexure at T = 750° C in an argon atmosphere. The deformation time was 2—3 min. The flexure axis was parallel to the [110] direction. The rate of cooling was 5° per minute. The dislocation density was determined from the etch pits on the (110) face with accuracy ± 20%. After deformation, an upper layer 200 μ thick was removed by grinding. The samples for the measurements were prepared in the form of bars measuring $8 \times 2 \times 1.5$ mm. Some samples were in the form of dumbbells. Prior to depositing the contacts, the samples were bright-dipped in CP-4A. The contacts were of In or 95% Sn + 5% Sb or 4% Au + 21% Sb + 75% Pb alloys. Samples with ohmic contacts were chosen for the measurements. The electric conductivity and the Hall constant were measured in the temperature

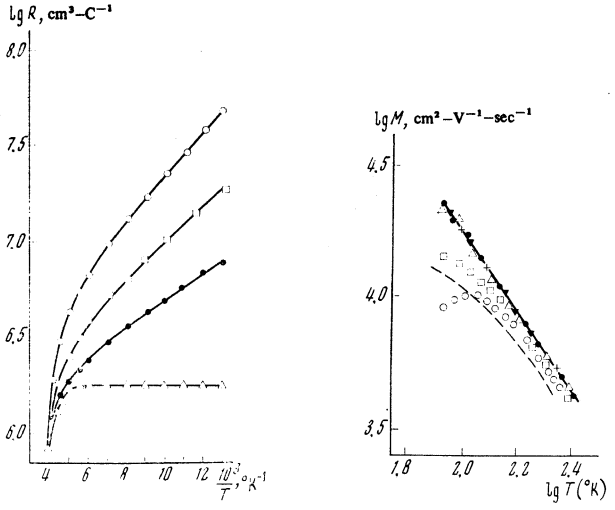

FIG. 2. Temperature dependence of the Hall constant for the control sample and the plastically deformed samples: Δ—control sample; ●, □, ○—deformed samples with dislocation densities 3×10^6, 6×10^6, and 1×10^7 cm^{-2}, respectively.

FIG. 3. Temperature dependence of electron mobility for control sample and for plastically deformed samples: Δ—control sample; ●, □, ○—deformed samples with dislocation densities 3×10^6, 6×10^6, and 1×10^7 cm^{-2}, respectively; the current lines are perpendicular to the flexure axis: +, ▼—deformed samples with dislocation density 3×10^6 and 1×10^7 cm^{-2}, respectively; the current lines are parallel to the flexure axis. The dashed curve takes into account the bending effect for a deformed sample with dislocation density 3×10^6 cm^{-2}.

interval 77—300°K on direct current by the usual null method. For high-resistance samples we also used a circuit with an electrometer and a dynamic capacitor. The magnetic field intensity was 6500 Oe.

3. EXPERIMENTAL RESULTS

Figure 2 shows in a semilogarithmic scale the temperature dependence of the Hall constant for four typical germanium samples, namely a control sample, one kept at the deformation temperature, and three deformed samples with dislocation densities 3×10^6 cm^{-2}, 6×10^6 cm^{-2}, and 1×10^7 cm^{-2} (the concentrations of the broken bonds were 7.5×10^{13}, 1.4×10^{14}, and 2.5×10^{14} cm^{-3}). Figure 3 shows the temperature dependence of the Hall mobility of the electrons with the directions of the electric and magnetic fields perpendicular to the direction of the flexure axis. In samples where the current lines were parallel to the flexure axis, the mobility coincided within the limits of experimental errors, regardless of dislocation density, with the mobility for the control sample.

As follows from the presented data, in the case of heat treatment the control sample does not experience any changes. In the deformed samples, the Hall constant increases with increasing dislocation density, corresponding to the introduction of certain acceptor centers. This result turned out to be independent of the material with which the sample was coated prior to deformation, thus indicating that there were no diffusion impurities from the surface. In addition, it can be seen that the slopes of the temperature dependence of the Hall constant do not correspond to levels of any of the impurities in germanium.

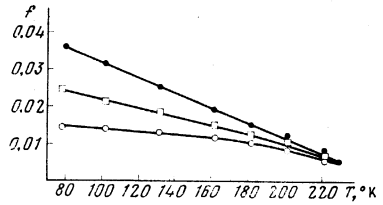

FIG. 4. Temperature dependence of the occupation coefficient for plastically deformed samples with different dislocation densities. The symbols are the same as in Fig. 2.

To ascertain the possible contribution made to the change of the electric conductivity by the point defects, the formation of which corresponds to plastic deformation, the samples were annealed after deformation at 550, 600, 650, and 750°C for 20 minutes. Annealing produced no changes in the Hall constant or in the mobility. It is obvious that the high deformation temperature, 750°C, suffices to anneal out the point defects during the deformation itself.

As seen from Fig. 3, the mobility curves obey the $T^{-3/2}$ law, i.e., it can be assumed that the mobility in the initial and in the control samples is determined by scattering by acoustic phonons. The decrease of the mobility when the electric field is perpendicular to the flexure axis comes into play at dislocation densities larger than 3×10^6 cm^{-2}. The mobility anisotropy observed by us is much smaller than that observed by others at the given dislocation density[2,10,11].

4. DISCUSSION OF RESULTS

As follows from the foregoing data, introduction of dislocations gives rise to an acceptor action.

Let us use the data of Fig. 2 to determine the temperature dependence of the occupation coefficient of the dislocation line by electrons, and let us determine from a comparison with the theory the position of the acceptor level of the dislocation in the forbidden band.

The occupation coefficient f is defined as the ratio of the number of electrons captured by the dislocations to the number of "dangling" bonds, i.e.,

$$f = \frac{N_d - \langle n \rangle}{N_a}, \qquad (1)$$

with $N_a = N_D/c$, where N_D is the dislocation density, c are the distances between the dangling bonds, and N_d is the donor concentration in the control sample.

Figure 4 shows the temperature dependence of the filling coefficient for the investigated samples. In the reduction of the experimental data, the Hall factor was assumed to be $3\pi/8$. Since the condition $cN_d/N_a \ll 1$ is satisfied for all samples, i.e., the number of dangling bonds per cm^3 is much larger than the number of free electrons, the occupation coefficient decreases in absolute magnitude with increasing dislocation density at the same value of the temperature. This also causes a weaker temperature dependence of f for samples with a large dislocation density. The maximum value of f for a sample with dislocation density 3×10^6 cm^{-3} is 0.038 at T = 77°K.

Read has previously developed[5,6] a number of approximate statistical methods for the determination of the occupation coefficient of dangling bonds of a disloca-

tion. In this case it is possible to use the Fermi-statistics approximation, which implies that all the electrons on the dislocations have the same energy. This is valid if $f\mathscr{E}_0 < kT$, where $\mathscr{E}_0$ is the electrostatic interaction energy of the electrons located on neighboring dangling bonds, k is Boltzmann's constant, and T is the temperature. For germanium at c = 4Å we have $\mathscr{E}_0 = 0.225$ eV. For a sample with minimum dislocation density at T = 77°K we have f = 0.038. Then $f\mathscr{E}_0 = 0.007$ eV, i.e., $f\mathscr{E}_0 \sim kT$ at $T \approx 100$°K. Since the occupation coefficient decreases and kT increases with increasing temperature and dislocation density, the use of this approximation is justified in our case. In the case of the indicated model, the occupation coefficient is determined from the equations obtained by Read:

$$\mathscr{E}^*(f) = \mathscr{E}_F - \mathscr{E}_2 + kT \ln(1/f - 1), \quad (2)$$

$$\mathscr{E}^*(f) = \mathscr{E}_0 f[3 \ln f / f_c - 0.232], \quad (3)$$

where $\mathscr{E}_F$ is the Fermi level, $\mathscr{E}_2$ is the acceptor level connected with the dislocation, and $\mathscr{E}^*$ is the potential energy of the electron located on the dislocation, in the field of the positive ions and of all other electrons in the dislocation plus the energy of all the electrons located on the dislocation ($f\mathscr{E}_0$),

$$f_c = c[\pi(N_d - N_A)]^{1/2}, \quad (4)$$

where N_A is the concentration of the acceptors in the initial sample.

Using Eqs. (2) and (3) at T = 0, $N_d - N_A = 10^{15}$ cm^{-3}, and $\mathscr{E}_2 = 0.225$ eV, Read obtained a value f = 0.1. Since f_c depends on $N_d - N_A$, we find from (2)–(4) that when $N_d - N_A$ decreases, the absolute value of f at T = 0 should decrease at $\mathscr{E}_2$ values within the upper half of the forbidden band. Thus, at $N_d - N_A \leq 10^{15}$ cm^{-3}, the occupation coefficient can be less than 0.1, but not more.

When the condition $f\mathscr{E}_0 \ll kT$ is satisfied, the energy $\mathscr{E}$ of the electron located on the dislocation is

$$\mathscr{E} = \mathscr{E}_2 + \mathscr{E}^*(f). \quad (5)$$

Then Eq. (1) takes the form

$$f = \left[1 + \exp\left(\frac{\mathscr{E} - \mathscr{E}_F}{kT}\right)\right]^{-1}. \quad (6)$$

Using (6), we determine the number of electrons located on the dislocation, namely

$$n_a = fN_a. \quad (7)$$

Substituting in the neutrality equation $N_d = \langle n \rangle + n_a$ the values of (7) and

$$\langle n \rangle = N_c \exp\left(-\frac{\mathscr{E}_c - \mathscr{E}_F}{kT}\right),$$

we obtain an expression for a determination of $\mathscr{E}$ from the experimental data:

$$\langle n \rangle \frac{N_a - N_d + \langle n \rangle}{N_d - \langle n \rangle} = N_c e^{\mathscr{E}/kT}, \quad (8)$$

where $N_c = 2 \times 10^{15}\, T^{3/2}$ for electrons in germanium. Knowing $\langle n \rangle$, we can determine $\mathscr{E}(f, T)$.

The table lists the values of $\mathscr{E}$ calculated from the experimental data in accordance with (8) for different temperatures and samples with different dislocation densities. The table also gives the corresponding values

T, °K	Dislocation density $3 \cdot 10^6$ cm^{-2}		$6 \cdot 10^6$ cm^{-2}		$1 \cdot 10^7$ cm^{-2}	
	f	$\mathscr{E}$	f	$\mathscr{E}$	f	$\mathscr{E}$
143	0.013	0.124	0.016	0.130	0.012	0.135
167	0.013	0.141	0.012	0.143	0.010	0.153
200	0.010	0.164	0.009	0.167	0.009	0.175
208	0.009	0.170	0.008	0.173	0.007	0.176
220	0.007	0.170	0.006	0.174	0.0055	0.178
230	0.005	0.173	0.005	0.175	0.0045	0.176

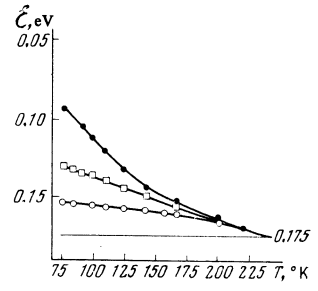

FIG. 5. Temperature dependence of the total energy of the electron $\mathscr{E}$ on the dislocation for samples with different dislocation densities. The symbols are the same as in Fig. 2.

of the occupation filling coefficients f. We see that with increasing temperature and with decreasing f, for all values of N_D, the value of $\mathscr{E}$ tends to a constant corresponding to the position of the dislocation level $\mathscr{E}_2$. At T > 220°K, the electrostatic increment $\mathscr{E}^*$ becomes smaller than 0.005 eV and the total energy practically coincides with $\mathscr{E}_2$, the value of which, as follows from the table, turns out to be 0.175 eV. At higher temperatures, the calculation of the energy from expression (8) can already lead to erroneous values, since the Fermi level will drop in connection with the fact that the intrinsic conductivity comes into play.

Figure 5 shows the temperature dependence of $\mathscr{E}$ calculated from the experimental data on the temperature dependence of the occupation coefficient f and in accordance with expressions (3) and (5). $\mathscr{E}_2$ is assumed to equal 0.175 eV. We see that the curves practically converge to the value of $\mathscr{E}_2$, and at low temperature they diverge in accordance with the dislocation density.

We can thus state that our experimental results concerning the influence of dislocations on the carrier density in germanium are in good agreement with Read's theory.

As to the Hall mobility of the carriers, in accord with the data of Fig. 3 it turns out that in the cases when the current lines are parallel to the flexure axis, even as high a dislocation concentration as 10^7 cm^{-2} has practically no influence on the mobility. In cases when the current lines at sufficient dislocation density are perpendicular to the flexure axis (curves 2 and 3), a certain decrease of the mobility is observed but, as already noted, it is much smaller than that given in[2,10,11].

A comparison of the results with the theory is meaningful only for the minimal dislocation density $N_D = 3 \times 10^6$ cm^{-2}. At large dislocation densities, owing to the low concentration of the donor electrons, the Read cylinders produced around the dislocations, within which the excess charge of the dislocation line becomes screened, begin to overlap one another. Under these conditions the calculation of the scattering processes on the basis of Read's model can lead to erroneous results.

The results of the calculation of the transverse mobility with allowance for the effect of the bending of the cylinders for $N_D = 3 \times 10^6$ cm^{-2} are shown in Fig. 3 by the dashed line. It was assumed there that the cylinders are absolutely impermeable to the electrons. However, at the temperatures at which our experiments were performed, the thermal energy of the electrons is sufficiently high and some of them penetrated through the cylinder. Allowance for this phenomenon should lead to a decrease of the effective radius of the cylinders. Quantitative estimates show that under these conditions the influence of the bending effect on the mobility becomes negligible, in agreement with the experimental data.

Our future experiments will be aimed at a more detailed study of the anisotropy of the carrier mobilities in samples with oriented dislocation structure.

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[1]R. A. Logan, G. L. Pearson, and P. A. Kleinman, J. Appl. Phys. **30,** 885 (1959).
[2]B. Podör, Acta Phys. **23,** (4), 393 (1967)
[3]P. Gondi, S. Mantowani, and F. Schintu, Nuovo Cimento B 2, 1 (1971).
[4]R. L. Bell and A. F. W. Willoughby, J. Mater. Sci. **5,** 198 (1970).
[5]W. T. Read, Phil. Mag. **45,** 775 (1954).
[6]W. T. Read, Phil. Mag. **45,** 1119 (1954).
[7]W. T. Read, Phil. Mag. **46,** 111 (1955).
[8]J. J. Duga, J. Appl. Phys. **33,** 169 (1962).
[9]V. I. Nikitenko and A. A. Polyanskiĭ, in Materialy Vsesoyuznogo soveshchaniya po defektam struktury v poluprovodnikakh (Materials of All-Union Conference on Structural Defects in Semiconductors), Novosibirsk, p. 382, 1969.
[10]L. I. Kolesnik, Candidate's Thesis, Moscow, 1966.
[11]R. M. Broudy, Adv. Phys. **12,** 135 (1963).

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