Effect of dislocations on the electric properties of p-germanium

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The effect of dislocations on the concentration and mobility of holes is studied in the 300–4 °K temperature range in germanium single crystals of the p type with a resistivity 50 Ω cm at room temperature. The dislocation effect is of the donor type at $T < 80$ °K and of the acceptor type at $T > 80$ °K. The level corresponding to a neutral dislocation state is 0.09 eV above the valence band ceiling. An exponential temperature dependence of hole mobility due to scattering by dislocations is observed in the region of donor action of the dislocations.

INTRODUCTION

Investigations of the effect of dislocations on the electric properties of germanium with n-type conductivity[1] have shown that the dislocations act as acceptors. A reduction of the experimental results on sufficiently pure n-Ge has shown that the results agree well with Reed's theory, based on the model wherein the dislocation is made up of a row of atoms with broken bonds capable of becoming attached to electrons[2].

For a better understanding of the mechanism whereby the dislocations influence the properties of the semiconductors, it is natural to attempt to study also p-germanium with dislocations. One of the experimental studies in this direction[3] has shown that donor action of dislocations also appears in p-germanium under certain conditions. The experimental conditions in the cited reference, however, were such that the electric properties could be altered also by other factors not connected with the direct action of the dislocations (annealing of point defects, diffusion of impurities from the outside, etc.).

We therefore deemed it advisable to perform experiments under more pure conditions and take measures to prevent contamination of the sample, choosing a plastic-deformation regime in which the heat treatment contributes to annealing of the point defects but does not change the dislocation density.

PROCEDURE

We investigated single crystals of pure p-germanium with resistivity 50 Ω-cm at room temperature. The differential acceptor concentration was $N_A = 2.2 \times 10^{12}$ cm^{-3} at total donor and acceptor concentrations $N_d = 1.28 \times 10^{13}$ cm^{-3} and $n_a = 1.5 \times 10^{13}$ cm^{-3}. The donor and acceptor activation energy was approximately 0.01 eV. The growth-dislocation density did not exceed 10 cm^{-2}. Prior to deformation, all the samples were coated with a thin layer of gold to prevent contamination from the outside during the time of deformation or annealing. The excess dislocations were introduced by plastic deformation (compression).

The compressed samples were bars measuring 9 × 3 × 3 mm, bounded by the planes (111), (110), and (112). The samples were compressed along the [110] axis. The deformation was produced in vacuum at a rate 5—20 μ/sec at T = 600° C. The dislocation density was determined from the etch pits on the (111) face, as well as with an electron microscope. The electron microscope has shown that the presence of shallow dislocation loops may cause the dislocation density in the volume of the sample to exceed by approximately 3.5 times the dislocation density determined from the etch pits. It is important also to note that no change was observed in the dislocation density and in the dislocation motion when the samples were heated up to 700° C.

After deformation, an upper layer of approximate thickness 0.2 mm was removed. The dimensions of the samples of the measurements were 8 × 2 × 1 mm. Before depositing the contact, the samples were polished in a CP-4A solution and were thoroughly washed. The contacts were of indium and of an alloy of indium with gallium, and formed together with germanium ohmic contacts for each sample, down to a definite temperature below which no measurements were made. The quality of the contact was verified with a "characteriograph." Prior to annealing, the contacts were removed from the samples, the samples were ground and polished, thoroughly washed, and then coated with a layer of gold evaporated in vacuum. The annealing was at a temperature equal to or higher than the deformation temperature, in an atmosphere of ultrapure argon, and lasted 10 minutes.

The electric conductivity and the Hall effect were measured in a helium cryostat in which the temperature could be regulated between 4.2 and 300° K. The temperature was determined with accuracy 0.1°. The sample was placed in helium vapor. To measure the emf we used an electrometer with a dynamic capacitor and with an input resistance ~10^{15}. The insulators were Teflon, sapphire, and epoxy resin. The measurements were performed at a magnetic field intensity 6200 Oe, which corresponded in all cases to the strong-field condition. A unity Hall factor was therefore assumed when the hole density was determined from the experimental data.

MEASUREMENT RESULTS

Figure 1 shows in a semilogarithmic scale the temperature dependence of the hole density p for the control and deformed samples. The smallest and largest dislocation densities were $N_D = 2.5 \times 10^7$ cm^{-2} (sample No. 1) and $N_D = 1.2 \times 10^8$ cm^{-2} (sample No. 4). Annealing of the samples at 700° C for 10 minutes did not affect the density and mobility of the holes in the control and deformed samples. The hole density in the deformed samples was smaller at low temperatures and larger at high temperatures than the hole density in the control sample, and at low temperatures each sample had a temperature dependence different from that of the others. The hole

density decreased noticeably with decreasing temperature at low temperatures and the larger the dislocation density the lower the hole density at the given temperature. For all samples there was a temperature region in which the dependence of log p on $10^3/T$ was a straight line, i.e., corresponded to a definite activation energy. The larger the dislocation density the higher the temperature of this region and the larger the slope of the linear section. Thus, the slope is 1.8 times larger for sample No. 3 than for sample No. 1. At high temperatures, where the hole density in the deformed sample exceeds the hole density in the control sample, a smooth growth of the hole density with increasing temperature and dislocation density is observed, and there is no linear dependence of log p on $10^3/T$ in this temperature interval. No saturation of the hole density was observed for any sample up to room temperature.

Figure 2 shows the temperature dependence of the Hall mobility of the holes in the investigated samples. In the control sample, the Hall mobility μ_0 retains its initial value. In the temperature range 200—100° K we have $\mu_0 \sim T^{-2.3}$, corresponding to scattering by acoustic and optical phonons. At $T < 80°$ K one observes a section with $\mu_0 \sim T^{-1.5}$, corresponding to scattering by acoustic phonons only. At the given degree of doping, the scattering by ionized impurities has no effect down to 30° K. In all the deformed samples, the hole mobility μ_h at $T > 80°$ K does not differ in practice from the mobility in the control sample. At $T < 80°$ K, the hole mobility μ_h decreases with increasing dislocation density, revealing the so-called "bell-shaped behavior" observed earlier[3]. Unlike in[3], however, at the maximum there is little difference between the mobilities of samples

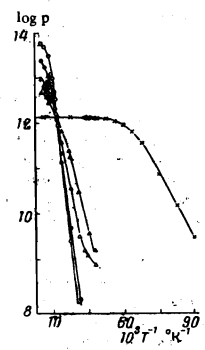

FIG. 1

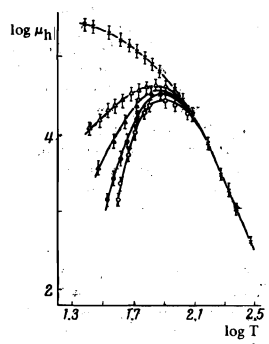

FIG. 2

FIG. 1. Temperature dependence of the hole density in the control sample (X) and in deformed samples having dislocation densities ▲—2.5 × 10^7 cm^{-2} (No. 1), Δ—4.2 × 10^7 cm^{-2} (No. 2), ●—8 × 10^7 cm^{-2} (No. 3), and ○—1.2 × 10^8 cm^{-2} (No. 4).

FIG. 2. Temperature dependence of the Hall mobility of the holes in the control sample (X) and in deformed samples with dislocations density Δ—5 × 10^6 cm^{-2}, ▲—2.5 × 10^7 cm^{-2}, ●—8 × 10^7 cm^{-2}, and ○—1.2 × 10^8 cm^{-2}.

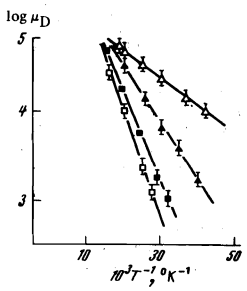

FIG. 3. Temperature dependence of Hall mobility due to scattering by dislocations in samples with dislocation density Δ—5 × 10^6 cm^{-2}, ▲—2.5 × 10^7 cm^{-2}, ■—8 × 10^7 cm^{-2}, and □—1.2 × 10^8 cm^{-2}.

having different dislocation densities. An appreciable difference appears at $T < 80°$ K, when a sharp increase in the slope of the plot of log μ_h against log T occurs with increasing dislocation density, besides a decrease in the absolute value of the mobility at the given temperature. Using the well-known formula for the addition of reciprocal mobilities, we can write

$$\frac{1}{\mu_h} = \frac{1}{\mu_D} + \frac{1}{\mu_0},$$

where μ_h is the experimentally determined Hall mobility in the deformed samples, μ_0 is the mobility in the control sample, and μ_D is the mobility due to scattering by the dislocations. The value of μ_D obtained in this manner is plotted in Fig. 3. It turns out that the plots of log μ_D against 10^3 T^{-1} approximate quite well straight lines with slopes that increase with increasing dislocation density, i.e., the mobility varies exponentially with temperature.

DISCUSSION

A. Temperature dependence of hole density

The germanium used in our experiments was a compensated semiconductor containing shallow donors ($N_d = 1.28 \times 10^{13}$ cm^{-3}) and acceptors ($N_a = 1.5 \times 10^{13}$ cm^{-3}) with approximate activation energy 0.01 eV. Since $N_a > N_d$, some of the acceptors remain uncompensated, and this is the reason for the hole conductivity. As to the position of the dislocation level, in spite of many years of study of plastically deformed semiconductors, its position in the forbidden band of germanium cannot be regarded as finally established. According to Shockley's classical model[5] a dislocation containing atoms with dangling bonds can act either as a donor or as an acceptor. For a long time, however, only acceptor properties of dislocations were observed in monatomic semiconductors. The donor action was observed first in 1967 in p-germanium[3].

In accordance with the foregoing, the energy scheme of a semiconductor with dislocations can be represented in the form shown in Fig. 4. The donor action of the dislocation can become manifest at low temperatures, since electrons from the dislocations can partly or completely fill the uncompensated acceptors at T = 0. Then the dislocations become positively charged. With increasing temperature, only a fraction of the acceptors (in the case of incomplete compensation) can be filled with electrons excited from the valence band. On the other hand, if the electrons from the dislocations compensate the acceptors completely, then the electrons from the valence band can be excited only at a higher dislocation level. Consequently, the hole density in the deformed sample is lower than that in an undeformed sample, as is indeed observed in the experiments (see Fig. 1) at $T < 80°$ K. In samples 1—3 there is apparently a partial compensation of the acceptors by electrons from the dislocations. Sample No. 4 corresponds to the case of complete compensation.

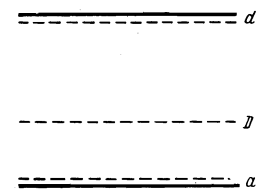

FIG. 4. Energy scheme of a semiconductor containing donors (d), acceptors (a), and dislocations (D).

At a definite temperature, the thermal transfer of the electrons from the valence band to the dislocation level causes the dislocation to accept electrons given up initially to chemical acceptors. In this state, the dislocation is electrically neutral, and the hole density in the deformed sample is equal to the hole density in the control sample. In our sample this occurs at T = 80° K. At T > 80° K, the dislocation continues to accept thermally-excited electrons from the valence band, leading to an increase in the concentration of the free holes in the deformed sample in comparison with the control sample. In this temperature range (up to room temperature), the hole density increases monotonically with increasing temperature and with increasing dislocation density, which is indeed characteristic of the acceptor action of dislocations.

The donor and acceptor actions of the dislocations are reflected in the special behavior of the filling coefficient f in p-germanium, namely, the dependence of the filling coefficient f on the temperature and on the dislocation density turns out to be different in the regions of the donor and acceptor action of the dislocations (see Fig. 5). At T < 80° K we have f < 0, and the absolute value of this coefficient decreases with increasing temperature and dislocation density. At T > 80° K we have f > 0, and its absolute value increases with increasing temperature and dislocation density. At T = 80° K, the filling coefficient is equal to zero. The filling coefficient is defined by the formula

$$f = (p - N_A)/N_0, \tag{1}$$

where N_0 is the concentration of the broken bonds. At T < 80° K we have $p < N_A$, and the absolute value of f is determined to a considerable degree by N_A and N_0. Since N_A does not depend on the temperature and on the dislocation density, the number of free places for electrons from the dislocations is the same in all samples, and therefore |f| decreases with increasing dislocation density. At T > 80° K the value of |f| is determined mainly by the densities p and N_0. But p, in turn, depends on the temperature and on the number of broken bonds, i.e., in this region (and also in the region where p and N_A are comparable), the decisive role is played not only by the number of places on the dislocations, but also by the number of electrons that can be transferred from the valence band at a given temperature.

Thus, the acceptor action of dislocations should be described differently in p-germanium than in n-germanium. In any case, however, the Fermi energy $\mathscr{E}_F$ in plastically deformed material can apparently be written in the form

$$\mathscr{E}_F = \mathscr{E}_0 + \mathscr{E}_e(f) + \mathscr{E}(T, f), \tag{2}$$

where $\mathscr{E}_0$ is the position of the dislocation level at f = 0, reckoned from the top of the valence band; $\mathscr{E}_e(f)$ is the electrostatic energy of the interaction of the electrons on the dislocations which is different for different screening of the dislocations, namely:

$$\mathscr{E}_e(f) = \frac{e^2}{\varepsilon a} f\left[\lg\frac{|f|\lambda}{a} + \frac{1}{4}\frac{N_d - N_a}{n-p} + 1\right] \tag{3}$$

when the screening is by free carriers[4] and

$$\mathscr{E}_e(f) = \frac{e^2}{\varepsilon a} f\left[\frac{3}{2}\lg\frac{1-f}{f} - 0.116\right] \tag{4}$$

when the screening is by ionized impurities[5]. Here e is the charge of the electron, a is the distance between the dangling bonds, ϵ is the dielectric constant, λ is the screening length, and n is the electron density in deformed n-type material.

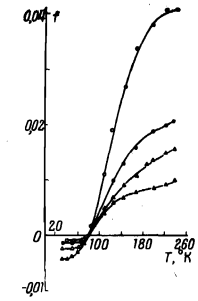

FIG. 5. Temperature dependence of the filling coefficient f for deformed samples. The notation is the same as in Fig. 1.

An important fact is that in any case $\mathscr{E}_e(f)$ is proportional to f, i.e., $\mathscr{E}_e(f) = 0$ at f = 0. The fact that $\mathscr{E}_e(f) \sim f$ explains qualitatively the increase of the slope of the plot of log p against 1/T with increasing dislocation density at T < 80° K. The $\mathscr{E}_e(f)$ term shifts the dislocation-filling boundary towards the valence band. The lower the dislocation density, the larger f, the larger $\mathscr{E}_e(f)$, the larger the shift of the filling boundary to the valence band, and the lower the temperature at which excitation of electrons from the valence band to the dislocation sets in. This is indeed observed in the experiment (see Fig. 1).

The problem is to evaluate the term $\mathscr{E}(T, f)$. In the Schröter-Labusch theory[4], this term is neglected, and in the Read theory[5] it is equal to $kT \ln[(1-f)/f]$ a quantitative estimate by Read's theory, which can be obtained quite arbitrarily, yields $\mathscr{E}_0 = 0.14$ eV at f = 0. On the other hand, the Schröter-Labusch theory yields $\mathscr{E}_0 = 0.09$ eV at f = 0, which agrees with the data of[3]. We have attempted to reduce the experimental results in accordance with this theory, but no quantitative agreement was observed.

B. Hall mobility of holes

As seen from Fig. 2, the effect of the dislocations on the hole mobility comes into play at T < 80° K and is manifest in an anomalous temperature dependence of μ_D (see Fig. 3). At these temperatures, the dislocations give up electrons to the acceptors, become positively charged, and are effective scattering centers for the holes.

The presently available theoretical calculations of the carrier mobility in scattering by dislocations yield the following expression:

$$\mu_D = CT^{3/2}/\lambda f^2 N_D, \tag{5}$$

where C is numerical constant, and λ is the screening length and equals $(f/\pi a N_A)^{1/2}$ if the screening is by ionized impurities and $(\epsilon kT/e^2 p)^{1/2}$ if the screening is by free carriers. Since the filling factor f depends little on the temperature at T < 80° K, where an anomalous dependence of μ_D on the temperature is observed (Fig. 5), we should have $\mu_D \sim T^{3/2}$ for the first mechanism and $\mu_D \sim Tp^{1/2}$ for the second. Thus, the exponential temperature dependence of μ_D can be interpreted as a manifestation of the second mechanism. At these temperatures, however, it turns out that the free-carrier dislocation screening length turns out to be much larger than the ionized-impurity screening length, i.e., the mechanism of screening by free carriers should apparently not be in operation. It can be suggested that the

anomalous behavior of the mobility is connected with the exponential temperature dependence of the number of scattering centers. Further research is necessary, however, before a quantitative theory based on this assumption can be constructed.

[1] R. A. Logan, G. L. Pearson and D. Kleinman, J. Appl. Phys. **30**, 135, 1963.

[2] Yu. A. Osip'yan and S. A. Shevchenko, Zh. Eksp. Teor. Fiz. **61**, 2330 (1971) [Sov. Phys.-JETP **34**, 1248 (1972)].

[3] W. Schröter, Phys. Stat. Sol. **21**, 211, 1967.

[4] W. Schröter and R. Labusch, Phys. Stat. Sol. **36**, 539, 1969.

[5] W. T. Read, Phil. Mag. **45**, 775, 1954.

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73