

Electronic phenomena on cleaved germanium surfaces in liquid helium

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We investigated clean germanium surfaces obtained by cleavage of a crystal in liquid helium. Regardless of the properties of the initial crystal, the surface electric conductivity, after intermediate heating in helium vapor at $T \leq 40$ K, was of p -type with $\sigma_m \approx 4 \times 10^{-4} \Omega^{-1}$, hole density $p = (6 \pm 10) \times 10^{12} \text{ cm}^{-2}$, and mobility $\mu = (400\text{--}250) \text{ cm}^2/\text{V}\cdot\text{sec}$. The general physical picture is approximately the same as on the intergrowth surface in a germanium bicrystal [B. M. Vul and É. I. Zavaritskaya, *Sov. Phys. JETP* **49**, 551 (1979)]. The valence electrons go from the subsurface layer to the surface, where they are pinned to broken valence bonds. The electric conductivity σ_m is determined by the motion of the holes that remain in the subsurface layer after the departure of the electrons to the surface.

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A surface is a boundary between two media. When a "clean" surface is investigated, one of the media tends to reduce to a minimum the influence of the other. For this reason, thorough cleaning of a surface and measurement of its properties are carried out in an ultra-high vacuum. To obviate the need for special cleaning of the surface, crystal samples are cleaved directly in a vacuum, and if the cleaving is performed in liquefied inert gas, there is even no need for ultra-high vacuum. Most such investigations were made in liquid nitrogen.^{1,2}

Obviously, a much cleaner freshly produced cleaved surface can be obtained by replacing the nitrogen with helium.³⁻⁵ Since helium is chemically higher inert, and all impurities freeze out at helium temperatures, the effect of the external medium on the surface properties is negligibly small under these conditions. However, mechanical actions accompanying low-temperature cleavage lead inevitably to certain damage to the crystal structure of the freshly produced surface.

1. In the present study, the investigated surfaces were obtained by cleaving germanium crystals in liquid helium. The cleavage setup and the sample shape were similar to those described in Ref. 1 for cleavage in liquid nitrogen, but additional provisions were made to ensure the needed hermetic sealing of the cryostat. The samples were plates of area $\sim 1 \text{ cm}^2$ and thickness 1–4 mm. The cleaving knives were made of fused quartz or hard metal alloys. The cleavage plane was (111) and mirror-smooth surfaces were usually produced. The contacts for the samples were made by fusing-in indium and were located as shown in Fig. 1.

The electric conductivity before and after the cleavage was measured for more than a hundred samples made of n - and p -germanium with electrically active impurity density from 10^{13} to $5 \times 10^{15} \text{ cm}^{-3}$. Typical current-voltage characteristics of the samples before and after the cleavage are shown in Fig. 2. As seen from these data, the sample resistance after cleavage is approximately doubled, since the cleavage decreases by one-half

the cross section through which the volume current flows. Thus, the surface conductivity σ_s , immediately after the cleavage is so low that it cannot be discerned at helium temperatures against the background of the bulk conductivity of the germanium. However, as seen from the data of Fig. 2, after intermediate heating in helium vapor the conductivity, measured again at 4.2 K increases substantially as a result of the contribution of the surface electric conductivity. The steep growth of the current at $V \approx 5$ volts is due to impact ionization of the impurity atoms in the germanium.

The dependence of the surface conductivity σ_s on the temperature T_i and the duration t of the intermediate heating in helium vapor is shown in Fig. 3 at several fixed values of T_i from 26 to 40 K. These as well as as other measurements of σ_s were made in liquid helium at $T = 4.2$ K. As seen from the data, after the samples are heated in the helium vapor, the surface electric conductivity increases to the same limiting value

$$\sigma_m \approx 4 \cdot 10^{-4} \Omega^{-1}$$

independently of the intermediate-heating temperature T_i . However, the heating time needed to reach the limiting value σ_m increases with decreasing T_i and reaches 10 hours at $T_i = 30$ K, as against only several minutes at $T_i = 40$ K. With further heating, for several hours at $T_i = 40$ K, the value of σ_m remains constant.

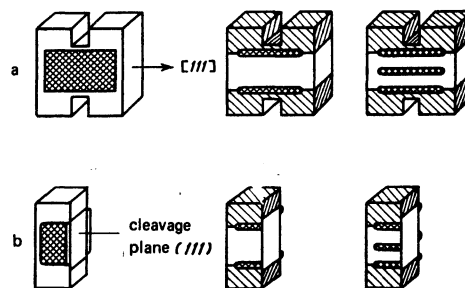


FIG. 1. Shape of sample and configuration of electrodes for the measurement of the electric conductivity and of the Hall effect: a) prior to cleavage, b) after cleavage.

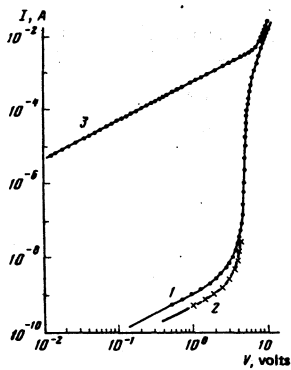


FIG. 2. Typical current-voltage characteristic at $T = 4.2$ K. 1) Prior to cleavage, 2) after cleavage, 3) after cleavage and intermediate heating.

2. In the temperature range $40 \leq T_i \leq 50$ K, the electric conductivity decreases by up to 1.5 times at a heating duration on the order of several hours. At $T_i \geq 55$ K the decreases of the electric conductivity the decrease of the electric conductivity becomes noticeable even after several minutes, as seen from the data shown in Fig. 4. If the sample is kept for a long time at $T_i \approx 100$ K, σ_s decreases sharply. The same effect was observed within a much shorter time when the cryostat was unsealed. The electric conductivity measured under such conditions at $T_i \approx 100$ K, shown in Fig. 5, reflects the influence of two factors—annealing of the defects upon heating, and contamination of the surface by contact with the air. If the sample stays in a helium atmosphere with air impurity for only 30–40 sec, the surface electric conductivity σ_s increases by several orders and reaches values equal to $\frac{1}{2}\sigma_m$. After heating the sample further for 1.5 min, the value of σ_s decreases by several times, and then drops abruptly and becomes again indiscernible against the background of the bulk conductivity of the germanium at helium temperatures. It is obvious that the decrease of the surface conductivity is due to contamination of the sample surfaces during their prolonged stay outside the liquid helium. As seen from our data, however, this contamination is nonexistent, or at any rate does not affect noticeably the surface conductivity σ_s , if the intermediate-heating temperature does not exceed substantially 40 K. Under these conditions, all the investigated germanium samples, independently of

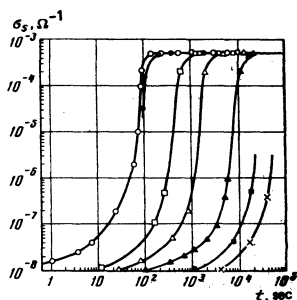


FIG. 3. Value of surface electric conductivity σ_s at $T = 4.2$ K as a function of the duration of the intermediate heating at the following values of T_i [K]: \circ) 38–40; \bullet) 35; \square) 32; \triangle) 31; \blacktriangle) 30; \blacksquare) 28; \times) 26.

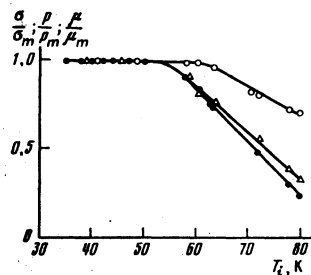


FIG. 4. Relative change of electric conductivity σ , of the density ρ , and of the hole mobility μ at $T = 4.2$ K vs. the temperature of intermediate heating for 5 minutes: \bullet) σ/σ_m , \triangle) ρ/ρ_m , \circ) μ/μ_m .

the type of conductivity and impurity density in the initial crystal, the limiting value of the surface conductivity is

$$\sigma_m = 4 \cdot 10^{-4} (\pm 30\%) \Omega^{-1}.$$

3. A set of measurements of the temperature dependence of the surface electric conductivity was made on samples subjected to intermediate heating. In n -type germanium, the surface conductivity σ_s retains its maximum value σ_m in the entire temperature region to $T \leq 40$ K. In p -germanium, $\sigma_s = \sigma_m$ only to $T \approx 9$ K. The independence of σ_s of the crystal-lattice temperature allows us to assume that so long as $\sigma_s = \sigma_m$ the hole gas in the subsurface layer is degenerate. The difference between the temperature intervals in which $\sigma_s = \sigma_m$ in n - and p -germanium is explained by the influence of the indium contacts.

4. Measurements of the Hall coefficient R have shown that the surface electric conductivity σ_s in germanium is due to hole motion. The measurements of R were made on 14 samples of n - and p -germanium with different donor and acceptor densities in the interval from 10^{14} to $3 \times 10^{15} \text{ cm}^{-3}$ at currents $10^{-6} \leq I \leq 10^{-3} \text{ A}$ and magnetic field intensities $0.1 \leq H \leq 7 \text{ kOe}$. For each of the samples R remained constant within the measurement range, and for different samples the values of R differed by an approximate factor of two.

Since the hole gas is degenerate, it can be assumed when the hole density is calculated from the relation $p = r/Re$ that the Hall factor $r = 1$. The hole density near the cleavage surface is then

$$p = (6-10) \cdot 10^{14} \text{ cm}^{-2},$$

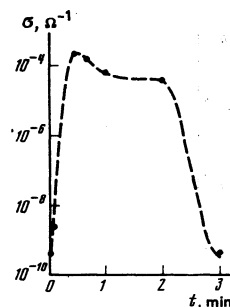


FIG. 5. Electric conductivity σ_s at $T = 4.2$ K vs. the duration of the intermediate heating at $T_i = 100$ K.

and the Hall mobility is

$$\mu = R\sigma_m = (400-250) \text{ cm}^2/\text{V} \cdot \text{sec}.$$

If the intermediate heating is at $T \ll 40$ K and is not long enough, the annealing is incomplete and the surface electric conductivity σ_s does not reach the value σ_m , but it increases with increasing heating duration and temperature. These intermediate values of σ_s likewise remain constant in liquid helium for many hours. Measurements of the Hall effect on surfaces with conductivity.

$$0.1\sigma_m \leq \sigma_s \leq \sigma_m$$

have shown convincingly that the hole density remains approximately constant in this case, and consequently the change of the surface conductivity with increasing duration of the intermediate heating, as seen from the data of Fig. 6, is due to the change of the carrier mobility. This result is apparently connected with the fact that cleaving the crystal is accompanied by structure defects that become frozen-in in the liquid helium and impede the hole motion. Intermediate heating in helium vapor anneals the defects, and it is this which makes it possible to observe the electric conductivity of the freshly produced surface.

5. Calculation shows that the effective thickness of the hole subsurface layer is $l \approx 40 \text{ \AA}$. As we have seen, σ_s reaches a value $4 \times 10^{-4} \Omega^{-1}$, which exceeds by an order of magnitude the minimum value e^2/h of the metallic conductivity in the two-dimensional model.⁶ The hole layer adjacent to the surface can in this case be regarded as a two-dimensional degenerate gas, the scattering in which is predominantly by charged centers. The carrier mobility under these conditions is described by the relation⁷

$$\mu = \frac{\kappa h (p_s)^{1/4}}{2(2\pi)^{1/2} e m_* N_i} \left(\arctg \frac{\kappa h^2 p_s}{4\pi e^2 m_* N_i^{1/2}} \right)^{-1},$$

where κ is the permittivity, h is Planck's constant, e is the electron charge, m_* is the effective mass of the carriers, p_s is the carrier density, and N_i is the density of the scattering centers. In first-order approximation it can be assumed that both on the germanium surface and in its volume we have $\kappa = 16$, the effective hole mass is $m_* = 0.4m_0$, and the density of the scattering centers is $N_i = p_s$. As seen from the data of Fig. 7, the calculated values of μ are approximately half

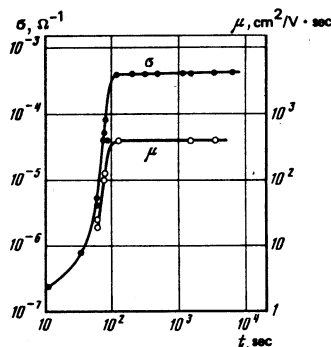


FIG. 6. Electric conductivity σ and hole mobility vs. the time of intermediate annealing at $T_i = 38$ K.

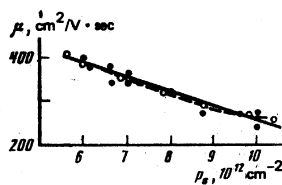


FIG. 7. Dependence of the hole mobility μ on their surface density p_s : \bullet) experimental data; \circ) double the value of μ calculated in accord with Ref. 7.

the measured ones. Under our rough approximation this can be regarded as satisfactory agreement.

6. The data on the negligibly small electric conductivity of freshly cleaved germanium surface pertain to samples with mirror-smooth cleavage surfaces along the (111) cleavage plane. In the case of an uneven rough surface with steps and other defects, which occur when inaccurately oriented samples are cleaved, a high conductivity is observed immediately after the cleavage in the liquid helium. Depending on the type of imperfection of the surface, its conductivity ranges from 10^{-7} to $3 \times 10^{-5} \Omega^{-1}$. On individual such surfaces, the conductivity in helium increases slowly with time from the instant of cleavage. All defective cleavage surfaces reveal, when illuminated with visible or near-infrared light, a residual photoconductivity that exceeds the dark value by dozens of times, but is much less than σ_m . After intermediate heating to $T \approx 40$ K, however, the conductivity of the samples with imperfect surfaces also becomes constant and equal to σ_m , just as for samples with a mirror-smooth surface.

7. The observed set of phenomena can be explained by assuming that when the crystal is cleaved in liquid helium the electrons go over from the valence band on the freshly formed surface and, releasing energy, are pinned there apparently on the broken valence bonds. This process continues until the negative-charge density accumulating on the surface is so large that, owing to repulsion, further transfer of electrons can no longer be offset by energy release when the electrons become pinned on the surface. Calculations made by us with I. I. Ivanchuk, in the Thomas-Fermi approximation, show that at the experimentally established surface-charge density $p_s = (6-10) \times 10^{12} \text{ cm}^{-2}$, the energy released when one electron is pinned on the surface is ~ 0.1 eV.

It is noteworthy that the electronic processes on the free germanium surface produced by the cleavage are qualitatively and quantitatively similar to the phenomena observed on the so-called internal cleavage surface in a germanium bicrystal.⁶ In the former case, however, the surface is between two media-germanium and liquid helium, while in the latter the difference reduces only to a small change of the crystalline orientation of the parts of the bicrystal relative to each other. It is obvious that in both cases the decisive role is played by the transition of the electrons to the broken bonds, regardless of whether these bonds are produced directly during the growth of the bicrystal or whether they are produced on the surface following cleavage in liquid helium.

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