Effect of hydrogen and oxygen adsorption on the electrical conductivity of a cleaved germanium surface

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The high surface conductivity of cleaved germanium crystals results from the adsorption of oxygen molecules.

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The electrical conductivity of a cleaved germanium surface in ultrahigh vacuum, $p \lesssim 10^{-12}$ Torr, is so low that it cannot be detected against the background of the volume conductivity, even after heating to $T_i \approx 120$ K, while in saturated helium vapor the surface begins to conduct as a metal after heating to $T_i \approx 40$ K (Ref. 1). Obviously, a freshly cleaved germanium surface does not itself exhibit an elevated conductivity; this elevated conductivity results from the adsorption of gas molecules. Analysis of the experimental results of Ref. 1 shows that it is not the helium itself but some undetermined impurity in it which has the dominant effect on the surface conductivity. The possibility that impurities in gaseous helium have an effect was also raised by Aristov *et al.*[2]

Hydrogen and oxygen might be the most probable impurities in helium. In this letter we are reporting a study of how the adsorption of these gases affects the surface conductivity of germanium at $T = 4.2$ K.

For the study of hydrogen adsorption we used the same apparatus as was used for the measurements in high vacuum and in low-pressure helium in Ref. 1. The germanium (1) was soldered to a copper heat sink (3) which was insulated from the container (2). As shown in Fig. 1, the sample was held between quartz knife-edges, a fixed one (4) and a movable one (5), in a hermetically sealed container inside a helium cryostat. The sample temperature was monitored by a thermometer (6) soldered directly to the sample. Leads from the thermometers, the heater (7), and the sample passed through platinum seals in glass (8) into the liquid helium.

The container was flushed with hydrogen three or four times; before each flushing it was pumped down to $p \simeq 10^{-6}$ Torr. The hydrogen was subjected to a special purification by passing it through a system of traps with activated charcoal and liquid nitrogen. The gas was injected into the container through a tube (9) slowly and in small portions. Before the cryostat was filled with liquid helium, the container was filled with hydrogen to a pressure of about two atmospheres at room temperature. The crystal was cleaved at $T \approx 4.2$ K by striking it with knife-edge 5, operated by a bellows (10).

Each time the sample was to be heated, the container was raised above the level of the liquid helium. Although the temperatures in the different parts of the container were not the same, it may be assumed that the hydrogen pressure in the container during an intermediate heating of the sample from 20 to 90 K was quite high, since the saturation vapor pressure of hydrogen is equal to atmospheric pressure at $T \approx 20$ K.

The surface conductivity σ_s was measured in all cases after the sample had been cooled to $T \approx 4.2$ K. Figure 2 shows the measurements of σ_s, plotted as a function of the temperature of the intermediate heating in hydrogen; also shown here are the results of corresponding measurements of σ_s with the container filled with gaseous helium. Comparison of these results shows that the increase and decrease of the surface conductivity in the hermetically sealed container as a function of the tem-
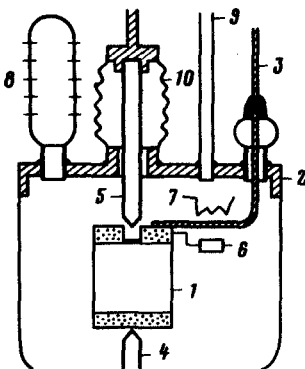

FIG. 1. Cutaway of the hermetically sealed container inside the helium cryostat.
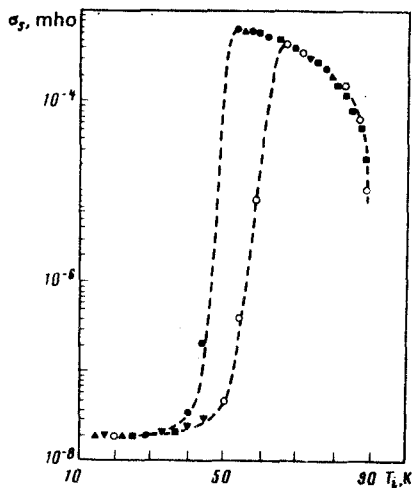
FIG. 2. Changes in the surface conductivity after heating in the container. ▲, ▼, ■—filled with hydrogen; ●, ○—filled with helium. The heating time at each temperature is 5–10 min.

perature of the intermediate heating occur essentially identically when the container is filled with either helium or hydrogen.

It may thus be considered established that the hydrogen, like the helium, does not itself have any significant effect on the surface conductivity of germanium.

It is extremely difficult to carry out a corresponding experiment in liquid helium with a container filled with oxygen, since the boiling point of oxygen is $T_b \approx 90$ K. In our experiments the oxygen was accordingly injected directly into the helium vapor in the upper part of the cryostat, where the sample was also positioned during the heating in this case Each heating session, lasting 10–20 s was carried out at $T_i \approx 90$ K, and then the sample was lowered into the liquid helium for the conductivity measurement. Figure 3 shows the measured values of σ_s, plotted here as a function of the total duration of the successive heating steps. We see that the surface conductivity reaches a maximum $\sim 3 \times 10^{-4}$ mho after the first 20–30 s of heating. Further heating causes σ_s to decrease monotonically, and after heating for about 2 min the conductivity drops sharply. Evidently, oxygen in the atmosphere around the sample is responsible for the change in the surface conductivity of germanium in these experiments.
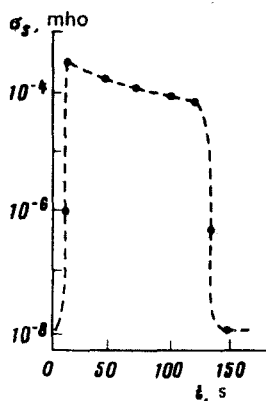

FIG. 3. Dependence of σ_s on the total duration of the successive heatings of the surface at $T_i \approx 90$ K in helium vapor with an oxygen admixture.

In our earlier measurements in helium vapor and oxygen, the changes in the conductivity occurred in the same way as in the experiments in which oxygen was deliberately introduced, but the changes occurred over a longer time; this longer time can be attributed to the very low concentration of the impurity oxygen in the gases that we used. Further confirmation for an effect of oxygen comes from the circumstance that in the range of intermediate-heating temperatures $30 \leqslant T_i \leqslant 40$ K, in which the saturation vapor pressure of oxygen rises sharply from 10^{-7} to 10^{-3} Torr (Ref. 3), we also observe an increase in the surface conductivity by four or five orders of magnitude.[4]

Boonstra[5] has reported qualitatively similar results on the effect of hydrogen and oxygen on the surface conductivity of germanium at room temperature.

All our experimental results conform to the following physical picture.

When crystals are cleaved in liquid helium, the fresh surface and the ruptured bonds at it appear at such a low temperature that the diffusion of impurities from the interior to the surface is ruled out, while the impurities in the liquid helium condense and precipitate out. The surface conductivity is not observed under these conditions, because the ruptured bonds are formed again at the surface. This process is apparently accompanied by the release of more energy than during a possible capture of electrons from the valence band of the crystal.

The conductivity changes which are observed after the intermediate annealing in helium and hydrogen can be attributed to a residual oxygen impurity in these gases, as mentioned earlier. This conclusion is confirmed by direct measurements in which oxygen was added directly to helium vapor. The adsorption oxygen on a germanium surface is evidently accompanied by the rupture of paired bonds at the surface and by the formation of new complexes, in which one of the ruptured bonds remains free. It is to this free bond that an electron comes from the valence band of the crystal, leaving a hole in the surface layer.

The transition of electrons from the valence band is limited by the appearance of an electrostatic field. The maximum electron density at the surface of germanium is $\sim 7 \times 10^{12}$ cm^{-2}, or 1% of the density of germanium atoms on the surface, $\sim 7 \times 10^{14}$ cm^{-2}. It may be assumed that the oxygen complexes are distributed quite uniformly over the surface and are relatively far apart.

A further adsorption of oxygen does not affect the conductivity σ_s as long as the interaction between oxygen complexes on the surface can be ignored. When the concentration of adsorbed oxygen reaches a sufficiently high level, however, such that the oxygen complexes are close together, the linking of theses complexes by free bonds becomes preferred over the capture of electrons from the valence band. The electrons which were previously held at these bonds are sent back into the valence band of the crystal; they reduce the concentration of free holes and suppress the surface conductivity.

Working from this model, we can find a qualitative estimate of how the hole concentration p at the surface depends on the concentration of adsorbed oxygen molecules, n. We assume that the concentration of adsorbed centers is N; then the total number of possible positions of oxygen complexes per unit surface area is

$$C_N^n = \frac{N!}{n! \, (N-n)!} \, ,$$

(1)

and the number of these positions in which two oxygen complexes are neighbors is

$$C_{N-2}^{n-2} = \frac{(N-2)!}{(n-2)! \, (N-n)!} \, .$$

(2)

The probability for this arrangement is the ratio

$$C_{N-2}^{n-2} \, / \, C_N^n = \frac{n(n-1)}{N(N-1)} \approx \left(\frac{n}{N}\right)^2 .$$

(3)

If each oxide complex can have four nearest neighbors, we have

$$p = n - \frac{2n^2}{N} \, .$$

(4)

It follows from (4) that the maximum hole concentration $p_m \approx 7 \times 10^{12}$ cm^{-2} is reached at

$$n_1 \approx p_m \quad \text{and} \quad n_2 \approx \frac{N}{2} \, .$$

(5)

If the concentration of adsorbed oxygen is $n < n_1$, the number of holes increases in proportion to n, since $n/N \ll 1$. In the interval $n_1 < n < n_2$ the hole concentration remains equal to p_m because of restrictions imposed by the surface electric field. At $n > n_2$, progressively more of the electrons previously captured by the surface are sent back into the valence band, and the hole concentration p approaches zero. If we assume that N is equal to the number of surface germanium atoms, the fraction of a monolayer sufficient for the disappearance of the holes is $2/k$, where k is the number of possible neighbors of the oxide complex.

These results add some detail to the physical picture drawn on the basis of the early work on this topic.

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