

Role of oxygen adsorption in the insulator–metal transition at a cleaved germanium surface

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The transition of a cleaved germanium surface from a nonconducting state to a metallic state at low temperatures is due to the adsorption of oxygen molecules in an amount of less than 1% of a monolayer.

The germanium surfaces produced by cleaving crystals in liquid helium undergo a transition^{1,2} from an insulating state to a metallic state after a brief heating in He vapor at $T=35$ K. Heating in ultrahigh vacuum ($P \ll 10^{-12}$ torr), in contrast, does not alter the surface properties; the surface remains insulating when the sample is heated to 120 K (Ref. 3). These experiments leave no room to doubt that this insulator–metal transition is due to an adsorption of gas molecules. In this letter we are reporting a study carried out to determine specifically which impurity in helium vapor is responsible for this transition.

At liquid–helium temperatures, cleaved crystal surfaces are of very high purity, since helium itself is inert, while impurities in it freeze and precipitate in solid form with a negligibly low saturation vapor pressure. An exceptional case is hydrogen, for which we have $P=2 \times 10^{-7}$ torr at $T=4$ K. In the case of interest here, however, hydrogen can be ignored, since direct measurements⁴ have shown that it plays no role in the conversion of a germanium surface into a 2D metal. As for impurities which affect the surface of Ge, we can discuss two at $T=30$ – 35 K: oxygen and carbon monoxide, whose saturation vapor pressures at $T=30$ K are 1.2×10^{-7} and 7×10^{-7} torr, respectively.⁵

We were able to solve the problem in which we were interested—determining the active impurity in Ge—by measuring the heat of sublimation of the adsorbing gas. For these experiments we used samples of nondegenerate *n*- and *p*-type germanium with an excess donor (or acceptor) concentration on the order of 10^{14} cm⁻³ and with an impurity ionization potential $E_i \sim 10$ meV. The electrical conductivity of these crystals at $T=4.2$ K does not exceed $\sigma \sim 10^{-9}$ S/cm. At ~ 10 K (and above), however, σ increases by several orders of magnitude, complicating efforts to distinguish the surface-conductivity component of the total conductivity of the sample. These properties of nondegenerate Ge crystals forced us to use more elaborate experimental conditions. Specifically, we heated the samples in helium vapor in accordance with a certain program, and in liquid helium we detected the changes caused in the surface conductivity of a sample by a heating of the samples in a certain procedure.

To heat the samples quickly to the given temperature we used two wire heaters with a power of more than 10 W. When they were turned on, the helium level in the cryostat dropped rapidly, and the sample warmed up very rapidly as soon as it

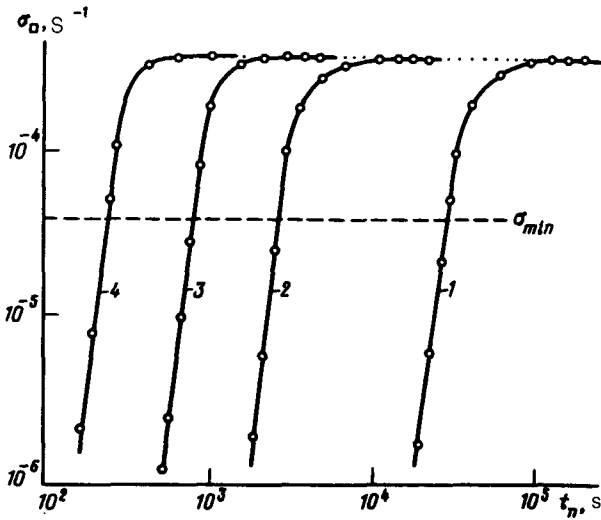


FIG. 1. Specific surface conductivity σ_{\square} in germanium versus the total duration of the heating of the sample in helium vapor at several temperatures T_i : 1—29.5 K; 2—31.5; 3—32.5; 4—34 K.

emerged above the liquid, in the saturated vapor. The sample temperature T_i which was reached in the course of this heating was varied from 20 to 40 K. Measurements were carried out with a miniature carbon thermometer soldered to the sample. The heating time for each given temperature was varied over a wide range from 1 s to 3–10 h. The heating procedure began with the minimum given temperature and the minimum heating time interval. In each successive heating of the sample the duration of the heating was increased. Since we were unable to remove the adsorbed layer which formed on the surface under these conditions by any method available to us, all successive heating cycles (at each new value of T_i) were carried out on new, freshly cleaved samples, with the same dimensions and the same positions of the contacts as for the first sample.

The results of these measurements are shown in Fig. 1. The measured values of σ_{\square} are plotted along the ordinate, while the abscissa shows the total heating time required to reach these values. Here we have allowed for the circumstance that each new, higher value $(\sigma)_n = F(t_n)$ is reached not exclusively over the duration of the n th heating but actually over the durations of all the preceding heating cycles. In other words, the heating time is actually $t_n = \sum_{i=1}^n t_i$. The dependence of the surface conductivity σ_{\square} on the total heating time t_n found in this manner is shown in Fig. 1 as four isotherms, corresponding to intermediate heatings at $T_1 = 29.5$ K, $T_2 = 31.5$ K, $T_3 = 32.5$ K, and $T_4 = 34$ K. The dashed line shows the value $\sigma_{\min} = e^2/h$, characteristic of the minimum metallic conductivity in a 2D medium.

We see from Fig. 1 that heating the freshly cleaved germanium surfaces in helium vapor at temperatures of about 30 K results in the appearance and rapid growth of a surface conductivity, up to $\sigma_{\square} \approx 10\sigma_{\min}$. The limiting value of the surface conductivity

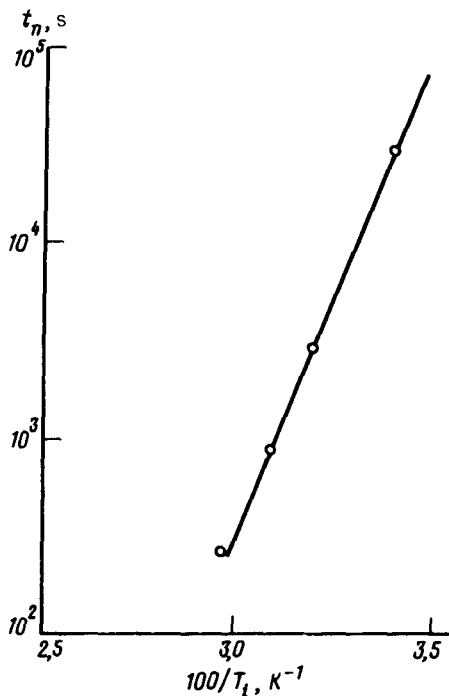


FIG. 2. Temperature dependence of the total heating time required to convert the Ge surface layer into a 2D metal with a conductivity $\sigma_{\square} = 1 \times 10^{-4}$ S.

in the selected range of T_i is independent of the temperature of the intermediate heating. On the other hand, the heating duration required to reach this value increases sharply with decreasing T_i , evidently because of a significant decrease in the concentration of adsorbed gas molecules.

We know that the number (N) of molecules which evaporate from the surface of a liquid (or a solid) is determined by the energy required to overcome the molecular adhesive forces in the condensed medium and is described by

$$N \sim \exp(-Q/RT), \quad (1)$$

where $R = 1.95$ cal/(mole · K) is the universal gas constant, Q is the heat of sublimation of the adsorbed impurity, and K is a degree Kelvin.

The time (t_n) required for the formation of the adsorbed layer is given under weak-adsorption conditions by

$$N \cdot t_n \simeq \text{const} \quad (2)$$

since the heating duration required increases with decreasing concentration of adsorbed impurity molecules.

Figure 2 shows the experimental results on the time t_n as a function of the reciprocal temperature of the intermediate heating. These results show that the increase in t_n with decreasing temperature is indeed exponential. The value calculated

for Q from the slope of the experimental straight line is 2.2×10^3 cal/mole, in agreement with the tabulated heat of sublimation of the β phase of solid oxygen in the temperature range⁵ $24 < T < 35$ K.

A detailed analysis of the data, incorporating the process by which the solid impurity and its vapor reach equilibrium and the influence of diffusion processes,⁶ furnishes quantitative support for this result. The calculations also show that the effect of other components of air, in particular, carbon monoxide, on the formation of the highly conducting germanium layer of interest here can be totally ignored.

The results of this study leave no room to doubt that the adsorption of oxygen is responsible for the insulator-metal transition on a clean Ge surface after it is heated in helium vapor. This adsorption gives rise to the formation of a 2D system in which there is a strong interaction between carriers.⁷

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