R. Kh. Burshtein, L. A. Larin, and G. F. Voronina

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R. Kh. Burshtein, L. A. Larin, and G. F. Voronina

CHEMISORPTION OF OXYGEN ON GERMANIUM

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It is known that the state of the surface has a great influence on the electrophysical properties of semiconductors. Therefore, the study of adsorption processes on germanium and the investigation of the properties of adsorbed layers are of considerable interest. In order to elucidate the mechanism of oxygen chemisorption on germanium, we investigated the kinetics of oxygen adsorption.

Since the surface of germanium is always covered with an oxide layer, in studying the adsorption of gases it is important to develop a method for cleaning the germanium surface. In a number of works (1) carried out recently, much attention has been devoted to this question. To clean the germanium surface, Farnsworth and co-workers (2) used a method of ion bombardment in argon followed by degassing in ultrahigh vacuum at high temperature. Schlier and Farnsworth (3), as well as Handler (4), point to difficulties associated with cleaning the germanium surface by ion bombardment. Law and Garrett (5) believe that a germanium surface treated by ion bombardment is not free from chemisorbed oxygen. There are also indications that after ion bombardment the germanium surface has a large number of defects (6).

The possibility of obtaining a clean germanium surface by depositing films also raises doubts, since during evaporation of germanium the film may capture gas released from the germanium upon heating.

A clean germanium surface for adsorption measurements can be obtained by crushing single crystals in ultrahigh vacuum (7). However, for cleaning the surface of oxide films, it was desirable to use a method that could be employed both for adsorption measurements and for investigation of electrophysical properties.

In our work, cleaning the germanium surface of oxide films was carried out by repeated reduction of germanium in hydrogen. After reduction of germanium for 1-2 hours at 400-450° prolonged degassing was performed in a vacuum of 10^{-7} mm at the same temperature. Reduction and degassing of the germanium were repeated 5-6 times. For complete cleaning of the surface, after reduction, degassing was carried out in a vacuum of 10^{-9} mm at 400-450°. Complete desorption of hydrogen adsorbed on germanium at 278° was observed by Timuni and Budar (8). According to these authors, the rate of desorption increases

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

rapidly with temperature. It also follows from the results of our experiments that by degassing at 400° it is easy to clean the germanium surface of adsorbed hydrogen.

We investigated the adsorption of oxygen on germanium powder obtained by crushing single crystals. The surface area of the germanium powder, determined by the BET method, was 620 cm^2/g. Adsorption experiments were carried out with 60.4 g of germanium. The presence of a large surface made it possible to study in more detail the mechanism of oxide-film formation. The investigation of oxygen adsorption on germanium was carried—

was carried out by the method we had used earlier in studying the adsorption of oxygen on iron (^{9}). This method was also applied by Rideal and Treppnel (^{10}) to investigate the adsorption of oxygen on tungsten.

In our experiments, after reduction and degassing, the germanium powder was cooled to room temperature; oxygen was then adsorbed in small portions, and the rate of uptake of each portion was studied. The initial pressure of each portion was approximately 0.07 mm. The results obtained in studying the adsorption of oxygen

Fig. 1. Adsorption kinetics of individual portions of oxygen on germanium (the curve numbers correspond to the serial numbers of the admitted oxygen portions).

Fig. 2. Dependence of $\lg 1/\tau$, where τ is the half-uptake time of individual oxygen portions, on the number of oxygen molecules adsorbed per 1 cm^2 of surface.

on germanium are shown in Fig. 1. From these data it is evident that on germanium there are two stages of oxygen uptake: a fast stage and a slow stage. The adsorption rate in the fast stage is practically independent of the degree of surface coverage. The amount of rapidly adsorbed oxygen corresponds to the formation of a monoatomic layer, on the assumption that one germanium atom sitting on the surface adsorbs one oxygen atom. The number of atoms on 1 cm^2 of the surface of germanium powder, in accordance with the data of Green, Kafalas, and Robinson (^{7}), was taken to be $7.7 \cdot 10^{14}$.

Figure 2 shows the dependence of $\lg 1/\tau$, where τ is the half-uptake time of each portion, on the amount of oxygen taken up. It is seen from Fig. 2 that the amount of slowly absorbed oxygen is equal to the amount of rapidly absorbed oxygen. It follows from our experiments that, in contrast to the data of Green, Kafalas, and Robinson (^{7}), the dependence $N \simeq \lg t$ (where N is the number of adsorbed molecules and t is the time from the beginning of the experiment) is valid only for the slow stage of adsorption. The total amount of oxygen chemisorbed on germanium powder purified by reduction in hydrogen, just as on germanium powder obtained by crushing single crystals in ultrahigh vacuum (^{7}), is equal to two monoatomic layers. Such agreement is further evidence that reduction in hydrogen followed by degassing can yield a clean germanium surface.

The question of whether the surface of germanium can be cleaned of oxide films by heating in vacuum was subjected to experimental verification. For this purpose, germanium powder on which fast and slow adsorption at room temperature had been completed was heated at 400° in vacuum for 2 hours. No desorption of oxygen was observed during heating. After the germanium powder heated in vacuum had cooled, its adsorption capacity with respect to oxygen at room temperature was again tested. It turned out that after heating, slow adsorption again occurs on the germanium powder.

Since desorption of oxygen does not occur during degassing, and removal of oxygen from the surface in the form of GeO (^{11}) is also practically not observed, it may be assumed that when germanium on which chemi-

chemisorbed oxygen, a change occurs in the character of the bond of the latter with the germanium surface.

The rapid stage of oxygen adsorption can be used to determine the surface area of germanium. The surface area of 1 g of germanium powder obtained by this method, equal to 630 cm^2, is in good agreement with data on surface determination by the BET method. In contrast to the chemisorption of oxygen at room temperature, for which, at a certain filling, complete cessation of the adsorption process is observed, at 400° no formation of a protective oxide film on the germanium surface is observed; rather, oxidation of germanium by oxygen proceeds to a considerable depth.

If it is assumed that the rapid stage of chemisorption corresponds to the reaction

$$2\mathrm{Ge} + \mathrm{O}_2 \rightarrow 2\mathrm{GeO}, \tag{1}$$

then the slow stage is apparently connected with the formation on the germanium surface of a layer of GeO_2 according to the reaction

$$2\mathrm{GeO} + \mathrm{O}_2 \rightarrow 2\mathrm{GeO}_2. \tag{2}$$

Both the adsorption-measurement data presented here and certain data on the influence of adsorbed oxygen on the electrophysical properties of germanium speak in favor of such an assumption.

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Institute of Electrochemistry
Academy of Sciences of the USSR

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