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# Physical Chemistry

R. Kh. Burshtein and L. A. Larin

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## Abstract

## Full Text

*Physical Chemistry*

R. Kh. Burshtein and L. A. Larin

# THE EFFECT OF ADSORBED OXYGEN ON THE ELECTRON WORK FUNCTION OF GERMANIUM

*(Presented by Academician A. N. Frumkin, October 7, 1959)*

A number of works have been devoted to the study of the effect of adsorbed gases on the electron work function of germanium <sup>(1-4)</sup>. However, these were not accompanied by an investigation of oxygen adsorption on germanium and therefore, when measuring the contact potential difference, the specific features of the process could not be revealed. In our previous work we investigated the kinetics of oxygen adsorption on germanium <sup>(5)</sup>. To elucidate the influence of various stages of oxygen chemisorption on surface properties, we investigated the effect of adsorbed oxygen on the electron work function of germanium.

To measure the contact potential difference, in our work we used the Kelvin vibrating-capacitor method. The principal disadvantage of this method when used for adsorption measurements is the adsorption of gases both on the electrode under investigation and on the reference electrode, which prevents correct results from being obtained regarding the effect of adsorbed gases on the electron work function. In order to eliminate this shortcoming, we used an apparatus developed earlier by us <sup>(6)</sup>, in which the reference electrode is sealed with glass. Since the adsorption of a number of gases on glass is considerably smaller than on metals, such a reference electrode is more stable. To eliminate interference, after heating at 400° the apparatus was kept in a shield. The use of an apparatus with a glass-covered reference electrode made it possible to investigate the effect of adsorbed oxygen on the electron work function of germanium over a wide temperature interval.

**Fig. 1.** Change in the contact potential difference between germanium and the reference electrode as a function of the logarithm of the oxygen pressure.

The method of cleaning the germanium surface is described in <sup>(5)</sup>. Our studies

showed, on a series of samples of *n*- and *p*-type germanium of different conductivity, that in all cases the clean germanium surface had a very constant contact potential difference relative to the reference electrode.

The electron work function both from *n*- and from *p*-type germanium was 0.73–0.75 V less than the work function from the reference electrode. The absence of a noticeable difference in the electron work function ( $\pm 0.02$  V), in the presence of a considerable difference in the position of the Fermi level for *n*- and *p*-type germanium, is explained by the high density of surface states (7). The results obtained in studying the change in the contact potential difference of the surface

of germanium during the process of oxygen adsorption at different pressures are shown in Fig. 1. These data refer to an *n*-type germanium specimen with  $\rho = 20 \Omega \cdot \text{cm}$ . Similar results (within  $\pm 0.02$  V) were also obtained on other *n*- and *p*-type germanium specimens of different conductivity.

The influence of adsorbed oxygen on the work function was studied in the pressure range from  $10^{-3}$  to 100 mm Hg. At each pressure the contact potential difference was measured for 20 min.

It follows from the data obtained that the electron work function of *n*- and *p*-germanium increases upon oxygen adsorption. The dependence between the contact potential difference and the logarithm of the oxygen pressure is expressed by a straight line over a considerable pressure interval.

A comparison of the data on measuring the work function with adsorption-measurement data indicates that the fast stage of oxygen adsorption on germanium, which corresponds to the formation of a monoatomic layer and, already at a pressure of  $10^{-3}$  mm Hg, is completed within no more than 5 min, leads to a change in the contact potential difference by 0.15 V. With a further increase in pressure and, consequently, an increase in the amount of adsorbed oxygen corresponding to the slow stage, the work function continues to rise and at a pressure of 100 mm increases by 0.48 V. The data we obtained are not in agreement with the data of Dillon (2), from which it follows that the maximum increase in the electron work function by 0.2 V is observed at a pressure  $P_{\text{O}_2} = 10^{-6}$  mm; at  $P_{\text{O}_2} = 10^{-5}$  mm the electron work function decreases by 0.1 V, and a further increase in pressure has no effect on the electron work function. According to Dillon and Farnsworth (3), upon oxygen adsorption the work function increases by 0.2 V. When the pressure is changed, in the authors' opinion, the contact potential difference does not change. However, these authors varied the pressure only from  $1 \cdot 10^{-7}$  to  $2 \cdot 10^{-5}$  mm. Under these conditions the slow stage of adsorption is difficult to observe.

According to our data, completion of the slow stage of oxygen chemisorption at a pressure of 0.07 mm requires several days. When the pressure is increased, the rate of the slow stage increases in proportion to  $P^{0.52}$  (8). This can explain the change in the contact potential difference with increasing pressure. The change in the contact potential difference upon completion of the fast stage is smaller than that corresponding to slow adsorption. The data obtained lead to

the conclusion that, when the second layer is formed on the germanium surface, a new compound is formed. If it is assumed that the fast stage of chemisorption corresponds to the reaction



then the slow stage of adsorption is apparently associated with the formation of a layer of  $\text{GeO}_2$  on the germanium surface according to the reaction



From the data obtained in measuring the contact potential difference it follows that oxygen adsorbed on the germanium surface at pressures up to 10 mm is adsorbed irreversibly. This is indicated by the fact that degassing to  $10^{-6}$  mm after oxygen adsorption does not lead to a change in the contact potential difference. However, in those cases where the influence of adsorbed oxygen on the contact potential difference was studied at pressures of the order of 100 mm and higher, along with irreversible adsorption, reversible adsorption was also observed, exerting some influence on the contact potential difference. Thus, for example, after adsorption at  $P_{\text{O}_2} = 100$  mm, degassing led to a decrease in the electron work function by 0.04-0.05 V, which is possibly associated with physical adsorption of oxygen on the oxide surface.

In order to investigate the behavior of oxygen chemisorbed on germanium at different temperatures, on the germanium surface there was adsorbed

a definite amount of oxygen was adsorbed at room temperature. The contact potential difference between germanium and the reference electrode was measured, and then the germanium with chemisorbed oxygen was heated at various temperatures in the absence of oxygen in the gas phase. After heating for 1 hour, the apparatus in which the germanium was located was cooled to room temperature and the contact potential difference was again measured. The results obtained in studying the effect of the heating temperature of germanium with chemisorbed oxygen on the electron work function are shown in Fig. 2. From the results obtained it follows that after heating (at temperatures of 100-400°) germanium on whose surface there is a layer of chemisorbed oxygen, the electron work function decreases (Fig. 2, 1), which can be explained both by the penetration of oxygen into germanium and by evaporation of germanium oxide from the surface, or by decomposition of the surface oxide. Upon heating to 200° the work function is lower by 0.2 V than before heating. After heating at 400° the work function is only 0.08 V higher than for a clean germanium surface.

**Fig. 2.** Change in the contact potential difference of the surface of germanium on which oxygen is chemisorbed, as a function of heating temperature. 1 – in a vacuum of  $1 \cdot 10^{-6}$  mm; 2 – in oxygen, 5-6 mm.

Fig. 2. Change in the contact potential difference of the surface of germanium on which oxygen is chemisorbed, as a function of heating temperature. 1—in a vacuum of  $1 \cdot 10^{-6}$  mm; 2—in oxygen, 5–6 mm

Figure 2: Fig. 2. Change in the contact potential difference of the surface of germanium on which oxygen is chemisorbed, as a function of heating temperature. 1—in a vacuum of  $1 \cdot 10^{-6}$  mm; 2—in oxygen, 5–6 mm

These data are in agreement with the data of Schlier and Farnsworth<sup>(9)</sup>, who, by the method of electron diffraction, showed that after heating at  $500^\circ$  in vacuum of germanium on which oxygen is chemisorbed, cleaning of the germanium surface apparently occurs. However, desorption of oxygen at  $400^\circ$ , on the basis of our pressure-change data, does not occur. Removal of GeO from the surface at  $400^\circ$ , according to Vol'skii<sup>(10)</sup>, also does not occur. Our adsorption measurements showed that after heating at  $400^\circ$  of germanium on which fast and slow adsorption has been completed, slow adsorption of oxygen again occurs at room temperature<sup>(5)</sup>. Since desorption of oxygen does not occur upon heating, it may be considered that upon heating the reaction occurs



The GeO formed, upon contact with oxygen at room temperature, is again converted into  $\text{GeO}_2$ .

Thus, when germanium is heated to  $400^\circ$  in vacuum, cleaning of the surface from chemisorbed oxygen does not occur; rather, the character of the bond of oxygen with germanium changes. On this basis, the change in the contact potential difference upon heating can be explained by reaction 3.

Different results are obtained when germanium is heated in the presence of a certain amount of oxygen in the gas phase (5 mm). These data are given by curve 2 in Fig. 2. From these data it is seen that, as the heating temperature increases, the electron work function of germanium increases by 0.9 V after heating at  $400^\circ$ , which apparently indicates an increase in the thickness of the  $\text{GeO}_2$  oxide layer.

Thus, it follows from our experiments that the electron work function of germanium continues to change even in the presence of several oxide layers on the surface. These data are in agreement with the data obtained by us earlier on the absorption of oxygen on iron and can be explained in accordance with Mott's concepts<sup>(11)</sup> concerning the diffusion of metal atoms—in the present case, a semiconductor—to the oxide surface.

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Institute of Electrochemistry

Academy of Sciences of the USSR

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