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Figure 1

Figure 1: Figure 1

Abstract

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THE INFLUENCE OF WATER VAPOR ON THE INTERACTION OF GERMANIUM WITH OXYGEN

(Presented by Academician A. N. Frumkin, January 28, 1960)

In previous works (1,2) we investigated the mechanism of oxygen chemisorption on germanium, and it was shown that on the surface of germanium, upon contact with dry oxygen at room temperature, a protective film is formed corresponding to the adsorption of two oxygen atoms per one germanium atom. Comparison of these data with data obtained in studying the effect of adsorbed oxygen on the electron work function from germanium permits the conclusion that the fast stage of adsorption leads to the formation on the germanium surface of a monolayer of composition GeO, while the slow stage leads to the formation of a monolayer of composition GeO_2.

Fig. 1. Dependence of the rate of oxygen adsorption on the coverage of the germanium surface. 1—on a clean surface; 2, 3—after adsorption of water vapor

It is known from a number of works that the properties of semiconductor germanium devices change upon their contact with atmospheric air containing water vapor (3). It was of interest to study the mechanism of this process and to determine the influence of water vapor both on pure germanium and on germanium covered with an oxide film. To clarify this question, the following experiments were carried out. On a clean germanium surface, freed from the oxide film by reduction in hydrogen with subsequent degassing, as we described earlier, oxygen was adsorbed in small portions in an amount sufficient to complete the fast and slow stages of adsorption (1). After this, the germanium surface was brought into contact with water vapor. After some time the water vapor was frozen out or pumped off, and the kinetics of oxygen uptake were again investigated.

The results of these experiments are given in Fig. 1, where the ordinate gives the reciprocal of the half-uptake time for each portion of oxygen, and the abscissa gives the total amount of oxygen absorbed by germanium. From these data it

Fig. 2

Figure 2: Fig. 2

is evident that if, after completion of the fast and slow adsorption processes represented by curve 1, germanium is brought into contact with water vapor, then after removal of the water vapor the adsorption rate increases. As new portions of oxygen act on the germanium, the rate of the process again decreases (Fig. 1, 2). However, subsequent interaction of germanium, covered with the newly formed passivating oxide film, with water vapor again leads to an increase in the rate of interaction of germanium with oxygen; in this case, too, passivation of the surface can be achieved by additional uptake of oxygen (Fig. 1, 3). Thus, these experiments showed that during adsorption of wa-

water vapor on the surface of germanium covered with an oxide film, the passivating properties of the oxide film are impaired, which leads to the formation of a thick oxide layer on the surface of germanium.

The impairment of the passivating properties of the oxide film under the action of water vapor can be observed especially clearly when these phenomena are studied by measuring the contact potential difference (c.p.d.). The latter was measured by the vibrating-capacitor method in an apparatus described by us earlier (4), with a reference electrode sealed with glass. The results relating to the effect of water vapor adsorbed by a clean germanium surface on the electron work function are presented in Fig. 2, 1. These data show that, as the water-vapor pressure is increased, a linear dependence is observed between the change in work function and $\lg P_{H_2O}$ in the pressure range from $1 \cdot 10^{-3}$ to 7 mm Hg. In this pressure interval the electron work function increases by 0.16 V. However, with a further increase in the pressure of water vapor, namely when the relative humidity changes from 50 to 100%, a sharp increase in the electron work function by 0.24 V is observed. Thus, the total increase in the work function upon adsorption of water vapor reaches 0.4 V. This change in the electron work function is reversible. When the water vapor is pumped out, the work function assumes the value corresponding to a clean germanium surface.

Fig. 2. Dependence of the c.p.d. on $\lg P_{H_2O}$: 1 —on a clean surface; 2 —on germanium covered with an oxide film; 3 —after repeated treatment.

The effect of water vapor on the electron work function from germanium covered with an oxide film has a different character. The results of these experiments are shown in Fig. 2, 2. Adsorption of oxygen on germanium in these experiments was carried out at a pressure of 0.1 mm for 15 h. In accordance with the results obtained earlier, under these conditions the shift of the c.p.d. is due to rapid adsorption of oxygen on germanium (by 0.15 V) and to partially slow adsorption. As is seen from Fig. 2, 2, the increase in the work function due to chemisorbed oxygen under these conditions corresponded to 0.28 V.

Fig. 3. Dependence of the c.p.d. on the amount of adsorbed water vapor. θ is

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

the number of molecular layers.

Adsorption of water vapor on the surface of germanium covered with an oxide film, when the pressure is changed from $1 \cdot 10^{-3}$ to 7 mm, leads to a change in the contact potential difference of only 0.02 V. When the pressure of water vapor is increased from 7 to 15 mm, a shift of the contact potential difference corresponding to 0.16 V is observed. Thus, upon adsorption of water vapor on the surface of germanium covered with an oxide film, the c.p.d. shift is approximately 2 times smaller than on a clean surface.

From Fig. 2 (curves 1 and 2) it is seen that at a water-vapor pressure in the range 7-15 mm ($\lg P_{H_2O} = 0.84$–1.18) there is a strong change in c.p.d. with increasing pressure. The results obtained can be explained on the basis of works (^{5}, ^{6}), from which it follows that, as the relative humidity is increased to 80%, the amount of adsorbed water vapor corresponds to the formation of three molecular layers, and when the relative–

humidity from 80 to 100%, the thickness of the water layer increases to 7 molecular layers. A comparison of our results with those of the Japanese authors (^{6}) is given in Fig. 3, which presents the dependence between $\Delta\varphi$ and the number of molecular layers of water adsorbed on germanium. As can be seen from Fig. 3, the considerable increase in the contact potential difference at higher pressures is caused by a substantial increase, under these conditions, in the adsorption of water vapor.

In contrast to the adsorption of water vapor on a clean surface, adsorption of water vapor on the surface of germanium covered with an oxide film, as can be seen from Fig. 2, leads to irreversible changes in the surface properties. This follows from the fact that after desorption of the water vapor the contact potential difference does not return to the value that corresponded to the surface before adsorption of the water vapor, but becomes only 0.07 V greater than the electron work function of the clean germanium surface, which indicates a disturbance of the structure of the oxide film and a change in its protective properties.

Fig. 4. Change in contact potential difference under repeated action of oxygen, water vapor, and vacuum on the surface of germanium. *a*–oxygen; *b*–water; *v* –vacuum.
1—$P_{O2} = 12$ mm; 2—$\tau = 120$ min.; 3—$P_{O2} = 3$ mm; 4–combined action of water vapor ($P_{H2O} = 15$ mm) and oxygen $P_{O2} = 3$ mm; 5—$P_{O2} = 1.5$ mm,

$\tau = 1000$ min.

It is possible that the smaller change in the contact potential difference under the action of water vapor on an oxidized germanium surface, in comparison with its action on a clean surface, is connected with the fact that, along with the increase in the work function occurring during adsorption of water vapor, there simultaneously occurs a decrease in the work function as a result of disturbance of the structure of the oxide film.

In accordance with the data of Fig. 1, this disturbance of the structure leads to the acquisition by the germanium surface of the ability to absorb oxygen additionally. After additional adsorption of oxygen, the increase in the electron work function of germanium again rises to 0.4 V. The process of successive action of oxygen, water vapor, and vacuum on the surface properties of germanium was followed over 12 cycles. The results of these experiments are shown in Fig. 4. With the exception of the cases indicated in Fig. 4, oxygen was adsorbed on germanium at a pressure of about $1 \cdot 10^{-1}$ mm for 15–30 min., and water at a relative humidity of 100% for 10–30 min. The sample was kept in vacuum for about 30 min. From the data of Fig. 4, as well as Fig. 1, it is evident that in the presence of water vapor it is impossible to attain a stable state of the germanium surface: as follows from the data on the value of the work function after desorption of water vapor, each time the oxidized surface comes into contact with water vapor, the protective properties of the oxide film are destroyed.

The results obtained in studying the influence, at various pressures, of the water-vapor potential on the contact potential difference after repeated treatment of germanium with oxygen and water vapor (11 cycles) are shown in Figs. 2 and 3. It follows from these data that, under conditions in which a thick oxide film forms on the surface of germanium, adsorption of water vapor even at high relative humidity leads to an increase in the work function of only 0.03 V, which is substantially less than the change in the work function in

in the first cycle. However, when the water vapor is pumped off, the work function continues to change by a considerable amount, although this change is smaller than in the first cycle. Whereas the change in the work function upon pumping off water vapor in the first cycle was 0.4 V, in the 10th cycle this change is 0.16 V.

A study of the combined effect of oxygen and water vapor on the work function of an electron from germanium was previously carried out by Brattain and Bardeen (7). In their experiments with germanium treated with oxygen in a spark discharge, the electron work function of germanium decreases both when germanium is held in an oxygen atmosphere and in an atmosphere of oxygen saturated with water vapor. The results of our experiments, however, indicate that adsorption of oxygen, as well as adsorption of water vapor on a clean germanium surface and on a surface covered with a not very thick oxide film, leads to an increase in the electron work function. Apparently, the indicated discrepancy is due to the fact that treatment of germanium in a spark discharge in an oxygen atmosphere substantially changes the surface properties of germanium.

It also follows from the data we obtained that adsorption of water vapor leads to destruction of the protective oxide film on the germanium surface. This, in turn, leads to the formation of thick oxide layers on the surface. It is possible that the deterioration of the parameters of semiconductor devices that occurs when they come into contact with the atmosphere is associated with the formation of such thick oxide layers.

In order to prevent the formation of thick oxide layers on the germanium surface, it was expedient to hydrophobize the surface. For this purpose, after completion of rapid and slow adsorption, vapors of trichloromethylsilane were adsorbed on the germanium surface. Hydrolysis and polymerization of trichloromethylsilane were then carried out in the presence of water vapor at 150° for 1.5 hours.

After the germanium surface is coated with a hydrophobic film, the activating effect of water vapor on the process of oxygen adsorption by germanium practically disappears.

The stability of the hydrophobic surface with respect to oxygen adsorption is retained under repeated exposure to water vapor and oxygen. Preliminary experiments also showed a favorable effect of silane treatment on the properties of germanium semiconductor devices.

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Note: Figure translations are in progress. See original paper for figures.