EFFECT OF OXYGEN AND WATER VAPOR ON THE SURFACE PROPERTIES OF GERMANIUM AND SILICON

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It is known that the state of the surface of germanium and silicon strongly affects their electrical properties. Therefore, studies of the mechanism of adsorption and of the properties of layers adsorbed on these semiconductors are of special interest.

Several papers have been published on the process of chemisorption of oxygen on germanium and silicon and work has been done on the influence of chemisorbed oxygen layers on the electron work function and the surface recombination velocity of these semiconductors.

However, the studies of their electrical properties have not been accompanied by parallel studies of the process of oxygen chemisorption and, therefore, the special features of the adsorption process, found in later work [1-4], have not been allowed for in measurements of the contact potential difference and the surface recombination velocity.

Moreover, the papers mentioned above dealt with surfaces subjected to different cleaning methods, which may have had considerable effect on the state of the surface.

From several published papers, it is known that the properties of semiconducting germanium devices are altered on contact with water vapor. In this connection, it was interesting to investigate, by adsorption and electrical methods, the effect of water vapor on the surface properties of germanium and silicon, and on the interaction of oxygen with these two semiconductors.

The kinetics of chemisorption and the influence of adsorbed oxygen and water vapor on the surface properties of germanium and silicon were studied in our laboratory. In these studies adsorption methods were used as well as methods employing the contact potential difference and the surface recombination velocity.

Since the surface of germanium or silicon is always covered with an oxide layer, it is important to develop a method of cleaning these semiconductors for the purpose of studying adsorption of gases. In recent work especial attention has been paid to this point. Farnsworth and co-workers [5], Handler [6], and others [7] used the ion bombardment method to clean the surface of germanium and silicon.

Law and Garrett [8] are of the opinion that the surface of germanium treated by ion bombardment is not free of chemisorbed oxygen. There are also indications that after ion bombardment the germanium surface has a large number of defects.

The method of obtaining a clean germanium surface by the condensation of films [9] is also unreliable because during the evaporation of germanium the growing film may capture the gases evolved on heating. A more reliable variant of this method is the technique developed very recently by Bennett and Tompkins [3].

This technique involves melting germanium in hydrogen, outgassing it and depositing it on a cool wall of a chamber. Some workers obtained clean surfaces for adsorption measurement by fragmenting single crystals in ultravacuum.

According to published data, the surface of a silicon single crystal also can be cleaned by ion bombardment or heating in vacuum.

To clean a semiconductor surface it is desirable to use a method which is convenient both for adsorption measurements and for studies of electrical properties.

In the present work we removed oxide layers from the surface of germanium by multiple reduction in hydrogen, both for investigations of oxygen chemisorption and for electrical measurements.

After the reduction at 400-450°C, a prolonged outgassing was carried out in 10^{-7} mm Hg vacuum at the same temperature. The reduction and the outgassing were repeated 5-6 times. In some experiments, for complete removal of hydrogen from the reduced germanium surface, a prolonged outgassing in 10^{-9} mm Hg vacuum at 400-450°C was carried out.

According to Tamaru and Boudart [10] the complete desorption of hydrogen from germanium is obtained even at 280°C. From the results of our experiments it also follows that outgassing at 400°C is capable of removing completely the adsorbed hydrogen from the surface of germanium.

This cleaning method is convenient because it is applicable both to single crystals and to powders. This allows us to start with the same initial surface in studies of the electrical properties of the surface and in studies of the chemisorption of oxygen on germanium. Other methods of surface cleaning are convenient only either for adsorption measurements or for electrical measurements.

The adsorption of oxygen was investigated using germanium powder prepared by crushing a single crystal and cleaning it by the method described above. The surface area of the powder, determined by the Brunauer, Emmett, and Teller (BET) method, was 620 cm^2/g. Adsorption tests were carried out using 60.4 g of germanium powder. The use of a large surface area allowed us to investigate the process of oxygen chemisorption in greater detail.

The adsorption of oxygen on germanium was studied by the method we employed earlier in investigating the adsorption of oxygen on iron [11]. This method was used also by Rideal and Trapnell [12] to study the adsorption of oxygen on tungsten.

In our experiment the germanium powder was cooled to room temperature after reduction and outgassing and then the oxygen was adsorbed in small portions and the rate of absorption of each portion was measured. The initial pressure of each oxygen portion was about 0.07 mm Hg. The results obtained for the adsorption of oxygen on germanium are given in Fig. 1. From these results it is clear that there are two stages of oxygen sorption in germanium: the fast and the slow. The rate of adsorption in the fast stage is practically independent of the degree of surface coverage. The rapidly adsorbed oxygen represents the formation of a monatomic layer on the assumption that one atom of germanium on the surface adsorbs one atom of oxygen. The number of atoms per 1 cm^2 of the germanium powder surface was taken to be 7.7×10^{14}, in accordance with the data of Green, Kafalas, and Robinson [1].

The fast stage of oxygen adsorption could be used to determine the surface area of germanium. The surface area of 630 cm^2 obtained for 1 g of germanium powder is in good agreement with the results obtained by the BET method. Figure 2 shows the dependence of $\log(1/\tau)$, on the amount of absorbed oxygen, where τ is the absorption time of half a portion of oxygen. This figure indicates that the amounts of slowly and rapidly absorbed oxygen are equal.

It follows from our experiments that the kinetics of the slow chemisorption stage is logarithmic: $N \approx \log t$, where N is the amount of adsorbed oxygen and t is the time from the beginning of the adsorption process. This result is in agreement with the data of Green, Kafalas, and Robinson [1], according to whom the fast stage of oxygen chemisorption on a surface prepared by crushing a single crystal in ultravacuum, represents the formation of 0.9 monolayer. In his later work, Tompkins has shown that the amount of oxygen chemisorbed

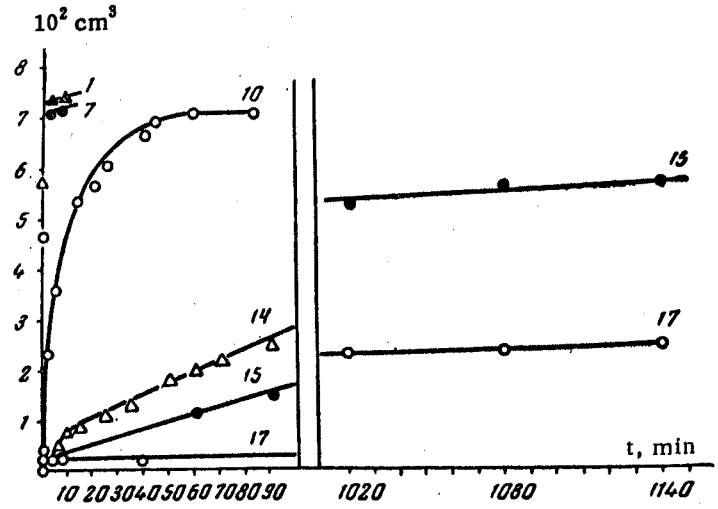

Fig. 1. Kinetics of the adsorption of separate portions of oxygen on germanium (the numbers by the curves give the order in which the oxygen portions were admitted).

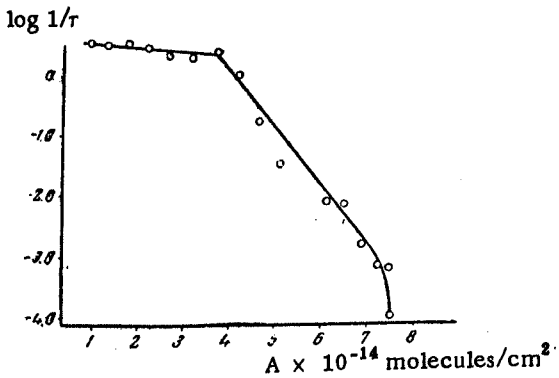

Fig. 2. Dependence of log $1/\tau$, where τ is the time necessary to absorb half a portion of oxygen, on the number of adsorbed oxygen molecules per 1 cm^2 of the surface.

in the fast stage increases from 0.3 to 1 monolayer as the temperature is raised from -78 to 0°C. And according to Brennan, Hayward, and Trapnell [4], the fast chemisorption stage represents a surface coverage of 0.83 monolayer; they found that the heat of adsorption in this range of surface coverage decreases from 123 to 100 kcal/mole. These data are obviously more accurate than those of Green et al. Thus both in our measurements and on surfaces cleaned by the other aforementioned methods, the fast chemisorption stage represents the formation of between 0.83 and 1 monatomic layer on the assumption that one surface atom of germanium adsorbs one atom of oxygen.

In the slow chemisorption stage, similar values are obtained for the amount of chemisorbed oxygen, representing about 1 monolayer for surfaces cleaned by our method and by the method of fragmentation of a single crystal in ultravacuum. Comparison of these various adsorption data is an additional verification of the cleanness of the surface used in our experiments.

The feasibility of the removal of oxide layers from the germanium surface by vacuum heating was investigated experimentally. For this purpose, the germanium powder, on which the fast and slow stages of adsorption were completed at room temperature, was heated at 400°C in vacuum for 2 hours. No desorption of oxygen was observed on heating. After cooling the powder, its ability to adsorb oxygen at room temperature was determined. It was found that after heating the germanium powder, the slow stage of adsorption occurred again.

Since the desorption of oxygen does not occur on outgassing, and there is practically no removal of oxygen from the surface in the form of GeO [13], we may assume that, on heating germanium on which oxygen was chemisorbed, the nature of the bonding between oxygen and the surface atoms of germanium is altered.

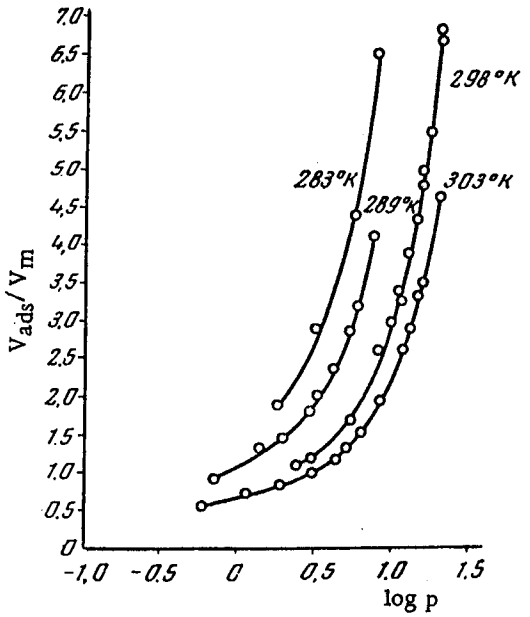

Fig. 3. Isotherm of the water vapor adsorption on the surface of germanium according to Law [14].

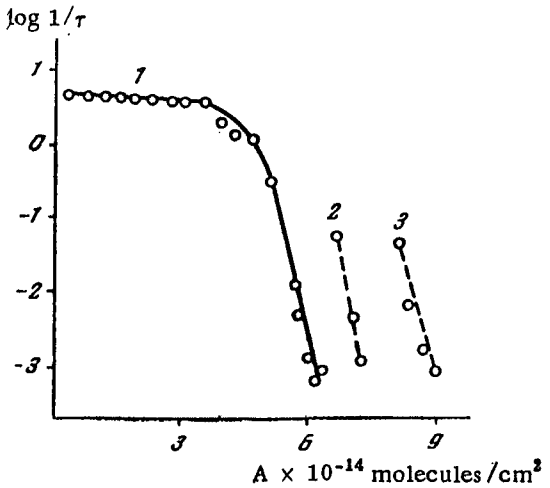

Fig. 4. Dependence of the oxygen adsorption rate on the surface coverage of germanium: 1) clean surface; 2) and 3) after adsorption of water vapor.

The adsorption of water vapor on the surface of germanium was investigated by Law [14] and Kawasaki et al. [15]. From their results it follows that, with the increase of the relative humidity to 80%, the amount of water vapor adsorbed on germanium increases to 3 molecular layers, and on further increasing the relative humidity to 100% the amount of adsorbed water increases to 7 molecular layers. The results of Law are given in Fig. 3.

The adsorption of water vapor on a cleaned surface of germanium is in practice reversible, as indicated by the measurements of the work function.

Preliminary tests on the adsorption of water vapor on an oxidized surface showed that in the presence of this vapor some irreversible changes of the surface properties of germanium take place. In connection with this, the process of the influence of water vapor on the interaction of germanium and oxygen was studied in detail. The adsorption tests were carried out as follows. On a clean surface of germanium freed from the oxide layer by reduction in hydrogen followed by outgassing (as described earlier), oxygen was adsorbed in small portions sufficient for completion of the fast and slow stages of adsorption. Then the germanium surface was placed in contact with water vapor. After some time the water vapor was frozen out or pumped out and again the kinetics of oxygen sorption was investigated.

The results of these tests are shown in Fig. 4, where the ordinate represents the reciprocal of the time necessary to adsorb half the oxygen in a given portion and the abscissa represents the total amount of oxygen adsorbed by the germanium surface. From these results it is clear that, if, after completion of the fast and slow adsorption processes represented by curve 1, the germanium is placed in contact with water vapor, then the rate of adsorption of O_2 increases after the removal of the water vapor [16]. As fresh portions of oxygen are adsorbed, the rate of adsorption decreases (Fig. 4, curve 2). However, a subsequent interaction of the germanium, covered anew by a passivating oxide layer, with water vapor again increases the rate of the germanium-oxygen interaction, but in this case the passivation of the surface may be reached by additional sorption of oxygen (Fig. 4, curve 3). Thus these tests show that on the adsorption of water vapor on a germanium surface coated with an oxide layer the passivating properties of the oxide layer are disturbed, which leads to formation of a thick oxygen layer on the surface if oxygen is present.

To find the effect of the various stages of oxygen chemisorption on the surface properties, we investigated the influence of adsorbed oxygen on the electron work function of germanium [17].

The contact potential difference was measured in the present work by the Kelvin vibrating capacitor method. The main disadvantage of this method is the adsorption of gases both on the test electrode as well as on the reference electrode, which makes it difficult to obtain correct results on the influence of adsorbed gases on the electron work function. In order to avoid this difficulty, we used a device developed earlier [18] in which the reference electrode is coated with glass. Since the adsorption of many gases on glass is considerably smaller than on metals, such a reference electrode is more stable. To avoid interference during measurements, the device was screened after heating at 400°C. The use of a glass-coated reference electrode made it possible to study the influence of adsorbed oxygen on the electron work function of germanium in a wide range of temperatures.

The electron work function of both n- and p-type germanium was 0.73-0.75 eV smaller than the work function of the reference electrode. The absence of a large difference in the electron work function (±0.02 eV) in spite of the considerable difference in the position of the Fermi level in n-type and p-type germanium is due to the high density of surface states [19]. The results obtained in the study of variation of the contact potential difference of a germanium surface during the adsorption of oxygen at various pressures, are given in Fig. 5. These results refer to an n-type germanium sample of ρ = 20 Ω·cm resistivity. Similar (within the limits of ±0.02 eV) results were obtained for other samples of n- and p-type germanium having various conductivities.

The influence of adsorbed oxygen on the work function was investigated in the pressure range 10^{-3}-10^{2} mm Hg. At each pressure the contact potential difference was measured over an interval of 20 min.

From the results obtained, it follows that the electron work function of n- and p-type germanium increases with the adsorption of oxygen. The dependence of the contact potential difference on the logarithm of oxygen pressure is linear over a wide range of pressures.

Comparison of the results on the work function with the results of the adsorption measurements indicated that the fast stage of oxygen adsorption on germanium changes the contact potential difference by 0.10-0.15 V. This fast stage represents the formation of a monatomic layer and ends after not more than 5 min even at a pressure of 10^{-3} mm Hg. On further increase of the oxygen pressure and the consequent increase of the amount of adsorbed oxygen, corresponding to the slow stage, the work function continued to rise and increased by 0.48 eV at 100 mm Hg. The results obtained do not agree with the data of Dillon [20], who found that the maximum increase of the electron work function by 0.2 eV occurred at the oxygen pressure of p = 10^{-6} mm Hg; for p_{O_2} = 10^{-5} mm Hg Dillon reported that the electron work function decreased by 0.06 eV and that further increase of the pressure did not affect the work function. According to Dillon and Farnsworth [21] the work function increases by 0.2 eV on the adsorption of oxygen. Dillon and Farnsworth believed that the contact potential was practically unaffected by pressure variation. However, these workers varied the pressure only from 1×10^{-7} to 2×10^{-5} mm Hg. Under these conditions the slow stage of adsorption is difficult to observe.

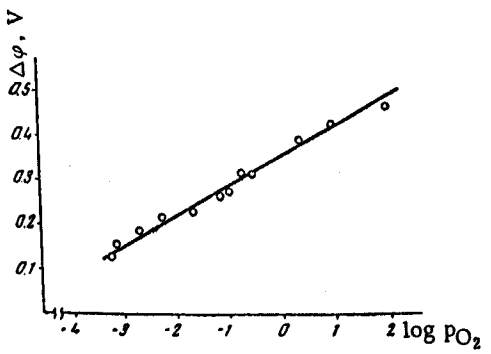

Fig. 5. Dependence of the contact potential difference between germanium and a reference electrode on the logarithm of oxygen pressure.

According to our results, several days are needed to complete the slow stage of oxygen chemisorption at 0.07 mm Hg. On increasing the pressure the rate of adsorption in the slow stage increases as $p^{0.52}$ [1, 3]. This may explain the variation of the contact potential difference as the pressure is increased. The change in the contact potential difference on completion of the fast stage is smaller than that produced in the slow stage. The results obtained lead us to conclude that during the chemisorption of the second layer of oxygen atoms on the germanium surface a new compound is formed. If it is assumed that the fast chemisorption stage corresponds to a reaction of the type

$$Ge + \frac{1}{2} O_2 \rightarrow GeO, \qquad (1)$$

then the slow adsorption stage is apparently related to

formation of a layer of the GeO_2 type by the reaction

$$GeO + \frac{1}{2} O_2 \rightarrow GeO_2. \quad (2)$$

From the results obtained by measuring the contact potential difference, it follows that at pressures up to 10 mm Hg oxygen is adsorbed irreversibly on the germanium surface. This is indicated by the fact that outgassing to 10^{-6} mm Hg after the adsorption of oxygen does not alter the contact potential difference. However, in those cases where the influence of adsorbed oxygen on the contact potential difference was studied at pressures of 100 mm Hg or more, there was also, apart from the irreversible adsorption, the reversible adsorption which has some effect on the contact potential difference. Thus, for example, after adsorption at p_{O_2} = 100 mm Hg outgassing reduced the electron work function by 0.04-0.05 eV, which may possibly have been due to physical adsorption of oxygen on the surface of the oxide.

In order to investigate the behavior of oxygen chemisorbed on germanium at various temperatures, a definite amount of oxygen was adsorbed on germanium at room temperature. The contact potential difference between germanium and the reference electrode was measured, and then germanium with chemisorbed oxygen was heated at various temperatures in gaseous media free of oxygen. After heating for 1 hour, the device in which germanium was placed was cooled to room temperature and the contact potential difference was measured again. The results obtained in this study of the effect of the temperature of heating of germanium with chemisorbed oxygen on the electron work function, are given in Fig. 6. From these results it follows that after heating at temperature of 100-400°C the electron work function of germanium with a layer of chemisorbed oxygen decreases (Fig. 6, curve 1), which may be explained either by penetration of oxygen into germanium or the evaporation of germanium oxide from the surface or the decomposition of the oxide. On heating to 200°C, the work function is reduced by 0.2 eV. After heating to 400°C, the work function is only 0.08 eV higher than that of a clean germanium surface.

These results are in agreement with those of Schlier and Farnsworth [5] who showed, by electron diffraction, that heating at 500°C in vacuum seemed to have cleaned a surface of germanium on which oxygen was chemisorbed. Our adsorption measurements showed that, after heating to 400°C the germanium on which the fast and slow adsorption stages were completed, oxygen was again adsorbed slowly at room temperature. Since the desorption of oxygen did not occur on heating, we may assume that heating produced the reaction

$$GeO_2 + Ge \rightarrow GeO. \quad (3)$$

The GeO formed on contact with oxygen at room temperature was again transformed into a compound of the GeO_2 type.

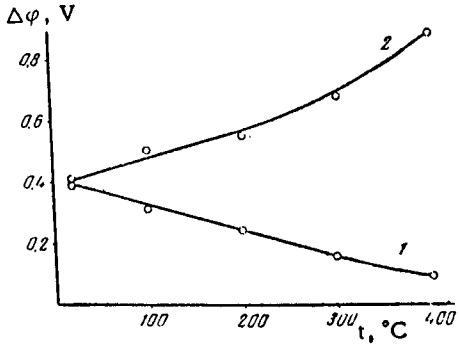

Fig. 6. Dependence of the contact potential of a germanium surface with chemisorbed oxygen on the heating temperature: 1) in 1×10^{-6} mm Hg vacuum; 2) in oxygen, p_{O_2} = 5 mm Hg.

Thus the heating of germanium to 400°C in vacuum did not remove the chemisorbed oxygen from the surface but altered the nature of the binding of the oxygen and germanium. On this basis the change in the contact potential difference can be explained by the reaction (3).

Different results were obtained on heating germanium in the presence of some oxygen in the gaseous phase (5 mm Hg). These results, shown by curve 2 in Fig. 6, indicate that as the heating temperature is increased (after preliminary heating at 400°C) the electron work function of germanium increases by 0.9 eV which suggests an increase of the thickness of the GeO_2 layer.

Thus it follows from our experiments that the electron work function of germanium continues to change even when there are several oxide layers on the surface. These results are in agreement with our earlier data on the adsorption of oxygen on iron and they may be explained by

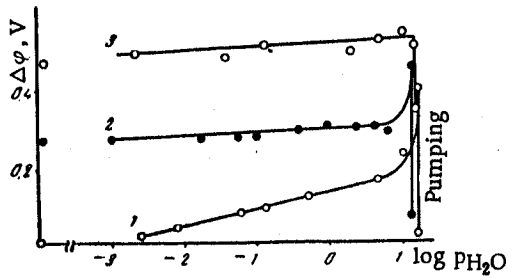

Fig. 7. Dependence of the contact potential difference on log P_{H_2O}: 1) clean surface; 2) germanium covered with an oxide layer; 3) after multiple treatment.

Mott's representation of the diffusion of metal atoms [22], in our case semiconductor atoms, to the surface of the oxide.

The conclusion, drawn above from the adsorption measurements, that the protective properties of oxide layers are disturbed in the presence of water vapor is very clearly confirmed by measurements of the contact potential difference [16].

The results on the influence of water vapor, adsorbed by a clean germanium surface, on the electron work function are given by curve 1 in Fig. 7. They show that as the water vapor pressure is increased the work function increases linearly with log (P_{H_2O}) in the pressure range from 1×10^{-3} to 7 mm Hg. In this range of pressures, the electron work function increases by 0.16 eV. However, on a further increase of the water vapor pressure (corresponding to an increase of the relative humidity from 50 to 100%) the electron work function increases more markedly (by 0.24 eV). Thus the total increase of the work function on the adsorption of water vapor amounts to 0.4 eV. This change of the electron work function is reversible. On pumping out the water vapor, the work function assumes a value close to that of a clean germanium surface.

The influence of water vapor on the electron work function of germanium covered with an oxide layer is different. The results of the relevant tests are given by curve 2 in Fig. 7. In these tests the oxygen was adsorbed on germanium for 15 hours at a pressure of 0.1 mm Hg. According to the earlier results the contact potential change under these conditions is due to the fast adsorption of oxygen on germanium (a change by 0.15 V) and partly due to the slow adsorption. As shown by curve 2 in Fig. 7 the increase of the work function due to chemisorbed oxygen is, under these conditions, 0.28 eV. The adsorption of water vapor on a germanium surface covered by an oxide layer changes the contact potential by only 0.02 V for a change of pressure from 1×10^{-3} to 7 mm Hg. On increasing the water vapor pressure from 7 to 15 mm Hg, the contact potential difference shifts by 0.16 V. Thus the adsorption of water vapor on the surface of germanium covered with an oxide layer produces a contact potential shift of about half that on a clean surface.

Curves 1 and 2 in Fig. 7 indicate that in the 7-15 mm Hg range of the water vapor pressure (log P_{H_2O} = 0.84-1.18) there is a strong variation of the contact potential difference with increasing pressure. The results obtained may be explained on the basis of the work of Law and of Kawasaki et al. [14, 15], from which it follows that with the increase of the relative humidity to 80% the amount of adsorbed water vapor represents the formation of three molecular layers and that with a further increase of the relative humidity from 80 to 100% the water layer thickness increases to seven molecular layers. Comparison of our results with those of the Japanese [15] is given in Fig. 8, which shows the dependence of $\Delta\varphi$ on the number of molecular layers of water adsorbed on germanium. It is seen in Fig. 8 that a considerable increase of the contact potential difference at higher pressures is due to a considerable increase of the adsorption of water vapor under these conditions.

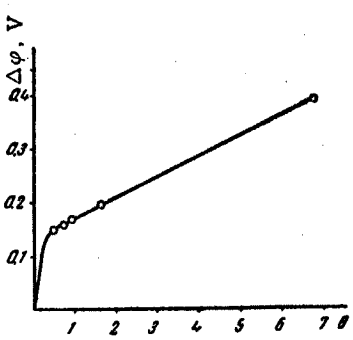

Fig. 8. Dependence of the contact potential difference on the number of adsorbed water molecules; θ is the number of molecular layers.

In contrast to the adsorption of water vapor on a clean surface, the adsorption of this vapor on a surface of germanium covered with an oxide layer produces irreversible changes of the surface properties (curve 2 in Fig. 7).

This follows from the fact that after the desorption of water vapor the contact potential difference does not return to the value before adsorption of the vapor, but remains 0.07 V higher than the

contact potential difference of a clean surface of germanium, which indicates that the structure of the oxide layer is disturbed and its protective properties are altered.

It is possible that the smaller change of the contact potential difference produced by the action of water vapor on an oxidized surface of germanium, compared with the effect on a clean surface, is related to the fact that in addition to the increase of the work function occurring on the adsorption of water vapor there is also the reduction of the work function due to the disturbance of the oxide layer structure.

According to the data in Fig. 4, this disturbance of the structure makes a germanium surface capable of additional sorption of oxygen. After additional adsorption of oxygen the value of the contact potential difference increases to 0.4 eV. The process of the consecutive action of oxygen, water vapor and vacuum on the surface properties of germanium was followed for 12 cycles. The outcome of these tests is shown in Fig. 9. Unless indicated otherwise in Fig. 9, oxygen was adsorbed on germanium at a pressure of the order of 0.1 mm Hg 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 results in Figs. 9 and 4, it is clear that in the presence of water vapor it is impossible to reach a stable state of the germanium surface; as indicated by the results on the value of the work function, after the desorption of water vapor, every time that the oxidized surface is placed in contact again with water vapor the protective properties of the oxide layer are destroyed.

The results obtained in a study of the effect of water vapor at various pressures on the contact potential difference after many treatments with oxygen and water vapor (11 cycles) are given by curve 3 of Fig. 7. Thus it follows that when a thick oxide layer is formed on a germanium surface the adsorption of water vapor even at a high relative humidity increases the work function by only 0.03 eV, which is considerably less than the change of the work function in the first cycle. However, on pumping the water vapor out, the work function continues to change by a considerable amount, although this change is smaller than in the first cycle: the work function changes by 0.4 eV on evacuation of the water vapor in the first cycle, but in the tenth cycle this change is 0.16 eV.

An investigation of the simultaneous action of oxygen and water vapor on the electron work function of germanium was carried out by Brattain and Bardeen [23]. In their experiments on germanium treated with oxygen in a spark discharge, the electron work function decreased both in an atmosphere of oxygen and in an atmosphere of oxygen saturated with water vapor. The results of our experiments indicate that the adsorption of oxygen and the adsorption of water vapor on a clean germanium surface and on a surface covered by a not too

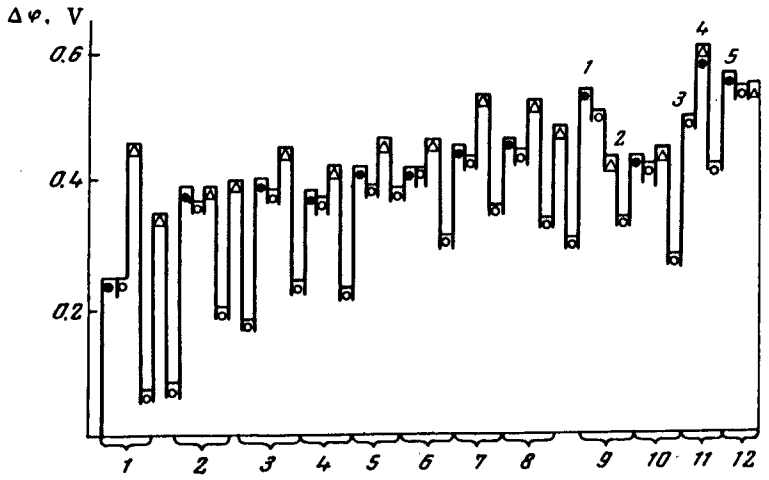

Fig. 9. Variation of the contact potential difference on repeated treatment of a germanium surface with oxygen, water vapor and vacuum: ● - oxygen; Δ - water; O - vacuum. 1) p_{O_2} = 12 mm Hg; 2) τ = 120 min; 3) p_{O_2} = 3 mm Hg; 4) simultaneous action of water vapor (15 mm Hg) and oxygen (3 mm Hg); 5) p_{O_2} = 1.5 mm Hg, τ = 1000 min.

thick oxide layer produces an increase of the electron work function. Obviously the difference between the two sets of results is related to the fact that treatment of germanium in a spark discharge in oxygen essentially alters the surface properties of germanium.

From our results, it follows that the adsorption of water vapor destroys the protective oxide layer 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 semiconducting devices in contact with the atmosphere is due to the formation of such layers.

It was interesting to find how various forms of chemisorbed oxygen affect the lifetime of minority carriers in germanium.

To investigate this problem the minority-carrier lifetime was studied on a clean germanium surface and on a surface which chemisorbed oxygen.

The influence of oxygen on the carrier lifetime, determined from the photoconductivity decay, was investigated by Madden and Farnsworth [24]. The germanium surface in their tests was subjected to ion bombardment followed by heating in vacuum; the oxygen pressure did not exceed 1.2×10^{-4} mm Hg. After such treatment the oxygen adsorbed at room temperature did not affect the carrier lifetime; but the oxygen adsorbed at 100°C reduced the minority-carrier lifetime on the germanium surface. One should note that in Madden and Farnsworth's work the tests were carried out at very low oxygen pressures, which should have reduced the chemisorption rate, particularly in the slow stage. To compare the results on the carrier lifetime with those on the chemisorption kinetics and the electron work function, it was necessary to carry out measurements of the lifetime under the same conditions as in our earlier tests.

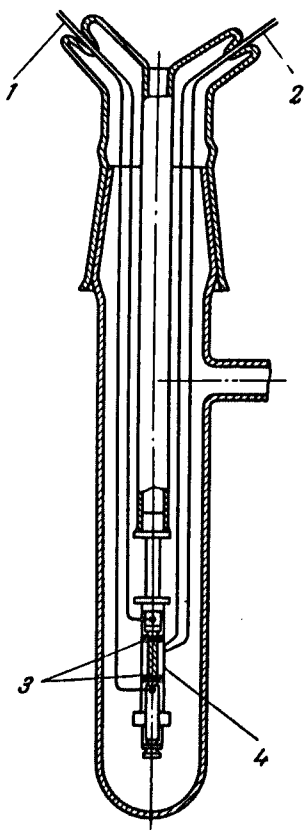

Fig. 10. Measuring device. 1) Lead to amplifier; 2) to pyrometer; 3) end contacts; 4) germanium sample.

The minority carrier lifetime was measured by the photogalvanomagnetic method [25, 26]. An electromagnet (B = 3200 G) provided the magnetic field. A 500 W projection lamp was used as the light source, and the light was modulated at 60 cps. To amplify the signal, a narrow-band amplifier with a gain of 6×10^4 was employed.

A rectangular germanium slab was placed in a special holder in a device shown in Fig. 10. The end contacts were used to pass direct current through the sample and to measure the photogalvanomagnetic effect and photoconductivity emf's. The temperature was measured with a thermocouple placed near the surface of germanium.

The tests were carried out on n-type germanium samples having ρ = 20 Ω·cm, L = 1.5 mm, and ρ = 48 Ω·cm, L = 3.2 mm.

The samples were ground and then etched in hydrogen peroxide.

The surface was cleaned by multiple reduction in hydrogen at 400°C followed by outgassing in 10^{-7} mm Hg at the same temperature. The carrier lifetime in germanium samples treated in this way was practically the same as on a freshly etched surface.

All measurements of the carrier lifetime were carried out at room temperature. A study was made of the effect, on the lifetime, of oxygen chemisorbed at various pressures in the temperature range 20-400°C. The results obtained at 20°C are given in Fig. 11, where the abscissa represents the logarithm of the oxygen pressure and the ordinate shows the effective lifetime. The lifetime was measured 10 min after the admission of gas.

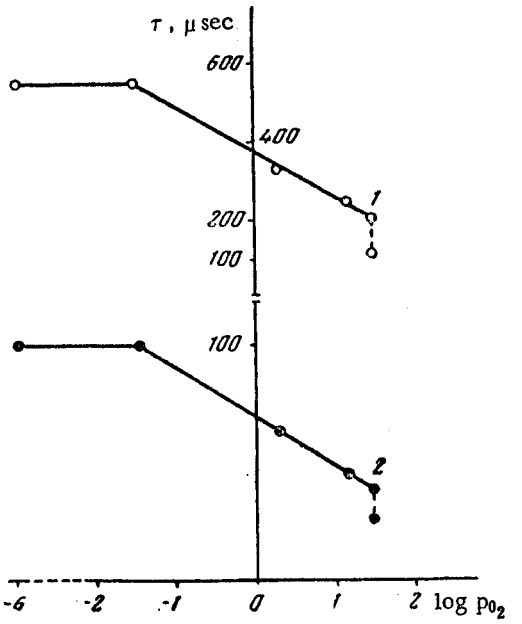

Fig. 11. Dependence of τ on log p_{O_2}: 1) n-type germanium, ρ = 48 Ω·cm; 2) n-type germanium, ρ = 20 Ω·cm.

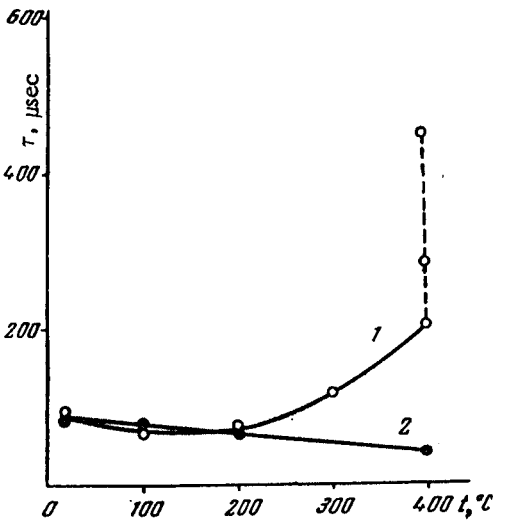

Fig. 12. Dependence of τ on the heating temperature: 1) in vacuum; 2) in oxygen.

From the results obtained it follows that the fast and slow stages of chemisorption affect in different ways the minority-carrier lifetime on the surface of germanium. From the data in Fig. 11, obtained after 5 min from the beginning of a test at a given pressure, it is clear that at oxygen pressures not exceeding 1 mm Hg the chemisorption of oxygen does not affect the lifetime. Under these conditions, mainly the fast stage of chemisorption takes place. At higher pressures corresponding to the slow adsorption, the lifetime decreases and this decrease depends on the duration of contact of germanium with oxygen. It is clear from Fig. 11 that after a long time in oxygen (17 hours), during which the slow adsorption increases, the reduction of the lifetime τ corresponds to the dashed parts of the curves.

A study was also made of the effect of 20-400°C heating in vacuum on germanium with chemisorbed oxygen. These experiments were carried out on n-type germanium samples having ρ = 48 Ω·cm, L = 3.2 mm. The results are given by curve 1 in Fig. 12. At each temperature germanium was heated for 1 hour. It is clear that with increase of the temperature of the heat treatment the lifetime increased. This increase was considerable at 400°C and the value of the lifetime after heating depended on the duration of heating. Heating in vacuum for 3 hours increased the lifetime to a value corresponding to a clean surface. An investigation was made also of the effect of oxygen adsorbed at high temperature on the lifetime of minority carriers. This showed that after the heating of germanium in the presence of gaseous oxygen (5 mm Hg), the lifetime decreased from 100 μsec at room temperature to 40 μsec after heating at 400°C (curve 2 in Fig. 12).

Comparison of the influence of the adsorbed oxygen on the work function and on the carrier lifetime allows us to conclude that the fast adsorption of oxygen, which does not affect the lifetime, produces a small change of the electron work function, while the slow chemisorption, during which a GeO_2-type layer is formed on the surface, considerably raises the work function and simultaneously strongly reduces the lifetime.

On vacuum heating of germanium with chemisorbed oxygen, i.e., on heating under conditions when the reaction (3) takes place, the work function decreases and the lifetime increases.

Heating of germanium in oxygen increases the work function and considerably reduces the lifetime. It has not yet been possible to draw a definite conclusion to what extent the results satisfy the theory of Garrett and Brattain [27], which established a relationship between the surface recombination velocity and the surface charge.

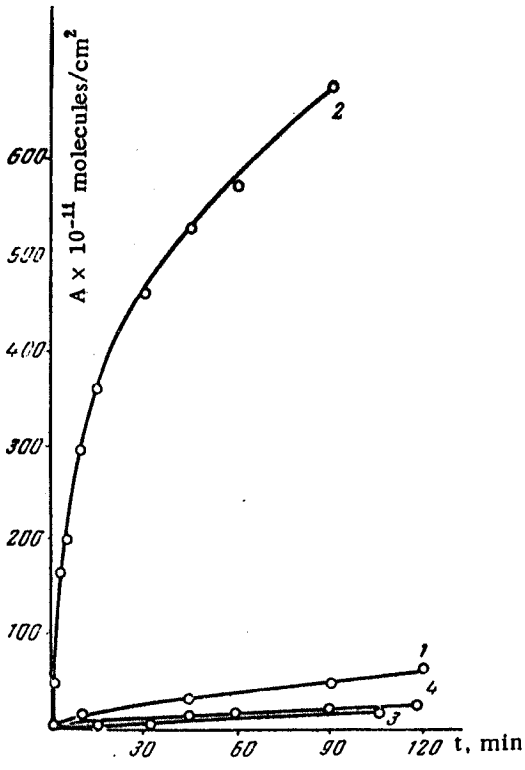

Fig. 13. Kinetics of oxygen adsorption on germanium. 1) Oxidized germanium surface; 2) after treatment with water vapor; 3) surface made hydrophobic; 4) hydrophobic surface after treatment with water vapor.

The results suggest that the change in the lifetime on adsorption of oxygen is related to a considerable degree to the formation of a GeO_2-type oxide on the germanium surface. The parts covered by this oxide are obviously surface recombination centers.

The mechanism of the influence of water vapor on the interaction of germanium with oxygen, described above, suggests that in order to prevent the formation of thick oxide layers on the surface of germanium under the influence of water vapor, it is desirable to make the surface hydrophobic. For this purpose trichlormethylsilane vapor was adsorbed on the surface after the fast and slow stages of oxygen adsorption were completed. Then trichlormethylsilane was hydrolyzed and polymerized at 150°C for 1.5 hours in the presence of water vapor.

The results on the kinetics of oxygen adsorption and the influence of water vapor on this adsorption are given in Fig. 13, where the ordinate represents the amount of adsorbed oxygen and the abscissa shows the time in minutes. Curve 1 represents the adsorption of oxygen on the oxidized germanium surface. Curve 2 shows how the kinetics of oxygen adsorption on the same germanium surface is affected by water vapor. Comparison of the results represented by curves 1 and 2 shows that the amount of oxygen chemisorbed on the germanium surface treated with water vapor exceeds by a factor of more than 130 the amount of oxygen chemisorbed during the same time (90 min) on the original surface. On the germanium surface which was made hydrophobic, the rate of adsorption after water-vapor treatment (curve 4) was practically the same as the rate of adsorption before water-vapor treatment (curve 3). Thus the activating effect of water vapor on the process of oxygen adsorption on germanium practically disappeared when the germanium surface was made hydrophobic. The stability of the hydrophobic surface with respect to oxygen adsorption was retained even after multiple treatments with water vapor and oxygen.

Experiments were also carried out to find the influence of adsorbed oxygen and water vapor on the surface properties of silicon.

To free the silicon surface from oxides we used heating in hydrogen at temperatures from 500 to 900°C followed by outgassing in 10^{-7} mm Hg vacuum at the same temperatures. The maximum duration of heat treatment was 100 hours.

According to Farnsworth the electrical properties of silicon surfaces treated in this way are close to properties of a surface subjected to ion bombardment.

A study of the interaction of oxygen with silicon showed that at room temperature there are two oxygen chemisorption stages (a fast one and a slow one), as in the case of germanium.

The results of one of the experiments, in which silicon powder was heated for 10 hours at 500°C, are given in Fig. 14, where the abscissa represents quantities proportional to the rate of oxygen adsorption (τ is the

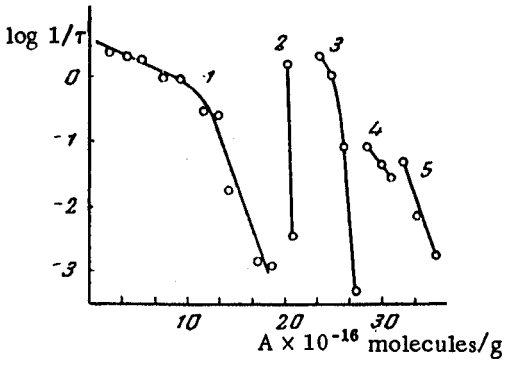

Fig. 14. Dependence of the oxygen adsorption rate on the surface coverage of germanium: 1) clean surface; 2) and 3) after adsorption of water vapor; 4) after heating at 200°C; 5) after heating at 500°C.

time for sorption for half a given portion of oxygen) and the ordinate shows the number of adso bed oxygen molecules per 1 g of silicon powder which had a specific surface area of 1200 cm^2/g.

The amount of rapidly adsorbed oxygen corresponded to 12×10^{16} molecules/g. After longer heating (100 hours) the amount of rapidly adsorbed oxygen increased to 20×10^{16} molecules/g. Comparison of the results obtained on adsorption of oxygen with the value of the surface area, determined by the BET method, indicates that under these conditions only half the silicon surface is cleaned. The rate of chemisorption in the fast stage depends little on the surface coverage. The rate of oxygen chemisorption at the end of the fast stage decreases by a factor of about 5-7 compared with that at the beginning of this stage. On the other hand, the rate of oxygen chemisorption at the end of the slow stage is 1000 or more times lower than at the beginning (curve 1 in Fig. 14).

At 0.1 mm Hg the fast stage ends in several minutes. Several days are required to complete the slow stage at the same pressure.

The results of adsorption measurements showed that the amount of chemisorbed oxygen depends on the conditions of preliminary treatment of silicon powder.

On increase of the temperature of vacuum heating in a quartz ampoule from 500 to 700°C (for the same duration of heating) the amount of oxygen chemisorbed on silicon increased. However, further increase of the heating temperature to 900°C poisoned the surface and the amount of chemisorbed oxygen was considerably reduced.

Heating of silicon, on which the fast and slow stages of oxygen chemisorption had been completed, for one hour at 200°C in vacuum produced (curve 4 in Fig. 14) a small additional chemisorption of oxygen. Repeated heating at a higher temperature (500°C) for 2 hours increased the adsorption of oxygen by an additional amount (curve 5 in Fig. 14).

The effect of water vapor on the oxidized surface of silicon at 20°C made silicon capable of sorbing further amounts of oxygen (curves 2 and 3 in Fig. 14).

An investigation of the influence of the adsorbed oxygen on the electron work function of silicon showed that this oxygen increases the work function: the increase corresponding to the fast adsorption stage amounts to 0.12-0.15 V, while the oxygen adsorbed in the slow stage increases the work function by a further 0.6 V. Thus the slow adsorption stage has a considerable influence on the surface charge on silicon. In the slow stage of oxygen adsorption on silicon, as in the case of germanium, there is a semilogarithmic dependence of the change in the work function on the oxygen pressure.

Heating of the oxidized silicon surface at 300 and 450°C for several hours in vacuum strongly reduced the work function (curve 1 in Fig. 15) making it approach the value for a clean surface. Such an effect can be explained, in full accord with the results given earlier for the adsorption measurements, by the appearance of silicon atoms on the oxidized surface of silicon either due to the penetration of oxygen into the lattice or the emergence of silicon atoms on the surface as the result of vacuum heating. A similar change of the structure of the oxide layer on the surface of silicon in the presence of water vapor can be used to explain the change in the electron work function and the additional adsorption of oxygen on silicon after the action of water vapor on an oxidized silicon surface.

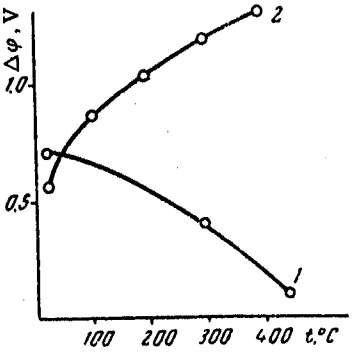

Fig. 15. Dependence of the contact potential of a germanium surface with chemisorbed oxygen on the heating temperature: 1) in 1×10^{-6} mm Hg; 2) in oxygen, 3 mm Hg.

The results obtained in measurement of the contact potential difference of silicon heated in oxygen at 3 mm Hg in the temperature range 100-400°C are given by curve 2 in Fig. 15.

After heating at 400°C the work function was 1.28 eV greater than the work function of a cleaned silicon surface. The increase of the work function on heating is obviously related, as in the case of germanium, to the formation of a thicker oxide layer on the silicon surface.

From the above results it follows that the fast and slow stages of the chemisorption affect in very different ways the surface properties of silicon and germanium. While the fast chemisorption affects little the work function and practically not at all the lifetime of carriers in germanium, the slow chemisorption affects the work function more strongly and produces a large change in the lifetime.

The adsorption and contact potential methods showed that in the presence of water vapor the protective properties of the oxide layer on the surface of germanium are disturbed and as a result of this a thick oxide layer is formed on the surface, which alters considerably the electrical properties of this semiconductor.

The disturbance of the protective oxide layer by water vapor may be due to the tendency of crystallization of the surface oxide or the penetration of semiconductor atoms to the surface of the oxide in the presence of water vapor.

The results obtained for germanium and silicon, together with the data for iron [29], suggest that it is more likely that water vapor promotes the penetration of semiconductor atoms to the oxide surface. This is supported by the agreement between the results on the effects of water vapor and of vacuum heating on an oxidized surface. Both these treatments produced the same changes in the surface properties, which are manifest as the reduction of the work function of the oxidized surface and as the ability to adsorb additional amounts of oxygen.

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