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The Effect of Oxygen Chemisorption on the Work Function and Electrical Conductivity of Titanium Dioxide

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As is known, the work function and the electrical conductivity of a semiconductor usually change under the influence of adsorption. This is attested by numerous experimental data. The origin of this effect is as follows ([1]). Chemisorption leads to the formation of a surface charge on the semiconductor surface, which in turn causes bending of the energy bands. In this case the position of the Fermi level relative to the energy bands in the near-surface layer of the crystal is shifted, which leads to a change in the conductivity in the near-surface layer. If the crystal dimensions are not very large, this may be reflected in the conductivity of the σ-sample as a whole.

As an example, Fig. 1 considers the case of adsorption of an acceptor gas, leading to negative charging of the surface, upward band bending, and an increase in ε_s. As is seen from the figure, an increase in ε_s causes an increase in the work function φ, since

$$\varphi = \varepsilon_s + \chi + \delta, \tag{1}$$

where

$$\varepsilon_s = \varepsilon_v + \Delta e. \tag{2}$$

Here ε_s and ε_v are the depth of the Fermi level below the conduction band at the surface plane ($x = 0$) and inside the crystal, far from the surface ($x = \infty$), respectively; Δe is the surface potential (surface potential relative to the bulk); χ is a constant depending on the nature of the semiconductor; δ is an additional potential drop caused by polarization of the adsorbed molecules (the electrical double layer creating a potential barrier at the semiconductor surface). Negative charging of the surface leads to an increase in Δe, while the quantities ε_v, χ, and δ in (1) and (2) remain unchanged.

Let us note that chemisorption of oxygen may be accompanied by penetration of oxygen atoms into the crystal lattice and their diffusion into the interior of

Figure 1

Figure 1: Figure 1

the crystal. It may also be accompanied by diffusion of positive impurity ions contained inside the crystal toward the surface and by their emergence onto the surface under the influence of the electric field created by the chemisorbed negative ions. In these cases the impurity content in the crystal changes (superstoichiometric oxygen appears; the amount of donor impurity decreases), which leads to an increase in ε_v and, consequently, to a decrease in σ and, as is seen from (1) and (2), to an increase in φ. These processes, governed by a diffusion mechanism, begin to play a significant role, however, only at sufficiently high temperatures.

The change in the work function during chemisorption may also occur, as is seen from (1), not only through a change in ε_s (i.e., surface charge), but also through a change in the dipole component δ. It should be noted that physical adsorption of dipolar and strongly polarizing molecules can also lead to a change in δ (under our conditions

physical adsorption is very small). Usually the component δ in expression (1) is neglected, although there are not sufficient grounds for this.

In order to study separately the charged and neutral forms of chemisorption (1), in the present work simultaneous investigations were carried out of changes in the work function and electrical conductivity occurring in the process of adsorption and desorption of oxygen on titanium dioxide, the nature of whose surface and adsorption properties had previously been studied in detail in our laboratory (2). Semiconducting crystalline titanium dioxide, both in the form of single crystals and in the form of highly dispersed powders, is of interest because it is widely used in various fields of radio electronics and catalytic chemistry.

Fig. 1. Energy diagram of a semiconductor with a negatively charged surface (FF is the Fermi level)

Measurements were carried out on the high-temperature modification of titanium dioxide—rutile. The sample was obtained by combustion of $TiCl_4$ in oxygen. The specific surface area of the sample, determined from low-temperature adsorption of nitrogen, was ~ 15 m^2/g. Thus, we were dealing with a very highly dispersed powder (the average particle size was $1 \cdot 10^{-4}$ cm). The sample was preliminarily subjected to repeated oxidation and vacuum pumping in the temperature interval 200–300° in order to stabilize the surface. Before the measurements, the sample was pumped for a long time in a vacuum of 10^{-5}–10^{-6} torr at a temperature of 300°. According to (2), the surface of the sample may be regarded as dehydrated to a considerable extent.

Fig. 2. Kinetics of changes in the work function φ (a) and electrical conductivity σ (b) during adsorption and desorption of oxygen on titanium dioxide

Figure 2

Figure 2: Figure 2

Measurements of the work function and electrical conductivity were carried out on the same initial sample. The work function was determined from measurements of the contact potential difference, for which the vibrating-capacitor method described in (3) was used. The gold reference electrode was passivated in oxygen (3). The electrical conductivity was studied on pressed pellets* by an alternating-current circuit (1 kHz). In the direct-current circuit the ohmicity of the contacts was checked. The kinetics of changes in φ and σ during adsorption and desorption of oxygen were measured simultaneously. All measurements were carried out at 20° and an oxygen pressure of 15 torr.

The results are shown in Fig. 2 (the work function of the gold reference electrode is denoted by φ_3). As can be seen from Fig. 2, admission of oxygen led, as was to be expected, to an increase in φ and to a decrease in σ. This unambiguously indicates that the adsorbate (oxygen) is an acceptor, and the adsorbent (titanium dioxide) is an *n*-semiconductor. Stationary values of φ and σ, indicating stabilization of the Fermi level, were established simultaneously. During desorption σ decreased, however, did not reach its initial value (Fig. 2a). In other words, the change in the work function ($\Delta\varphi$) caused by adsorption proved to consist of two parts: a reversible part ($\Delta\varphi_0$), which disappears upon desorption, and an irreversible part ($\Delta\varphi_\text{n}$), which remains after many hours of pumping. In contrast to φ, the change in σ caused by adsorption proved, at this temperature, to be completely irreversible: the established stationary value of σ remained unchanged during pumping (Fig. 2b).

The only possible mechanism, under our conditions, by which adsorption can affect electrical conductivity is the charging of the surface during chemisorption and the accompanying bending of the energy bands. As was noted above, a decrease in σ caused by a change in the concentration of donor impurities as a result of diffusion processes cannot make a substantial contribution at room temperature. Thus, from the results obtained (Fig. 2b) it follows, first, that a charged form of chemisorption is present and, second, that this form is practically completely irreversible under the conditions of our experiment.

From a comparison (Fig. 2b and a) it follows that, along with the irreversible (charged) form of chemisorption, there exists a certain reversible (and therefore uncharged) form, which does not affect the electrical conductivity but makes its own contribution to the work function through a change in the dipole component δ. Thus, if the charged form of chemisorption is responsible for the term ε_s in expression (1) (the irreversible part of the work function), then the neutral form,

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* The authors express their gratitude to N. S. Gorbunov for preparing the pellets on a vibrational stand.

to which the term ε_s is insensitive, is responsible for the term δ (the reversible part of the work function). As we see, under our conditions the change in the dipole component is not negligible in comparison with the total change in the work function.

These results are in qualitative agreement with the predictions of the electronic theory of chemisorption (^{1}). It was shown (^{4}) that, in the case of an ideal surface, electronic equilibrium and, at the same time, the relative content of the neutral and charged forms of chemisorption characteristic of adsorption equilibrium are disturbed during desorption. In this case only the neutral form is desorbed, whereas the charged form proves to be practically irreversible.*

It should be noted that, under the conditions of our experiment, the reversible part of the work function cannot be caused by physical adsorption. The dipole moment μ induced in an oxygen molecule during physical adsorption cannot provide the change in the height of the potential barrier that is observed experimentally (see Fig. 2a). A simple calculation shows that, if one starts from the effective electric-field strength above the rutile surface $E = 2.72 \cdot 10^5$ CGSE (^{5}) and from the polarizability of the oxygen molecule $a = 1.57 \cdot 10^{-24}$ cm^3, then for the idealized case of a monomolecular layer consisting of N parallel-oriented dipoles ($N = 10^{15}$ cm^{-2}), the value of $\Delta\varphi_0$ is found to be, in order of magnitude, equal to 1 eV. In our case the degree of coverage, determined from direct adsorption data, was about 0.5% of a monolayer, which gives for $\Delta\varphi_0$ a value of the order of ~ 0.01 eV. The experiment, however, gives $\Delta\varphi_0 = 0.4$ eV. We note that the dipole moment of quantum-mechanical origin arising in the neutral form of chemisorption may exceed the magnitude of the induced dipole moment in physical adsorption by a factor of 10–100 (^{6}), which gives the correct order of magnitude for $\Delta\varphi_0$.

The reversible part of the work function ($\Delta\varphi_0$ in Fig. 2a) also cannot be due to a change in φ_3, as might appear at first sight. Indeed, one can be confident that, under our conditions, the work function of the reference electrode φ_3 remains, during gas admission and during pumping,

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* The same result can, generally speaking, also be obtained in the case of a defective surface.

constant; even if this were not so, desorption of oxygen from gold could lead only to a decrease in φ_3, i.e., to an increase in CPD (where CPD $= \varphi - \varphi_3$), and not to a decrease, as is actually the case (see Fig. 2a).

In investigating the electrophysical characteristics of a semiconductor, chemisorbed particles manifest themselves only from the standpoint of their acceptor or donor role; the nature of the chemical bonds in such investigations remains hidden. In this connection, studies of infrared spectra and, in particular, EPR spectra are very promising; we are conducting these jointly with the Institute of Chemical Physics of the USSR Academy of Sciences.

The first results showed (⁷) that, upon adsorption of oxygen on a partially reduced specimen of titanium dioxide (anatase), two signals appear in the EPR spectrum, one of which disappears completely on evacuation, while the other is retained even upon heating to 200°. It is possible that this is also connected with the presence of reversible and irreversible forms of chemisorption.

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