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ELECTRONIC PROCESSES AT THE SURFACE OF A SEMICONDUCTOR DURING CHEMISORPTION*

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1. INTRODUCTION

THE surface of a semiconductor (the specific topic of this article) is of interest, both scientifically and practically, from two completely different standpoints.

First of all—from the standpoint of semiconductor physics and design of semiconductor devices. Unstable properties of the surface and uncontrollable changes in it under the influence of the environment are the reasons for unstable operation of semiconductor devices. Design of semiconductor devices, so to speak, hinges on the problem of the surface. To learn to control the properties of the surface is one of the primary problems in the semiconductor industry.

At the same time, the surface of a semiconductor is of interest from another standpoint as well. It is the arena in which catalytic processes take place. Indeed, most semiconductors are catalysts for chemical reactions. Even when a metal is being used as the catalyst, the process often actually occurs on the surface of a semiconductor, since most metals are most often covered by a semiconductor coating.

To learn to control the catalytic properties of the surface is one of the primary problems in the chemical industry. The importance of this problem will be evident if we recall that almost all modern chemical production is based on using catalytic processes. Almost all industrial chemistry is catalytic chemistry.

The surface of a semiconductor is the boundary between two phases: a solid and a gas (we are restricting ourselves to the case in which the semiconductor is in a gaseous medium). As with any boundary, it can be approached from two sides: from the solid side—this is how the semiconductor specialists approach the surface (they come out at the surface from inside the semiconductor); and from the gas side—this is how the physical chemists approach the surface, concerning themselves with problems of adsorption and catalysis.

However, actually the properties of the surface are determined both by what lies beneath and by what lies above: it is in equilibrium with both phases. The surface, being the boundary between the two phases, is at the same time the boundary between two sciences:

physics and chemistry. The surface of a semiconductor is the meeting place of physicists and chemists. Here, in Lomonosov's words, "physics and chemistry are so interwoven that neither can exist without the other."

2. CRITERIA OF CHEMISORPTION

a) Heat of adsorption. Contact of a semiconductor with a gas phase results first of all in adsorption of particles of the gas on the surface of the semiconductor. This alters the properties of the surface, and thereby alters some of the bulk properties of the semiconductor. The influence of the environment on the properties of the semiconductor is effected by adsorption.

The concept of adsorption is rather broad. Generally speaking, this term covers varied phenomena. First of all, we must distinguish physical and chemical adsorption.[1] The difference between them lies in the distinction between the forces holding the gas molecule to the surface. They can be forces of electrostatic origin (van der Waals forces, electrostatic polarization forces, and electric image forces). In this case we speak of physical adsorption. However, if the forces responsible for adsorption are of chemical nature (exchange forces), we are dealing with the so-called chemical adsorption (chemisorption). In this latter case, the adsorption is a chemical combination of the gas molecule with the solid.

The theoretical treatment of physical and chemical adsorption requires essentially different approaches. In physical adsorption, the adsorbed molecule and the crystal structure of the adsorbent can be treated as two independent systems. The action of the adsorbent on the substance being adsorbed can be treated in this case as a weak perturbation, and the problem can be solved by the methods of perturbation theory. However, in chemisorption the adsorbed molecule and the crystal structure form a single quantum-mechanical system, and must be treated as a whole.

As for the experimental criteria for physical and chemical adsorption, they are often indistinct and not always unambiguous. The heat effect is usually used as such a criterion: the molecule is bound to the surface more firmly in chemisorption than in physical adsorption. In physical adsorption the binding energy amounts to 0.01—0.1 eV, and in chemisorption it amounts to as much as several eV.

However, one cannot always determine the true

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*A lecture given at a session of the Belgian Chemical Society in Brussels, and also at a session of the Polish Chemical Society in Krakow.

binding energy from the energy liberated during adsorption. As an example: let us imagine that the molecule AB dissociates upon adsorption (as is often the case):

$$AB + L \rightarrow AL + BL.$$
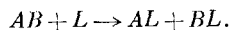
Here L denotes the crystal structure. The amount of energy liberated in this process is denoted by Q. Evidently,

$$Q = (q_A + q_B) - D_{AB},$$

where q_A and q_B are the binding energies of the atoms A and B to the crystal, and D_{AB} is the dissociation energy of the AB molecule. Here the terms q_A and q_B can be individually rather large, whereas the total heat effect Q proves to be small.

b) The activation energy. The existence of an activation energy is commonly taken as another criterion for chemisorption. This is why chemical adsorption is often called activated adsorption. One can determine the presence or absence of an activation energy from the nature of the kinetics. When there is no activation energy, adsorption takes place very quickly (and faster with decreasing temperature), so that equilibrium between the adsorbate and the gas phase is established practically instantaneously. However, when an activation energy exists, equilibrium is established slowly. Adsorption proceeds at a measurable rate, and faster at higher temperatures.

However, we note that the existence of an activation energy is not a necessary sign of chemical adsorption: cases are possible in which chemisorption occurs without activation. Indeed, activation is not required in every reaction nor at all times. Substitution reactions such as

$$AB + C \rightarrow AC + B,$$
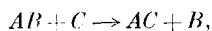
in which old bonds have to be broken to form new ones, are always characterized by a certain activation energy. However, combination reactions such as

$$A + B \rightarrow AB$$
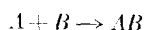
can often occur without any activation.

Thus, the experimentalist cannot always draw a sharp line between physical and chemical adsorption. Along with the extreme, evident cases, intermediate cases are found in which this line is rather blurred.

We shall limit our treatment to chemical adsorption alone. In this case, the chemisorbed particle forms a quantum-mechanical unity with the crystal. Thus it acquires the role of a surface defect, or in other words, of a surface "impurity". The chemisorbed particles can be considered as local defects in the strictly periodic structure of the surface. In this sense, they are not to be distinguished in principle from structural defects of "historical" origin. The distinction consists only in the fact that the chemisorbed particles can escape from the surface to enter the gas phase, and to arrive from the latter

at the surface, whereas "historical" defects can be considered to be firmly bound to the surface, and not to exchange with the gas phase. Chemisorption alters the entire system of surface states, and this is its specific role. In speaking of chemisorption on semiconductors, we shall discuss three aspects of the topic. First we shall take up the different forms of chemisorption. Our problem is to elucidate the properties and role of the different forms. Second, we shall discuss the properties of a semiconductor that are altered by chemisorption. We shall discuss the mechanism of this influence. The problem consists in altering the properties of the semiconductor by treating it with some particular gaseous medium. Finally and thirdly, we shall take up the problem of the chemisorptive capacity of the surface of a semiconductor. The problem is that of how many gas particles the surface can bind under given external conditions. What determines this capacity? What does it depend on? The final problem consists in learning how to control the chemisorptive capacity of a surface by treating the semiconductor with various agents.

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3. DIFFERENT FORMS OF CHEMISORPTION

a) The electrically-neutral and charged forms. The chemisorbed particles, in acquiring the role of a surface "impurity", thereby perform the function of localization centers for free electrons or holes in the crystal structure (they act as traps for electrons or holes). The existence of chemisorbed particles on the crystal surface is reflected in the energy spectrum: they correspond to local surface levels of acceptor or donor type (this depends on the nature of the particles).

Acceptor levels are populated by electrons to some degree; donor levels by holes. Thus, a certain fraction of the particles chemisorbed on the surface of the semiconductor is always in a charged state, and the rest are in the neutral state. Thus, chemisorption contributes to the charge on the surface. The existence of such a charge is characteristic of every real surface.

Chemisorption alters the absolute magnitude (and sometimes even the sign) of this surface charge. This is highly essential. Further on we shall discuss the consequences of this.

We shall denote by N^0 the number of neutral particles, and by N^- or N^+ the number of charged particles chemisorbed per unit of surface. When electronic equilibrium has been established, we have

$$N^{\mp} = N^0 \exp \left(\frac{v^{\mp} - \varepsilon_s^{\mp}}{kT} \right), \tag{1}$$

where the upper sign corresponds to acceptor particles, and the lower sign must be taken for donor particles. The meaning of the symbols used here is evident from Fig. 1a, which shows the energy spec-
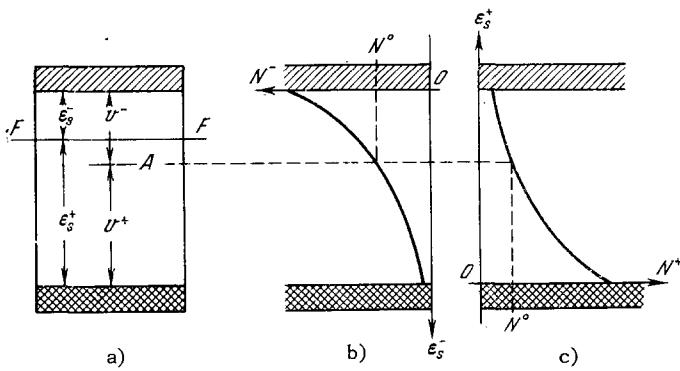
FIG. 1

trum of the surface: FF is the Fermi level, A is the local level of the chemisorbed particle (acceptor or donor), and ϵ_s^- and ϵ_s^+ denote the distances from the Fermi level to the bottom of the conduction band and to the top of the valence band, respectively.

We note that only the natural form of chemisorption takes part in exchange with the gas phase.[1] Thus, under conditions of adsorption equilibrium the amount of the neutral form of chemisorption on the surface (i.e., the quantity N^0) is unambiguously fixed by assigning the temperature T and the pressure P:

$$N^0 = N^0\,(T,\,P).$$

However, the amount of the charged form under constant external conditions (i.e., for given N^0) is determined, as we see from (1), by the position of the Fermi level. That is, it depends on the state of the system as a whole. By acting on the semiconductor with factors that shift the Fermi level (e.g., by adding an acceptor or donor impurity to the bulk substance), we can thereby regulate the amount of the charged form of chemisorption on the surface. The relations of N^- and N^+ to the position of the Fermi level at the surface of the crystal (i.e., to ϵ_s^- or ϵ_s^+) are shown schematically, according to (1), in Figs. 1b and 1c, respectively).

Thus, the Fermi level enters into the theory of chemisorption, and as we shall see below, it takes on a dominant role there.

b) "Weak" and "strong" forms. We note (and this is important) that the strength of the bond of the chemisorbed particle to the crystal structure of the adsorbent differs in the neutral and charged states. The localization of a free carrier (electron or hole) at the chemisorbed particle always strengthens the bond, as we can show. Thus, we must distinguish between "weak" and "strong" forms of chemisorption. If we denote the energy of the "weak" bond by q^0 and the energy of the "strong" bond by q^- and q^+ for acceptor and donor particles, respectively, then

$$q^\mp = q^0 + v^\mp. \tag{2}$$

Thus, when forming a "strong" bond, the chemisorbed particle binds a free electron or free hole on

or near itself. Here the latter are directly involved in the chemisorptive bond.

However, in "weak" chemisorption, the bond between the particle and the adsorbent crystal is formed without participation of free electrons or holes in the crystal. Rather, it involves deformation of the electronic orbitals, such that the electron cloud is drawn from the chemisorbed particle into the adsorbent crystal, or conversely, from an atom of the adsorbent acting as the adsorption center to the chemisorbed particle. One can show[2] that the bond becomes stronger as this deformation becomes greater.

An essential point is that a chemisorbed particle forming such a "weak" bond with the surface acquires a certain dipole moment while remaining electrically neutral. The moment is of purely quantum-mechanical origin in this case. As has been shown,[2] this moment can exceed the dipole moment induced in physical adsorption by several orders of magnitude.

c) The valence-saturated and radical forms. We note further (and this is also very important) that, among the different coexisting forms of chemisorption, we should distinguish the forms in which the chemisorbed particle sits on the surface as a radical or an ion-radical from the forms in which the same particle forms a valence-saturated entity with the surface. This is due to the role played by the free electrons and holes of the crystal: they perform the function of free valencies in the chemical transformations occurring on the surface of the crystal.

We shall explain this for a very simple example. Let us consider an NaCl crystal made of Na^+ and Cl^- ions having closed electron shells. The presence of a free electron in this crystal implies the presence of an "extra" electron attached to an Na^+ ion outside the closed shell and transforming the Na^+ ion into a neutral Na atom. This electron migrates through the crystal, moving from one Na^+ ion to a neighboring Na^+ ion, and can be treated as a migrating free (positive) valency. The presence of a hole implies that one electron has been removed from the closed shell of one of the Cl^- ions. This hole can also be treated as a free (now negative, rather than positive) valency.
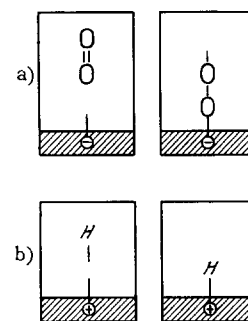

FIG. 2

Consequently, the "weak" form of chemisorption is the form that doesn't involve free valencies of the surface. "Strong" chemisorption implies that a free valency of the surface is involved in the bond, this valency being thereby localized and combining with a valency of the adsorbed particle. The involvement of a free valency of the surface in the chemisorptive bond has the result that a valence-saturated particle is transformed into an ion-radical, while conversely, a radical is converted into a valence-saturated, and moreover, electrically-charged entity. This is illustrated by Fig. 2, which shows as examples in terms of valence diagrams the "strong" chemisorption of an oxygen molecule and a hydrogen atom, respectively.

One might suppose that the radical and ion-radical forms show enhanced reactivity, whereas the valence-saturated forms can be considered reactively inert. This is essential in the theory of catalysis.

d) The reversible and irreversible forms. When we are dealing with semiconductors, adsorption equilibrium (i.e., equilibrium between the surface and the gas phase) often does not set in. As a rule, chemisorption on the surface of a semiconductor takes place very slowly, and the experimenter much more often deals with the kinetics of chemisorption than with an established adsorption equilibrium.

Furthermore, electronic equilibrium at the surface of the semiconductor may prove to be likewise disturbed. As we know, it is not maintained during adsorption or desorption if the probability of desorption of the chemisorbed particle is greater than the probability of transition from one charge state to another (from the neutral to the charged state, or vice versa). The author and Peshev have recently studied this case.[3] Here the establishment of electronic equilibrium does not keep up with the course of adsorption or desorption. Indeed, the arrival of new molecules from the gas phase at the surface during adsorption, or conversely, the loss of molecules from the surface into the gas phase during desorption continually disturbs the electronic equilibrium at the surface, while the electronic transitions tend to restore it. If this second process does not keep up with the first, electronic equilibrium continues to be disturbed.[3]

In this case, practically only the neutral form escapes from the surface during desorption. And only later, as the unbinding proceeds, do particles that are in the charged state leave the surface. Thus, hindered electronic transitions can retard the desorption process. If desorption of the charged form (i.e., desorption of particles occurring on the surface in the charged state) proceeds slowly enough, then we can consider the charged form to be practically irreversible. Here we must raise the temperature considerably in order to remove all of the adsorbate completely from the surface. Thus, under certain condi-
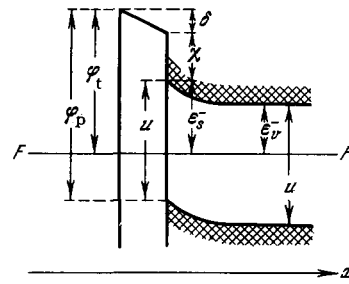

FIG. 3

tions the neutral and charged forms of chemisorption can play the roles of the reversible and the irreversible form, respectively.

Thus, we should distinguish the following forms of chemisorption: a) electrically-neutral and charged, b) "weak" and "strong", c) valence-saturated and radical, and d) reversible and irreversible.

4. EFFECTS CAUSED BY CHEMISORPTION

a) Interaction of the surface and the bulk material. We shall now discuss the effects caused by chemisorption. The existence of chemisorbed particles on a surface generally alters the charge on the surface. This has a number of consequences.

The surface charge (of whatever origin, adsorptive or historical) gives rise to bending of the energy bands in the layer of the semiconductor near the surface. These bent bands are shown in Fig. 3. The diagram refers to the case in which the surface has a negative charge. In turn, the bending of the bands leads directly to two effects: it alters the electrical conductivity of the specimen (by altering the electrical conductivity of the subsurface layer), and it alters the thermoelectric work function (denoted in Fig. 3 by φ_T; FF is the Fermi level). Both of these effects result from the shift in the Fermi level at the surface of the crystal caused by the subsurface bending of the bands: in Fig. 3 the depth of the Fermi level below the conduction band near the surface is denoted by ϵ_s^-, and within the crystal (far enough from the surface) by ϵ_V^-.

The quantities ϵ_s^- and ϵ_V^- are determined as follows. The value of ϵ_V^- is fixed by the condition that the interior of the crystal is neutral:

$$\rho(\epsilon_v^-) = 0, \tag{3a}$$

where ρ is the space charge density. The value of ϵ_s^- (for a given ϵ_V^-) is fixed by the condition that the system as a whole is neutral:

$$\sigma(\epsilon_s^-) + R(\epsilon_s^-, \epsilon_v^-) = 0. \tag{3b}$$

Here σ is the surface charge density, and R is the space charge in the subsurface layer of the crystal (per unit of surface).

Eq. (3b) is of physical interest: this equation relates ϵ_s^- to ϵ_v^-. That is, it relates the surface properties of the crystal to its bulk properties. The catalytic activity, the adsorptive capacity of the surface, and the relative amount of the different forms of chemisorption on the surface, which depend on ϵ_s^-, prove to be related to the electrical conductivity and to the impurity concentration within the crystal, which fix the value of ϵ_v^-.

We note that the relation between ϵ_s^- and ϵ_v^- (i.e., between the surface and bulk properties of the semiconductor) can cease to hold for a surface having a high density of surface states. Bardeen[5] pointed this out as early as 1947. In 1957, the author and Sh. M. Kogan[6] studied such a surface in detail. We called it a "quasi-isolated" surface. For such a surface, the quantities ϵ_s^- and ϵ_v^- are determined not by the two interrelated equations (3a) and (3b), but can be determined by two independent equations:

$$\rho(\epsilon_v^-) = 0, \tag{4a}$$

$$\sigma(\epsilon_s^-) = 0, \tag{4b}$$

Of these, the former depends only on the parameters characterizing the bulk of the semiconductor, and the latter only on the parameters characterizing the surface. Thus, the relation between ϵ_s^- and ϵ_v^- vanishes in this case.

b) <u>Change in the electrical conductivity</u>. The existence of chemisorbed particles on the surface alters ϵ_s^- while leaving ϵ_v^- constant. Adsorption of acceptor particles shifts the Fermi level at the surface of the crystal downward (increasing ϵ_s^-), while adsorption of donor particles shifts it upward (decreasing ϵ_s^-). In turn, an increase in ϵ_s^- diminishes the electron component of the conductivity and increases the hole component; a decrease in ϵ_s^- has the opposite effect. We see that the manner in which chemisorption influences the conductivity depends on the nature of the absorbed particles (acceptor or donor particles) and on the nature of the semiconductor (n or p-type semiconductor).

We note that if chemisorption decreases the conductivity when the fraction of the surface occupied is small, then when the occupancy is great enough, the same adsorbate on the same adsorbent can, conversely, increase the conductivity. This effect is due to inversion of the conduction in the subsurface layer of the semiconductor (i.e., n conduction is changed into p conduction, or vice versa). This occurs when the bending of the bands is sufficient, i.e., when enough of the surface is covered by the adsorbate.

Further, we note that in some cases an acceptor gas can act as though it were a donor by shifting the Fermi level at the surface of the crystal upward, rather than downward, as was shown above. In turn, a donor gas can play the role of an acceptor, by shifting the Fermi level downward upon adsorption, rather than upward. This can happen when acceptor

particles are being adsorbed on acceptor defects of the surface, or donor particles on donor defects. Here, as adsorption progresses, the energy spectrum of the surface loses the levels of the defects acting as adsorption centers. New levels appear in their place in the same quantity (the levels of the chemisorbed particles), and they have the same nature as the original levels, but they occupy different positions in the energy spectrum. One can easily show that this can lead to an anomalous shift in the Fermi level.

c) <u>Changes in the work function</u>. We shall now discuss changes in the thermoelectric and photoelectric work function produced by chemisorption. Let us return to Fig. 3. In this diagram φ_t and φ_p denote the thermoelectric and photoelectric work functions, respectively. By definition, φ_t and φ_p have the form

$$\varphi_t = \epsilon_s^- + \chi + \delta, \tag{5a}$$

$$\varphi_p = u + \chi + \delta. \tag{5b}$$

The meaning of the symbols introduced here is evident from the diagram. Here χ and u are parameters fixed by the nature of the crystal (u is the width of the forbidden region between the bands), and δ is the so-called "dipole component" of the work function, which is the potential differential due to the polarization of the adsorbed molecules.

According to (5a), the change in the thermoelectric work function $\Delta\varphi_t$ due to adsorption is made up of two components:

$$\Delta\varphi_t = \Delta\epsilon_s^- + \Delta\delta, \tag{6a}$$

whereas, according to (5b), the change in the photoelectric work function is

$$\Delta\varphi_p = \Delta\delta. \tag{6b}$$

We note that the term $\Delta\epsilon_s^-$ in (6a) originates from the charged form of chemisorption, and that form alone, whereas the neutral form of chemisorption contributes to the term $\Delta\delta$. Thus we see (cf. (6a) and (6b)) that parallel measurements of $\Delta\varphi_t$ and $\Delta\varphi_p$ permit us to distinguish the effect due to the charged form from the overall effect due to chemisorption.

One can also distinguish the neutral and charged forms of chemisorption by kinetic measurements. Let us suppose that we are making a parallel study of the changes in the thermoelectric work function φ_t and those in the electrical conductivity κ during adsorption and desorption. We shall assume that the charged form of chemisorption plays the role here of the irreversible form (as has been discussed above, cf. Sec. 3d).

The kinetic curves in this case must have the form shown in Fig. 4 (the diagram refers to the case of adsorption of an acceptor gas on an n-type semiconductor). At the instant t = 0, the gas is admitted into the adsorption vessel (adsorption begins). Adsorption equilibrium has been established by the instant t_0. At the instant t_0 the pressure is released (desorption
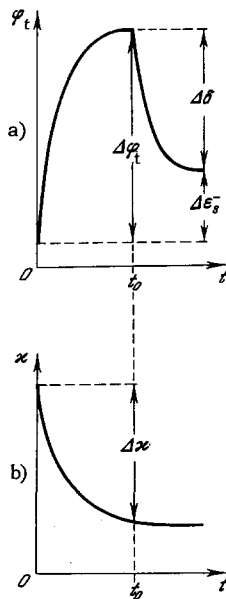
FIG. 4

begins). We should observe complete irreversibility in the electrical conductivity (Fig. 4b) and partial reversibility in the work function (Fig. 4a), since the change in the electrical conductivity is due to the charged form of chemisorption (which is not removed by outgassing), while the neutral form contributes to the change in the work function, and escapes from the surface upon outgassing.

In Fig. 4, the symbols $\Delta\kappa$ and $\Delta\varphi_t$ denote the changes in the electrical conductivity and the work function due to adsorption. Here, as we see from the diagram, $\Delta\varphi_t$ is made up of a reversible $(\Delta\delta)$ and an irreversible $(\Delta\epsilon_s^-)$ fraction. The reversible fraction is the dipole component of the work function, which is due to the neutral form of chemisorption.

Curves similar to those shown in Fig. 4 have been obtained recently by E. N. Figurovskaya and V. F. Kiselev.[7] They studied the kinetics of adsorption and desorption of oxygen on titanium dioxide. These experimental curves are shown in Fig. 5. Here φ_{Au} (Fig. 5a) is the symbol for the work function of the reference (gold) electrode.

d) Redistribution of impurities. We shall discuss another effect due to chemisorption. Let us imagine a semiconductor containing an impurity uniformly distributed throughout its volume, and as is always the case, partially ionized. Far from a surface, or at an electrically neutral surface, this uniform distribution of the impurity (concentration constant throughout the volume) is at the same time an equilibrium distribution. The existence of chemisorbed particles on the surface alters the surface charge. The electric field of this extra surface charge that arises during chemisorption penetrates to a certain depth within the crystal. In the subsurface layer of the semiconductor, where this field is not completely compensated by the

space charge arising in the semiconductor, the initial impurity distribution is disturbed.

In fact, particles of an ionized impurity of charge opposite in sign to the surface charge will be attracted to the surface. Impurity particles of the same sign as the surface charge will conversely be repelled from the surface into the interior of the crystal. The impurity concentration in the subsurface layer will prove to be raised or lowered. Of course, this effect may be noticeable only at not too low temperatures.

The problem of the equilibrium distribution of an impurity within a semiconductor in the presence of chemisorbed particles on its surface has been discussed by V. B. Kuznetsov and V. B. Sandomirskiĭ.[8] They showed that the redistribution of an impurity caused by chemisorption in turn alters the chemisorptive capacity of the surface. Thus, we have here a problem of self-consistency. This is still another example of the problem of surface-volume interaction.

We note that the redistribution of an impurity can be accompanied by emergence of the impurity at the surface, leading again to a change in its adsorptive and catalytic properties. Garner and many other authors [9,10] have repeatedly referred to this process, which accompanies the chemisorption process (at high enough temperatures).

5. THE CHEMISORPTIVE CAPACITY OF A SURFACE

a) Effect of impurities. We shall now return to the problem of the chemisorptive capacity of the surface of a semiconductor. We shall characterize the chemisorptive capacity for molecules of a given type by the number N of molecules of this type bound per unit of
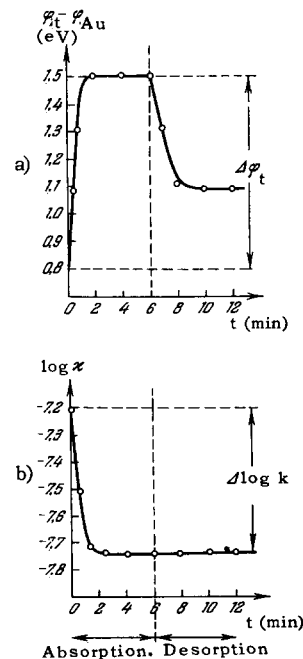

FIG. 5

surface under given external conditions (temperature and pressure). What determines the chemisorptive capacity of a semiconductor? What external influences on the semiconductor can alter it?

As has been mentioned, the amount N^0 of the neutral form of chemisorption on the surface is fixed by the pressure and temperature. The neutral form is supplemented by a certain proportion of the charged form (N^- or N^+), the amount of which is determined by the Fermi level (when electronic and adsorption equilibrium have been established). According to (1), we have:

$$N = N^0 + N^\mp = N^0 \left[1 + \exp \left(\frac{v^\mp - \varepsilon_s^\mp}{kT} \right) \right], \quad (7)$$

where

$$\varepsilon_s^\mp = \varepsilon_v^\mp \pm V_s. \quad (8)$$

Here V_S is the bending of the band at the surface (Fig. 6). In Eqs. (7) and (8), the upper or lower sign should be taken, depending on whether the local level (level A in Fig. 6) is an acceptor or donor level, respectively.

We see from (7) and (8) that the chemisorptive capacity of the surface is regulated by factors shifting the Fermi level ε_v^- within the crystal, and by factors changing the degree of bending V_S of the bands.

An example of a factor affecting the value of $\varepsilon_v^\mp$ is an impurity introduced within the crystal. Here the word "impurity" should not be taken too literally. It does not necessarily nor only mean chemically-foreign atoms introduced into the structure. In semiconductor physics, the concept of "impurity" has a broader meaning. We are bearing in mind any local defects in the strictly periodic crystal structure.

Acceptor levels shift the Fermi level downward (they increase ε_v^- or decrease ε_v^+). Foreign particles dissolved in the crystal play the roles of acceptors or donors, depending on their nature, or if their nature is fixed, depending on their manner of incorporation within the crystal. The very same foreign atom in the very same crystal can perform the function of an acceptor of a donor. Furthermore, the acceptor of

FIG. 6

donor role of the foreign atom is determined not only by its nature nor by its manner of incorporation into the structure, but also by the nature of the crystal into which it has been introduced.

Here are some examples. Lithium atoms introduced into the nickel oxide structure are donors if they are located in the interstices of the structure (form an interstitial solution). However, the same lithium atoms are acceptors if they are located at the atomic sites of the structure, replacing nickel atoms (substitution solution). Gallium atoms forming a substitution solution play the role of donors in the zinc oxide structure, whereas they play the role of acceptors in the germanium structure.

We note that the term V_S in (8) is itself a function of $\varepsilon_v^\mp$:

$$V_s = V_s(\varepsilon_v^\mp), \quad (9)$$

Here, as we can show,[6]

$$\frac{d\varepsilon_s^\mp}{d\varepsilon_v^\mp} \geqslant 0. \quad (10)$$

As long as the condition (10) holds, the electrical conductivity of the specimen (which is fixed by $\varepsilon_v^\mp$) and its adsorptive capacity (which is determined by $\varepsilon_s^\mp$) are correlated: on going from sample to sample, the adsorptive capacity for acceptor molecules varies symbatically with the electron conductivity, while the adsorptive capacity for donor molecules varies symbatically with the hole conductivity.

However, as one can show,[6] we note that condition (10) holds only as long as the factors shifting the Fermi level $\varepsilon_v^\mp$ within the crystal leave the system of surface levels unchanged. If this is not so, then condition (10) can be violated, and along with it the correlation between the electrical conductivity and the adsorptive capacity will fail.

b) The effect of an external electric field. While the introduction of an impurity is an example of a factor affecting the first term in the summation of (8) (the term $\varepsilon_v^\mp$), an example of a factor affecting the second component (the term V_S) is an external electric field. Indeed, one can control the degree of bending of the bands with an external field (the so-called "field effect"). Thus, we should expect changes in the chemisorptive capacity of a surface when an external electric field is applied normal to the adsorbing surface.

The author and V. B. Sandomirskiĭ[11] have calculated this effect for the case in which the semiconductor is put between the plates of a condenser, and thus maintains its electrical neutrality upon application of the electric field. V. G. Baru and I[12] have recently discussed this effect (we called it the "electroadsorption effect"), as applied to the field-effect technique with the semiconductor under study serving as one of the electrodes, and thus acquiring an induced charge when the field is applied.
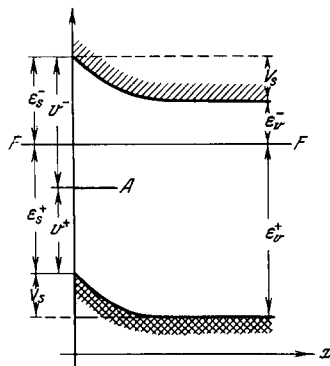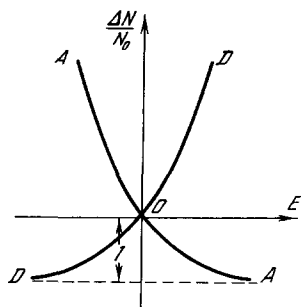
FIG. 7

Figure 7 shows the theoretical curves for this latter case. They give the relative change in the adsorptive capacity of the surface $\Delta N/N_0$ as a function of the applied field intensity E. Here N_0 is the adsorptive capacity in the absence of a field, and ΔN is the increment (positive or negative) caused by the field. In Fig. 7 the positive field direction is that for which the semiconductor is positively charged. The curve AA refers to the case where the adsorbed particles are acceptors, and the curve DD is for donor particles.

In connection with these theoretical results, we should mention the study by V. I. Lyashenko, O. A. Serba, and I. I. Stepko,[13] and the recent study by É. P. Mikheeva and N. P. Keĭer,[14] who detected an electroadsorption effect experimentally. The authors studied the adsorption of various gases on germanium. Application of a field brought about an additional adsorption or desorption.

c) The effect of illumination. We shall take up another factor that can alter the chemisorptive capacity of a surface. This factor is illumination. This is the so-called photoadsorption effect. As a rule, the photoadsorption effect is elicited by photoelectrically-active frequencies, i.e., frequencies causing an internal photoeffect (photoconduction) in the semiconductor. The photoadsorption effect is usually detected by the change in pressure in the adsorption vessel observed when the illumination is turned on or off. In some cases, turning on the illumination is accompanied by a pressure drop (photoadsorption); in other cases, conversely, by a pressure rise (photodesorption). Thus we must distinguish between positive and negative photoadsorption effects.

At present the photoadsorption effect has already been studied experimentally rather well. According to the experimental data, the absolute magnitude and sign of the effect depend on the choice of system, the conditions of experiment, and also on the prior history of the specimen being illuminated. The author and Sh. M. Kogan[15] have studied the mechanism of this effect, as have the author and I. V. Karpenko[16] subsequently. When the crystal is illuminated with photoelectrically-active light, free electrons and holes

are generated in it. These diffuse into the interior of the crystal and then recombine. Under steady-state conditions, a certain concentration gradient of non-equilibrium carriers is generated in the semiconductor, and the concentration of the electron and hole gases at the surface of the crystal is altered. Thus the amount of the charged form of chemisorption at the surface is altered.

The sign of the effect depends on the relation between the concentrations of the non-equilibrium electrons and non-equilibrium holes in the plane of the surface. The criteria determining the sign of the effect have been given in[16]. It was shown that the sign of the effect depends on the location of the Fermi level in the original specimen, other conditions remaining constant. When an acceptor gas is being adsorbed on an n-type semiconductor, an upward shift of the Fermi level in the forbidden region between the bands can reverse the sign of the effect: photoadsorption is replaced by photodesorption.

In connection with this theoretical result, it is of interest to cite some new experimental data of the well-known Japanese investigator Kwan.[17] Kwan has studied the photoadsorption effect in the adsorption of oxygen on zinc oxide. Zinc oxide specimens containing lithium as the impurity gave a positive effect, while samples containing an aluminum impurity gave a negative effect, other conditions being the same. These results agree with the theoretical predictions. Indeed, replacement of lithium by aluminum, i.e., of an acceptor impurity by a donor, is always accompanied by an upward shift of the Fermi level.

We note that there are a number of factors in the photoadsorption effect that haven't yet been interpreted theoretically. For example, according to the data of many investigators, photodesorption is always reversible, whereas photoadsorption is irreversible as a rule. This means that the additional amount adsorbed that appears on the surface after the illumination is turned on does not leave the surface after it is turned off, but is held there. This fact is as yet outside the framework of the theory.

We note also that the experimental data of different authors working in the field of the photoadsorption effect often disagree. Thus, e.g., a simultaneous study of photoconductivity and photosorption leads V. A. Kotel'nikov[18] to conclude that photosorption and photoconductivity vary symbatically (oxygen on cadmium sulfide). However, Yu. P. Solonitsyn[19] observes no such relation: according to his data, there is no correlation between photoconductivity and photosorptive capacity (oxygen on zinc oxide).

Further studies of the photoadsorption effect (experimental and theoretical) are of great interest, since the electronic nature of chemisorption is manifested here more clearly and in a less obscured fashion than in any other phenomenon.

6. CONCLUSION

In conclusion, we shall discuss the role that chemisorption plays in semiconductor physics and in the design of semiconductor devices. Every defect in the crystal structure (in particular, on its surface too) disturbing the strict periodicity of the structure and represented by a local level in the energy spectrum can play the role of a recombination center, i.e., the site of meeting and annihilation of a free electron and a free hole. The capture cross-sections of these centers cover a wide range.

Molecules chemisorbed on the surface of a semiconductor are no exception in this regard. Their existence on the surface alters the conditions of recombination: new recombination centers are created, or old ones are blocked. This interferes with stability of function of semiconductor devices, and renders them out of control.

In this regard we should emphasize that the energy spectrum of the surface (the position and concentration of surface local levels) can serve to characterize the surface only under strictly fixed conditions. The slightest changes in the history of the surface, as well as contact with the external medium (chemisorption), can completely distort the entire pattern. In other words, the energy spectrum of the surface of a semiconductor is a typical so-called "structure-sensitive" characteristic of the specimen.

We note that a molecule physically adsorbed can also play the role of a recombination center, just like a chemisorbed molecule. It is wrong to think (although this opinion is widespread) that a physically adsorbed molecule cannot be reflected in the spectrum of the crystal, inasmuch as the wave functions of a physically adsorbed molecule and those of the structure of the adsorbent do not overlap (according to the very definition of physical adsorption). If the molecule is polarized, it can create a potential well at the surface of the crystal by virtue of its electric field (although not a very deep one), and a free electron or hole can fall into this well. This implies the creation of a local level (as a rule, rather shallow), which will be an acceptor or donor level, respectively.

We should bear in mind the fact that physical adsorption and the "weak" form of chemisorption are experimentally hard to distinguish, although they are of completely different origin. The difference in the origin of these two forms of adsorption can be explained by the following analogy. The analog in the first case is an H atom and an H^+ ion separated by a great distance, with the H^+ ion polarizing the H atom by means of its field. In the second case, the same H atom and H^+ ion are close enough to form a single, quantum-mechanical system, the molecular ion H_2^+. In physical adsorption and "weak" chemisorption, the binding energies can be rather similar. However, the distinction can be manifested in the size of the dipole moment of the molecule: in physical adsorption it never attains the values that it can have in the "weak" form of chemisorption.

It should be evident from this article what role chemisorption plays in the properties of a semiconductor, and what role free electrons and holes in a semiconductor play in chemisorption phenomena. They are the leading actors here. In the final analysis, they govern the process.

In conclusion, we note again that the problem of the surface of a semiconductor is in no way to be treated as a two-dimensional problem. It is essentially a three-dimensional problem. The properties of the surface are determined by the properties of the two phases that it separates. The surface of a semiconductor is the meeting place of two different sciences (physics and chemistry) and of investigators of two different types. Its behavior can be deciphered only by their joint efforts.

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Translated by M. V. King