Reports of the Academy of Sciences of the USSR

F. F. VOL’ KENSHTEIN and V. B. SANDOMIRSKII

1958

SovietRxiv

Fig. 1. Scheme of energy levels in the absence of an external electric field (a) and in the presence of a field (b)

Figure 1: Fig. 1. Scheme of energy levels in the absence of an external electric field (a) and in the presence of a field (b)

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1958. Volume 118, No. 5

PHYSICAL CHEMISTRY

F. F. VOL' KENSHTEIN and V. B. SANDOMIRSKII

ON THE INFLUENCE OF AN EXTERNAL ELECTRIC FIELD ON THE ADSORPTION CAPACITY OF A SEMICONDUCTOR

(Presented by Academician N. N. Semenov, 25 VII 1957)

According to the electronic theory of chemisorption, an external electric field applied to a semiconductor, by changing the concentration of free charge carriers at the surface, should consequently affect its adsorption capacity ([1]). The possibility of the existence of such an effect was already indicated earlier by one of the authors ([2]).

If a semiconductor plate is placed in an external homogeneous electric field directed perpendicular to its surface, then the concentration of charge carriers at one surface will increase, while at the other it will decrease. The adsorption capacities of each of the surfaces change correspondingly. These changes in adsorption capacity do not compensate one another, and as a result the adsorption capacity of the semiconductor as a whole in an electric field will prove to be different from that in the absence of a field.

Fig. 1. Scheme of energy levels in the absence of an external electric field *(a)* and in the presence of a field *(b)*

We shall call an increase or decrease of the adsorption capacity in an electric field, respectively, electroadsorption and electrodesorption. The purpose of the present note is to estimate the experimental possibility of observing this effect, which depends on the magnitude of the change in pressure in the reactor upon application of the field and on the corresponding field values.

Let us consider the adsorbent in the form of a semiconductor plate of thickness $2L$ in the direction of the x-axis and of sufficiently large dimensions in the directions of the y- and z-axes. On the surface $x = \pm L$ (see Fig. 1), adsorption of molecules takes place, to which local surface levels E correspond. For definiteness we shall consider adsorption of acceptor molecules on an n-type semiconductor. The crystal is in an external homogeneous electric—

field of strength F, directed perpendicular to the surface.

To simplify the calculation, we shall make the following assumptions: a) the thickness of the crystal is much greater than the screening length l; hence it follows that at the center of the crystal the position of the Fermi level μ (relative to the energy bands) does not change when the field is applied; b) the distribution of electrons over all energy levels in the bulk of the crystal is Boltzmannian (both in the absence of an electric field and in an electric field); c) surface bands are absent; d) there exist only two types of bonding of adsorbed molecules with the surface: "weak" and "strong" acceptor bonding (3).

The schemes of the energy levels in the absence and in the presence of an electric field are given in Fig. 1. We shall denote the potential energy of an electron by $V(x, F)$. Let $V(0,0) = V(0,F) = 0$. Obviously, $V(-L, 0) = V(L, 0)$.

We shall assume that the crystal is in a reactor of constant volume v, filled with a gas at pressure p_0. After the field F is applied, the gas pressure becomes equal to p. The problem is to find the dependence of p/p_0 on F. From the condition of adsorption equilibrium at not too high pressures we have (4):

$$N_1(0) = N_2(0) = \frac{\gamma p_0}{1-\eta(0)}, \quad N_1(F) = \frac{\gamma p}{1-\eta_1(F)}, \quad N_2(F) = \frac{\gamma p}{1-\eta_2(F)}, \tag{1}$$

where $N_1(F)$ and $N_2(F)$ are the numbers of molecules adsorbed per unit of the left and right surfaces, respectively (see Fig. 1); $\eta_1(F)$ and $\eta_2(F)$ are the fractions of molecules in the state of strong bonding (5) on the corresponding surfaces (obviously, $\eta_1(0) = \eta_2(0) = \eta(0)$); γ is the adsorption coefficient in the Langmuir equation.

From the equation of state of an ideal gas and on the basis of (1) we find:

$$\frac{p_0}{p} = \frac{1}{2}\left\{\frac{1-\eta(0)}{1-\eta_1(F)} + \frac{1-\eta(0)}{1-\eta_2(F)}\right\}. \tag{2}$$

In deriving (2) it is assumed that $\gamma kT\dfrac{S}{v} \gg 1$, where S is the area of each of the two adsorbing surfaces, k is Boltzmann' s constant, and T is the absolute temperature. (We note that the opposite limiting case $\gamma kT\dfrac{S}{v} \ll 1$ leads to disappearance of the effect: $\dfrac{p}{p_0} = 1$.)

Writing Poisson' s equation for the volume of the semiconductor and integrating it once, we obtain, respectively, from the two boundary conditions at $x = \pm L$, two equations containing the unknowns $\eta_1(F)$, $\eta_2(F)$, and p. These two equations, together with equation (2), form the complete system of equations describing the effect under consideration. However, since it proves impossible in the general case to find the analytic form of the dependence of p/p_0 on F, we shall consider a special case.

Let us assume that

$$\eta(0) \ll 1. \tag{3}$$

This means that, in the absence of a field, the overwhelming majority of the adsorbed molecules are in the state of "weak" bonding with the surface. From (3) it follows that $\eta_2(F) < \eta(0) \ll 1$, and therefore, according to (2),

$$\frac{p_0}{p} = \frac{1}{2}\left[\frac{1}{1-\eta_1(F)} + 1\right]. \tag{4}$$

It is seen from (4) that $p_0/p \geq 1$, i.e., within the framework of the chosen model only electroadsorption can occur. We shall consider the case

$$\frac{p_0}{p} \gg 1, \tag{5}$$

corresponding to a large magnitude of the effect.

Using the explicit expression for $\eta_1(F)$ (5) and assumption (5), from (4) we obtain:

$$\frac{p}{p_0} = 2e^{\frac{E-\mu+V(-L,F)}{kT}}. \tag{6}$$

From one of the equations obtained as boundary conditions after integration of Poisson' s equation, it is easy to find, under the assumption

$$\frac{|V(-L,F)|}{kT} \gg 1 \tag{7}$$

the expression for $e^{-\frac{V(-L,F)}{kT}}$. Substituting this expression into (6), we obtain the desired dependence of the magnitude of the effect on F:

$$\frac{p}{p_0} = 2\left(\frac{\varepsilon kT}{ql}\right)^2 e^{\frac{E-\mu}{kT}}\frac{1}{F^2}. \tag{8}$$

Here ε is the dielectric constant of the semiconductor, and q is the absolute value of the electron charge.

It is not difficult to show that assumptions (3), (5), and (7), according to (8), have respectively the following meaning:

$$p_0 \gg \frac{\varepsilon kT}{4\pi q^2 \gamma l}\, e^{-\frac{E-\mu}{2kT}}; \tag{9}$$

$$F \gg \begin{cases} \dfrac{\varepsilon kT}{ql}\, e^{\frac{E-\mu}{2kT}} + 8\pi q\gamma p_0, & \text{for } E \geq \mu; \\ \dfrac{\varepsilon kT}{ql} + 8\pi q\gamma p_0, & \text{for } E \leq \mu. \end{cases} \tag{10}$$

Thus, under conditions (9) and (10), the effect is certainly large and is described by expression (8).

Let us carry out a numerical estimate. Put $\varepsilon = 10$, $T = 300$°K, $l = 10^{-4}$ cm, $\gamma = 10^{-2}$ mm Hg/Å^2, $E - \mu = 0.1$ eV. Then from (9) and (10) we have $p_0 \gg 1.5 \cdot 10^{-6}$ mm Hg, $F \gg 10^2$ V/cm. The calculation presented shows that, under certain conditions, the electroadsorption effect can apparently be detected experimentally.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
18 VII 1957

CITED LITERATURE

1. F. F. Volkenshtein, *Problems of Kinetics and Catalysis*, **8**, 79 (1955).
2. F. F. Volkenshtein, *Problems of Kinetics and Catalysis*, **8**, 201 (1955).
3. F. F. Volkenshtein, S. Z. Roginskii, *ZhFKh*, **29**, No. 3 (1955).
4. F. F. Volkenshtein, Sh. M. Kogan, *Izv. AN SSSR, OKhN*, **1957**, 916.
5. V. B. Sandomirskii, *Izv. AN SSSR, Ser. Fiz.*, **21**, 211 (1957).

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