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ON THE SHIFT OF ADSORPTION EQUILIBRIUM ON THE SURFACE OF A SEMICONDUCTOR UNDER THE INFLUENCE OF ILLUMINATION

(Presented by Academician M. M. Dubinin, 28 VII 1965)

A number of experimental works have been devoted to the photoadsorption effect on semiconductors (for a summary of experimental data see in ([1,2])). At present the existence of the effect is not in doubt. However, the effect has still not been experimentally investigated sufficiently comprehensively. A whole series of works ([2–5]) has also been devoted to an attempt to construct a theory of the effect on the basis of the electronic theory of chemisorption ([2]). The present note is one further link in this series.

We shall characterize the photoadsorption effect by the quantity

$$\Phi = \frac{N - N_0}{N_0} = \frac{\Delta N}{N_0},$$

which represents the relative change in the adsorption capacity of the surface caused by illumination. Here N_0 and N are the surface concentrations of chemisorbed particles of the given kind, respectively in the absence and in the presence of illumination (assuming that the other conditions remain unchanged). Depending on the sign of Φ, we are dealing with a positive or negative effect (respectively, with photoadsorption or photodesorption). The criterion for the sign of the effect was derived in ([3]). In the present note the absolute magnitude of the effect is calculated as a function of the parameters characterizing the state of the adsorbent and the conditions of the experiment. In doing so we remain within the framework of the same assumptions as in ([3]) (we restrict ourselves to the case of established adsorption equilibrium; we assume that absorption of a light quantum leads to transfer of an electron from the valence band to the conduction band).

Fig. 1

Figure 1: Fig. 1

As was shown (4,5):

$$\Phi = \eta_0^{\mp}(\mu^{\mp 1} - 1), \tag{1}$$

where

$$\eta_0^{\mp} = [1 + \exp(\varepsilon_s^{\mp} - v^{\mp})]^{-1} \tag{2}$$

is the relative content on the surface of the charged form of chemisorption in the absence of illumination, and

$$\mu = (1 + a + a \cdot \Delta p_s / p_{0s}) \big/ (1 + a + \Delta n_s / n_{0s}) \,. \tag{3}$$

Here the following notation has been adopted:

$$a = \exp(\varepsilon_s^- - v^+) = \exp(v^- - \varepsilon_s^+). \tag{4}$$

By n_{0s} and p_{0s} are denoted the concentrations, respectively, of free electrons and holes in the plane of the semiconductor surface in the absence of illumination; by Δn_s and Δp_s, the increments to the corresponding concentrations, caused by illumination. Note that

$$\begin{aligned} n_{0s} &= C_n \exp(-\varepsilon_s^-), \\ p_{0s} &= C_p \exp(-\varepsilon_s^+). \end{aligned}$$

The meaning of the remaining notation is clear from Fig. 1, which shows the energy diagram of a semiconductor: A is the surface local level of the chemisorbed particle, FF is the Fermi level in the unilluminated sample. In the formulas given above (and below), all energy quantities are expressed in units of kT; in all these formulas the upper signs should be taken if the chemisorbed particles are acceptors, and the lower signs if they are donors.

Fig. 1

The quantities $\Delta n_s / n_{0s}$ and $\Delta p_s / p_{0s}$ were calculated in (3). Taking $C_n = C_p = C$, we have:

$$\left.\begin{aligned} \Delta n_s / n_{0s} &= I \exp \varepsilon_v^-, \\ \Delta p_s / p_{0s} &= I \exp \varepsilon_v^+, \end{aligned}\right\} \tag{5}$$

where the notation adopted is

$$I = \sqrt{\tau/D}\,(I_0 + j_s)/C. \tag{6}$$

Here τ and D are the lifetime and diffusion coefficient for minority carriers; I_0 is the intensity of the incident light (number of quanta per 1 cm^2 per 1 s); j_s is the flux of electrons and holes in the surface plane, determined by the recombination conditions at the semiconductor surface, and, as is easy to show,

$$|j_s| \ll I_0. \tag{7}$$

Substituting (4) and (5) into (3), and then substituting (3) and (2) into (1), we obtain

$$\Phi = \frac{(xy-1)y}{(x+y)(1+ax+bx)}; \tag{8}$$

where the following notation has been adopted:

$$\left.\begin{aligned} x &= \exp(\varepsilon_v^{\mp} - v^{\mp}), \quad & a &= (1/I)\exp(-v^{\pm}), \\ y &= \exp(\mp V_{0s}), & b &= (1/I)\exp(-v^{\mp}). \end{aligned}\right\} \tag{9}$$

Function (8) gives us the desired dependence of the magnitude of the photoadsorption effect Φ on the parameters characterizing the nature of the adsorbent and adsorbate $(\tau, D, C, v^{\mp})$, the state of the system as a whole $(V_{0s}, \varepsilon_v^{\mp})$, and the experimental conditions (I_0, T).

Let us turn to the analysis of function (8). In Fig. 2, according to (8) and (9), the dependence of the magnitude of the photoadsorption effect Φ on the position of the Fermi level $\varepsilon_v^{\mp}$ inside the crystal in the initial (unilluminated) sample is shown schematically. In Fig. 2, as in Fig. 1, the conduction band is indicated by oblique hatching; the valence band by double hatching; A is the local level of the chemisorbed particle, and, for definiteness, it is assumed that

$$v^{\mp} < u$$

and, moreover:

$V_{0s} \geq 0 \ldots$ in the adsorption of acceptor particles
$V_{0s} \leq 0 \ldots$ in the adsorption of donor particles.

Fig. 2a refers to the case in which the adsorbed particles are acceptors; Fig. 2b, to the case in which they are donors. The two curves in Figs. 2a and b

Fig. 2

Figure 2: Fig. 2

correspond to two different values of V_{0s}, the curves being numbered in order of increasing V_{0s}.

We see that the magnitude and sign of the effect, for a specified nature of the adsorbent and adsorbate and for specified experimental conditions, are determined by the values of $\varepsilon_v^{\mp}$ and V_{0s}, i.e., by the initial state of the sample. Thus, by subjecting the sample to one treatment or another (introduction of impurities, disturbance of stoichiometry), we can control its photoadsorption properties to one degree or another.

Fig. 2

This is in agreement with the experimental results of Romero-Rossi and Stone, Barry, Kwan and Feit, Terenin and Solonitsyn, which have already been analyzed in ([3]). Also in agreement with the theory are new data of Kwan (oral communication), who studied the adsorption of oxygen on ZnO: ZnO samples containing Al as an additive gave a negative effect (photodesorption), whereas on samples containing Li, under the same conditions, a positive effect (photoadsorption) was observed. Replacement of aluminum (a donor) by lithium (an acceptor) is known to lead to a lowering of the Fermi level in the sample (to an increase of ε_v^-) and may cause, in Fig. 2a, a shift from point a to point b, which apparently did occur in Kwan' s experiments. Within the framework of the theory, the results of the recent work of Haber and Kowalska ([6]) can also be understood; dealing with the same system (oxygen on ZnO), they observed a change of the positive effect to a negative one upon oxidation of the sample. Indeed, if one assumes that in the experiments of Haber and Kowalska oxidation affected mainly the surface layer of the sample, then the authors were obviously dealing with an increase in the surface potential V_{0s}, i.e., with a transition from curve 1 to curve 2 in Fig. 2a (for example, from point c to point a: replacement of photoadsorption by photodesorption*).

Let us note that a factor making it possible to change over very wide limits the surface potential V_{0s} (while leaving the position of the Fermi level $\varepsilon_v^{\mp}$ inside the crystal unchanged) is an external electric field normal to the adsorbing surface. Therefore, the representation–

* Let us note that treatment of a sample may lead (and, as a rule, does lead in reality) to a simultaneous change (and in the same direction) of both parameters: both ε_v^- and V_{0s} (see ([3])).

it would be of interest to investigate the photoadsorption effect in combination with the field effect, i.e., to investigate the combined action on a semiconductor of illumination and an external field. When the field strength is changed, we move in Fig. 2 horizontally to the right or to the left, which may lead, as is seen from Fig. 2, to a change in the magnitude and sign of the photoadsorption effect. Thus, one may expect that in certain cases, on one and the same specimen and under the same external conditions, both photodesorption and photoadsorption may occur, depending on the magnitude and direction of the electric field applied to the specimen.

Let us further note that the quantity V_{0s}, to within a constant term, coincides with the electron work function, and thus Fig. 2 testifies to the existence of a correlation between the work function (when the dipole component of the work function is neglected) and the magnitude of the photoadsorption effect on a given surface. Experimental searches for this theoretically expected correlation would be of interest: specimens with differently treated surfaces, differing in work function, should differ, generally speaking, in the magnitude of the photoadsorption effect.

One may also expect a correlation of the magnitude of the photoadsorption effect with the initial (dark) conductivity of the specimen, since the latter is determined by the parameter $\varepsilon_v^{\mp}$. For acceptor particles the photoadsorption effect, as is seen from Fig. 2a, should be the greater in its algebraic magnitude the larger ε_v, i.e., the greater the hole and the smaller the electron components of the conductivity; in the case of donor particles this relation, as is seen from Fig. 2b, proves to be the opposite. It would be of interest to detect experimentally this theoretically expected correlation: a study of the photoadsorption effect on different specimens of one and the same semiconductor, differing in the magnitude of the dark conductivity.

Let us return once more to Fig. 2. The point O, at which the sign of the effect is inverted, is determined, as is seen from Fig. 2, by the condition

$$\varepsilon_v^{\mp} = v^{\mp} \pm V_{0s},$$

which is in agreement with the result obtained in (3). We see that, by subjecting the surface of a specimen to one or another treatment, we can shift the point O along the vertical axis in Fig. 2. The effect reaches its maximum value (in algebraic magnitude), as is seen from Fig. 2, at $\varepsilon_v^{\mp} = u$ (point M in Fig. 2). At the same time, as can be shown on the basis of (8):

$$\Phi = \Phi_M = y/b = I \exp\left(v^{\mp} \mp V_{0s}\right).$$

We see that, as a result of one or another treatment of the specimen, the point M may be shifted to the left or to the right horizontally in Fig. 2.

In conclusion, let us note that at present the experimental material on the photoadsorption effect is clearly insufficient for carrying out any detailed comparison of theory with experiment. It should be emphasized that in the photoadsorption effect, more vividly than in any other phenomenon and in the least veiled form, the electronic nature of chemisorption is manifested. Therefore, a comprehensive experimental study of the photoadsorption effect is important not only for constructing a theory of the effect, but also for verifying and substantiating the electronic theory of chemisorption in general.

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