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ELECTRICAL CONDUCTIVITY OF n-SEMICONDUCTORS DURING CHEMISORPTION OF ATOMS AND RADICALS

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Chemisorption of atoms and radicals, as our study has shown, entails a considerably larger change in conductivity than chemisorption of molecules. The change in conductivity during chemisorption of molecules in many cases apparently is determined by the degree of dissociation of the chemisorbed molecules into atoms or radicals ([1]).

In the present work the effect of chemisorption of atoms and radicals on the electrical conductivity of electron semiconductors of the ZnO, TiO_2 type was investigated in order, bypassing the stage associated with dissociation of chemisorbed molecules, according to the scheme:

$$M_2 \rightleftarrows (M_2)_s \rightleftarrows 2(M)_s \rightleftarrows 2(M)'_s + 2n_0, \tag{1}$$

where M_2 and M are molecules and atoms, the subscript s denotes the chemisorbed state, $(M)'$ are ions, and n_0 are free current carriers, to attempt to clarify, from the change in electrical conductivity of the adsorbent, the behavior of atoms and radicals on its surface, assuming that the change in conductivity in this case will be determined only by chemisorption of the atoms and radicals themselves and by transitions of current carriers between the adsorbent and the chemisorbed particles.

The experiments were carried out with atomic hydrogen, nitrogen, and methyl radicals. Atomic hydrogen and nitrogen were obtained in a stream of molecular hydrogen and nitrogen (pressure 0.7 mm Hg) by means of a silent discharge in a low-power discharge tube (length 40 cm, diameter 2 cm), and also under static conditions under the action on nitrogen and hydrogen of a powerful cobalt γ-source* at a gas pressure of 1 atm.

Methyl radicals were generated in a quartz cell by photolysis of acetone vapor. Samples of the semiconductor adsorbents ZnO and TiO_2 were prepared in the

Fig. 1

Figure 1: Fig. 1

form of thin (3-5 μ) films by applying (spraying) aqueous suspensions of the corresponding oxides onto quartz tube substrates (length 20-25 mm, diameter 5 mm).

The adsorption cells, with the films placed inside them, were thermostated. The temperature was monitored with thermocouples whose junctions were located on the films. The electrical conductivity of the films was recorded in direct current with the aid of a compensation bridge and a loop oscillograph.

In processing the experimental data, the change in electrical conductivity caused by chemisorption of atoms or radicals was associated with a change in the surface conductivity of films having a mosaic structure. The basis for this was provided by specially designed experiments on the alternating-current conductivity of ZnO at various frequencies in the presence of oxygen ([2]).

* A. Kh. Breger, V. A. Belynskii, V. L. Karpov, S. D. Prokudin—unpublished.

Before the experiments with atomic hydrogen and nitrogen, the film samples were heated for some time and kept under the experimental conditions (temperature, pressure).

In the presence of hydrogen or nitrogen, switching on the discharge or introducing a γ-source into the chamber led to an increase in conductivity* (Fig. 1A). In preliminary experiments on γ-irradiation of films in vacuum, no noticeable change in conductivity was found. After switching off the discharge or removing the source, at room temperature and below, the conductivity in the gases remained unchanged, and only after heating and subsequent cooling of the film to room temperature did its conductivity return to its former value. At temperatures above 200°, after removal of the sources of atoms, the conductivity decreased at a noticeable rate to its former value without preliminary heating. The higher the temperature, the faster the return.

The kinetics of the increase in conductivity (far from equilibrium) during chemisorption of atoms and of its decay in the absence of atoms in the bulk agrees well with equations of the form:

$$\Delta\sigma = k_1[\mathrm{H}]_s t, \qquad \frac{1}{\Delta\sigma} = k_2 t + \mathrm{const}, \tag{2}$$

where $\Delta\sigma = \sigma - \sigma_0$, σ_0 is the conductivity in the molecular gas, k_1 and k_2 are kinetic constants, and $[\mathrm{H}]_s$ is the stationary concentration of chemisorbed atoms.

Fig. 1. Changes in the conductivity of ZnO in H_2 and N_2 under γ-irradiation and in a discharge. γ-irradiation (A). For H_2: 1 –17°; 2 –200°; 3 –350°; for

N_2: 4 –17°. In a discharge (B). For H_2: 1 –without discharge, 2 –discharge intensity $i = 1$; 3 $-i = 2$; 4 $-i = 3$ (in arbitrary units); for N_2: 5 –without discharge, 6 –in a discharge, $i = 1$.

These equations are associated with the ionization reaction of chemisorbed atoms, proceeding as a first-order reaction, and with the recombination reaction. The activation energies for the increase in conductivity during chemisorption of H atoms and for its decay in the absence of H atoms in the bulk are, respectively, 2 and 36 kcal. Figure 1B shows the change in conductivity caused by chemisorption of atoms as a function of temperature at different discharge intensities in the tube.

The discharge intensity was monitored by the saturation current using two plate probes introduced into the discharge tube perpendicular to the direction of the field causing the discharge. The decrease in the slope of the rectilinear portions of the curves with increasing stationary concentration of chemisorbed H atoms is apparently connected with the known regularity (3) of a decrease in the activation energy of semiconductor conductivity with increasing impurity concentration. In the present case, however, this effect is associated with surface impurities–chemisorbed atoms (4)–and surface conductivity.

* No noticeable change in the temperature of the film due to recombination of atoms on its surface and absorption of γ-radiation occurred.

At temperatures above 300° the increase in conductivity for one and the same value of the stationary concentration of H atoms in the bulk decreases. Such a course of the change in conductivity with temperature is, in all probability, connected with the following competing reactions in the bulk and on the surface:

$$\begin{aligned}
&\text{(a)}\quad M_2 \rightsquigarrow 2M;\\
&\text{(b)}\quad M + M \xrightarrow{\text{third body}} M_2;\\
&\text{(c)}\quad M \to (M)_s;\\
&\text{(d)}\quad M + (M)_s \to M_2;\\
&\text{(e)}\quad (M)_s + (M)_s \to (M_2)_s \to M_2;\\
&\text{(f)}\quad (M)_s \rightleftarrows (M)_s^+ + e.
\end{aligned} \tag{3}$$

With increasing temperature the concentration of M atoms in the bulk practically does not change (the activation energies of reactions (a) and (b) are close to zero), whereas the stationary concentration of chemisorbed atoms $(M)_s$ decreases appreciably, since reactions (e) and (d) have significant activation energies, due to migration of atoms and rupture of bonds with the surface. At the same time, an increase in temperature shifts equilibrium (f) toward an increase in the concentration of electrons in the conduction band.

Fig. 2. Change in the conductivity of ZnO when alcohol vapor is admitted into the reaction vessel.

Fig. 2

Figure 2: Fig. 2

1—390°; 2—370°; 3—350°; 4—320°; 5—admission of hydrogen at 390°

In addition to the experiments mentioned, it was of interest to investigate the change in the conductivity of sorbents under the influence of H atoms formed on the surface as a result of heterogeneous chemical reactions, for example, the reaction of alcohol dehydrogenation. For this purpose, vapors of isopropyl alcohol were admitted into the small volume in which the ZnO film was located (pressure in the volume $5 \cdot 10^{-2}$ mm Hg). The change in conductivity was recorded with a loop oscillograph (see Fig. 2). It had been verified beforehand that the decomposition products of the alcohol (acetone and hydrogen), in the concentrations obtained upon complete decomposition of the alcohol, changed the conductivity (in comparison with H atoms) only very slightly (in the case of H_2—see Fig. 2). When the alcohol pressure was increased by a factor of 5-10, the "conductivity spike" effect decreased, which is apparently connected with an increase in the rate of recombination of chemisorbed H atoms (proportional to the square of the concentration) and chemisorption of alcohol vapors (which lower the conductivity). The activation energy of the increase in conductivity is 46 kcal (a value close to the activation energy for dehydrogenation of isopropyl alcohol on ZnO ([6]))*; that of the decrease in conductivity is 37 kcal (a value close to that obtained for the activation energy of the decrease in conductivity in the discharge experiments).

Figure 3 gives the results of experiments on the chemisorption of methyl radicals. Chemisorption of methyl radicals decreases the conductivity. This result is obtained both in the case of photolysis of acetone and in the case of cracking of dimethyl ether. At room temperature, switching off the light does not lead to a reverse change in conductivity (heating of the film is necessary). The decrease and increase in the conductivity of an n-semiconductor film with time are satisfactorily consistent with equations of the form.

$$\begin{gathered} \lg\sigma = -k_1'[\mathrm{CH}_3]_s t + \mathrm{const}, \\ \frac{1}{\Delta\sigma} = k_2 t + \mathrm{const}, \end{gathered} \tag{4}$$

where k_1' and k_2 are kinetic constants depending on temperature; $[\mathrm{CH}_3]_s$ is the stationary concentration of chemisorbed radicals; $\Delta\sigma = \sigma_0 - \sigma$; σ_0 is the conductivity of the film in the absence of radicals, and the subscript s denotes the chemisorbed state.

* This was to be expected, since the activation energy of the reaction $H \rightarrow (H)_s^+ e$ is small ($\sim$ 2 kcal), and therefore the limiting stage in the increase of ZnO conductivity in this process is the decomposition of alcohol molecules.

Fig. 3

Figure 3: Fig. 3

These equations can be associated with the reactions $(CH_3)_s + e \rightarrow (CH_3)_s^-$ and $2(CH_3)_s^- \rightarrow C_2H_6 + 2e$, if one assumes that in the impurity-conduction region $(CH_3)_s^- = [e]_0 - [e] = \Delta\sigma$.

As the temperature is increased, the quantities $k_1 = k_1' \cdot [CH_3]_s$ first increase (Fig. 3A, section of curve $1a$), and then decrease (section $1b$); the values of the stationary conductivity increase with temperature at first slowly and then rapidly (Fig. 3B). Such a change in k_1 and in the stationary conductivity with temperature is connected, as in the case of chemisorption of H radicals (see scheme (3)), with the presence in the bulk and on the surface of several competing reactions with different activation energies, leading, as the temperature increases, to a decrease in the stationary concentration of chemisorbed radicals $(CH_3)_s$, and, consequently, to a decrease in the values of k_1 and an increase in the stationary conductivity (see Fig. 3B, curve 2), owing to the shift of the equilibrium $(CH_3)_s + e \rightleftarrows (CH_3)_s^-$ toward an increase in the concentration of electrons in the conduction band.

Fig. 3. Change in the conductivity of ZnO upon chemisorption of methyl radicals. A —dependence of k_1 $(1a, b)$ and k_2 (2) on $1/T$; B —dependence of the stationary conductivity of ZnO on temperature: 1 —in acetone vapor; 2 —in acetone vapor in the presence of CH_3 radicals

The activation energies of the surface elementary reactions calculated from the results of conductivity measurements are as follows: (I) $CH_3 \rightarrow (CH_3)_s \rightleftarrows^{+e} (CH_3)_s^-$; (II) $2(CH_3)_s^- \rightarrow (C_2H_6)_s + 2e$ have the following values: 5 kcal, 27 kcal.

The data obtained in the present work make it possible to draw the following conclusions:

1. The processes of chemisorption of atoms and radicals with their subsequent ionization (formation, for example, of $(H)_s^+$, $(N)_s^+$, $(CH_3)_s^+$) proceed with considerably lower activation energies (from 2 to 5 kcal) than the corresponding processes for molecules (for H_2, 30 kcal (^{1}); in the case of chemisorption of C_2H_6 the change in conductivity is small; in the case of N_2 it is practically absent).
2. Monitoring and measuring the conductivity of semiconductors in the course of chemical reactions proceeding by a radical mechanism may serve as a convenient method for detecting atoms and radicals, measuring their concentration, and studying the elementary stages of surface processes in chemisorption and catalysis.

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