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Abstract

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Adsorption of Alkyl Radicals on Oxide Semiconductors

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In paper (1) it was shown that adsorption of atoms and radicals on the surface of semiconducting oxide films of the ZnO type (an n-semiconductor) is accompanied by a considerable change in their electrical conductivity. On the basis of these data, in the present work an investigation was undertaken of the quantitative relation between the stationary concentration of radicals and the electrical conductivity of ZnO films placed at various distances from the source of radicals in atmospheres of different gases. Alkyl radicals (methyl, ethyl), when chemisorbed on ZnO, decrease its electrical conductivity (the electron affinity energy of the radical CH_3 is 25 kcal/mole). This means that active particles of this kind form electron traps (acceptor impurities) on the surface of the semiconductor.

The indicated phenomenon for a self-activated semiconductor may be connected with the following processes:

$$\begin{aligned} &\text{a)} \quad \mathrm{Zn} \rightleftarrows \mathrm{Zn}^+ + e \\ &\text{b)} \quad \mathrm{R} + e \rightleftarrows \mathrm{R}^- \\ &\text{c)} \quad \mathrm{R}^- + \mathrm{Zn}^+ \rightleftarrows (\mathrm{R}^- \ldots \mathrm{Zn}^+) \\ &\text{d)} \quad \mathrm{R} + \mathrm{Zn} \rightleftarrows (\mathrm{R}^- \ldots \mathrm{Zn}^+) \end{aligned} \tag{1}$$

where R is a radical, e is an electron of the conduction band, Zn^+ is an ionized impurity zinc atom, and $(\mathrm{R}^- \ldots \mathrm{Zn}^+)$ is a surface compound of a radical with an impurity atom (the plus and minus signs do not at all imply an ionic character of the bond, but indicate only the preferential distribution of charges).

Assuming that the rate of the forward reaction (1) is proportional to the concentration of radicals in the gas phase n, to the degree of free surface $1-\theta$, and to the concentration of impurity zinc atoms, while the rate of the reverse reaction is proportional to the concentration of chemisorbed radicals $[(\mathrm{Zn}^+ \ldots \mathrm{R}^-)]$, for the stationary process we obtain an expression relating the impurity electrical conductivity of the near-surface layer of the semiconductor to the concentration of radicals in the gas phase*:

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

$$\sigma^2/\Delta\sigma = \text{const}/n(1-\theta), \qquad (2)$$

where $\Delta = \sigma_0 - \sigma$, σ_0 is the electrical conductivity of the sample in the absence of radicals on the surface. Under the condition $\sigma_0 \gg \sigma$ and $\theta \ll 1$, formula (2) is transformed into the approximate expression

$$\sigma = \text{const}/\sqrt{n}. \qquad (3)$$

The validity of expression (3) is shown in this work by the example of the chemisorption of methyl radicals. Methyl radicals were obtained by photolysis of acetone vapor in the reaction vessel shown in Fig. 1.

The pressure of acetone vapor was varied from 0.1 to 100 mm Hg, the pressure of inert gases from 1 to 200 mm, and the temperature from 200 to 300° (at ex— at high temperatures the value of θ is small). The distance of the ZnO films from the radical source (the distance from filter Φ_2) was from 1 to 15 cm. The thickness of the ZnO films deposited on the strips of quartz frame 4 was $\sim 5\,\mu$.

Fig. 1. Photocell (1) with movable quartz frame (3); 2—quartz windows; 4—strips; 5—glass-covered weight; 6—guide; 7—ground joint; 8—ruler; 9—soldered contacts; Φ_1—filter for the incident light; Φ_2—removable black filter; L—PRK-2 lamp; T—thermostat.

Fig. 2. Dependence of the conductivity of ZnO under conditions of acetone photolysis on the light intensity I (in relative units) at $t = 300°$, $P_{\text{acetone}} = 5$ mm Hg; a—for $\Delta\sigma = \sigma_0 - \sigma$ (1—increase of I, 2—decrease of I); b—for two specimens differing in thickness by a factor of 1.5 (1—increase of I, 2—decrease of I).

According to the data of (3), during the photolysis of acetone under the indicated conditions (temperature, pressure), the principal reactions are:

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* At large degrees of coverage, expressions (2) and (3) should not be fulfilled, since in this case reactions of the type

$$(\text{R}^- \ldots \text{Zn}^+) + \text{R} \rightarrow \text{R}-\text{R} + \text{Zn}^+ + e; \qquad 2[\text{Zn} \ldots \text{R}] \rightarrow \text{R}-\text{R} + 2\text{Zn} + 2e$$

will also occur (interaction of adsorbed radicals), and, in addition, for large θ it is necessary to take into account the influence of the double electric layer (2).

$$\begin{array}{ll} \text{a) } CH_3COCH_3 \xrightarrow{h\nu} CH_3CO + CH_3; & \text{b) } CH_3CO \to CO + CH_3; \\ \text{c) } 2CH_3 \to C_2H_6; & \text{d) } CH_3COCH_3 + 2CH_3 \to CH_4 + CH_3COC_2H_5. \end{array} \tag{4}$$

The quantum yield of the primary photolysis process is close to unity. The disappearance of methyl radicals proceeds mainly according to the law of the bimolecular reaction c) (4).

The change in the stationary concentration of radicals with the intensity of the absorbed light I under this condition follows the law $n \sim \sqrt{I}$. Substituting this expression into (3), we obtain a relation connecting I with the electrical conductivity (σ) of the semiconductor film, i.e.,

$$\sigma = \text{const}/\sqrt[4]{I}. \tag{5}$$

An experimental verification of formula (5) is shown in Fig. 2. The tangent of the angle of inclination of the straight line in Fig. 2b is −0.26. This means that formula (5) is satisfactorily fulfilled. This, in turn (for the case under consideration), indicates the validity of formulas (2) and (3).

To estimate the sensitivity of semiconductor films to methyl radicals, the concentration of radicals under steady-state conditions was calculated on the basis of measurements of the energy of the incident and absorbed light. For the established process of acetone photolysis, the following expression is valid:

$$(I_0/V)(1 - e^{-\alpha dp}) = k_1 n^2 + k_2 np, \tag{6}$$

where $V = 20$ cm^3 is the volume of the illuminated sector; $\alpha = 0.94 \cdot 10^4$ cm^2/mol is the absorption coefficient (λ 3100 Å); $d = 3$ cm is the thickness of the absorbing layer; $P = 5$ mm Hg is the vapor pressure of acetone; $I_0 = 3 \cdot 10^{15}$ quanta/sec is the energy of the incident light (the absorbed energy per 1 cm^3 was $\sim 1 \cdot 10^{12}$ quanta/sec); $k_1 = 5 \cdot 10^{13}$ mol^{-1} cm^3 sec^{-1} and $k_2 = 10^8$ mol^{-1} cm^3 sec^{-1} are the rate constants of reactions 4c and 4d for $t = 300°$ (4,5).

The calculation shows that the steady-state concentration of radicals n at the maximum light intensity in our experiments was no greater than 10^{10} radicals/cm^3. Under these conditions the electrical conductivity of the ZnO film ($t = 300°$) changed by 300-400% relative to the dark value. Consequently (in accordance with formula (3)), with a semiconductor indicator it is possible to measure radical concentrations equal to 10^6–10^7 radicals/cm^3, i.e., 7 orders of magnitude lower than can be done at present by existing methods. Such a high sensitivity of ZnO films to alkyl radicals is also confirmed by comparing the activation energies of the electrical conductivity of ZnO in the presence of oxygen molecules (6) (electron affinity energy of O_2, 20 kcal/mol) and methyl radicals (1) (electron affinity energy of CH_3, 25 kcal/mol). Experiment shows that in an oxygen atmosphere at a pressure of 10^{-6} mm (10^{10} molecules/cm^3) the electrical conductivity of ZnO films decreases by 30-50%, and consequently, in the presence of CH_3 radicals, all other conditions being equal, the same change in conductivity will correspond to radical concentrations below 10^{10} radicals/cm^3.

An increase in the acetone pressure under photolysis conditions (the frame was lowered into the lower part of the vessel) first leads to a decrease in electrical conductivity (the dark conductivity changes practically not at all), which indicates an increase in the radical concentration due to an increase in the absorption of active radiation, and then to an increase, which is associated with an increase in the rates of reactions 4c and 4d and with the interaction of acetone vapor with chemisorbed radicals. An increase in the pressure of inert gases under analogous conditions leads only to an increase in electrical conductivity (see Fig. 3), with a correlation observed between the activity of the inert gas with respect to increasing the conductivity of the film under conditions of acetone photolysis and the atomic weight of the gas. The increase of σ with the pressure of the inert gas is probably connected with the fact that, in addition to processes (4), triple collisions of two radicals with an atom of the inert gas as the third body also play a role in the disappearance of CH_3 radicals. From this point of view, the correlation can be explained by the fact that in the series He—Ne—Xe, with increasing atomic weight the kinetic diameter of the particle increases (2.20; 2.60; 4.91 Å), and the number of triple collisions

$$Z_{\text{III}} \sim d_{1,2}^5 m_{1,2}^{-1/2}.$$

As a result, Z_{III} increases from He to Xe.

Figure 4 shows the change in σ of the film as the distance (x) from the lower part of the vessel increases (Fig. 4a) and as the pressure of the inert gas increases (Fig. 4b). The concentration of radicals n_0 in the lower part of the vessel during these experiments was maintained constant.

Under these conditions, according to the data of (^{7}), the relative concentration of radicals ($n_x/n_{x=0}$) changes with distance as follows: $n_x/n_{x=0} = \exp[-(\beta\gamma^{1/2}x)]$ —surface recombination of first order; $n_x/n_{x=0} = [1 + (n_{x=0}bp/6D)^{1/2}x]^{-2}$ – volume recombination (triple collision), where b and γ are recombination coefficients; $\beta = (\bar{v}C/4SD)^{1/2}$; $\bar{v}$ is the mean velocity of the radicals; p is the gas pressure; C and S are, respectively, the perimeter and the cross section of the reaction vessel.

If a semiconductor film is used as the probe, then these formulas, in accordance with formula (3), are transformed into the following*:

$$(\sigma_{x=0}/\sigma_x)^2 = \exp[-(\beta\gamma^{1/2}x)]$$

and

Fig. 3. Dependence of the conductivity of ZnO under conditions of acetone photolysis on pressure: a—acetone, b—inert gases ($P_{\text{acetone}} = 5$ mm Hg) at $t = 300°$ (frame in the lower part of the vessel). 1—He, 2—Ne; 3—Xe; 4—dark conductivity

Figure 2: Fig. 3. Dependence of the conductivity of ZnO under conditions of acetone photolysis on pressure: a—acetone, b—inert gases ($P_{\text{acetone}} = 5$ mm Hg) at $t = 300°$ (frame in the lower part of the vessel). 1—He, 2—Ne; 3—Xe; 4—dark conductivity

Fig. 4. Dependence of the conductivity of ZnO films: a—on the distance x to Φ_2; b—on the pressure of neon at t = 300°, P_acetone = 5 mm Hg. *σ{x=0}(n*{x=0}) = const (frame in the upper part of the vessel)

Figure 3: Fig. 4. Dependence of the conductivity of ZnO films: a—on the distance x to Φ_2; b—on the pressure of neon at t = 300°, P_acetone = 5 mm Hg. *σ{x=0}(n*{x=0}) = const (frame in the upper part of the vessel)

$$(\sigma_x/\sigma_{x=0}) = 1 + (n_{x=0}bp/6D)^{1/2}x$$

or

$$\Delta\sigma = (bp/6D)^{1/2}kx,$$

where $\Delta\sigma = \sigma_x - \sigma_{x=0}$, $k = \text{const}$ (see formula (2)). For a bulk bimolecular reaction of methyl radicals, instead of the quantity bp one should substitute the recombination constant of methyl radicals.

Verification of the derived relationships, using alkyl radicals as an example, has so far been carried out only for the case of bulk recombination. From Fig. 4 it is evident that the derived relationship is confirmed by experiment to a sufficient degree. This means that the processes of recombination and the reactivity of radicals in the presence of various gases can be investigated by the semiconductor-probe method.

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Fig. 4. Dependence of the conductivity of ZnO films: *a*—on the distance x to Φ_2; *b*—on the pressure of neon at $t = 300°$, $P_{\text{acetone}} = 5$ mm Hg. $\sigma_{x=0}(n_{x=0}) = \text{const}$ (frame in the upper part of the vessel)

The proposed method can also be used to study active particles arising both in the process of pyrolysis or radiolysis of chemical substances and in certain heterogeneous reactions. Experience shows that different alkyl radicals behave differently with respect to their influence on the conductivity of films, and therefore it becomes possible to identify them at very low concentrations.

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* At small values of $\Delta\sigma$, formula (2) should be used.

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