PHYSICAL CHEMISTRY

E. E. GUTMAN, I. A. MYASNIKOV

1963

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

E. E. GUTMAN, I. A. MYASNIKOV

EFFECT OF ADSORPTION OF FREE RADICALS ON THE CONTACT POTENTIAL OF n-SEMICONDUCTORS

(Presented by Academician V. A. Kargin, 18 V 1963)

It has been shown in ([1],[2]) that, under the influence of chemisorption of free atoms and radicals, the electrical conductivity of semiconductors in the impurity region changes to a considerably greater extent than during the chemisorption of most molecules. Such a large change in conductivity upon adsorption of radicals should be expected only for specimens whose crystal thickness is comparable with the screening length. Such specimens may be either semiconductors possessing a microstructure (sintered oxide films), or elemental semiconductors (Ge, Si) made in the form of thin filaments. The magnitude of the electron work function, as is known, is not associated with this limitation, and its change most fully characterizes surface processes.

The present work is the first step in applying the electron work-function method to the study of the behavior of active particles (radicals, atoms, ions) in the gas phase and in the adsorbed layer.

Apparatus. To measure the work function, the method of the contact potential difference (c.p.d.) was used ([3]). The cell is a glass vessel (Fig. 1), in which the vibrating electrode is a gold plate attached by a molybdenum wire to a molybdenum rod. Vibration of the electrode with an amplitude of about 0.1 mm is produced through an ebonite rod by means of a mechanical-oscillation generator (GMK-1), supplied from an audio generator ZG. To avoid industrial interference, the work was carried out at a frequency of 80 Hz. The parameters of the vibrating electrode were chosen so that the frequency of 80 Hz was the natural oscillation frequency of the electrode. For the same purpose, a movable platinum rider was provided.

Fig. 1. Photocell and electrical circuit for measuring the contact potential difference.
1 –quartz window; **2** –removable black-glass filter; **3** –quartz-molybdenum-glass transition; **4** –quartz table with the semiconductor deposited on it; **5** –vibrating gold electrode; **6** –platinum rider; **7** –molybdenum rod 3 mm in

Fig. 2

Figure 2: Fig. 2

diameter; **8** –molybdenum wire 0.5 mm in diameter; **9** –audio generator ZG-12; **10** –mechanical-oscillation generator GMK-1; **11** –ebonite rod for transmitting oscillations; **12** –narrow-band amplifier; **13** –EO-7 oscillograph, serving as a sensitive null instrument; **14** –dc potentiometer (for compensation and readout of the c.p.d.); **15** –furnace heated by direct current; **16, 17** –shields against industrial and atmospheric interference.

The second electrode was a quartz table with a film of pure, self-activated zinc oxide, free of foreign impurities, deposited on its surface. The entire apparatus was carefully shielded. The temperature of the vessel was maintained by a furnace heated by direct current.

The experiments were carried out with methyl radicals, which were generated in the quartz part of the cell by photolysis of acetone vapor. To avoid the influence of light on the contact potential difference inside the cell, a black-glass filter was placed there; its design is shown in Fig. 1. Illumination was provided by an optical system consisting of a DRSh-500 mercury lamp, a water filter, a quartz condenser, and calibrated grids.

The main drawback of the method is the possible adsorption of radicals on the reference electrode. In the present work we did not investigate the behavior of radicals on gold, since the aim of the work was to detect the very effect of the influence of chemisorption of radicals on the contact potential difference (ZnO–Au). However, the properties of alkyl radicals studied earlier and in the present work make it possible to improve the method and eliminate the indicated drawback.

Fig. 2. Change in the contact potential of ZnO during and under the conditions of photolysis of acetone at various temperatures. $P_{\text{acet}} = 0.5$ mm.
1 –270; 2 –200; 3 –100; 4 –23° C

It is known that the lifetime, and hence the path length, of a radical are limited. Consequently, by making one of the plates of the capacitor in the form of a movable carriage traveling along guide rails, it is possible to adsorb radicals only on the sample deposited on the carriage, and then to "deliver" it to the reference electrode, to which the radicals do not reach. The path length of radicals in the vessel can be regulated by additions of inert gases (volume recombination of radicals).

This manner of carrying out the experiments will be most effective at temperatures not above 200° (for methyl radicals on ZnO), when the reverse processes associated with the disappearance of radicals from the adsorbent surface do not proceed at an appreciable rate. Only with very careful preparation of the experiment did we succeed in detecting the effect of the influence of radical adsorption on the contact potential difference ZnO—Au.

The indicated difficulty is associated with the fact that radicals, being active, unstable particles, were readily lost in quartz cells with tungsten leads, in cells washed with hydrofluoric acid, etc. In parallel with measurement of the contact potential difference, the conductivity of the sample was measured.

Results. When ultraviolet light was switched on in acetone vapor, we observed a new phenomenon—the change in the contact potential difference ZnO—Au under the influence of radical adsorption (Fig. 2).

The observed effect directly indicates that chemisorption of radicals, even when their concentration in the gas phase is extremely small (of the order of 10^9 radicals/cm^3 in our experiments), charges the zinc oxide surface negatively by a considerable amount. After the light is switched on—at temperatures above 200° the contact potential difference and the resistance of the film decreased at an appreciable rate (the higher the temperature, the faster the return); below 200° this rate is small, and heating of the film is required for the contact potential difference and conductivity to return to their former values.*

In Fig. 3 are given the results of experiments on the influence of light intensity on the kinetics of change of the contact potential difference ZnO—Au. Attenuation of the light intensity by factors of 10 and 20 (curves 2 and 3) considerably lowers both the initial rate of change of the contact potential difference and the value of the contact potential difference under stationary conditions.

Comparison of the data obtained with the results of work [4] on the influence of radical adsorption on the electrical conductivity of zinc oxide leads to the conclusion that adsorption of radicals on the reference electrode apparently does not make a substantial contribution to the change in c.p.d., and consequently to the change in the electron work function of gold.

Therefore we considered it possible to carry out a preliminary analysis of the data obtained, assuming that a substantial part of the change in c.p.d. in our experiments is associated with adsorption of radicals on ZnO.

The process of chemisorption of radicals on zinc oxide with capture of an electron from the conduction band may be represented by the following scheme:

$$\mathrm{R}_v \to \mathrm{R}_s \xrightarrow{+e} \mathrm{R}_s^- \xrightarrow{+\mathrm{Zn}^+} (\mathrm{R}_s^- \ldots \mathrm{Zn}^+),$$

where R_v is a radical of the gas phase; R_s is an adsorbed radical; R_s^- is an adsorbed radical that has captured a free electron; e is an electron of the conduction band; Zn^+ is an ionized impurity zinc atom; $(\mathrm{R}_s^- \ldots \mathrm{Zn}^+)$ is a surface

---

* The influence of molecular products of photolysis on the contact potential difference was not observed, owing to the small fraction of ketone conversion.

Fig. 3

Figure 3: Fig. 3

compound of the radical with the impurity atom (the plus and minus signs do not at all indicate an ionic character of the bond, but only point to the predominant distribution of charges).

As electrons accumulate on the adsorbed particles, a double electric layer is formed at the semiconductor surface, which creates a potential barrier for the transition of electrons into the space-charge region of the semiconductor (^{5}). The height of the barrier E, or the magnitude of the change in electron work function $e\Delta\varphi$, where e is the electron charge, will in first approximation be proportional to the surface concentration of ions $[\mathrm{R}_s^-]$.

Fig. 3. Change in the contact potential of ZnO with time and under conditions of acetone photolysis at different intensities of illumination (in relative units) at 270°C. $P_{\text{acet}} = 0.5$ mm. 1—100 (without attenuation of intensity), 2—10; 3—5

Assuming that the limiting stage of the entire process of radical chemisorption is not the adsorption of radicals (^{4}), but electron transitions through the barrier, we obtain for a nondegenerate semiconductor:

$$\frac{d\varphi}{dt} = \frac{d[\mathrm{R}_s^-]}{dt} = k[\mathrm{R}_s][e] \cdot \exp\left\{-\frac{E_0 + E}{kT}\right\}$$

or

$$\frac{d\varphi}{dt} = k' \exp\left\{-\frac{e\Delta\varphi}{kT}\right\},$$

where $\frac{d\varphi}{dt}$ is the rate of change of the electron work function, $[\mathrm{R}_s]$ is the stationary concentration of adsorbed radicals, $[e]$ is the concentration of conduction-band electrons, E_0 is the height of the energy barrier before chemisorption of radicals, and k and k' are kinetic constants*.

With increasing coverage, the quantity $e\Delta\varphi$ will increase, while $\frac{d\varphi}{dt}$ will decrease, approaching zero (the slow part of adsorption). Fig. 4 shows the agreement of this expression with experiment.

The disappearance of radicals from the semiconductor surface, accompanied in our experiments by a decrease in the work function and an increase in conductivity, may occur as a result of three possible processes: desorp-

---

Fig. 4. Dependence of the rate of change of the contact potential of a ZnO film during the process at $T = 270°\text{C}$.

Figure 4: Fig. 4. Dependence of the rate of change of the contact potential of a ZnO film during the process at $T = 270°\text{C}$.

* Assuming that $[\mathrm{R}_s]$ is a stationary quantity (by virtue of the assumption about the limiting stage) and that the change in the pre-exponential quantity $[e]$ is small compared with the change in the exponential term, we obtain

$$k' = k[\mathrm{R}_s][e] \cdot \exp\left\{-\frac{E_0}{kT}\right\}$$

—a kinetic constant depending only on temperature.

of radicals, surface recombination of radicals, and the interaction of radicals with molecules and radicals arriving from the gas phase.

A decrease in the work function, only indirectly connected with these processes, will occur as a result of the reverse transition of an electron from the adsorbed particle into the conduction band. Within the framework of the adopted model, the rate of the reverse process does not depend on the height of the barrier and will be determined mainly by the rate of occurrence of the chemical reactions. Investigation of the reverse process by the method of electrical conductivity and of the work function confirms the validity of the scheme adopted.

Fig. 4. Dependence of the rate of change of the contact potential of a ZnO film during the process
$T = 270°\text{C}$

On the basis of measurements of the c.p.d. ZnO—Au, it is possible to estimate, very approximately, the magnitude of the surface concentration of ions $[R_s^-]$, assuming that the adsorbed radicals $[R_s]$ are not polarized on the surface. The calculation shows that if, for our zinc oxide samples, one takes the screening length to be $1\,\mu$, the dielectric constant $\varepsilon = 10$, then for the experimental value $\Delta\varphi = 0.16$ V the desired quantity will be approximately 10^{10} radicals/cm^2. The concentration of surface regular atoms is 10^{15} cm^{-2}. Consequently, under the conditions of our experiments the maximum coverage* is $10^{-3}\%$ of the number of surface atoms. It should be noted that the surface concentration of irregular (interstitial) zinc atoms in ZnO, responsible for impurity conductivity, is 10^{10}–10^{11} cm^{-2} (calculated from the volume concentration).

This interesting result requires further experimental verification.

Physical-Chemical Institute
named after L. Ya. Karpov

Received
13 IV 1963

REFERENCES CITED

1. I. A. Myasnikov, DAN, **120**, 1298 (1958).

2. I. A. Myasnikov, E. V. Bolshun, DAN, **135**, 1164 (1960).

3. B. M. Tsarev, *Contact Potential Difference*, 1955; V. I. Lyashenko, I. I. Stepko, Izv. AN SSSR, ser. fiz., **16**, 211 (1952); E. Kh. Enikeev, in: *Surface Properties of Semiconductors*, Publ. House of the Academy of Sciences of the USSR, 1960.

4. I. A. Myasnikov, E. V. Bolshun, E. E. Gutman, *Kinetics and Catalysis*, **4**, no. 5 (1963).

5. K. Hauffe, H. J. Engel, *Zs. Electrochem.*, **56**, 366 (1952).

---

* From the data of work (1) it follows that, at the same light intensity and, consequently, concentration of radicals in the volume, and at the temperature of the experiment for which the calculation was made, the value found for the surface coverage is a maximum, since a further increase in light intensity and decrease in temperature do not lead to a change in the quantity $\Delta\sigma = \sigma_0 - \sigma$ (σ_0 is the electrical conductivity of the sample in the absence of radicals on the surface), and consequently to further adsorption associated with electron capture.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.