KINETICS OF OXIDATION-REDUCTION REACTIONS IN THE SYSTEM IMPURITY SEMICONDUCTOR - ELECTROLYTE SOLUTION

(UDC 541.13:621.395.592)

R. R. Dogonadze and A. M. Kuznetsov

Institute of Electrochemistry, Academy of Sciences, USSR

Translated from Élektrokhimiya, Vol. 1, No. 6,
pp. 742-744, June, 1965
Original article submitted February 9, 1965

In [1], the current and transport coefficients were calculated for oxidation-reduction reactions proceeding on an electrode prepared from the semiconductor itself. In this work we considered the case when the half-width of the forbidden zone Δ_0 is significantly smaller than the energy of overpolarization E_s.

In this work, these results are generalized for the case of an impurity semiconductor, where together with the case $\Delta_0 \ll E_s$, we shall also consider the case $\Delta_0 \sim E_s$. Moreover, we shall consider the exchange of electrons between the surface states of the semiconductor and the solution. Since the calculations for impurity and intrinsic semiconductors differ little, we shall not take up the details of the calculations and shall immediately present the results. Just as in [1], we shall consider that the deviation from equilibrium in the semiconductor is small. Generalization to the case of deviation from equilibrium in a semiconductor also presents no difficulties. To simplify the expressions, we shall also consider that the ψ_1-effect is absent.

The expressions for the currents for a semiconductor with a nondegenerate surface take the form:

$$i_{\text{sп}}{}^{p} = G_p \cdot n_p{}^0 \cdot \exp\left(-\beta_p \cdot e\eta_K / kT\right), \tag{1}$$

$$i_{\text{sп}}{}^{e} = G_e \cdot \exp\left(-\beta_e \cdot e\eta_K / kT\right) \cdot n_e(\eta), \tag{2}$$

where η and η_K are the overvoltages in the volume of the semiconductor and on the contact, where

$$G_{p,e} = e \cdot l \cdot |L|^2 \cdot \left(\frac{8\pi}{\hbar^2 kT}\right)^{1/2} \cdot \frac{E_s \cdot \exp\left[\dfrac{\Delta_{p,e} \mp e(\varphi_{\text{п}}{}^0 - \varphi_K{}^0)}{kT}\right]}{[E_s + \Delta_{p,e} \mp e(\varphi_{\text{п}}{}^0 - \varphi_K{}^0)]^{1/2}}$$
$$\times \exp\left\{-\frac{[E_s + \Delta_{p,e} \mp e(\varphi_{\text{п}}{}^0 - \varphi_K{}^0)]^2}{4E_s kT}\right\} \cdot c_z^{1-\beta_{p,e}} \cdot c_{z-1}^{\beta_{p,e}}. \tag{3}$$

The upper sign pertains to the first subscript, the lower sign to the second; n_p^0 is the concentration of holes at the contact at equilibrium; $n_e(\eta)$ is the electron concentration at the contact in the absence of equilibrium; $\Delta_{p,e}$ are the distances from the Fermi level to the top of the valence zone and from the bottom of the conduction zone to the Fermi level, respectively; φ_π^0 and φ_K^0 are the equilibrium potentials in the volume of the semiconductor and on the contact; L is the matrix element of the perturbation; l is the size of the reaction region; c_z and c_{z-1} are the ion concentrations in the volume of the solution.

The quantities $\beta_{p,e}$ take the form

$$\beta_{p,e} = \frac{1}{2} \pm \frac{\Delta_{p,e} \pm e(\varphi_{\text{п}}{}^0 - \varphi_K{}^0)}{2E_s}. \tag{4}$$

These quantities are coefficients of proportionality between the change in the activation energy and the heat of the reaction, i. e., coefficients contained in the Bronsted function [2]. As can be seen from (4), β_p, generally speaking, does not coincide with β_e; moreover, the values $\beta_p > 1$ and $\beta_1 < 0$ are impossible in principle. The dependence of the current on the potential is determined by the transport coefficients $\alpha_{p,\,e}$

$$\alpha_e = 1 - (1 - \beta_e)\, d\eta_K / d\eta \tag{5}$$

$$\alpha_p = \beta_p d\eta_K / d\eta. \tag{6}$$

In the absence of surface states, the derivative $d\eta_K/d\eta$ is very small. However, from the standpoint of the last observation with respect to the quantities $\beta_{p,e}$ the opposite case is more interesting, in which $d\eta_K : d\eta \approx 1$, i. e., $\alpha_{p,e} \approx \beta_{p,c}$. In this case, an unusual dependence of the current on the potential may appear in principal. Actually, let the reaction proceed for any reason (for example, as a result of the fact that the matrix element L for the conduction zone is equal to zero) with the participation of the electrons only of the valence zone, and let $\beta_p > 1$. Then the expression for the current takes the form

$$i^p = i_0{}^p \left[e^{e(1-\beta_p)\eta/kT} - e^{-e\beta_p\eta/kT} \right]. \tag{7}$$

As can be seen from (7), as η increases, the current first increases, then reaches a maximum, and begins to fall.

The fact that the electronic or hole currents may possess a maximum was obtained from the qualitative considerations of Gerischer [3], who considered a semiconductor without surface states, and considered that the current may reach a maximum when the surface of the semiconductor degenerates. Gerischer obtained no expressions for the quantities $\beta_{p,\,c}$.

Let us consider the relationship between the exchange currents for the case $\Delta_0 \ll E_S$.

$$i_0{}^e / i_0{}^p \approx \exp\{-(1 + \Delta_0 / E_s)\,[e(\varphi_{\text{п}}{}^0 - \varphi_K{}^0) - (\Delta_p - \Delta_e) / 2] / kT\}. \tag{8}$$

In the absence of surface states, the derivative $d\varphi_K / d\varphi_\pi$ is very small. Hence, the quantity $\varphi_K{}^0$ may be considered approximately constant with variation of $\varphi_\pi{}^0$. Then, when the concentration of impurities in the semiconductor varies, the quantity $c\,(\varphi_\pi{}^0 - \varphi_K{}^0)$ will vary exactly as $(\Delta_p - \Delta_e)/2$. Hence, the ratio of the electronic exchange current to the whole current will remain approximately constant. At a large concentration of surface states, when $d\varphi_K/d\varphi_\pi \approx 1$, the quantity $e(\varphi_\pi{}^0 - \varphi_K{}^0)$ will remain approximately constant, as the dependence of $i_0{}^c/i_0{}^p$ on the concentration of impurities will be determined by the change in the quantity $(\Delta_p - \Delta_e)/2$.

In conclusion, let us briefly consider the current at the surface levels. For the sake of definition, we shall consider that there are only donor states on the surface of the semiconductor, with a constant concentration N_d and an energy $E_d{}^0$. The expression for the current $i_{s\pi}$ may be written as follows

$$i_{s\text{п}} = i_{s\text{п}}{}^p + i_{s\text{п}}{}^e + i_{s\text{п}}{}^d,$$

where $i_{s\pi}{}^d$ is the current related to transition of electrons from the donor levels to the solution. We shall consider that the exchange of electrons between the donor states and the zones is rapid. Then, for $i_{s\pi}{}^d$, we can write (to simplify the expressions, we shall consider that $|E_d - \varepsilon_F| \ll E_s$, ε_F is the Fermi level)

$$i_{s\text{п}}{}^d = G^d \cdot \left[1 + \exp\left\{ \frac{E_d{}^0 - \varepsilon_F + e(\varphi_{\text{п}}{}^0 - \varphi_K{}^0) + e(\eta - \eta_K)}{kT} \right\} \right]^{-1} \times \exp(-e\eta_K/2kT). \tag{9}$$

$$G^d = e \cdot l \cdot |L_d|^2 \cdot N_d \sqrt{c_z \cdot c_{z-1}} \times \exp\left\{ -\frac{[E_s - E_d{}^0 + \varepsilon_F - e(\varphi_{\text{п}}{}^0 - \varphi_K{}^0)]^2}{4E_s kT} \right\}. \tag{10}$$

Estimates show that if $L_d \sim L$, then at a concentration $N_d \sim 10^{14}$–10^{15} cm^{-2}, for sufficiently low-lying levels, the current $i_{s\pi}{}^d$ may be of the same order as the current $i_{s\pi}{}^e$ or even greater. Moreover, for levels E_d lying above the Fermi level, the dependence of the current $i_{s\pi}{}^d$ on the overvoltage is the same as for $i_{s\pi}{}^e$, while for the levels lying below the Fermi level, the dependence is the same as for $i_{s\pi}{}^p$.

LITERATURE CITED

1. R. R. Dogonadze, A. M. Kuznetsov, and Yu. A. Chizmadzhev, Zh. Fiz. Khimii, 38, 1195 (1964).
2. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, Kinetics of Electrode Processes [in Russian], Moscow (1952).
3. H. Gerischer, In Advances in Electrochemistry and Electrochemical Engineering, I (1961).
