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R. R. DOGONADZE, Yu. A. CHIZMADZHEV

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Abstract

Full Text

PHYSICAL CHEMISTRY

R. R. DOGONADZE, Yu. A. CHIZMADZHEV

KINETICS OF CERTAIN ELECTROCHEMICAL OXIDATION-REDUCTION REACTIONS ON SEMICONDUCTORS

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The theoretical study of the kinetics of oxidation–reduction reactions on semiconductors is, above all, of independent interest in connection with the developing experimental investigations in the electrochemistry of semiconductors. In addition, extending the theory developed for metals ([1]) to semiconductors will considerably broaden the possibilities for comparison with experiment. Indeed, in ([1]) it was shown that the exchange current depends on the nature of the metal mainly through the density of electronic states ρ_f, which changes only slightly in going from one metal to another. Comparison of theory with experiment on this point is also made difficult by the fact that, for ρ_f of a number of metals that are of greatest interest electrochemically, there are no experimental data. By comparing the kinetics of reactions on metals and semiconductors, we obtain the possibility of studying the influence of the energy spectrum of a solid on kinetic regularities.

The presence of a forbidden band in a semiconductor leads to the fact that, first, the concentration of free carriers is usually small in comparison with the concentration of ions in solution; second, electrons passing from the solution to the electrode may enter both the conduction band and the valence band, where holes are present. Thus the total anodic current will consist of two components:

$$i = i^e + i^p, \tag{1}$$

where i^e and i^p denote the currents associated with the transition of electrons, respectively, into the conduction band and into the valence band. Since there exist experimental methods that make it possible to measure separately the electron current i^e and the hole current i^p ([2]), their calculation is of interest.

The potential distribution at the electrolyte–semiconductor interface obeys the following simple law:

$$\frac{\Delta\varphi_s}{\Delta\varphi} \simeq \left(\frac{c_{\mathrm{p}}\varepsilon_{\mathrm{p}}}{c_s\varepsilon_s}\right)^{1/2}, \tag{2}$$

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Figure 1

Figure 1: Figure 1

where $\Delta\varphi$ is the total difference of Galvani potentials at the electrolyte–semiconductor interface, and $\Delta\varphi_s$ is the potential drop in the solution; ε_s and c_s denote, respectively, the dielectric constant of the solution and the number of ions in 1 cm^3, while ε_p and c_p are the corresponding quantities for the semiconductor. For germanium, $\varepsilon_\mathrm{p} \simeq 16$, $c_\mathrm{p} \simeq 10^{13}$ cm^{-3}, so that for $c_s \simeq 10^{19}$ cm^{-3} ($\simeq 0.01$ N) we obtain $\Delta\varphi_s \simeq 5 \cdot 10^{-4}\Delta\varphi$, i.e., only 1/2000 of the total potential difference falls in the solution. Therefore, in what follows we shall assume that the entire potential difference is concentrated in the semiconductor.

Let us consider the reaction $A^{+2} \rightarrow A^{+3} + e$ (in the semiconductor). We shall assume that this reaction is not accompanied by adsorption of the reactants on the electrode, by the breaking or formation of chemical bonds, or by deformation of bonds in the first coordination sphere of the ion. To calculate the rate of this reaction we shall use the method developed earlier ([3]), which differs from

used in the theory of absolute reaction rates. To clarify the differences between these two approaches to the problem, let us briefly analyze the basic premises of the theory of absolute rates using homogeneous reactions as an example. Suppose that, in a volume V, particles C and D are present in the gaseous state and are capable of reacting according to the scheme $C + D \rightarrow CD$. The rate of this reaction is determined by the formula:

$$K \sim \exp\left[-\frac{\Delta E^*}{kT}\right],$$

where ΔE^* is the activation energy, whose magnitude is determined by the law of interaction of particles C and D. According to the Maxwell distribution, there are particles in the gas whose energy is sufficient to overcome the activation barrier. Thus, the activated state is reached owing to the motion of the reacting particles. These same ideas are transferred in the theory of absolute rates to reactions in solutions as well; here only a static role is assigned to the solvent: the solvent affects the character of the interaction between the reacting particles, but does not take part in creating the activated state, since the motion of the solvent particles is not taken into account. Such a treatment is not applicable to reactions between charged particles in polar media, since vibrations of the dipole molecules of the solvent cause more significant changes in the energy of the reacting particle than does the thermal motion of the particle itself.

Fig. 1. *a*—potential distribution at the electrolyte-semiconductor boundary; *b* —band structure of the semiconductor

Thus, in reality the solvent plays an essential dynamic role, ensuring the creation of the activated state. It is precisely this idea of the dynamic role of the solvent

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that underlies the method used here. Treating the medium outside the first coordination sphere of the ion as continuous, we shall describe it by means of the polarization $\mathbf{P}(\mathbf{r}, t)$, which changes with time. This change of $\mathbf{P}(\mathbf{r}, t)$ with time plays here a role analogous to the thermal motion of the reacting particles in the theory of absolute reaction rates. Then the process of electron transfer from A^{+2} (the initial state) into the semiconductor (the final state) may be represented as follows. As a result of changes in $\mathbf{P}(\mathbf{r}, t)$ with time, an activated state is created, i.e., such a state in which the energies of the system in the initial and final states are equal (by the system we mean the electron, the solvent, and the ion). The probability of electron transition w_{sf} is represented [3] as the product of the probabilities of creating the activated state and of the actual electron transition, which is possible only in the activated state:

$$w_{sf} = \left(\frac{\pi}{\hbar^2 kTE_s}\right)^{1/2} |L|^2 \exp\left\{-\frac{(I_f - I_s + E_s)^2}{4E_s kT}\right\}, \tag{3}$$

where I_f and I_s are the equilibrium energies in the initial and final states, respectively, and E_s is the reorganization energy, equal to $\frac{c}{8\pi}\int(\mathbf{D}_{03} - \mathbf{D}_{02})^2\, dv$; $\mathbf{D}_{02}$ and $\mathbf{D}_{03}$ denote the field induction values of the ions A^{+2} and A^{+3}; L is the exchange integral (3).

Since the transition probability (3) contains as a factor the matrix element L, which rapidly decreases with increasing distance $|x|$ from the electrode surface, we shall assume that electrons from the solution pass into states located at the surface of the semiconductor. According to [1,3]

$$I_f - I_s = \Delta I = \varepsilon_f - \varepsilon_F + kT \ln\frac{c_2}{c_3} - e\eta, \tag{4}$$

where η is the overvoltage, ε_f is an arbitrary energy level in the semiconductor, ε_F is the Fermi level; the method of counting energies is indicated in Fig. 1b. It is now not difficult to calculate the electronic exchange current:

$$i_0^e = e\delta c_2 \rho_e \int_{\varepsilon_1^k}^{\infty} w_{sf}\, d\varepsilon_f, \tag{5}$$

where δ is the distance from which the electron transfer mainly occurs, ε_1^k is the energy of the bottom of the conduction band at the contact, and ρ_e is the density of electron states. The occupation of electron states in the conduction band is not taken into account in formula (5). Integration of (5) gives:

$$i_0^e = ec_2^{1/2-\Delta_0/2E_s} c_3^{1/2+\Delta_0/2E_s} \delta \frac{kT}{h}\left(\frac{16\pi^3}{kTE_s}\right)^{1/2} |L_e|^2 \rho_e \exp\left[-\frac{(E_s + \Delta_0 + e\Delta\varphi^0)^2}{4E_s kT}\right]. \tag{6}$$

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This formula has been obtained under the assumption that $E_s \gg \varepsilon_1^k - \varepsilon_F$ and $e(\varphi_n^0 - \varphi_s) = e\Delta\varphi^0 \ll \Delta_0$, where Δ_0 is the half-width of the forbidden band. In calculating the hole current it is necessary to take into account the concentration of holes in the valence band, which gives

$$i_0^p = ec_2\delta\rho_p \int_0^{\varepsilon_2^k} w_{sf} \exp\left[\frac{\varepsilon_f - \varepsilon_F}{kT}\right] d\varepsilon_f, \tag{7}$$

where ε_2^k is the energy of the top of the valence band. Integrating, we obtain:

$$i_0^p = ec_2^{1/2+\Delta_0/2E_s} c_3^{1/2-\Delta_0/2E_s} \delta \frac{kT}{h} \left(\frac{16\pi}{kTE_s}\right)^{1/2} |L_p|^2 \rho_p \exp\left[-\frac{(E_s + \Delta_0 - e\Delta\varphi^0)^2}{4E_s kT}\right]. \tag{8}$$

Neglecting the pre-exponential factors, one may write the ratio of the electronic exchange current to the hole current in the form:

$$\frac{i_0^e}{i_0^p} \simeq \exp\left[-\frac{e\Delta\varphi^0}{kT}\left(1 + \frac{\Delta_0}{E_s}\right)\right]. \tag{9}$$

Thus, if $\Delta\varphi^0 > 0$ and $\Delta\varphi^0 \gg kT$, the exchange current is practically entirely a hole current. Comparing (6) with the expression for the exchange current on a metal (1), one can see that

$$i_0^{\mathrm{p}} \simeq i_0^M \exp\left[-\frac{\Delta_0}{2kT}\right]. \tag{10}$$

Thus, the exchange current at a semiconductor electrode is smaller than the exchange current at a metal, owing to the presence of the forbidden band.

When considering currents under nonequilibrium conditions, we encounter a number of new regularities that are characteristic of semiconductors.

Let us consider the system under anodic polarization. The magnitude of the overvoltage η is determined by the equality $\eta = \varphi_n - \varphi_n^0$. In Fig. 1b the dashed line shows-

reflected in a shift of the bottom of the potential well upon polarization. The bands in the bulk of the semiconductor will shift downward by the amount $-e\eta$ (the energy of an electron infinitely far from the semiconductor being taken as zero). At the contact, evidently, the bands will not shift. At small overvoltage the equilibrium distribution of carriers in the semiconductor will be preserved, so that the concept of the Fermi level may still be used.

In the presence of overvoltage, formula (5) takes the form:

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$$i_a^e = ec_2\delta\rho_e \left(\frac{\pi}{\hbar^2 kTE_s}\right)^{1/2} |L_e|^2 \int_{\varepsilon_1^k+e\eta}^{\infty} \exp\left[-\frac{\left(\varepsilon_f - \varepsilon_F + kT\ln\frac{c_2}{c_3} - e\eta + E_s\right)^2}{4E_s kT}\right] d\varepsilon_f. \tag{11}$$

Let us make a change of variables according to the formula: $\varepsilon_f - e\eta = \varepsilon'_f$. Then formula (11) assumes the form:

$$i_a^e = ec_2\delta\rho_e \left(\frac{\pi}{\hbar^2 kTE_s}\right)^{1/2} |L_e|^2 \int_{\varepsilon_1^k}^{\infty} \exp\left[-\frac{\left(\varepsilon'_f - \varepsilon_F + kT\ln\frac{c_2}{c_3} + E_s\right)^2}{4E_s kT}\right] d\varepsilon'_f. \tag{12}$$

Comparison of this expression with the exchange current (5) shows that $i_a^e(\eta) = i_0^e$, i.e., the transfer coefficient $\alpha_e = 0$. For the hole anodic current we obtain

$$i_a^p = i_0^p \exp\left[-\frac{e\eta}{kT}\right], \tag{13}$$

i.e., $\alpha_p = 1$. This result is obvious, since we assumed that the electron transition occurs only into states lying at the very surface of the semiconductor. In this approximation all the overvoltage drops outside the "reaction" region, and the dependence of the hole current on the overvoltage is connected only with the dependence of the number of holes at the contact on the overvoltage. Allowance for electronic transitions into states remote from the surface should lead to a deviation of α_e from 0 and α_p from 1. However, since the transition probability decreases at distances much smaller than the Debye lengths, it may be asserted that α_e is close to 0, and α_p is close to 1.

The ratio of the electron current to the hole current, in contrast to (4), has the form

$$\frac{i_a^e}{i_a^p} = \frac{(i_a^e)^0}{(i_a^p)^0} \exp\left[-\frac{e\eta}{kT}\right] = \exp\left[\frac{e\Delta\varphi^0}{kT}\left(1 + \frac{\Delta_0}{E_s}\right) + \frac{e\eta}{kT}\right]. \tag{14}$$

Since no special experiments have been carried out with systems of the type considered, for the present one can speak only of a qualitative agreement of the theory with experiment ([2]).

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Institute of Electrochemistry
Academy of Sciences of the USSR

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[1] R. R. Dogonadze, Yu. A. Chizmadzhev, DAN, **145**, No. 4 (1962).
[2] Yu. V. Pleskov, DAN, **130**, 62 (1960); ZhFKh, **35**, 2576 (1961).
[3] R. R. Dogonadze, Yu. A. Chizmadzhev, DAN, **144**, No. 5 (1962).
[4] H. Gerischer, Z. phys. Chem., N. F., **26**, 325 (1960).

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