THE KINETICS OF SOME ELECTROCHEMICAL OXIDATION – REDUCTION REACTIONS ON SEMICONDUCTORS

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A theoretical study of the kinetics of the oxidation-reduction reactions occurring on semiconductors is primarily a matter of special interest in connection with the developing experimental investigations of the electrochemistry of semiconductors. In addition, the extension of the theory developed for metals [1] to the case of semiconductors greatly increases the possibility of comparison with experimental results. It was in fact shown in [1] that the exchange current depends on the nature of the metal, particularly with reference to the density of the electronic states ρ_f, which is only slightly changed in moving from one metal to another. Comparison between theory and experiment on this point is complicated by the fact that no experimental data are available for the value of ρ_f for a number of metals of particular interest from an electrochemical point of view. By comparing the kinetics of reactions on metals and semiconductors, however, the possibility arises of studying the effect of the energy spectrum of a solid on the kinetic regularities.

The presence of a forbidden zone in semiconductors results, first of all, in the fact that the concentration of free conductors is usually low compared with the concentrations of ions in solution; and, secondly, in the fact that electrons moving from the solution to the electrode must make contact both with the conductivity zone and the valence zone in which holes occur. Thus, the total anode current consists of two components:

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

in which i^e and i^p represent the currents due to transfer of electrons in the conductivity and valence zones respectively. Since experimental methods exist for measuring the electronic current i^e, and the hole-current i^p, separately [2], the calculation of these is a matter of interest.

The distribution of potential at the electrolyte-semiconductor boundary obeys the following simple relation:

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

where $\Delta\varphi$ is the total difference in potential at the electrolyte-semiconductor boundary, and $\Delta\varphi_s$ is the potential drop in the solution; ε_s and c_s denote the dielectric constant of the solution and the number of ions per cm^3 respectively; and ε_π and c_π denote the corresponding values for the semiconductor. For germanium $\varepsilon_\pi \simeq 16$, $c_\pi \simeq 10^{13}$ cm^{-3}, so that if we take $c_s \simeq 10^{19}$ cm^{-3} (roughly 0.01 N), we obtain $\Delta\varphi_s \simeq 5 \cdot 10^{-4}\ \Delta\varphi$, : that is, the potential drop in the solution amounts to only 1/2000 of the total potential difference. We shall therefore from now on assume that the entire potential difference is concentrated within the semiconductor.

We consider the reaction $A^{2+} \rightarrow A^{3+} + e$ (in the semiconductor). If we suppose that this reaction is not accompanied by adsorption of the reagents at the electrode, and that there is neither destruction nor formation of chemical bonds, nor deformation of bonds in the first coordination sphere of the ion, we may then calculate the rate of this reaction by means of a method developed earlier [3], which is different from that used in the theory of absolute reaction rates. To show clearly the difference between these two approaches to the problem, we shall carry out briefly an analysis of the fundamental postulates of the theory of absolute rates to the case of homogeneous reactions. Let a volume V in the gas state containing particles C and D which are able to react according to the scheme $C + D \rightarrow CD$. The rate of this reaction is determined by the equation:

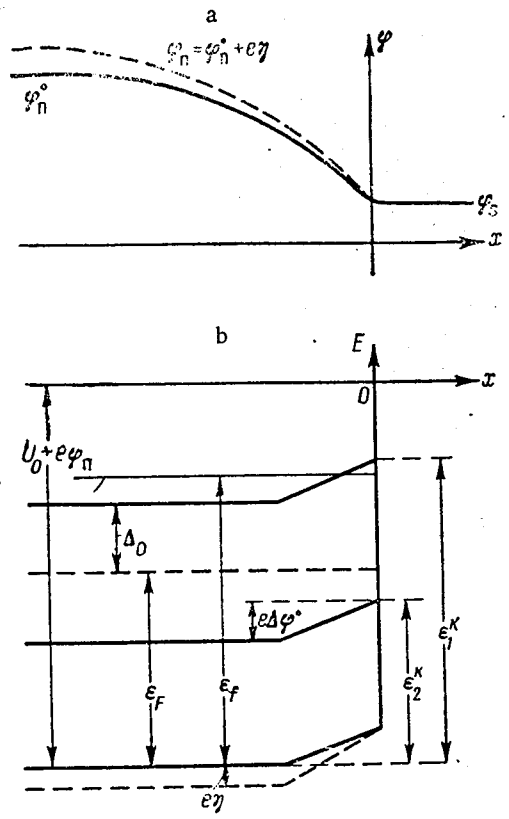

Fig. 1. a) Distribution of potential at the electrolyte–semiconductor boundary; b) zone structure of the semiconductor.

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

where ΔE^* is an activation energy whose magnitude is determined by the regularity governing the interaction of the particles C and D. According to the Maxwell distribution, there are present in the gas particles of sufficient energy to pass over the activation barrier. Thus, the activated state is attained through the movements of the reacting particles. The same assumptions may be transferred to the theory of absolute rates of reactions occurring in solution also, the solvent being ascribed a merely statistical role: the solvent is regarded as affecting the nature of the interaction between the reacting particles, but not as participating in the creation of the activated state, since the movement of the solvent particles does not enter into the calculation. This assumption is not applicable to the reaction between charged particles in polar media, since the oscillations of the dipolar molecules of the solvent produce a more significant change in the energies of the reacting particles than do the thermal, movements of the particles themselves. Hence the solvent actually plays a significant dynamic role in bringing about the formation of the activated state. This notion of the dynamic role played by the solvent lies at the basis of the method applied here. If we regard the medium outside the first coordination sphere of the ion as continuous, we may describe it by means of the polarization $\mathbf{P}(r, t)$, which is variable with respect to time. The variation in the function $\mathbf{P}(r, t)$ with respect to time here plays a role analogous to the thermal movement of the reacting particles in the theory of absolute reaction rates. The process of electron transfer from A^{2+} (the initial state) to the semi-conductor (the final state) may then be represented in the following way: In consequence of the variation in $\mathbf{P}(r, t)$ with respect to time, an activated state is created – that is, a state in which the energies of the system in the initial and final states are equal (the system being understood to include electron, solvent and ion). The probability of the electron transfer w_{sf} may be presented [3] in the form of the product of the probabilities of the creation of the activated state and of the electronic transition proper, which may only occur in the activated state:

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

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

Since the probability of transfer (3) includes as a co-factor the matrix element L, which rapidly dies away with increase in the distance |x| from the electrode surface, it may be supposed that the electrons from the solution are transferred into a state lying at the semiconductor surface. According to [1, 3]:

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

where η is the overpotential, ε'_f is any energy level in the semiconductor, and ε_F is the Fermi level. The method of deriving the energy is given in part (b) of the figure. It is not now 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 at which electronic transfer may basically occur, ε_1^k is the energy of the base of the conductivity zone of the contact, ρ_e is the density of the electronic states. No account is taken of the degree of filling of the electronic state in the conductivity zone in Eq. (5). Integration of (5) gives

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

This formula has been obtained on the assumption that E_s is much greater than $\varepsilon_1^k - \varepsilon_F$ and that $e(\varphi_\pi^0 - \varphi_s) = e\Delta\varphi^0$ is much less than Δ_0, the half-breadth of the forbidden zone. In a calculating the hole-current it is necessary to take account of the concentration of holes in the valence zone, 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 zone. On integration we obtain:

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

Ignoring the pre-exponential factors, the ratio of the electronic exchange current to the hole-current may be expressed in the form

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

Thus, if $\Delta\varphi^0$ is greater than zero, and $\Delta\varphi^0$ is much greater than kT, the exchange current is made up practically completely of the hole-current. By comparing Eq. (6) with the expression for the exchange current on a metal [1], it may be seen that

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

The exchange current at a semiconductor is thus less than that at a metallic electrode, because of the presence of the forbidden zone.

In considering the currents under nonequilibrium conditions we arrive at a number of new regularities characteristic of semiconductors.

We consider a system in which anode polarization occurs. The magnitude of the overpotential η is determined by the equality: $\eta = \varphi_\pi - \varphi_\pi^0$. Part (b) of the figure shows by means of a dotted line the shift of the base of the potential minimum when polarization occurs. The zones in the body of the semiconductor are shifted downwards to a value $e\eta$ (taking the energy of an electron infinitely far away from the semiconductor as equal to zero). At the contact it is obvious that the zones will not be shifted. For low overpotential in the semiconductor the equilibrium distribution of the carriers is maintained, so that it is possible as before to make use of the Fermi-level concept.

Equation (5), in the presence of overpotential, assumes the form

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

When we exchange variables by means of the formula: $\varepsilon_f - e\eta = \varepsilon_f'$. Eq. (11) assumes the form:

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

Comparison of this expression with the exchange current according to (5) shows that $i_a^e(\eta) = i_0^e$, that is, the transfer coefficient $\alpha_e = 0$. The anodic hole-current is given then by:

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

that is, $\alpha_p = 1$. This result is evident, since we have assumed that electronic transfer takes place only for the state lying at the surface of the semiconductor itself. With this approximation the whole overpotential falls away outside the "reaction" region, and the relationship between the hole-current and the overpotential depends only on the relationship between the number of holes at the contact and the overpotential. Calculation of electronic transitions in states distant from the surface should be carried out with variation of α_e from 0 and of α_e from 1. But since the probability of transition decreases at distances considerably less than the Debye-distances, it may be regarded as certain that α_e is near to 0, and α_p is near to 1.

The ratio between the electronic current and the hole-current, in distinction to (4), takes the form:

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

Since special experiments have not been carried out on systems of the type considered, we may for the present only speak of the qualitative agreement between theory and experiment.

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LITERATURE CITED

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