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Abstract

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CAPACITANCE, RESISTANCE, AND INJECTION COEFFICIENT OF A SEMICONDUCTOR ELECTRODE IN OXIDATION-REDUCTION REACTIONS

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Semiconductor electrodes, unlike metallic ones, have the distinctive feature that the electrochemical processes occurring on them are closely connected with the electronic structure of the semiconductor. This is manifested in the fact that both electrons of the conduction band and of the valence band (holes) can participate in an electrochemical reaction. The ratio of the current of minority carriers at the contact to the total current, called ([1]) the injection coefficient and denoted by γ, is decisive for the course of electrochemical processes. As is shown in the present work, γ can be introduced not only in the case of a steady current, but also when an alternating periodic signal passes. Calculation of the basic characteristics of the contact—the diffusion capacitance and resistance—shows that they also depend on the value of γ.

Let us suppose that a steady current of density $\bar{i}$ flows across the electrolyte-semiconductor boundary, upon which a small periodic signal $\tilde{i}$ is superposed, with $\tilde{i} \sim e^{i\omega t}$, where ω is the frequency of the periodic signal. In this case all quantities appearing in the problem can be represented as the sum of two terms, one of which depends only on $\bar{i}$, and the other also on $\tilde{i}$. To exclude the influence of natural convection, let us assume that the electrolyte is enclosed in a capillary of length l, and that at its open end a constant concentration is maintained both of oxidizer ions (C_∞) and of reducer ions (C'_∞). The oxidation-reduction reaction on the electrode surface proceeds according to the scheme Ox+$me \rightleftarrows$ Rd. The total current i passing through the contact is $i = \vec{i} - \overleftarrow{i}$, where $\vec{i}$ and $\overleftarrow{i}$ are, respectively, the forward and reverse reaction currents, determined by the relations

$$\vec{i} = me\left[k_1 \frac{n_s}{n_\infty} C_s + k'_1 C_s\right], \qquad \overleftarrow{i} = me\left[k_2 C'_s + k'_2 \frac{p_s}{p_\infty} C'_s\right]. \tag{1}$$

The values of all quantities at the contact will be supplied with the subscript s; p_∞ and n_∞ denote the concentrations of holes and electrons in the bulk of the semiconductor; k_1, k'_1, k_2, and k'_2 are quantities characterizing the reaction rate.

Equation (1) assumes that the potential drop in the Helmholtz layer is small in comparison with the potential drop in the semiconductor and that the currents passing through the contact are proportional to the concentrations of the reacting components.

The expression $k_1 \dfrac{n_s}{n_\infty} C_s$, for example, describes the reduction of ions by electrons of the conduction band, while the expression $k_1' C_s$ describes the reduction of ions by electrons of the valence band. The two other terms have an analogous meaning.

For what follows it is convenient to represent the total current in the form $i = i^+ - i^-$, where i^+ and i^- are the hole and electron currents. Using (1), we find:

$$i_s^+ = me\left[k_1' C_s - k_2' C_s' \frac{p_s}{p_\infty}\right] = i_0^{(p)}\left[\frac{C_s}{C_\infty} - \frac{C_s' p_s}{C_\infty' p_\infty} e^{eU/kT}\right],$$

$$i_s^- = me\left[k_2 C_s' - k_1 C_s \frac{n_s}{n_\infty}\right] = i_0^{(e)}\left[\frac{C_s'}{C_\infty'} - \frac{C_s n_s}{C_\infty n_\infty} e^{-eU/kT}\right]; \qquad (2)$$

here U is the equilibrium potential; $i_0^{(p)} = emk_1' C_\infty$ and $i_0^{(e)} = emk_2 C_\infty'$ are exchange currents characterizing, respectively, electron transitions from ions

into the conduction band and electrons into ions from the valence band. We shall call the sum of these currents i_0 the total exchange current $i_0 \equiv i_0^{(p)} + i_0^{(e)}$.

Let the x-axis be directed perpendicular to the contact plane into the semiconductor; choose the point $x = 0$ on the surface of the semiconductor. We shall assume that in the solution there is an excess of foreign electrolyte and that the migration of ions discharged at the electrode may be neglected. Then C_s and C_s' are found from the solution of the one-dimensional diffusion equation $\partial C/\partial t = D\,\partial^2 C/\partial x^2$ (the equation for C' is analogous) with the following boundary conditions: at the open end of the tube $C(-l) = C_\infty$, $C'(-l) = C_\infty'$; at the electrode the current is related to the concentration gradient by the relation:

$$i = -e\left[zD\left(\frac{\partial C}{\partial x}\right)_s + z'D'\left(\frac{\partial C'}{\partial x}\right)_s\right] \qquad (3)$$

(z and z' are the charges of the oxidant and reductant ions, $z - z' = m$). If there is no adsorption, $D(\partial C/\partial x)_s = -D'(\partial C'/\partial x)_s$, since for each Ox ion there is one Rd ion and their fluxes are directed in opposite directions. Taking into account that $C = \overline{C} + \widetilde{C}$, with $\partial\overline{C}/\partial t = 0$, and $\partial\widetilde{C}/\partial t = i\omega\widetilde{C}$, we obtain

$$\overline{C}_s = C_\infty \left(1 - \frac{\overline{i}}{i_{\text{lim}}}\right), \qquad \widetilde{C}_s = -\frac{\widetilde{i}_s}{me(D\omega)^{1/2}}\, e^{-i\pi/4}, \tag{4}$$

where $i_{\text{lim}} \equiv meDC_\infty/l$. The solution for $\widetilde{C}$ is valid under the condition $\omega \gg D/l^2$, which in practice imposes no restrictions on ω.

In an analogous way, for the reductant ions we have

$$\overline{C}'_s = C'_\infty \left(1 + \frac{DC_\infty}{D'C'_\infty}\frac{\overline{i}}{i_{\text{lim}}}\right), \qquad \widetilde{C}'_s = \frac{\widetilde{i}_s}{me(D'\omega)^{1/2}}\, e^{-i\pi/4}. \tag{5}$$

The hole concentration at the contact is $p_s = p_d e^{-e\varphi_s/kT}$, where $p_d = \overline{p}_d(\overline{i}) + \widetilde{p}_d(\overline{i}, \widetilde{i})$ is the hole concentration at the boundary of the space-charge region and the diffusion region. If $i_{\text{lim}} \ll i_p$, then one may set $p_d = p_\infty$. Here $i_p \equiv eD_+p_\infty/L$ is the limiting hole current (D_+ is the hole diffusion coefficient, L the diffusion length).

Let $\widetilde{i}_s$ be so small that $|e\widetilde{\varphi}_s/kT| \ll 1$. Then, to first-order small quantities, we obtain:

$$\overline{p}_s = p_\infty e^{-e\overline{\varphi}_s/kT}, \qquad \widetilde{p}_s = \overline{p}_s \left(\frac{\widetilde{p}_d}{p_\infty} - \frac{e\widetilde{\varphi}_s}{kT}\right). \tag{6}$$

Analogous relations may also be written for electrons; in this case, by virtue of the condition of quasineutrality of the diffusion region, $\widetilde{p}_d = \widetilde{n}_d$.

With the aid of (1), using the values of the constant concentrations from (4), (5), and (6), it is easy to find the current-voltage characteristic of the contact

$$\overline{i}_s = \frac{i_0^{(p)}\left(1 - e^{-e(\overline{\varphi}_s - U)/kT}\right) - i_0^{(e)}\left(1 - e^{e(\overline{\varphi}_s - U)/kT}\right)}{1 + \frac{1}{i_{\text{lim}}}\left[i_0^{(p)}\left(1 + \frac{DC_\infty}{D'C'_\infty} e^{e(-\overline{\varphi}_s + U)/kT}\right) + i_0^{(e)}\left(\frac{DC_\infty}{D'C'_\infty} + e^{e(\overline{\varphi}_s - U)/kT}\right)\right]}. \tag{7}$$

According to (7), as $\overline{\varphi}_s \to \infty$, $\overline{i} \to i_{\text{lim}}$; as $\overline{\varphi}_s \to -\infty$, $\overline{i} \to -\dfrac{D'C'_\infty}{DC}\, i_{\text{lim}}$, i.e., the contact has rectifying properties. The ratio $\overline{i}_s(\overline{\varphi}_s = \infty)/i_s(\overline{\varphi}_s = -\infty)$ does not depend on the properties of the semiconductor.

Let us consider the laws governing the passage of an alternating signal. For the alternating components, taking (6) into account, we obtain:

$$\widetilde{i}_s^+ = me\left[k'_1\widetilde{C}_s - k'_2\widetilde{C}'_s\frac{\overline{p}_s}{p_\infty} - \overline{k}'_2\overline{C}'_s\frac{\overline{p}_s}{p_\infty}\left(\frac{\widetilde{p}'_d}{p_\infty} - \frac{e\widetilde{\varphi}_s}{kT}\right)\right],$$

$$\tilde{i}_s^- = me\left[k_2\widetilde{C}_s' - k_1\widetilde{C}_s\frac{\overline{n}_s}{n_\infty} - k_1\overline{C}_s\frac{\overline{n}_s}{n_\infty}\left(\frac{\tilde{p}_d}{p_\infty} + \frac{e\widetilde{\varphi}_s}{kT}\right)\right]. \tag{8}$$

The value of the hole current $\tilde{i}_d^+$ at the boundary of the space-charge region in the diffusion region in an n-type semiconductor is given by expression (2):

$$\tilde{i}_d^+ = e\tilde{p}_d\left[D_+(i\omega + \tau^{-1})\right]^{1/2}, \tag{9}$$

where τ is the hole lifetime. With the aid of (6) and (9) it can be shown that, when the condition

$$\frac{d}{L}(\omega\tau)^{1/2}e^{-e\varphi_s/kT} \ll 1$$

is satisfied (d is the dimension of the space-charge region), the fraction of holes expended in changing the space charge is negligibly small, so that $\tilde{i}_d^+ = \tilde{i}_s^+$.

Substituting in (8) $\tilde{i}^- = \tilde{i}^+ - \tilde{i}$ and eliminating $\tilde{\varphi}_s$ from two relations, we represent the current $\tilde{i}_s^+$ in the form $\tilde{i}_s^+ = \gamma\tilde{i}_s$. For γ, taking into account the condition $n_\infty \gg p_\infty$, we obtain the expression

$$\gamma = \frac{k_2'\bar{C}_s'\dfrac{\bar{p}_s}{p_\infty} + \left(k_2'\dfrac{\bar{p}_s}{p_\infty}\dfrac{\tilde{i}^-}{\sqrt{D'}} - k_1\dfrac{\bar{n}_s}{n_\infty}\dfrac{\tilde{i}^+}{\sqrt{D}}\right)\dfrac{e^{-i\pi/4}}{me\omega^{1/2}}}{k_1\bar{C}_s\dfrac{\bar{n}_s}{n_\infty} + k_2'\bar{C}_s'\dfrac{\bar{p}_s}{p_\infty} + k_1k_2'\bar{C}_s\bar{C}_s'\dfrac{m}{p_\infty}\left[D_+(i\omega + \tau^{-1})\right]^{-1/2}}. \tag{10}$$

Expressing $\tilde{p}_d$ through $\tilde{i}_s$ by means of (9) and (10), and $\tilde{C}_s$ and $\tilde{C}_s'$ through $\tilde{i}_s$ by means of (4) and (5), and using (8), we represent the relation of the current $\tilde{i}_s$ to the potential $\tilde{\varphi}_s$ in the form $\tilde{i}_s = \hat{Z}\tilde{\varphi}_s$, where

$$\hat{Z} = \left(k_2'\bar{C}_s'\frac{\bar{p}_s}{p_\infty} + k_1\bar{C}_s\frac{\bar{n}_s}{n_\infty}\right)\frac{e^2m}{kT}\left\{\left(k_1' + k_1\frac{\bar{n}_s}{n_\infty}\right)\frac{e^{-i\pi/4}}{(D\omega)^{1/2}} + 1 + \right.$$

$$\left. + \left(k_2 + k_2'\frac{\bar{p}_s}{p_\infty}\right)\frac{e^{-i\pi/4}}{(D'\omega)^{1/2}} + \frac{k_2'\bar{C}_s'\dfrac{\bar{p}_s}{p_\infty}\dfrac{1}{p_\infty} - k_1\bar{C}_s\dfrac{\bar{n}_s}{n_\infty}\dfrac{1}{n_\infty}}{\left[D_+(i\omega + \tau^{-1})\right]^{1/2}}\gamma m\right\}^{-1}. \tag{11}$$

If the contact under study is described by an equivalent circuit consisting of a capacitance C_D and a resistance R connected in parallel, then $\hat{Z} = 1/R + i\omega C_D$. Hence, with the aid of (10) and (11), one can find R and C_D in the general form.

The quantity C_D thus found is a purely diffusion capacitance. The total capacitance C is composed of C_D and the electrostatic capacitance C_0 associated with the presence of space charge in the semiconductor. The quantity C_0 has been calculated, for example, in (3).

We shall assume that the relation

$$i_0 \ll i_p(1+\omega\tau)^{1/2} \ll i_D \tag{12}$$

is satisfied.

Here $i_D \equiv emC'_\infty\sqrt{D'\omega}$. Condition (12) is usually satisfied, since the exchange currents at semiconductor contacts are small (4, 5), while $i_p\sqrt{1+\omega\tau} \ll i_D$ already at very low concentrations of reacting ions.

It was previously assumed that $|e\varphi_s/kT| \ll 1$. With the aid of (11) and (12) it is easy to find that this inequality is in any case satisfied if $\tilde{i}_s/i_0 \ll 1$.

When (12) is satisfied, with the aid of (2) and (10) it can be shown that the expression for γ is simplified if the following relation holds:

$$i_0^{(e)} \ll \left| \frac{em(DD'\omega)^{1/2}\bar{C}'_s\, C_\infty\, e^{e(-\bar{\varphi}_s+U)/kT}}{\sqrt{D}\, C_\infty \left(\dfrac{\bar{C}_s}{C'_\infty} e^{e(-\bar{\varphi}_s+U)/kT} - \dfrac{\bar{C}_s}{C_\infty}\right) - \sqrt{D'}\, C'_\infty \left(\dfrac{\bar{C}_s}{C_\infty} e^{e(\bar{\varphi}_s-U)/kT} - \dfrac{\bar{C}'_s}{C'_\infty}\right)} \right|. \tag{13}$$

Condition (13) is in any case satisfied at potentials close to equilibrium, and also at large negative potentials. Let us emphasize that (13) imposes no restrictions on the magnitude of $i_0^{(p)}$. When the···

Substituting (13) into (10), for γ we obtain

$$\gamma = -\frac{k'_2\overline{C}'_s\overline{p}_s/p_\infty}{k_1\overline{C}_s\overline{n}_s/n_\infty + k'_2\overline{C}'_s\overline{p}_s/p_\infty}. \tag{14}$$

As follows from (14), the quantity γ does not depend on frequency, and the ratio of the alternating hole current to the total alternating current does not change during the period. This is due to the fact that, under the assumptions made, the imaginary part of γ is negligibly small. At the equilibrium potential, as one would expect, $\gamma = i_0^{(p)}/i_0$. At large negative potentials $\gamma \to 1$.

Let us find the diffusion capacitance and resistance of the system, assuming that $\gamma \sim 1$ and is given by relation (14). There are two limiting cases. Let

$$\frac{i_0^{(p)}}{i_p(1+\omega\tau)^{1/2}} e^{e(U-\overline{\varphi}_s)/kT} \ll 1.$$

This condition is in any case satisfied near the equilibrium position. For C_D and R, from (11) we obtain

$$C_D = \frac{e\left[i_0^{(p)}\right]^2}{kTi_p}\tau\frac{\left[1+\tau(\tau^{-2}+\omega^2)^{1/2}\right]^{1/2}}{\left[1+\tau(\tau^{-2}+\omega^2)^{1/2}\right]^2+(\omega\tau)^2}, \qquad \frac{1}{R} = \frac{e}{kT}\frac{1}{\gamma}\frac{1}{\overline{C}'_\infty}\overline{C}'_s e^{e(-\overline{\varphi}_s+U)/kT}. \tag{15}$$

Let now the condition

$$e^{e(U-\overline{\varphi}_s)/kT}\frac{i_0^{(p)}}{i_p(1+\omega\tau)^{1/2}} \gg 1$$

be satisfied (the case of large negative potentials). From (11) we obtain

$$C_D = \frac{e^2 p_\infty}{kT}\frac{1}{\gamma^2}\left(\frac{D_+}{2}\right)^{1/2}\frac{1}{\left[\tau^{-1}+(\tau^{-2}+\omega^2)^{1/2}\right]^{1/2}},$$

$$\frac{1}{R} = \frac{e^2 p_\infty}{kT}\frac{1}{\gamma^2}\left(\frac{D_+}{2}\right)^{1/2}\left[\tau^{-1}+(\tau^{-2}+\omega^2)^{1/2}\right]^{1/2}. \tag{16}$$

In both cases the diffusion lag is connected wholly with the semiconductor. The result has a clear physical meaning: since $\gamma \sim 1$, holes take a substantial part in the reaction. On the other hand, according to (12), $i_D \gg i_p(1+\omega\tau)^{1/2}$, i.e., the reacting ions are present in excess. Hence the lag is caused only by hole diffusion.

Consider the case $|\gamma| \ll 1$, which occurs if

$$i_0^{(p)} e^{-2e(\varphi_s-U)/kT} \ll i_0^{(e)},$$

or if the condition opposite to (13) is satisfied. From (11) we obtain

$$C_D = \frac{1}{R}\frac{1}{\omega^{3/2}}\left[\left(k'_1+k_1\frac{\overline{n}_s}{n_\infty}\right)\frac{1}{(2D)^{1/2}}+\left(k_2+k'_2\frac{\overline{p}_s}{p_\infty}\right)\frac{1}{(2D')^{1/2}}\right],$$

$$\frac{1}{R} = \frac{e}{kT}\left[i_0^{(p)}\frac{\overline{C}'_s}{\overline{C}'_\infty}e^{e(U-\overline{\varphi}_s)/kT}+i_0^{(e)}e^{e(\overline{\varphi}_s-U)/kT}\frac{\overline{C}_s}{\overline{C}_\infty}\right]. \tag{17}$$

As should also have been expected in accordance with what was said, at $|\gamma| \ll 1$ the diffusion effects turn out to be connected wholly with the electrolyte. C_D decreases as $\sim \omega^{-3/2}$. For the resistance at the equilibrium potential, from (17) and (15) we obtain the well-known expression $R = kT/ei_0$. A comparison of relations (15), (16), and (17) shows that the diffusion capacitance C_D increases with increasing $|\gamma|$ and with increasing cathodic potential, reaching values of the order

$$C_D \sim \frac{e\tau}{kT} i_p.$$

Estimates show that in the latter case the diffusion capacitance may considerably exceed the space-charge capacitance.

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