POLARIZATION CURVE OF THE ANODIC DISSOLUTION OF GERMANIUM OF FINITE DIMENSIONS

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Abstract

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POLARIZATION CURVE OF THE ANODIC DISSOLUTION OF GERMANIUM OF FINITE DIMENSIONS

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In work (1) the process of dissolution of germanium was considered under the assumption that the semiconductor adjoining the electrolyte has unbounded dimensions. Below, we shall consider the process of dissolution of germanium in the case when the length of the semiconductor is comparable with the diffusion length or smaller than it. Such investigations have been carried out by a number of experimenters, for example in works (2, 3). It therefore seems reasonable to carry out numerical calculations for this case. One may also hope that the study of the dissolution processes of semiconductors of finite length will shed further light on the understanding of the kinetics of semiconductor dissolution. Indeed, as we shall see below, the limiting current depends on the dimensions of the semiconductor. The value of the limiting current is connected with the magnitude r/m (1), i.e., with the ratio of electrons and holes which, respectively, are evolved or consumed when a germanium atom passes into solution. By comparing the theory with experiment, it may be possible to investigate the degree of participation of electrons and holes in the reaction as a function of various physical characteristics, for example of the magnitude of the electric fields at the contact, etc.

We shall henceforth consider a one-dimensional problem. Let us introduce the x-axis, perpendicular to the germanium—electrolyte boundary. We shall assume that the plane $x = 0$ corresponds to the germanium—electrolyte interface. In the region $x < 0$ the electrolyte is located, and in the region $x > 0$ there is n-type germanium. In the plane $x = w$ there is an ohmic contact.

In accordance with works (4, 5) we shall characterize the ohmic contact by the magnitude of the surface recombination velocity. In other words, we shall assume that the hole current flowing through the ohmic contact is determined by the relation

$$j_p = e[p(w) - p_n]S, \tag{1}$$

where e is the absolute value of the electron charge; p_n is the concentration of holes in a homogeneous equilibrium semiconductor; $p(w)$ is the concentration of holes in the plane of the ohmic contact; S is the constant of the surface recombination velocity.

The region adjoining the ohmic contact is uncharged, and minority carriers in this region move by the diffusion mechanism. We therefore have the following equation relating the hole current to the change in the concentration of holes in the diffusion region:

$$j_p = -eD_p \frac{dp}{dx}. \tag{2}$$

Here D_p is the diffusion coefficient of holes in the diffusion region. When holes pass through the diffusion region, recombination takes place.

holes. This process, as usual, is described by the equation

$$\frac{\partial p}{\partial t} = -\frac{p - p_n}{\tau_p}, \tag{3}$$

where τ_p is the lifetime of holes; dp/dt is the number of holes absorbed per unit time.

The continuity equation for holes has the form

$$\frac{dj_p}{dx} = e\,\frac{p_n - p}{\tau_p}. \tag{4}$$

Using (2), we obtain

$$\frac{p_n - p}{\tau_p} + D_p \frac{d^2 p}{dx^2} = 0. \tag{5}$$

Equation (5) determines the law of variation of the hole concentration along the semiconductor and is a second-order equation. Its solutions contain two arbitrary constants, for whose determination boundary conditions must be formulated.

In the plane of the ohmic contact, evidently, the relation

$$-eD_p \left.\frac{dp}{dx}\right|_{x=w} = w = e[p(w) - p_n]S. \tag{6}$$

must hold.

Equation (6) is a boundary condition for our problem. To describe the distribution of holes in the near-contact Debye layer, one should use the equation

$$j_p = eu_p pE - eD_p \frac{dp}{dx}. \tag{7}$$

The germanium surface is strongly enriched with holes at the contact. Since the change in the hole concentration occurs over distances of the order of 10^{-4} cm, there are large gradients of the hole concentration; therefore the diffusion currents are always large in comparison with all currents j_p used in electrochemistry, and the latter may be neglected. Putting $j_p = 0$ in (7), we immediately arrive at the Boltzmann-law distribution of holes. These considerations make it possible to relate the hole concentration at the contact to the concentration at the boundary of the diffusion region.

At equilibrium, in accordance with what was said above, we have the relation

$$p_k(j = 0) = p_n e^{-e\varphi/kT}, \tag{8}$$

where $p_k(j = 0)$ is the equilibrium concentration of holes at the contact with the electrolyte, φ is the equilibrium potential difference dropping in the semiconductor.

When an external potential u is applied, a current j begins to flow through the system. The concentration at the contact is related to the concentration at the boundary with the quasineutral region $p(x_a)$ by the dependence

$$p_k(j) = p(x_a) e^{-e(\varphi+u)/kT}. \tag{9}$$

Eliminating the quantity $e^{e\varphi/kT}$ from relations (8) and (9), we obtain

$$p(x_a) = \frac{p_k(j)}{p_k(j = 0)} p_n e^{eu/kT}. \tag{10}$$

Equation (10) is the boundary condition for equation (5) on the side of the germanium-electrolyte contact.

As in work (^{1}), we assume that recombination of electrons and holes in the Debye region is negligible. Therefore the equality is obvious

$$j_p(x = 0) = j_p(x_a), \tag{11}$$

which means that the hole current does not change in passing through the Debye region.

The solution of equation (5) with boundary conditions (6) and (10) has the form

$$p(x) = p_n + p_n \left[\frac{p_k(j)}{p_k(j=0)} e^{eu/kT} - 1 \right] \frac{D_p \operatorname{ch} \frac{x-w}{L_p} - SL_p \operatorname{sh} \frac{x-w}{L_p}}{D_p \operatorname{ch} \frac{w}{L_p} + SL_p \operatorname{sh} \frac{w}{L_p}}. \qquad (12)$$

With the aid of equations (2) and (12), one can find the hole current at the point $x = x_a$. We have

$$j_p(x_a) = j_p(x=0) = \left[\frac{p_k(j)}{p_k(j=0)} e^{eu/kT} - 1 \right] j_1, \qquad (13)$$

where j_1 is determined by the formula

$$j_1 = \frac{eD_{pp}n}{L_p} \frac{D_p \operatorname{sh} \frac{w}{L_p} + SL_p \operatorname{ch} \frac{w}{L_p}}{D_p \operatorname{ch} \frac{w}{L_p} + SL_p \operatorname{sh} \frac{w}{L_p}}. \qquad (14)$$

In obtaining relations (13) and (14) we used the fact that $x_a \ll L_p$, $x_a \ll w$.

To obtain the polarization curve, we must find the dependence of the total current j on the magnitude of the applied total voltage. In doing so it should be remembered that the total potential ψ is equal to $\psi = u + \Delta\psi_1$, where $\Delta\psi_1$ is the potential drop in the Helmholtz part of the double layer.

In accordance with work (^{1}), we shall assume that the ratio of the electron current to the hole current is a prescribed quantity, i.e., we suppose that the relation

$$\frac{j_p(0)}{j_e(0)} = \frac{r}{m}, \qquad (15)$$

is satisfied, where j_e is the electron current. Hence we obtain

$$j_p(0) = j \frac{r}{m+r}, \qquad (16)$$

where j is the total current flowing through the contact.

With the aid of relations (13) and (15), one can find the dependence between the total current j and the voltage drop in the semiconductor. For the potential we have the expression

$$\frac{eu}{kT} = -\frac{\ln p_k(j)}{p_k(j=0)} + \ln\left(1 + \frac{j}{j_1} \frac{r}{m+r}\right). \qquad (17)$$

To obtain the total potential drop, one must add also the potential drop in the Helmholtz region. This potential drop $\Delta\psi_1$ is related to the total current by the relation from the theory of slow discharge (^{1})

$$j = -j_0 \left(\frac{p_k(j)}{p_k(j=0)} \right)^{\rho} e^{\beta(\Delta\psi_1 + \Delta\psi_0)/kT}.$$

Determining $\Delta\psi_1$ from this and adding this value to the left-hand side of equation (17), we find the total voltage drop

$$\psi = \frac{1}{\beta} \ln \left(-\frac{j}{j_0} \right) + \left(1 - \frac{\rho}{\beta} \right) \ln \frac{p_k(j)}{p_k(j=0)} - \ln \left(1 + \frac{j}{j_1} \frac{r}{m+r} \right). \tag{18}$$

Expression (18) is, strictly speaking, the polarization characteristic of the anodic dissolution of germanium. Indeed, it can be shown that the quantity $\ln \frac{p_k(j)}{p_k(j=0)}$ is, generally speaking, a quantity that varies only weakly in comparison with the first and third terms. This can be done by investigating the behavior of holes and electric fields in the Debye layer.

Let us now proceed to consider the polarization characteristic. At small currents, when $|j/j_i| \ll 1$, a logarithmic dependence of the current on the voltage should be observed, i.e., the usual Tafel law.

Since the current $j < 0$, the presence of the third term indicates the existence of a limiting current, whose value is equal to:

$$j_{\text{lim}} = \left(1 + \frac{m}{r} \right) \frac{eD_p p_n}{L_p} \frac{D_p \operatorname{sh} \frac{w}{L_p} + SL_p \operatorname{ch} \frac{w}{L_p}}{D_p \operatorname{ch} \frac{w}{L_p} + SL_p \operatorname{sh} \frac{w}{L_p}}. \tag{19}$$

One can find the dependence of the limiting current on distance for $w \to \infty$. In this case the formula for j_{lim} has the form

$$j_{\text{lim}} = \left(1 + \frac{m}{r} \right) \frac{eD_p p_n}{L_p} = e^2 n_i^2 D_p \mu \frac{\rho}{L_p} \left(1 + \frac{m}{r} \right).$$

This expression coincides with the result obtained in work (^{1}).

In the limiting case $w \ll L_p$, the hyperbolic cosines and sines can be expanded in series, and for the limiting current the expression obtained is

$$j_{\text{lim}} = \left(1 + \frac{m}{r} \right) \frac{eD_p p_n}{L_p} \frac{D_p \frac{w}{L_p} + SL_p}{D_p + Sw}. \tag{20}$$

For $S \to \infty$, the limiting current tends to the value

$$j_{\text{lim}} = \left(1 + \frac{m}{r}\right) \frac{eD_p p_n}{L_p} \operatorname{cth} \frac{w}{L_p}. \tag{21}$$

For small S, expression (19) can be expanded in a series, and we find:

$$j_{\text{lim}} = \left(1 + \frac{m}{r}\right) \frac{eD_p p_n}{L_p} \left(\operatorname{th} \frac{w}{L_p} + \frac{SL_p}{D_p \operatorname{ch}^2 \frac{w}{L_p}} \right).$$

The expressions obtained determine the limiting current in different cases.

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CITED LITERATURE

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