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Abstract

Full Text

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On the Theory of the Anodic Dissolution of Silicon

(Presented by Academician A. N. Frumkin, 11 III 1961)

The process of the anodic dissolution of silicon differs substantially from the analogous process of germanium dissolution. In silicon, as was shown in papers ([1,2]), recombination of carriers in the near-contact region plays a significant role, whereas in germanium this process is, on the contrary, negligible. In germanium the holes needed for dissolution are supplied to the contact from the bulk by the forces of the electric field and by the diffusion mechanism. In the dissolution of silicon these two mechanisms also occur; however, it is absolutely necessary to take into account the generation of carriers in the Debye layer. It is evident that allowance for the latter process leads to an increase in the maximum possible current flowing through the contact.

Indeed, without taking into account the current associated with the generation of holes, the formula for the saturation current would have the same form as for germanium ([3])

$$j_{\text{sat}} = \frac{r+m}{r} n_i^2 D_+ e^2 u_- \frac{\rho}{L}, \tag{1}$$

where n_i is the number of carriers in intrinsic silicon. n_i is related to the band-gap width ΔE by the relation

$$n_i \approx e^{-\Delta E/2kT}. \tag{2}$$

Since for silicon the band-gap width is considerably larger than for germanium, in accordance with formulas (1) and (2), other conditions being equal, the saturation current for silicon should be considerably smaller than for germanium.

However, it is known from experiment that the limiting currents for germanium and silicon are quantities of the same order. This reasoning also indicates the necessity of taking into account carrier generation in the semiconductor. Carrier generation may occur as a result of surface and bulk recombination. Flynn ([2]) estimated the value of the surface recombination needed to pass the observed currents in silicon. The value found, in his opinion, is too large to be observed in practice. By examining formula (23) of paper ([3]), one can arrive at an analogous conclusion. Thus, it is evident that carrier generation must be taken into account in the near-contact layer.

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Let us now proceed to the calculation of the current-voltage characteristic of the anodic dissolution of electronic silicon. In silicon in contact with an electrolyte there are two characteristic lengths: the diffusion length and the Debye length, the first being considerably larger than the second. At distances of the order of the diffusion length, the density of majority carriers changes essentially not at all. In the diffusion region (called quasineutral) there are weak electric fields. The equations characterizing the physical quantities in this region are analogous to the equations in the theory of germanium (equations $(1')$–$(4')$ of paper [3]).

The relation between the hole density and the hole current is given by the relation ((3); below we use the notation adopted in this work)

$$p = b + \frac{\lambda_+}{\sqrt{AK}}. \tag{3}$$

In the region adjacent to the electrolyte, in the Debye layer, the main potential drop occurs and the carrier density changes substantially. In this same region the n–p junction is located. We shall further assume that in silicon, as in germanium, the surface at the contact is enriched with holes. As in germanium, the region immediately adjacent to the quasineutral one is depleted of carriers. For silicon in this region their generation is substantial.

In this depleted region $n \ll 1$; $p \ll 1$. To describe the processes we have the following equations:

$$\frac{dz}{dt} = zy + \lambda_-; \tag{4}$$

$$\frac{dp}{dt} = -py - \frac{1}{k}\lambda_+; \tag{5}$$

$$\frac{d\lambda_-}{dt} = A_1(zp - b); \tag{6}$$

$$\frac{dy}{dt} = z - p - 1, \tag{7}$$

where, in accordance with work [4], the quantity A_1 is equal to

$$A_1 = \frac{e_1}{\left[(n + n_1)\tau_{p_0} + (p + p_1)\tau_{n_0}\right] u_- kT\chi^2}.$$

Here

$$n_1 = \frac{n_i}{N_-} \exp\frac{E_t - E_i}{kT}; \qquad p_1 = \frac{n_i}{N_-} \exp\frac{E_i - E_t}{kT};$$

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n_i is the number of electrons in the intrinsic semiconductor; N_n and $pN_$ are, respectively, the densities of electrons and holes at the points where recombination occurs; τ_{n_0} is the lifetime of electrons introduced into an n-type specimen; τ_{p_0} is the lifetime of holes introduced into a p-type specimen; E_t is the trap energy; E_i is the Fermi level in the intrinsic semiconductor.

In accordance with the usual assumptions used in the physics of silicon rectifiers, we take $n \ll n_1,\ p < p_1$. Then we obtain:

$$A_1 = \frac{eN_}{n_i\left[\tau_{p_0}\exp\frac{E_t-E_i}{kT}+\tau_{n_0}\exp\frac{E_i-E_t}{kT}\right]V_kT\chi^2}.$$

In accordance with what was said earlier, in equation (7) one may neglect the quantities z and p in comparison with unity. Since the entire potential applied to the contact falls over distances of the order of 10^{-4} cm, in this region we have strong electrolytic fields. Therefore, in equations (4) and (5) one may also neglect the terms λ_+ and $\lambda_$. Under these assumptions we find the distribution of charge density as a function of the electric field

$$z = e^{-y^2/2}; \tag{8}$$

$$p = \left[b + \frac{\lambda_+(t_0)}{\sqrt{Ak}}\right]e^{y^2/2}; \tag{9}$$

here $\lambda_+(t_0)$ is the value of the hole current at the boundary of the quasineutral and Debye regions. Substituting the values of z and p into equation (6) and integrating it, we find the dependence of the hole current on the electric field

$$\lambda_+ = \frac{A_1\lambda_+(t_0)y}{\sqrt{Ak}}. \tag{10}$$

As in the theory of germanium dissolution at large currents, the potential drops in the carrier-depleted layer and is equal to[3]

$$\psi = -\ln\left(b + \frac{\lambda_+(t_0)}{\sqrt{Ak}}\right) = \frac{y_k^2}{2}, \tag{11}$$

while the potential drop taking into account the Helmholtz layer is equal to

$$\psi = \psi_0 + \frac{1}{\beta}\ln\frac{-\lambda}{\lambda_0} - \ln\left[b + \frac{\lambda_+(t_0)}{\sqrt{Ak}}\right].$$

Assuming that the hole current at the contact is related to the electronic one by the ratio

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$$\frac{\lambda_+(0)}{\lambda_-(0)} = \frac{r}{m}, \tag{12}$$

we obtain two equations relating y_k and λ_+ to the total current λ:

$$\frac{r}{m+r}\lambda = A_1 \frac{\lambda_+(t_0)}{\sqrt{Ak}}\, y_k; \tag{13}$$

$$y_k = -2\ln\left(b + \frac{\lambda_+(t_0)}{\sqrt{Ak}}\right). \tag{14}$$

Equations (11), (13), and (14) are parametric equations determining the potential ψ as a function of the total current λ. At relatively large potentials and currents, in the case when the relation

$$b - \frac{\lambda_+(t_0)}{\sqrt{Ak}} = \eta \ll b,$$

is satisfied, the equations can be solved, and we find

$$\psi = -\frac{1}{2b^2A_1^2}\left(\frac{r}{r+m}\right)^2 \lambda^2 + \frac{1}{\beta}\ln\frac{-\lambda}{\lambda}. \tag{15}$$

The results obtained agree qualitatively with experiment. Indeed, at small λ the first term in (15) is insignificant, and we observe a logarithmic dependence of the current on the voltage. At large currents, however, the parabolic dependence of the current on the voltage becomes decisive. One can estimate the value of the current λ_1 at which the transition from the logarithmic dependence to the parabolic one occurs. For this, the derivatives should be equated:

$$\frac{d}{d\lambda}\frac{1}{\beta}\ln\lambda = \frac{d}{d\lambda}\frac{1}{2b^2A_1^2}\left(\frac{r}{m+r}\right)^2\lambda^2.$$

In order of magnitude we obtain from this the value

$$\lambda_1 \simeq bA_1,$$

or, passing to dimensional variables, we find

$$j_1 = \frac{en_i}{\left[\tau_{p_0}\exp\frac{E_t-E_i}{kT} + \tau_{n_0}\exp\frac{E_i-E_t}{kT}\right]\varkappa}, \tag{16}$$

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where $1/\varkappa$ is the length of the charged Debye region. Formula (16) agrees with Flynn' s data[2]. In work[2], the following values are adopted for the characteristics of the semiconductors used in the experiments: $1/\varkappa = 10^{-4}$ cm, $E_t - E_i = 4.6\,kT$, $\tau_{p_0} = 1.2 \cdot 10^{-8}$ sec, $\tau_{n_0} = 4.3 \cdot 10^{-6}$ sec.

In this case the current j_1 proves to be equal to $j_1 = 0.6 \cdot 10^{-6}$ A/cm^2, which is in good agreement with experiment.

Using formula (15), one can find the dependence of the current on the resistance of silicon in the parabolic region. Approximately, the following dependence holds:

$$j \sim \sqrt{R_\varphi}.$$

In work ([1]), an increase in current with increasing silicon resistance was indeed observed. A more precise quantitative comparison of theory with experiment is at present difficult.

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

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