Soviet-era science, translated into English

A. A. YAKOVLEVA, T. I. BORISOVA, and V. I. VESELOVSKII

1960

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196001.93952

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

PHYSICAL CHEMISTRY

A. A. YAKOVLEVA, T. I. BORISOVA, and V. I. VESELOVSKII

THE ACTION OF OPTICAL RADIATION ON AN ANODICALLY POLARIZED GERMANIUM ELECTRODE

(Presented by Academician A. N. Frumkin, March 18, 1960)

The anodic behavior of a germanium electrode in electrolyte solutions has been studied by many authors ([1–6]), and, although the mechanism of anodic dissolution is not yet entirely clear, it may be asserted that this process proceeds, first, with consumption of holes and that the existing saturation current for the n-type is determined by their bulk thermal generation, and, second, that germanium passes into solution in the form of a complex oxygen ion. It is known that anodically polarized n-Ge possesses great photosensitivity; however, the principal photoelectrochemical relationships are, with few exceptions ([1]), absent from the literature.

The investigation undertaken in the present work had as its aim to determine the influence of irradiation on the structure of the germanium–electrolyte phase boundary and on the mechanism of the anodic dissolution process of germanium. When various kinds of radiation are used, it is desirable to be able to irradiate the electrode in such a way as to avoid the action on it of components of radiolysis of the solution (in the case of ionizing radiation). For this purpose a method was developed which permits irradiation of the specimen both from the dry side and from the solution side.

The apparatus consisted of a Teflon cylindrical vessel, one end face of which was a quartz window, the other–the specimen under study, in the form of a disk of various thicknesses with crystallographic orientation (111). On the dry side of the specimen a circular ohmic contact was soldered. All investigations were carried out on single-crystal n-type germanium of various specific resistivities in $0.1\,N$ NaOH in a nitrogen atmosphere. The specimens were ground and etched in the standard CP-4 etchant, after which they were thoroughly washed with bidistillate. Monochromatic radiation from an incandescent lamp was used in the wavelength interval 0.4—$0.7\,\mu$. Irradiation was carried out either at constant current through the system or at constant potential of the system. As can be seen from Fig. 1, the system is photosensitive over the entire range of polarization applied. Upon illumination of the n-anode the entire potential barrier is removed by the light, i.e., the potential in the saturation region everywhere falls

Figure 1

Figure 1: Figure 1

Fig. 2

Figure 2: Fig. 2

to the constant value 0.5 V. Above the breakdown potential the effect rapidly dies away.

Fig. 1. Dependence of photoelectrochemical parameters on polarization for n-Ge 3/07 in 0.1 N NaOH.

The process of anodic dissolution can be represented by the overall reaction (^{2}):

$$\mathrm{Ge} + 2\mathrm{OH}^- + 2e \rightarrow \mathrm{Ge(OH)}_2^{2+} + 2e.$$

Under illumination, in the initial portion of the polarization curve (the Tafel region), the value of the slope "b" decreases from 110 mV in the dark to 80 mV under intense illumination (Fig. 2). In this region the rate of the anodic reaction is not limited by the concentration of minority carriers. However, in the nonequilibrium state, when anodic current passes, part of the measured potential drop occurs in the space-charge region of the semiconductor. In this case, as was shown earlier by one of the authors (^{7}), the rate of the anodic reaction may be represented by the dependence

$$i = ke^{-\Delta\psi F/RT} e^{-\alpha \Delta H F/RT}, \tag{1}$$

where $\Delta\psi$ is the change in potential in the space-charge region of the semiconductor, and ΔH is the change in potential in the ionic double layer.

Fig. 2. Dependence of i_t (1) and i (2) on potential in the Tafel region

Fig. 3. Dependence of Δi (1, 2, 3) and $\Delta\varphi$ (4, 5, 6) on intensity for potentials 0.5, 3, and 5 V, respectively

In turn, $\Delta\psi$ is related to the change in carrier concentration at the surface by the relation

$$C \quad = C \; e^{-ne\Delta\psi/kT}. \tag{2}$$

Fig. 3

Figure 3: Fig. 3

Thus, all factors that affect the surface concentration of electrons and holes (surface treatment, polarization, illumination) must change $\Delta\psi$ and the total measured potential difference $\Delta\varphi$.

Light, being absorbed in the surface layer, changes the concentration and distribution of carriers, as a result of which the energy levels change in such a way that, for an n-anode, the measured potential difference decreases owing to a reduction of its share in the space-charge region of the semiconductor. It follows from equation 1 that, with a decrease in $\Delta\psi$ under illumination, the magnitude of the slope "v" must also decrease.

The dependence of the photoelectrochemical characteristics Δi_{sv} and $\Delta\varphi_{\text{sv}}$ on the intensity of the incident radiation for all polarization regions is shown in Fig. 3. In all cases the photoelectrochemical current increases linearly with an increase in the number of absorbed quanta. The relation of $\Delta\varphi_{\text{sv}}$ to intensity is more complicated. In the Tafel region, $\Delta\varphi_{\text{sv}}$ changes exponentially with intensity; in the saturation-current region, $\Delta\varphi_{\text{sv}}$ tends toward a certain limiting value at high intensities; above the breakdown potential, the potential barrier changes little with decreasing intensity.

Table 1

L_{inc}, cal/cm · sec	Δi (theor.)	Δi_{sv} (meas.)	$h\nu$, eV	K
$1.2 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$	$3.6 \cdot 10^{-4}$	1.8	2.6
$0.6 \cdot 10^{-4}$	$7 \cdot 10^{-5}$	$18.2 \cdot 10^{-5}$	1.8	2.6
$0.3 \cdot 10^{-4}$	$3.5 \cdot 10^{-5}$	$9.1 \cdot 10^{-5}$	1.8	2.6
$1.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$4.55 \cdot 10^{-5}$	1.8	3.2
$0.6 \cdot 10^{-5}$	$0.7 \cdot 10^{-5}$	$2.6 \cdot 10^{-5}$	1.8	3.7
$0.3 \cdot 10^{-5}$	$0.35 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$	1.8	4.5

An important characteristic of the system is the quantum yield of the photoelectrochemical process. Table 1 gives the values of the quantum yield for different intensities of absorbed radiation at the potential of the saturation region. The quantum yield increases with decreasing intensity at small L and remains constant at large L. Evidently, in this case recombination effects are enhanced. Table 2 gives

Table 2

φ_{t}	L_{abs}	$h\nu$, eV	Number of incident quanta	Δi_{sv}	Electron yield	K
0.45	$0.6 \cdot 10^{-4}$	1.8	$8.65 \cdot 10^{14}$	$10.4 \cdot 10^{-5}$	$6.4 \cdot 10^{14}$	0.73

SovietRxiv

Fig. 4

Figure 4: Fig. 4

φ_t	L_{abs}	$h\nu$, eV	Number of incident quanta	Δi_{sv}	Electron yield	K
3	$0.6 \cdot 10^{-4}$	1.8	$8.65 \cdot 10^{14}$	$36.0 \cdot 10^{-5}$	$22.3 \cdot 10^{14}$	2.6
6	$0.6 \cdot 10^{-4}$	1.8	$8.65 \cdot 10^{14}$	$18.2 \cdot 10^{-5}$	$11.3 \cdot 10^{14}$	1.3
0.45	$0.6 \cdot 10^{-5}$	1.8	$8.65 \cdot 10^{13}$	$17.5 \cdot 10^{-5}$	$10.8 \cdot 10^{13}$	1.24
3	$0.6 \cdot 10^{-5}$	1.8	$8.65 \cdot 10^{13}$	$4.55 \cdot 10^{-5}$	$28.2 \cdot 10^{13}$	3.2
6	$0.6 \cdot 10^{-5}$	1.8	$8.65 \cdot 10^{13}$	$2.5 \cdot 10^{-5}$	$15.8 \cdot 10^{13}$	1.8

the values of K for two intensities. K has a maximum in the saturation region. The magnitude of the quantum yield, which is greater than unity and varies from one and a half to four, is noteworthy. The nature of this phenomenon is apparently the same as that of the so-called current multiplication factor noted by a number of authors ($^{1-3}$). In our experiments this quantity varied from one and a half to four, depending on the experimental conditions. In the present communication there is no possibility of discussing this question; however, it should be noted that if the very fact of multiplication is apparently connected with the nature of the electrochemical reaction, then the absolute magnitude of the coefficient depends on the conditions of carrier recombination at the surface. Since the excess carriers created by light are in thermal equilibrium with the lattice for the overwhelming part of the time, they participate in multiplication

of current by the same mechanism as the dark currents, which explains the high value of the quantum yield.

For a broader use of the method described, it was of interest to determine the dependence of the photoelectrochemical parameters on the electrode thickness when irradiated from the dry side. Obviously, in this case the photoelectrochemical current Δi_{sv} will depend strongly on recombination effects in the bulk of the sample and on its surface.

Fig. 4. *a*—dependence of Δi_{sv} on electrode thickness for low-resistance Ge; *b*—for high-resistance Ge: 1 and 3—$\Delta \varphi_{sv}$ and Δi_{sv} from the dry side, 2 and 4—the same from the electrolyte side.

In the case of high-resistance germanium ($\rho = 28\ \Omega \cdot \text{cm}$ and diffusion length

1.8 mm), already at a plate thickness of 0.5 mm the difference in the values of Δi_{sv} and $\Delta\varphi_{\text{sv}}$ under irradiation from the dry side and from the solution side is insignificant (Fig. 4b). For a low-resistance germanium sample with $\rho = 2\ \Omega \cdot \text{cm}$ and $L = 0.5$ mm, the obtained relation of Δi_{sv} to the electrode thickness is presented in Fig. 4a. As is evident from the figure, Δi_{sv} increases linearly with an increase in the reciprocal thickness of the electrode. Thus, no differences were found in the character of the action of radiation from the dry side and from the electrolyte side, and complete quenching under irradiation from the dry side occurs at plate thicknesses several times greater than the diffusion length of the minority carriers.

Physical-Chemical Institute
named after L. Ya. Karpov

Received
18 III 1960

REFERENCES

1. W. Brattain, G. Garret, Bell Syst. Techn. J., **34**, 129 (1955).
2. D. R. Turner, J. Electrochem. Soc., **103**, No. 4, 252 (1956).
3. B. F. Vinin, J. Electrochem. Soc., **105**, No. 12, 715 (1958).
4. J. Bardeen, Zs. phys. Chem., **17**, 39 (1958).
5. E. A. Efimov, I. G. Erusalimchik, ZhFKh, **32**, 1103 (1958).
6. H. Gerischer, F. Beck, Zs. Electrochem., **63**, No. 4 (1959).
7. V. I. Veselovskii, ZhFKh, **22**, 1427 (1948).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.