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Abstract

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Kinetics of Electrode Processes and the Mechanism of Self-Dissolution of Germanium of n- and p-Types with Different Resistivity

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In our previous works ([1,2]) it was shown that the processes of hydrogen evolution and hydrogen peroxide reduction on hole-type germanium are strongly inhibited, i.e., they proceed at a considerably lower rate than on n-type germanium. Since, in their chemical composition and surface state, n- and p-germanium practically do not differ from each other, the differences in their semiconductor properties must be invoked to explain the results obtained.

In a number of works ([3,4]) the supposition is expressed that the difference in the rate of hydrogen evolution on n- and p-germanium is connected with participation in this reaction only of electrons from the conduction band. For n-type germanium, free electrons are the majority charge carriers; their concentration here is sufficiently high, and therefore reduction reactions on n-type germanium involving free electrons should proceed without hindrance.

For hole-type germanium, the rate of the cathodic process under such a reaction mechanism is limited by the low concentration of free electrons. Analogously to the limiting current for holes for electron-type germanium under anodic polarization, on the cathodic polarization curves for p-germanium there should in this case be observed a region corresponding to the "limiting" current for free electrons. The magnitude of the "limiting" cathodic current should depend on the resistivity of the specimen, increasing with increasing resistivity ρ at the same value of the diffusion length L of the minority carriers, or with increasing ratio ρ/L ([5]).

Proceeding from general concepts of semiconductor physics, however, in cathodic reduction reactions on semiconductors, not only free electrons but also electrons from the valence band can in principle participate, which in a number of cases has been confirmed experimentally ([6,7]). Energetically this is possible provided that the energy level to which the electron passes in the reduction process lies below the Fermi level of germanium. The share of the participation of electrons from the different bands in this case will be determined by the type of conductivity of the germanium, the energy position of the level to which the electron passes in the reduction process, and the magnitude of the potential of the given cathodic reaction, i.e., it depends on the nature both of the semiconductor and of the ion being reduced.

On the basis of these concepts, we suggested that in the reaction of cathodic reduction of hydrogen peroxide on *p*-germanium, electrons from the valence band take part preferentially (1). In this case, with an increase in the resistivity of hole-type germanium

(i.e., when the concentration of holes in it decreases) the rate of the cathodic process should decrease, owing to the formation of a greater depletion of holes in the near-surface layer of the electrode. The change in the rate of the cathodic process on *p*-germanium as a function of its resistivity may thus be an indirect criterion of the correctness of one of the above mechanisms of the cathodic reaction.

Fig. 1. Cathodic polarization of germanium in an H_2SO_4 solution (pH = 1.0). *p*-type germanium: 1—$\rho = 1.3\ \Omega \cdot \text{cm}$; 2—$\rho = 12\ \Omega \cdot \text{cm}$; 3—$\rho = 20\ \Omega \cdot \text{cm}$. *n*-type germanium: 4—$\rho = 1.0\ \Omega \cdot \text{cm}$; 5—$\rho = 10\ \Omega \cdot \text{cm}$; 6—$\rho = 20\ \Omega \cdot \text{cm}$.

Fig. 2. Cathodic polarization of germanium in an H_2SO_4 solution (pH = 1.0) $+0.2\,N$ H_2O_2. *p*-type germanium: 1—$\rho = 1.3\ \Omega \cdot \text{cm}$; 2—$\rho = 20\ \Omega \cdot \text{cm}$. *n*-type germanium: 3—$\rho = 1\ \Omega \cdot \text{cm}$; 4—$\rho = 20\ \Omega \cdot \text{cm}$.

In the present work we carried out polarization measurements and determined the rate of self-dissolution for *n*- and *p*-germanium with different resistivities.

Below is given the characterization of the germanium used in our work*.

	Germanium *n*-type	Germanium *p*-type
Resistivity ρ, $\Omega \cdot \text{cm}$	1.0; 10.0; 20.0	1.3; 12.0; 20.0
Diffusion length L, mm	0.5; 1.3; 1.5	0.4; 1.0; 1.5
ρ/L	2.0; 7.7; 13.3	3.2; 12.0; 13.3

All experiments were carried out in solutions: H_2SO_4 (pH 1.0); H_2SO_4 (pH 1.0) $+0.2\,N$ H_2O_2; $0.5\,N$ Na_2SO_4 + $0.05\,N$ $K_3Fe(CN)_6$, and, in procedure, corresponded to the conditions of our previous measurements (1).

The results obtained are presented in Figs. 1, 2, 3. For *n*-type germanium the rate of the cathodic process is practically independent of its resistivity**. For hole-type germanium (Figs. 1, 2) the degree of retardation

* It should be noted that, for these germanium samples, the change in resistivity considerably exceeded the change in diffusion length.

** In all figures, the polarization curves are given with allowance for the ohmic potential drop in the bulk of the sample.

Fig. 3

Figure 1: Fig. 3

of the cathodic reactions of hydrogen evolution and reduction of H_2O_2, the higher the resistivity of *p*-germanium, i.e., the lower the concentration of majority carriers in it. The cathodic polarization curves for *p*-germanium in an H_2SO_4 solution (pH 1.0) and in H_2SO_4 (pH 1.0) + 0.2 N H_2O_2 have a constant slope and do not show a region corresponding to a limiting current due to free electrons. The rate of cathodic reduction of $[Fe(CN)_6]^{3-}$ on *p*-germanium over a wide range of current densities proves to be even higher than on *n*-type germanium and, for hole germanium, does not depend on its resistivity (Fig. 3). The sharp change in the slope of the polarization curves for *n*- and *p*-germanium is connected in this case with attainment of the limiting current for $[Fe(CN)_6]^{3-}$ ions.

Fig. 3. Cathodic polarization of germanium in a solution of 0.5 N Na_2SO_4 + 0.05 N $K_3[Fe(CN)_6]$. *p*-type germanium: $1 - \rho = 1.3$ ohm · cm; $2 - \rho = 12$ ohm · cm; $3 - \rho = 20$ ohm · cm. *n*-type germanium: $4 - \rho = 1$ ohm · cm; $5 - \rho = 10$ ohm · cm; $6 - \rho = 20$ ohm · cm.

The decrease we observed in the discharge rate of hydrogen ions and in the reduction of H_2O_2 on hole germanium as its resistivity increases (or, correspondingly, as the ratio ρ/L increases), and the absence on the curves of a limiting current for minority carriers, shows that the assumption that only free electrons participate in these reactions is apparently incorrect. The experimental results obtained confirm our hypothesis of the predominant participation in these cathodic processes of the majority current carriers, i.e., free electrons for *n*-germanium and electrons from the valence band for *p*-type germanium.

The higher polarizability of *p*-germanium in comparison with *n*-type germanium in the reactions

$2H^+ + 2e^- \rightarrow H_2$

and

$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$

may in this case be caused by an additional ohmic potential drop in the near-surface layer of the electrode depleted of holes. A hole-depleted layer on *p*-germanium arises in the course of its cathodic polarization, i.e., with negative charging of the surface of *p*-germanium relative to the solution. The presence of such a layer, directed into the depth of the semiconductor, is equivalent to an increase in the effective resistance at the germanium—solution interface and therefore leads to a certain additional ohmic potential drop, which, at constant density of the polarizing current, is the greater the higher the resistivity of the initial *p*-germanium.

The magnitude of the potential at which depletion of the near-surface layer of *p*-germanium in holes begins to appear is determined by the position of the zero point of germanium under the given conditions and may differ for different solutions. On a positively charged surface of *p*-germanium, a hole-depleted layer is not formed. The absence of inhibition of the reduction reaction of $[\mathrm{Fe(CN)}_6]^{3-}$ on *p*-germanium (Fig. 3), apparently, is explained by the fact that, owing to the very positive value of the reduction potential of this ion on the germanium electrode, depletion of the *p*-germanium surface in holes in this case is extremely small or entirely absent.

The rate of anodic dissolution of *p*-germanium in all the above-indicated

in solutions does not depend on its specific resistance. For electron-type germanium in these same solutions, as was to be expected, the anodic saturation current is the greater, the higher the specific resistance (or the ratio ρ/L) of the starting material.

It is shown below that the rate of self-dissolution of germanium in a solution of H_2SO_4 (pH 1.0) $+0.2\,N\,H_2O_2$ is practically independent of its type of conductivity and specific resistance.

	Ge *n*-type	Ge *p*-type
Rate of self-dissolution, mg/cm^2·h, at $\rho = 1.0$ ohm · cm	0.91	0.98
Rate of self-dissolution, mg/cm^2·h, at $\rho = 20.0$ ohm · cm	0.87	0.92

For Ge *n*-type at $\rho = 1.0$ ohm · cm, $I_{\text{sat}} \simeq 0.4$ mA/cm^2; at $\rho = 20.0$ ohm · cm, $I_{\text{sat}} \simeq 1.2$ mA/cm^2.

For *n*-type germanium with a specific resistance of 1.0 ohm · cm, the rate of self-dissolution, moreover, exceeds the value of the anodic saturation current by a factor of 3.

The results obtained show that, in the process of self-dissolution, the specific influence of the semiconductor properties of germanium is not manifested, and the electrode reactions, both for germanium with electron conductivity and for germanium with hole conductivity, proceed in this case without retardation.

We associate the latter with the presence of a positive charge on the surface of *n*- and *p*-germanium at the stationary potential in a solution of H_2SO_4 (pH 1.0) $+0.2\,N\,H_2O_2$, i.e., with an increased surface concentration of holes under these conditions.

The rate of self-dissolution of germanium in the presence of hydrogen peroxide, for both the *n*- and *p*-type, should in this case be determined by the kinetics of the cathodic process on *n*-germanium and of the anodic process on *p*-type germanium. The values of the stationary potential and of the rate of self-dissolution of *n*- and *p*-germanium in a solution of H_2SO_4 (pH 1.0) $+0.2\,N\,H_2O_2$, obtained from the polarization diagram constructed according to this principle, agree well with the data of direct measurements.

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