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REDUCTION REACTIONS AT A GERMANIUM CATHODE

(Presented by Academician A. N. Frumkin on 17 IX 1959)

In electrochemical processes at a semiconductor electrode, free electrons and holes may take part. It was previously suggested ([1]) that reduction reactions at a germanium electrode proceed with the participation of free electrons. According to another hypothesis ([2]), during the reduction of $K_3Fe(CN)_6$ at a germanium cathode, electrons pass to the $Fe(CN)_6^{3-}$ ions from the valence band of germanium, leaving holes in it. In an earlier work by the author ([3]), the presence of hole injection into n-type germanium during the reduction of $Fe(CN)_6^{3-}$ and MnO_4^- ions was proved by a direct method. Thus, the germanium–electrolyte interface can serve, as it were, as an emitter in the occurrence on it of certain reduction processes.

The aim of the present work was to investigate the kinetics and to measure the injection coefficient (the fraction of valence electrons in the total current) of certain reduction reactions at a germanium electrode.

Experimental method

The electrodes for measuring the injection coefficient were disks 6 mm in diameter and about 0.12 mm thick, made of single-crystal n-type germanium with specific resistance $\rho = 2.5\ \Omega \cdot$cm and hole diffusion length $L = 0.5$-0.7 mm; crystallographic orientation (111). Along the circumference of the disk there was an annular ohmic nickel contact soldered with tin. On one side of the germanium plate, at the center, there was a p–n junction formed by alloying indium (junction diameter about 3 mm). The quality of both contacts was checked by recording current-voltage characteristics in direct current, and also in alternating current with the aid of a cathode oscillograph. The entire surface of the electrode was coated with silicone varnish and paraffin, except for a circle 1-2 mm in diameter on the side opposite the p–n junction. This free surface was placed in the electrolyte, in which there were an auxiliary electrode for polarization and a reference electrode. When cathodic current was passed through the germanium–electrolyte boundary, it served as an emitter; the p–n junction

Fig. 1. Change in the reverse collector current as a function of the reduction current; 1 –$KMnO_4$; 2 –$K_3Fe(CN)_6$; 3 –KI_3; 4 –quinone; 5 –$K_2Cr_2O_7$

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served as the collector. The change in the reverse current of the collector ΔI_{coll} (at a bias $V_{\text{coll}} = 3$ V) as a function of the reduction current I_{red} was recorded with an electronic polarograph PE-312; from the data obtained, the current gain coefficient

$$\alpha = \left(\frac{\Delta I_{\text{coll}}}{I_{\text{red}}} \right)_{V_{\text{coll}}}$$

of this peculiar triode was calculated (all measurements were made in direct current). Since the distance from the p–n junction to the electrolyte did not exceed 70–80 μ, almost all the holes injected into the electrode by the electrochemical reaction reached the collector (the transfer coefficient in planar triodes of analogous design is 0.96–0.99). Therefore, the measured values practically coincide with the injection coefficient γ, provided that the rate of surface recombination at the germanium–electrolyte boundary is small. A slight

the value of ΔI_{coll} upon immersion of a dry electrode in the solutions under study (at $I_{\text{red}} = 0$), as well as literature data ([4], [5]), show that this assumption is apparently justified (in the absence of adsorbed hydrogen on the electrode).

Polarization curves were recorded with a PE-312 polarograph on rotating disk electrodes made of platinum and single-crystal n-type germanium ($\rho = 1.8\ \Omega$·cm, $L = 0.3$ mm) and p-type germanium ($\rho = 2.8\ \Omega \cdot$ cm, $L = 0.3$ mm).

Before the measurements the germanium electrodes were etched in an CP-4 mixture. Reagents of high purity were used. All measurements were carried out in an atmosphere of purified nitrogen, in the dark. Electrode potentials are given relative to the normal hydrogen electrode.

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Results obtained

Measurement of the injection coefficient

Figure 1 gives curves of the dependence of ΔI_{coll} on I_{red} for 5 different oxidizing agents. In all cases α lies between 0 and 1 and, except for $Cr_2O_7^{2-}$, does not depend on I_{red} (Table 1).

Reduction of H_2O_2 does not affect I_{coll} and, consequently, is not accompanied by injection of holes into germanium. In the case of $K_3Fe(CN)_6$ and $KMnO_4$, the concentration of the oxidizing agent has some influence on α; in the case of KI_3, α does not depend on its concentration.

Table 1

Reducing substance	Conc. of reducing substance, mol/l	Indifferent electrolyte	Germanium potential, V	Injection coefficient γ	Maximum value of i_{red}, mA/cm^2
$KMnO_4$	0.12	1 N H_2SO_4	0.2	0.78–0.88	13.5
$K_3Fe(CN)_6$	0.28–0.56	1–2 N KOH	−0.2	0.66–0.80	8.6
KI_3	0.1–0.33	1 N KJ	0.2	0.42	22
Quinone	0.4	1 N H_2SO_4	−0.4	0.38	3.3
$K_2Cr_2O_7$	0.04–0.12	1 N H_2SO_4	−0.4	0.03–0.08	83
H_2O_2	0.4	0.3 N K_2SO_4	−0.7	0	20

The measured values of α are very sensitive to the state of the electrode surface. With an increase in the negative potential of germanium, as the hydrogen-evolution potential is approached, α begins to decrease (Fig. 1, 5). Hydrogen evolved at the germanium cathode, by being adsorbed on the semiconductor (or by entering the crystal lattice), sharply increases the rate of surface recombination ([6]), which is accompanied by a change in the electrochemical properties of germanium ([3], [5]). Evidently, hydrogen adsorption begins at less negative potentials than its visible evolution on the electrode and causes a decrease in the transfer coefficient of the electrodes used, and consequently also in α. It is possible that the small values of α in the case of reduction of $K_2Cr_2O_7$ and the absence of injection during reduction of H_2O_2 are explained by the fact that these reactions proceed at very negative potentials, close to the hydrogen-evolution potential, and, consequently, on a hydrogenated electrode.

Polarization curves for all the substances studied (the composition of the solutions is given in Table 1) on platinum and n-type germanium electrodes have the form of a well-defined wave, and the limiting-current density i_{lim} on both metals is the same (the reduction curve of $KMnO_4$ on germanium contains 2 waves). The limiting-current density is proportional to the square root of the angular velocity of electrode rotation, ω (Figs. 2, 4); consequently, the limiting rates of the reduction reactions on Pt and n-type Ge are determined by the rate of diffusion in solution of the particles of the reducible substances to the electrode surface (7) and do not depend on the electrode material. Illumination of the electrode does not change the wave height and has almost no effect on the shape of the polarization curve on n-type germanium.

Fig. 2. Dependence of the limiting current of reduction of KJ_3 (0.096 N) on

Fig. 2. Dependence of the limiting current of reduction of KJ_3 ($0.096\,N$) on a rotating disk germanium electrode on $\sqrt{\omega}$. 1—p-type Ge; 2—the same (with moderate illumination of the electrode); 3—the same (hydrogenated electrode); 4—n-type Ge

Figure 2: Fig. 2. Dependence of the limiting current of reduction of KJ_3 ($0.096\,N$) on a rotating disk germanium electrode on $\sqrt{\omega}$. 1—p-type Ge; 2—the same (with moderate illumination of the electrode); 3—the same (hydrogenated electrode); 4—n-type Ge

a rotating disk germanium electrode on $\sqrt{\omega}$. 1—p-type Ge; 2—the same (with moderate illumination of the electrode); 3—the same (hydrogenated electrode); 4—n-type Ge.

The reduction curves of $K_3Fe(CN)_6$, $K_2Cr_2O_7$, quinone, and H_2O_2 on hole germanium also contain 1 wave (the $KMnO_4$ curve contains 2 waves), and the value of i_{lim} is the same as on Pt and n-type Ge electrodes up to current densities of $20\,\text{mA/cm}^2$ (in the case of $K_3Fe(CN)_6$, up to $100\,\text{mA/cm}^2$). The limiting current is proportional to $\sqrt{\omega}$. However, the curves are shifted by 0.2-0.3 V toward negative potential values in comparison with the curves on n-type Ge; upon illumination of the electrode they approach the corresponding curves obtained on electronic germanium.

The height of the reduction wave of KJ_3 on p-type Ge (Fig. 3, 1) is less than on n-type Ge and depends little on stirring of the solution (Fig. 2, 1). Upon illumination of the electrode, the curve is not only shifted toward positive potential values, but the value of the limiting current also increases and reaches a value corresponding to Pt and n-type Ge electrodes (Fig. 3, 2). Preliminary hydrogenation of the electrode has the same effect on the KJ_3 reduction wave (at a current density of $10\,\text{mA/cm}^2$ for 1-2 min). On strongly illuminated or hydrogenated p-type germanium, the limiting current is proportional to $\sqrt{\omega}$ over almost the entire range of current densities used (Fig. 2, 3). With moderate illumination of the electrode, a direct proportionality between i_{lim} and $\sqrt{\omega}$ is observed over a small range of i_{lim} (Fig. 2, 2).

Discussion of Results

The values of the injection coefficient given above show that, in all the cases considered (except H_2O_2), both free and valence electrons are involved in the reduction reaction on the germanium electrode. The fractional and not always constant values of γ apparently do not permit the fraction of free and valence electrons to be related to any particular molecular scheme of the reaction. Probably the reaction proceeds simultaneously by two paths, with the proportion of one and the other depending in each individual case on the position of the energy level occupied by the reducible ions or molecules relative to the energy bands of the semiconductor.

Fig. 3

Figure 3: Fig. 3

It has been stated more than once ([1,5]) that the lower rate of reduction reactions on electrodes made of p-type germanium, in comparison with electron-conducting germanium, is explained by the lower concentration in the hole material of free electrons, which participate in cathodic processes. The circumstance that the reduction of $KMnO_4$ and $K_3Fe(CN)_6$ on p-type germanium is not retarded is connected with the fact that these reactions proceed mainly with the participation of valence electrons. The limiting current for the reduction of quinone, $K_2Cr_2O_7$, and H_2O_2 is reached on a hydrogenated electrode with a high rate of surface recombination and therefore does not depend on the type of conductivity of Ge. The larger overvoltage on p-type Ge as compared with n-type is possibly explained by a potential drop in the surface layer depleted of free carriers, arising during cathodic polarization of a hole semiconductor relative to the solution ([8]). Illumination of the electrode is accompanied by generation of free carriers and eliminates this effect.

Fig. 3. Polarograms of the reduction of KJ_3 ($2.07 \cdot 10^{-2}$ N) on a rotating disk electrode of p-type germanium: 1 —in the dark, 2 —under illumination. Electrode rotation speed 440 rpm.

In the reduction current of KJ_3 the fraction of free electrons is very large (about 60%). The limiting current of this reaction on p-type germanium in the dark (Fig. 2, 1) is almost independent of stirring of the solution and is determined by the rate of diffusion of free electrons from the bulk of the semiconductor to the electrode surface, where they enter into reaction. On an illuminated or preliminarily hydrogenated electrode, free electrons are generated in excess, respectively, by light or in a layer with a high recombination rate, and the rate of the electrode reaction is determined by the slower stage—the diffusion of J_3^- ions in the solution to the electrode surface.

The data obtained make it possible to draw some conclusions about the mechanism of chemical etching of germanium. As a rule, etching mixtures include the oxidants HNO_3, H_2O_2, J_2, Br_2, $K_2Cr_2O_7$, etc. ([9]). It is possible that the reduction of many oxidants on germanium proceeds with the participation of valence electrons and is a source of holes, which then participate in the dissolution of n-type germanium. However, in the case of H_2O_2 such a mechanism does not seem probable.

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