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Abstract**Full Text**

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PHYSICAL CHEMISTRY

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GERMANIUM ELECTRODE WITH A p-n JUNCTION

(Presented by Academician A. N. Frumkin, May 23, 1958)

In earlier work ^(1,2) it was shown that the process of anodic dissolution of germanium depends on the concentration of holes at the surface of the semiconductor. In this connection it seemed interesting to investigate the behavior of a germanium electrode with a p-n junction created on it, by means of which it would be possible both to inject holes and to create in germanium a region depleted of carriers.

In the present work the experiments were carried out on a germanium plate of the electronic type of conductivity, with a specific resistance of $20 \Omega \cdot \text{cm}$ and a diffusion length of 1 mm. The initial thickness of the plate was 250μ . On one side of the plate, by alloying indium, a p-n junction with a total area of about 0.04 cm^2 was created. On the same side of the electrode a ring-shaped ohmic contact (base) was alloyed in. The entire germanium plate with leads was insulated with silicone varnish, except for the region opposite the p-n junction and equal to it in area. The electrical circuit made it possible to measure the electrode potential at various current densities, both when a reverse bias was applied to the p-n junction and when the external circuit of the junction was open. All experiments were carried out in $0.1 N \text{ HCl}$ at 20° in an atmosphere of nitrogen.

Figure 1 gives polarization curves for the process of anodic dissolution of germanium, recorded in the current-density interval 10^{-6} – 10^{-2} a/cm^2 for different ways of connecting the p-n junction. Curve 2 shows the change in the potential of the germanium anode when the positive pole of the current source is connected to the ring-shaped ohmic contact, while the external circuit of the p-n junction (between the ring-shaped base contact and the alloyed indium) is open. At current densities of about $3 \cdot 10^{-3} \text{ a/cm}^2$, this curve deviates toward more positive potential values because of the shortage of holes at the germanium surface at high rates of the anodic process ⁽²⁾. If a reverse bias of 30 V is applied to the p-n junction located on the opposite side of the plate, the polarization

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

curve obtained under these conditions coincides with curve 2. This phenomenon is observed only for plates thicker than 100μ .

Since the rate of anodic dissolution of germanium is limited by the number of holes arriving per unit time at the surface of the semiconductor ^(1,2), it should be expected that any injection of holes into germanium must lead to a decrease in the polarization of the electrode reaction. Curve 1 of Fig. 1 was obtained when the positive pole of the current source was connected not to the ring-shaped base contact but to the indium alloyed into the germanium, i.e., to the p-region of the germanium. Here the p-n junction is connected in the forward direction and injects holes toward the germanium-electrolyte interface. These holes will be consumed in the electrochemical reaction and will accelerate the process of anodic dissolution of germanium. Therefore the electrode reaction here will proceed at almost the same rate as for p-type germanium. This explains the fact that curve 1 differs almost not at all from

analogous curve obtained for the process of anodic dissolution of p-type germanium in work ⁽²⁾.

Curve 3 was taken on the same electrode as curve 2, but the thickness of the germanium plate was reduced to 25μ by chemical etching. The positive pole of the current source was connected to the base, and the external circuit of the p-n junction was open. Under these conditions the process of anodic dissolution of germanium at $I > 10^{-3} \text{ A/cm}^2$ proceeds with a higher polarization than for thick germanium plates (curve 2). This phenomenon is associated with a decrease in the number of holes generated throughout the entire volume of the semiconductor owing to the reduction in the geometrical dimensions of the electrode.

Fig. 1. Polarization curves for a germanium electrode with a p-n junction. Explanations in the text

Fig. 2. Capacitance and potential of a germanium electrode as a function of the magnitude of the reverse bias applied to the p-n junction. Explanations in the text

If a reverse bias of 30 V is simultaneously applied to the p-n junction of such an electrode, then the curve $\varphi - \lg I$ (Fig. 1, 4) will deviate from a linear form toward high values of the potential at lower current densities ($I \approx 10^{-4} \text{ A/cm}^2$). As the reverse bias is applied to the p-n junction, the width of the zone depleted of current carriers increases. This further decreases the volume

of the semiconductor in which the holes consumed in the anodic reaction are generated, which cannot but affect the magnitude of the saturation current. It should be emphasized that this effect is observed only on very thin plates.

The width of the depleted layer of space charge for an alloyed p–n junction⁽³⁾ is equal to

$$D = \sqrt{2\varepsilon\mu\rho u_{\text{rev}}}, \quad (1)$$

where ε is the dielectric constant, μ is the mobility of the majority current carriers, ρ is the specific resistance of germanium, and u_{rev} is the reverse bias.

It follows from this that, by increasing u_{rev} , one can expand the space-charge region so much that it will reach the germanium surface in contact with the electrolyte. In order to trace the behavior of the electrode under these conditions, we measured its potential (Fig. 2, 1) and capacitance at a frequency of 5000 Hz (Fig. 2, 2) at different values of the reverse bias on the p–n junction. The experiments were carried out in 0.1 N HCl on a germanium plate 25 μ thick. No external voltage was applied to the electrolyzer.

As is seen from Fig. 2, as u_{rev} is increased to 15–20 V, the capacitance of the electrode drops sharply and then becomes constant. In contrast to this, the electrode potential does not change up to $u_{\text{rev}} = 15 \div 20$ V and then begins to rise slowly. Such a course of the curves is connected with the emergence of the space charge of the p–n junction at $u_{\text{rev}} \approx 15 \div 20$ V at the germanium–electrolyte interface. Indeed, according to equation (1), at $u_{\text{rev}} = 20$ V and $\rho = 20 \Omega \cdot \text{cm}$, the width

of the space-charge layer is $\sim 20 \mu$, which corresponds to the thickness of the *n*-layer of germanium in the electrode used.

The decrease in capacitance with increasing width of the space charge up to its emergence at the electrode surface is apparently caused by an increase in the distance between the ionic plate of the layer and the centers of positive charges on the germanium surface, owing to the drawing-in of holes by the *p–n* junction. After the space charge reaches the surface, the depleted layer, devoid of current carriers, occupies the entire thickness of the plate. The carriers of positive charges in this layer are ionized donor atoms, which cannot change their position in the lattice. This accounts for the constancy of the double-layer capacitance values at reverse biases greater than 20 V.

When the space charge reaches the surface, the process of self-dissolution of germanium slows down owing to the lack of holes, and the electrode potential acquires a more positive value (Fig. 2, 1).

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

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