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Abstract

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STUDY OF THE STATE OF THE SURFACE OF ANODICALLY POLARIZED GERMANIUM IN ALKALINE SOLUTIONS

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Recently, alkaline solutions have been widely used for the electrochemical etching of germanium in the production of semiconductor devices. Nevertheless, the literature contains very little information on the state of the surface of a germanium electrode during electrochemical etching.

Turner, Bardel' ben, and other investigators carried out all experiments on the study of the state of the surface of anodically polarized germanium in acidic solutions.

Irzha (^1), who studied the behavior of the germanium anode in NaOH and NH_4OH solutions, came to the conclusion that, during the dissolution of germanium, a layer of germanium monoxide forms on its surface. Beck and Gerischer (^2), discussing the mechanism of anodic dissolution of germanium in alkaline solutions, assert that this process necessarily passes through a stage involving the formation of surface oxygen compounds of germanium.

In the present work, the method of charging curves was used to study the state of anodically polarized germanium in alkaline solutions. All experiments were carried out on a polycrystalline degenerate germanium electrode in a 0.1 N KOH solution at 20°C.

The concentration of impurities in degenerate germanium, which does not possess semiconductor properties, is close to 0.01%; therefore, from the chemical point of view, it is very pure. Degenerate germanium was used by us in order to exclude all possible complications in electrode processes associated with the passage of current in a semiconductor electrode. Preliminary experiments showed that the kinetics of anodic dissolution of degenerate germanium and of p-type germanium are identical. Thus, for both types of germanium the φ–$\lg I$ curves practically coincide, which is quite natural, since the kinetics of anodic

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

dissolution of *p*-type germanium is not hindered by a shortage of holes at the semiconductor—electrolyte boundary.

The germanium electrode was subjected to anodic polarization at various current densities for a certain time, after which the charging curve was recorded with an ENO-1 oscillograph, the cathodic current density being 10^{-3} A/cm^2. Before the beginning of each experiment, the germanium electrode was etched in a CP-4-type etchant and then brought by careful cathodic polarization to a stationary potential (~ -0.55 V).

Figure 1 presents cathodic charging curves obtained after preliminary anodic polarization for 10, 20, 60, and 120 sec at potentials of −0.350 V and −0.330 V. In all cases, at a potential close to −0.75 V, a retardation of the potential increase is observed, associated with the removal of oxygen from the surface of germanium. At an anodic polarization potential $\varphi = -0.35$ V, the quantity of electricity required for

for this purpose is $\sim 4.5 \cdot 10^{-4}$ coul/cm^2 and does not depend on the duration of polarization. The charging curves obtained after polarization at a more negative anodic potential outwardly resemble curve 1 in Fig. 1. However, the amount of electricity expended on removing the adsorbed oxygen will be lower here. Thus, at $\varphi = -0.420$ V it is $2 \cdot 10^{-4}$ coul/cm^2.

A potential of ~ -1.4 V corresponds to the potential of the hydrogen-evolution process on a clean germanium surface in 0.1 N KOH at $I = 10^{-3}$ A/cm^2.

Fig. 1. Charging curves obtained after preliminary anodic polarization at $\varphi = -0.35$ V and $\varphi = -0.33$ V. 1 $-\varphi = -0.35$ V, 10-120 sec.; 2 $-\varphi = -0.33$ V, 10 sec.; 3 $-\varphi = -0.33$ V, 20 sec.; 4 $-\varphi = -0.33$ V, 60 sec.; 5 $-\varphi = -0.33$ V, 120 sec.

Fig. 2. Charging curves obtained after preliminary anodic polarization at $\varphi = -0.18$ V and $\varphi = -0.15$ V. 1 $-\varphi = -0.18$ V, 10 sec.; 2 $-\varphi = -0.18$ V, 20 sec.; 3 $-\varphi = -0.18$ V, 10 sec.; 4 $-\varphi = -0.15$ V, 10 sec.; 5 $-\varphi = -0.15$ V, 60 sec.

The course of curve 1 in Fig. 1 indicates that all the oxygen adsorbed on the germanium surface is removed during cathodic polarization, and that the amount of deposited oxygen depends on the potential of anodic polarization. The character of curve 1 in Fig. 1 makes it possible to suppose that at $\varphi \leq -0.35$ V ($I \leq 10^{-4}$ A/cm^2) electrochemical adsorption of oxygen takes place. It is easy to calculate (3) that in this case there will be 1 oxygen atom per 1 germanium

Fig. 3

Figure 3: Fig. 3

atom.

Fig. 3. Charging curves obtained after preliminary anodic polarization at $I = 2.5 \cdot 10^{-2}$ A/cm^2. 1 –10-60 sec.; 2 –120 sec.

When the potential of the preliminary anodic polarization is increased to -0.330 V ($I = 2.5 \cdot 10^{-4}$ A/cm^2), a horizontal plateau appears on the charging curves (curves 2, 3, 4, 5 in Fig. 1) at $\varphi \approx -0.75$ V, and the total amount of electricity required to remove oxygen from the electrode surface increases by approximately an order of magnitude. In addition, it increases with the time of the preliminary anodic polarization (from 10^{-3} coul/cm^2 at $\tau = 10$ sec. to $7 \cdot 10^{-3}$ coul/cm^2 at $\tau = 120$ sec.). With a further increase in the potential of the anodic polarization to $\varphi \approx -0.20$ V, the character of the cathodic charging curves does not change, although the total amount of electricity expended on the arrest increases to $1.2 \cdot 10^{-2}$ coul/cm^2.

The appearance of a horizontal arrest on curves 2, 3, 4, 5 in Fig. 1 makes it possible to suppose that at anodic potentials more positive than -0.33 V, part of the electrochemically adsorbed oxygen is more strongly bound to the surface. The amount of electricity expended on the horizontal arrest does not exceed $4.4 \cdot 10^{-4}$ coul/cm^2. This indicates that a monolayer of a surface oxide compound is formed on the germanium electrode, in which there is 1 oxygen atom per 1 germanium atom (3).

A horizontal arrest at $\varphi = -0.75$ V is observed on the cathodic charging curves obtained upon anodic polarization to a potential

not above $\varphi = -0.180$ V (Fig. 2). With an increase in the duration of anodic polarization or an increase of its potential to $\varphi = -0.15$ V, $I = 10^{-2}$ A/cm^2, the horizontal plateau disappears (curves 3, 4, 5 in Fig. 2), although the total amount of deposited oxygen remains approximately the same.

Figure 3 shows charging curves obtained after anodic polarization at $I = 2.5 \cdot 10^{-2}$ A/cm^2 ($\varphi = -0.03$ V). If the duration of anodic polarization is increased to 120 sec, then, because of concentration phenomena associated with the slow diffusion of OH^- ions to the electrode surface$^{(2)}$, the electrode potential increases to $\sim +0.6$ V, and a new plateau appears on the charging curve (Fig. 3, 2) at $\varphi = -0.25$ V.

Such a sharp decrease in the reduction potential is evidently associated with a significant change in the pH of the solution in the near-electrode layer owing to prolonged anodic polarization.

From the experimental data obtained it is clear that the total amount of oxygen adsorbed on germanium can reach 10 or more monolayers. It is therefore realistic to assume that, during the anodic dissolution of germanium, a layer of phase oxide is formed on its surface, which begins to undergo cathodic reduction at $\varphi = -0.75$ V.

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