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THE ROLE OF MINORITY CURRENT CARRIERS IN THE PROCESS OF ANODIC DISSOLUTION OF ELECTRONIC GERMANIUM

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Studies of the anodic dissolution of germanium have shown that this process proceeds with the participation of holes. At a sufficiently high current density of anodic dissolution of n-type germanium, in which holes are the minority carriers, the germanium–electrolyte interface is a kind of hole collector; moreover, "current multiplication" takes place at the collector, associated with the participation in the reaction of free electrons of the semiconductor as well. In other words, a germanium atom passing into solution transfers electrons simultaneously to the valence band (for which holes are necessary) and to the conduction band. The overall reaction equation (in an acidic medium) is

$$\mathrm{Ge} + x \oplus + 3\mathrm{H_2O} \rightarrow \mathrm{H_2GeO_3} + (4 - x) \ominus + 4\mathrm{H}^+.$$

For the current multiplication coefficient $\alpha'_0 = 4/x$ (equal to the ratio of the limiting current of anodic dissolution to the limiting current of hole diffusion from the bulk of the semiconductor to its surface), different authors ($^{1-4}$) give values from 1.3 to 4.4. Attempts have been made to relate the value of α'_0 to one or another molecular scheme of the reaction (^{3,5}). The purpose of the present work was to study the dependence of α'_0 on the conditions of anodic dissolution of germanium.

Experimental procedure

To measure α' we used the method proposed by Brattain and Garrett (^{1}). An electrode of electronic germanium with a specific resistivity of 3 ohm · cm and a hole diffusion length of 0.7 mm was made in the form of a thin disk (about 0.1 mm thick) 8 mm in diameter; on one side of it there was a p—n junction, while the other side was immersed in the solution. A ring-shaped ohmic contact, soldered with tin, was placed around the circumference of the electrode. The quality of the contacts was checked by recording current-voltage characteristics

Fig. 1

Figure 1: Fig. 1

in direct and alternating current. The surface of the electrode (except for the region immersed in the electrolyte) was insulated with pure paraffin. The area of the germanium–solution interface was 0.25 cm^2, and the area of the p—n junction was 0.2 cm^2. The anodic dissolution of germanium was carried out at a constant potential corresponding to the limiting dissolution current; as potentiostat we used a PE-312 electronic polarograph. By means of the p—n junction connected in the forward direction, holes were injected into the n-type region; these holes diffused to the surface of the germanium–solution interface and took part in the dissolution reaction. The increase in the anodic dissolution current ΔI_a as a function of the injection current I_p was recorded automatically*. From the data obtained we calculated the current gain coefficient $\alpha = d(\Delta I_a)/dI_p$ of our system, which can be written in the form $\alpha = \gamma\beta\alpha'$, where γ is the efficiency of the emitter (the fraction of hole current in the current of the p—n junction), β is the transmission coefficient–

* For greater accuracy, in the experiment we measured not $\Delta I_a'$, but the quantity $\Delta I_a - I_p$ (by means of a corresponding arrangement of the electrical circuit), i.e., the increase in the anodic current through the electrode surface.

tion (the fraction of holes injected by the emitter that reach the collector without recombining), α' is the current multiplication coefficient at the collector (the increase in the reverse collector current when the hole current is increased by unity). In planar triodes of analogous design, the emitter efficiency γ and the transmission coefficient β are very close to 1, so that the flux of hole injection to the germanium-solution surface is, to within 2-3%, equal to the transmission current of the p–n junction, I_p. The rate of surface recombination at the germanium-aqueous solution boundary is small, as follows from the literature ([3,6]) and from our indirect data. Consequently, the experimentally measured quantity $d(\Delta I_a)/dI_p$ practically coincides with the current multiplication coefficient α' of the anodic dissolution reaction.

Results obtained

Figure 1 gives the dependence of $\Delta I_a - I_p$ on I_p for the anodic dissolution of germanium in $1\,N$ H_2SO_4 in the dark and under illumination of different intensity E; in Figs. 2 and 3–the dependences calculated from these data

Fig. 1. Acceleration of the anodic dissolution of germanium (μa) in $1N$ H_2SO_4 as a function of the injection current through a p–n junction. Electrode illumination (in arbitrary units): 1–0; 2–3.5; 3–5.8; 4–7.5

of $d(\Delta I_a)/dI_p$ on I_p and E. The illumination E was determined from the increase in the reverse current I_s of the p–n junction under illumination (at a reverse bias of 3 V) and is given in arbitrary units $\Delta I_s/I_s^{\mathrm{dark}}$.

It is seen from Fig. 1 that at small values of I_p ($I_p \ll I_a^0$)* there is a direct proportionality between ΔI_a and I_p, noted earlier ([1]), i.e. $d(\Delta I_a)/dI_p$ retains a constant value. The current multiplication coefficient

$$\alpha_0' = [d(\Delta I_a)/dI_p]_{I_p=0},$$

calculated from curve 1 (Fig. 1), is 1.6-1.7 (Fig. 2), which agrees well with the results of the direct measurements of Brattain and Garrett ([1]) (1.4-1.8) and is close to the value 1.4 obtained by Uhlir by a less direct method ([4]), as well as to the value 1.6-2.5 calculated from the indirect data of Gerischer and Beck ([2,8]) with allowance for our work ([7])**. The magnitude α_0' does not depend on the potential of the ger-

* In the absence of injection, the normal limiting current of anodic dissolution of the electrodes used, I_a^0, was about 90 μa.

** In works ([2,8]), injection of holes into germanium was performed not by means of a p—n junction, but as a result of the reduction reaction of $K_3Fe(CN)_6$, which proceeds with the participation of valence electrons. The ratio ΔI_a to the reduction current of $K_3Fe(CN)_6$ was 1.3-1.7. According to our data ([7]), the fraction of valence electrons in the reduction of $K_3Fe(CN)_6$ at a germanium electrode is 0.6-0.8 (and not 1, as assumed by the authors of works ([2,8])).

of germanium (in the interval 1-3 V) and is the same for dissolution in 1 N H_2SO_4 and 1 N KOH; in a 48% HF solution $\alpha_0' = 1.3^*$.

With an increase in I_p relative to I_a^0, $d(\Delta I_a)/dI_p$ decreases and at $I_p \simeq 5I_a^0$ is 1.15, while at $I_p \simeq 10I_a^0$ it is only 1.03. Illumination of the electrode does not change the character of the dependence of $d(\Delta I_a)/dI_p$ on I_p (Fig. 2); however, the absolute value of $d(\Delta I_a)/dI_p$ decreases with increasing illumination E (Fig. 3).

It is seen from Fig. 1 that, with increasing injection current, the quantity $\Delta I_a - I_p$ tends to a certain limit; extrapolation of curves 1-4

Fig. 2. Dependence of current multiplication on the current through the p—n junction I_p. Illumination of the electrode:
1—0; 2—3.5; 3—5.8; 4—7.5.

Fig. 3. Dependence of current multiplication on electrode illumination E. Current through the p—n junction: 1—0; 2—200 μA; 3—300 μA.

(Fig. 1) to $I_p \to \infty$ (by plotting these curves in the coordinates

$$\frac{1}{\Delta I_a - I_p}, \quad \frac{1}{I_p}$$

) gives a limiting value of about 200-250 μA (which is 2-3 times greater than I_a^0).

Discussion of the Results

The dependence we observed of the current multiplication coefficient α' for anodic dissolution of germanium on the injection current of holes is qualitatively confirmed by the results of the recently published work of Beck and Gerischer ([8]). According to these authors, the acceleration of anodic dissolution of n-type germanium in 0.1 N NaOH in the presence of $K_3Fe(CN)_6$ depends on the concentration of the latter; moreover, with increasing concentration and, consequently, the rate $I_{\text{red.}}$ of ferricyanide reduction, the value $\Delta I_a / I_{\text{red.}}$ decreases. However, in the cited work the question of the fraction γ of valence electrons in the reduction current of $K_3Fe(CN)_6$ was not investigated. If it is assumed that γ changes little when the ferricyanide concentration is varied, then the decrease in $\Delta I_a / I_{\text{red.}} = \alpha'\gamma - 1$ is associated mainly with a decrease in α' as the rate of hole injection by reduction of $K_3Fe(CN)_6$ increases.

The derivative $d(\Delta I_a)/dI_p$ characterizes the dependence of the electron component I_n of the total anodic dissolution current $I_a = I_p' + I_n$ on the hole current through the surface: $d(\Delta I_a)/dI_p = 1 + d(\Delta I_n)/dI_p$. Its decrease with increasing I_p means that, as the flux of holes to the surface of the dissolving germanium increases, it is predominantly the hole component of the dissolution current that increases. From the experimentally measured

From the value $\alpha_0' = 1.65$ it follows that, in the process of anodic dissolution (without injection), when one atom of germanium passes from the crystal lattice into solution, 2.4 holes are consumed and 1.6 electrons pass into the conduction band. With increasing injection (by means of a p—n junction or by illumination), the fraction of holes and free electrons changes and, at the maximum value of I_p attained in the present work, amounts, respectively, to 3.9 and 0.1. The continuous change in the macroscopic value α' (i.e., the derivative $d(\Delta I_a)/dI_p$) while the composition of the solution, the potential, and other dissolution conditions (apart from the injection magnitude) remain constant obviously does not allow this quantity to be associated with any definite molecular scheme of the dissolution reaction—for example, by assuming that some intermediate stage proceeds exclusively with the participation of holes ([3,5]). Apparently, the process proceeds simultaneously along two paths (with charge transfer into the valence band and into the free band of the semiconductor).

On the other hand, the increase in the absolute value of the electronic component of the dissolution current with increasing hole current serves as a known

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* According to our data, the limiting current of anodic dissolution of germanium in HF is 4-5 times higher than in H_2SO_4 and KOH, which may be explained by the considerable rate of recombination at the germanium-HF solution interface.

confirmation of Dewald' s point of view (9), according to which the hole and electronic currents do not correspond to two independent paths of anodic dissolution, but are connected with the elementary act of the reaction. It may be assumed that the observed decrease in $d(\Delta I_n)/dI_p$ with increasing dissolution rate is due to the fact that, at high currents, substantial recombination occurs through the germanium—electrolyte surface in the space-charge layer, the magnitude of which is usually taken to be insignificant, and the number of holes participating in the reaction proves to be smaller than the injection current. In this case the microscopic value of the current multiplication coefficient α' (which is determined by the number of holes and free electrons participating in the elementary act of the reaction) differs from the experimentally measured values given above.

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