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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE PECULIARITIES OF THE ELECTROCHEMICAL DISSOLUTION OF n-TYPE SILICON

(Presented by Academician A. N. Frumkin, 8 IX 1959)

The question of the nature of the holes consumed during the anodic dissolution of a semiconductor is of particular interest for studying the mechanism of the electrochemical reaction at germanium and silicon electrodes.

At present, direct proof has been obtained (1–3) that, during the anodic dissolution of germanium, the holes required for the electrochemical reaction are supplied mainly from the bulk of the semiconductor. The same cannot be said of silicon. Thus Flynn (4), who studied the anodic dissolution of n-type silicon in 5% HF, found a hole saturation current of the order of 10^{-5} a/cm^2. This experimental value of the saturation current and a number of theoretical calculations carried out by the author led him to the idea that, in the process of silicon dissolution—unlike germanium—the holes chiefly consumed are those formed as a result of generation in the space-charge layer of the semiconductor, near the boundary with the electrolyte, and that only an insignificant number of the holes consumed arise from generation in the bulk of the semiconductor.

Flynn’ s hypothesis can be tested experimentally, and an unambiguous answer obtained, if a thin plate of n-type silicon with a p—n junction is used as the electrode under investigation.

In the present work, the method described in (3) was mainly used. The experiments were carried out on a plate of silicon of electronic type conductivity, with a resistivity of $3\ \Omega \cdot$ cm and a minority-carrier lifetime of about 100 μsec. On one side of the plate, a p—n junction with a total area of 0.03 cm^2 was produced by alloying with aluminum. On the same side of the electrode a ring-shaped ohmic contact (base) was alloyed in. The entire plate with leads was insulated with silicone varnish and then with paraffin, except for a region opposite the p—n junction and slightly smaller in area. The thickness of the n-type silicon layer between the boundary of the p-region and the electrolyte was 20—25 μ.

All experiments were carried out in $2.5\,N$ HF at 20°. The electrolyzer and all parts of the cell were made of Teflon. The potential was measured against a saturated calomel half-cell, with subsequent recalculation to the hydrogen scale. The electrical circuit made it possible to measure the electrode potential both

Fig. 1. Anodic polarization during dissolution of n-type silicon (explanations in the text)

Figure 1: Fig. 1. Anodic polarization during dissolution of n-type silicon (explanations in the text)

when a reverse bias was applied to the p—n junction and when the external circuit of the junction was open. Before each experiment the electrode surface was treated in a mixture of nitric and hydrofluoric acids (4 : 1), and then in concentrated hydrofluoric acid.

Figure 1 presents polarization curves for the process of anodic dissolution of silicon in the current-density range 10^{-6}—$5 \cdot 10^{-4}$ a/cm^2. Curve 1 was obtained when the external circuit of the p—n junction was open and the positive pole of the current source was connected to the ohmic contact.

Curve 2 was obtained when a reverse bias of 100 V was applied to the p—n junction. It coincides completely with curve 1. In other words, applying a reverse bias to the p—n junction has no effect on the potential of anodic dissolution of silicon. For comparison, the same figure also gives curves recorded on ordinary silicon electrodes with resistivities of 3 $\Omega \cdot$cm (curve 3) and 10 $\Omega \cdot$cm (curve 4). As is readily seen from Fig. 1, a sharp change in the thickness of the electrode at the same silicon resistivity has practically no effect on the process of anodic dissolution (curves 1, 3), in contrast to what was observed for a germanium electrode (^{3}).

Fig. 1. Anodic polarization during dissolution of n-type silicon (explanations in the text)

These experimental data quite clearly show that the holes consumed in the electrochemical reaction are formed mainly in the surface layers of the electrode, and not in its bulk. If this assumption were not true, then a decrease in the thickness of the electrode and, especially, an increase in the width of the zone depleted of current carriers upon application of a large reverse bias to the p—n junction would sharply reduce the volume of the semiconductor in which the holes consumed in the reaction are generated. In turn, such a phenomenon would lead to a noticeable decrease in the magnitude of the saturation current, as is the case for germanium (^{3}). The noticeable increase in the saturation current of holes when the resistivity of silicon is raised from 3 $\Omega \cdot$ cm (Fig. 1, 3) to 10 $\Omega \cdot$ cm (Fig. 1, 4) is evidently associated with an increase in the thickness of the space-charge layer at the boundary with the electrolyte, in which the holes consumed in the anodic reaction are generated (^{5}).

If it is assumed that all the holes consumed in the anodic dissolution of silicon are formed only as a result of surface generation, then the magnitude of the saturation current would hardly depend so strongly on the resistivity of the silicon. Moreover, as Flynn has shown, such an assumption leads to inadmissibly high values of surface recombination on silicon. The fact that the holes consumed in the anodic dissolution of silicon are formed mainly in the space-charge region of the semiconductor at the boundary with the electrolyte must have a special influence on the nature of the action of additives of reducing agents and oxidizing agents. As was shown in (^{6}), the presence of the ion $C_2O_4^{2-}$ in solution causes an increase in the saturation current of holes on n-type germanium. The authors associated this phenomenon with the arrival at the surface, from the depth of the semiconductor, of an additional number of holes as a result of the action of a strong electric field. Obviously, such a phenomenon should not be observed on a silicon electrode, since holes generated in the bulk participate hardly at all in the anodic process. The experimental data fully confirm this assumption. The anodic curves recorded on silicon with $\rho = 10\ \Omega \cdot \mathrm{cm}$ and $\rho = 3\ \Omega \cdot \mathrm{cm}$ in $2.5\,N$ HF + $1.0\,N$ $K_2C_2O_4$ coincide with curves 3 and 4 of Fig. 1, obtained without additions of potassium oxalate.

On the other hand, the phenomenon of an increase in the saturation current of holes upon the introduction into solution of oxidizing agents of the $K_3Fe(CN)_6$ type, discovered by Gerischer and Beck (^{7}), should also occur for the silicon electrode, since in this case an additional number of holes arises directly at the surface of the semiconductor. This is confirmed by the course of curves 5 and 6 in Fig. 1, obtained

in a solution of $2.5\,N$ HF + $0.05\,N$ $K_3Fe(CN)_6$. Both curves, recorded with a reverse-biased p–n junction and with the circuit open, coincide.

Thus, as a result of the experiments carried out, direct proof has been obtained of the fact that the holes consumed in the anodic dissolution of silicon are generated mainly in the space-charge region at the boundary with the electrolyte, and not in the bulk of the semiconductor.

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