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E. N. Paleolog, K. S. Korotkova, and N. D. Tomashov

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Abstract

Full Text

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Kinetics of Electrode Processes on a Silicon Electrode in Acidic and Alkaline Solutions

(Presented by Academician A. N. Frumkin, March 3, 1960)

There have been no systematic studies of the electrochemical behavior of silicon in electrolyte solutions. In this respect, however, one may expect a fairly close analogy with germanium, since silicon and germanium are similar in both their semiconductor and chemical properties. Recently this assumption was experimentally confirmed by Flynn (^1), who showed that holes take part in the reaction of anodic dissolution of silicon, as in the case of germanium.

The distinctive features of the electrochemical behavior of the silicon electrode, as compared with germanium, must be associated with the presence on its surface of a film of silicon dioxide, which is insoluble in most aqueous solutions. According to Archer (^2), under ordinary conditions in air the surface of silicon is covered with a phase oxide film about 30 Å thick. An oxide film on silicon is also readily formed during its anodic treatment in a number of acidic solutions, which leads to strong polarizability of the silicon anode under these conditions ([3],4). The SiO_2 film is insoluble in most aqueous solutions; however, it is readily soluble in hot alkalis and in hydrofluoric acid. These solutions are used mainly for etching silicon.

In the present work we studied the rate of the hydrogen-ion discharge reaction on silicon and the rate of anodic dissolution of silicon in solutions of 0.2 *N* H_2SO_4, 1.0 *N* HF, and 5.0 *N* KOH. Measurements were carried out on single-crystal silicon of *n*- and *p*-types with different resistivities (0.2, 10.0, and 23.0 ohm · cm) and a diffusion length of 0.5 mm.

Silicon specimens 4–5 mm thick were cut from the middle of the cross section of a single crystal and had the same crystallographic orientation. The silicon surface was polished on boron carbide powders Nos. 100, 180, and 240. To provide electrical contact, one side of the silicon specimen was coated with a layer of electrolytic rhodium, to which a copper wire was soldered. Before each measurement, each specimen was checked for the absence of a rectifying contact. The specimen was then embedded in epoxy resin, resistant in both acidic and alkaline solutions. The experiments were carried out under thermostated conditions, in an intensively stirred solution, in the dark, in an air atmosphere. The electrode potential was measured 30 sec after changing the current density.

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Fig. 1. Cathodic polarization of n-type silicon.

Figure 1: Fig. 1. Cathodic polarization of n-type silicon.

Figure 1 gives the cathodic polarization curves of *n*-type silicon with different resistivities in a solution of 0.2 *N* H_2SO_4 and 5.0 *N* KOH*. The silicon surface was studied both immediately after mechanical grinding and after preliminary etching in a hot alkaline solution (KOH 400 g/l; temperature 80°, time 1 min.).

The results obtained show that in sulfuric acid solution at 25° the reaction of hydrogen-ion discharge on silicon with a polished (unetched—

* All polarization curves given below were constructed with allowance for the ohmic potential drop in the bulk of the specimen. The potential values are given on the hydrogen scale.

surface is strongly inhibited, and to a greater degree the higher the resistivity of the silicon (Fig. 1a). This inhibition in the present case is apparently associated with the presence of an oxide film on the electrode surface, since the slope of the polarization curves decreases appreciably on the reverse run, i.e., after partial reduction of the film, and also after preliminary removal of the film from the specimen during etching (Fig. 1b). The greatest decrease in polarization after etching occurs for silicon with a resistivity of 23.0 ohm · cm, since the film on such silicon is apparently especially perfect.

In a 5.0 N KOH solution at 50° (Fig. 1b), i.e., under conditions in which the oxide film on silicon is readily soluble, the rate of discharge of hydrogen ions on a silicon electrode depends little on its resistivity, and the cathodic behavior of *n*-type silicon under these conditions does not differ in principle from that of a metallic electrode.

Fig. 2 gives the curves of cathodic polarization of *p*-type silicon. We see that both in sulfuric acid and in 5.0 N KOH solution, hole-type silicon is polarized more strongly than *n*-silicon, and with increasing resistivity the slope of the polarization curves increases. The nature of the solution has only a slight effect on the kinetics of discharge of hydrogen ions on *p*-silicon. It should be noted that in sulfuric acid solution *p*-type silicon becomes a strongly polarizable cathode only after preliminary etching, whereas for a mechanically polished, unetched surface the cathodic polarization curves for *n*- and *p*-type silicon differ little. The latter is explained by the fact that in the process of preliminary etching not only the oxide film is dissolved, but also the surface layer of silicon with a lattice deformed (after mechanical polishing) is removed. For 5.0 N KOH solution at elevated temperature (50°), owing to the high rate of self-dissolution of silicon under these conditions, preliminary etching of the electrode has no effect.

Fig. 1. Cathodic polarization of *n*-type silicon.
a—surface after mechanical polishing, $t = 25°$; solution—0.2 N H_2SO_4; resistivity: 1—0.2 ohm · cm, 2—10 ohm · cm, 3—23 ohm · cm, 4—0.2 ohm · cm (hydrogen

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Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

atmosphere); points—curves of the reverse run.
b—surface after etching, resistivity: 1—1′—0.2 ohm • cm, 2—2′—10.0 ohm • cm, 3—3′—23.0 ohm • cm, 4—0.2 ohm • cm (hydrogen atmosphere); $1, 2, 3, 4$—0.2 N H_2SO_4 solution, $t = 25°$; $1', 2', 3'$—5 N KOH solution, $t = 50°$.

Analysis of the results obtained shows that the hydrogen-ion discharge reaction on *n*-silicon apparently proceeds with the participation of free electrons. The relatively low cathodic efficiency of *n*-silicon in sulfuric acid solution, as already indicated above, may be associated with the presence on the electrode surface, under these conditions, of a poorly conducting oxide film, which in turn also has semiconductor properties.

Fig. 2. Cathodic polarization of *p*-type silicon. Solution 0.2 N H_2SO_4, $t = 25°$, resistivity: 1—0.2 Ω · cm; 2—10.0 Ω · cm; 3—0.2 Ω · cm; $1, 2$—after etching, 3—without etching. Solution 5.0 N KOH, $t = 50°$, resistivity: 4—0.2 Ω · cm; 5—23.0 Ω · cm; $4, 5$—after etching. Dashed lines—reverse-scan curves.

Fig. 3. Anodic polarization of *n*-type $(2, 5, 6)$ and *p*-type $(1, 3, 4)$ silicon with a preliminarily etched surface. Solution 0.2 N H_2SO_4, $t = 25°$, resistivity: 1—10.0 Ω · cm, 2—1.0 Ω · cm, 3—10.0 Ω · cm; 3—protection under a gold solution. Solution 1.0 N HF, $t = 25°$, resistivity: 4—10.0 Ω·cm; 5—1.0 Ω·cm; 6—1.0 (under illumination).

All factors that promote removal or weakening of this film simultaneously increase the cathode efficiency of *n*-type silicon as well. The sharp decrease in the rate of hydrogen-ion discharge on *p*-type silicon may be explained both by a deficiency of free electrons (provided that they take predominant part in the given cathodic reaction) and by an additional ohmic potential drop in the near-surface layer of *p*-silicon depleted of holes. In this latter case, the main participation in the hydrogen-ion discharge reaction on *p*-silicon must belong to electrons from the valence band. The formation on *p*-silicon of a near-surface layer with a lower concentration of holes than in the bulk occurs in the course of cathodic polarization of the silicon electrode, and this is equivalent to the successive inclusion in the electrode circuit of a variable ohmic resistance. The decrease in the rate of the cathodic reaction on *p*-silicon observed in 5.0 N KOH solution at 50° (i.e., under conditions in which the oxide film proves to be readily soluble) with increasing resistivity allows one to consider the second assumption —i.e., the predominant participation in the hydrogen-ion discharge reaction on *p*-silicon of electrons from the valence band—to be the more probable. A similar view was also expressed in work (5).

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Proceeding from the structural features of a lattice with covalent bonds of the diamond type, one may expect that the process of anodic dissolution of silicon, as of germanium, will proceed with the participation of holes. The latter should be manifested in strong inhibition of the anodic dissolution reaction of electronic-type silicon. The peculiarity of the behavior of the silicon electrode consists

in the easy formation on the anode of oxide films that passivate the electrode and greatly increase the ohmic resistance of the electrode. The effect of the hole concentration under anodic polarization of n-type silicon may therefore appear only under conditions in which this anodic film is not formed on the silicon electrode (i.e., in electrolytes that readily dissolve silicon dioxide) and when the silicon-dissolution process is the principal anodic reaction. In sulfuric acid of any concentration the indicated film does not dissolve; therefore, in $0.2\,N$ H_2SO_4, irrespective of the type of conductivity and the state of the electrode surface, silicon is very strongly polarized and is practically an insoluble anode (Fig. 3). On the anode in this case a film of high ohmic resistance is formed, and oxygen is simultaneously evolved.

To confirm that, in a sulfuric acid solution, the strong anodic polarizability of p-silicon is in fact determined by the formation of a film on the anode, experiments were carried out on anodic polarization of a silicon electrode (p-type) with simultaneous mechanical cleaning of its surface under the solution [6]. The results obtained show (Fig. 3, 3) that up to a current density of about 15 mA/cm^2 the slope of the polarization curve under cleaning conditions decreases markedly, which is connected with continuous removal of the film during polarization and with some activation of the electrode surface. However, even under these conditions the film continues to form on the anode. At current densities above 15 mA/cm^2, the polarizability of p-silicon, even with cleaning, proves to be very high, since at this current density the rate of film formation apparently begins to greatly exceed the rate of its removal by cleaning.

On the basis of the results obtained, it may be considered that, in sulfuric acid solution in the range of potentials investigated by us, the high anodic polarizability of silicon with both hole and electronic conductivity is a consequence of passivation of the electrode. The principal electrode reaction under these conditions is oxygen evolution.

As was to be expected, different behavior of silicon with electronic and hole conductivity under anodic polarization is observed in $1.0\,N$ HF solution. Owing to the good solubility of silicon dioxide in hydrofluoric acid, p-type silicon, under anodic polarization in this solution, is not passivated up to a current density of 30 mA/cm^2.

For silicon of the electronic type, already at a current density of about 1.0 mA/cm^2 the anodic process begins to be strongly inhibited; by analogy with germanium this may be connected with the attainment of a limiting current for the holes participating in the electrode reaction of silicon dissolution. For n-type silicon, holes are minority charge carriers, and the rate of their

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delivery to the boundary with the solution determines the rate of anodic dissolution of n-silicon.

The data obtained thus show that the electrochemical behavior of silicon in electrolyte solutions is fundamentally similar to that of germanium and, as for germanium, is determined by its type of conductivity. The principal difference in the electrochemical behavior of silicon as compared with germanium is that, owing to the high chemical inertness of SiO_2, silicon under most conditions is characterized by the presence of an oxide film on the surface. The presence of such a film, possessing high ohmic resistance, leads to additional inhibition of the cathodic and anodic reactions on the silicon electrode.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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