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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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PECULIARITIES OF THE PHOTOELECTROCHEMICAL BEHAVIOR OF THE SILICON–ALKALI INTERFACE

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The photoelectrochemical behavior of silicon during self-dissolution and in the initial region of the passive state depends strongly on the nature of the processes occurring at the surface, which are determined by the potential, the composition of the solution, and the temperature (^1).

In studying the influence of light on the silicon—alkali interface, a dual effect of irradiation was found, consisting in the fact that light can both passivate an etching electrode and completely activate a passive system. The process of photopassivation is illustrated in Fig. 1 (curve 1), from which it follows that illumination initially shifts the potential ϕ^* of silicon toward more cathodic (n-Si) or positive (p-Si) values, in accordance with the type of conductivity. The subsequent, slower displacement of the photopotential ϕ__c into the anodic region is evidently caused by suppression of the etching process, which is especially noticeable after the light is switched off, when ϕ abruptly passes into the range of values characteristic of the passive state in the dark. Photopassivation of the electrode is observed only when an anodic current $i_a < i_{a\,\mathrm{max}}$ is applied and at high light intensities. Consequently, it may be concluded that light passivates the system at insufficient dark currents (Figs. 1 and 2). Moreover, the rate of photopassivation (determined from the change in ϕ__c), inversely proportional to the irradiation time, increases with increasing potential and light intensity. Figure 2 (curve 3) gives the change in the number of absorbed light quanta (Z) that cause photopassivation with increasing polarization ($i_a \to i_{a\,\mathrm{max}}$). The same figure shows the decrease of i_{cp} when ϕ is shifted to less negative values. From Fig. 2 it follows that a slight increase in i_a with ϕ leads to an exponential decrease in i_{cp}: $i_{\mathrm{cp}} = k_1 e^{-\varphi}$. At the same time, the quantum yield of photopassivation increases

Fig. 1. Curves of photopassivation of n-Si in 10 N KOH (30° C) (1); 2—

Fig. 2

Figure 2: Fig. 2

photoactivation (light parameters: $\lambda = 525$—530 mμ, $E \sim 2$ eV, light intensity $6.3 \cdot 10^{-3}$ cal/sec $\cdot$ cm^2)

$$K = \frac{\Delta i_a}{Z}$$

($\Delta i_a = i_{a\,\max} - i_a$—additional light current promoting passivation of the electrode, with $i_a \to i_{a\,\max}$, $\Delta i_a \to 0$). From the experimentally established linear dependence of Δi_a on $\lg Z$ and $\lg Z$ on the potential shift $\Delta\varphi$ from the stationary φ_{st}, one can obtain an expression relating Z to i_a:

$$Z = k_2 e^{\Delta i_a} = k_2 e^{i_{a\,\max} - i_a}, \quad \text{and} \quad i_{a\,\max} = k_3 i_{\text{cp}}$$

$$(\Delta\varphi = \varphi_{\text{st}} - \varphi = \Delta\varphi_{\text{oz}} + \Delta\varphi_{\text{g}} + \Delta\varphi_{\text{os}},$$

where $\Delta\varphi_{\text{oz}}$—change in the potential jump—

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* Values of ϕ are given relative to the hydrogen alkaline electrode.

potential in the bulk, $\Delta\varphi_{\text{H}}$—in the Helmholtz double layer, $\Delta\varphi_{\text{ox}}$—in the oxide layers). Photopassivation occurs for all concentrations from 10^{-3} to $20\,N$ and temperatures (20-80°C), and is practically independent of the preliminary treatment of the electrode surface. The necessity of a definite irradiation time indicates that passivation by light develops with time, since there is an opposing factor—the etching action of the alkali, which increases with increasing temperature. Evidently, as the temperature rises, photopassivation is effected at higher light intensities.

In contrast to photopassivation on the ascending branch of the anodic polarization curve, illumination in the initial region of the passive state (descending branch) leads to activation of the electrode.

Fig. 2. **1**—Anodic polarization curve, **2**—decrease in the self-dissolution rate i_{cp}, **3**—change in the number of light quanta passivating the electrode, with potential φ

As shown in Fig. 1 (curve 2), photoactivation of passive silicon is observed. As can be seen from the figure, short-term irradiation of the system causes complete activation of Si, which is manifested in the transition of φ into the range of values characteristic of the etching process with hydrogen evolution. Complete photoactivation occurs in a definite region of potentials (100-300 mV); at

Figure 3

Figure 3: Figure 3

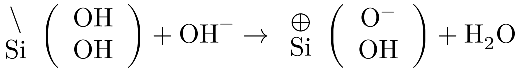
more anodic values (400-600 mV), incomplete photoactivation is observed (a temporary shift of φ toward less anodic values after the light is switched off). With a further increase in polarization, photoactivation disappears completely. When the temperature is increased in $10\,N$ KOH, the interval of φ in which light completely activates the electrode expands considerably. In dilute solutions (10^{-3}-$1\,N$), with increasing temperature (60°), complete photoactivation is observed only in $1\,N$ KOH and in a very narrow region. At low temperatures (20-30°) in these same concentrations, light does not cause even incomplete activation. Photoactivation depends substantially on φ and on the light intensity. Thus, the more anodic φ is (under conditions of complete photoactivation), the longer the illumination time at $Z = \text{const}$; and, conversely, at $\varphi = \text{const}$, an increase in temperature promotes activation at considerably lower Z.

It is natural to suppose that photopassivation and photoactivation may be due to the manifestation of acceptor or donor properties by oxygen passivating the surface in the process of anodic polarization. In this connection, data on the measurement of resistance R and capacitance C in alternating current (0.2-100 kHz) in combination with the action of

light. Figure 3 shows changes in the resistance, capacitance, and photoeffect (ΔV_c) for both types in $10\,N$ KOH (30°). Under stationary etching conditions, ΔV_c on n-Si is practically absent, whereas on p-Si it is 600 mV (^{1}). Accordingly, the RC values measured at high frequencies (f = 40 kHz) will differ for the two types. Indeed, if C of n-Si is of the order of 1 μF/cm^2, then for p-Si $C = 3.0$-$4.0 \cdot 10^{-2}$ μF/cm^2. Under anodic polarization up to $\varphi = 150$-200 mV, when the positive charge (n-Si) increases and the negative charge (p-Si) decreases in the space-charge layer, the behavior of RC and ΔV_c is quite regular and basically reflects the change in the space-charge parameters with potential. Consequently, under these conditions electrochemically adsorbed oxygen plays the role of an electron acceptor. However, at a potential of 150-200 mV a sharp violation of the regular change in RC occurs for both types, manifested in an increase of C for n-Si and a decrease for p-Si. Equally unusual is the change in ΔV_c at these potentials, consisting in a decrease on n-Si and constancy or an increase for p-Si, contrary to what should have been observed under anodic polarization. Evidently, such an anomalous course of the change in the parameters of the system with potential in the initial stage of the passive state (150-300 mV) compels one to assume that oxygen in this region changes from an acceptor into an electron donor (^{2}). Thus, from the data considered it follows that in the potential interval where passivating oxygen—an electron acceptor—is present, a process of photopassivation is observed, whereas in the region where donor properties appear there is photoactivation, which disappears after oxygen again becomes an acceptor at potentials above 400 mV.

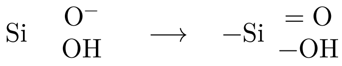
Fig. 3. Dependence curves C—φ (1), R—φ (2), 3 –change in ΔV_c under anodic polarization; A –for n-Si, B –for p-Si (the RC values are given from the parallel circuit)

The acceptor nature of oxygen can be established from the fact that the electrode is passivated by small anodic currents, two orders of magnitude smaller than the self-dissolution currents i_{sr} (Fig. 2). This, apparently, is due to the formation of a negatively charged oxygen dipole as a result of discharge of OH^- ions of the solution on the OH radicals adsorbed during self-dissolution, with localization of the hole



$$\overset{\backslash}{\mathrm{Si}}\begin{pmatrix}\mathrm{OH}\\ \mathrm{OH}\end{pmatrix} + \mathrm{OH}^- \rightarrow \overset{\oplus}{\mathrm{Si}}\begin{pmatrix}\mathrm{O}^-\\ \mathrm{OH}\end{pmatrix} + \mathrm{H_2O}$$

It is generally known that the ion-radical O^- has a high passivating ability, manifested in the impeded interaction of OH^- with silicon atoms over a considerable portion of the surface adjacent to O^- (^{3}). With an increase in the anodic current ($i_a \rightarrow i_{a\,\mathrm{max}}$), the amount of adsorbed O^- increases; moreover, with an insignificant increase in the concentration of dipole oxygen on the surface, the self-dissolution current i_{cp} decreases exponentially (Fig. 2). A further increase in the anodic potential leads to withdrawal of charge from a certain part of the surface O^-, which depletes the surface of holes as a result of their recombination with the electrons of O^-.



$$\mathrm{Si}\begin{matrix}\mathrm{O}^-\\ \mathrm{OH}\end{matrix} \longrightarrow -\mathrm{Si}\begin{matrix}=\mathrm{O}\\ -\mathrm{OH}\end{matrix}$$

The decrease in the negative charge of the surface, with a simultaneous decrease in the positive charge in the space-charge layer, is manifested in the anomalous course of RC and ΔV_c for both types. Consequently, under certain conditions the ion-radical O^- can be converted from an acceptor into an electron donor. Despite the strengthening of the bond upon the transition of O^- into uncharged O, the passivating ability decreases because the etching process is inhibited only at the adsorption sites.

Proceeding from the concepts developed, it is natural to assume that the photopassivation of silicon is caused by the additional formation of O^- under the action of light according to the mechanism given above. Consequently, illumination acts in the same way as external anodic polarization, i.e., in the light a directed photoelectrochemical current is excited,

$$i_{\mathrm{ph}} = \Delta i_a = i_{a\,\mathrm{max}} - i_a,$$

superimposed on the polarizing anodic current i_a. In the initial region of the passive state, characterized by the anomalous course of RC and ΔV_c (Fig. 3), illumination converts the oxygen acceptor O^- into a donor. Indeed, in the above-mentioned region the passive state in the dark is maintained by a definite concentration of O^- and O on the surface. The action of light promotes an additional decrease of O^-, as compared with the dark. Removal of charge from O^- leads to the fact that, at sites previously passive because of the long-range effect, the etching process begins with the participation of Si—OH groups. Since the anodic current for maintaining the passive potential is $i_{\mathrm{an}} < i_{a\,\mathrm{max}}$, the electrode ultimately begins to be actively etched. Obviously, complete or incomplete photoactivation depends on the amount of O^- (with an overall increase of passivating oxygen on the surface); moreover, with a decrease in O^- the efficiency of photoactivation decreases. In addition, the rate of photoactivation will increase with increasing temperature and KOH concentration.

Thus, electrochemically adsorbed oxygen may be an electron acceptor or donor, and depending on the manifestation of these properties, a process of photopassivation or photoactivation takes place. The action of light irreversibly changes the nature of the passivating oxygen, determined by the character and strength of its bond with the lattice, which affects in different ways the structure of the silicon–alkali interface and, thereby, the process of self-dissolution.

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CITED LITERATURE

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