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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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Electrochemical and Photoelectrochemical Behavior of a Silicon Electrode

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The study of electrochemical and photoelectrochemical parameters in the process of silicon etching in alkali is of interest from the standpoint of elucidating the mechanism of self-dissolution and the influence of changes in the surface state on the photogalvanic activity of the system. Of the few works ([1–6]) devoted to the electrochemical behavior of silicon, only one ([6]) considers the influence of optical radiation on a silicon electrode in the absence of an external electric field in alkaline solutions.

Fig. 1. 1 —change in potential during etching in 10 N KOH of ground specimens; 2 —for pre-etched specimens; 3 —decrease in the self-dissolution current during etching of ground specimens.

The object of the study was single-crystal silicon of n- and p-types with $\rho = 1\ \Omega \cdot \text{cm}$. The crystallographic orientation of the surface was (111). An incandescent lamp served as the source of undecomposed light of high intensity ($\sim 10^{-1}$ cal/cm$^2 \cdot$ s). The following methods of surface treatment were used: etching in hot KOH or HF + HNO_3, and mechanical grinding with abrasive powder.

The process of silicon self-dissolution with hydrogen evolution was studied in KOH solutions of various concentrations (0.01—10 N). Figure 1 shows, for n- and p-Si, the practically coincident course of the change in potential with time from −550— − 500 mV, which is the immersion potential, to a constant value of −300— − 320 mV in 10 N KOH for ground specimens (curve 1) and etched specimens (curve 2). As KOH is diluted, less negative values of the stationary potentials are established (−200—50 mV), which is associated with the greater oxidized character of the surface owing to the lower rate of self-dissolution. The self-dissolution current, measured from the rate of hydrogen evolution, decreases with time from a maximum value of $5—6 \cdot 10^{-3}$ A/cm^2 to a stationary value of $1 \cdot 10^{-3}$ A/cm^2 upon attainment of a stable potential (Fig. 1, 3). As is seen from Fig. 1, the observed shift of the potential during etching toward a less cathodic

Fig. 2. Anodic polarization curves: 1 and 3—for freshly immersed polished specimens; 2 and 4—after attainment of stationary conditions; 5 and 6—dependence of the rate of hydrogen evolution on potential

Figure 2: Fig. 2. Anodic polarization curves: 1 and 3—for freshly immersed polished specimens; 2 and 4—after attainment of stationary conditions; 5 and 6 —dependence of the rate of hydrogen evolution on potential

Fig. 3. Increase of ΔVc with time during etching of polished specimens: 1—course of potential change; 2—p-Si; 3—n-Si

Figure 3: Fig. 3. Increase of ΔVc with time during etching of polished specimens: 1—course of potential change; 2—p-Si; 3—n-Si

stationary value for ground specimens is accompanied by a change in the rate of self-dissolution. This change may be caused both by a decrease in the true surface as a result of etching away the mechanically disturbed layer and by an enhancement of a possible oxidation process. The shift of the po-

potential is due exclusively to the greater oxidation of the surface under stationary conditions of self-dissolution. The opposite course of the change of potential with time for etched specimens, from less cathodic to the stationary value, is explained by considerable dissolution of the oxide film produced by preliminary chemical etching and by exposure in air ([7]). Figure 2 gives the anodic polarization curves for both types, recorded immediately after immersion (curves 1, 3) and after the same electrode had reached the stationary state (curves 2, 4), showing suppression of the self-dissolution process and transfer of silicon into the passive state. It follows from Fig. 2 that, at lower rates of self-dissolution under conditions of stationary etching, the maximum current required for passivation of the electrode is substantially reduced ($6—10 \cdot 10^{-6}$ A/cm^2) in comparison with the current passivating a freshly immersed polished electrode ($75—85 \cdot 10^{-6}$ A/cm^2), while in both cases these currents are approximately two orders of magnitude smaller than the self-dissolution currents.

Fig. 2. Anodic polarization curves: 1 and 3—for freshly immersed polished specimens; 2 and 4—after attainment of stationary conditions; 5 and 6—dependence of the rate of hydrogen evolution on potential

Fig. 3. Increase of ΔV_c with time during etching of polished specimens: 1—course of potential change; 2—p-Si; 3—n-Si

It is interesting that the potential of the maximum of the anodic curve for the p-type is 200 mV more positive than for n-Si. Apart from this difference and the somewhat higher current values for p-Si, as is seen, no fundamental difference is observed between n- and p-Si under anodic polarization. Measurements of the rate of hydrogen evolution simultaneously with the recording of the polarization curves show that currents shifting the potential by 100 mV into the anodic region for the n- and p-types are 500-600 times smaller than the self-dissolution

Fig. 4

Figure 4: Fig. 4

current, equal to $1 \cdot 10^{-3}$ A/cm^2. Moreover, it turned out that the rate of hydrogen evolution is practically unaffected by a shift of the potential by 230 mV (n-Si) and 420 mV (p-Si) into the anodic region (Fig. 2, 5, 6). The slowing of self-dissolution begins at potentials 80-90 mV more cathodic than the maximum of the polarization curves. Complete cessation of the gas-evolution process occurs with time only in the region of the potentials of the maximum. Cathodic polarization to -1—-1.5 V (p-Si) and 0.6 V (n-Si) also has almost no effect on the rate of self-dissolution. However, the currents under cathodic polarization of the n-type are one to one and a half orders of magnitude greater than for p-Si and become comparable with the self-dissolution currents. In other words, under cathodic polarization the nature of the conductivity becomes sharply manifest.

In addition to changes in the potential and in the rate of self-dissolution, the photogalvanic activity ΔV_c of the system also changes during the etching process. For polished p-type specimens, ΔV_c increases from zero to a constant value of 600 mV under stationary conditions of self-dissolution (Fig. 3, 2). For n-Si under these same conditions the maximum value of ΔV_c does not exceed 10-15 mV (curve 3). The more dilute the alkali solution, the smaller ΔV_c is for the p-type and the larger it is for n-Si in comparison with 10 N KOH, which is evidently connected with the greater oxidation of the surface. It should be especially noted,

that the rate of hydrogen evolution practically does not change under the action of optical radiation, despite the shift of the measured potential of the system into the anodic region up to $+250 \div 300$ mV at $\Delta V_c = 600$ mV (p-Si). Oxidation of the surface, both by anodic polarization and by preliminary chemical etching and the introduction of oxygen into the solution, noticeably affects the photoeffect, increasing ΔV_c for n-Si (50-100 mV) and decreasing it for the p-type (200-400 mV). In the process of dissolution of the oxide film, with a simultaneous rise of the potential to the initial stationary value, the photoeffect increases for the p-type (Fig. 4, 1) and decreases for n-Si (Fig. 4, 2).

Fig. 4. Change in ΔV_c during dissolution of the oxide film for:
1 —p-Si; 2 —n-Si

The specificity of the electrolyte has a strong effect on the electrochemical and photoelectrochemical parameters. In contrast to KOH, in H_2SO_4 the process of self-dissolution is practically absent, owing to which the anodic polarization curves do not pass through a maximum, the stationary potentials are positive, and the surface properties specified by the treatment are almost preserved. The shift of the potential with time into the anodic region, independent of the treatment, is evidently associated with further oxidation of the surface in the solution. The maximum value $\Delta V_c = 500$ mV is observed only for etched n-type material;

whereas for p-Si ΔV_c is strongly reduced (150-250 mV), and under constant illumination a further decrease occurs. The anodic current for the return of the light potential to the dark value decreases from $70\text{-}80 \cdot 10^{-6}$ A/cm^2 to $2\text{-}3 \cdot 10^{-6}$ A/cm^2 because of the growth of the oxide film in this case. Anodic polarization introduces substantial changes into the parameters of the system, and in the case of H_2SO_4 the correlation between the degree of oxidation of the surface and ΔV_c, observed in KOH, disappears.

Thus, from the results presented it follows that the rate of the process of self-dissolution of silicon in alkali is practically the same for p- and n-Si, is not controlled by the measured potential over a considerable interval, and does not change substantially under the action of optical radiation. The practical coincidence of the self-dissolution rate for n- and p-Si indicates the independence of this process from the type of conductivity. The energy of the leading act of the chemical interaction of silicon atoms with OH^- in the overall self-dissolution process

$$Si + 2OH^- + H_2O = SiO_3^{2-} + 2H_2$$

ensures the occurrence of the compensating coupled cathodic reaction of hydrogen-ion discharge, which proceeds with consumption of electrons released by the anodic reaction from the valence band. In explaining the mechanism of the cathodic reaction of self-dissolution, certain difficulties arise. The observed difference (by an order of magnitude and more) in the currents under cathodic polarization of both types indicates that, apparently, in the process of self-dissolution there is no transfer of electrons into the conduction band or realization of surface energy levels. Consequently, owing to the coupling in a single act of silicon ionization and proton discharge, the cathodic reaction of self-dissolution proceeds with consumption of electrons, probably directly from the valence band. Under cathodic polarization, however, electrons are taken from the conduction band, which is manifested in the above-mentioned difference in the behavior of n- and p-type material. However, additional investigations are necessary to clarify these questions.

The absence of a fundamental difference in the course of the anodic curves for n- and p-silicon (Fig. 2) and the passivation of the surface by currents by two orders

lower self-dissolution currents under stationary etching conditions may be caused by further electrochemical oxidation. The somewhat greater polarizability of the p-type (a shift of the maximum of the anodic curve by 200 mV into the anodic region) and the independence of the rate of hydrogen evolution on the ascending branches of the curves are associated with a predominant change in the potential drop in the space-charge region. An analogous conclusion can be drawn when considering the effects of optical radiation. The substantial difference in ΔV_c for p- and n-Si in the absence of an external electric field is due to the fact that, in the process of self-dissolution, the surface of p-Si

approaches the n-type, whereas oxidation acts in the opposite direction, namely: toward a decrease in ΔV_c for p-Si and an increase for n-Si. It follows from this that, although the measured stationary potentials are practically identical for both types, the distribution of potential drops at the silicon–solution interface is different. Etching away the mechanically defective layer, by reducing surface recombination, leads to an increase in ΔV_c for p-Si. Evidently, light acts mainly on the space-charge region, as follows from the practical invariance of the rate of hydrogen evolution upon illumination.

It follows from the foregoing that it is precisely the presence of two conjugate oxidation and reduction reactions in the irreversible process of self-dissolution of silicon in alkali that determines the independence of the dissolution rate from the type of conductivity and, along with the state of the surface, the photogalvanic activity of the system.

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