

Electrolytic Growth and Dissolution of Oxide Layers on Silicon in Aqueous Solutions of Fluorides

H. Gerischer and M. Lübke

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-1000 Berlin 33, Federal Republic of Germany

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The growth and dissolution of oxide layers on silicon has been studied under illumination and in the dark by analyzing current transients at different voltages in solutions of NH_4F of various concentrations at pH values between 1 and 4.5. When the oxidation rate of the silicon at high enough anodic bias and, for n-type specimens, high enough illumination intensity exceeds the rate of oxide dissolution in the fluoride, the film grows until it has reached a thickness where the dissolution is rate-determining for the net process. At higher voltages the current begins to oscillate. The data give some insight into the composition of the oxide layers and their electronic and ionic properties.

Introduction

The electrochemistry of silicon in contact with aqueous electrolytes is complicated by the great tendency to form oxide layers [1–4]. This can only be prevented in the presence of hydrofluoric acid in which the oxide dissolves forming $[\text{SiF}_6]^{2-}$ ions [5–7]. In a recent investigation we have studied the behavior of n-type silicon in slightly acidic ammonium fluoride solutions [8]. Anodic oxidation in such solutions occurs only under illumination. No oxide layer is formed as long as the photocurrents do not exceed a critical height at which oxide formation can no longer be prevented. The mechanism of the photooxidation in this range has been analyzed, and it was confirmed that two of the four oxidation steps transforming silicon into $[\text{SiF}_6]^-$ ions are controlled by the supply of holes while two consecutive steps can be performed by electron injection into the conduction band [9]. If the light intensity and the thus generated photocurrent at n-type materials exceeds this critical value, an oxide grows on top of the silicon which allows the anodic photocurrent to decrease until a steady state is reached in which the dissolution of the oxide becomes the rate-controlling step. The same happens at p-type materials under anodic bias, if the rate of oxidation exceeds the same critical limit for direct formation of the silicon fluoride. In the present investigation we have studied the growth and the dissolution of the oxide layers formed on silicon with the intention of analyzing the mechanism of its growth and the composition of the oxide produced on the surface.

Experiment

The experiments were performed in a similar way as reported previously [8]. N-type silicon specimens with a donor density of $4 \cdot 10^{15} \text{ cm}^{-3}$ from Heliotronic GmbH (Wacker Chemie) in the form of thin slices with a (111) surface orientation have been used. Photocurrent or dark current transients were measured under potentiostatic control at a rotating electrode. Potentials are given vs. the Saturated Calomel Electrode (SCE). The electrolyte solutions were prepared from p.a. grade ammonium fluoride and triply distilled water. The pH was adjusted by addition of sufficient amounts of HCl. Oxygen was removed by passing pure nitrogen through the electrolyte. Illumination was performed with a Xenon lamp XB0 150 using neutral filters for varying the light intensity.

Results

If the photocurrent exceeds the critical value starting from an oxide-free Si surface, a rapid decay of the photocurrent is observed

in the transient with a short step after the first rapid decay. The current finally reaches a constant value which is independent of the illumination intensity. This is shown in Fig. 1. The initial step is connected with the photocurrent multiplication on the oxide-free silicon surface as long as surface atoms can directly interact with fluoride ions from the solution [6]. The height of this stationary current steeply increases with increasing fluoride concentration. This is shown in Fig. 2 for a solution with constant pH.

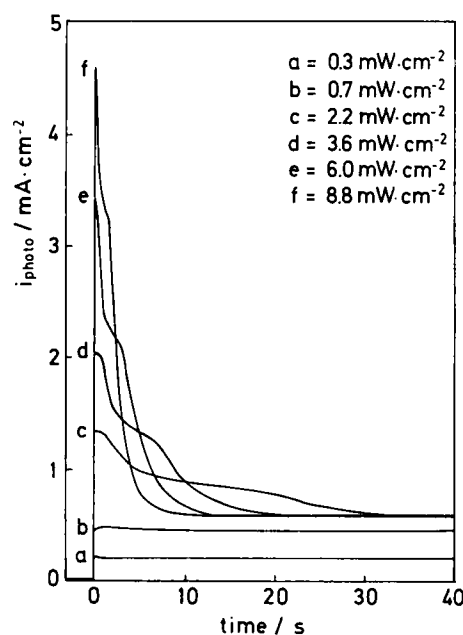


Fig. 1
Photocurrent transients on n-type Si at different illumination intensities in 0.13 M NH_4F , pH = 4, $U = 2.75 \text{ V}$

The photocurrent in the stationary state depends also on the pH as shown in Fig. 3 for different fluoride concentrations. At pH values below 2.4 we found a decay of the stationary current, which is not yet understood. We did not investigate this range in more detail.

The stationary current under high enough illumination depends also on the applied voltage. This is shown in Fig. 4. The decay of the stationary current below 0 V is connected with the decay of the photocurrent due to a too small band bending in the silicon at this bias. The minimum between 0 and 1 Volt may be connected with the formation of recombination centers in the oxide layer which is being formed or by the shift of the band edge position connected thereto. We mainly investigated the range above 1.5 V, where the stationary current continuously decreases with increasing bias.

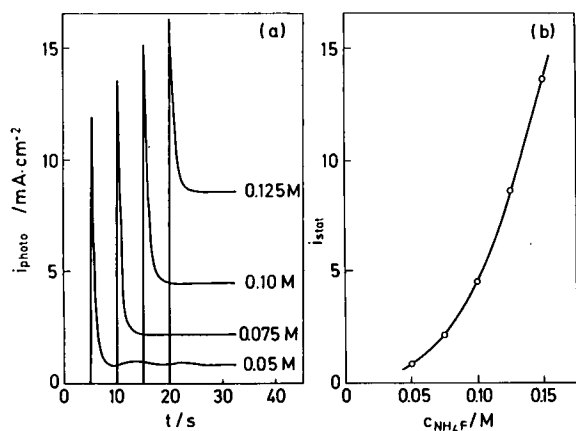


Fig. 2

- a) Photocurrent transients at $U = 2 \text{ V}$ and $\text{pH} = 3.5$ in different concentrations of NH_4F .
 b) Dependence of the stationary current on the fluoride concentration; n-type Si under illumination

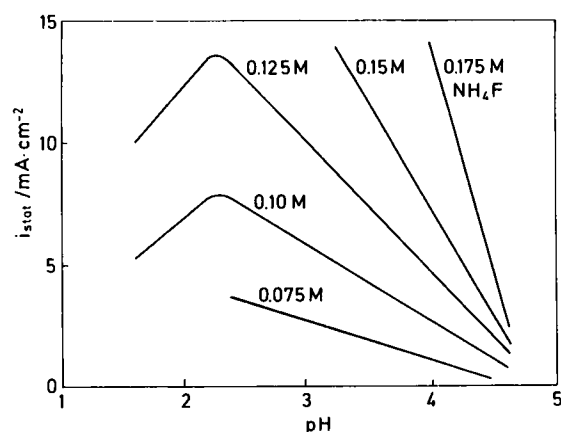


Fig. 3

Influence of the pH on the stationary currents of illuminated n-Si at $U = 2 \text{ V}$ for different fluoride concentrations

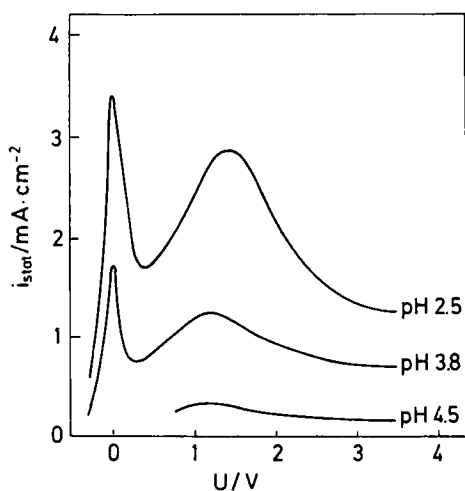


Fig. 4

Voltage dependence of the stationary current in $0.1 \text{ M NH}_4\text{F}$ for different pH values; n-Si under illumination

At higher voltages no stationary state was reached. Oscillations appeared instead as shown in Fig. 5. The amplitude of these oscillations increased with increasing bias. The frequency of the oscillations became more rapid with increasing fluoride concentration parallel to the increase of the stationary current at lower bias.

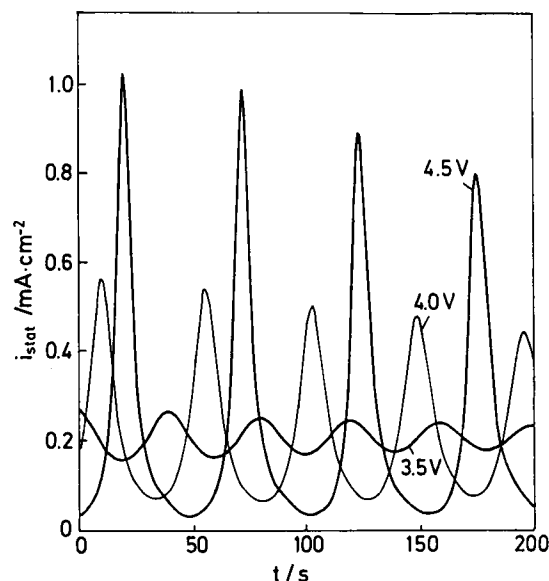


Fig. 5

Oscillations of the oxidation current on illuminated n-Si in $0.1 \text{ M NH}_4\text{F}$, at $\text{pH} = 4$ for different bias applied

As the light was interrupted but the bias kept constant, the photocurrent suddenly dropped to nearly zero. However, after some time a current arose in the dark passing a maximum until it decayed to a very small value, which corresponded to a rate of oxidation of the silicon at this voltage in the dark (these electrodes did not have a perfect blocking character). This behavior is shown in Fig. 6 for the same electrode at different bias. At higher voltages, where the layer is thicker, the current transient appears at a later time. Similar observations have already been made by Matsumura and Morrison [9]. This transient current is obviously connected with the dissolution of the oxide layer and indicates that during the dissolution some oxidation of silicon in the oxide layer still occurs. We calculated the integral charge in these transients which is given as an insert in Fig. 6. The numbers show that the amount of electricity needed for the oxidation of the not fully oxidized silicon in this oxide layer remains approximately constant with a slight increase when higher voltages are applied.

If one assumes that the dissolution rate of the oxide remains constant during its formation period, i.e. until the steady state has been reached, one can calculate the electric charge Q , which is

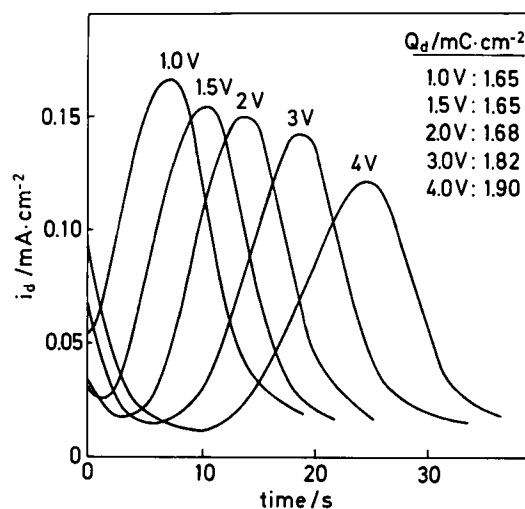


Fig. 6

Current after interruption of the illumination of n-Si in $0.1 \text{ M NH}_4\text{F}$ at $\text{pH} = 4$ for oxide layers formed at different voltages, which were kept constant. Q_d = current time integrals

stored in the oxide layer, by an integration of the excessive photocurrent before the steady state is reached. This procedure is demonstrated in Fig. 7, on the left-hand side for two different voltages applied to the same electrode in the same electrolyte and on the right-hand side for experiments at the same voltage in two different electrolytes. If one plots the charge, in this way calculated for the oxide formation, versus the applied voltage, one obtains the result represented in Fig. 8 for three different concentrations of the fluoride. This figure shows an approximately linear increase of this charge with the bias applied and relatively small differences in different electrolytes. This is surprising insofar as the stationary current between a 0.1 M and a 0.4 M NH_4F solution at pH 4 differs by a factor of 5–10.

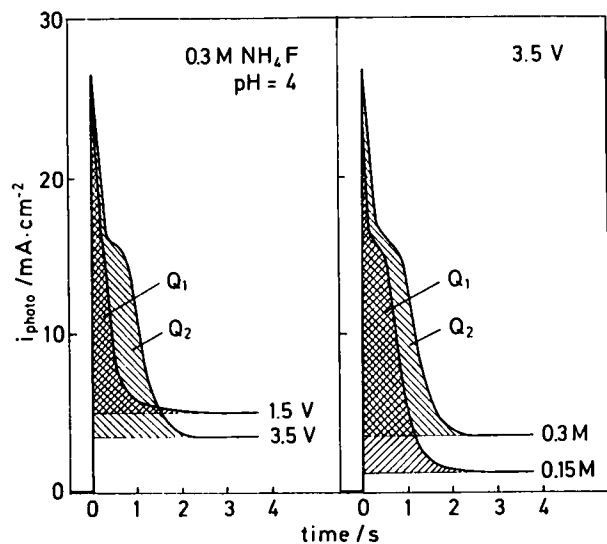


Fig. 7

Procedure for measuring the electric charge Q stored in the oxide layer at the steady state

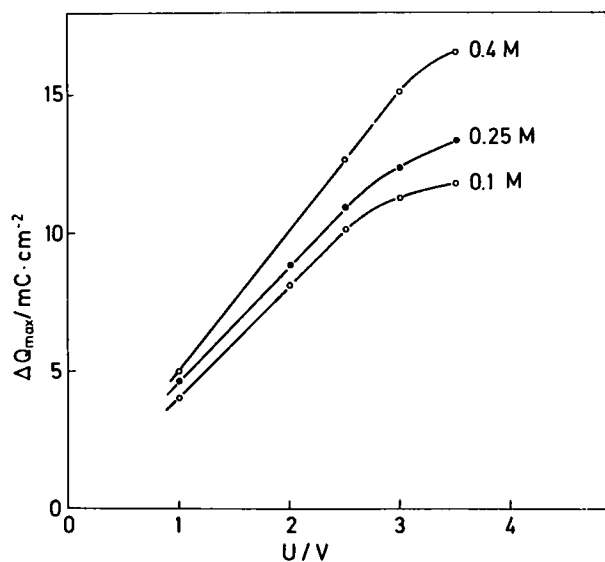


Fig. 8

Dependence of the stored charge Q in the oxide layer on the applied voltage for different concentrations of NH_4F at pH = 4

In order to check whether the assumption that the dissolution rate of the oxide layer during the dark period remains approximately constant, the illumination was interrupted for different periods, τ , after the steady state situation had been reached. Then the illumination was switched on again and the excess photocurrent was measured and integrated until the steady state had been

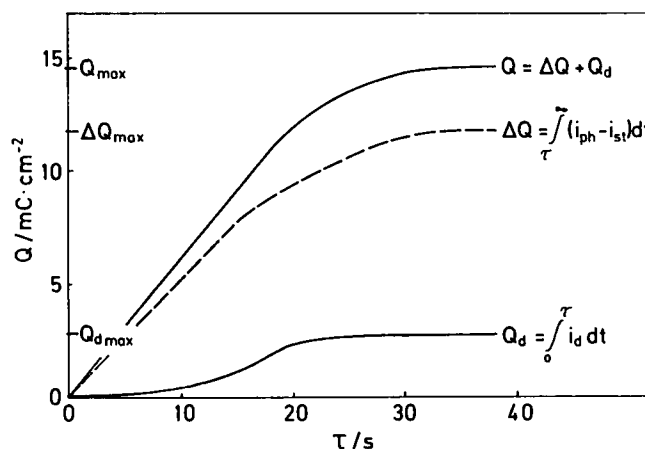


Fig. 9

Amount of electricity, ΔQ , needed for restoring the steady state situation after an interruption of the illumination for the period τ ; integral of the dark current, Q_d , for the period τ . N-type Si in 0.07 M NH_4F at pH = 3.8; $U = 3$ V

reached. This integral is shown in Fig. 9 together with the integral of the dark current during the period of the interruption of the illumination. The plot of Fig. 9 is made for conditions under which the oxide layer dissolved relatively slowly in order to make the transients longer and easier to integrate. The results were similar under other conditions and at higher dissolution rates of the oxides. Fig. 9 also contains the sum of both integrals which corresponds to the whole electric charge stored in the oxide layer, if one assumes that the oxide dissolves only in the form of tetra-valent Si and the current flowing during dissolution of the oxide in the dark (cf. Fig. 6) is due to the oxidation of silicon from a lower valence state inside the oxide layer to Si^{4+} . The linear increase of ΔQ in the first part of the figure can be taken as the proof that the dissolution rate of the oxide remains constant, at least during this period.

The behavior of p-type specimens was very similar with the only difference that no illumination was needed for the anodic process. The current on the oxide-free specimen is initially controlled by the applied bias. At high enough bias, however, the anodic current dropped rapidly to a stationary value which depended on the electrolyte composition in a way very similar to that found for n-type specimens under illumination. An example of the current transient and the dependence of the stationary current on the voltage applied for two different fluoride concentrations is given in Fig. 10. The

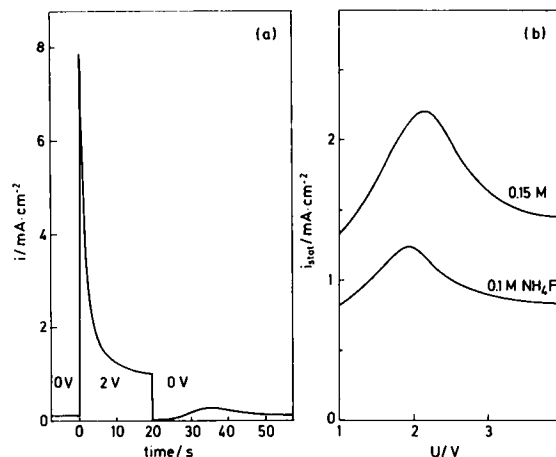


Fig. 10

- Current transients for p-type Si in 0.1 M NH_4F at pH = 3.8 during a voltage step between $U = 0$ and $U = 2$ V.
- Voltage dependence of the steady state current for two NH_4F concentrations at pH = 3.8

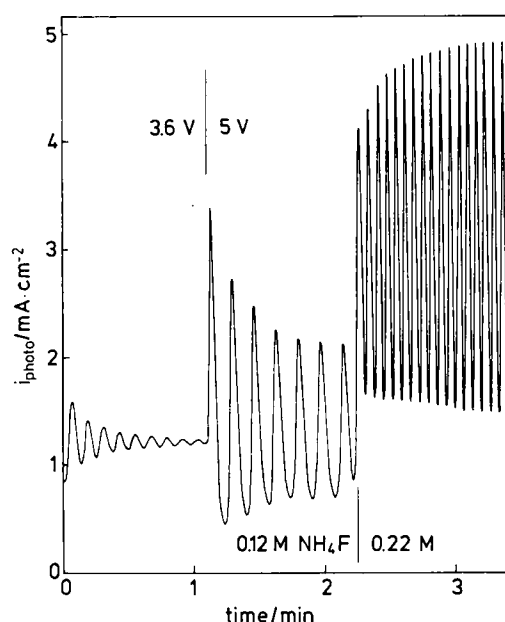


Fig. 11

Current oscillations on p-type Si in 0.12 M, or respectively 0.22 M NH_4F at pH = 3.8 for two different voltages

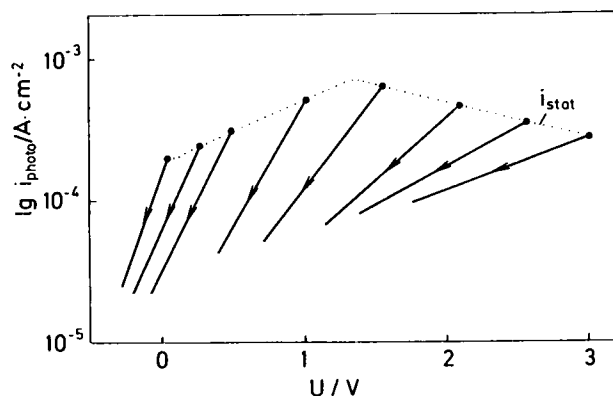


Fig. 12

Potentiodynamic current voltage curves of n-Si starting from the steady state under illumination with a rapid potential scan (1 V s^{-1}) into negative direction from different voltages. 0.1 M NH_4F ; pH = 1

current during dissolution of the oxide layer can in this case only be observed after reduction of the bias to a value where the current on the oxide-free surface would be negligible. In such an experiment shown in the transient of Fig. 10a a current maximum appears some time after the voltage step to low bias indicating that parts of the oxide are further oxidized during the dissolution in the same way as was seen in Fig. 6 for the n-type specimens.

At higher anodic bias, oscillations are also generated on the p-type samples, as seen in Fig. 11 where at first the bias is increased and afterwards the fluoride concentration. The latter change increases the frequency.

Discussion

The experiments demonstrate that the dissolution rate of the silicon oxide becomes the rate-determining step if sufficient holes are available at the contact between silicon and the oxide. This is achieved for n-type materials by illumination, at p-type materials just by the forward bias applied. In the steady state, the formation of new oxide as well as the transport of silicon ions through the oxide layer regardless of the mechanism of this transport [10, 11] must match

the rate of dissolution. The main driving force for the transport of these ions through the oxide layer is the electric field in this layer. This can easily be demonstrated by measuring dynamic current voltage curves starting from the potential applied in the steady state with a fast linear sweep into negative direction. A typical result is shown in Fig. 12 for different starting potentials. The current decreases exponentially as shown in the semilogarithmic plot but the slope of the logarithm of the currents decreases with starting from higher anodic potentials. The results of Figs. 8 and 9 show that at higher voltages the oxide layer is thicker. This is confirmed by the different slopes of Fig. 12 since the field strength in the film should be about the same for equal transport rates of ions through the film. Consequently, the local field strength decreases slower when starting the scan from a higher voltage with equal scan rate.

The decrease of the stationary current with increasing voltage in the same electrolyte seen in Fig. 4 and also seen in Fig. 12 by the decrease of the starting current with increasing voltage indicates that the rate of dissolution of the oxide must be affected by the voltage. This should most probably occur by a change in composition. The transport of ionic charge through the oxide depends on the disorder in the oxide, which under the conditions of its formation will have a great concentration of oxygen vacancies. The distribution of these oxygen vacancies cannot be homogeneous. This was already indicated by the current transients in the dark (cf. Fig. 6). The increase of the dark current in the later stage of the dissolution of the oxide demonstrates that a kind of suboxide exists close to the silicon contact, as one should expect from the mechanism of oxide formation.

If we realize that the composition of the oxide will vary and probably become closer to SiO_2 the thicker the oxide layer is, we can imagine that the dissolution rate and the rate of ion transfer through the oxide will decrease somewhat with thickening of the layer. On the other hand, the observation that the thickness of the layer does not change much, although the dissolution rate in fluoride solutions of different concentration varies drastically, suggests that also the composition of the oxide layer and its ionic conductivity varies considerably with the composition of the electrolyte. It is most probable that the oxide incorporates increasing amounts of fluoride with increasing fluoride concentrations in solution and also with decreasing pH, with the result that the concentration of oxygen ion vacancies increases and the transport of oxygen ions through the oxide grows in parallel. This variation in composition and ionic conductivity of the oxide layer during its formation can even explain the appearance of oscillations which can only be caused by non-linear correlations between formation and dissolution of the oxide.

We can make an attempt to get some idea about the composition of the oxide on the basis of our experimental results shown in Fig. 9. The average composition of the oxide $\text{SiO}_{\bar{n}}$ during the dissolution process at a time, τ , is given by

$$\bar{n} = 2 \frac{\Delta Q_{(\max)} - \Delta Q(\tau)}{Q_{\max} - Q(\tau)} \quad (1)$$

This value calculated from Fig. 9 is 1.62, initially, decreasing during the first period of dissolution and increasing later, when the film has already become rather thin, at which point this procedure becomes very uncertain. The local composition, n , will depend on the distance from the silicon contact, since the oxidation current in the dark increases in the later stage of the dissolution. If we assume that n will be very close to 2 at the contact to the electrolyte and may decrease to approximately 1, if one approaches the silicon contact, one can get from the average \bar{n} data an idea of the composition of the oxide during the dissolution process at different times, τ , corresponding to different thicknesses. This is shown in Fig. 13, where the average composition is indicated for the four situations together with a guess of the real distribution of the oxygen deficiencies.

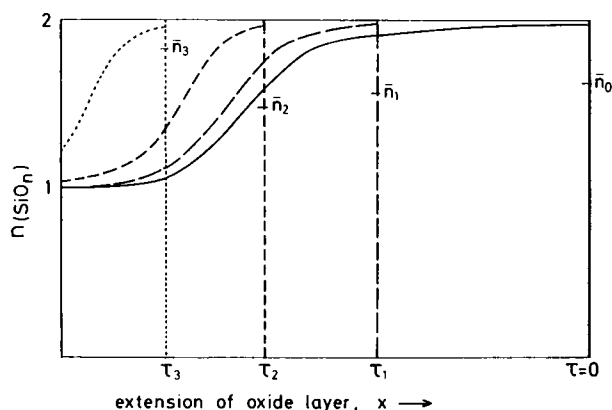


Fig. 13

Suggested composition of the SiO_n layer in dependence of the distance from the silicon for 4 different thicknesses of the oxide during the dissolution process together with the average value of \bar{n}

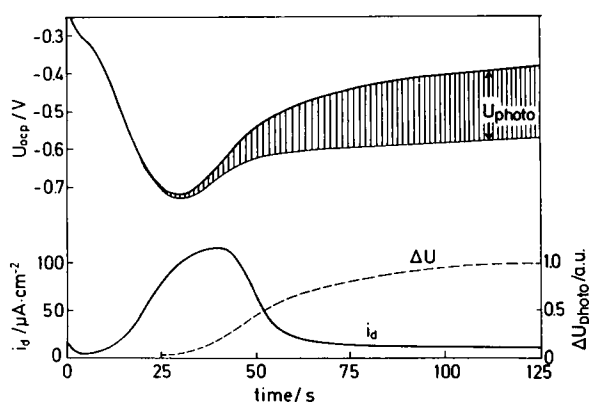


Fig. 14

The photopotential determined by short light pulses at open circuit of an n-type Si electrode during the dissolution of the oxide after switching off the illumination and the respective current in the dark. 0.13 M NH_4F solution, pH = 4

If the assumption is correct that the Si ions in the oxide only dissolve in the tetra-valent state, the current flowing during the dissolution period in the dark seen in Fig. 6 on n-Si, or in Fig. 10a at the reduced bias on p-Si, must be an electronic current to the silicon. The oxide must have enough electronic conductivity in this part, where oxidizable Si ions exist. The model of Fig. 13 contains Si^{n+} ions close to the Si contact with $n < 4$, which can be considered as states with trapped electrons. These electrons can be excited by interaction with O^{2-} ions and can reach the silicon contact via a hopping mechanism. The Si/SiO_n contact behaves electronically like an ohmic contact, which could be demonstrated by measuring the photovoltage at open circuit during the dissolution of the oxide layer. The result is shown in Fig. 14, where one sees that the open circuit potential drifts to rather negative values during the first stage of dissolution and turns into less negative direction only when the anodic current during the respective experiment under anodic bias in the dark has nearly reached its maximum. Only at this stage does a photovoltage appear, indicating that a depletion layer on the n-type silicon begins to be formed which reaches a barrier height at open circuit of about 300 mV in the final state where a slow corrosion proceeds [8].

Within the model developed on the basis of these experiments the electrode behavior of Si electrodes with anodically formed oxide layers can satisfactorily be interpreted in a qualitative way. A closer inspection of the composition of the oxide layer and its suggested content of fluoride would be most useful for the examination of this model, and a continuous registration of the thickness of the layer during the oscillations would be very helpful for understanding their origin.

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