Catalysis and Pore Initiation in the Anodic Dissolution of Silicon in HF

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ABSTRACT

A mechanism for the (photo)anodic dissolution of silicon in HF containing solutions is proposed, which explains the dependence of both the photocurrent quantum yield and the efficiency for hydrogen evolution on the flux of absorbed photons. The model assumes that the chemical oxidation of an Si(II) intermediate to an Si(IV) product, which is accompanied by the formation of a hydrogen molecule, is catalyzed by a mobile Si(I) dissolution intermediate. The surface chemistry, corresponding to the proposed mechanism of anodic dissolution, is discussed. Furthermore, it is shown that the mechanism may provide an explanation, based on chemical kinetics, for initiation of pores during anodic etching.

Introduction

The anodic dissolution of silicon in HF-containing solutions is characterized by several remarkable features.¹⁻²⁸ First of all, the anodic etching reaction is a multistep process which involves charge-transfer reactions both via the valence band (hole capture) and via the conduction band (electron injection).^{2-5,7,9,14,17,18,20,22} In addition, hydrogen evolution has been observed at potentials far more positive than the Nernst potential for the H^+/H_2 couple.^{8,14,17,18} Finally, the morphology of the etched silicon surface strongly depends on the anodization conditions.^{11,13,15,16,18-20,23-26} For example, thick nanoporous silicon layers can be formed, which exhibit interesting optical properties, viz. strong visible photoluminescence¹¹ and electroluminescence.^{29,30} Although the mechanism for pore propagation during porous silicon etching seems reasonably well understood,^{15,18,19} the origin of pore initiation remains a subject of speculation;^{24,26-28} even on ideally flat surfaces it is possible to etch very inhomogeneous, highly porous structures.

Anodic dissolution of n-type silicon occurs only at a considerable rate when the electrode is illuminated,^{1-3,8,9,22} which means that a valence band hole is required for the etching reaction. During dissolution of n-type silicon in HF solutions, photocurrent multiplication has been observed; more than one charge carrier per absorbed photon contributes to the photocurrent measured in the external circuit.^{2-5,7-9,14,17,22} Photocurrent quantum efficiencies Q (the number of charge carriers measured per absorbed photon) of up to four have been found with n-type silicon electrodes.^{2,4,9,14,17} An explanation for the current quadrupling effect has been sought in terms of a model involving four consecutive electrochemical dissolution steps.^{4,9,14,17} In the initial step, a photogenerated hole is captured in a surface bond and a surface intermediate is formed. This intermediate is further oxidized to an Si(IV) species by three consecutive electrochemical steps, in which electrons are thermally excited to the conduction band. As a consequence, four charge carriers can be measured as photocurrent in the external circuit per absorbed photon. The photocurrent quantum efficiency Q is dependent on the incident photon flux;^{2,4,9,14} at low light intensity the quantum efficiency is almost 4, but drops to 2 as the photon flux is increased. This phenomenon has been explained by assuming that electron injection from, and hole capture by surface intermediates are competing processes in two of the three charge-transfer steps.^{4,9} The hole capture rate is proportional to the product of the surface hole concentration p_s and the rate constant k_p , while electron injection is a thermally activated process, depending only on the rate constant k_n . At low intensity the product $k_p p_s$ is smaller than k_n , but as the number of incident photons increases, $k_p p_s$ increases and, eventually, hole capture will become the predominant process.

The above mechanism has proven successful in explaining the results obtained with other semiconductors.³¹⁻³⁴ However, during photoanodic etching of n-type silicon at sufficiently high light intensity a photocurrent quantum efficiency of 2 is found and hydrogen is evolved at a considerable rate; for each silicon atom dissolved a H_2 molecule is formed.^{8,14,17,18} This means that the efficiency for hydrogen evolution η_{H_2} (the number of H_2 molecules formed per absorbed photon) is 1. Several models for the dissolution reaction have been proposed to account for these results.^{13,18,21,22,25} From Fourier transform infrared (FTIR) measurements it is well established that the silicon surface is mainly hydrogen-terminated (Si-H) during anodic dissolution and pore formation.^{6,12} Lehmann and Gösele¹³ and Gerischer *et al.*²² proposed models for the silicon dissolution in HF, which account for the hydrogen termination and for a photocurrent quantum yield of 2 and a H_2 yield of 1 as observed at high intensity. In both models it is assumed that a valence band hole is captured in an Si-H surface species, resulting in an electron-deficient Si-H bond.^{13,22} The main difference between the two descriptions of the surface chemistry is the position of the positive charge in the electron-deficient Si-H bond. Lehmann and Gösele assume that the positive charge is located on the silicon side of the bond, resulting in a hydrogen radical.¹³ Gerischer *et al.* assume that hole trapping in the Si-H bond results in a silicon surface radical species and a proton.²² In both cases the hole capture step is followed by injection of an electron into the conduction band, thereby accounting for the observed photocurrent doubling. Further chemical oxidation of the divalent silicon intermediate to a tetravalent dissolution product is accompanied by the formation of one H_2 molecule, in accordance with the experimental results at high light intensity. The models of Lehmann and Gösele¹³ and Gerischer *et al.*²² can account for the fact that the photocurrent quantum efficiency is 2 and the hydrogen yield is 1 during photoanodic dissolution of n-type silicon at sufficiently high light intensity.

However, Stumper and Peter¹⁴ have found, with rotating ring-disk voltammetry, that not only the photocurrent quantum efficiency, but also the efficiency for hydrogen evolution η_{H_2} depends on the photon flux. The experimental results are summarized in Fig. 1.¹⁴ Hydrogen is not evolved when Q is approximately 4 at low light intensity. At higher light intensity, as Q decreases, hydrogen evolution is observed and the efficiency for hydrogen evolution η_{H_2} increases with increasing photon flux. When the photon flux is sufficiently large, Q is approximately 2 and the efficiency for hydrogen evolution η_{H_2} is 1. It was remarked by the authors^{14,17} that it is impossible to explain the light intensity-dependence of both the photocurrent quantum efficiency Q and the efficiency for hydrogen evolution η_{H_2} (as shown in Fig. 1) with the hitherto proposed models. Both the rate of electron injection from and the rate of

Fig. 1. Intensity-dependence of the photocurrent quantum efficiency Q (■) and the efficiency for hydrogen evolution η_{H_2} (▲) for n-type silicon in 1 M NH_4F . Results were taken from Ref. 14. The calculated intensity-dependence of Q (solid line) and η_{H_2} (dashed line) were obtained from Eq. 15 and 16 with $k_0/(k_1 k_2) = 6 \times 10^{-14} \text{ cm}^2 \text{ s}$.

proton reduction by a surface intermediate are simply proportional to the concentration of this intermediate. Hence, the competition between both processes is expected to be independent of the photon flux, in contrast to the experimental results (Fig. 1). The results suggest that the hydrogen evolution reaction is of higher order in the concentration of intermediate species than the electron injection process.^{14,17}

We have reconsidered the results of Stumper and Peter¹⁴ and developed a kinetic scheme, which accounts for the observed decrease of Q and the simultaneous increase of η_{H_2} with increasing light intensity. The key step in the kinetic model is the chemical oxidation of an Si(II) surface intermediate to an Si(IV) dissolution product with H_2 formation, a reaction catalyzed by another dissolution intermediate. The surface chemistry corresponding to the kinetic model is discussed in relation to previously proposed models. Furthermore, the implications of the autocatalytic step for the dissolution process and the resulting morphology of the etched silicon surface are mentioned.

Kinetic Model

In the kinetic model, unoxidized silicon surface atoms are represented by Si(O). As mentioned in the introduction the anodic dissolution of n-type silicon in HF solutions only occurs under illumination, so the first step obviously involves the capture of a valence band hole by an Si(O) surface species

We assume that the hole is captured in a Si-Si bond and the Si(I) intermediate then corresponds to an electron-deficient Si-Si back bond; hole capture in a back bond has been reported in studies of the anodic dissolution of III-V semiconductors.^{31,34} The assumption of an electron-deficient Si-Si bond is different from that proposed by Lehmann and Gösele¹³ and Gerischer *et al.*,²² who assumed hole capture by a Si-H bond. The photocurrent quantum efficiency is approximately 4 at very low light intensities; four charge carriers are measured in the external circuit for each photon absorbed. This can only be achieved if the initial hole capture is followed by three consecutive electron injection steps

In the last step, a completely oxidized Si(IV) species is formed, which enters solution as a dissolution product

(SiF_6^{2-}) and a new, unoxidized Si(O) species is exposed at the electrode surface.

The concentration of Si(I) intermediates will increase with increasing light intensity (reaction 1). If this intermediate is able to move along the silicon surface, it may interact with other dissolution intermediates. The surface mobility of Si(I) is determined by the ease with which a bonding electron can pass from an unbroken Si-Si surface back bond to a neighboring electron-deficient surface bond. From work on III-V semiconductors it is known that in many cases such mobile intermediates are involved in anodic dissolution.³¹ To account for the decrease of the photocurrent quantum efficiency and the formation of hydrogen as the photon flux becomes larger, a reaction is required which is second order in concentration of the intermediate. We assume that an Si(II) intermediate is chemically oxidized to an Si(IV) dissolution product while two protons are reduced to H_2 in a reaction which is catalyzed by an Si(I) surface intermediate. The overall reaction can be written as

If reaction 5 competes with the electron injection step 3, the photocurrent quantum efficiency will decrease from 4 to 2 and the efficiency for hydrogen formation will increase from 0 to 1 with increasing photon flux.

The problem can be treated quantitatively. From the reactions 1-5 described above we can deduce equations which describe the time-dependence of the concentration of reaction intermediates. In the steady-state, the concentration of the intermediates is constant and we obtain the following relations

$$\frac{dp}{dt} = j_h / e - k_0 s_0 p = 0 \quad [6]$$

$$\frac{ds_1}{dt} = k_0 s_0 p - k_1 s_1 = 0 \quad [7]$$

$$\frac{ds_2}{dt} = k_1 s_1 - k_2 s_2 - k_4 s_1 s_2 = 0 \quad [8]$$

$$\frac{ds_3}{dt} = k_2 s_2 - k_3 s_3 = 0 \quad [9]$$

where the concentrations of the Si(O), Si(I), Si(II), and Si(III) intermediates are denoted by s_0 , s_1 , s_2 , and s_3 , respectively. The photon flux is given by the hole current divided by the elementary charge e , which we denote as $j_h/e = j'_h$. In the analysis the contributions from hole capture processes, which may compete with the electron injection steps 2-4, are not taken into account. The photocurrent quantum efficiency Q is given by

$$Q = \frac{j'_h + k_1 s_1 + k_2 s_2 + k_3 s_3}{j'_h} \quad [10]$$

and the efficiency for hydrogen evolution η_{H_2} , which we defined as the number of H_2 molecules formed per absorbed photon, is

$$\eta_{H_2} = \frac{k_4 s_1 s_2}{j'_h} \quad [11]$$

We now have to calculate the steady-state concentration of Si(I), Si(II), and Si(III) intermediates and insert these into Eq. 10 and 11 to obtain expressions for Q and η_{H_2} as a function of j'_h .

From Eq. 6 and 7 it is found that

$$s_1 = \frac{j'_h}{k_1} \quad [12]$$

and when we insert this into Eq. 8 it follows that

$$s_2 = \frac{j'_h}{k_2 \left(1 + \frac{k_a}{k_1 k_2} j'_h \right)} \quad [13]$$

Finally, the combination of this expression for s_2 and Eq. 9 yields an expression for the concentration of Si(III) intermediates

$$s_3 = \frac{k_2}{k_3} s_2 = \frac{j'_h}{k_3 \left(1 + \frac{k_a}{k_1 k_2} j'_h \right)} \quad [14]$$

The photocurrent quantum efficiency Q and the efficiency for hydrogen evolution η_{H_2} follow directly from Eq. 10-14

$$Q = 2 + \frac{2}{1 + \frac{k_a}{k_1 k_2} j'_h} \quad [15]$$

$$\eta_{H_2} = \frac{\frac{k_a}{k_1 k_2} j'_h}{1 + \frac{k_a}{k_1 k_2} j'_h} \quad [16]$$

The two limiting cases, mentioned above, can be distinguished. At low light intensities, j'_h becomes small and we find that $Q = 4$ and $\eta_{H_2} \approx 0$. On the other hand, when the photon flux is sufficiently large ($j'_h/e > k_1 k_2/k_a$) the photocurrent quantum efficiency decreases to 2 while the efficiency for hydrogen evolution reaches a limiting value of 1. With Eq. 15 and 16 it is now possible to evaluate Q and η_{H_2} in the whole range of light intensity. Note that both expressions contain only one variable parameter $k_a/(k_1 k_2)$. By fitting the data of Fig. 1 to these equations with $k_a/k_1 k_2$ as a parameter, a value $k_a/(k_1 k_2) = 6 \times 10^{-14} \text{ cm}^2 \text{ s}$ was found (see Fig. 1). It is clear that the calculated curves agree quite well with the experimental results. The kinetic scheme presented above explains the observed relationship between Q and η_{H_2} in the entire range of light intensity. Taking into account that the reaction intermediates must be mobile along the surface, we have also derived expressions for Q and η_{H_2} as a function of the photon flux, based on other second-order reactions, but none of these were able to account for the experimental results.

Discussion

In the first part of the discussion, the chemical implications of the mechanism are investigated. The importance of the mechanism for initial pore formation is then considered.

Surface chemistry.—Here, we consider the surface chemistry of a (100) silicon surface in the context of our kinetic scheme. The likely initial steps of the etching mechanism are given, after which a distinction is drawn between low and high light intensities, corresponding to the two limiting cases mentioned in the kinetic analysis. From *in situ* FTIR measurements on silicon electrodes in HF containing electrolytes, it was concluded that the electrode surface is to a large extent covered with hydrogen and that anodic dissolution in the region of porous silicon formation also results in a hydrogen terminated surface.^{6,12} The surface atoms of a (100) silicon electrode have two back bonds to deeper lying silicon atoms and two Si-H bonds. These silicon surface atoms correspond to the Si(O) entity, introduced in the kinetic model.

Figure 2 describes the formation of an Si(II) intermediate from an Si(O) surface atom. In the first step, a valence band hole is captured by an Si(O) entity, resulting in an electron-deficient Si-Si surface bond. As mentioned before this is distinctly different from other models, in

which it is assumed that the hole capture results in an electron-deficient Si-H bond.^{13,22} This process of hole capture corresponds to reaction 1 of the kinetic scheme and the electron-deficient bond corresponds to the Si(I) intermediate. It is assumed that this Si(I) intermediate is mobile within the layer of surface back bonds. Electron transfer between neighboring Si-Si bonds may not be the only process occurring. It is also possible that an electron is transferred from one of the Si-H surface bonds to the Si-Si bond, which yields an electron-deficient Si-H species, similar to that mentioned by Lehmann and Gösele¹³ and Gerischer *et al.*²² There will probably be an equilibrium between the two aforementioned cases, as denoted in Fig. 2 by the double arrow. In the following step, corresponding to reaction 2 of the kinetic scheme, an electron is thermally excited to the conduction band, while

Fig. 2. Schematic representation of the first steps of the mechanism for anodic dissolution of n-type (100) silicon in HF solutions.

a fluorine ion bonds to the surface silicon atom. The attack of one of the Si-Si back bonds by HF is the final step in Fig. 2. The Si(II) intermediate is hence a silicon atom bonded to another silicon atom, two fluorine atoms and one hydrogen atom.

Figure 3 shows the further steps of the dissolution mechanism, which are assumed to occur at low light intensity. In this case the electron injection step 3 dominates over the catalyzed reaction 5. The Si-H bond on the HSiF_2 species, which is still attached to the surface, is destabilized due to the strongly polarized Si-F bonds as well as the interaction with the solution. Oxidation of this destabilized Si-H species is accompanied by electron injection into the conduction band. The two electron excitation steps of Fig. 3 correspond to reactions 3 and 4 of the kinetic scheme. Deprotonation and bonding with a fluorine ion transforms HSiF_2 into SiF_3 . The high electronegativity of fluorine induces a strong polarization in the Si-Si back bond. Attack on this back bond by an HF molecule (final step of Fig. 3) yields an SiF_4 molecule, which is further complexed by two fluorine ions forming the soluble SiF_6^{2-} species and a new Si-H surface bond. The net result of the reactions shown in Fig. 2 and 3 for low photon flux can be represented by reaction 17

Fig. 3. Schematic representation of the further steps of the mechanism for anodic dissolution of n-type (100) silicon in HF solutions at low light intensity.

From this it is clear that the quantum efficiency is 4, while no hydrogen gas is evolved, in agreement with the experimental results and the kinetic model.

Peter *et al.*⁹ performed a detailed study of the kinetics of the electron injection steps during photoanodic dissolution of n-type silicon in NH_4F solutions of pH 4. They found that the rate constants of the subsequent electron injection steps decrease considerably with increasing degree of oxidation of the intermediate: $k_1 = 2 \times 10^4 \text{ s}^{-1}$, $k_2 = 500 \text{ s}^{-1}$, $k_3 = 0.5 \text{ s}^{-1}$. This seems to be in accordance with the surface chemistry proposed in Fig. 2 and 3. The first electron injection step involves a surface radical with only one Si-F bond, the second and third injection steps involve intermediates with 2 Si-F bonds. It is reasonable to assume that the high electronegativity of fluorine decreases the rate of thermally activated electron injection. Furthermore, it must be remarked that the Si(II) intermediate proposed in Fig. 2 and 3 is relatively stable with respect to anodic charge-transfer processes.

At high light intensity, the concentration of photogenerated holes becomes large and the surface concentration of Si(I) intermediates increases (Eq. 12). In Fig. 4 likely steps of the etching mechanism at high photon flux are given. Due to the higher Si(I) concentration, the probability that this mobile intermediate interacts with an Si-SiHF_2 [Si(II)] species becomes significant. If this is the case, an electron from the Si-Si bond, linking the HSiF_2 to the surface, may be transferred to the electron-deficient interme-

Fig. 4. Schematic representation of the further steps of the mechanism for anodic dissolution of n-type (100) silicon in HF solutions at high light intensity.

diate. If a fluorine ion is bound to the outermost silicon atom in this process (the second step in Fig. 4), an HSiF_3 molecule is detached from the surface and an unpaired electron is left behind on one of the new surface atoms. The formation of this HSiF_3 intermediate has also been proposed by Lewerenz *et al.*⁴ and Peter *et al.*⁶ It was, however, impossible to detect this species with *in situ* FTIR experiments.¹² In the last step, the surface radical reacts with a proton and the Si(I) intermediate is restored. The silicon surface remains fully hydrogenated, in agreement with experimental evidence.^{12,17} In the reactions of Fig. 4, no free charge carriers are involved, in contrast to what is proposed for low light intensity. If we summarize the reactions in Fig. 2 and 4 the following overall equation for the anodic dissolution of silicon in HF solutions is obtained

In this reaction the Si(I) intermediate participates but is not consumed, so it can be regarded as a surface catalyst for the anodic etching reaction at higher light intensity. Only one electron is injected for each hole consumed, which implies a quantum efficiency of 2. Due to the strong polarization of the Si-H bond in the HSiF_3 molecule, which is formed in the final reaction of Fig. 4, it is easily attacked by HF to form hydrogen

The SiF_4 is further complexed by 2 fluorine ions, again forming the soluble SiF_6^{2-} species. The sum of Eq. 18 and 19 gives the overall anodic dissolution reaction occurring at sufficiently high light intensity

From Eq. 20 it is evident that the efficiency for hydrogen evolution η_{H_2} , defined as the number of H_2 molecules evolved per absorbed photon, amounts to 1 and that the photocurrent quantum yield is 2. This is in agreement with the kinetic model and the experimental results at high light intensity. Reaction 20 involves a sequence of (electro)chemical steps. It follows from our kinetic analysis that the step in which a relatively stable Si(II) intermediate reacts with an Si(I) intermediate must determine the rate of the self-catalyzed branch of the dissolution mechanism, which competes with electron injection from Si(II) , in order to explain the observed relationship between Q and η_{H_2} .

Pore initiation.—The physical background of pore propagation in silicon under conditions of (photo)anodic etching is rather well understood.^{15,18,19} However, the fact that porous silicon can be formed photoanodically, starting from nearly atomically flat silicon surfaces with spatially homogeneous surface properties is not yet understood.^{24,27,28} The observation that porous etching is possible with p-type and n-type silicon crystals with large variations in doping density suggests that the primary initiation of pores has a chemical, rather than physical origin. We now investigate if pore initiation can be rationalized within the framework of the mechanism of photoanodic etching presented in previous sections. The essential steps of the mechanism can be summarized as follows

From a detailed kinetic study using intensity modulated photocurrent spectroscopy, Peter and co-workers found that the thermal injection of an electron from a surface bond of the Si(II) intermediate (reaction 3) is relatively slow, at least much slower than the injection of an electron from an Si(I) intermediate.^{14,17} Electron injection from the

Si(I) intermediate may involve a half-broken bond or an Si-SiHF radical species, while the Si(II) species already has two Si-F bonds. It is assumed here that the chemical oxidation of an Si(II) intermediate catalyzed by an Si(I) intermediate (the competitive reaction 5) is much faster than the electron injection (reaction 3) from the Si(II) intermediate into the conduction band. Since the catalyzed reaction 5 leads to a new Si(O) entity, a new Si(II) intermediate can be readily formed by reaction 1 (hole trapping) and reaction 2 (electron injection). This would imply that anodic dissolution proceeds much faster in a surface region round an Si(I) intermediate. Such an active region can be characterized by a radius which is determined by the diffusion length $L_{\text{Si(I)}}$ of the mobile Si(I) intermediate. The diffusion length is defined as

$$L_{\text{Si(I)}} = \sqrt{D_{\text{Si(I)}} \times \tau_{\text{Si(I)}}} \quad [21]$$

where $D_{\text{Si(I)}}$ is the surface diffusion coefficient of the Si(I) intermediate and $\tau_{\text{Si(I)}}$ is the lifetime, given by

$$\tau_{\text{Si(I)}} = (k_{\text{a}S_2} + k_{\text{i}})^{-1} \quad [22]$$

Inhomogeneous etching will occur if the diffusion length of the Si(I) intermediate is smaller than the average distance between these intermediates

$$\sqrt{D_{\text{Si(I)}} \times \tau_{\text{Si(I)}}} < \frac{1}{\sqrt{s_1}} \quad [23]$$

or, using Eq. 22, 12, and 13

$$D_{\text{Si(I)}} \leq \frac{k_{\text{i}}}{j_{\text{h}}} \left(k_{\text{i}} + \frac{k_{\text{a}}k_{\text{i}}j_{\text{h}}}{k_{\text{i}}k_{\text{2}} + k_{\text{a}}j_{\text{h}}} \right) \quad [24]$$

In the framework of our model, anodic dissolution occurs with formation of pores for anodic currents up to $j_{\text{h}} = 2ek_{\text{i}}^2/D_{\text{Si(I)}}$. It would be interesting to investigate whether this maximum current density corresponds to the value which determines the region of porous silicon formation.¹⁸ This will, however, require a reliable value of the surface diffusion coefficient of the Si(I) intermediate. The model for pore initiation may be verified by measuring the initial density of pores as a function of the anodization current in the primary stages of porous etching. It should be possible, we believe, to perform these measurements using scanning tunneling microscopy of atomic force microscopy, or maybe other surface imaging techniques.

It can be concluded that the mechanism of porous etching, which we have proposed here for explaining the unique relationship between η_{H_2} and Q , may also provide an explanation for pore initiation. Since the basis for pore nucleation relies on (electro)chemical kinetics, the explanation pertains to both n-type and p-type silicon in HF, independent of the doping density.

Conclusions

We have developed a kinetic scheme for the dissolution of silicon in HF containing solutions. From measurements on n-type silicon it has previously been found that both the photocurrent quantum efficiency Q and the number of hydrogen molecules formed per absorbed photon, referred to as η_{H_2} , are dependent on the light intensity. The kinetic analysis yields expressions for Q and η_{H_2} which explain the experimental results. The key step in the kinetic scheme is a chemical reaction of an Si(II) surface intermediate with two protons to give an Si(IV) dissolution product and H_2 , a reaction which is catalyzed by a mobile surface intermediate Si(I) . Based on the kinetic model a mechanism is proposed for the anodic dissolution of silicon in HF and the corresponding surface chemistry is discussed. The possible implications of this mechanism and, in particular, the autocatalytic step for the dissolution process and the resulting morphology are mentioned. We showed that this mechanism may provide an explanation based on chemi-

cal kinetics, for initiation of pores during the anodic etching of silicon in HF solutions.

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