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PHYSICAL CHEMISTRY OF WET CHEMICAL ANISOTROPIC ETCHING OF SILICON

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ABSTRACT

In this paper we explain a view to understand the anisotropy of the etching of silicon in certain wet chemical agents (such as KOH). The starting point is the assumption that the $\langle 111 \rangle$ face of silicon is a flat face, the etch rate of which is then governed by a nucleation barrier. We review the atomic surface structure of the $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ face, with the result that the $\langle 111 \rangle$ face is the only flat face. We discuss the consequence of the assumption of steps on the orientation dependence of the etch rate, and we show that the observed experimental facts perfectly fit to this idea. We also review recent *in situ* STM images of slightly misaligned $\langle 111 \rangle$ -n-silicon that show moving steps, and an increasing number of etchpits as a function of the voltage difference between silicon and an NaOH solution, reaching a maximum close to the passivation voltage. This observation is discussed in terms of the driving force for etching and the step free energy. Finally, the order of magnitude of the step free energy is discussed.

INTRODUCTION

When trying to interpret wet chemical anisotropic etching of single crystals such as silicon, quartz and gallium arsenide, no reference is made to the roughening transition of crystal faces. In the science of crystal growth and surface science, roughening is a well known phenomenon, and its impact of surface kinetics such as crystal growth and dissolution is well established. Crystals generally have a surface free energy ("surface tension") Γ that is anisotropic, and the anisotropy has a peculiar property: the

minima are singular points (Herring 1951), as a function of the orientation of the surface, Γ varies as

$$\Gamma \propto |\sin \Omega| \quad (1)$$

As a consequence of this singularity, in equilibrium crystals are bound by flat faces (Wulff 1901). The faces are flat on an atomic/molecular scale. This in turn means that it costs energy to form steps on the surface, otherwise the surface cannot be flat. Hence a flat face is associated with a step free energy γ which is related to the surface energy by

$$\gamma = \partial \Gamma / \partial \Omega \quad (2)$$

Growth or etching occurs in a non equilibrium situation described by a difference in chemical potential $\Delta \mu$ of the atoms or molecules in the crystalline phase of the fluid phase, whether or not the atom/molecule is bound in a chemical compound such as in the case e.g. in etching of silicon. When growing one has to add atoms/molecules to a flat face, when etching one has to remove atoms/molecules from a flat face. Both processes give rise to a step.

The roughening transition now occurs at a temperature T_r where γ vanishes. At $T > T_r$ the surface is rough on an atomic scale, it does not require work to add a step on a rough surface. Growing or etching a flat face therefore is a layer mechanism. Once a start is made a layer can be added or removed by lateral motion of a step. The rate of etching or growth is controlled by a nucleation barrier, and it is proportional to (de Haan et al. 1974)

$$R \propto (1 - \exp(-\beta)) \exp\{-\gamma v^2 / \beta\} \quad (3)$$

where we have normalised the relevant energies to the temperature,

$$\beta = \Delta\mu/kT$$

and

$$\psi = \gamma/kT$$

with kT the Boltzmann constant times the absolute temperature.

The first term on the right hand side of (3) stems from the phenomenological equations that state that a current density must be proportional to a chemical potential difference. The second term describes the nucleation barrier. In fact, $kT\psi^2/\beta$ is the free energy of the critical nucleus of a radius

$$r_c = a\zeta\psi/\gamma \quad (4)$$

with a the length of the atom in a step and ζ a number of order one which has to do with the symmetry of the face in question.

Therefore $kT\psi^2/\beta$ represents the activation energy necessary to overcome the nucleation barrier. The idea that a nucleation barrier is responsible for the slow etching of the {111} face of silicon has been introduced earlier by the author (Elwenspoek 1993).

The kinetics of rough faces are not controlled by a nucleation barrier. Every atom/molecule at the solid-fluid interface that feels a smaller chemical potential can change its thermodynamic phase without the need to find a step. If $\psi = 0$, on a particular face, the kinetics are obviously much faster than if $\psi > 0$. This observation constitutes the large anisotropy in the kinetics - whether growth or etching - of all single crystals. The anisotropy of growth rate and etch rate is a universal phenomenon. In most cases, the minima in the etch rate and in the growth rate occur in identical crystallographic directions.

In the second term of the product in eq. (3), we have to deal with the ratio of ψ^2 to β . Nucleation becomes unimportant if this ratio is of order one or smaller. In this case one speaks of kinetic roughening (Balibar et al 1990), and the etch rate (and growth rate) starts to approach the maximum possible rate (i.e. controlled by diffusion of material and heat). This is the case for isotropic etching.

In anisotropic wet chemical etching of silicon, the chemical potential difference consists of two parts: one is for the chemical reaction itself and the other one has to do with the dissolution of the etch product. Currently there is no consensus in the literature of the mechanism of the chemical reaction when etching silicon; in a most recent publication (Bressers et al.) it was suggested that it is simply a reaction with water. For a silicon atom with 3 backbonds to the solid and one dangling bond, the net reaction reads



The oxidation enthalpy of silicon is very large, it is close 3 eV, and generally it is assumed that the formation of the $\text{Si}(\text{OH})_4$ gives an energy gain of the same order, perhaps less because of the dissociation of water. The energy could be smaller because the fourth bond of the silicon atom at the surface is certainly not dangling. Recent work (Rappich et al 1993, Allongue et al 1993)

gives very strong evidence that the $\langle 111 \rangle$ face of silicon is hydrogenated (while earlier it was generally expected that the surface is hydroxylated). Therefore we assume a wide margin for the chemically caused chemical potential difference (the "driving force") to of the order of 1 eV, very much larger than kT . So the first term in eq. (3) is fairly close to one. Note however that this is the only term in which the temperature explicitly plays a role. In the case of silicon anisotropic wet chemical etching, obviously, ψ must be equal to 5 at least. It is the aim of this paper to put forward arguments that support such a large step free energy.

In the following section we discuss the crystallography to show that the $\langle 111 \rangle$ face of silicon is the strongest candidate to have a step free energy larger than zero. The $\langle 001 \rangle$ and $\langle 110 \rangle$ silicon faces which appear to be flat under certain conditions will be discussed below. The section that follows deals with some of the experimental facts that support the idea of steps and show that the assumption of steps makes the major phenomena of anisotropic wet chemical etching (i.e. the anisotropy and the variation of the etch rate with the crystallographic orientation) transparent.

CRYSTALLOGRAPHY

The flat character of the {111} faces in the diamond lattice follows directly from the analysis of the crystal structure. In fig. 1 we show the unit cell of diamond. The crystal structure of silicon is of the diamond type with lattice constant of 5.43 Å.

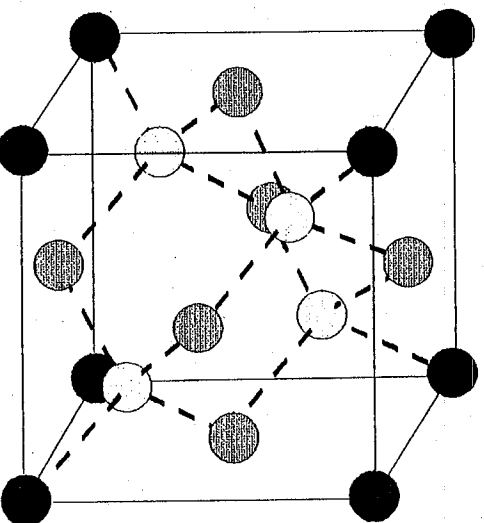


Fig. 1. Unit cell of the diamond lattice

The following analysis is due to Hartman and Perdock (in Hartman 1974), and has been extended for complex crystal structures by Bemmema et al (1987). We shall now draw the atomic configuration of an (001) face (fig. 2.) In the upper part we show a flat, undisturbed (001) face. Only the dangling bonds are shown. We see that each atom has two dangling bonds and two backbonds. Atoms that have an equal number of bonds to the solid phase as to the fluid phase are said to be in a kink position. They are in a position where they can change the phase most easily. The theory of crystal growth (e.g. Cabrera, Burton and Frank 1951) kink positions are assumed to be sinks of atoms in the case of growth, and sources of atoms in the case of

dissolution. Obviously, the (001) face of silicon only has kink positions. Further it is easily seen that this surface should be rough (in reality, sometimes it is not rough, but this has to do with surface effects, such as adsorption or reconstruction (Giling and van Enkevort 1985); we ignore this problem here). This is demonstrated in the lower part of fig. 2, where we have taken one atom out of the face, a process that requires the energy to two times the energy of a covalent bond Φ_{SiSi} , and replaced it somewhere else. The replacement gives us the energy of twice the covalent bond energy, and the total procedure can be performed without doing work. Evidently, the (001) must be rough, since the entropy of a face full of these excitation pairs is much larger than that of a perfectly flat face (the entropy of which is exactly equal to zero). The (001) face of the diamond structure is an example for a "K-face", with K from kink, in the nomenclature of Hartman and Perdock.

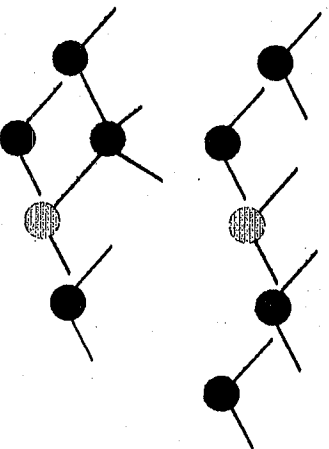


Fig. 2. Atomic configuration of the (001) face of silicon. Only the dangling bonds are shown. Upper part: flat configuration, lower part: configuration with one excitation.

Fig. 3 shows the atomic structure of the (110) face. We see here that the (110) face is built up by parallel running bond chains. The bond chains are bonded with a third backbond per atom to the body of the crystals, and there is one dangling bond per atom. Note that the chains do not cross: there is no direct link between the chains. This fact allows us cut a whole chain from the crystal, which costs us one bond per atom, and replace the chain somewhere on the crystal surface, regaining the energy of one bond per atom. Again we have an operation that does not require work. The surface therefore will be stepped along the $\langle 110 \rangle$ direction. Such faces are called "S-faces", with S from steps.

Let us finally analyse the {111} face. Here the three bondchains form a triangular connected net. Each atom is connected with three bonds to his next neighbour in the face, and every second atom has a dangling bond, the other atoms have one bond that connect the two-dimensional net to the body of the crystal. The excitation, i.e. taking one atom out of the face and replacing it somewhere else, now definitely costs energy, twice the bond energy of one covalent bond, which is -2.34 eV per covalent bond. Therefore, this is a flat face. In fact, the $\langle 111 \rangle$ face is the only flat face in the diamond lattice (starting from crystallography alone, thus neglecting additional surface effects such as adsorption and surface reconstruction). The (111) face of silicon is called an "F-face", with F from flat.

The energy to create the first excitation state of the surface ΔE divided by kT is known as the α -factor of Jackson (1967). The α -

factor describes the energy of the surface ignoring entropy effects. Therefore it is related to the step free energy by

$$\alpha = 2\psi/(T=0)$$

We can define an α -factor that corresponds to roughening of the face,

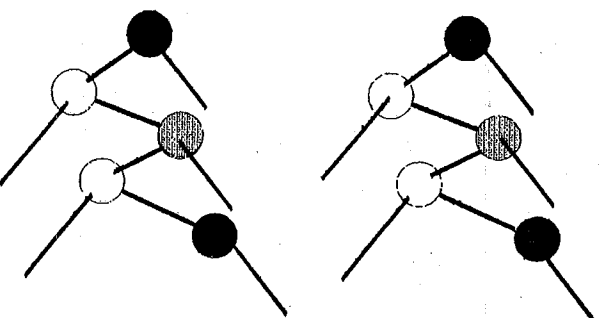


Fig. 3. Atomic configuration of the (110) face of silicon. The dangling bonds are shown and those that connect the atoms in the (110) face directly to each other, leading to a chain-like structure. The third backbond is not shown, these connect the chains to the bulk of the crystal.

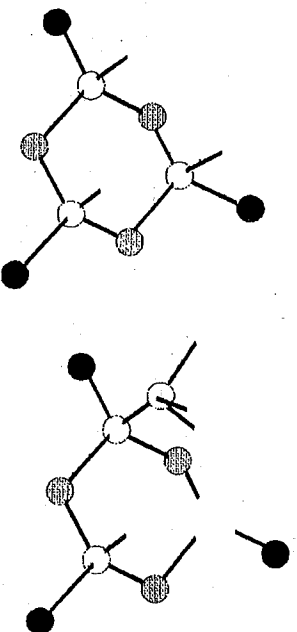


Fig. 4. Atomic structure of the (111) face. Left the completely flat face, right with one excitation. Each second atom has three backbonds and one dangling bond. The other atoms have four backbonds. Only the zigzagging back bonds that connect the surface atoms directly are shown, and the dangling bonds.

$$\alpha_F = \Delta E/kT$$

(6)

Based on Monte Carlo simulation of crystal surfaces, van de Erden has shown that α_R only depends on the symmetry of the face in question (van de Erden 1976). For the diamond lattice, he found

$$\alpha_{R<010>} = \infty; \alpha_{R<110>} = \infty; \alpha_{R<111>} = 4.2.$$

This is in agreement with our analysis of the (110) and the (001) face. An infinitely large α_R means $\Gamma_R = 0$, the face is rough at all temperatures. If $\alpha > \alpha_R$, the face is flat. In vacuum at room temperature, ignoring the 7x7 surface reconstruction, we would have $\alpha_{<111>} \approx 2001$

It is maybe instructive to mention the following: Both, the (110) and the (111) have one and one half, res., dangling bond per atom. The number of dangling bonds alone cannot account for the differences in the etch rate. From the same reason, it has been proved to be very difficult to find a satisfactory purely (electro)chemical model to explain the anisotropy of the etch rate. It has been argued that the bonds running parallel in the (110) face must not be counted as backbonds, but we do not see any reason why this should be: Why could the bond energy of these bonds be so much smaller than the bonds to the body of the crystal? Why should this be so much different from the (111) face, where three bonds run nearly parallel to the surface?

The analysis we described here for the diamond lattice is universal. Since the papers of Hartman and Perdock appeared some 30 years ago, a vast number of crystal structures has been investigated predicting correctly the flat faces of crystals. Deviations could mostly be understood in terms of surface effects. In particular, quartz has been analysed by Hartman, leading to prediction of all flat faces except one. These are precisely the faces where etch rate minima occur.

It is also worth noting that it is not the minimum of the surface tension that directly causes the etch rate minimum. Orientational variations of the surface tension is rather small, within a factor of two, as has been noted by several authors (e.g. Hesketh 1993). Orientational variation of the step free energy or the critical α -factor, however is very large.

It rests to estimate the α -factor for the etching situation. With our current knowledge this turns out to be an impossible task. According to Rappich et al (1993) the (111) face is covered by a layer of hydrogen; the bond energy per hydrogen atom is -3 eV. The first excitation offer in total four more bonds to react with hydrogen than the flat face. This would give

$$\Delta E = 4\Phi_{SH} - 2\Phi_{SIS} \approx -8eV \quad (7)$$

with Φ_{xy} the bond energy between x and y. A negative ΔE would mean that the surface breaks up spontaneously. Two effects make ΔE considerably larger: (i) Certainly there are no free hydrogen atoms in the solution, so they have to be created, which costs energy to be added to the r.h.s. of (7). If this came from the dissociation of water, the energy would be very large. The reaction enthalpy of the formation of one water molecule from $1/2 O_2 + H_2$ equals 2.4 eV, and the dissociation of H_2 in 2H requires another 4.4 eV. Hydrogen could also result from dissociation OH^- ions. The energy required to form H-atoms to adsorb at the silicon surface must be somewhere between 1 and 3 eV. (ii) Certainly, there is not enough space in the hole formed in the right hand side of fig. 4 for three hydrogen atoms to bond to the silicon, at most

there can be 2, maybe even only one hydrogen atom. (i) and (ii) would lead to

$$\Delta E = \xi\Phi_{SH} - \xi\Phi_{HX} - 2\Phi_{SIS} \quad (8)$$

where ξ is between 2 and 3, X is the partner of the hydrogen before it adsorbs at the silicon. Φ_{HX} for $HX = 1/2 H_2O$ would equal to 4.6 eV, resulting in $\Delta E = 1.6\xi + 4.7$ eV. This is certainly much too large, since we neglected any activity. In conclusion, all Φ 's are of the same order of magnitude, and ΔE can be well a few tenths of an eV or even larger.

EXPERIMENTAL EVIDENCE FOR STEPS I: etch rate diagram

Here we review and discuss some experimental results of relevance for our subject.

Silicon etch rates have been studied using three basic methods. Starting from a sphere (Hesketh et al 1993), the fast etching orientations are most easily revealed, however, it turns out that it is quite difficult to give data on the etch rate as a function of orientation. The final shape of the sphere takes the form of a polyhedron with the vertices pointing in the slowly etching orientations ($<111>$ and $<001>$ in KOH at small temperatures and a little pronounced maximum pointing to $<110>$ at higher temperature) and the faces governed by the fast etching orientations, which are the $<110>$ in KOH at low temperature and $<114>$ at higher temperature.

The most widely used method to study etch rates as a function of the orientation is Kendall's wagon wheel method (Kendall 1979, Seidel et al 1990), which shows the characteristic butterfly shape when applied to a $<001>$ oriented wafer. Using photolithography a pattern is generated on the silicon wafer which opens the mask in the form of a wagon wheel. The spokes are undercut which gives one the undercut rate as a function of the orientation. The interpretation of these experiments are much more straight forward than curved features as used by e.g. Weirauch (1975). If the width of the spokes increases radially, the spokes are undercut completely if they are normal to a fast etching orientation, and stay a long time if they are oriented along a slowly etching orientation. Due to the cubic symmetry of silicon the length of the spokes left after etching gives immediately the etch rate along the orientation of the spoke. The wagon wheel method is a powerful one, however it gives information only in one crystallographic zone.

Is it even more powerful to etch silicon starting from a (negative) hollow sphere. Similar to the positive sphere, all orientations are offered to the etchant, and one sees immediately the minima of the etch rates. By scanning the profile of the etched negative sphere we get complete information about the etch rate as a function of the orientation (Sato et al 1989). The results of all three method are at least quantitatively in agreement.

Close to the $<111>$ orientation the etch rate varies quickly with the orientation. It has been demonstrated several times (Seidel et al 1990, Uenishi et al 1994, Kendall 1975) that the etch rate varies linearly with the orientation Θ (in $<111+ \Theta ->$) and in a wider range as $|\sin \Theta|$ apart from a narrow range of $\pm 0.3^\circ$ where the etch rate appears to be finite and constant. This interesting fact will be addressed elsewhere, but here we ignore it for the

sake of simplicity. It has to do with the spontaneous formation of steps.

This dependency of the etch rate of the orientation is immediately transparent if the concept of moving steps on a flat face is accepted. In fig. 5 we give a schematic of a flat face with steps on it. These steps are due to a misorientation which is imposed by the experiment (the orientation of the spokes). The etching proceeds by movement of the steps (height h), and the average distance between the steps is λ . The speed of the steps v is given by

$$v = \lambda/\tau \quad (9)$$

where τ is the time a step needs to move the distance λ . After time τ the crystal surface has moved a distance D , and the etch rate E is given by

$$E = D/\tau \quad (10)$$

Elementary geometry now gives the following expression of the etch rate:

$$E = v |\sin\Theta| \equiv v |\Theta|. \quad (11)$$

The last equality applies for a small misalignment.

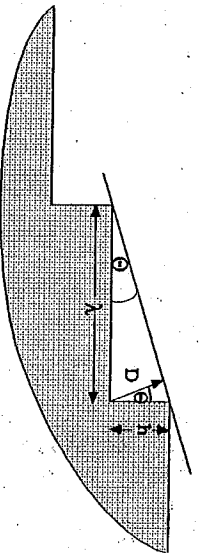


Fig. 5. Illustration for the derivation of the relations between step height h , distance between steps λ , angle of misorientation Θ and the proceeding of misoriented crystal front D , when the step has moved the distance λ .

The absolute value comes because a misalignment in $-\Theta$ has the same consequence.

In fig. 6 we demonstrate the prediction of eq. (11) over a larger range of misorientation. The data were extracted from the paper of Koide et al (Koide 1992). The etchrate nearly follows the line of $\sin \Theta$.

In conclusion, the simple idea of steps seems to explain the whole etch diagram, once the flat faces are known.

EXPERIMENTAL EVIDENCE FOR STEPS II:

in situ STM

The steps do exist. A recent paper of Allongue et al (1993) shows STM images of a slightly misoriented $\langle 111 \rangle$ n-silicon wafer while being etched in NaOH at room temperature. The authors demonstrate that the $\langle 111 \rangle$ face is etched by movement of steps on this face and they were able to record sequences of images that show the advancing steps. They did the experiments in an electrochemical set-up, so they were able to show the effect of a bias. When etching n-silicon, the etch rate drops if the bias of

silicon with respect to a standard calomel electrode becomes more negative (and seems to be independent of the bias for p-silicon). At a potential $V_{pp} \approx 0.8V$ a passivating silicon oxide layer forms, the growth rate of which starts to compete with the etching. When scanning the surface at a potential negative of the OCP (open circuit potential), only motion of steps can be seen, however at less negative potentials etchpits occur between the steps that are due to the misalignment. As a result, the number of etchpits depends exponentially of the potential. Although at the smallest voltage that was experimentally accessible to STM-imaging the surfaces look rather rough, they are quite flat: the etchpits all where only one (double-)layer deep, and the density of pits was only 2×10^{11} pits/cm², this corresponds to 1 pit per 10,000 sites! Analysis showed that the etch rate was proportional to the pit density, hence, the etch rate is controlled by the probability of nucleation.

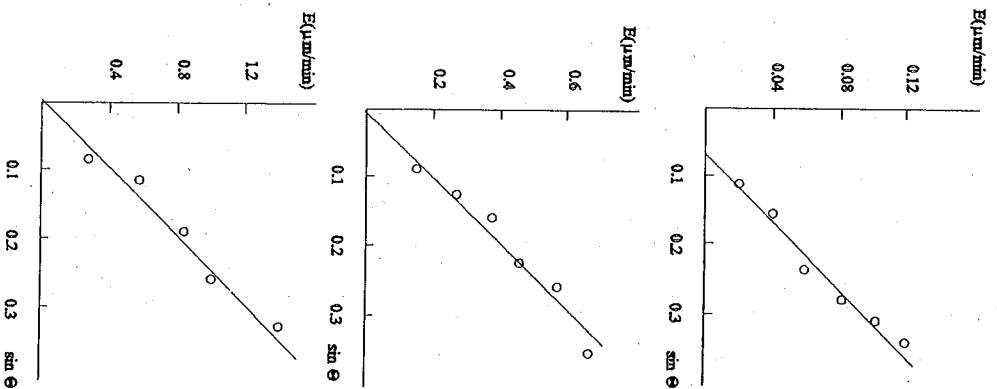


Fig 6. Etchrates of $\langle 111 \rangle + \Theta \rangle$ silicon as a function of the orientation. Data were taken from Koide et al. (1992).

ESTIMATE OF STEP FREE ENERGY

When plotting the log of the pit density as a function of the voltage, the data lie on a line, however, when we plot the same data, \log (pit density) versus $1/V$, the data points again lie on a

line, see fig. 7. This must be expected from eq. (3), if the electrical potential has something to do with the chemical potential. The latter would be the case if (i) charge transfer is associated with the chemical reaction, i.e., if the reaction is electrochemical and (ii) if there were a large voltage drop across the interface. (i) is not established, but an electrochemical route parallel to a chemical route of the reaction sequence must exist (Allongue et al 1993, Glambocki et al 1985). What regards assumption (ii) we have the difficulty that generally one believes that the voltage drops across a space charge layer at the surface, so the voltage drop directly at the surface is believed to be very small. The latter might be not true. If we identify the voltage with $\Delta\mu$ we would arrive at γ of the order of 0.3 eV, in the range we require for layer controlled etching.

Alternatively, the voltage could increase the bondstrength of the hydrogen atoms adsorbed at the surface. This would lead to

$$\gamma = \gamma_0 - \delta eV \quad (12)$$

with δ a (small) numerical factor, e the elementary charge and V the voltage/SCE. Eq. (12) would lead to the observed dependency of the etchpit density together with eq. (3) and equally account for the drop of the etch rate at increasing anodic voltage. Both interpretations are in a somewhat premature state, and more research is required to support one of them (or to discard both). An interesting experiment would be to study the etch rate diagram using the wagon wheel method with n-silicon as a function of the voltage. The anisotropy should increase with the anodic voltage, and the maximum etch rate in the $\langle 111 \rangle$ orientation should drop slower with the anodic voltage.

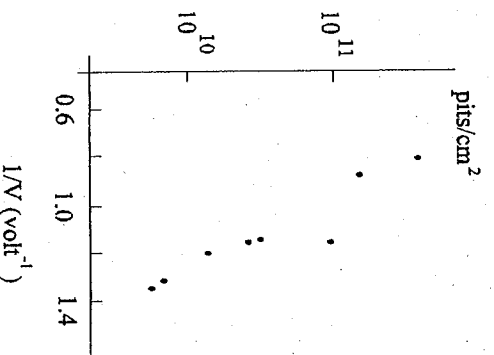


Fig. 7. Etchpit density on $\langle 111 \rangle + 0.7^\circ$ oriented silicon as a function of reciprocal voltage with respect to an SCE-electrode. Data were taken from fig. 13, ref. Allongue et al (1993)

An alternative estimate for the step free energy can be gained from the temperature dependence of the step velocity from fig. 6. The activation energy of the velocity of steps (i.e. the derivative of the plots in fig. 6) is 0.6 eV, very close to the activation energy of the the etchrate of the $\{110\}$ and $\{001\}$ in KOH, and 0.1 eV

larger than the activation energy of the $\{111\}$ etchrate. This fact points to the following interpretation: the etchrate of the $\{110\}$ and $\{001\}$ are dominated by the chemical reaction rate since they are (nearly) rough. Also the velocity of steps is governed by the chemical reaction rate: both should have similar activation energies, and the etchrate of the flat $\{111\}$ must have a larger activation energy. Hence, the height of the nucleation barrier, $kT\psi^2/\beta$, is equal to 0.1 eV.

In conclusion, we have overwhelming experimental evidence for the existence of steps, from both, indirectly from etch rate diagrams, and from direct observation using STM.

So: there are steps, the step free energy therefore must be larger than zero, and etching of silicon in hydroxides is at an undersaturation smaller than the undersaturation where kinetic roughening starts, i.e.

$$\psi_{\langle 111 \rangle} > \sqrt{\beta} \quad (13)$$

DISCUSSION AND CONCLUSION

The experimental evidence for steps, separating atomically flat terraces, on Si $\langle 111 \rangle$ faces when being etched in anisotropic etching solutions is overwhelming. A flat face with isolated steps inevitably means that a step free energy is associated to the face, and the face is being etched at an undersaturation (the driving force) below kinetic roughening. Simple arguments based on the crystallographic structure of silicon - arguments originally due to Hartman (1965) - show that the $\langle 111 \rangle$ face is the only flat face in the diamond structure. Etch rate minima in $\langle 001 \rangle$ directions (found in KOH (Seidel et al 1990) and $\langle 110 \rangle$ (as found in EDP or KOH + isopropanol solutions Bäcklund and Rosengren (1992))), must be due to either surface reconstruction or adsorption effects as will be discussed elsewhere. The kinetics of flat faces however are governed by a nucleation barrier. If the driving force is given by the reaction free energy of the etch process, one must expect a very large $\Delta\mu$. Therefore the step free energy must be at least a few tenths of eV. We have put forward arguments that show that γ easily can be even larger. Allongue et al. (1993) found in electrochemical etch experiments of $\langle 111 + 0.7^\circ \rangle$ n-Si that the density of etchpits depends exponentially of the voltage. These results can be quantitatively understood if one assumes that the voltage difference either changes the driving force or the step free energy.

We do not make any attempt here to discuss the chemical reaction, and its rate. With the theory presented here we only aim to the explanation of the anisotropy of the etchrate. We claim here that it is not the chemical reaction which causes the anisotropy, but the physical state of the surface: rough or smooth. The theory differs therefore radically from models presented by other authors (e.g. Seidel et al (1990), Glambocki et al (1985) and Allongue et al. (1993)). The theory is somewhat closer related to cellular automata models, see e.g. Than and Bittgenbach (1994). Probably these models also would lead to steps and an orientational dependence of the etchrate as given in eq. (11). However, these are $T = 0$ models without roughening transition, and a background etch rate of the $\langle 111 \rangle$ orientation must be artificially inserted into the model. The greatest difficulty in my view is the $\langle 110 \rangle$ face with its three backbonds per atom. Than (1994) just states that because (in contrast to the $\langle 111 \rangle$) all atoms have one backbond, these backbonds will be weaker than the

backbonds in the $\langle 111 \rangle$, without giving an argument for this. In our view it is the rough character of this face causes its large etchrate.

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