Table II. Silicon nitride film properties.

Film property	720°C LPCVD	780°C LPCVD	480°C PECVD	580°C PECVD
Index of refraction	1.980	2.008	1.984	2.004
Wet etch rate (nm/min)	2.0	1.3	9.8	4.1
Nonuniformity (3σ)	2.4%	2.4%	2.9%	3.2%
Stress (dynes/cm^2)	1.46×10^{10} (T)	1.22×10^{10} (T)	1.49×10^9 (T)	-1.55×10^9 (C)
Hydrogen content (N-H, Si-H bonds $\times 10^{21}$/cm^3)	2.77, 1.01	2.04, 0.44	5.42, 4.17	4.14, 3.02
Conformality	≃100%	≃100%	62%	69%
Foreign material (1 μm particles)	10-20	100-300	0-10	0.-10

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On the Mechanism of Anisotropic Etching of Silicon

M. Elwenspoek[a]

Department of Electrical Engineering, Uppsala University S-751 21 Uppsala, Sweden

ABSTRACT

A new model is proposed that explains the anisotropy of the etch rate of single crystalline silicon in certain etchants. It is inspired from theories of crystal growth. We assume that the (111)-face is flat on an atomic scale. Then the etch rate should be governed by a nucleation barrier of one atomic layer deep cavities. The origin of the nucleation barrier is that the formation of a too small cavity increases the free energy of the system due to the step-free energy. The step-free energy and the undersaturation governs the activation energy of the etch rate. Having the largest step-free energy, the (111)-face etches the slowest. The model explains qualitatively why the etching is isotropic in certain etchants and anisotropic in others.

In papers on anisotropic etching of silicon many authors are puzzled by the strong anisotropy of the etch rate (see the discussion in Ref. 1 and references therein). In some etchants [the most well-known are aqueous solution of KOH and ethylene diamine pyrocatechol (EDP)], the etch rate of the (111) planes is much smaller than in the other crystallographic directions. Depending on concentration of the etchant and the temperature the (111) direction etches slower than the other ones by a factor 100 and more. This fact is widely being used to micromachine tiny mechanical devices.[2] Etch rate and temperature dependence (described by an Arrhenius law) are anisotropic: slow etching goes with large activation energies.

Recently, papers appeared which deal with the mechanism of anisotropic etching of silicon.[1,3,4] The basic idea is that in the (111)-plane of silicon there is only one dangling bond per silicon atom. Therefore there are three bonds to break for dissolution, while other planes [except the (110)] have more dangling bonds, accordingly a smaller number of bonds must be broken.

[a] Present address: MESA-Research Institute, University of Twente, NL-7500 AE Enschede, The Netherlands.

The anisotropy cannot be understood by this fact alone because in the dissolution process transferring a silicon atom from the solid to a molecule dissolved in the liquid the backbonds are not broken simultaneously.

Seidel *et al.*[1] have proposed that in the rate-determining step the electronic state of the complexed silicon depends on the number of backbonds. The anisotropy of the activation energy and of the etch rate itself could be explained by such a model. A serious problem however arises if one realizes that on the (110) plane there are also three backbonds, but the etch rate is large [comparable to (100)] and the activation energy corresponds to a fast etching direction.

The activation energy of the etch rate in anisotropic etching solutions depends on the etching system. This dependence is attributed to diffusion that plays a greater role in EDP than in KOH based solutions. However one should expect that at least the slow etch rates are not due to diffusion in the solution but to surface reactions, and diffusion should have a minor effect on the activation energy.

There are other etchants in which silicon etches isotropically (aqueous solutions of HF:HNO_3). Here, the chemical reaction is different; HNO_3 acts as an oxidizer and the sili-

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con oxide is dissolved subsequently by HF. No reasons are given in the literature why this system etches isotropically.

A simple explanation may be available that could clarify the points addressed above, and that opens a route for new research. I propose it is the physical state (being atomically flat or rough) of the various surfaces that are finally responsible for the anisotropy of etch rates and activation energies.

It is a nucleation barrier on the (111)-plane that inhibits the etching and gives rise to a larger activation energy of the etch rate. The situation may be similar to the growth of crystals.

The similarity between kinetics of crystal growth and crystal dissolution may not be obvious since usually we observe a rounding off of the crystal while dissolving: if sugar crystals are thrown into your coffee, the edges and corners of the crystals are etched away quickly. The dissolution process appears to be isotropic. However, the edges and corners dissolve quicker than the facets. The facets disappear from the crystal. The etch rate seems to be isotropic because only nonfaceted faces are etched. If you throw a sugar crystal into a supersaturated solution, facets develop, and the crystal is bounded by the slowly growing faces. The similarity becomes apparent if one compares growth forms starting from convex forms and dissolution forms starting from concave forms (as is usually done in micromaching). In both cases the crystal is bounded by the slow growing and the slow etching planes, respectively. Parallels in the process of etching and growing of crystals, slowly growing crystal faces also etch slowly, has been mentioned by several authors.[5,6] Here we claim that slow growing faces also etch slowly for similar reasons.

This paper is arranged as follows: in the next Section the etch-inhibiting mechanism of a nucleation barrier is explained. The basic notion introduced is the step-free energy, which plays a key role in kinetics of crystal growth and dissolution. It is the key notion to understanding the anisotropy of etch rates (and growth rates) of single crystals. The theory we explain here can be applied in principle to the etching of all single crystalline materials such as quartz and gallium arsenide, materials also of importance for micromachining. Two Sections reviewing thermal and kinetic roughening follow. In these Sections we describe circumstances in which the nucleation barrier becomes unimportant. Here the reasons are given why the degree of anisotropy can be so great. Only in special circumstances can the etching of single crystals be isotropic. It is not necessary to look for reasons for the anisotropy in details of the chemical reactions that are relevant in the dissolution process. Also guidelines for estimation of the step-free energy, and whether a particular crystal facet is smooth or rough, are given.[b] Finally, discussion and conclusion follow.

The Nucleation Barrier

The basic kinetics of crystal growth is well established[7]. There are two different states of surfaces giving rise to two different growth mechanisms: the surface can be either atomically rough or smooth.[8] A smooth face is seen on the crystal form as a facet. If the surface-free energy (surface tension) is plotted as a function of the orientation (Gibbs-Wulff plot), these faces manifest themselves in minima at the positions of the facets.

Now, imagine that you have a flat face and you want to misorient it. This can be done only by adding steps to the crystal face, therefore misorientation costs the free energy of steps. Since steps can be added only in whole portions, the smallest misorientation that can be achieved costs a finite amount of free energy, the free energy of one step This is true for all directions of misorientation, therefore the minimum in the surface-free energy of a flat face is a singular point. The minima of flat faces are sharp. These sharp minima are called cusps, and the slope close to the cusps is proportional to the step-free energy of the face.[9] The step-free energy is of central importance to crystal growth and etching. Faces that are atomically rough may have minima in the Gibbs-Wulff plot but these are regular minima if at all, no cusps. Accordingly, the step-free energy is equal to zero on these faces. On the equilibrium form of a crystal, a rough face is round (if it ever appears on the equilibrium form). An illustration is given in Fig. 1.

[b] Much of the material given in these Sections (especially the explanation of the nucleation barrier) is basic and well known to researchers active in crystal growth; however, this knowledge is not common to researchers active in micromachining. To make this paper easily readable we discuss these basic but relevant features.

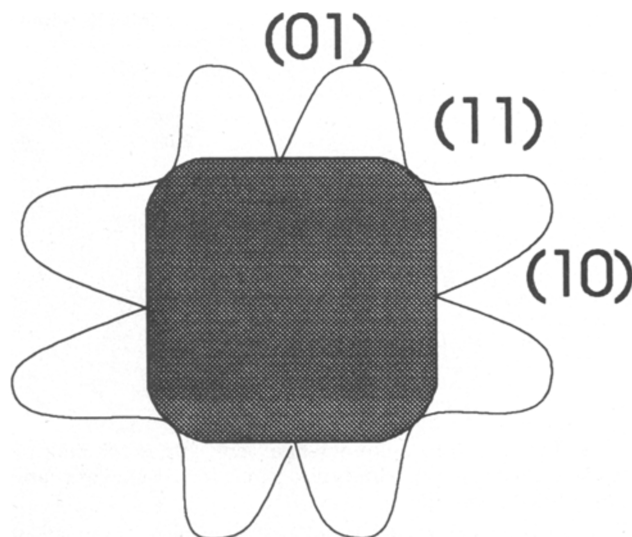

Fig. 1. Schematic diagram of a Gibbs-Wulff plot showing the surface-free energy as a function of the crystal orientation. Singular minima at flat (10) faces and nonsingular minima at rough (11) faces are indicated.

Between smooth and rough faces, there is a phase transition, the so-called roughening transition.[10-12]

Steps play a key role in the kinetics of crystal growth and dissolution of flat faces.[7] Obviously, an atom at the edge of a step has a smaller binding energy to the crystal than the atoms in a flat face. Furthermore, steps are never straight because they are essentially one-dimensional structures. One-dimensional structures have no phase transitions[9], therefore steps are probably always rough, except at $T = 0$. Accordingly, there are many atoms along a step in convex corners, which are bonded even more loosely to the crystal. The consequence is that the kinetics of crystal growth and dissolution is governed by the kinetics of steps: the kinetics of the formation of steps and their velocity. Therefore, if crystal surfaces are flat, one does not have to worry much about how to remove an atom from the flat face, and how to break all these bonds, but how to make steps, and, if there are steps, how to remove atoms from the weakest sites of a step. These atoms may leave the step by diffusing on the surface, reducing thereby the number of bonds even further.

The growth and etch mechanism of a smooth face is characterized by a nucleation barrier. To grow a new layer on a flat face, an island has to form. For etching, it is the same: to etch a layer of a flat face, one must dig a cavity and transport the atoms into the undersaturated surrounding. The total free energy is decreased by the chemical potential difference, and increased by the presence of a step on the crystal surface. This is shown schematically in Fig. 2. In any case the free energy change g, by adding an island or digging a cavity (of circular shape in an isotropic face) of radius r, is given by

$$g = -N\Delta\mu + 2\pi r\gamma \quad [1]$$

where N is the number of atoms in the island, or removed from the cavity, $\Delta\mu$ is the chemical potential difference between silicon atoms in the solid state and the solution (whether or not bonded in a molecule), and γ is the step-free energy. We have

$$N = \pi r^2 h\rho \quad [2]$$

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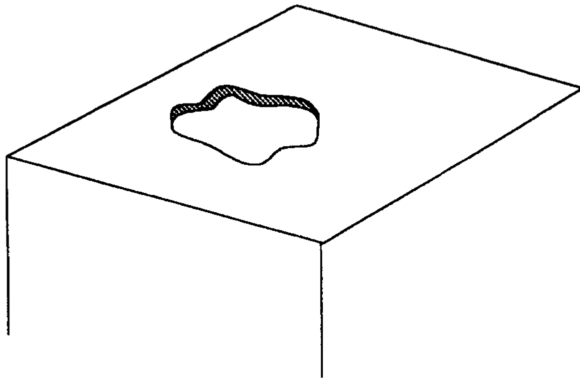

Fig. 2. Etching a cavity into a flat crystal face.

where h is the height of a step and ρ is the density (atoms per cm^3) of the solid material. The result is

$$g = -\pi r^2 h \rho \Delta\mu + 2\pi r \gamma \qquad [3]$$

Note that $\Delta\mu$ is counted positive and γ is positive in any case; $g(r)$ is shown in Fig. 3. Equation 3 has a maximum at

$$r^\star = \gamma / h \rho \Delta\mu \qquad [4]$$

At $r^\star$ the free energy is

$$g^\star = g(r^\star) = \pi\gamma^2 / h\rho\Delta\mu \qquad [5]$$

Hence there is an island of critical size, and there is a cavity of critical size. If by chance a cavity is dug into the crystal which is smaller than $r^\star$ it is filled rather than growing, since this is the easy way to decrease the free energy. This fact is well known in nucleation theories. The difference in free energy of a silicon atom in the crystal compared with that in a $Si(OH)_4$ is large, but if the nucleus of critical size is not too small (see below), the state of a one-atom cavity is unfavorable. It is the same for growth: islands smaller than the critical size have a much greater chance to dissolve than to continue to grow. Islands or cavities with $r = r^\star$ do not know what to do, and once $r > r^\star$ the islands or cavities can grow until the whole layer is filled or removed. What we have described here is the nucleation barrier to growth or dissolution of flat crystal faces. The theory is known as the classical nucleation theory, and works as well for nucleation of crystals and liquids from a supersaturated environment.

In the light of the nucleation barrier theory it is practically impossible to remove atoms directly from a flat face[c], since the created cavity increases the free energy of the system and the filling of the cavity is more probable than the removal of a second adjacent atom.

The growth and etch rates of flat faces are proportional to

$$\exp(-g^\star/kT)$$

Since $g^\star$ is proportional to γ^2 the activation energy of the etch rate of different flat faces differs, the etch rate and the activation energy are both anisotropic. The influence of various etchants is reflected in the (isotropic) parameter $\Delta\mu$ and in the (anisotropic) parameter γ.

The origin of the anisotropy of the etch rate therefore is due to the anisotropy of the step-free energy, rather than surface-free energy. These free energies are related: comparing flat faces, those having a large surface-free energy have a small step-free energy, and vice versa.

The most important difference in these quantities is that the step-free energy is zero for rough faces, while the surface energy remains finite.

If there are screw dislocations emerging at the crystal surface, the etch mechanism is different: screw dislocations serve as continuous step sources. The growth and etch rate are much larger in the presence of screw dislocations, but still smaller than those of rough faces. However, in silicon the density of dislocations is small. Screw dislocation serving as a continuous source of steps may play no role for silicon etching.

[c] Except if the critical nucleus is too small, see Section on kinetic roughening.

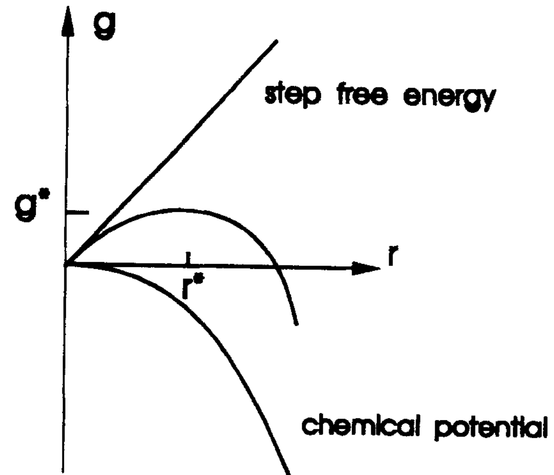

Fig. 3. Free energy as a function of the size of a cavity in a flat crystal face.

The Roughening Transition

What are the smooth faces of silicon? This question is not so easy to answer. We must know the roughening temperature T_R. To estimate T_R one can use the following argument.

A crystal face may be characterized by its so called α-factor of Jackson[13], which is the binding energy of a crystal slice with orientation (hkl) divided by the temperature. A simple visualization of the meaning of α is given in Fig. 4. It is equal to energy of the first excitation state of a surface. An atom is taken out of the crystal face and laid down somewhere on the crystal face, so that the chemical potential is not changed. For excitation of the surface, as shown in Fig. 4, only lateral bonds must be broken, the bonds normal to the face are left unchanged. Therefore, α is related to the step-free energy, and at a very low temperature, where entropy effects can be ignored, $kT\alpha$ is proportional to γ.

If one takes into account only nearest neighbor interaction, whose energy in a lattice gas model for the fluid can be denoted by ϕ_{ss}, ϕ_{ff}, and ϕ_{sf}, s and f refer to solid and fluid, respectively, we have[14]

$$\alpha_{hkl} = \frac{1}{kT} \Sigma_{slice}[\phi_{sf} - \frac{1}{2}(\phi_{ss} + \phi_{ff}) \qquad [6]$$

where the sum runs over the bonds in the slices with orientation (hkl). In a fluid mixture, ϕ_{sf} and ϕ_{ff} must be replaced by[15]

$$\phi_{ff} = X_A^2\phi_{AA} + X_B^2\phi_{BB} + 2X_AX_B\phi_{AB} \qquad [7]$$

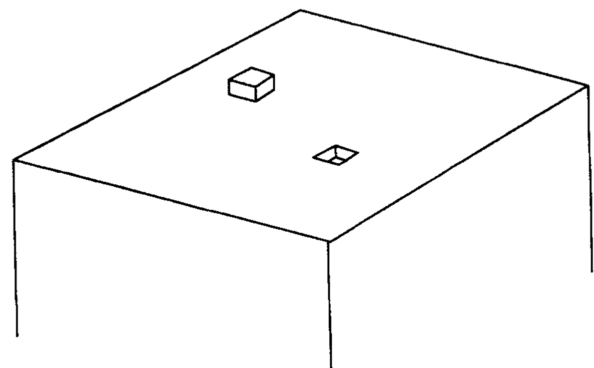

Fig. 4. Illustration of the definition of the α-factor of Jackson.

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and

$$\phi_{sf} = X_A \phi_{sA} + X_B \phi_{sB} \quad [8]$$

X_A and X_B are the mole fractions of the solute (subscript A) and solvent (subscript B), respectively. By assuming complete wetting[14], $\phi_{sA} = \phi_{AA}$ and $\phi_{sB} = \phi_{AB}$, one can show that[15]

$$\alpha_{hkl} = \xi_{hkl}\, \Delta H_{diss}/kT \quad [9]$$

where ξ_{hkl} is the anisotropy factor is defined by

$$\xi_{hkl} = \frac{\sum_{slice} \phi_{ss}}{\sum \phi_{ss}} \quad [10]$$

and ΔH_{diss} is the heat of dissolution.

Since α is proportional to the inverse temperature, it decreases if the temperature is raised. If T is larger than T_R, α_{hkl} is smaller than a critical number α_R, and the face is atomically rough. Computer simulations[10] have revealed that α_R depends on the symmetry of the face in question, *e.g.,* for the (111) face in the diamond structure, $\alpha_R = 4$; for square symmetry it is close to 3.[10] If in a particular face there are nearest neighbor bonds only in one lateral direction, we have $\alpha_R = \infty$, as is the case if there are no lateral bonds at all in a face. This corresponds to a roughening temperature $T_R = 0$.

If the real silicon faces are approximated by the faces one obtains by simply cutting along a particular crystal plane (hkl), the (111) plane is the only plane with a finite α_R or a roughening temperature $T_R > 0$.[16] However, real crystal faces are more complicated than one obtained simply by cutting. The surface reconstruction on silicon (111) and (100) faces are well known and generally, they decrease the surface-free energy. Of importance here, the formation of dimers on the (100) face can have the consequence that there are periodic bonds in more than one direction, raising the step-free energy from zero to a finite value.[17] Flat (100) faces on silicon have been observed in chemical vapor deposition (CVD) experiments.[18,19] These experiments revealed many flat faces, including the (110) and (331). It appears from these experiments that the (111) face is the strongest one. The appearance of the (110) face is not understood but may be attributed to absorption of chemicals[19].

A liquid environment is much different from a vapor environment. First, ΔH_{diss} is much larger (up to two orders of magnitude) in vapors than in liquids. Unfortunately we cannot give any values of ΔH_{diss} in any etchant. Second, the reconstruction on the (111) and (100) faces have been found in high vacuum only, and no one knows what happens to them in the relevant etchants. Anyway, there is a good chance that the (111) face is flat, and if it is flat, there is no doubt that it has the largest step-free energy; the (100) and the (110) faces may be flat also.

Rough crystal faces grow and dissolve by a mechanism that differs from that of flat faces. There is no nucleation barrier because the step-free energy is equal to zero. New units may be added and removed freely to the surface without changing the number of steps. Rough crystal faces grow and dissolve with a rate proportional to $\Delta\mu$. Growth and etching of flat faces therefore proceeds slower than growth and etching of rough faces.

Kinetic Roughening

Our remarks on α_R and the state of the surface below and above the roughening temperature apply to a thermal equilibrium situation. Etching of silicon is far from equilibrium. However, the most important change here is kinetic roughening.[20-22] This roughening occurs if the super or undersaturation is so large that the thermally created islands or cavities are of the size of the critical nucleus. One can show[21] that if the super- or undersaturation is larger than $\Delta\mu_c$, given by

$$\Delta\mu_c = \pi f_0 \gamma^2/kT \quad [11]$$

(f_0 is the area one atom occupies in a given crystal plane), the growth and etch mechanism changes from a nucleation barrier controlled mechanism to a direct growth/etch mechanism. The growth and etch rate is then proportional to the chemical potential difference.

We expect therefore that if the undersaturation becomes high enough, the (111) face etches by direct dissolution of the atoms out of a rough surface. The etch rate increases very much in this case, approaching the etch rate of the other (rough) faces. The etching becomes isotropic. We expect that this is the case in mixtures of HF and HNO_3, which are known to etch isotropically.[23] However, it is difficult to estimate the undersaturation in isotropic and anisotropic etchants. It should be related to the solubility of silicon or its reaction products with the etchant, but these data do not seem to be easily available. Furthermore, $\Delta\mu$ is time dependent and the effective $\Delta\mu$ is given by precise chemical reactions, the concentration of the reactants at the silicon surface, and their thermodynamic properties. Therefore reliable estimates of $\Delta\mu$ deserve further research.

Discussion

Fortunately there is some indication on the state of the (111), (100) and (110) faces in contact with EDP and KOH solutions from an experimental viewpoint.

We can infer from the etch experiments of Seidel *et al.*[1] on the state of the (111) face in alkali-based etchants and EDP. Seidel *et al.* conducted careful measurements of the etch rate around the minimum in the (111) direction and they found a beautiful cusp: the etch rate varied linearly with the misalignment angle, showing a singular point (within the experimental accuracy), see Fig. 11 of Seidel's paper, Ref. 1. That is what one expects from flat faces. A misalignment means that there are steps on the surface. The number of steps is proportional to the misalignment angle, therefore the etch rate (and the growth rate, as is well established) should vary linearly with the misalignment, showing a singular point at perfect alignment. Seidel's results give us strong evidence that at least the (111) face in KOH and EDP at this very high undersaturation are flat indeed.

The linear dependence of the etch rate in KOH close to the (111) direction on the misorientation angle has been found and discussed by Kendall[24]. In this paper there is also a demonstration that the motion of macrosteps (ledges) is responsible for the etching of misoriented (111) faces. This point deserves some further comment. In practice one always has some misorientation with respect to the (111) plane, and the actual etch rate is governed by the number of steps one has due to the misorientation. The better the orientation the greater is the anisotropy of etching. However, that the (111) plane is flat is the reason for the minimum of the etch rate. Because the face is flat, the etch rate is proportional to the angle of misorientation.

The results on etch rates of misaligned (100) faces are less conclusive. If etched in KOH, minima in the etch rate appear in the (100) direction. Inspecting Fig. 10 in Ref. 1 it appears that the minima are smooth at a KOH concentration of 50%. Unfortunately, the authors do not give their data points but present a (probably eye-guided) curve. Therefore I suggest to either inspect the raw data or to perform new experiments with a refined angular resolution. The depth of the minimum of the etch rate around the (100) faces depends on the KOH concentration, and the minimum may be singular (cusped) at higher concentrations[25] and nonsingular at smaller concentrations. If we perform etch experiments with slight misorientation around the (100) direction at higher KOH concentration, we may gain more precise information on the form of the minimum. If it is a cusp, it is likely that there is a surface reconstruction as in high vacuum even in the harsh etching environment.

Similar remarks apply to the (110) face. In EDP, Seidel *et al.* observe minima of the etch rate in the (110) direction. These minima seem to be nonsingular, c.f., Fig. 8 and 9 in Ref. 1. Again, it would be interesting to know about the character of this minimum and whether it changes with concentration and/or temperature.

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There is a point that is not well understood by theories of crystal growth. A rough crystal face should grow or etch with the maximum rate, that is governed only by transport of species active in the etch or growth process to and from the crystal surface. However, according to Monte Carlo simulations (as an example) on the growth of crystals,[8] the growth rate at a temperature higher than the roughening transition is smaller than the maximum growth rate. Although the step-free energy is equal to zero, there remains some anisotropy in the growth rate. This has not been discussed in the literature. Here the study of etching of silicon or quartz may shed some light on this fundamental question.

Interesting experiments could deal with the temperature dependence of the etch rate as a function of the orientation. The activation energy of the etch rate of a flat face is dominated by the free-energy barrier of the critical nucleus. Further, the etch rate is proportional to the velocity v of the propagating steps on the surface. If the face is misaligned, steps need not to be created by nucleation, and the etch rate is proportional to the absolute value of the angle of misorientation times v, without the inhibiting exponential factor. That means that close to the orientation of a flat face, the activation energy of the etch rate could vary rapidly, raising to a maximum at the flat face. That means that it is difficult to measure the activation energy of the etch rate of a flat face, since a slight misorientation should reduce the observed temperature dependence. This could be an explanation for the spread of the activation energy found in the literature dealing with the etch rates of quartz.[26]

One may have noticed that in a plot of the growth/etch rate *vs.* the crystal orientation flat faces have a cusp-like minimum and rough faces have a smooth (parabola-like) minimum. This plot is similar to the Gibbs-Wulff plot. Hence, equilibrium forms are similar to some extent to convex growth/concave dissolution forms: often knowledge of the surface-free energy of a crystal is sufficient to give a reasonable first approximation to nonequilibrium forms. This may be the reason for the success previous authors[3,4] had in interpretation of the anisotropy of the etch rate. Their argument was based on quantities related directly to the surface tension, hence their results are in estimates of the equilibrium form.

We expect that $\Delta\mu$ is largest in isotropic etching solutions, so that all faces are kinetically rough. This statement implies that if the undersaturation in these etchants can be lowered by some means (*e.g.*, by using a solution that has etched silicon a sufficiently long time, so that it becomes more or less saturated), the etch rate should become anisotropic. Such an effect has been observed by Hashimoto *et al.*[27] They etched silicon through small holes in the mask, trying to etch semispherical cavities. If the hole in the mask was large enough they succeeded but they observed that the cavities revealed some anisotropy if the holes in the mask were very small. This is a case where aging of the solution may be visible, since the small hole in the mask hinders the transport of fresh solution to the silicon surface.

We also expect that $\Delta\mu$ is smaller in EDP than in KOH, since the former etchant is known to age (saturate) much quicker than KOH.[1] This difference seems to fit perfectly to the steeper minimum of the etch rate in the (111)-direction in EDP,[1] but contradicts the larger activation energy of the etch rate in KOH solutions.[1] Without knowledge of thermodynamic data (at least ΔH_{diss} and c_0) no firm conclusion on this point can be drawn, because besides $\Delta\mu$ the step-free energy also depends on the etchant. In Ref. 1 the difference in activation energy in the KOH and EDP systems is attributed to the fact that transport in the liquid phase plays a greater role in EDP than in KOH. For the total etch rate the reciprocal rates of the bulk transport and the surface reactions must be added, $R^{-1} = (R_{surface})^{-1} + (R_{bulk})^{-1}$. An influence of transport on the activation energy of R is only expected if $R_{surface}$ and R_{bulk} are of comparable order. If this were the case for the fast etching crystallographic orientations, it is certainly not true for the slow etching ones. The activation energy for R_{bulk} should be close to that for the self-diffusion constant, which in turn should be close to the activation energy of the viscosity of the etchants. I expect this activation energy to be similar to that for water, which is 0.2 eV, considerably smaller than the activation energy observed for the etch rates. Therefore I find the explanation given in Ref. 1 not satisfactory.

There is a difference of the sensibility of rough and flat faces with respect to absorbed impurities that may have important technological implications. On flat faces impurities can have a greater effect than on rough faces. This effect can be seen from a simple argument. If the growth or etch mechanism is controlled by the movement of steps, it is a one-dimensional structure that reacts on absorption of impurities. The impurity concentration at the steps can be much larger than the impurity concentration in the three-dimensional fluid bulk. A blocking mechanism of moving steps due to impurity absorption at steps has been proposed by Cabrera and Vermilyea[28], their model results in totally blocking of crystal growth at a given impurity concentration below a threshold supersaturation. The central idea is that a step moving on a surface on which impurities are absorbed, the step has to bend to move between two sites with absorbed impurities. If the impurites are closer to each other than twice the critical radius $r^\star$, they cannot keep on moving, they are blocked and the crystal face stops growing or etching. A similar mechanism could provide a possible explanation of the rough appearance of the (100) faces after etching, and the consequences of adding pyrazine to EDP for etch anisotropy and morphology of the (111) face.

Conclusion

In this paper an alternative interpretation of the anisotropy of the etch rate is given, inspired by current theories of crystal growth. We have put forward arguments that the key to understand nonequilibrium forms is the step-free energy γ of crystal faces. Flat faces grow and etch with a rate proportional to $\exp\,[-\pi\gamma^2/h\rho kT\Delta\mu]$, which predicts that faces with large step-free energy grow and etch much slower than faces with a smaller step-free energy. Certainly, the (111) face of Si has the largest step-free energy. Above a certain temperature T_R, the roughening temperature, crystal faces are rough, and these grow and etch with a different mechanism, so that the rate is proportional to $\Delta\mu$ and much larger than that of flat faces.

γ and $\Delta\mu$ both depend on temperature and the ambient solution, so the degree of anisotropy should depend on the etchant. If the under/supersaturation exceeds a certain limit, faces also become rough. This roughening may explain why silicon is etched isotropically in certain etchants and anisotropically in others. It is expected that the undersaturation in isotropic etching solutions is largest and therefore the difference in chemical potential. Then kinetic roughening of the (111) face may explain the isotropic etch rate.

Since the solubility of silicon in EDP solutions is smaller than in KOH solutions, we expect that $\Delta\mu$ is larger in KOH, from which a smaller activation energy in KOH would follow, if γ where independent from the etchant. Since the activation energy in KOH is larger than in EDP one could expect that the heat of dissolution of silicon in KOH is larger. For more quantitative discussion of the influence of the etchant, thermodynamic data of the etch products of silicon in the etchants are needed to estimate α, γ, and $\Delta\mu$.

The (111) face is probably flat. This result is suggested by Hartman's PBC-analysis[16], and by CVD growth experiments[18,19], and it is evident from the linear dependence of the etch rate on the misorientation angle close to (111). If the plots for the etch rate close to the (110) (EDP) and (100) (KOH) are realistic (no cusps but regular minima), these faces are rough in the respective etchants. The (111) plane would be the only flat face in this case, and the kinetics must be much slower on this face, in agreement with experimental results. In principle, similar remarks (although not detailed here) can be made on etching on single crystalline quartz (see *e.g.*, Ref. 29). We suggest a reinspection of raw

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data of the etch rates close to Ref. the (100) and the (110) faces to get a firmer insight into the character of these faces, whether flat or rough. One could get indications on the existence of dimer reconstruction on the (100) face. Knowledge about whether faces are rough or flat gives one the chance to understand the action of additives in the fluid, which act strongly on the kinetics of steps. In case the (100) and/or the (110) faces are flat, one could find additives that absorb preferentially on one face and block the etching.

There are more open questions. We already mentioned the anisotropy of growth and etch rates of atomically rough faces, a phenomenon for which there is as yet no good theory. Further, it is unclear why the maxima in the etch rate appear at the observed crystallographic directions. As observed in our own laboratories as well as in scanning electron micrographs in the literature (*e.g.* Fig. 4.1.1. in Heuberger's textbook[30]) seemingly smooth faces emerge from convex etch forms. These facts point to cusps at maxima in the etch rate as a function of the orientation.

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