Etchant Anisotropy Controls the Step Bunching Instability in KOH Etching of Silicon

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STM investigations of vicinal Si(111) surfaces etched in KOH solutions under controlled flow conditions show that step bunching instability is due to inhomogeneities that develop in the etchant as the result of highly step-site-specific etching reactions. Other previously postulated mechanisms for step bunching, including anisotropic surface diffusion, surface strain, and impurity deposition, are conclusively ruled out. The inhomogeneities locally accelerate etching near surface steps. Kinetic Monte Carlo simulations of this process qualitatively reproduce the observed morphologies.

The control of surface morphology during growth and processing has received considerable attention over the past decade. From a fundamental standpoint, growth and etching processes are susceptible to many intriguing instabilities that can lead to the formation of complex but surprisingly regular surface morphologies, such as step bunches, hillocks, and even pyramids. From a technological standpoint, the control of these morphologies is important to the successful fabrication of many commercial devices, including inkjet nozzles, solar cells, and transistors. In spite of their importance, the fundamental processes that govern the development of surface texture during processing are, in many cases, poorly understood.

For example, aqueous KOH solutions find widespread use in micromachining, as these solutions selectively attack all silicon surfaces *except* {111} planes. Because of this property, KOH can be used to selectively produce precisely aligned and oriented Si{111} surfaces, in some cases with near-atomic smoothness. In spite of their widespread use, KOH etchants have defied simple explanation for a number of reasons. First, these etchants produce surprisingly regular, micron-scale etch features [e.g., randomly distributed pyramids on (100) faces, ridges on vicinal (110) faces, and macrosteps on vicinal (111) faces] whose size and structure depend sensitively on etchant concentration and temperature [1]. What controls the length scale of these features? Can their size be controlled chemically? Their shape? Their formation? Second, the kinetics of this very simple etchant cannot be explained by a simple chemical mechanism. For example, the etchant has a maximum rate at intermediate KOH concentrations; 12% (w/v) KOH is a significantly faster etchant than either 50% or 5% (w/v) KOH [1,2]. The etchant anisotropy (i.e., face-specific etch rates) also has a complicated concentration and temperature dependence, even though measurements of the kinetic isotope effect strongly suggest that all silicon surfaces etch by the same chemical mechanism [1].

In this Letter, we show that the KOH etching of silicon surfaces is subject to a new type of etching instability which is caused by inhomogeneities that develop in the etchant as a result of the highly anisotropic (i.e., site-specific) etching reactions. Because the etchant preferentially attacks step sites on the surface, inhomogeneities in the etchant, which may be due to etchant depletion, product buildup or local heating, are most severe in regions of high step density. The inhomogeneities have a surprisingly large magnitude and extend laterally for microns across the etching surface. As a result, KOH etching is inherently nonlocal and inherently unstable to the formation of macroscopic surface features. On vicinal Si(111) surfaces, these inhomogeneities lead to step bunching and macrostep formation.

To conclusively separate the effects of etchant inhomogeneities from all other effects, silicon surfaces were etched under controlled flow conditions. A vicinal Si(111) surface miscut by 3.5° toward the $\langle 11\bar{2} \rangle$ direction was first mounted in a cylindrical Teflon sample holder and cleaned thoroughly following standard procedures [1]. The sample holder was then placed in a fresh sample of room temperature, 50% (w/v) aqueous KOH and rotated at a constant angular frequency ω about the sample centerline. In this geometry, forced laminar convection draws the etchant towards and across the surface in a vortex pattern as sketched in Fig. 1. This controlled
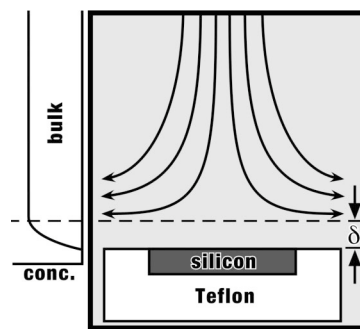

FIG. 1. Schematic diagram of etchant flow in the rotating disk geometry. The laterally averaged concentration of the etchant as a function of height is plotted at left.

flow creates a stagnant, unstirred layer of thickness δ, known as the diffusion layer, above the surface. Transport in this layer is diffusional. According to a hydrodynamic analysis first presented by Levich [3] and verified by many subsequent electrochemical experiments [4] the thickness of the diffusion layer is constant across the entire surface, proportional to $\omega^{-1/2}$, and given by

$$\delta = 1.61 D^{1/3} \omega^{-1/2} \nu^{1/6}, \tag{1}$$

where D is the diffusion constant, and ν is the kinematic viscosity. At high rotational frequencies, transport perpendicular to the surface is facile, and etchant inhomogeneities are suppressed. In contrast, unstirred solutions develop much larger inhomogeneities.

Figure 2 shows representative scanning tunneling microscopy (STM) images of initially flat, vicinal Si(111) surfaces etched for 5 min under controlled flow conditions in room temperature KOH. During etching, the samples were rotated at 0, 200, and 800 rpm, respectively. All surfaces developed macrosteps (i.e., step bunches) during etching; however, the average height and density of the macrosteps were strongly dependent on the rate of sample rotation. This effect is relatively independent of the initial step spacing, as step bunching is also seen on samples miscut by 0.35° — a tenfold decrease in step density. Samples etched in an unstirred etchant, where the largest inhomogeneities were expected, developed large macrosteps separated by nearly atomically flat terraces. In contrast, samples rotated at 800 rpm developed significantly smaller bunches, whereas intermediate height macrosteps were formed on samples rotated at 200 rpm. Importantly, the morphologies were independent of the direction of etchant flow.

These experiments rule out a number of previously observed mechanisms for step bunching. For example, step bunching on clean silicon surfaces has been previously attributed to anisotropic surface diffusion induced by an Ehrlich-Schwoebel barrier to step crossing [5,6]. A surface diffusion based mechanism cannot explain these results, as surface diffusion should not couple to sample
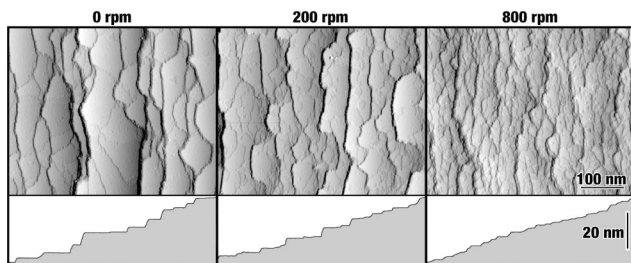

FIG. 2. STM images (upper) and cross-sections (lower) of vicinal Si(111) surfaces etched for 5 min in room temperature 50% (w/v) KOH in the rotating disk geometry as a function of rotational frequency. In this geometry, increased rotational frequency suppresses the development of etchant inhomogeneities.

rotation. The same argument can be used to rule out strain-mediated step bunching [7]. Similarly, these experiments cannot be explained by impurity-induced step bunching [8,9], as the flux of impurities from the etchant, and thus the magnitude of the bunches, should *increase* with decreasing diffusion layer thickness. The experiments show the opposite trend.

In this system, macrostep formation is driven by a kinetic instability that is similar to the instability that causes traffic jams on crowded highways. KOH solutions are step-flow etchants; they etch step sites much more quickly than terrace sites as evidenced by the low density of etch pits on the surface. Since the etching reactions are localized at the steps, the etchant concentration and temperature are both perturbed in the vicinity of each step. When the steps are equidistant, these perturbations have no morphological effect. All of the steps are affected equally, and they propagate at the same velocity. When a random fluctuation brings two steps close to one another, though, the inhomogeneities overlap and are enhanced. As a result, the step pair will begin to etch faster or slower, depending on the net effect of the inhomogeneities, which may be complex. (For example, product buildup might cause an autocatalytic reaction to accelerate.) This faster (slower) motion will allow the pair to catch up to the next step, creating an even more quickly (slowly) propagating step trio, and so forth [10].

This type of instability was proposed essentially simultaneously by Frank, who described step bunching during etching, and by Cabrera and Vermilyea [11] who described growth. Using a continuous, one-dimensional model of step-flow etching, they predicted the formation of step bunches in any system where the velocity of step propagation, ν_{step}, is dependent on step density, ρ_{step}. In cases where step bunching locally accelerates etching (i.e., $\partial\nu_{\text{step}}/\partial\rho_{\text{step}} > 0$), this model predicts the formation of concave step bunches. In contrast, convex bunches were predicted for decelerating kinetics (i.e., $\partial\nu_{\text{step}}/\partial\rho_{\text{step}} < 0$).

The macrosteps produced by KOH etching of vicinal Si(111) are not consistently concave or convex. Instead, most macrosteps have a roughly constant slope which varies from bunch to bunch. This experimental observation is consistent with recent two-dimensional simulations of the instability [12], which failed to reproduce the concavity predicted by one-dimensional models.

To determine whether step bunching leads to local acceleration or local deceleration and to obtain further insight into the magnitude and lateral extent of this effect, we devised a second type of experiment, which is sketched in Fig. 3(a). In this experiment, five equally spaced, 750-nm-wide, 100-μm-long lines were opened into an inert silicon nitride mask covering a silicon surface. When this masked substrate was placed in the etchant, a concentration gradient was generated in the
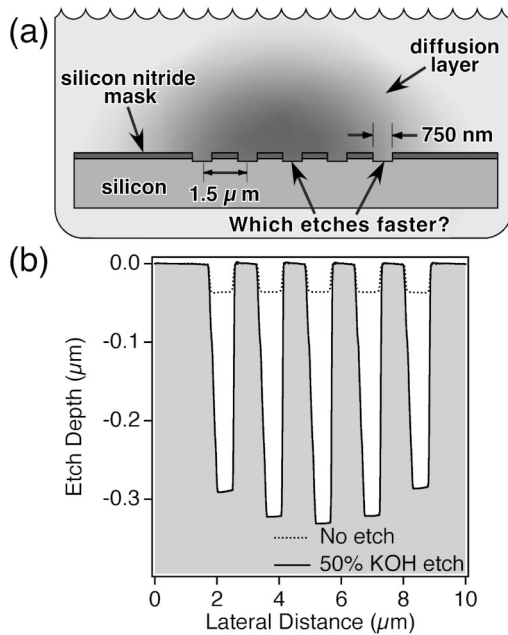
FIG. 3. (a) Schematic of trench etching experiment; (b) AFM image of trench profile with and without etching in room temperature 50% (w/v) KOH. These data show that etching leads to local acceleration, as the center trench etches at least 15% faster than the outer trenches.

near-surface region. If etchant inhomogeneities lead to local acceleration, the center trench should etch fastest, whereas if they lead to deceleration, the outer trenches should etch fastest. If diffusional effects are negligible on this length scale, all trenches should etch at the same rate.

The results of one such experiment in room temperature, 50% w/v KOH are shown in Fig. 3(b). Clearly, the etchant inhomogeneities had a *dramatic accelerating effect* on etching; the center trench etched *at least 15% faster* than the outer trenches even though the trenches were almost 1 μm apart. Indeed, this accelerating effect was seen for trench spacings up to 6 μm—the largest spacings examined to date. Furthermore, when the masked samples were rotated about their centerline during etching, the magnitude of the acceleration decreased, further confirming that this effect is due to etchant inhomogeneities. Although the sign of this effect is somewhat surprising, it is consistent with the observed macroscopic kinetics—decreasing the concentration of a 50% (w/v) KOH solution leads to an acceleration of the macroscopic silicon etch rate.

To further confirm the proposed mechanism, the morphological effects of this inhomogeneity driven instability were modeled using an atomistic, kinetic Monte Carlo simulation of silicon etching [12]. These simulations used a hybrid model of aqueous silicon etching that combined an atomistic model of the site-specific surface reactions to a qualitative, coarse-grained model of etchant inhomogeneity. Like the original model proposed by Frank [10],

this model assumed that the etchant inhomogeneities were proportional to the local density of step or defect sites. In the simulation, the etch rate of a specific site, k_{site} was determined by two factors: the etch rate of that type of site (e.g., kink, step, terrace) in the absence of inhomogeneities (i.e., under well-stirred conditions), k_{site}^{KMC}, and the local step density according to

$$k_{site} = [1 + a\rho_{step}(N)]k_{site}^{KMC}, \qquad (2)$$

where a is an adjustable parameter that controlled the coupling to the inhomogeneity. The distance over which the step density is averaged is controlled by the adjustable parameter N. Further details of the simulation are given in Ref. [12].

A comparison between the experimental and simulated morphologies are shown in Fig. 4, and a movie showing the development of macrosteps on an initially flat surface is available [13]. In the simulation, the site-specific etch rates were chosen to simulate a step-flow etchant producing meandering steps. In the absence of etchant inhomogeneities, no step bunching was observed; the etched steps remained roughly equidistant, in agreement with previous studies [14]. When the effects of etchant inhomogeneities were included, rapid step bunching was observed. To simulate the experiments, the characteristic size of the inhomogeneities, which was controlled by the parameter N, was adjusted to yield the best fit to experiment, while all other parameters were held fixed.

The agreement between simulation and experiment is surprisingly good given the simplicity of the model. Nevertheless, the numerical value of N should be interpreted with caution. Experimentally, the macrosteps con-
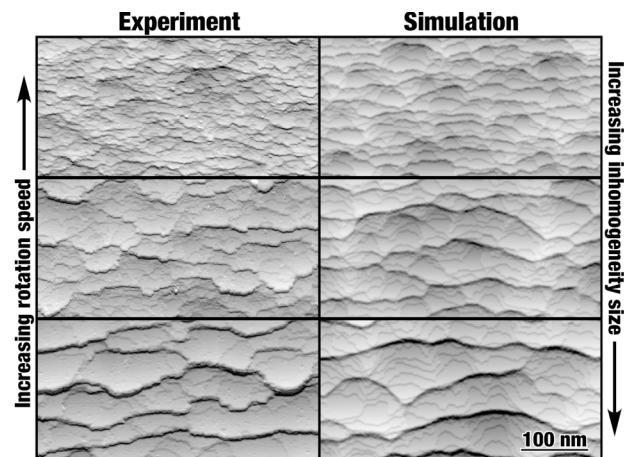

FIG. 4. Comparison of experimental and simulated morphologies of KOH-etched Si(111) surfaces showing the pronounced effect of diffusion on the etch morphology. The experimental images correspond to 800, 200, and 0 rpm, respectively, whereas the corresponding simulations had characteristic inhomogeneity length scales (see Ref. [13] for definition) of ~50, 100, and 150 Å.

tinue to grow with increased etch time, whereas the finite size of the simulation restricts further bunching.

Why are etchant inhomogeneities so important in what should be a rapidly diffusing system? The answer to this question may lie in an underappreciated aspect of silicon chemistry. Although the elementary steps in KOH/Si etching are controversial, the net reaction [2] is believed to be

$$Si + 2H_2O + 2OH^- \rightarrow 2H_2 + Si(OH)_2O_2^{-2}.$$
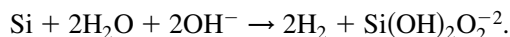
Importantly, the soluble product of this reaction, silicic acid, is unstable to further polymerization reactions of the type [15]

$$-SiOH + HOSi- \quad \rightarrow \quad -SiOSi- + H_2O.$$
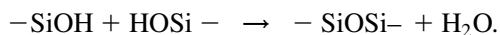
As a result, the dissolution of substantial quantities of silicon in KOH leads to the production of a viscous substance known as *wasserglas* or soluble glass [16,17]. We hypothesize that this polymerization reaction increases the viscosity of the etchant in the near-surface region, thereby slowing transport and promoting the formation of inhomogeneities. As the wasserglas diffuses from the surface, it is redissolved by the KOH solution; the bulk viscosity of the etchant is unaffected unless large quantities of silicon are etched.

This solution-phase reaction may explain the unusual concentration dependence of KOH/Si etching as well. The rate of the initial polymerization reaction should be quadratic in the concentration of silicic acid in the near-surface region. The extent of polymerization will therefore be determined by the competition between silicic acid production (i.e., the rate of etching) and the rate of diffusion away from the surface. As a result, high etch rates will favor polymerization. On the other hand, extensive polymerization will also increase the local diffusion constant and suppress diffusive transport of the etchant to the surface. This will tend to lower the etch rate. The combination of these effects may lead to a maximum etch rate at intermediate KOH concentration; however, more information about the polymerization reaction would be needed to quantitatively model this effect.

In summary, the morphology of etched silicon surface is strongly affected by inhomogeneities in the etchant that are the result of anisotropic etching reactions. These inhomogeneities may be enhanced by solution-phase reactions that locally increase the etchant viscosity near the surface. As a result, the surface etching reactions are inherently nonlocal.

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[13] See EPAPS Document No. E-PRLTAO-93-086441 for a movie showing the formation of macrosteps on a vicinal Si(111) surface. A single terrace is colored red to aid visualization. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/ epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information. An alternate repository is http://www.chem.cornell.edu/ mah11/KOHetch.html.

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