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Anisotropic Etching of Silicon on {111} and Near {111} Planes

Songsheng Tan, Robert Boudreau and Michael L. Reed[1,*]

Packaging and Assembly Core Technology Corning Inc. Corning, NY 14831 USA
[1]Department of Electrical and Computer Engineering, University of Virginia, P.O. Box 400743
Charlottesville, VA 22904-4743 USA

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We present silicon etch rate measurements from wagon-wheel patterns and widely separated V-grooves etched in potassium hydroxide solutions. The data indicates there is a reactant depletion effect when using wagon-wheel patterns, which obscures the true surface-reaction-rate-limited etch rate. Etch rates obtained from widely separated V-grooves, which are less influenced by reactant transport, indicate that the activation energy of {111} etching is less than that of {100} etching, in contrast to previous reports. Our experiments yield activation energies of 0.53 eV for {111} planes and 0.62 eV for {100} planes. The apparent activation energy is highly sensitive to slight angular misalignments off the {111}.

1. Introduction

The anisotropic etching of silicon in potassium hydroxide and other solutions has been broadly used in our laboratory and elsewhere to fabricate V-grooves for optoelectronic devices, including silicon waferboards,(1) 1 × N optical fiber splitters, 1 × N optical switches and 2 × 2 optical refractive plate switches.(2) Knowledge of the behavior of anisotropic etching of {111} and near {111} planes is necessary for the fine design and precise control of V-groove etching.

The fact that the etch rate of {111} silicon planes is much lower than the etch rate of other crystallographic planes is a fundamental property of anisotropic etching. It is because of this behavior that deep V-grooves can be fabricated with a precisely defined

*Corresponding author

apex angle. Despite the importance of this fact, the fundamental mechanisms underlying the crystallographic etch rate anisotropy are still controversial. Interestingly, two of the leading theories of anisotropic etching, formulated by Seidel *et al.*[3] and Elwenspoek,[4] both invoke the idea that the activation energy of etching {111} planes is larger than that for {100} and {110} etching.

Data in the literature describing the activation energy of {111} silicon etching is sparse. Faust[5] determined the activation energies of {100}, {110}, and {111} silicon etched in NaOH, based on etch pit data. No difference in activation energies was found for these three orientations. The activation energy for the 10% NaOH solution was 0.56 eV, for 25% and 50% NaOH, the energy was 0.73 eV. Seidel *et al.*[3] described their experimental results as follows: "... for KOH solutions, <110> etches about 60% faster than <100>, with nearly identical activation energies of 0.61 and 0.59 eV, respectively. The activation energy of <111> is approximately 0.7 eV." (Page 3617 in Ref. 3) These results were obtained from etch rate experiments measured with wagon-wheel shaped mask patterns, consisting of V-grooves with different angles arranged in a spoke configuration. When this kind of mask pattern is used, the etched areas are physically very close to each other near the center of the pattern. Nearly identical values were later published by Camon *et al.*[6] Clark and Edell[7] found activation energies ranging from 0.39 to 0.92 eV for {111} etching of Si in KOH, depending on the concentration. Tabata *et al.*[8] also found a dependence of the activation energy on concentration for Si etching in TMAH, with values ranging from 0.36 to 0.50 eV for {111} planes.

In this work, we investigated widely separated V-groove etch rates, in addition to etch rates obtained with a wagon-wheel mask. We found that closely spaced V-grooves consistently etch at a slower rate than widely spaced V-grooves, which implies that reaction rates are affected by the diffusion of reactant and/or product species. To obtain accurate estimates of the true reaction-rate-limited etch rates, these diffusion effects must be minimized. Also, we found that errors arising from the slight misalignment of the wafer flat must also be taken into consideration. When these corrections are made, our results indicate that the activation energy of {111} silicon etching is less than that of {100}. This paper describes our experiments, and discusses the discrepancy between our results and previous estimates of the {111} etch rate activation energy.

2. Experimental Procedure

One hundred millimeter, N-type, float-zone silicon wafers were obtained from Topsil. The wafers were single-side polished, with the polished side oriented within ±1° of the (100) crystalline plane. The major flat on the wafers was specified to be within ±1° of the $(01\bar{1})$ plane. Electrical resistivity was approximately 5000 Ω-cm. The wafers were coated with LPCVD silicon nitride and patterned before etching.

Three major sets of patterns were used:

(1) A first set of open-ended V-grooves consisted of 27 patterns over an angular range of ±0.65° in fine increments of 0.05°. Each pattern was 70 μm wide and 3 mm long, and was separated from adjacent patterns by approximately 1500 μm. This large separation

of the patterns, considerably larger than the individual V-groove widths, is key in interpreting our etch rate results.

(2) A second set of 69 open-ended V-grooves over an angular range of ±17.0° in coarser increments of 0.5°. The size and spacing of the patterns are otherwise identical to the first set.

(3) A third set of 360 V-grooves arranged in a wagon-wheel pattern with an angular increment of 1.0°. Each pattern was 40 μm wide and approximately 12 mm long; the overall wagon-wheel diameter was 25 mm.

To reduce the effect of wafer misorientation off the surface (100) plane on the measurement results, each set of designs was duplicated, with one set parallel to the major flat, and the other perpendicular to the major flat. An additional prealignment pattern was used to ensure the mask alignment along the [110] crystal direction to within 0.05°.[9]

A Rowley 5-liter quartz reflux condenser was used for the etching experiments. A Fluoroware 100-mm wafer carrier was placed inside the vessel to hold the sample vertically during etching. The entire system was placed in a Lauda M20 constant temperature bath with a controller capable of holding the solution temperature constant to within 0.1°C. The large volume of the quartz condenser was helpful in maintaining a constant etch temperature. A Teflon-coated type-J thermocouple was inserted through the center tube of the condenser cap into the solution to measure the actual temperature near the etched wafer.

The 35 wt% KOH etching solutions were prepared by mixing VLSI low-particulate-grade potassium hydroxide solution (45%) with deionized water for a total volume of 5 liters inside the quartz condenser. Then, 500 ml of 2-propanol was poured inside the condenser to oversaturate the solution. Although cooling water was kept flowing continuously through the cap of the reflux condenser at all times, the 2-propanol was occasionally topped off to maintain a cap of alcohol on the top of the KOH solution.

V-groove widths were measured with an Olympus model BX60M optical microscope equipped with an OSM-4 Filar Micrometer. The total V-groove underetch was determined by the width differences before and after etching, or by measuring the width of the overhanging mask layer. (The silicon nitride used as a mask layer has a negligible etch rate in KOH.) The minimum resolvable linewidth increment which could be obtained with our instrument is 0.1 μm.

We measured the V-groove width at five separate points along each groove. Typically, the standard deviation of these five measurements was less than 0.15 μm. In the next section, we describe our procedure for determining the etch rate of near {111} planes from a set of grooves; depending on the particular set of structures, we used from 75 to 380 individual measurements to obtain a set of etch rates at a particular temperature.

The depth of the etched patterns was measured with a surface profilometer, a Tencor P-10, which could measure depths up to 300 μm. Ten measurements of etch depth were taken for each wafer. The average standard deviation of etch depth measurements was less than 2 μm. Since the etch depth values were about forty times higher than the underetch dimensions, the relative precision of the depth measurements was slightly greater than the lateral V-groove measurements.

3. Experimental Results

3.1 *Separated V-grooves and wagon-wheel patterns*

Lateral underetching was measured from the second (coarse) set of V-grooves and wagon-wheel patterns on the same wafer. A typical set of results is plotted in Fig. 1; the widely separated V-groove data is shown in circles, while the wagon-wheel data is indicated with boxes. In this and other experiments, it was found that the underetch rate of widely separated V-grooves always exceeded that of the corresponding wagon-wheel pattern.

These results demonstrate that the measured etch rate depends on the lithographic pattern. Closely spaced patterns, such as those found in a standard wagon-wheel mask, result in etch rates slower than the true surface-reaction-rate-limited value. This is to be expected if transport effects limit the amount of reactant available for the etch reaction.

3.2 *Underetch rates near {111} planes*

To accurately measure the underetch rates near {111} planes, the wafers were aligned with a prealignment mask and pre-etched to account for the misalignment angle between the wafer flat and the true $(01\bar{1})$ crystal plane. In this way, the etching mask would be aligned with the true crystal orientation to within 0.05°. Measurements of the near {111} undercut rates were performed using the first set of patterns, with widely separated V-

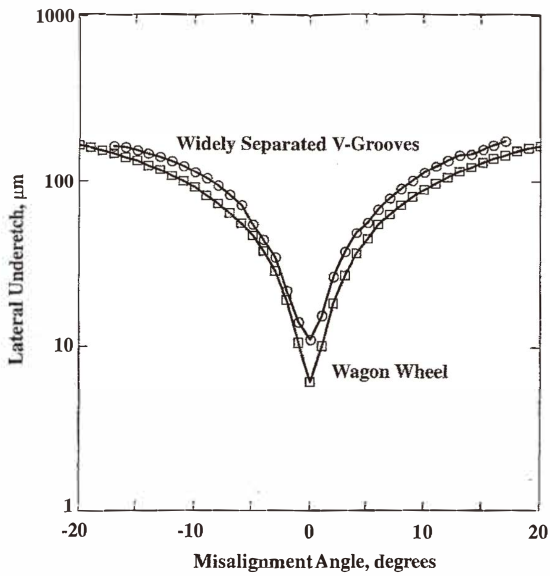

Fig. 1. Lateral undercut rates of separated V-groove and wagon-wheel patterns. In every case, closely spaced wagon-wheel patterns etch more slowly than widely separated V-grooves. (Etch conditions: 35% KOH, 38.4°C, 48 h)

grooves ranging from –0.65° to +0.65° in fine angular increments of 0.05°. A typical result is shown in Fig. 2, along with a least-squares fitted curve:

$$u = 0.545 + 0.639(\theta - 0.030)^2, \quad (1)$$

where u is the undercut rate (in μm/hr), and θ is the misalignment angle in degrees. (Again, each one of the circles in Fig. 2 represents five separate measured data points.) The minimum of this curve, 0.545 μm/hr, corresponds to the underetch rate of a V-groove perfectly aligned to a <110> direction, with faces composed of {111} crystal planes. This minimum occurs at 0.030 degrees, well within the 0.05-degree alignment tolerance afforded by the prealignment masking procedure.

Using this procedure, the determination of the {111} etch rate uses the full set of 75 measurements for each etch temperature. In addition, we can use the least-squares fitted curve to extract the etch rate of crystal planes slightly misaligned from the {111}. The fitted parabolas each have correlation coefficients in excess of 0.992, confirming the robustness of the experimental data.

3.3 *Activation energies of {111} and {100} in 35% KOH solutions*

The {111} etch rate can be related to the one-side lateral underetch rate of a <110>-oriented V-groove by the following equation:

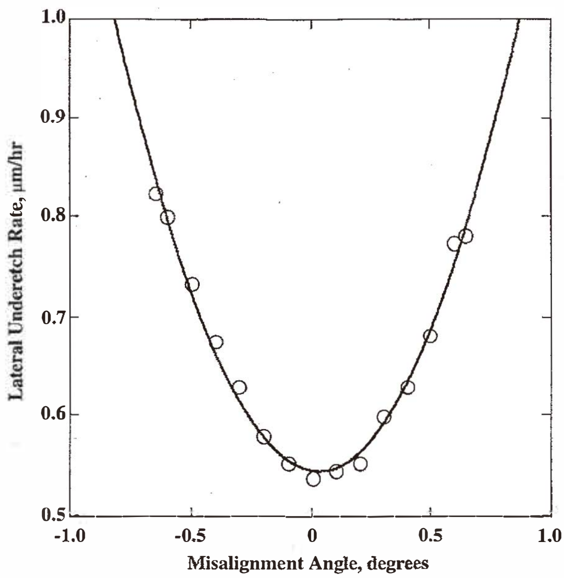

Fig. 2. Lateral underetch rates in the vicinity of {111} crystal planes measured on a (100) wafer. The solid line is a least-squares fit to the experimental data. (Etch conditions: 35% KOH, 70.3°C, 260 min)

$$r_{\{111\}} = u_{<110>} \sin\alpha, \quad (2)$$

where $r_{\{111\}}$ is the etch rate of the {111} crystal planes, $u_{<110>}$ is the lateral underetch rate of a perfectly <110> aligned V-groove, and $\alpha = 54.7°$ is the dihedral angle between {111} faces exposed by the etch and the surface (100) crystal plane. We used the minimum values of the lateral etch rate as a function of misalignment angle, from Fig. 2, for the value of $u_{<110>}$. {100} etch rates were determined from direct measurements of the V-groove etch depths.

A series of controlled temperature experiments were carried out to obtain the apparent activation energies of {111} and {100} etch rates. The etch time was varied with the temperature in order to obtain a similar amount (approximately 5 μm) of underetch in those V-grooves aligned in the <110> crystal directions. This was done to avoid errors which could result if widely different amounts of undercut (which would be the case if isochronal etching were performed) were measured with different magnification settings. The approximate etch time for each temperature was estimated by assuming a {111} activation energy of 0.7 eV.[3]

In practice, the {111} etch rates are based on a large set of experimental measurements. A series of underetch measurements for various V-groove misalignment angles were taken and plotted. For each temperature, a least-squares parabola was fitted to the data, similar to that shown in Fig. 2. The minimum in this curve corresponds to the lateral underetch rate of a perfectly aligned <110> V-groove, which is subsequently converted into a {111} etch rate using eq. (2). This procedure eliminates mask and wafer flat misalignment as a possible source of error; in addition, the {111} etch rate values at each temperature are the result of numerous (≥75) measurements, at many misalignment angles, and are not derived from measurements of a single V-groove which could be misaligned.

Our results are listed in Table 1, which shows the equations describing least-squared-error parabolas derived from this set of experiments. Due to the prealignment procedure, almost all patterns were well controlled with [110] misalignment angles of less than 0.05°; the single exception, wafer 4, had a slightly larger mask misalignment. The {100} etch rates are based on the depth measurements of V-grooves on the same wafers, and are not sensitive to mask misalignments. The temperature dependence for the {111} and {100} etch rates are plotted in Fig. 3. The calculated activation energy for the {100} etch rate is 0.62 eV, which is comparable to Seidel *et al.*'s[3] result of 0.61 eV in 34% KOH solution. In

Table 1
Lateral undercut rate as a function of temperature.

Wafer	Experimental conditions	Undercut rate, μm/h	Correlation coefficient
1	85.2ºC, 90 min	$u = 1.18 + 3.21 * (\theta - 0.03)^2$	0.992
2	70.3ºC, 260 min	$u = 0.545 + 0.639 * (\theta - 0.03)^2$	0.995
3	60.2ºC, 8.5 h	$u = 0.303 + 0.398 * (\theta + 0.04)^2$	0.993
4	50.2ºC, 21 h	$u = 0.188 + 0.168 * (\theta + 0.10)^2$	0.996
5	40.2ºC, 48 h	$u = 0.100 + 0.071 * (\theta - 0.01)^2$	0.994

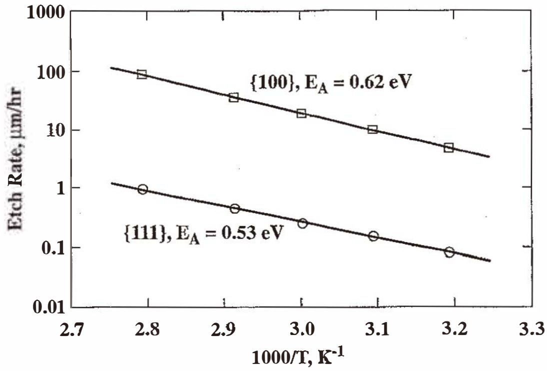

Fig. 3. Arrhenius plot of {100} and {111} etching rates in 35% KOH obtained from widely separated V-grooves.

the same experiment, the activation energy of {111} etching is 0.53 eV. For both orientations, we estimate the standard error to be ±0.01 eV.

The {111} results are replotted in Fig. 4, with lines representing both the calculated 0.53 eV activation energy derived from the data, and the reported value of 0.7 eV.[(3)] Error bars are not included on the graph because they would be too small to see; the standard error in our measurements falls within the radius of the circles representing the etch rates. We observe that there is no way for the {111} experimental data to accommodate an activation energy significantly higher than 0.53 eV.

Based on the equations of the fitting curves listed in Table 1, the apparent activation energies of V-groove etching with misalignment angles from 0.1° to 0.6° have been calculated and are listed in Table 2. We see that even minor misalignments off the {111} result in different activation energies, closer to the {100} value of 0.62 eV than the true {111} value. This again illustrates the importance of accurate mask/crystal alignment in all determinations of etch behavior.

4. Discussion

Figure 1 shows two sets of lateral underetch data, measured on the same wafer. This experiment clearly indicates that the {111} etch rate of widely separated V-grooves is larger than that of closely spaced wagon-wheel patterns. This result can be explained as follows. During chemical etching, the reacting species are continually consumed at the surface. As a result, a concentration gradient directed from the reacting surface into the bulk of the solution is established; this concentration gradient is the force which drives the reacting species towards the surface by diffusion. The overall kinetics of the etch will be determined by the slower of the two processes of reaction and diffusion. There is a general criterion[(10)] to distinguish the kinetics of aqueous chemical processes: the apparent activa-

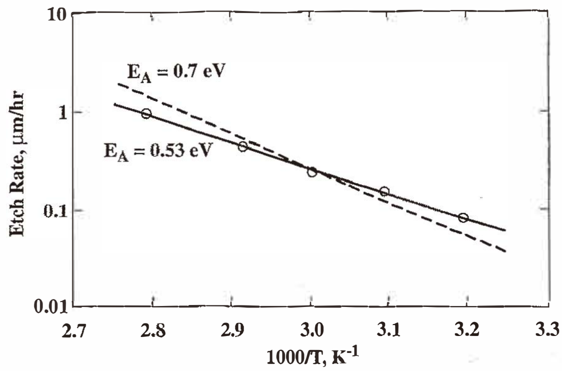

Fig. 4. Arrhenius plot of {111} etching data, with lines representing rates corresponding to activation energies of 0.53 eV (solid) and 0.7 eV (dotted).

Table 2
Apparent activation energy of etching near {111} planes and {100} planes.

Crystallographic plane	Apparent activation energy
(111)	0.53 eV
V-groove sidewall with 0.1° misalignment	0.53 eV
V-groove sidewall with 0.2° misalignment	0.54 eV
V-groove sidewall with 0.3° misalignment	0.56 eV
V-groove sidewall with 0.4° misalignment	0.57 eV
V-groove sidewall with 0.5° misalignment	0.59 eV
V-groove sidewall with 0.6° misalignment	0.61 eV
(100)	0.62 eV

tion energy is about 0.13 – 0.26 eV for diffusion-limited processes, but higher, about 0.43 – 0.86 eV, for reaction-limited processes. The activation energy of {111} etching found in our experiments, 0.53 eV, is in the range of a surface-reaction-limited process. In experiments with wagon-wheel patterns or closely spaced V-grooves, the presence of nearby patterns causes competition for available reactant species. This competition results in a local depletion of reactant, driving the reaction more slowly than for widely spaced patterns where there is ample supply of reactant.

This explanation is in agreement with other observations of diffusion-limited etching of semiconductors. Shaw,[11] Tan *et al.*[12] and Findler *et al.*[13] all observed etch profiles where the etch depth in the center of etched patterns is more shallow than at the edge. This effect can be explained in terms of the difference between the diffusion-limited transport of reactants near the mask edge and the center of the etched pattern. Seidel *et al.* (page 3, 618 in ref. 3) also reported that "some depletion effects are observable" during KOH etching.

Experiments incorporating wagon-wheel or closely spaced patterns provide technologically important measurements of etch rate, if these measurements are applied to processes using comparably spaced patterns. This is often the case in silicon micromachining where the aim is to maximize device density. However, the presence of diffusion effects renders these results less useful for investigating the fundamental physical processes at the surface which govern anisotropic etching. Here, clarifying the energetics of the surface-reaction-limited process is the desired goal; it is therefore important to minimize transport effects to obtain accurate values of the activation energy.

When this is carried out, we observe the unambiguous result that $E_{A,\{111\}} < E_{A,\{100\}}$, (0.53 eV and 0.62 eV, respectively). This result is significant as the slower etch rate of {111} surfaces is conventionally explained in terms of physical processes requiring more energy than {100} etching.

Since our samples have both widely spaced V-grooves and closely spaced wagon-wheel patterns, we can compare the etch behavior observed with the two mask patterns. Owing to the coarseness of the angular increment in the wagon-wheel pattern, we cannot quote a quantitative value of the activation energy for {111} etching from the closely spaced patterns. However, it is possible to make a strong qualitative statement about the relative activation energies for {111} and {100} etching. Figure 5 illustrates wagon-wheel patterns after etching for two etch temperatures. The dotted circles indicate the extent of lateral underetching for {111} planes; the radii of these circles are proportional to the

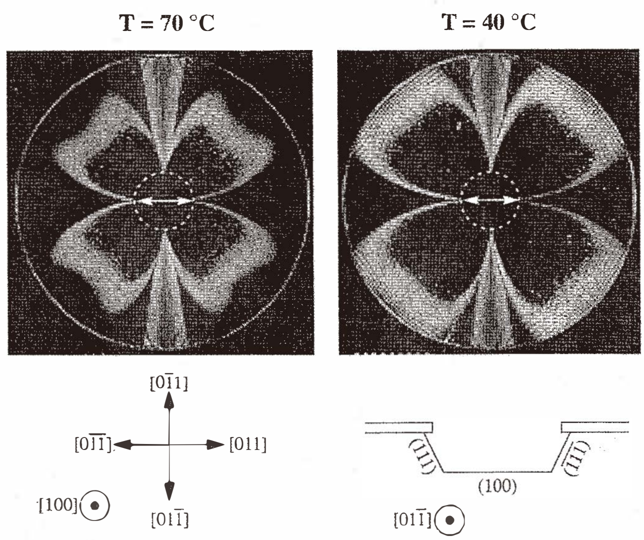

Fig. 5. Appearance of wagon-wheel mask patterns after etching in 35% KOH. The etch depths (i.e., in the [100] direction, into the plane of the paper) are 155 μm for the sample on the left (etched at 70.3°C) and 227 μm for the sample on the right (etched at 40.2°C). The diagrams illustrate the four <110> directions in the (100) plane; V-grooves aligned along these directions have sides defined by {111} planes. The length of the radius from the center to the pattern cusp along these directions is proportional to the {111} etch rate.

{111} etch rates. In this experiment, the etch times were adjusted to keep the underetch on {111} planes approximately constant, hence the two circles are about the same size. The corresponding etch depths, which are a measure of the {100} etch rates, are 155 μm for the sample etched at 70.3°C and 227 μm for the sample etched at 40.2°C. We observe that

$$\left.\frac{R_{100}}{R_{111}}\right|_{70°C} < \left.\frac{R_{100}}{R_{111}}\right|_{40°C}, \tag{3}$$

i.e., a higher degree of etch anisotropy is observed at the lower temperature. This result indicates that $E_{A,\{111\}} > E_{A,\{100\}}$ for the closely spaced patterns, in agreement with Seidel *et al.*'s[3] result. Taken with the widely spaced V-groove results, it also provides further evidence that etch rate measurements are highly dependent on pattern spacing.

5. Conclusions

By comparing the underetch rates measured from wagon-wheel and separated V-groove patterns, we conclude that underetch rates near {111} planes measured from the separated V-groove patterns provide more accurate estimates of the surface-reaction-rate-limited activation energy, owing to reduced effects of reactant transport. Our experiments with anisotropic Si etching, performed in 35% KOH saturated with 2-propanol, result in activation energies of 0.62 eV for {100} planes, and 0.53 eV for {111} planes. Qualitative results for wagon-wheel patterns show higher activation energies on {111} than on {100}, in agreement with previously reported results.[3]

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