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# Change in Orientation-Dependent Etching Properties of Single-Crystal Silicon Caused by a Surfactant Added to TMAH Solution

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***Key words:*** silicon, anisotropic etching, tetramethyl ammonium hydroxide (TMAH), surfactant, orientation dependence

We measured the etching rates of single-crystal silicon for a number of orientations using tetra-methyl-ammonium-hydroxide (TMAH) water solutions with and without the surfactant NCW601-A containing 30% poly-oxethylene-alkyl-phenyl-ether. It was observed that the anisotropy in etching rate changed with the addition of the surfactant. A significant decrease in etching rate was observed for orientations (jj1), where j>1. The (100) orientation no longer exhibited a local minimum in etching rate following the addition of the surfactant. The etched surface roughness also changed as a result of using the additive, depending on the orientation.

## 1. Introduction

It is empirically known that some surfactants are effective in improving the smoothness of etched surfaces. It was recently reported that a small amount of surfactant added to a tetra-methyl-ammonium-hydroxide (TMAH) water solution resulted in a strikingly suppressed etching rate of silicon (110) compared to other orientations, in addition to an improvement in smoothness.(1) However, the measured etching rates were for three principal orientations only.

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We measured the etching rate change for a number of crystallographic orientations, and clarified the selectivity in the suppression of the etching rate as a function of orientation. The surfactant used was NCW601-A containing 30% poly-oxethylene-alkyl-phenyl-ether. We also measured the effect of the surfactant on the etched surface roughness.

## 2. Experimental Method

We used a hemispherical single-crystal silicon specimen(2) to evaluate the effect of the surfactant for a number of crystallographic orientations. Etching rates were calculated from the change in the hemispherical profile of the specimen by measuring the profile before and after etching, as shown in Fig. 1. Flat silicon wafers oriented to (100), (110) and (111) were also used in parallel with the hemispherical specimen to verify the etching rate and roughness calculated from the hemispheres.

Etching conditions were as follows.

- TMAH concentration in water solution: 25 %
- Concentration of NCW601-A: 0.1–5.0% of total solutions
- Etching temperature: 80°C

The spherical profile measurement was carried out using a UPMC550-CARAT (Carl Zeiss) three-dimensional measuring machine. The etched surface roughness was evaluated using a Dektak(3) ST profilometer (Veeco) and an optical microscope.

## 3. Results and Discussion

### 3.1 *Etching rates*

The effects of the surfactant concentration on the change in etching rate are shown in Fig. 2 for three different orientations of flat silicon chips. Adding 2% of NCW601-A to a

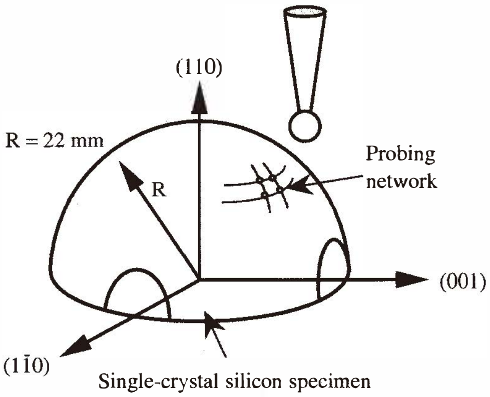


Fig. 1. Etching rate measurement scheme using a hemispherical specimen.

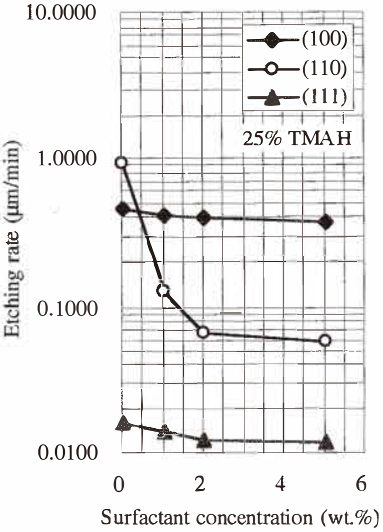


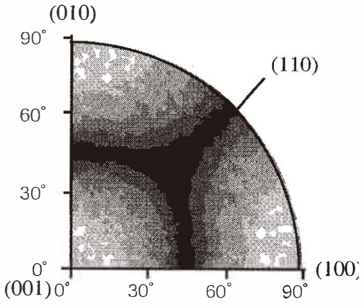
Fig. 2. Effects of the NCW601-A surfactant on the etching rate of silicon for three principal orientations.

25%TMAH water solution caused a significant change in the etching rate ratio of (110) to (100). The ratio was 2 without surfactant, and it decreased to 0.18 with the surfactant.

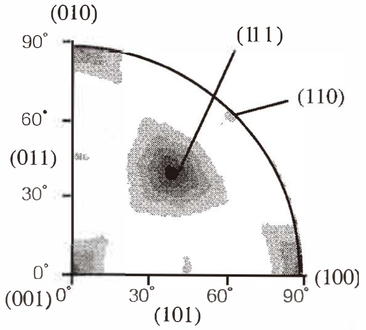
Etching rates for a number of orientations were obtained using a hemispherical specimen. We draw contour maps of etching rates as a function of orientation. Figure 3 shows the contour maps for TMAH solution with and without surfactant. The anisotropy in the etching rate changed significantly with the addition of the surfactant. A valley centered at (111) had triangular contours in cases both with and without the surfactant. However, the triangular contour is rotated by 60 degrees between the two maps. Following the addition of the surfactant, the valley extended toward the (110) orientation. Consequently, orientations having Miller indexes of (jj1), where j is a number larger than 1, showed very small etching rates, and thus resulted in a significant decrease in the etch rate for the (110) orientation.

The (100) orientation usually shows a local minimum in etching rate for both pure KOH and TMAH solutions.(2,3) However, following the addition of the surfactant, it is no longer a local minimum. The phenomena can be observed in Fig. 4 which shows cross sections of the contour maps in Fig. 3.

Our experimental results that (jj1) orientations show extremely low etching rates following the addition of the surfactant well explain the fact that undercutting of the square-cornered mask on the (100) wafer can be suppressed with this additive. The undercut profiles etched with and without surfactant are shown in Fig. 5. The vertex profile extending from the square-cornered mask can include any of the (jj1) orientations. When any (jj1) has a substantial etching rate, the vertex will be severely etched. However,



(a) 25%TMAH+NCW



(b) 25%TMAH (without surfactant)

Fig. 3. Etching rate contour maps with (a) without (b) the surfactant.

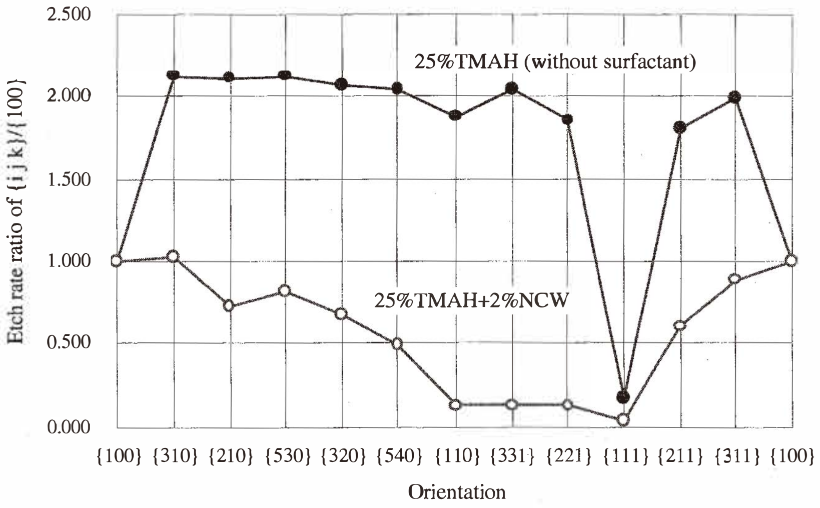


Fig. 4. Change of etching rate for different orientations after the addition of the surfactant.

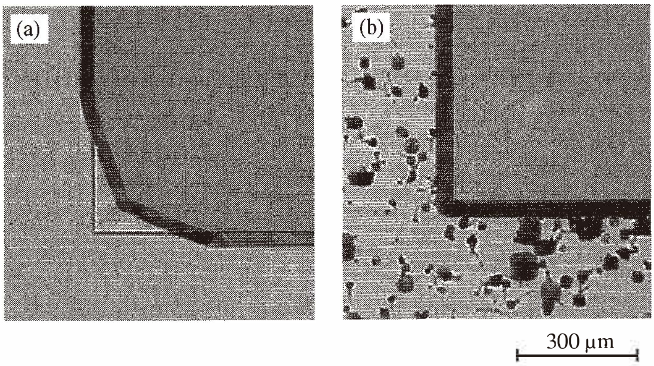


Fig. 5. Effects of surfactant on undercutting of a squre-cornered mask on a (100) wafer: (a) 25% TMAH, (b) 25% TMAH +2% NCW.

etching was suppressed, as shown in Fig. 5, when the additive was used. This is because all (jj1) orientations have extremely low etching rates.

### 3.2 *Etched surface roughness*

Hemispherical silicon surfaces etched with and without surfactant are compared in Fig. 6. The silicon surface became smoother when the additive was used, for many orientations. It should be noted that differences between the surface morphologies with and without surfactant are clear, in particular, for those at (jj1) orientations. Striation patterns observed under the two conditions are oriented perpendicular to each other. This suggests that the orientation dependence of etching rate may be related to the macroscopic surface morphology of the etched surfaces.

On the other hand, micropyramids started to grow on the (100) surface as a result of using the additive. This is due to the extremely low etching rates on (jj1) orientations. The growth mechanism is similar to that of the suppression of the corner undercut, as mentioned above.

## 4. Conclusions

The anisotropy in the etching rate markedly changed upon the addition of surfactant. A significant decrease in the etching rate was observed for orientations (jj1), where j>1. The (100) orientation no longer exhibited a local minimum in the etching rate following the addition of the surfactant. The etched surface roughness also changed as a result of using the additive, depending on the orientation. Roughness decreased for many orientations, except in the vicinity of (100) where micropyramids started to appear as a result of using the additive.

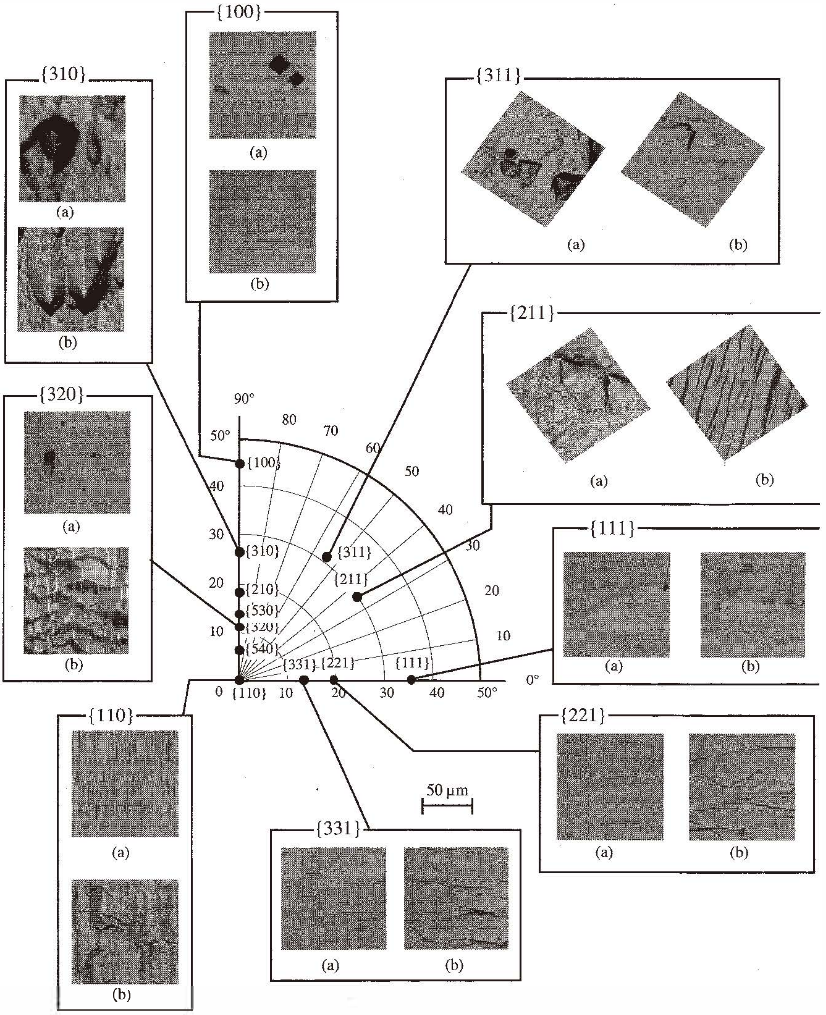


Fig. 6. Surface morphologies of the hemispherical specimens etched with and without the surfactant: (a) 25% TMAH+ NCW, (b) 25% TMAH.

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