A UNIVERSAL PARAMETER FOR SILICON ANISOTROPIC ETCHING IN ALKALINE SOLUTIONS

D. Cheng[1], M. A. Gosálvez[1], M. Shikida[2] and K. Sato[1]*
[1]Department of Micro-Nano Systems Engineering, Nagoya University, Japan
[2]EcoTopia Science Institute, Nagoya University, Japan

ABSTRACT

We propose a new explanation for the difference between the etching properties of potassium-hydroxide (KOH) and tetramethyl-ammonium-hydroxide (TMAH) by focusing on the volume fraction occupied by the corresponding cations, K^+ for KOH and TMA^+ (with molecular structure $N(CH_3)_4^+$) for TMAH. We have found experimentally that the differences in the surface morphology of Si(111) after etching can be explained by considering the cation volume fraction and that this parameter can also be used to explain the changes in the etch rates between different etchants, or between different concentrations of the same etchant, suggesting a universal behavior for any etching system. This finding simplifies the understanding of the mechanism of silicon anisotropic etching.

1. INTRODUCTION

Anisotropic wet chemical etching of single-crystal silicon is one of the key technologies for fabricating micromechanical structures such as diaphragms and cantilevers. KOH and TMAH are the two most popular etchants for anisotropic wet chemical etching of silicon [1-4]. We have previously constructed an etching rate database for KOH and TMAH solutions and reported the orientation dependence of the rates in a wide range of KOH and TMAH concentration and with temperature [1, 2]. We also reported the differences in anisotropic etching properties of these two etchants in a previous paper [5]. However, the fundamental mechanism behind their similarities and differences still needs to be understood. Due to the alkaline nature of these solutions, the two etchants show similar etching characteristics in both (100) and (110) orientations, although at different concentrations. As shown in Table 1, the etching rates of (100) and (110) are almost equal in 20wt% TMAH and 50wt% KOH at 80°C, and the etched surface morphologies are similar too, showing a smooth mirror-like surface in (100) and a striped zigzag pattern in (110). However, in the case of the (111) orientation, the triangular pits characteristic of this surface are rotated 60 degrees when the etched morphologies are compared, even if the two surfaces look equally smooth and do indeed yield similar roughness values.
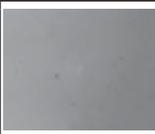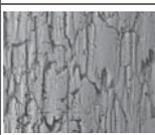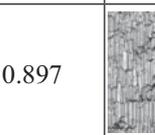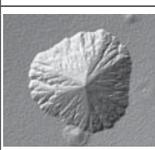
2. DIFFERENT ATOMIC STEPS ON Si(111)

We have previously reported the difference in activated atomic steps on Si(111) during KOH and TMAH etching [6]. Since the (111) orientation is the most stable against etching, the removal of terrace atoms (a process known as "pit nucleation") is a very rare event. Once it occurs, it is extremely difficult to etch deeper and etching must proceed side-wise in a process known as "step flow", resulting into the formation and growth of hexagonal pits. The sides (steps) of the hexagonal pits on the (111) surface are classified into two groups, those that are perpendicular to the $[\bar{1}\bar{1}2]$-direction family and those are perpendicular to the $[11\bar{2}]$ family. As depicted in Fig. 1, the step sites of the first group have three back-bonds and are traditionally referred to as step-monohydrides "SM", reflecting the fact that these atoms have one hydrogen terminating them during etching. The sites in the second group have two back-bonds and are known as step-dihydrides "SD", having two terminating hydrogens.

Normally, the speed of step flow (etching-rate) of these two groups shows much difference. Because one group will be removed faster than the other, the hexagonal pits grow asymmetrically and eventually become triangular, displaying only the slow, stable steps, as schematically shown in Fig. 2. The relative stability of the SM and SD sites depends on the etching solution. As shown in Table 1 for (111), in the case of 50wt% KOH, the SMs are more stable than the SDs. However, the situation is the opposite in the case of 20wt% TMAH. As a result, the triangular pits appear to be rotated 60 degrees between these two conditions. Since the etching rate of the surface is directly related to the rate of step propagation under the current step flow conditions, a rotation

Table 1: Etching rates and etched surface morphology in 20wt% TMAH and 50wt% KOH.

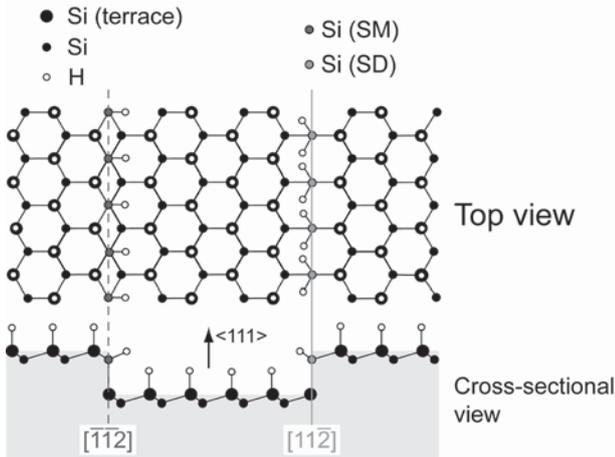|	TMAH 20wt%		KOH 50wt%	
	Etching rate (µm/min)	Surface morphology	Etching rate (µm/min)	Surface morphology
(100)	0.603		0.478	
(110)	1.037		0.897	
(111)	0.017		0.014	
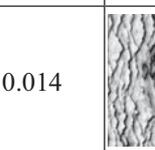
Figure 1: The atomic scale models of etch steps on the (111) silicon surface.

of the three-fold triangular symmetry is also observed when comparing the etching rate contour maps of the two etchants [6]. As a matter of fact, the relative stability of the SM and SD sites depends also on the etchant concentration for a fixed etchant. Typically, the pits are SM-terminated at low concentration and SD-terminated at high concentration. This is shown in Fig. 3, where the etch pits point to the right for low KOH and TMAH concentrations, and to the left for high concentrations. The Figure shows that the weight-per-cent (wt%) concentration of KOH has to reach large values (approx. 60-70) in order to induce the pit rotation whilst the rotation can be observed for TMAH already at a concentration as low as 15wt%. Note that in the case of KOH, it is necessary to rise the temperature to 130°C in order to use such highly concentrated solutions. As will be shown later, this concentration behavior applies to more etchants to the point that the orientation of the etch pits can be used as a measure of the relative concentration of two different etchants. As an example, we may classify the concentration as (i) low, if the etch pits are triangular and point to the right (SM-terminated); (ii) medium, if the pits are roughly hexagonal (both SM and SD terminated); and (iii) high, if the pits are triangular and point to the left (SD-terminated). We may roughly conclude from Fig. 3 that the wt% concentration (w) of KOH is low, medium and high when $w \leq 50$, $50 \leq w \leq 60$ and $w \geq 60$, respectively. The corresponding values for the wt% concentration of TMAH are roughly $w \leq 10$, $10 \leq w \leq 15$ and $w \geq 15$, respectively. For typical KOH and TMAH concentrations (about 30wt% and 15wt%, respectively) the triangular pits are rotated 60 degrees in the two etchants.

Although the largest difference between KOH and TMAH at typical concentrations is the relative rotation of the pits on the (111) surface, the previous results show that the two etchants would become essentially equivalent if only a universal parameter would be identified to successfully describe the concentration dependence of the etching process. Since wet etching takes place in water solutions, it is natural to expect that the concentration dependence should correlate with the pH value, or, what is equivalent, with the pOH. In deed, there are many wet etching studies where a number of variables are presented as a function of the pH value [7]. In the present case, however, Fig. 3 shows that the molarity (which measures the concentration of hydroxyls in the solution) plays no role as there is no correlation between the molarity values quoted for KOH and TMAH, and the rotation of the pits. We conclude that the concentration dependence of the triangular pit morphology is not a function of the pH or the molarity and, therefore, it is not controlled by the hydroxyl groups only.

3. AN EFFECT FROM THE CATIONS

As an alternative to the molarity, we have focused on the size of the cations in the different etchants as an explanation. We assume that different cations with different size in different alkaline solutions can cause a reduction in the etching rates by physically or chemically blocking the silicon surface during the etching process [8]. If we assume that the cations prefer to chemically link more actively with the step-dihydrides than with the step-monohydrides, a larger volume of cations in the etching solution will lead to a lower etching rate for the SD sites as compared to the SM sites. This can explain the rotation of the pits on the (111) silicon surface as the concentration is increased in any etchant. It can also explain why the etching rate of (100) decreases when the TMAH concentration increases. We are currently carrying out ab-initio studies in order to understand the details of the interaction between the different cations (such as K+ and TMA+) and the H-terminated and/or OH-terminated step sites. According to preliminary results, the hydroxyls (OH) favor H-substitution at the SD steps better than at the SM steps and, as a result, the cations (K+, TMA+,…) are attracted to the SD steps (due to the partial negative charge of O in the hydroxyl group). This stabilizes
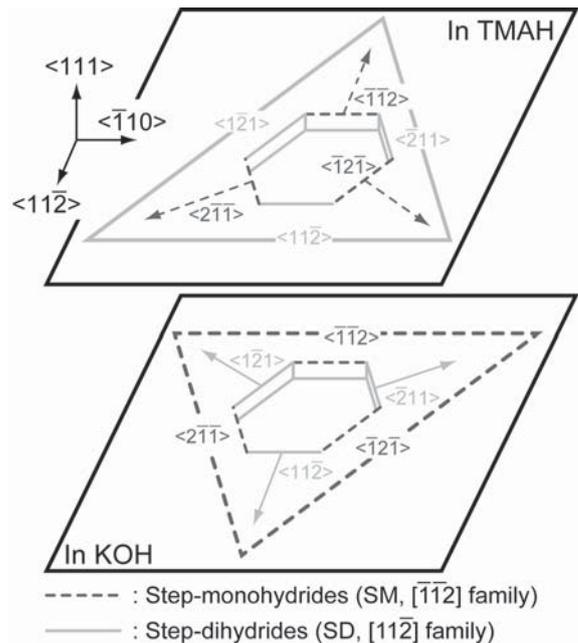

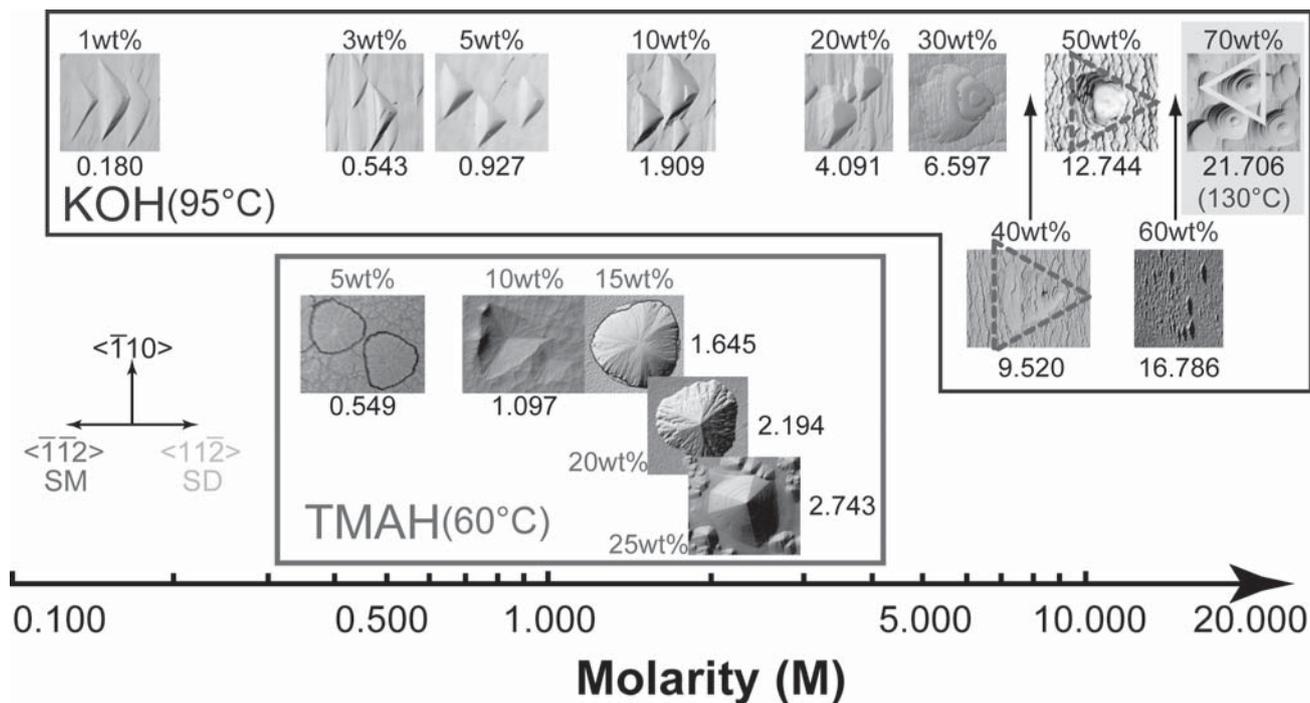*Figure 2: Difference in triangular etch pits between KOH and TMAH.*

Figure 3: Etch pits obtained by etching Si(111) sorted according to the etchant molarity.

the SD sites. Stabilization is further promoted by increasing the etchant concentration, due to the increased presence of both cations and hydroxyls. The size of the cation plays a role by directly blocking a larger or smaller region of the step, thus affecting the step reactivity.

4. EXPERIMENTAL METHOD

We have calculated the cation volume fractions (in the solution) for a number of weight concentrations of KOH and TMAH, as shown in Fig. 4. The result is the two linear data groups displayed. The Figure demonstrates that even in very strong KOH solutions (e.g. 60wt%), the K^+ volume fraction is just about equal to the TMA^+ ($N(CH_3)_4^+$) volume fraction in a weak TMAH solution (10wt%). In order to test our explanation, we consider more data points between these two data groups. Probably a good choice would be the use of ammonium hydroxide water (NH_4OH), whose cation (NH_4^+) size is just between K^+ and TMA^+. However, ammonium water is difficult to control. Besides, as a very weak alkaline solution, dissociation is less than 100% and its cation volume fraction is difficult to be calculated and controlled in an experiment. As an alternative for the use of ammonium water, we have added 25wt% TMAH into different concentrations of KOH. In this way, we have produced etchants with almost the same weight concentration but largely different total cation volume concentrations which lye between the two data groups for KOH and TMAH, as shown in Fig. 4.

5. RESULTS AND DISCUSSION

Etch pits obtained in each of the three etching solutions are shown in Fig. 5. It is apparent that the direction of the etch

pits rotates at about 10% of the volume concentration of cations in TMAH, KOH and the mixed etchant. These results show that the etchant cations have a preference to chemically block the SD sites, and that the etching of the SD sites is strongly suppressed when the cation volume fraction reaches a value of about 10%. We can now explain why the etching-rate of Si(110) increases more than that of Si(100) with increasing concentration in KOH, since (100) has a large surface fraction of SD sites and etching of these sites is suppressed whilst (110) has a large fraction of SM sites, which are not so dramatically affected. Also, we can now explain why the etching-rate of Si(100) strongly decreases in TMAH with small increments in the concentration, since a bigger cation volume fraction will block and stop the etching of SDs rather effectively.
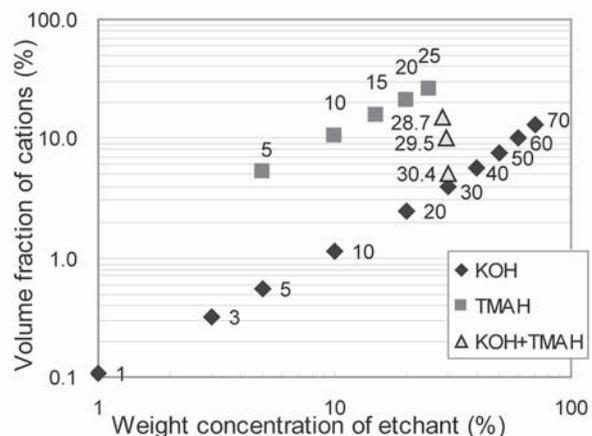

Figure 4: Cation volume concentration as a function of weight concentration for three different etchants.
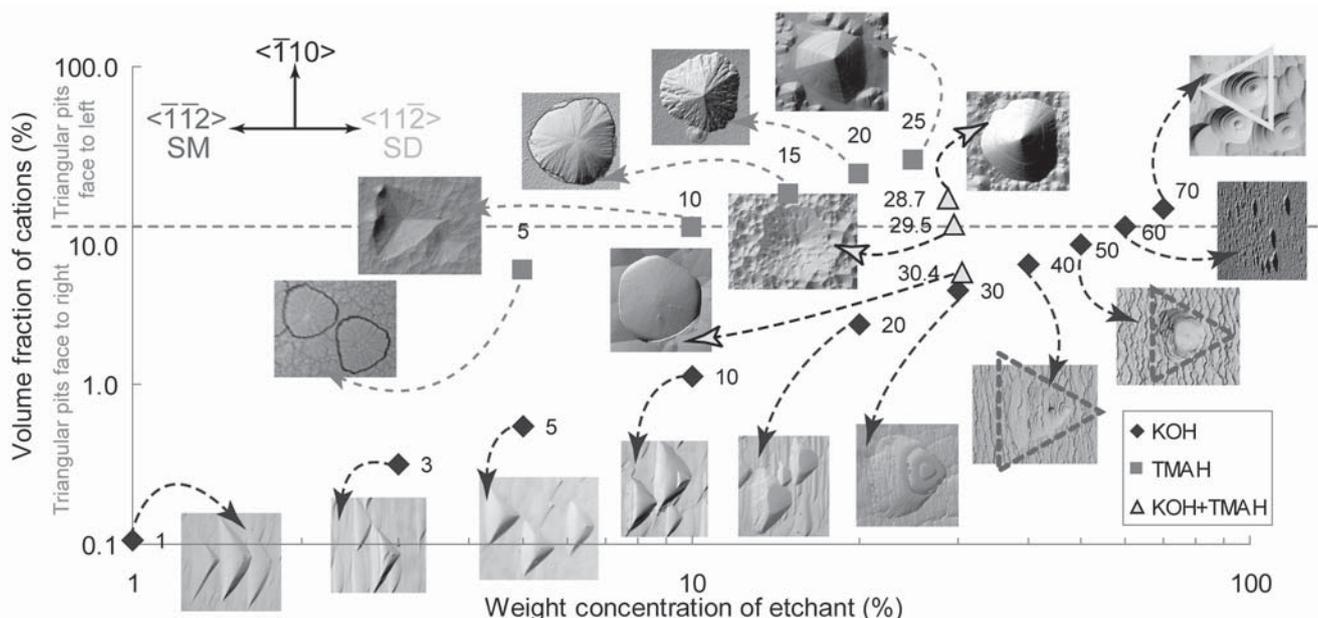
Figure 5: Etch pits on Si(111) obtained by etching in the three different etching solutions.

6. CONCLUSIONS AND FUTURE WORK

Our study shows that the cation volume fraction is a good candidate for a universal parameter that would make all etchants equivalent. This finding simplifies the understanding of the mechanism of silicon anisotropic etching. By using this parameter we are now able to explain the changes in the surface morphology of etched Si(111) between different etchants. We also can now explain the changes in the etch rates between different etchants, or, between the same etchants with different concentrations.

To prove that our model of the cations effect is completely right, we need to test other types of etchants with a very different cation size as compared to K^+ and TMA^+. Since ammonium water is hard to control, we have focused on one alkaline solution whose cation size is much bigger than TMA^+. We will use this etchant to test the rotation of the etch pits on Si(111) at a very low concentration. In addition, we are currently using DFT and Kinetic Monte Carlo simulations in order to find out how the cations link to the silicon surface and why the cations have a preference to chemically block the SD sites.

ACKNOWLEDGEMENTS

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