Fast Si (100) etching with a smooth surface near the boiling temperature in surfactant-modified tetramethylammonium hydroxide solutions

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The etching characteristics of the commonly utilised Si (100) facet at high temperatures near the boiling point in surfactant-modified tetramethylammonium hydroxide (TMAH) solutions are investigated. Solutions of 25 wt% TMAH are selected because of the etching stability and the rate of addition of the surfactant Triton-X-100 [$C_{14}H_{22}O(C_2H_4O)n$, $n = 9–10$] ranges from 0.01 to 1% v/v. The etching rates of Si (100) facets close to the boiling point are three to four times higher than those at 80°C in the surfactant-modified 25 wt% TMAH solutions. In particular, at 115°C, the very near temperature of the boiling point, the silicon sample possessing a high etching rate of 1.45 µm/min and the smooth etched Si (100) surface with an average roughness of about 1 nm is obtained. Moreover, the samples do not demonstrate much undercut difference at the etched convex corners near the boiling point. These results are useful for the fabrication of microelectromechanical systems and indeed provide an efficient etching method for industry products.

1. Introduction: Although there have been advances in the dry etching process, the wet etching process has good controllability and uniformity in etching depth, provides special types of etching profile and has an equipment cost advantage, all of which are very significant in the microelectromechanical systems (MEMS) industry. Owing to the complementary metal-oxide-semiconductor (CMOS) compatibility, tetramethylammonium hydroxide (TMAH) solution is very attractive for the fabrication of numerous MEMS devices [1–3]. This anisotropic etchant has experienced great advancement where various kinds of surfactants have been added to alter the etching behaviour, particularly in terms of undercutting at convex corners [4–6]. Recently, the orientation-dependent adsorption of surfactant molecules has been found, explaining the difference between the etching in surfactant-modified TMAH etchants and that in pure TMAH solutions [7–9]. The application of pure and surfactant-added TMAH has been exploited for the formation of MEMS components with new shapes [10]. Although the volume production of MEMS devices can be fabricated using the TMAH etching method, the main disadvantage is that the etching rates in TMAH solutions are low; especially the Si (100) facet generally used in MEMS devices, consequently causing the etching to be a time-consuming process. The means of ultrasonic agitation and microwave irradiation of the etchants have been studied, but they either broke the existing fragile structures or introduce irradiation damage [11, 12]. Tanaka *et al.* observed the etching results at high temperatures of KOH solutions, which showed much change of the etching characteristics at near the boiling point in KOH solutions [13]. However, the etching at high temperatures of surfactant-modified TMAH solutions has not been studied. In this Letter, we investigate the etching characteristics of Si (100) at ultra-high temperature ranges from 80°C to the near boiling point 115°C in surfactant-modified TMAH solutions.

2. Experimental method: 4-inch, *N*-type Czochralski-grown single crystalline silicon (100) wafers of resistivity 1–10 Ω cm and thickness 400 ± 10 µm are used. The 25 wt% TMAH solution exhibits good etching stability than the lower TMAH solutions. Among the various ionic (e.g. anionic SDSS, cationic ASPEG etc.) and non-ionic (e.g. Triton-X-100, NCW etc.) surfactants, the non-ionic ones are promising because they do not leave any residual ions on silicon surfaces after deionised (DI) water rinsing [14]. Moreover, Triton-X-100, one of the non-ionic surfactants is more popular because of its easy handling and less toxicity [15]. Thus, a 25 wt% TMAH and a Triton-X-100, which involves a hydrophobic chain and a hydrophilic chain in a molecular formula, are selected as the main etchant and surfactant, respectively. To investigate the effect of surfactant concentrations, 0.01, 0.1 and 1% v/v Triton-X-100 concentrations are utilised. Each wafer is thermally oxidised to reach a 1 µm thickness oxidation layer. Then the wafer is patterned to expose the centre part of 50 mm × 50 mm with arrays of the square shape 2 mm × 2 mm. Before immediately immersing in the solution, the wafer is dipped into 5% hydrofluoric (HF) acid to remove any trace amount of native oxide. The etching equipment mainly contains a Teflon bath with a covered reflux condenser, a thermometer and a constant temperature mineral oil bath (±1°C), which assists in reaching the high temperatures in this work. All of the samples are etched to more than 100 µm to ensure the precision of the results. The thickness of each sample is measured by a profilometer. The surface morphology of the etched silicon samples is investigated qualitatively by an optical microscope and a scanning electron microscope (SEM), and quantitatively by an atomic force microscope (AFM).

3. Results and discussion: Principally the etching characteristics of a silicon wafer include etching rate, etched surface roughness and the etched profile at the convex corners. The boiling points of 25 wt% TMAH + 0.01% v/v Triton-X-100, 25 wt% TMAH + 0.1% v/v Triton-X-100 and 25 wt% TMAH + 1% v/v Triton-X-100, checked by bringing the solutions to the boil, are almost the same at 118°C. Therefore the highest temperature in this work is 115°C.

Fig. 1 shows the dependence of the Si (100) etching rate on the temperature ranging from 80°C to the near boiling point 115°C in Triton-X-100-modified TMAH solutions. The deviation of the data in Fig. 1 is <0.03 µm/min. For temperatures of lower than 100°C, the etching rates demonstrate a linear increase with steps of about 0.15 µm/min, which are independent of the concentration of Triton-X-100. However, once the etching is performed at the temperature higher than 100°C, the etching rate appears to abruptly increase. The etching rates at 115°C are three to four times higher than those at 80°C in different Triton-X-100 modified 25 wt%

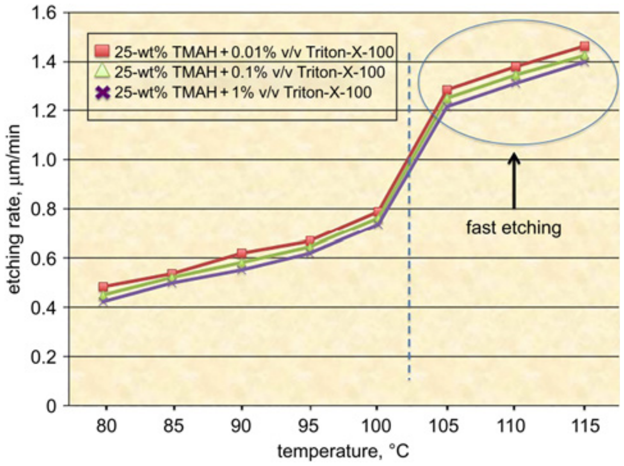

Figure 1 *Dependence of Si (100) etching rate on temperature*

TMAH solutions, respectively. This is the first time that etching rates of higher than 1 µm/min are achieved in surfactant-modified TMAH solutions. In the three solutions, the activation energies including the near boiling temperatures (80–115°C) are calculated as approximately 0.34 eV. When compared with the activation energies in the etching at less than 100°C (about 0.19 eV), the activation energies including the near boiling temperatures are higher, although still lower than the activation energies in pure TMAH solutions. This may explain the fast Si (100) etching at near boiling temperatures. The altered etching characteristics in TMAH + surfactant have been studied and the effect of the surfactant molecules has been analysed as a monolayer that modifies the input and output of the reactants and products, respectively. We argue that the fast etching at near the boiling temperature results from the much faster movement velocity of the reactants and products.

Fig. 2 shows the etched Si (100) surface roughness at temperatures from 80 to 115°C, where the samples typically in 25 wt% TMAH + 0.1% v/v Triton-X-100 at 80°C (A) and at 115°C (B) are measured by an optical microscope, a SEM and an AFM, respectively. The deviation of the data in Fig. 2*a* is less than 1 nm. Interestingly, the surface roughness is greatly improved at 115°C, reaching about 1 nm. In fact, the transition point of the surface roughness appears at between 100°C and 105°C, which is almost the same with the transition point of the etching rate. The concentration of Triton-X-100 does not influence the etched surface roughness much. The extremely smooth surface perhaps results from the good tension adjustment of the surfactant layer to oppose the formation of large hydrogen bubble masks, which have been considered as the main reason for the surface roughness during the wet etching process. The smooth etched silicon surface is beneficial for the fabrication of optical microdevices. Moreover, it is very useful for commercial products that the fast etching rate of higher than 1 µm/min and the small surface roughness of about 1 nm have been obtained under the same etching circumstance.

It is a simple and effective method that uses TMAH + Triton-X-100 solutions to protect the convex corners on Si (100) wafers without any corner compensation parts. This can be explained by the stronger adsorption of surfactant molecules on (110) and its vicinal planes that makes the etch rates of (110) and its vicinal planes low. The dependence of the undercut ratio at the convex corner on the temperature is shown in Fig. 3. The deviation of the data in Fig. 3*a* is less than 0.02. In 25 wt% TMAH + 0.1% v/v Triton-X-100, the undercut ratios at the convex corner on Si (100) wafers at the temperatures of 80 and 115°C are marked as A′ and B′, respectively. It is obvious from Fig. 3*b* that the etched area at the convex corner is larger at 80°C than that at 115°C. The undercut ratio of the sample at 115°C is really smaller, which can be

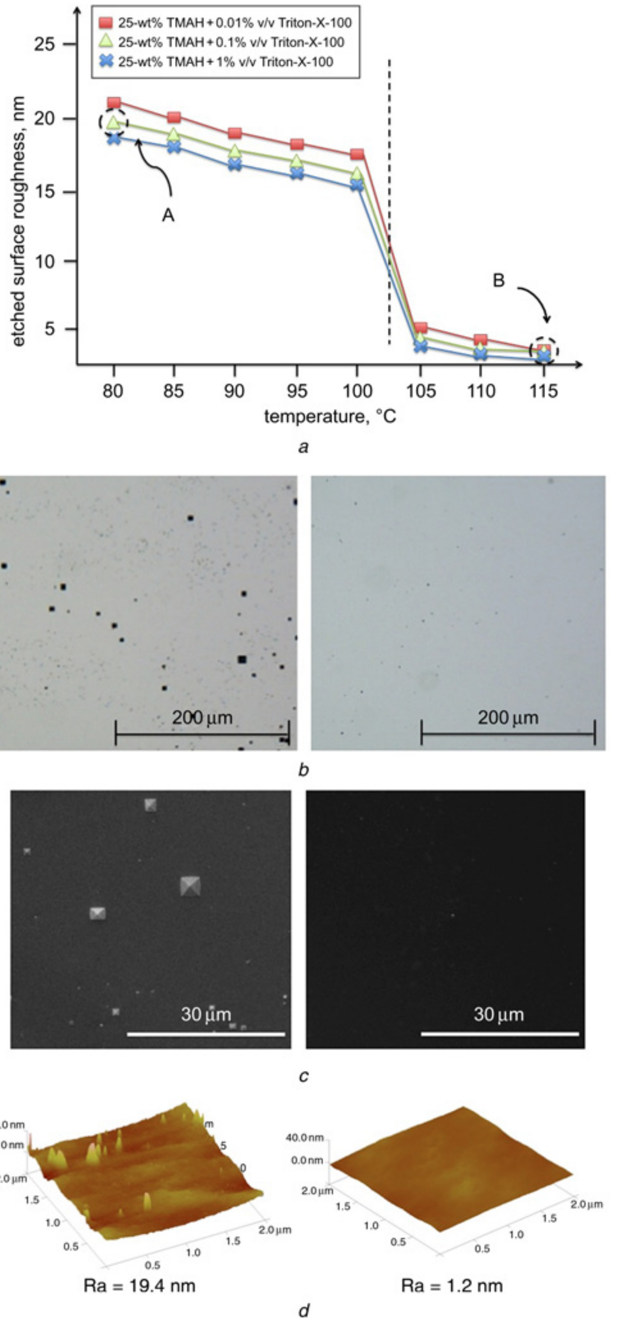

Figure 2 *Dependence of etched Si (100) surface roughness on temperature*
a Relationship between etched surface roughness and temperature
b Contrast of optical micrographs between samples A and B
c Contrast of SEM micrographs between samples A and B
d Contrast of AFM results between samples A and B

observed in Fig. 3*c*. In another view, it can be seen that the etched surface at near the boiling temperature is smoother than that at other temperatures, corresponding to the results in Fig. 2. This means that the higher the temperature, the lower the undercut ratio at the convex corner. The Triton-X-100 concentration between 0.01 and 0.1% v/v is considered as the value that reaches adsorption saturation on silicon surfaces. Thus, the Triton-X-100 with 0.1% v/v is generally used. If the concentration of Triton-X-100 is higher, the undercut ratio becomes smaller. This may be because more surfactant molecules are adsorbed on the silicon (110) and its vicinal surfaces. Note that at near boiling temperatures, high etching rates, extremely smooth surfaces and very small undercut ratios on Si (100) are gained simultaneously in Triton-100-X modified

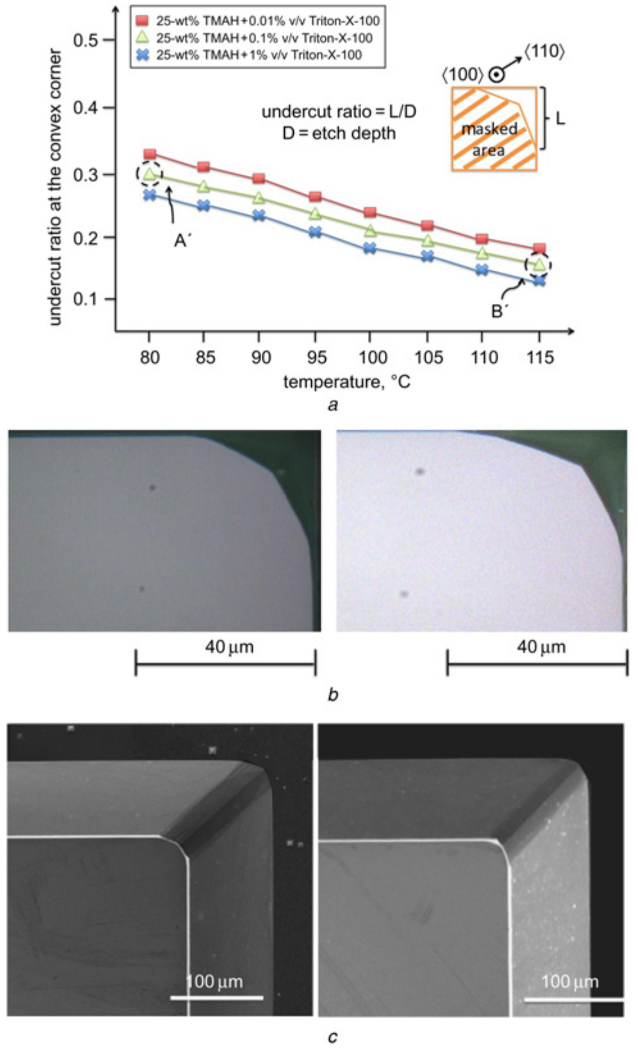

Figure 3 *Dependence of the undercut ratio at the convex corner of Si (100) on temperature*
a Relationship between the undercut ratio at the convex corner and temperature
b Contrast of optical micrographs between samples A′ and B′
c Contrast of SEM micrographs between samples A′ and B′

25 wt% TMAH solutions. This etching method is useful for the fast fabrication of microstructures [16, 17]. For example, during the process of a capacitive accelerometer, mass with very little corner undercut and a beam with a smooth surface are expected by this etching [18]. Therefore it provides a very profitable wet anisotropic etching method in CMOS-compatible MEMS fabrication.

4. Conclusion: In this Letter, the etching characteristics of the Si(100) facet at high temperatures near the boiling point in surfactant-modified TMAH solutions are studied. The etching rate of about 1.45 µm/min at 115°C, which is three to four times higher than that at 80°C in the Triton-X-100 modified 25 wt% TMAH solutions, is obtained for the first time. The activation energy value in the etching at higher temperatures is larger than that in the etching at lower temperatures. Further, it is intriguing that an extremely smooth surface with a surface roughness of about 1 nm and a very small undercut ratio of 0.2 at the convex corner emerge at near the boiling temperature as well. The wet anisotropic etching at near the boiling temperature in the surfactant-modified TMAH solutions has great potential in microdevice fabrication, especially for CMOS and microdevice integration processes.

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