

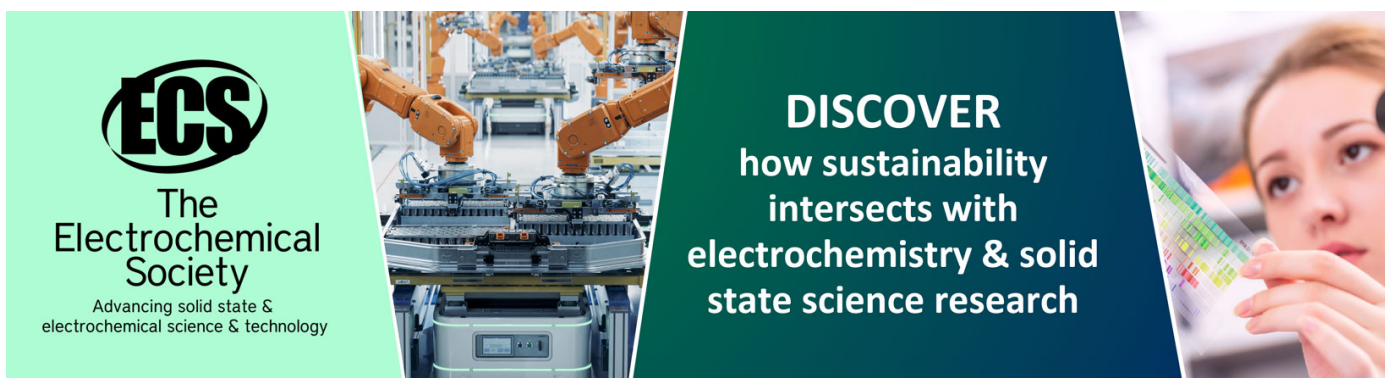
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Fabrication of novel microstructures based on orientation-dependent adsorption of surfactant molecules in a TMAH solution

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Abstract

In this work, the orientation-dependent adsorption of surfactant molecules on the silicon surface during etching in surfactant-added tetramethylammonium hydroxide (TMAH) is investigated. Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$, $n = 9-10$) and 25 wt% TMAH are used as surfactant and main etchant, respectively. The crystallographic planes affected by the surfactant molecules are determined by analyzing the etching behavior of different mask patterns on Si{1 0 0} wafers and silicon hemispheres in pure and surfactant-added TMAH. Taken together, the shapes of the etched profiles and the analysis of the hemispherical etch rates confirm that thick and dense adsorbed surfactant layers are typically formed on both the exact and vicinal Si{1 1 0} surfaces. In addition, the results indicate that the adsorbed surfactant layer behaves as a permeable mask, partially slowing down the etch rate of the affected surface orientation/s and thus enforcing their appearance on the etching front. The peculiar etching properties of surfactant-added and surfactant-free TMAH are then utilized for the fabrication of advanced micromechanical structures with new shapes on Si{1 0 0} wafers and polydimethylsiloxane based on complex Si{1 0 0} molds.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recent research in surfactant-added tetramethylammonium hydroxide (TMAH) is enhancing the applications of wet etching in microelectromechanical systems (MEMS) [1–4]. The etching properties of the TMAH solution are altered dramatically when a very small amount of surfactant is added (e.g. 0.01–0.1 vol%) [1–10]. Recent research in surfactant-added etching is focused on the study of the etching mechanism using *in situ* Fourier transform infrared spectroscopy (FTIR) and *ex situ* spectroscopic ellipsometry measurements [11–15]. Both studies confirm the existence of

orientation-dependent adsorption of the surfactant molecules during etching. Based on the idea that the relative hydrophobicity of two silicon surfaces determines their relative ability to adsorb the surfactant molecules, the orientation and concentration dependence of the adsorption density was correlated with crystallographic and etchant-related differences in the hydrophobic character of the surfaces at the atomistic scale: (i) differences in the H-termination densities, merely dictated by the particular crystallography of each surface; and (ii) differences in the number of OH-terminated surface atoms, mostly dependent on the relative reactivity of the atoms and the relative number of reactant molecules in the

solution, which are concentration-dependent features. This model was confirmed for commonly available wafer surfaces, such as $\{100\}$, $\{110\}$ or $\{111\}$, and the interaction of the surfactant molecules with other planes was extrapolated by taking into account the particular shapes of the 3D etched profiles.

From a theoretical perspective, the purpose of this paper is to offer additional experimental evidence for the validity of the previous hydrophobicity model for the vicinal $\{100\}$, $\{110\}$ and $\{111\}$ surfaces. In order to study the surfactant behavior for the whole range of crystallographic planes, the analysis of the etching characteristics of silicon hemispheres in pure and surfactant-added TMAH (or, simply, TMAH and TMAH+Triton) is arguably the most appropriate choice, in terms of experimental simplicity and data throughput [16, 17]. As previously demonstrated by the Wulf–Jaccodine method [18], the etch rate data from the etched hemispheres can be directly used to understand (and even simulate) which planes will appear at the edges of different mask patterns. Thus, we simultaneously study the etching behavior for different mask patterns on Si $\{100\}$ wafers and for the whole range of crystallographic planes on the hemispherical silicon specimens. The combination of the etch rates from the spherical specimen and the Wulf–Jaccodine method allows us to explore and understand (i) the formation of the sidewalls by the exact and vicinal $\{110\}$ surfaces at sharp convex and rounded concave corners in TMAH+Triton, and (ii) the effects of a pre-adsorbed surfactant layer on those sidewalls. As shown below, the results of this study confirm that the vicinal $\{110\}$ surfaces adsorb the surfactant molecules in a similar manner as $\{110\}$ itself, thus confirming the validity of the hydrophobicity model.

On the application side, pure and surfactant-added TMAH solutions provide different etching characteristics, particularly in terms of (i) the undercutting at curved edges and sharp convex corners, and (ii) the etch rates of the exact and vicinal $\{110\}$ planes. Pure TMAH, especially at high concentration (20–25 wt%), provides severe undercutting at curved and non- $\{110\}$ edges, and at extruded corners, while TMAH+Triton exhibits minimum undercutting at these edges and corners [1–4, 6–8]. In this case, $\{110\}$ planes are formed at $\{100\}$ mask edges, where the planes make an angle of 45° with respect to the $\{100\}$ wafer plane [3–6]. For the fabrication of MEMS structures using wet etching, the requirements for suppression or enhancement of undercutting depend on the type of structure. For instance, the fabrication of suspended structures (e.g. SiO₂ or P⁺-Si cantilevers) requires large undercutting in order to obtain as fast release as possible, while undercutting is undesirable for the realization of microstructures such as meandering channels or proof masses for accelerometers. Hence, the etchant can be selected accordingly. The availability of the two extremes for the TMAH solution enables the realization of newly shaped structures using wet etching only. Additionally, TMAH-based etchants have two significant advantages: (1) CMOS process compatibility, and (2) large etching selectivity between silicon and silicon dioxide as a mask material. Based on these features, this paper demonstrates the advanced applications

of surfactant-added TMAH in wet bulk micromachining by presenting novel shapes of MEMS structures realized in Si $\{100\}$ wafers and in polydimethylsiloxane (PDMS).

2. Experimental details

25 wt% TMAH with and without 0.1 vol% Triton-X-100 are used as the etchants in order to study the adsorption selectivity and for the fabrication of novel structures. In this paper, the etchants are referred to as pure TMAH and surfactant-added TMAH, respectively. Etching is performed at 70°C in 1 l of the etching solution. The etchant is kept in a cylindrical Teflon bowl placed inside a constant temperature water bath. A reflux condenser made of thick acrylic plastic walls and equipped with a narrow opening at the top is used to avoid changes in the etchant concentration during etching.

2.1. Characterization of TMAH+Triton etching

The investigation of orientation-dependent adsorption is performed on both Si $\{100\}$ wafers and silicon hemispheres. For the wafers, mask patterns containing both sharp convex and rounded concave corners, as shown in figure 1, are etched in TMAH+Triton. This enforces the emergence of the slowly etched, exact and vicinal $\{110\}$ planes at the two corner types, as schematically depicted in figure 1(a) and explained in section 3.1. The vicinal $\{110\}$ planes are of type $\{h h 1\}$, where $h > 2$, including examples such as $(3 3 1)$ and $(4 4 1)$. In the particular case of etching in TMAH+Triton, also $\{1 1 1\}$ vicinal planes, of type $\{h+2 h+2 h\}$ with $h > 1$, have very low etch rates and appear on the corner sidewalls. For this reason, in this paper we refer to both surface families $\{h h 1\}$ and $\{h+2 h+2 h\}$ as ‘vicinal $\{110\}$ ’. The samples are then cleaned in H₂SO₄+H₂O₂ (piranha) to remove any trace amount of impurities and surfactant molecules [11]. Thereafter, samples are dipped in a 5% HF (hydrofluoric acid) solution for 1 min in order to remove the oxide layer grown by the H₂SO₄+H₂O₂ cleaning process. Now, the samples are divided into two groups. The samples in group I are etched in pure TMAH. The samples in group II are dipped in Triton-added de-ionized (DI) water for 15 min. This process, which is referred to as the ‘surfactant treatment’, leads to selective surfactant adsorption on the exposed silicon depending on the local orientation of the exposed surface. To remove loosely adsorbed surfactant molecules, several gentle dips in pure DI water are performed. The Triton-treated samples are then etched in pure TMAH. Just prior to TMAH etching and prior to surfactant treatment, samples are dipped in a 5% HF solution in order to remove native oxide.

Silicon hemispheres of 44 mm diameter are etched in TMAH and TMAH+Triton in order to study the changes in the etch rates of different crystallographic planes. The surface profile of the sphere is measured using a UPMC550-CARAT (Carl Zeiss) three-dimensional measuring machine. The surface profile is probed every 2° of latitude ranging from 0° to 70° and every 2° of longitude ranging from 0° to 360° . The etch rates at different locations of the hemisphere (corresponding to different surface orientations) are calculated by taking the difference between the probed positions before

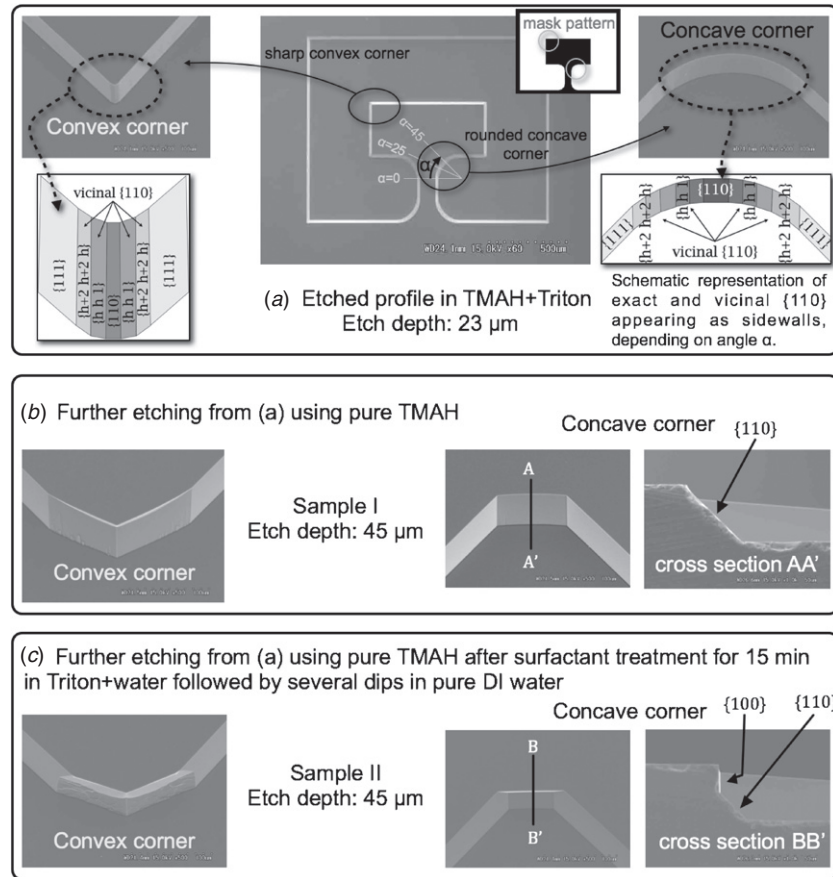


Figure 1. Etched profiles of sharp convex and rounded concave corners at different stages for samples I and II under various etching conditions. (a) Etched profile in TMAH+Triton, showing the definition of angle α and schematic representations of the exact and vicinal $\{110\}$ planes appearing as sidewalls at the sharp convex and rounded concave corners. (b) Further etching from state (a), using TMAH. (c) Further etching from state (a), using TMAH after surfactant treatment (15 min in Triton+DI water, followed by several dips in pure DI water).

and after etching, and dividing by the etching time. Further details are described in [16].

2.2. Applications of the proposed etching system

2.2.1. 3D structures by two-step etching. Since the etching characteristics of surfactant-added TMAH are different from those of pure TMAH, complex 3D shapes can be realized for advanced applications by using one- and two-step etching processes [3, 4]. Both steps can be performed in pure TMAH or in surfactant-added TMAH or in both, depending on the particular features of the desired etched profile. For one-step etching, oxide-deposited wafers are used, while nitride-deposited wafers are employed for two-step etching. For one-step etching, the oxide layer is patterned using photolithography and oxide etching steps. The nitride layer is etched either by dry etching or using hot phosphoric acid (H_3PO_4). In this work, hot phosphoric acid is used for nitride etching. Hence, in order to pattern the nitride layer for two-step etching, an oxide layer using plasma-enhanced chemical vapor deposition (PECVD) is deposited. PECVD oxide is patterned using photolithography followed by oxide etching in buffered hydrofluoric acid (BHF). The patterned oxide over the nitride layer works as a mask for selective removal of nitride in hot phosphoric acid. The patterned wafers are then etched in

pure or Triton-added TMAH, depending on the undercutting requirements, up to the required etch depth.

The process steps for the fabrication of freestanding SiO_2 and fixed silicon structures on $\text{Si}\{100\}$ wafers using two-step etching are illustrated in figures 2 and 3, respectively. Firstly, the nitride layer is patterned. Being aligned along the $\langle 110 \rangle$ direction with a tolerance of $\pm 1^\circ$, the primary flat is used as a reference to align the mask patterns/edges along $\langle 110 \rangle$. Thereafter, the first step of silicon etching is performed. In both cases (figures 2 and 3), etching is carried out in TMAH+Triton, as minimum undercutting is required at the mask edges in the corresponding applications. After the first step of silicon etching, local oxidation of silicon (LOCOS) is performed in order to deposit an oxide layer on the exposed silicon. For the freestanding structures, the oxide layer works as a structural layer. Hence, thick oxide of about 1–1.5 μm thickness is grown. In the case of fixed structures (figure 3), the oxide layer is used only as an etching mask and, correspondingly, a thin oxide (about 0.1 μm thick) can be used. After the LOCOS step, the nitride layer is removed and the second step of etching is performed. In this work, nitride etching is carried out in hot phosphoric acid (H_3PO_4) as it provides high nitride-to-oxide selectivity. It can be etched out by dry etching too; however, the nitride-to-oxide etching selectivity should be high. The process presented here does

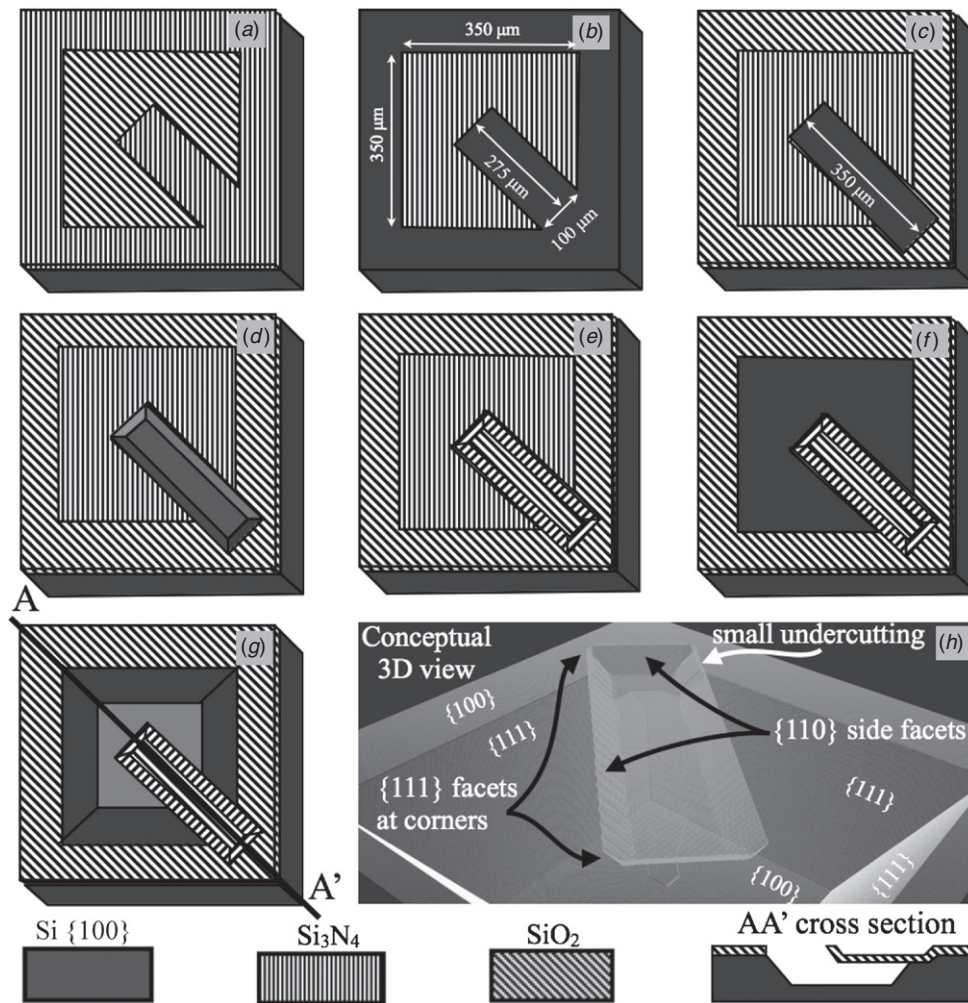


Figure 2. Fabrication steps for the realization of suspended SiO_2 structures on $\text{Si}\{100\}$ wafers: (a) deposition of Si_3N_4 and SiO_2 followed by patterning of oxide, (b) Si_3N_4 etching followed by oxide removal in BHF, (c) thermal oxidation and patterning of oxide, (d) anisotropic etching of silicon in 25 wt% TMAH + 0.1 vol% Triton, (e) thermal oxidation for the deposition of thick oxide, (f) selective etching of Si_3N_4 , (g) anisotropic etching of silicon in pure 25 wt% TMAH in order to release the structure from the substrate. (h) Conceptual 3D view of the final structure.

not depend on the etching method for silicon nitride. Again, the selection between pure and Triton-added etchant depends on the particular requirement of the desired shapes. As an example, the fabrication of the structures shown in figure 2 requires a large amount of undercutting for their fast release. Hence etching is performed in pure TMAH (figure 2(g)). On the other hand, the structures of figure 3 require minimum undercutting in order to maintain the shape of the convex corners. Therefore, the second step of etching is performed in TMAH+Triton (figure 3(d)).

Note that figures 2(d)–(g) show only a schematic representation of the main geometric features of the developed cantilever structure. Under closer inspection, small, flat $\{111\}$ facets will be formed at the four corners of the cantilever cavity, as shown in the 3D view of figure 2(h). Similarly, a small amount of undercutting will occur at the joint region between the cantilever base and the original $\{100\}$ surface. The two features result from the fact that the etch rate of the $\{110\}$ cantilever sidewalls has a finite value (not zero), thus forcing the timid appearance of the $\{111\}$ facets and undercutting.

2.2.2. Sharp-edged silicon molds for PDMS. Silicon micromachining is a promising technology for the fabrication of mold patterns for the realization of PDMS stamps for soft lithography. This type of lithography has gained much interest due to its great versatility, high throughput and potential low cost based on the use of the master and replication approach [19–21]. Moreover, silicon is suitable as a master material in a hot embossing process due to its high mechanical stability and rigidity. Simple 3D structures, such as pyramidal pits and V/U-shaped channels/grooves with a sidewall angle of 54.7° , are easily achieved by wet anisotropic etching of $\text{Si}\{100\}$ surfaces masked by SiO_2 and/or Si_3N_4 in alkaline solutions (e.g. KOH, TMAH, etc) [19, 21]. More advanced silicon micromachining would be desirable in order to realize more sophisticated mold (or master) patterns, such as bent V-grooves, 45° sidewalls, etc. As discussed earlier, the introduction of the TMAH+surfactant solution effectively enables the realization of new shapes on $\text{Si}\{100\}$ wafers. In this work, we show that a wide range of fixed structures containing perfectly sharp edges and grooves can be easily

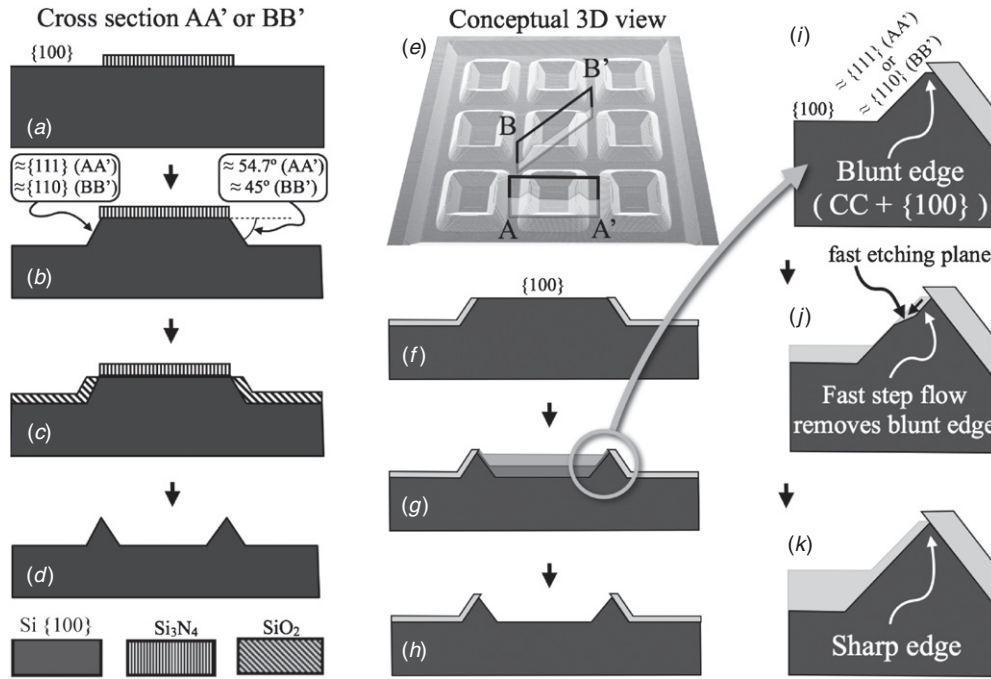


Figure 3. Fabrication concept for sharp-edged structures using two-step etching in Si{100} wafers: (a) patterning of the silicon nitride layer, (b) etching in TMAH+Triton, (c) local oxidation, (d) removal of nitride followed by silicon etching in TMAH+Triton and strip-off of the oxide in BHF, (e) conceptual 3D view, (f)–(h) graphical evolution of the etch front, (i)–(k) graphical explanation of the self-repairing etching mechanism that leads to a sharp edge in the event that a blunt edge is temporarily formed. CC = convex corner.

utilized as molds in order to realize sharp-edged PDMS structures.

The PDMS mixture is prepared by mixing two components (base and curing agent) in the standard ratio of 10:1 and degassed in a vacuum desiccator for 1 h. The degassed PDMS is poured onto the silicon mold patterns, followed by degassing again for 1 h to remove bubbles trapped in the sharp patterns. Thereafter, the PDMS is cured for 24 h at room temperature. The PDMS is then peeled off very slowly from the silicon mold patterns to prevent any tearing of the polymer.

3. Results and discussion

3.1. Surfactant adsorption

Figure 1 shows the etched profiles of the convex and concave corners for group I and group II samples, as described in section 2.1. The effect of the surfactant treatment is clearly visible as different etch profiles are developed for samples I and II. The difference in the profile indicates that the surfactant molecules are strongly adsorbed on the planes that emerge at both concave and convex corners in TMAH+Triton (figure 1(a)). The sidewalls of the rounded concave corners in figure 1(a) are formed by the exact and vicinal {110} surfaces (see figure 1(a)), as these planes have minimum etch rates among all possible orientations enforced by the rounded mask edges. This is shown in figures 4(a)–(c) for the particular case of the {110} planes appearing at the center of the rounded sidewalls. The angle α is defined in figures 4(a), (b) in order to refer to any vertical cross section of the etching profile

as well as any vertical cross section of the three-dimensional distribution of etch rates. The cross section of the etch rate data shown for $\alpha = 45^\circ$ is obtained from a three-dimensional distribution of etch rates for TMAH+Triton, as shown in figures 5(a), (b). These etch rates are obtained experimentally using the hemispherical silicon specimen. Based on a standard Wulf–Jaccodine analysis [18], figures 4(b), (c) show that the low etch rate of {110} is directly responsible for the formation of the {110} sidewall at the center of the rounded concave corner ($\alpha = 45^\circ$). For other values of α , especially for $25^\circ < \alpha < 45^\circ$ (see α in figures 4(a), (b) and 5(a)), similar cross sections of the etch rate data and of the etching front will be obtained. In particular, the low etch rates for the vicinal {110} orientations along path B in figures 5(a), (b) (going from {110} to {111}) explain the formation of the {h h 1} and {h+2 h+2 h} sidewalls schematically shown in figure 1(a), corresponding to other cross sections in the range $25^\circ < \alpha < 45^\circ$.

According to the previously reported hydrophobicity model [13, 14], the formation of an adsorbed layer on {110} is correlated to a small etch rate for {110} in TMAH+Triton and the development of {110} sidewalls on the etching front. Figures 5(a) and (e) demonstrate that the etch rates of the vicinal {110} surfaces (i.e. {h h 1} and {h+2 h+2 h} along path B between {110} and {111}) have also very small etch rates, and figure 1(a) shows that these vicinal surfaces appear as the sidewalls of the etched front region around the two types of corners, a feature that is readily explained by the Wulf–Jaccodine analysis. Thus, we conclude that the vicinal {110} surfaces adsorb the surfactant molecules in a similar manner as {110} itself.

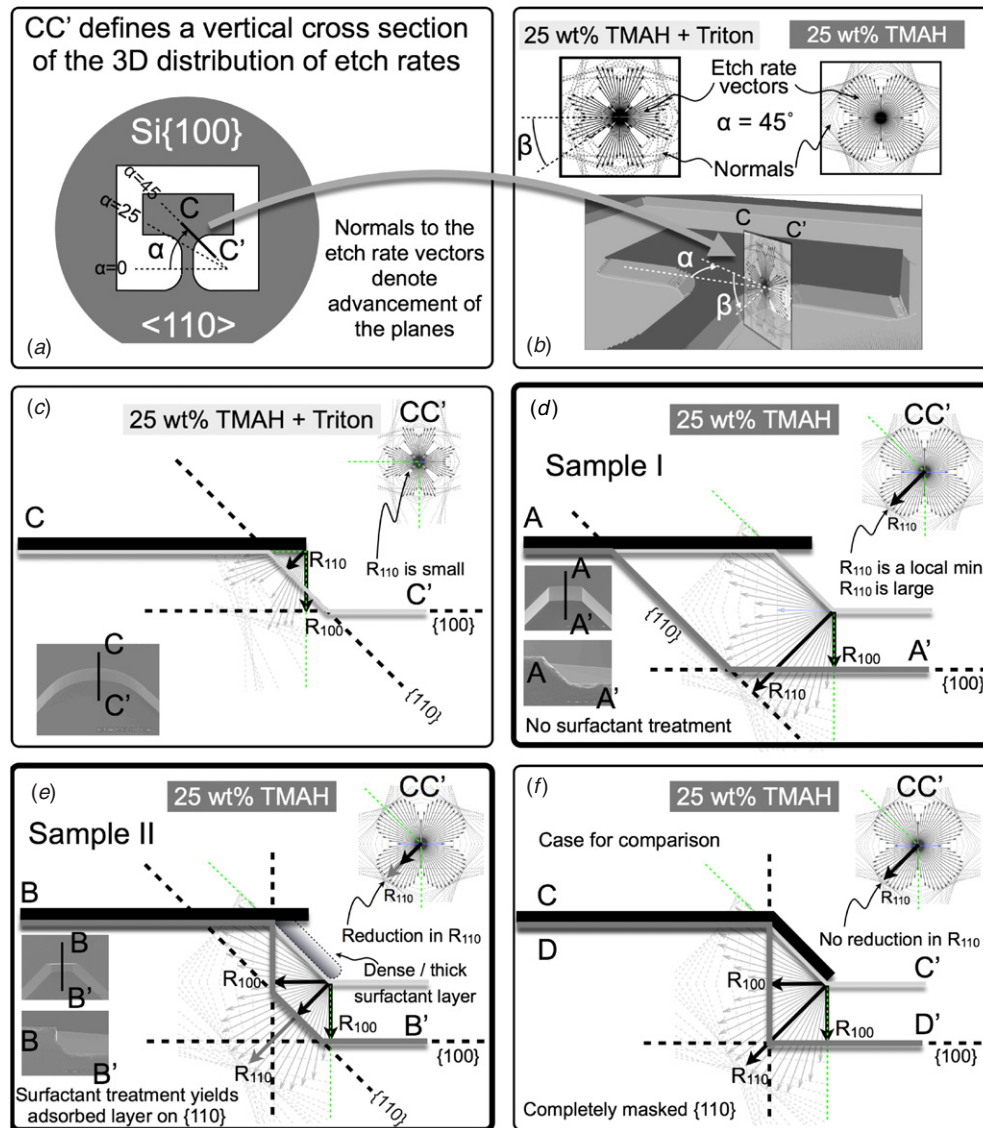


Figure 4. Explanation of the difference in the etched profiles for samples I and II. (a) Conceptual setup, showing the mask pattern and the definition of angle α . (b) Conceptual 3D view of the result obtained in figure 1(a), showing the definition of angles α and β , and the etch rate vectors for the CC' cross section of the etch rate data corresponding to $\alpha = 45^\circ$, cf figures 5(b), (c). (c) Application of the Wulf-Jaccodine method to derive the shape of the etch front for the CC' cross section defined in parts (a) and (b), corresponding to figure 1(a). (d) Same as (c), after additional TMAH etching (sample I, cf figure 1(b)). (e) Same as (c), after the surfactant treatment and additional TMAH etching (sample II, cf figure 1(c)). (f) Same as (c), after deposition of silicon oxide on the sidewalls shown in (b) and additional etching in TMAH (theory only, no experiment). R_{110} and R_{100} are the etch rates of $\{1\ 1\ 0\}$ and $\{1\ 0\ 0\}$, respectively.

According to [12–14], there exists a correlation between the hydrophobicity of the surface and the thickness of the adsorbed surfactant layer, resulting in the following hierarchy: (i) the exact and vicinal $\{1\ 1\ 1\}$ surfaces have the thickest and densest adsorbed layers, (ii) the exact and vicinal $\{1\ 1\ 0\}$ orientations exhibit medium adsorption, and (iii) the exact and vicinal $\{1\ 0\ 0\}$ planes experience very low or no adsorption. The underlying atomistic mechanism behind this orientation dependence of the surfactant adsorption is the difference in the hydrophobicity of the silicon surfaces due to differences in the density of H-terminations and in the number of OH-terminated atoms. See [12–14] for further details.

When the initial corners obtained in TMAH+Triton are etched in pure TMAH (sample I), $\{1\ 1\ 0\}$ planes emerge

as the main orientation and, as observed from the top, the rounded edge becomes straight (figure 1(b)). As explained in figure 4(d), while pure TMAH provides a large etch rate for $\{1\ 1\ 0\}$, this etch rate is actually a local minimum, thus ensuring that the initially exposed $\{1\ 1\ 0\}$ plane in the CC' profile of figure 4(c) will remain in the etched profile AA' of figure 4(d) in pure TMAH. As shown in figures 5(c), (d), the etch rate of $\{1\ 1\ 0\}$ in pure TMAH is also a local maximum along line E (i.e. as the angle α is varied). As a result, the vicinal $\{h\ h\ 1\}$ and $\{h+2\ h+2\ h\}$ planes originally present in the rounded corner for the other cross sections ($0 < \alpha < 45^\circ$) are replaced by $\{1\ 1\ 0\}$ and the rounded edge becomes straight (figure 4(c)).

When the same initial rounded corners obtained with TMAH+Triton are subject to the surfactant treatment, an

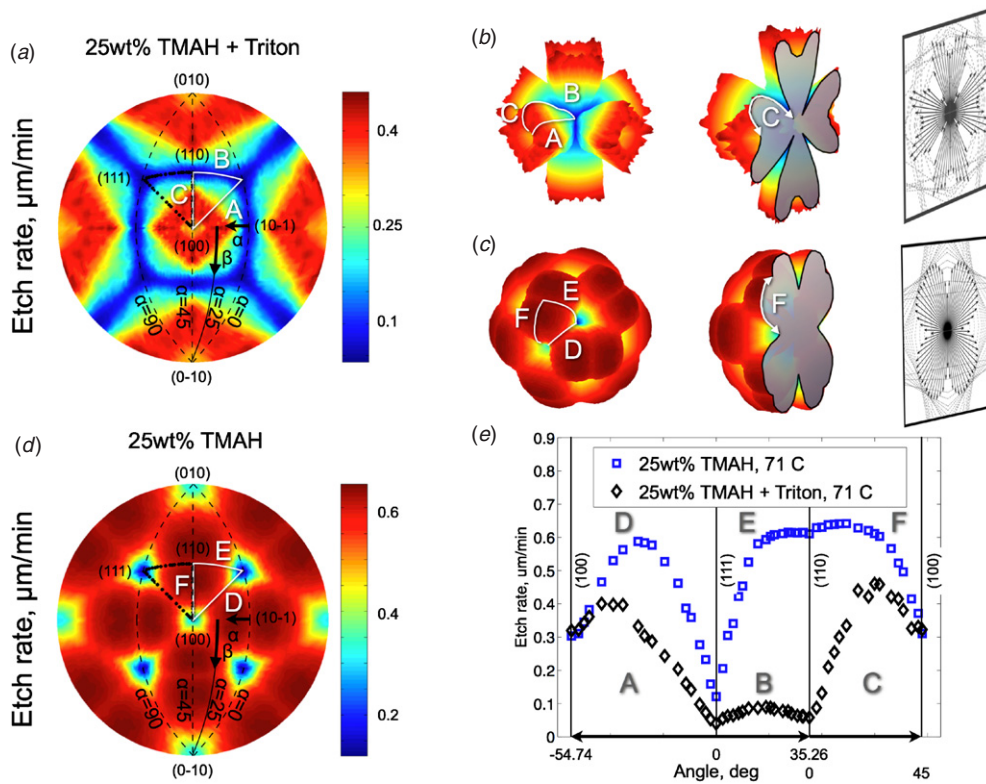


Figure 5. 3D distribution and 2D plot of the etch rates for different surface orientations in TMAH and TMAH+Triton at 71 C.

(a) Stereographic projection of the etch rates in TMAH+Triton. (b) 3D plot of the etch rates in TMAH+Triton, showing a principal cross section of the data and the corresponding etch rate vectors and normals used by the Wulff–Jaccodine method in figure 4. (c) Same as (b), this time for TMAH. (d) Stereographic projection of the etch rates in TMAH. (e) 2D plot of the etch rates for TMAH and TMAH+Triton along the A, B, C, D, E and F paths indicated in parts (a)–(d).

adsorbed layer of Triton molecules is formed on $\{110\}$ and its vicinal planes $\{h h 1\}$ and $\{h + 2 h + 2 h\}$, as concluded in the second paragraph of this section. The shape of the etched profile obtained after further etching in TMAH (figure 1(c)) strongly indicates that the adsorbed Triton layer acts as a *permeable mask*. Except for the presence of the $\{110\}$ plane, the etched profile BB' in figure 4(e) is equivalent to the etched profile DD' in figure 4(f) that would be obtained if a nitride/oxide mask covered the sidewall formed after the initial etching in TMAH+Triton. According to the Wulff–Jaccodine analysis for $\alpha = 45^\circ$, the $\{110\}$ planes will disappear in figure 4(f) as the etch rate of $\{110\}$ (R_{110}) is large in pure TMAH. However, the presence of the adsorbed surfactant layer in figure 4(e) slows down the etch rate of $\{110\}$, thus enforcing its appearance on the etched front. This means that the adsorbed surfactant layer (prior to etching in pure TMAH) acts as a permeable mask that can be used to alter the etched profile of sharp and concave corners. As described below, this result is in agreement with previous studies of the adsorption selectivity of Triton on silicon surfaces [12–15].

The etch rates for the whole range of crystallographic planes in pure and Triton-added TMAH are shown in figure 5. The range of the planes affected by the surfactant molecules is clearly visible. While the etch rates of the exact and vicinal $\{100\}$ planes are almost unaffected, the etch rates of the exact and vicinal $\{110\}$ planes are reduced significantly. These

results indicate that the surfactant molecules are adsorbed more densely (or more strongly, or both) on exact and vicinal $\{110\}$, in comparison to exact and vicinal $\{100\}$. Densely adsorbed surfactant molecules protect the surface from the reactants during etching, resulting in a dramatic reduction in the etch rates. This is in agreement with a previous ellipsometry study [15], where the surfactant layer thicknesses were measured on the three principal surfaces $\{111\}$, $\{110\}$, and $\{100\}$, thus concluding that the surfactant molecules form a thicker (and denser) layer on $\{111\}$ and $\{110\}$ surfaces in comparison to $\{100\}$. As a result of the present study, figure 5 reveals exactly which planes are affected by the surfactant molecules. Although the surfactant molecules are adsorbed strongly on exact and vicinal $\{111\}$, the effect on the etch rate is less significant since the etch rate of $\{111\}$ planes in pure TMAH is already very low. In contrast, the effect of the addition of the surfactant in TMAH is considerably prominent for the exact and vicinal $\{110\}$ planes, since their etch rates are quite large in pure TMAH.

Although the concept of figure 1 has already been used in [15], the new format used in the present paper describes more properly the key differences in the processing steps between samples I and II. Furthermore, figure 1 establishes the necessary background for the interpretation of figures 4 and 5. To our best knowledge, it is the first time that a comprehensive explanation is given for the profiles obtained in figure 1, based

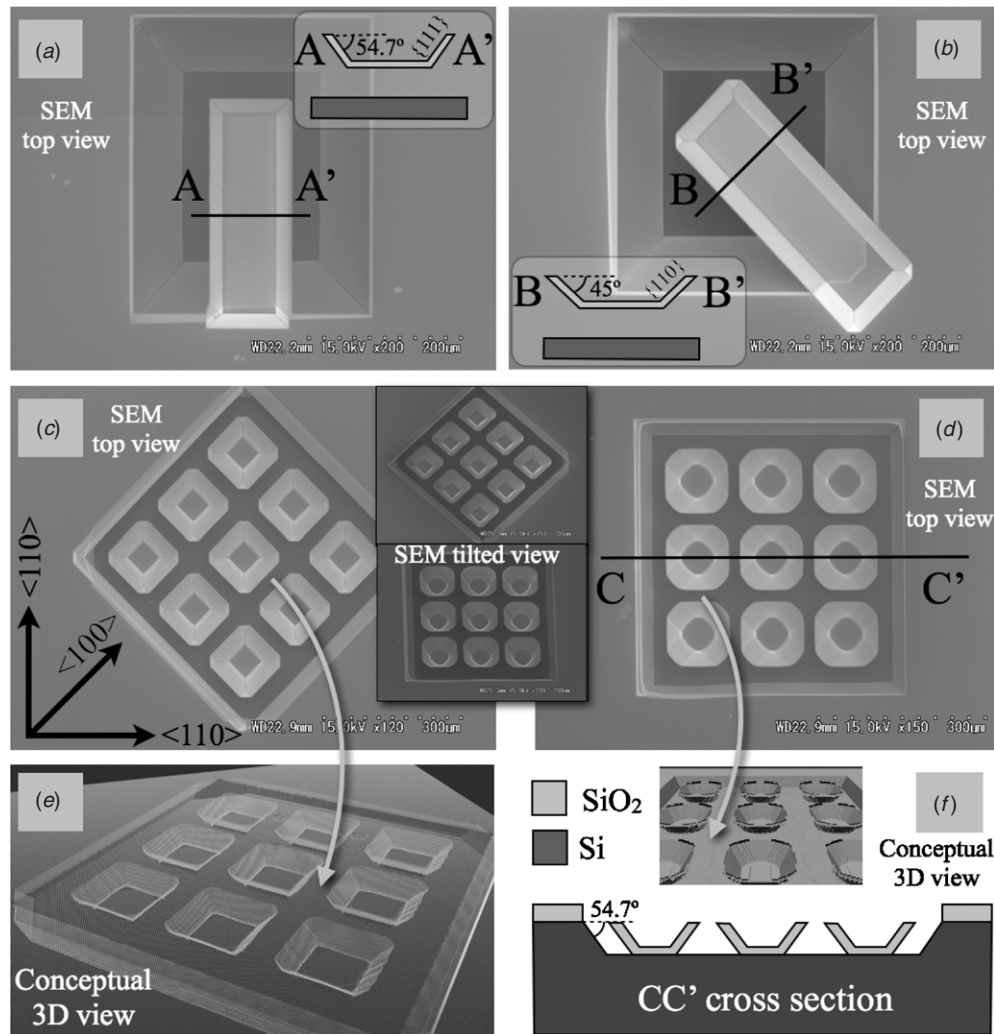


Figure 6. SEM pictures of various shapes of freestanding and side-released SiO_2 structures: (a) tray-shaped cantilever with $\{111\}$ sidewalls ($L = 300 \mu\text{m}$, $W = 100 \mu\text{m}$) (b) diagonal tray-shaped cantilever with $\{110\}$ sidewalls ($L = 350 \mu\text{m}$, $W = 100 \mu\text{m}$), (c)–(d) top view of the square and circular cups, with inserts showing tilted views. (e) Conceptual 3D view of the square cups. (f) Conceptual 3D view and cross section information for the circular cups.

on the Wulf–Jaccodine method and a novel description of the adsorbed surfactant layer as a permeable mask, as shown in figures 4 and 5.

The present study establishes that relatively thick and dense adsorbed surfactant layers are formed not only on exact $\{110\}$ surfaces but also on vicinal $\text{Si}\{110\}$ surfaces, thus corroborating and supplementing the conclusions of previous studies [12–15]. The surfactant layer partially slows down the etch rate of the underlying surface orientation/s and thus enforces the appearance of these plane/s on the etching front. Furthermore, this study shows for the first time that a pre-adsorbed surfactant layer can be understood and used as a permeable mask. Even in small numbers, the adsorption of surfactant molecules on pre-etched silicon surfaces can be sufficient to alter the shape of an etched profile. This perspective has the potential to expand the number of design possibilities for MEMS structures in the future.

3.2. Applications

3.2.1. 3D structures by two-step etching. New shapes of silicon dioxide fabricated on $\{100\}$ wafers are shown in figure 6. Each structure is obtained by following a similar process flow as that described in figure 2 for the diagonal cantilever cavity. All the structures in figure 6 are released in pure TMAH. In order to define the mold shape (figure 2(d)) for the growth of the LOCOS oxide layer (figure 2(e)), one can use pure or surfactant-added TMAH for the first silicon etching step (figure 2(c)), depending on the particular target features of the etching profile. In the case of the tray-shaped oxide cantilever beam shown in figure 6(a), the first etching step can be performed in either TMAH solution as only $\{111\}$ planes are developed in the etching front. For the rest of the structures (figures 6(b)–(d)) the first etching must be performed in TMAH+Triton in order to conformally keep the intended shapes. The sharp-edged silicon structures shown in

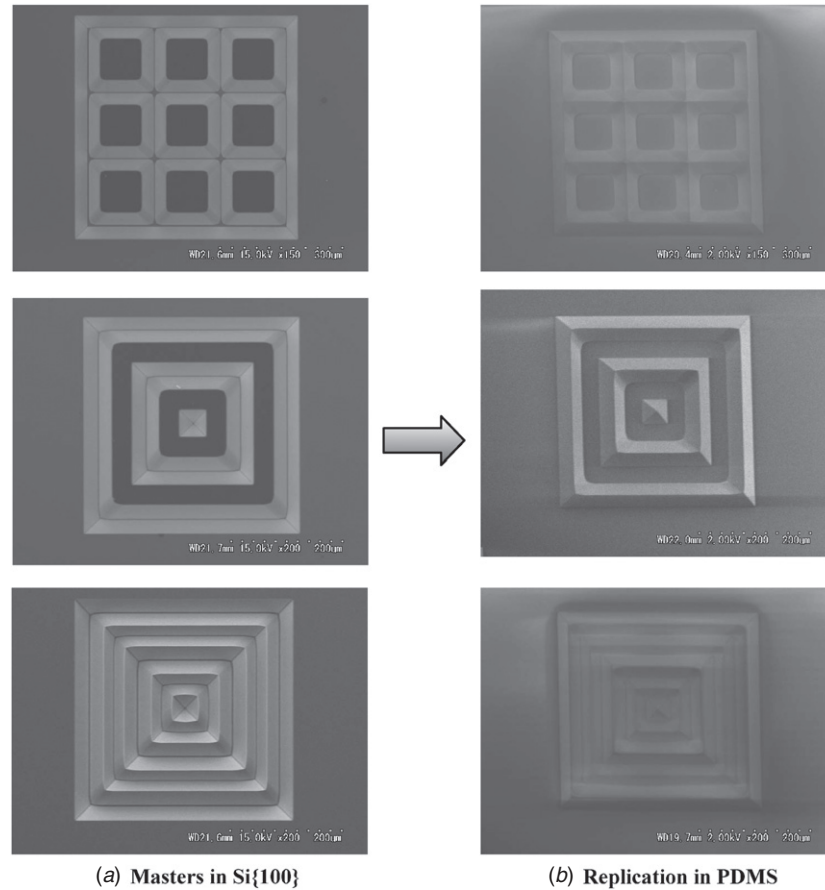


Figure 7. Sharp-edged PDMS structures fabricated using silicon molds created by wet etching of Si{100} in TMAH+Triton. (a) Masters in Si{100}. (b) Replication in PDMS.

figure 7(a) are obtained by using TMAH+Triton in both silicon etching steps in order to maintain the shape of the bent V-grooves. The experimental results show that any mask pattern shape can be etched conformally in TMAH+Triton, albeit with slanted sidewalls in the range between 54.7° and 45° , for {111} and {110} sidewalls, respectively.

We are not aware of any previous report containing the structures shown in figure 6. The experiments performed in this study serve to demonstrate that new shapes and structures can be fabricated by simple, affordable, single-sided, two-step wet etching. A possible application of the developed cantilevers is the ability to tune the main oscillation frequency by adding/removing a load to the cantilever basin, such as by using a microfluid. Elongated cantilever basins with wall angles of 45° and 54.7° can be realized for such purposes by simple wet etching.

3.2.2. Sharp-edged silicon molds for PDMS. This section provides experimental proof that the pattern transfer to the PDMS material is successful for several examples of complex silicon molds obtained by the general process described in figure 3. A selection of wet-etched silicon molds and their PDMS replicas is shown in figure 7. Since the mold patterns contain bent V-grooves and the V-grooves cross

each other, these geometries are not possible in pure TMAH and/or KOH due to the inherently large undercutting of these etchants. In general, the fabrication of convex corners in pure TMAH and KOH is based on the corner compensation method. However, this requires a large amount of space for the compensation patterns, making their use impossible in practice for the case of contiguous bent V-grooves. As surfactant-added TMAH provides minimum undercutting, a very small compensating geometry can be used, easily fitting in the reduced available space [4]. To our best knowledge, the shown PDMS replicas have not been demonstrated before. By taking advantage of low and high undercutting in pure and surfactant-added TMAH, new processes can be developed for the fabrication of sophisticated mold patterns in silicon wafers and corresponding PDMS structures.

The structures shown in figure 7 exhibit relatively sharp edges. This feature can be qualitatively explained as follows. When the system is observed from a distance, figures 3(f)–(h) describe the formation of the sharp edges as a result of the fast propagation of the horizontal section of the front, corresponding to the {100} orientation, and the slow retrieval of the developing sidewalls, which are made of slow etching planes such as {111} for the AA' cross section and {110} for BB' (see figure 3(e)). The slanted geometry of the oxide protection layer enforces the inverted 'V' shape.

Should a blunt edge be temporarily formed, figures 3(i), (j) explain graphically the existence of a self-repairing etching mechanism that will return the system to a sharp edge soon afterwards. A blunt edge not only exposes the {100} orientation at the top but also a convex corner (CC), as indicated in figure 3(i). The CC leads to the formation of a fast etching plane, as indicated in figure 3(j), thus resulting in the fast removal of the extra material on the sidewall. In other words, a blunt edge is unstable and correspondingly will induce a fast step flow process along the sidewall. As a result, the edges of the fabricated structures remain sharp.

4. Conclusions

The orientation-dependent adsorption of surfactant molecules is investigated. The use of silicon hemispheres in the present research reveals how the etch rate for the whole range of crystallographic orientations is influenced by the surfactant molecules. For the first time, it is shown that a pre-adsorbed surfactant layer can be understood and used as a permeable mask. Based on this concept and the use of the well-established Wulff–Jaccodine method, a new explanation is given for the dramatic effects that the surfactant adsorption has on the etching profiles. This potentially expands the number of possibilities for the design of MEMS structures using wet etching in the future. Advanced applications of pure and surfactant-added TMAH are demonstrated by fabricating microstructures with new shapes in Si{100} wafers. A thick layer of thermally grown oxide is utilized for the fabrication of suspended structures, and new shapes of wet-etched patterns in Si{100} are utilized as molds for the fabrication of sharp-edged PDMS structures. In this work, the credit for the advanced applications of wet etching goes to surfactant-added TMAH, which exhibits etching characteristics different from traditional etchants, such as pure TMAH and KOH. In the future, more exciting applications of pure and surfactant-added TMAH in MEMS fabrication will be investigated based on the dramatically different undercutting behavior of the two etchants.

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