Systematic study of the etching characteristics of Si{111} in modified TMAH

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Wet bulk micromachining on Si{111} is done to fabricate simple to complex microstructures for applications in sensors and actuators. In this work, it has been performed a systematic study of Si{111} in modified 5 wt% tetramethyl-ammonium hydroxide (TMAH) with varying concentration of NH_2OH for achieving improved etching characteristics especially high lateral undercutting at mask edges aligned along non-⟨110⟩ directions. The concentration of NH_2OH is varied from 5 to 20% in step of 5%. The lateral undercutting, which is highly desirable for the quick release of freestanding microstructures from the substrate, is increased considerably with the addition of NH_2OH in TMAH solution. In addition, the incorporation of NH_2OH improves etched surface morphology. Moreover, the effect of etchant ageing on the etching characteristics is investigated. Suspended microstructures are fabricated to demonstrate the application of modified TMAH solution for silicon wet bulk micromachining. The results presented in this work are highly useful where Si{111} wafer is used for the fabrication of microstructures.

1. Introduction: Wet anisotropic etching is a key step in the fabrication of various kinds of components for applications in microelectromechanical systems (MEMS) [1, 2]. Tetramethylammonium hydroxide (TMAH) and potassium hydroxide (KOH) are the most commonly used etchants in wet anisotropic etching for the fabrication of microstructures [2–15]. In silicon wet anisotropic etching, Si{111} planes are the slowest etch rate planes in all kinds of alkaline etchants. Among three principle orientations namely {100}, {110} and {111}, {100}-oriented wafers are most frequently used. Si{110} wafers are employed for specific applications such as microstructures with vertical sidewalls. As the Si{111} planes have slowest etch rate in all kinds of wet anisotropic etchants, Si{111} wafers are used for explicit applications and to fabricate complicated structures in combination with deep reactive ion etching (DRIE) prior to wet etching [16–22]. In these structures, gap between freestanding structure and bottom surface can be controlled precisely. In the case of Si{111} wafer, six {111} planes appear at the mask edges aligned along ⟨110⟩ directions and the freestanding structures are released through lateral undercutting at the mask edges not comprising {111} planes, for example, ⟨112⟩ mask edges as illustrated in Fig. 1. The cross-sections of etched profile along ⟨110⟩ direction are shown in Fig. 1*c*. In our previous work, we reported the etching characteristics of Si{100} and Si{110} in TMAH solution without and with addition of NH_2OH [23, 24]. It was found that the addition of NH_2OH improves the etch rate and undercutting. High etch rate is very useful for the fabrication of deeper cavity in less time, while high undercutting is needed for the fast release of the structures. Si{111} wafers have been explored for the fabrication of complicated structures using DRIE assisted wet etching [17–22]. Hence, it is very important to study the etching characteristics of Si{111} in pure and modified alkaline solution.

In the present work, we have investigated the etching characteristics of Si{111} in low concentration TMAH without and with addition of different concentrations of NH_2OH. The main objective of this work is to obtain high lateral undercutting rate at the mask edges aligned along non-⟨110⟩ directions, which is essential for the fast release of microstructures. The dependence of etching characteristics on etchant age has also been investigated.

2. Experimental: Four inch, Czochralski grown, and one side polished silicon {111} wafers with a resistivity of 1–10 Ω-cm are used for the experiments. An oxide layer of 1 µm thickness is grown using thermal oxidation process. Lithography technique is used to pattern the oxide layer. Oxide etching is performed in buffered hydrofluoric acid. Subsequently, the wafers are cleaned thoroughly in deionised (DI) water. After oxide etching, the photoresist is removed with acetone and then thoroughly rinsed in DI water. The wafers are diced using a dicing saw into 2×2 cm^2 pieces. The diced samples are cleaned in a piranha bath (H_2SO_4: H_2O_2::1:1) followed by DI water rinse to remove any trace of organic material and unwanted particles on the surface. Now, the cleaned samples are dipped into 1% HF for 1 min to remove the native oxide, which is grown during piranha cleaning. Subsequently, the samples are thoroughly rinsed in DI water. Silicon wet anisotropic etching is carried out in 5 wt% TMAH without and with varying concentrations of NH_2OH (5–20%) at 70 ± 1°C. In order to examine the effect of etchant ageing on the etching characteristics, optimal concentration of NH_2OH is used. A constant temperature water bath is used to maintain the uniform temperature throughout the experiment. A reflux condenser made of thick glass equipped with a double layered narrow opening is used to avoid any changes in the etchant concentration due to continuous heating of the etchant during experiments. Finally, the etched samples are characterised using a 3D measuring laser microscope (OLYMPUS OLS4000), optical microscope (OLYMPUS MM6C-PC), scanning electron microscope (SEM).

3. Results and discussion: The etch depth, undercutting length at mask edges and surface roughness are investigated using 3D laser scanning microscope and the etched surface morphology is studied using SEM. Etch rate is a very important parameter when etching is involved in the fabrication process. It is used to estimate the etching time. In this work, the etch rate of Si{111} is measured

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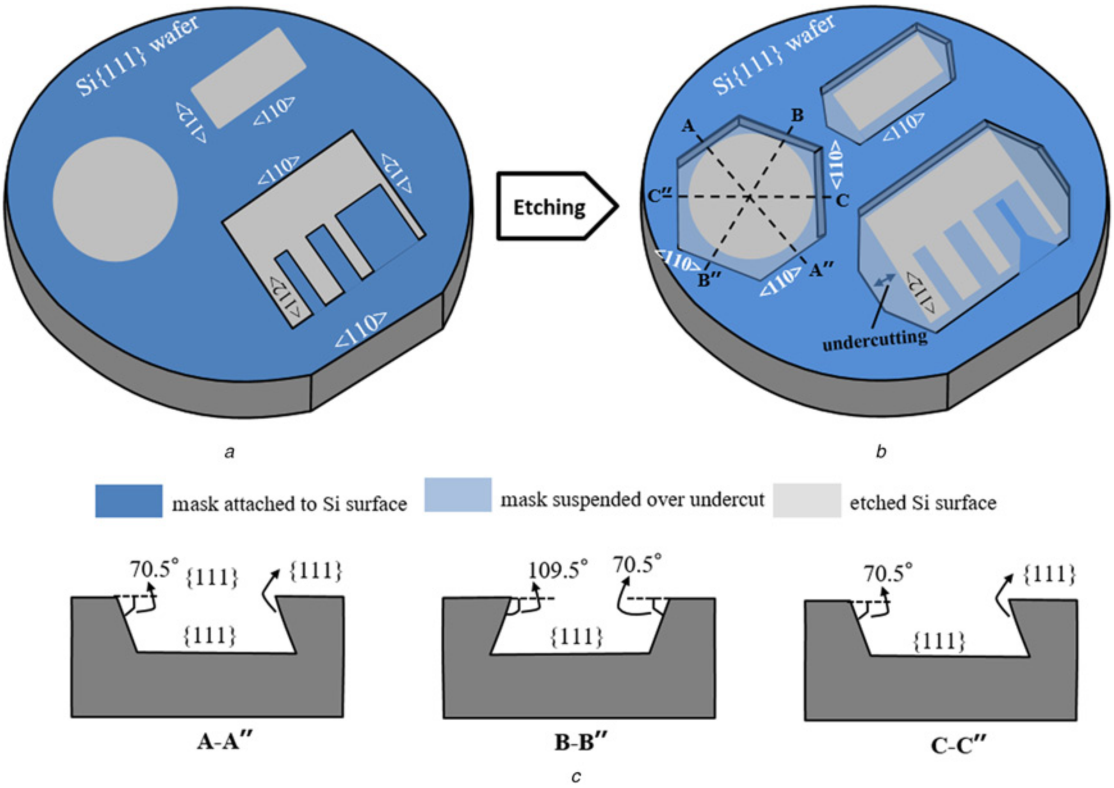

Fig. 1 *Schematic representation of the wet anisotropically etched profiles of different shapes mask geometries on Si{111} wafer*
a Mask pattern on wafer surface
b Etched profile after wet anisotropic etching
c Cross-sectional view of etched profiles. Undercutting at the mask edges aligned along ⟨112⟩ direction helps to remove the underneath material for the fabrication of freestanding structures (e.g. cantilever beams)

in pure and NH_2OH-added TMAH solution. Fig. 2 shows the etch rate of Si{111} without and with varying concentration of NH_2OH. The etch rate increases as the concentration of NH_2OH increases until saturation when the concentration reaches up to 10%. In pure alkaline solution (e.g. TMAH), water (H_2O) and hydroxyl ions (OH^-) play a vital role in the removal of silicon atoms. The maximum etch rate appears at intermediate concentration, where the OH^- and H_2O are in an optimal ratio (or an optimal balance) [8]. In the case of NH_2OH-added TMAH solution, NH_2O^-, OH^- and H_2O are the main species playing a key role in the removal of silicon atoms [23, 24]. The maximum etch rate is obtained when the concentration of NH_2OH is around 10%, which can be assumed as optimal concentration of NH_2OH in 5 wt% TMAH to obtain highest etch rate of silicon. As per the experimental results presented in Fig. 2, NH_2OH concentration affects optimal balance of main species and therefore the etch rate decreases if NH_2OH concentration is decreased/increased below/above 10%.

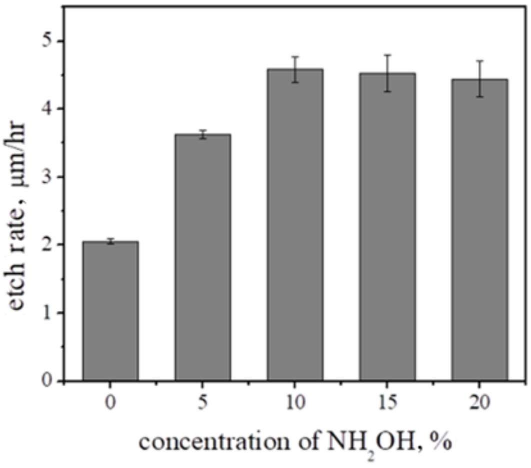

Fig. 2 *Etch rate of Si{111} in 5 wt% TMAH without and with varying concentrations of NH_2OH at 70 ± 1°C*

The main objective of the present study is to investigate the etching characteristics of Si{111} for the engineering applications of wet etching in MEMS. Therefore, the etching mechanism is not the main focus of this Letter. However, we have given a brief explanation about the most possible reason behind the increase of etch rate. In the presence of alkaline solutions, NH_2OH gives NH_2O^- ions and H_2O molecules. Thus, the reactive species, which are greatly accessible in NH_2OH-added alkaline solution, are NH_2O^- ions, OH^- ions and H_2O molecules [25–28]. As the number of reactive species in NH_2OH-added alkaline solution is more in comparison to that in pure alkaline solution, the etch rate significantly increases in the presence of NH_2OH. In addition to these species, other intermediate compounds (NH_2NHOH, HNO and NH_2O radical) may also participate in the etching reaction and might be helping to improve the etch rate.

The etched surface morphology is an important factor for optics-related applications. Fig. 3 presents the average surface roughness (R_a) and corresponding surface morphologies of the silicon samples etched in pure and various concentrations of NH_2OH-added TMAH. It is measured using 3D measuring laser microscope and the standard deviation is calculated by scanning $200 \times 200\ \mu m^2$ area at six different locations on the same chip. It can easily be noticed from the graphs that the low surface roughness is achieved in 10% NH_2OH-added TMAH solution, while further increment in NH_2OH concentration increases surface roughness, but lesser than that in pure TMAH.

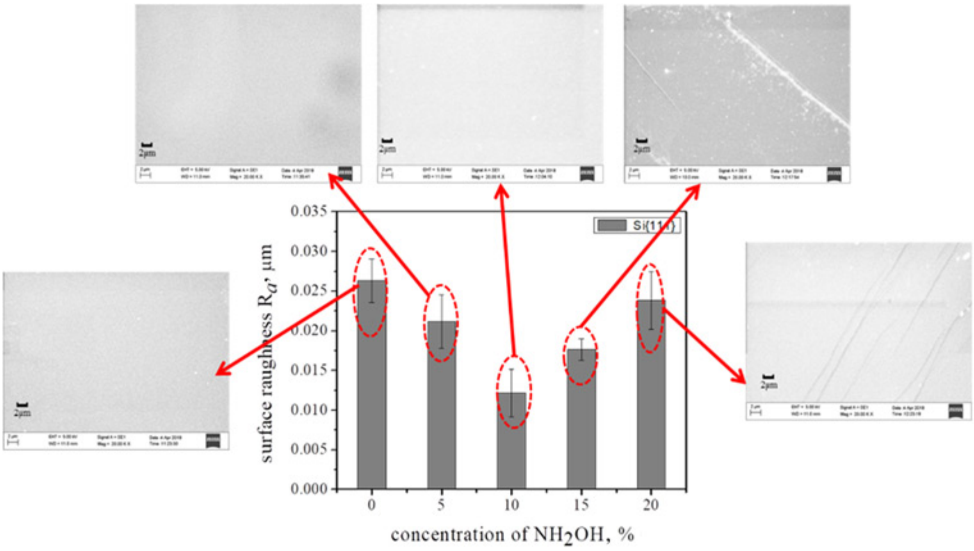

Fig. 3 *Etched surface roughness and morphology of Si{111} etched in 5% TMAH without and with different concentrations of NH_2OH at 70 ± 1°C*

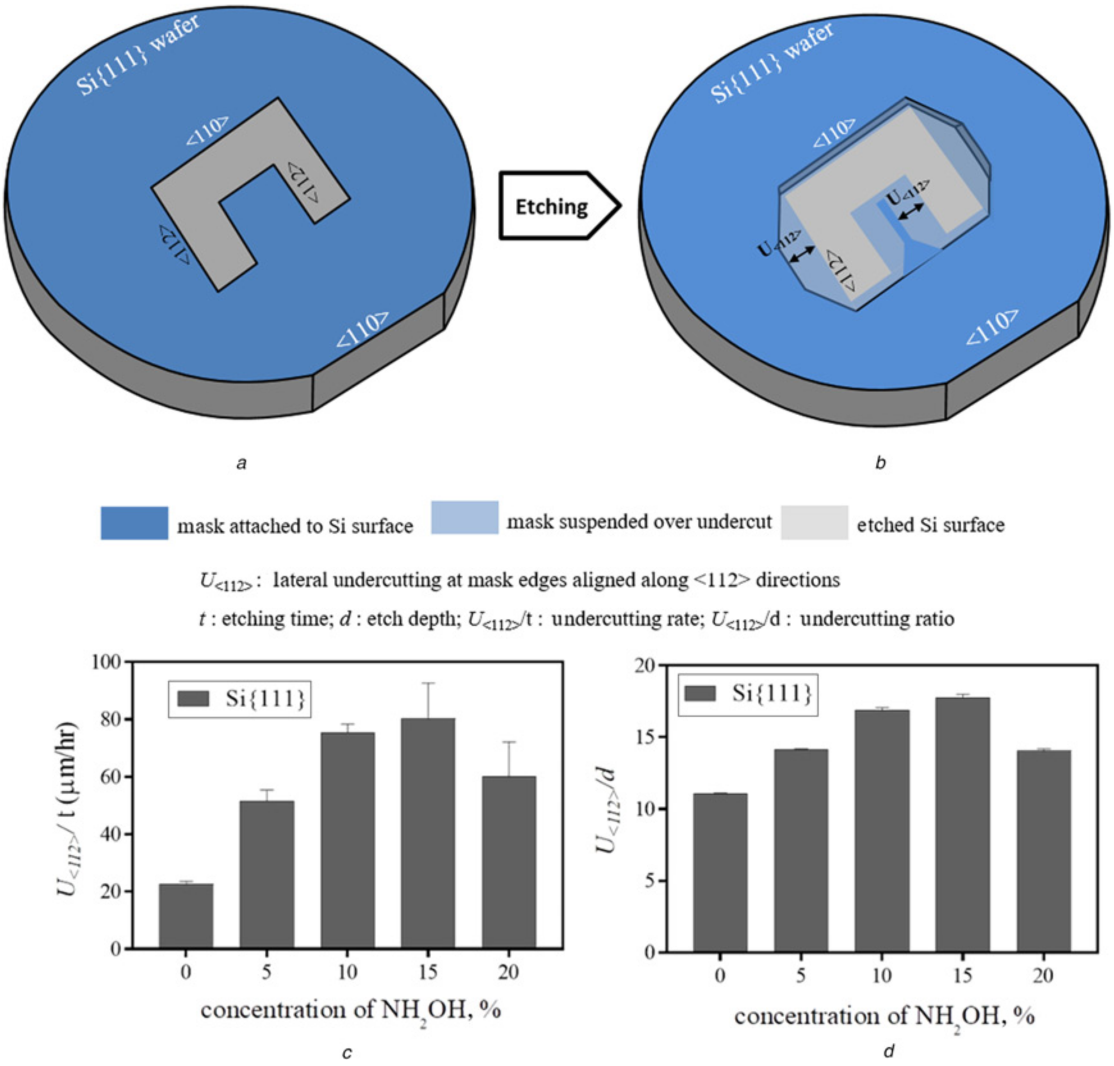

Fig. 4 *Undercutting at mask edges aligned along ⟨112⟩ direction on Si{111} wafer etched in 5 wt% TMAH without and with varying concentrations of NH_2OH at 70 ± 1°C*
a Mask pattern on wafer surface
b Etched profile after wet anisotropic etching
c Lateral undercutting rate
d Lateral undercutting ratio

Apart from etch rate and surface roughness, another important factor to be considered in silicon wet bulk micromachining for MEMS applications is undercutting for the removal of underneath material to release the microstructure from the substrate [29, 30]. In the fabrication of overhanging structures made up of materials such as SiO_2, Si_3N_4, undercutting is highly desirable to remove the underneath silicon. A lot of research has been done to study the undercutting on Si{100} and Si{110} wafer surfaces [29–50], but no study is performed on Si{111} wafer. Schematic view of lateral undercutting, undercutting rate and undercutting ratio at the mask edges aligned along ⟨112⟩ directions are presented in Fig. 4. It can easily be understood from Figs. 4*c* and *d* that the undercutting rate and undercutting ratio increase significantly with the increment of NH_2OH and get saturated at higher concentration of NH_2OH (i.e. 10% NH_2OH). As mentioned earlier, high undercutting is very useful for the fast release of the microstructure that increases productivity. The main reason behind the increase in undercutting on addition of NH_2OH is the same as explained for increase in etch rate, i.e. the reactive species increase on addition of NH_2OH that result in increase of the undercutting at mask edges.

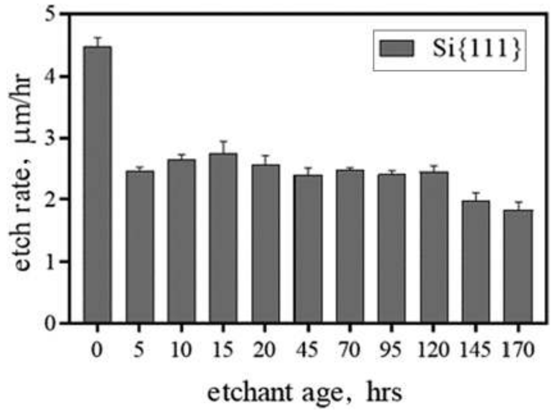

Fig. 5 *Averaged etch rate of Si{111} etched in 5% TMAH + 10% NH_2OH at 70 ± 1°C at different time interval in the same solution to study the effect of etchant ageing*

Hydroxylamine (NH_2OH) is unstable by nature in the presence of alkaline solutions [25–28]. Hence, it is important to study the behaviour of etchant ageing on the etching characteristics. As discussed in previous sections, 5 wt% TMAH with 10% NH_2OH is an optimal composition to achieve high etch rate and undercutting in comparison to pure TMAH. Hence, this composition is employed to study the ageing effect. In order to know the effect of etchant ageing on the etching characteristics of Si{111}, etching experiments are performed at different time interval in the same solution, which is used for 170 h. Figs. 5–7 present the etch rate, surface roughness and lateral undercutting rate at mask edge along ⟨112⟩ directions with increasing etchant age, respectively. It can be noticed from Figs. 5 and 7 that the etch rate and lateral undercutting reduces significantly with increasing etchant age. Fig. 6 shows the average surface roughness and the corresponding morphologies of the Si{111}. It can be seen from Fig. 6 that the surface roughness fluctuates within the sample in all cases. Since the etch rate and lateral undercutting is reduced with the age of the etchant, it can be recommended here that the NH_2OH-added solution should be used immediately to achieve high lateral undercutting for quick release of microstructures.

To demonstrate the application of high undercutting for the fabrication of MEMS structures, different kinds of SiO_2

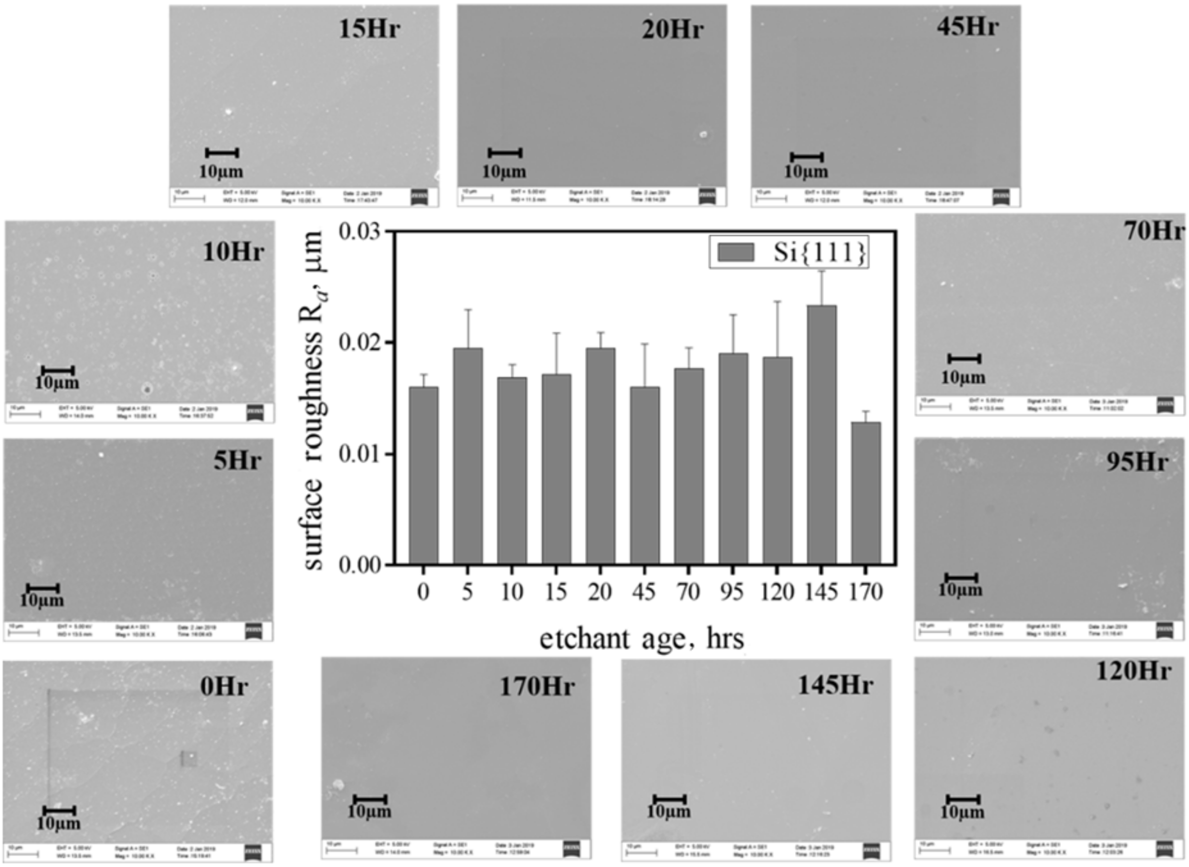

Fig. 6 *Etched surface roughness versus etchant ageing for Si{111} etched in 5% TMAH + 10% NH_2OH at 70 ± 1°C at different time interval in the same solution*

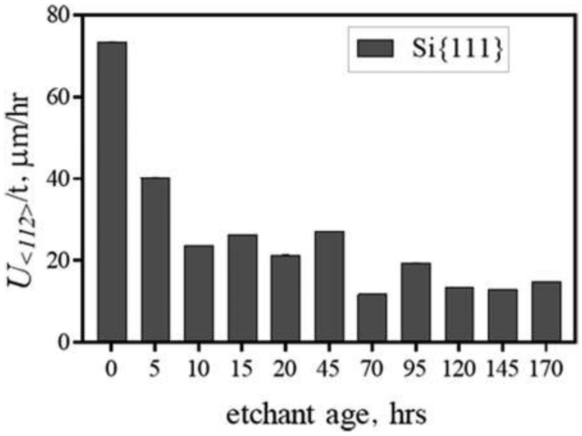

Fig. 7 *Lateral undercutting at ⟨112⟩ mask edges as a function of etching time (i.e. etchant ageing) in 10% NH_2OH-added 5 wt% TMAH at 70 ± 1°C*

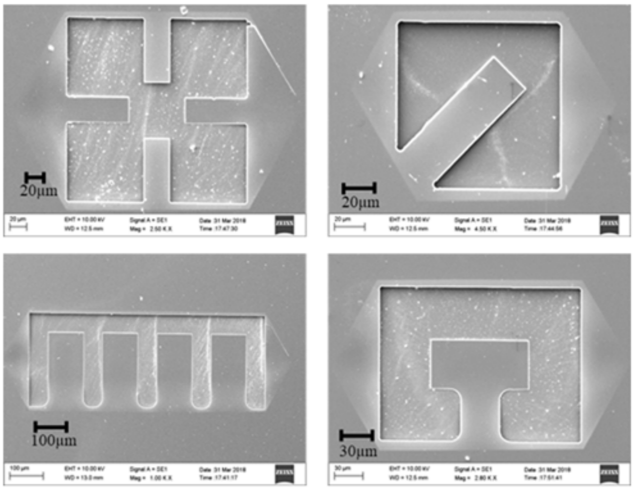

Fig. 8 *SEM micrographs of suspended SiO_2 microstructures on Si{111} released in 5 wt% TMAH + 10% NH_2OH*

microstructures are released in 10% NH_2OH + 5 wt% TMAH. SEM images of freestanding SiO_2 structures released in NH_2OH-added TMAH are shown in Fig. 8.

4. Conclusions: The etching characteristics of Si{111}, which is useful to fabricate simple and complex microstructures for MEMS applications, are investigated in low concentration TMAH without and with addition of reducing agent NH_2OH with varying concentrations (5–20% in step of 5%). The etchant is characterised by evaluating the etch rate, etched surface morphology and the lateral undercutting at mask edges aligned along ⟨112⟩ directions. 10% NH_2OH-added TMAH is an optimal choice to achieve high undercutting and smoother etched surface morphology. Significant increment in the undercutting in NH_2OH-added TMAH is a very useful characteristic for the fabrication of microstructures in less time that leads to the improvement in productivity. Furthermore, the effect of etchant ageing on the etch rate and etched surface roughness has been studied for 10% NH_2OH-added 5 wt% TMAH solution. The etch rate and lateral undercutting at mask edges are decreased with etchant age. However, the etchant ageing does not affect the surface roughness considerably. To the best of our knowledge, it is the first time, etching characteristics including lateral undercutting at mask edges are studied in NH_2OH-added TMAH for application in silicon wet bulk micromachining for the fabrication of microstructures.

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