Anisotropic etching in low-concentration KOH: effects of surfactant concentration

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Potassium hydroxide (KOH) provides high anisotropy between the Si{111} and Si{100} planes in comparison to tetramethylammonium hydroxide (TMAH). Moreover, the etch rate of Si{100} is higher in KOH than in TMAH, which is indispensable for high productivity to reduce the cost of end products. The etching study of pure and surfactant-added low-concentration KOH is presented. Triton X-100, with formula $C_{14}H_{22}O(C_2H_4O)_n$, where $n = 9$, 10, is used as the surfactant. This research focuses on the investigation of the effect of surfactant on the etching characteristics of low-concentration KOH. The value of the surfactant concentration ranges from 100 ppb to 1000 ppm and the etching temperature ranges from 60 to 76°C. The low-concentration KOH is selected because of its low cost and because of its use as an oxide layer and as an etch mask. Furthermore, the etchant is explored for the fabrication of silicon dioxide micromechanical structures. The addition of a small amount of surfactant reduces the undercutting at the convex corners. This property is explored to perform almost conformal etching to fabricate microstructures with minimum undercutting at mask edges and corners.

1. Introduction: In the fabrication of microelectromechanical systems (MEMS) using wet chemical silicon bulk micromachining, alkaline solutions, such as potassium hydroxide (KOH) [1–10], tetramethylammonium hydroxide (TMAH) [8–16] and ammonium hydroxide [17] are used. In addition to micromachining, alkaline solutions are employed for surface texturisation of monocrystalline silicon to reduce reflectance and to improve light trapping for high-efficiency silicon solar cells [18–20]. In alkaline solutions, TMAH and KOH are most widely used for wet anisotropic etching. TMAH solution is employed when CMOS compatibility is a concern and the thermal oxide is used as a masking layer [11–13]. To achieve a high etch selectivity of between {111} and {100} (i.e. $R_{\{111\}}/R_{\{100\}}$) and a significant etch rate of Si{100}, KOH is preferred over TMAH [4]. The maximum etch rate of Si {100} is observed at about 18 wt% concentration [5]. The etch rate decreases when the concentration of KOH is increased or decreased beyond this concentration. The etched surface morphology improves as concentration increases. A highly smooth surface is obtained at a concentration close to or more than 30 wt%. Silicon nitride shows excellent etching selectivity with silicon and is therefore preferred as the mask material if etching is carried out for longer periods. Thermally grown silicon dioxide, which is very convenient to deposit and pattern, can be used as an etch mask if etching is performed for a short period. The dissolution rate of oxide increases with the concentration of KOH solution [5].

Isopropyl alcohol (IPA) is often added into KOH to reduce the etch rate of {110} and high index planes (e.g. {221} {331}, {441} etc.} to minimise the undercutting at convex corners and to get 45° sidewalls at ⟨100⟩ mask edges [6, 10]. The addition of a small amount of surfactant also alters the etching characteristics of KOH solution [7, 21, 22]. In the fabrication of silicon microstructures, etch rate, etched surface morphology and corner undercutting are the major parameters considered while selecting an etchant. These parameters primarily depend on the concentration, type of additives and the etching temperature. A high-concentration KOH (i.e. about 30 wt%) is broadly explored for the fabrication of various kinds of MEMS components and to achieve a smooth surface morphology [5]. To use silicon dioxide as an etching mask and the structural layer for the fabrication of MEMS structures, the study of low-concentration KOH with and without additives is desirable.

In this Letter, the etching characteristics (e.g. etch rate, surface morphology, undercutting) of low-concentration KOH (5–10 wt%) with and without surfactant have been studied. The effect of surfactant concentration is investigated from ppb to ppm levels. This research is aimed at exploring the low-concentration KOH in silicon micromachining for MEMS applications.

2. Experimental: In this work, {100} and {110} oriented p-type Czochralski-grown silicon wafers of 4-inch diameter with 5–10 Ω cm resistivity are used. Thermally grown silicon dioxide of thickness of 1 μm is used to explore it as a mask and structural layer. Photolithography is employed to pattern the oxide layer. After patterning of the oxide layer, the wafer is diced into small chips of size 1×1 cm^2. KOH pellets are dissolved in deionised (DI) water to prepare 5 and 10 wt% KOH solutions. Triton X-100, with formula $C_{14}H_{22}O(C_2H_4O)_n$, where $n = 9$, 10, is used as the surfactant and its concentration in the etchant ranges from 100 ppb to 1000 ppm. All etching experiments are performed in a cylindrical container made of Teflon and equipped with a reflux condenser to prevent evaporation of the solution (or to avoid concentration change) during the etching process as shown in Fig. 1.

Each time 1 l of fresh etchant is used. The Teflon container is partially inserted into a constant temperature water bath. The etching is carried out at different temperatures from 60 to 76 ± 1°C without any agitation/stirring. In all experiments, the samples are held vertically in a PFA made chip holder containing multiple slots to etch many samples at a time to ensure the same etching conditions. Prior to immersion in the etchant, the samples are dipped in 1% hydrofluoric acid (HF) to remove native oxide and subsequently rinsed in DI water. After the etching process, the samples are thoroughly rinsed in DI water. To determine the etch rate of the thermal oxide layer, oxide thickness is measured using ellipsometry. Surface morphology, undercutting and etch depth are measured using three-dimensional (3D) measuring laser microscope.

3. Results and discussion: An anisotropic etchant is characterised by measuring various parameters, such as the etch rates of different

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Figure 1 *Constant temperature bath for anisotropic etching*

crystallographic planes and the masking layer, etched surface morphology and undercutting at the mask corners. The measurements of these parameters in pure and surfactant-added KOH are discussed in the following sections.

3.1. Etch rates of Si{100} and Si{110}: In MEMS fabrication, {100} and {110} wafers are commonly used. The study of the etch rates and the surface morphology of these orientations is significantly important from the point of view of applications. The etch rates of Si{100} and Si{110} in KOH of different concentrations with and without a wide range of surfactant

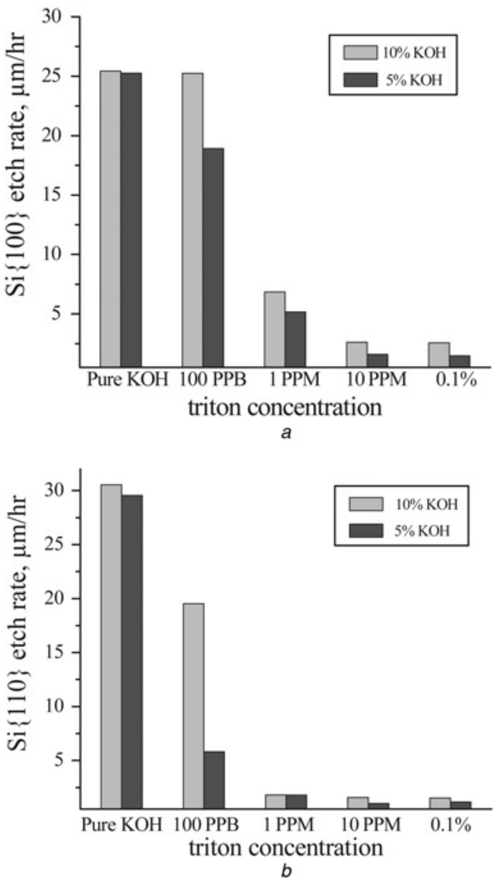

Figure 2 *Effect of the surfactant concentration on the etch rates of*
a Si{100}
b Si{110} in 5 and 10 wt% KOH at 60°C (surfactant concentration: 100 ppb–1000 ppm)

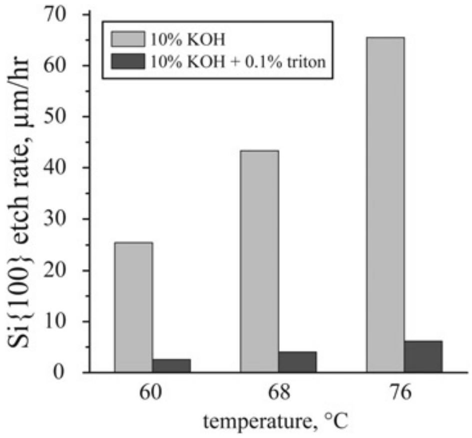

Figure 3 *Effect of the temperature on the etch rate of Si{100} in 10 wt% KOH without and with 0.1% v/v surfactant*

concentrations at 60°C are presented in Figs. 2*a* and *b*, respectively. It can be noticed that the etch rate of {110} in pure KOH is higher than that of Si{100}. The etch rate of individual orientation is almost the same in both concentrations (i.e. 5 and 10 wt%). However, the etch rate of both orientations (i.e. {100} and {110}) is reduced with an increase in the surfactant concentration. It is saturated when the surfactant concentration reaches equal to or greater than 10 ppm.

In several studies, it has been confirmed that the surfactant molecules adsorb at the solid–liquid interface [23–27]. These studies are performed in surfactant-added water and TMAH solutions. The adsorption of the surfactant at the silicon–etchant interface hampers the reaction between OH ions and silicon. As a result, less reactants reach the surface and the etch rate is strongly reduced. In other words, we can say that the reduction in the etch rate is mainly due to the adsorption of surfactant molecules on the surface being etched. Fig. 3 shows the etch rate of {100} silicon in pure and 0.1% v/v surfactant added 10 wt% KOH solution at different temperatures.

3.2. Surface morphology: The etched surface morphology is a major concern, especially in optical MEMS and for the high-efficiency solar cell. Fig. 4 shows the etched surface roughness and morphology of Si{100} in different concentrations of KOH solutions with and without varying concentrations of surfactant Triton-X-100. It can be noticed that the surface roughness decreases with increasing concentration of the surfactant. The surface is quite rough and full of hillocks in pure KOH solution, while it improves with increasing concentration of the surfactant. A highly smooth surface (roughness <5 nm) is obtained in 0.1% v/v surfactant-added KOH solution. The same trend is observed in the case of the Si{110} surface as presented in Fig. 5. Several papers have been published to report the main cause of surface roughness in the wet etching process. They explain that the micromasking by the hydrogen bubbles and/or impurities on the surface during the etching process are the major factors for worsening the surface roughness [5, 28]. The addition of surfactant to the etchant reduces the surface tension that results in high wetting capacity of the etchant. Increased wettability minimises the formation of bubbles attaching to the etched surface and thus provides a highly smooth surface [29–31].

3.3. Undercutting at convex corners: In bulk micromachined structures, two kinds of corners, namely concave and convex, are frequently encountered and their etching characteristics are completely opposite to each other. The convex corners in the mask patterns encounter significant lateral undercutting, while no

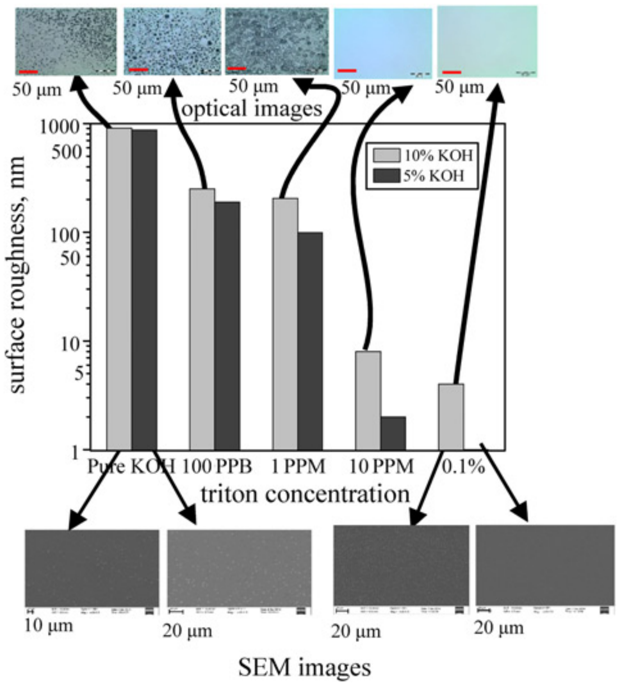

Figure 4 *Etched surface roughness of Si{100} in pure and surfactant-added KOH solutions at 60°C (etch time: 2 h)*

undercutting is observed at the concave corners. A significant amount of research has been done in this area. The undercutting at the convex corners plays a major role in the fabrication of freestanding structures. This process helps to remove the underneath material. The undercutting rate defines the release time and therefore should be sufficiently high to minimise the etching time for the complete release of the structure. The undercuttings measured along the ⟨110⟩ direction at the convex corner in different concentrations of KOH solutions with and without the addition of various surfactant concentrations are presented in Fig. 6. It can be noticed that 10 wt% KOH shows a

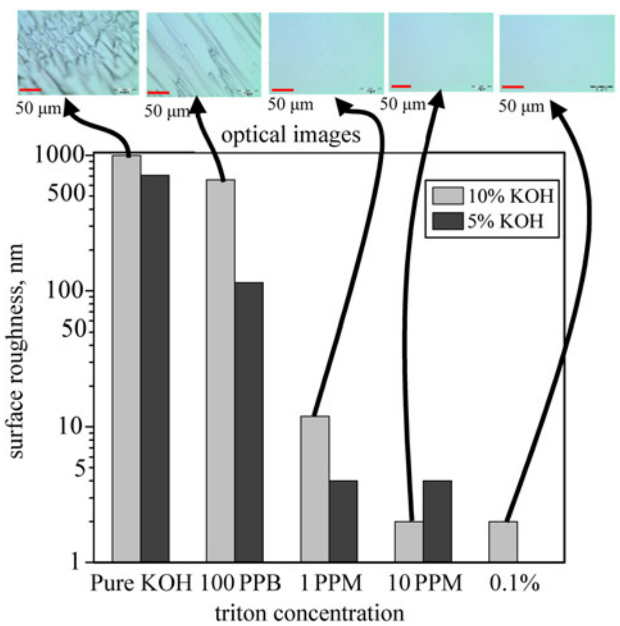

Figure 5 *Etched surface roughness of Si{110} in pure and surfactant-added KOH solutions at 60°C (etch time: 2 h)*

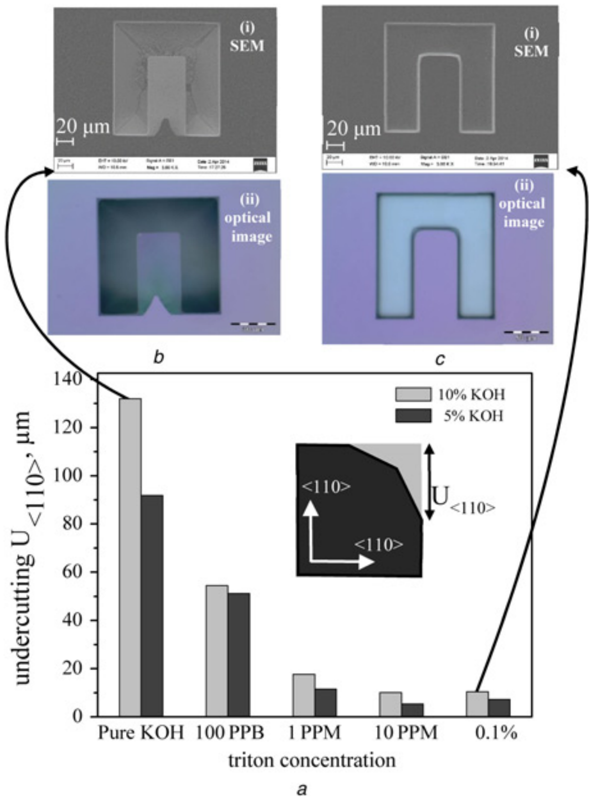

Figure 6 *Undercutting at the convex corners along ⟨110⟩ direction in pure and surfactant-added 5 and 10 wt% KOH at 60°C (surfactant concentration: 100 ppb–1000 ppm, etching time: 2 h)*

high undercutting in comparison to 5 wt% KOH. The undercutting has reduced to its minimum level when the surfactant is added to the etchant. The reduction in undercutting is significantly larger at the surfactant concentration equal to or greater than 10 ppm. The drastic decrease in undercutting at the convex corner can be explained in the same way as described in the previous section for the etch rate reduction. The undercutting at convex corners is controlled by vicinal {110} planes, namely, {331}, {441}, {221} and so on. These orientations are the examples of $\{h\ h\ 1\}$ and $\{h+2\ h+2\ h\}$ surfaces with $h \geq 3$ and $h \geq 2$, respectively [27, 32]. In other words, the undercutting at the convex corners occurs because of the appearance of high index planes [33]. The surfactant molecules form a dense layer on these types of orientations. This surfactant layer inhibits the etchant to react chemically with the silicon atoms that results in dramatic reduction in the etch rates of these orientations [10, 27–32]. The significant reduction in the etch rates of $\{h\ h\ 1\}/\{h+2\ h+2\ h\}$ planes suppress the undercutting at convex corners. In summary, the adsorption of surfactants on the silicon surface is believed to be responsible for modifying the etch rates, etched surface morphology and undercutting.

It can be easily concluded from Fig. 6 that the pure 10 wt% KOH is the best choice for the fast release of the suspended structures as it provides high undercutting, while surfactant-added solution is an appropriate choice for the formation microstructures with minimum undercutting as shown in Fig. 6*c*. If the pure KOH is used to realise the convex corners, a corner compensation method can be employed [33]. This method relies on a time-delayed etching of the convex corner through extra geometry. Fig. 7 shows the mesa structures fabricated using different kinds of compensation geometries. In the mask design, the sizes of the compensation structures were different and therefore the heights of mesa structures are not same. As can be seen from scanning electron microscope (SEM) images, none of the compensation design

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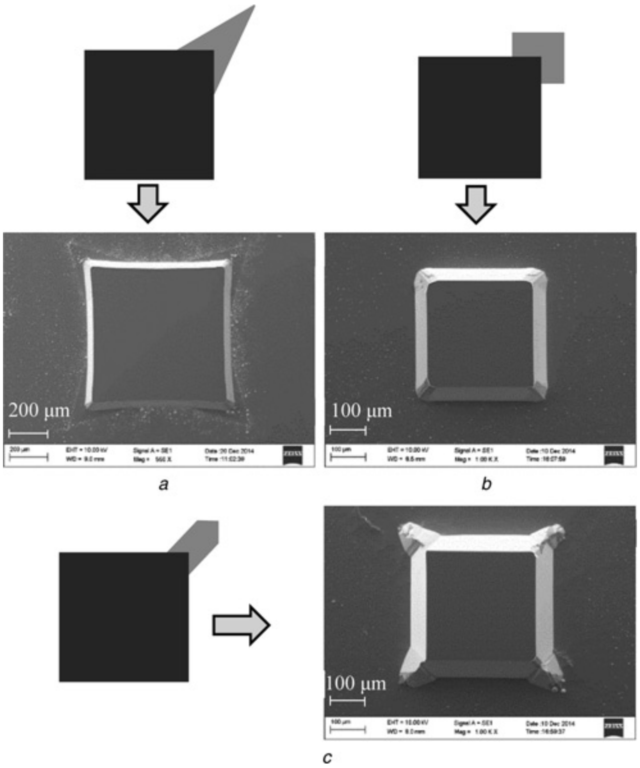

Figure 7 *Mesa structures fabricated in 10 wt% KOH by adding corner compensation patterns at convex corners*
a Triangular
b Square
c ⟨100⟩ beam

provides sharp-edged convex corners. However, the triangular shape geometry offers better shape corners.

3.4. Etch rate of thermal oxide: Thermally grown oxide is one of the best options for masking layer in anisotropic etching as it can be easily grown and patterned by photolithography followed by oxide etching in buffered HF (BHF). Since 10 wt% KOH provides high undercutting, the etch rates of oxide layer at different temperatures are studied in this etchant concentration with and without incorporation of 0.1% v/v Triton-X-100 and the results are shown in Fig. 8. The etch rate of SiO_2 increases with temperature, but is almost unaffected by the addition of surfactant. The etch rate selectivity between thermal oxide and Si {100} at various temperatures is presented in Fig. 9. It can be easily noticed that the etching selectivity is very high at low temperatures.

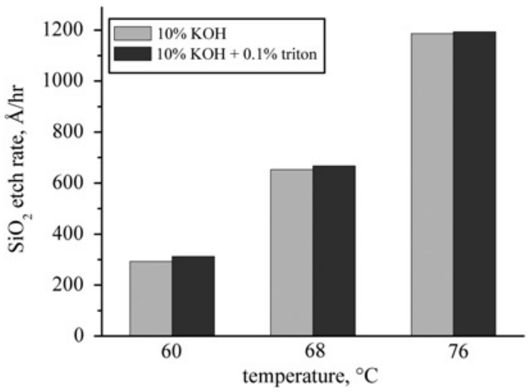

Figure 8 *Etch rates of SiO_2 in pure and 0.1% v/v Triton added 10 wt% KOH at different temperatures*

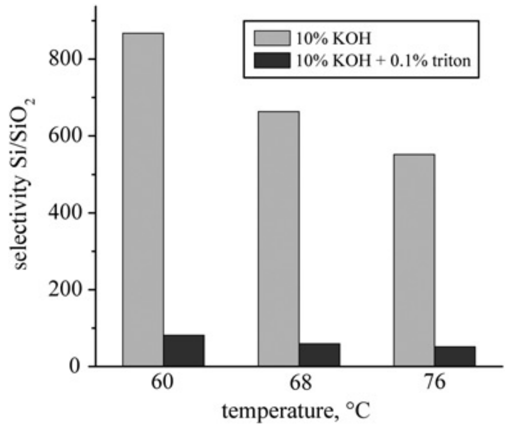

Figure 9 *Ratio of the Si and SiO_2 etch rates, determined from the data shown in Figs. 3 and 8*

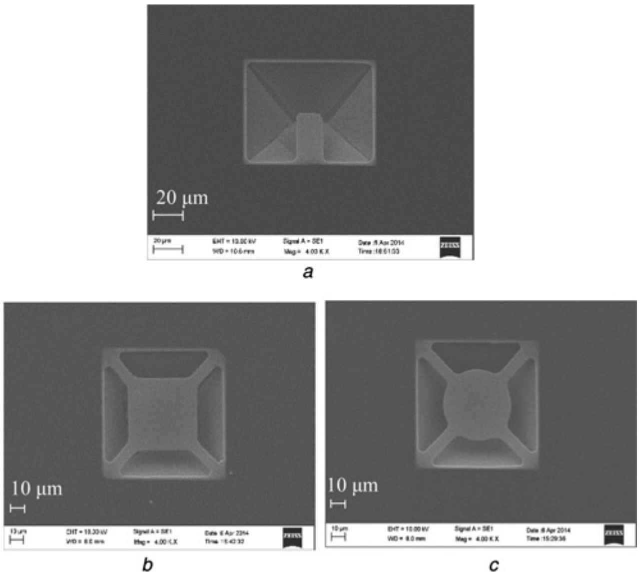

Figure 10 *Different shapes SiO_2 freestanding structures released in 10 wt% KOH*

After analysing the above characteristics, it can be concluded that 10 wt% KOH at 60°C is an optimal choice for the fabrication of SiO_2 freestanding structures, as this condition provides high etching selectivity and reasonably high etch rate of Si{100}. Fig. 10 shows suspended SiO_2 structures of various shapes fabricated in pure 10 wt% KOH at 60°C. It should be emphasised here that thermal oxide has an intrinsic compressive stress. This stress results in various effects on the released structures, such as cracking, deformation and strain [34, 35]. However, the bending of the structure due to the compressive stress depends on the type of structures. In some cases, it is relieved by the design, while in other cases it is too small to be clearly observed in SEM images. The same etching condition employed for the realisation of suspended structures can be used to fabricate the cavities/grooves using the SiO_2 as the mask layer. The surfactant-added KOH is most appropriate for the formation of microstructures with minimum undercutting at the corners as shown in Fig. 6*c*, but only for shallow depth as the etch rate of Si{100} is low in this composition. To fabricate microstructures with high etch depth and minimum undercutting, surfactant-added 25 wt% TMAH can be a better choice [29].

4. Conclusions: The etching characteristics of low-concentration KOH with and without a wide range of surfactant concentration are investigated for possible applications in silicon bulk micromachining for the fabrication of MEMS structures. The undercutting at convex corners and the etch rates of Si{100} and Si{110} are reduced to a considerably low level when a very small amount of surfactant is added to the KOH solution. However, the reduction in undercutting is disadvantageous for the fabrication of suspended structures; it is a desirous effect to fabricate microstructures with sharp corners. In this study, pure 10 wt% KOH at 60°C is explored for the fabrication of suspended oxide structures, while 10 wt% KOH + 0.1% v/v Triton-X-100 at 60°C is proposed to form microstructures with minimum undercutting.

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