Charge Transport in Uniform Metal-Assisted Chemical Etching for 3D High-Aspect-Ratio Micro- and Nanofabrication on Silicon

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Recently, metal-assisted chemical etching (MaCE) has been proposed as a promising method for micro- and nanostructures fabrication on silicon (Si) with high aspect ratio, high geometric uniformity and low cost. In MaCE, electron holes (h+) are injected into Si through catalytic reduction of H2O2 on metal catalyst thin film patterns. Si beneath the metal is etched through a redox reaction where h+ are involved. This work investigated a fundamental electrochemical process during MaCE: the transport of h+, and revealed its unique correlation with the 3D profile of the etching results. It is discovered that under the uniform etching condition, etching occurs both in the Si beneath the catalysts as well as on the sidewall of the etched space. On N-type Si, the sidewall etching is intrinsically depressed, and highly vertical HAR structures are formed; on P-type Si and undoped Si, the sidewall tapering becomes significant as the pattern number and density increase. The variation of the 3D profile can be explained by the CT during etching using a Schottky junction model, which show dependence on the intrinsic properties of the Si. CT involved in the two etching process can further be correlated by diffusion or drift of h+, which explains the influence of catalysts geometry.

Fabrication of micro- and nanostructures on silicon (Si) is a key step in manufacturing of modern electronic and optoelectronic devices. Especially, the high-aspect-ratio (HAR) structures, of which the vertical dimension is much larger than the lateral dimension, enable orders-of-magnitude higher integration density and superior system performance compared to that of traditional planar structures by utilizing the space inside Si. HAR structures, such as deep trenches and deep holes, have been widely used in advanced Si-based devices. For example, deep trenches are the core structures in the microelectromechanical systems; 4 deep holes serve as the interconnect routes in the emerging 3D integration technology in microelectronic packaging. 5 Most of these HAR structures are fabricated by selective removal of certain volume of Si from the bulk Si substrate, which is generally referred to as the etching of Si. Until now, the major applicable Si etching method for HAR structures fabrication is the deep reactive ion etching (DRIE). 3,4 In DRIE, Si is put in a gas chamber and etched by plasma. Although DRIE is able to fabricate a wide range of HAR structures, it is suffered from high cost. On the other hand, metal-assisted chemical etching (MaCE), a novel low-cost wet chemical etching method, has attracted attention from both academia and industry. 5,6 In MaCE, a thin layer of noble metal is deposited on top of Si. When the metal-loaded Si substrate is immersed in a hydrofluoric acid (HF)-hydrogen peroxide (H2O2) mixture solution, H2O2 is catalytically reduced on the metal surface and electron holes (h+) are generated. With the presence of h+, Si underneath the metal catalysts is etched by HF. MaCE for fabrication of HAR nanostructures on Si, such as nanowires, 9-16 nanogratings 17 and nanoparticles, 18 have been extensively studied. Recently, capability of MaCE in fabricating uniform micrometer-scale HAR structures was demonstrated. 19-22

The geometry of HAR structures in the 3D space plays the key role in the performance of the devices where they are involved. Thus, controllability over the 3D geometry of the etching profile (referred to as “3D profile” in the following discussion) is essential for any HAR Si etching method. In DRIE, the 3D profile can be controlled by the chemistry of plasma. 23 In MaCE for nanostructures fabrication (referred to as nano-MaCE), it has been reported that the 3D profile could be influenced by the etchant composition, 24 the doping type and doping level of Si substrates, 25 the chemistry in micro-MaCE is fundamentally different from nano-MaCE. Here we define ρ = [HF]/[HF] + [H2O2], where [HF] and [H2O2] are the concentration of HF and H2O2 in mol/L, respectively. In nano-MaCE, etchant with high ρ (generally, over 0.60) is preferred for high shape-transfer fidelity. 13 However, if micro-MaCE was conducted in such high-ρ etchant, deformation and disintegration of the catalysts were observed. 20 In order to obtain decent etching uniformity, ρ has to be lowered to ensure the stable movement of catalyst in micro-MaCE. The use of low-ρ etchant can be regarded as a uniform MaCE (UMaCE) condition. In the low-ρ etchant solution, the sidewall of the 3D profile can be either vertical or tapered. 20,21 In the context of MaCE for microstructures fabrication (referred to as micro-MaCE), controllability of the 3D profile has not been well studied.

In this work, we propose that under the UMaCE condition, the 3D profile in micro-MaCE can be correlated to the charge transport process during etching. Considering the fact that MaCE is essentially a redox reaction where electron holes (h+) are involved, the transport of h+ may critically influence the 3D profiles of MaCE. In this paper, we refer to the transport of h+ as the charge transport process (CT). To investigate the correlation between the CT and the 3D profile, the effects of two sets of “intrinsic” parameters are investigated in this work: the intrinsic property of the Si substrates and the geometry of the catalyst. A series of experiments under the UMaCE condition are conducted on Si substrates with different dopant type and doping level, straight-line shapes Au catalysts with different number of patterns, width and spacing distance are used in each experiment. Interestingly, the 3D profiles in these experiments show sharp contrast as presented below.

Experimental

All the Si substrates in this work were single crystalline with (100)-orientation from University Wafer, MA. The received Si was washed in Piranha solution (H2SO4 (96%wt): H2O2 (32%wt), volumetric ratio 1:1) at 120°C for 10 min and rinsed by deionized (DI) water. After dried in N2 gas, a layer of photoresist (Shipley S1813) was spin-coated onto the Si and exposed under 405 nm light in a Karl Suss Mask Aligner for photolithography. After developing in MF-319 developer (Shipley), the Si was cleaned by argon/oxygen plasma (Advanced Vacuum Vision RIE system). A layer of Au was then deposited by a Denton Explorer E-Beam evaporator at a rate of 0.5 Å/sec in a vacuum chamber of 3 × 10−6 Torr. The nominal thickness of all the Au film used in the work is 10 nm. Atomic force microscope (AFM) image of the Au film was collected from a Veeco Dimension Edge AFM system with a Si tip (Bruker MPP 11100-10). The Au-loaded Si substrates were cut into pieces (1 × 2 cm2 in lateral size) and directly immersed in HF-H2O2 etchant solution for MaCE of 10 min. Each piece contains one block of line-shaped patterns with same geometry, HF and H2O2 were provided by VWR International and directly used.

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without further processing. All the MaCE experiments were conducted in the mixture solution of 1.5 mol/L HF and 3.1 mol/L H₂O₂ in DI water with a total volume of 32 mL at room temperature with ambient light illumination. No significant effect of illumination was observed in the etching profile. It should be noted that the etching tests were done in a well-ventilated fume hood to avoid the hazard of HF to any personnel. After MaCE, the samples were rinsed by DI water and the photoresist was lift off by acetone. The etching results were observed under scanning electron microscope (SEM, Hitachi SU8010). For the cross sectional SEM images, Si samples were mechanically cleaved by a scriber along the direction that was perpendicular to the line patterns. Au layer is not removed because it is too thin (only ~10 nm) to make any difference in the SEM images that describe the overall geometry of etching profile. In the real application where Au needs to be removed, Au can be facilely removed by immersion in potassium iodide (KI, 10.0 wt%)/iodine (I₂, 2.5 wt%) aqueous solution needs to be removed, Au can be facilely removed by immersion in potassium iodide (KI, 10.0 wt%)/iodine (I₂, 2.5 wt%) aqueous solution.

### Results and Discussion

As listed in Table I, n-type and p-type doped Si with resistivity are labeled as N-Si and P-Si for the convenience of discussion. Undoped Si is named as U-Si, while the heavily doped n-type and p-type Si are named as (N⁺)-Si and (P⁺)-Si. To study the effect of Si type and catalyst geometry, all the other experimental conditions were strictly fixed as described in the Experimental section, including the catalyst thickness and morphology, etchant solution composition and volume, etching time, temperature and etc. The overall processing flow is illustrated in Scheme 1. At the initial step, blocks of line patterns are transferred onto Si by photolithography. Each block contains a certain number (n) of parallel line patterns (“lines” for short) with the same line width \( w_0 \) and line spacing distance \( s \). Each block is named by its \( n \), \( w_0 \) and \( s \) value in the format of \( w_0 \times n@s \). Within the lines, bare Si surface is exposed; while the Si surface outside the lines is covered by photoresist. The photoresist has been proven to block the etching of Si in MaCE of 2 hr. After deposition of Au, only the Au in the line pattern (referred to as “Au lines”) is in direct contact with Au, while the Si surface are covered by photoresist in other darker area (the same in the following images); (b) a 2 \( \mu \text{m} \times 1 \text{ pattern}; (c) magnified image of the red-circled area in (b), showing the smooth edge of photoresist; (d) magnified image of the red-circled area in (c), showing the nanoporous morphology of Au catalysts; (e) a 5 \( \mu \text{m} \times 1 \text{ pattern}; (f) a 10 \( \mu \text{m} \times 1 \text{ pattern.}

#### Table I. IDs, dopant type and doping level of the Si substrates used in this work.

| Substrate ID | Dopant     | Resistivity (Ω cm) | Doping Density (cm⁻³)⁶ |
|--------------|------------|--------------------|------------------------|
| U-Si         | Undoped    | >3000              | <10¹³                  |
| P-Si         | Boron      | 1–10               | 10¹⁵–10¹⁶             |
| N-Si         | Phosphorus | 1–10               | 10¹⁵–10¹⁵             |
| P(+) Si      | Boron      | 0.001–0.005        | 10¹⁵–10²⁰             |
| N(+) Si      | Phosphorus | 0.007–0.020        | 10¹⁹–10³⁹             |

⁶The doping density is estimated from the resistivity using the table in Ref. 31.

![Figure 1.](image-url) **Figure 1.** Top-view SEM images of Si sample after photolithography and Au deposition: (a) a 2 \( \mu \text{m} \times 5@20 \) \( \mu \text{m} \) pattern. The brighter area are the Si that are in direct contact with Au, while the Si surface are covered by photoresist in other darker area (the same in the following images); (b) a 2 \( \mu \text{m} \times 1 \) pattern; (c) magnified image of the red-circled area in (b), showing the smooth edge of photoresist; (d) magnified image of the red-circled area in (c), showing the nanoporous morphology of Au catalysts; (e) a 5 \( \mu \text{m} \times 1 \) pattern; (f) a 10 \( \mu \text{m} \times 1 \) pattern.
0.2 μm. The real thickness of Au catalyst on all Si is measured to be 13.3 ± 0.5 nm by AFM. Nanoporous morphology of the Au catalyst can be observed under high-magnification SEM (Figure 1d). These nanopores allow the access of HF to remove the oxidized Si beneath the Au catalyst, which also ensures the uniformity of MaCE.20

After MaCE, Au was found moving vertically into the Si and deep trenches were formed. Cross-sectional SEM images of the etching profile on U-Si. The name of blocks are labeled on top of each corresponding figure. All the scale bars have a length of 5 μm.

Figure 2. Cross-sectional SEM images of the etching profile on U-Si. The name of blocks are labeled on top of each corresponding figure. All the scale bars have a length of 5 μm.

Several trends can be derived from Figure 5: (a) for P-Si and U-Si, with keeping the same decreasing trend against n-Si (Figure 5e); (b) for P-Si and U-Si, while showing little dependence on n on P-Si (Figure 5c); (c) for P-Si in MaCE of the blocks which contain 50 lines with w₀ of 2 μm, ∆w₁ sharply decreases with the increasing s on P-Si and U-Si (Figure 5f); (e) as shown in Figure 5e and Figure 5f), if the w₀ increases to 5 μm and 10 μm while keeping n = 50, the absolute value of ∆w₁ also increases accordingly on P-Si and U-Si, with keeping the same decreasing trend against s. However, with the same s, ∆w₁(P-Si) > ∆w₁(U-Si). For N-Si, ∆w₁ remains much lower than U-Si and P-Si through Figures 5c to 5f, and showing little dependence on n, s and w₀.

To understand these trends, it is necessary to review the chemistry of MaCE. In MaCE, the chemical reactions can be written as:

\[ \text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + 2\text{H}_2\text{O} + 2\text{H}^+ \]  \hspace{1cm} [1]

\[ \text{SiF}_2 \cdot \text{HF} \rightarrow \text{SiF}_6^{2-} + 6\text{H}^+ \]  \hspace{1cm} [2]

From Eq. 2, HF and h⁺ can be identified as the chemical species that directly induce the etching. Thus, the 3D profile is related to the distribution of HF and h⁺ in the 3D space. In this regard, an orthogonal Cartesian coordination system is established where the origin is set at the geometric center of a line, and the y and z axis are set along the line and perpendicular to the Si surface, respectively (Figure 8a). The etching rate at position (x, y, z) and time t can be expressed as a vector \( \vec{r} \):

\[ \vec{r} \cdot \left( x, y, z, t \right) = C \cdot \text{c}_{\text{HF}}(x, y, z, t) \cdot \text{c}_{\text{H}^+}(x, y, z, t) \]  \hspace{1cm} [3]

Where \( \text{c}_{\text{HF}}(x, y, z, t) \) and \( \text{c}_{\text{H}^+}(x, y, z, t) \) are the concentration of HF and h⁺ at position (x, y, z) and time t, respectively; while C, a and
Figure 3. Cross-sectional SEM images of the etching profile on P-Si. The name of blocks are labeled on top of each corresponding figure. All the scale bars have a length of 5 μm.

Figure 4. Cross-sectional SEM images of the etching profile on N-Si. The name of blocks are labeled on top of each corresponding figure. All the scale bars have a length of 5 μm.
$b$ are constants to be determined. The vector $\vec{r}$ is the unit vector that points to the direction of the $h^+$ movement. We further set the start time of MaCE as $t = 0$. At $t = 0$, $\vec{r} 
abla (x, y, z, 0) = 0$. Since $\Delta w_1$ is larger than 0 in all the etching results, the trenches width after etching is always larger than $w_0$. The increase in $w$ during MaCE indicates that the Si both beneath the Au catalysts and on the sidewall are etched. We refer to these two etching processes as the vertical etching and sidewall etching. Conceivably, $d$ and $\Delta w_1$ can be related to the reaction rate of vertical etching and sidewall etching, i.e. the components of $\vec{r}$ along the $z$- and $x$-axis:

$$|\vec{r}_z (x_b, y_b, z_b, t)| = \frac{\Delta V_z}{\Delta t} = \frac{(w \cdot l) \cdot \Delta d}{\Delta t}$$

$$= C \cdot c_{HF}(x_b, y_b, z_b, t) \cdot c_{HF} (x_b, y_b, z_b, t)^b$$ \[4\]

$$|\vec{r}_x (x_b, y_b, z_b, t)| = \frac{\Delta V_x}{\Delta t} = \frac{(l \cdot d) \cdot \Delta w}{\Delta t} = \frac{\Delta w_1}{\Delta t}$$

$$= C \cdot c_{HF}(x_b, y_b, z_b, t) \cdot c_{HF} (x_b, y_b, z_b, t)^b$$ \[5\]

where $w$, $l$ and $d$ are the dimension along $x$, $y$ and $z$ axis, $V$ is volume of Si being etched, while $\Delta d$, $\Delta w$ and $\Delta V$ are the infinitesimal increase in $d$, $w$ and $V$ within the infinitesimal time period $\Delta t$, $(x_b, y_b, z_b)$ and $(x_b, y_b, z_b)$ refer to the arbitrary positions at the bottom of the etching profiles (i.e. the Au-Si interface) and on the sidewall, respectively. It has been demonstrated that under current UMaeC condition, $|\vec{r}_z|$ is constant within 10 min.\[9\] Then we can assume that the vertical etching is under a steady state: $c_{HF}(x, y, z, t)$ and $c_{HF}(x, y, z, t)$ in Eq. 5 are constant over time. For HF, since the initial concentration of HF equals to that in bulk solution, then:

$$c_{HF}(x, y, z, t) = c_{HF}(x, y, z, 0) = 1.5 \text{ mol/L}$$ \[6\]

Eq. 6 means that during the MaCE within 10 min, although the Au catalyst keeps moving into Si substrate, the etchant solution can quickly flow into the etched space above Au and a steady state is established within every infinitesimal time period, so that the local concentration of HF at the Au–Si interface maintains the constant value. It is conceivable that the $c_{HF}(x, y, z, t)$ in Eq. 5 also equals to $c_{HF}(x, y, z, 0)$, since the sidewall and Au-Si are subjected to the same etchant solution.
Figure 6. (Top) Cross-sectional SEM images of the etching profile in 10 μm × 50@50 μm block on N(+)-Si with magnified image detailing the red-circled area; (Bottom) cross-sectional SEM images of the etching profile in 2 μm × 50@50 μm block on P(+)Si with magnified image detailing the red-circled area.

To further confirm the steady state of MaCE within 10 min, a study on the evolution of etching depth (d) over etching time (t) in MaCE of 2 μm × 1 pattern on N-Si is conducted. The d-t curve is shown in Figure 7. The solution is kept at static state without agitation. Within the etching time of 10 min, the etching keeps constant. The result is consistent with our previous results of MaCE on circular patterns with diameter of 30 μm. At the point of t = 15 min, the etching rate starts to drop. At the point of t = 40 min, the etching rate significantly dropped. It should be noted that the consumption of the etchant solution is negligible over the MaCE of 40 min. To confirm this point, we immersed a 2 μm × 1 sample in the etchant solution after MaCE of 40 min, the etching rate is identical to that in MaCE with freshly prepared etching solution. In contrast, in our previous etching experiment of 2 μm × 1 pattern, an etching depth of 32 μm is reached after MaCE of 40 min with stirring of the etching solution, much higher than the depth here in the static etching solution. These facts indicate that within 10 min, MaCE is reaction-controlled, while the process becomes diffusion-controlled as the etching proceeds. One of the probable factors that cause the transition is that as the etching proceeds, the aspect ratio of the etched trench is increasing and the difficulty of HF and H₂O₂ molecules diffusion to the etching front, i.e. the Au-Si, is also increasing. By agitation of the solution, the diffusion of HF and H₂O₂ can be promoted and a higher etching rate over long-time etching can be achieved. The reaction-controlled mechanism validates the assumption that HF concentration inside the etching profile keeps constant within 10 min (Eq. 6).

If we assume that the etching is homogeneous along the y-axis, we can focus our study of etching rate on a 2D plane that is perpendicular to the y-axis (i.e. the x-z plane). Then Eqs. 4 and 5 can be simplified to:

\[
\frac{\partial}{\partial z} (x_b, z_b, t) = \frac{w_0 \cdot \Delta d}{\Delta t} = \frac{w_0 \cdot d}{t} = C \cdot c_{HF}(x_b, z_b, t)^a \cdot c_{H_2O_2}(x_b, z_b, t)^b = C_1 \cdot c_{HF}(x_b, z_b, t)^a
\]

Where \(C_1\) is a constant. Eqs. 7 and 8 show that under the UMaCE condition where the vertical etching is in steady state, the 3D profile is only related to the \(c_{HF}(x, z, t)\), which is determined by CT during MaCE.

It should be noted that in the HF-H₂O₂ etching solution, HF will undergo the following reaction:

\[
\text{HF} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{F}^-, \quad K_1 = \frac{[\text{HF}] [\text{F}^-]}{[\text{HF}]} \quad \text{(9)}
\]

\[
\text{HF} + \text{F}^- = \text{HF}_2^-, \quad K_2 = \frac{[\text{HF}_2^-]}{[\text{HF}] [\text{F}^-]} \quad \text{(10)}
\]

where \(K_1\) and \(K_2\) are the equilibrium constant of Eqs. 9 and 10, respectively. \([\text{HF}]\), \([\text{F}^-]\), \([\text{HF}_2^-]\) refer to the activity of the corresponding species. Thus the fluoride species that are actually involved in the dissolution of oxidized Si (Eq. 2) may contain HF, F⁻ and HF⁻. To qualitatively evaluate the effect of fluoride species concentration distribution, we did the MaCE on N-Si in etchant solution with H₂SO₄, NH₄•H₂O and NH₄F as additives, respectively. We adopted the value of 1.3 × 10⁻³ and 0.104 for \(K_1\) and \(K_2\), respectively, at the ionic strength of 1 M. Here we neglect the change of these value over the ionic strength in the solution, and substitute all the activity terms with concentration in the expression of \(K_1\) and \(K_2\). Then the two values can be used to estimate the concentration of each fluoride species. It has been reported that in HF solution with concentration over 1 M, some polymer of HF (HF)ₙF⁻, \(n = 2–6\) can be formed. Here the formation of HF is not taken into account to simplify the calculation of fluoride species concentration. Due to the low acidity of H₂O₂, the contribution of H⁺ from H₂O₂ is also neglected. The calculated concentration of etching solution is listed in Table II. In the etchant solution used in the aforementioned MaCE experiments without any additives, the majority fluoride species is HF. With addition of H₂SO₄, the c(HF) slightly increase, while c(HF⁻) and c(F⁻) sharply decrease. The etching depth slight decreases with the addition of H₂SO₄. However, the etching depth has a significant increase with the addition of NH₄•H₂O or NH₄F, where c(H⁺) decreases but c(HF⁻) and c(F⁻) increase. The results may be explained by the fact that HF⁻ dissolves the oxidized Si much faster than HF. Considering the fact that H⁺ is also involved in the reduction of H₂O₂ (Eq. 1), the relation between c(H⁺) and etching depth indicates that the dissolution of oxidized Si (Eq. 2) may be the rate limiting step in MaCE. In order to simplify the following discussion, however, the term HF is used to represent all the fluoride species. This generalization of terminology will not impair the validity of the conclusion derived from the data in Figure 5, because all the etching experiments are conducted in the etchant solution with the same composition.
CT in vertical etching and sidewall etching are illustrated in Figure 8a and labeled as CT1 and CT2, respectively. To study the \( c_{h}(t) \) in CT1 and CT2, the source of \( h^+ \) needs to be clarified first. Although it has been reported that the bare Si surface without the coverage of metal could also be etched in HF-H\(_2\)O\(_2\), its etching rate is on the order of 0.1–1.0 nm/min,\(^{28}\) which is negligibly small compared to that of MaCE. Thus, \( h^+ \) in CT1 is primarily originated from the catalytic reduction of H\(_2\)O on Au surface (Eq. 1). It follows that in CT1 \( h^+ \) is transported from Au to Si, rather than from etchant solution to Si. It has long been known that CT through a metal-semiconductor interface can be described by the Schottky junction model.\(^{29}\) In the context of vertical etching, metal and semiconductor correspond to Au and Si, respectively. Since \( h^+ \) are transported from Au to Si, Si can be regarded as negatively biased against Au (Figure 8a). The negative bias raises up the energy level of both the valence band and conduction band of the Si, regardless of its doping type. For N-Si, the negative bias favors the transport of \( h^+ \) from Au to Si (referred to as a “forward bias” for N-Si); for P-Si, however, the negative bias increases the difficulty in the \( h^+ \) transport (referred to as a “reverse bias” for P-Si).\(^{6,29}\) Then \( c_{h}(t) \) in Eq. 7 follows the order of: \( c_{h}(t)_{(P-Si)} < c_{h}(t)_{(U-Si)} < c_{h}(t)_{(N-Si)} \). Accordingly, we have \( d(P-Si) < d(U-Si) < d(N-Si) \), which is consistent with the results in Figure 5a.

Regarding CT2, etching on the sidewall have been attributed to the dissolution and redeposition process of metal catalyst in literature about nano-MaCE where silver (Ag) was used as the catalyst.\(^{25,30}\) It was assumed that Ag at the bottom of the etching profile could be partially dissolved by HF-H\(_2\)O\(_2\) and redeposited on the sidewall. Once deposited by Ag, \( h^+ \) is transported from Ag to Si by a process similar to that in CT1. In the present work, if the sidewall etching is induced by the dissolution and redeposition of Au, CT2 should resemble CT1 and the variation of \( \Delta u \) should be the same as that of \( d \). However, as can be clearly observed in Figure 5b, the order of \( \Delta u \) follows the order of: \( \Delta u \) (P-Si) < \( \Delta u \) (N-Si) < \( \Delta u \) (U-Si); in Figures 5c–5f, the order of \( \Delta u \) (P-Si) < \( \Delta u \) (N-Si) < \( \Delta u \) (U-Si) holds. Both trends are in sharp contrast to that of \( d \). Then the charge transport from Au to Si can be excluded in CT2. As mentioned before, under the UMaCE condition, low-\( \rho \) etchant is used and the \( h^+ \) generated from H\(_2\)O\(_2\) on Si surface cannot be completely consumed by the vertical etching process. The excessive \( h^+ \) from Au have a chance to be transported to the sidewall and induce the sidewall etching. In this sense, contrary to the vertical etching, the sidewall etching is a pure electrochemical process as described in Eq. 2, where \( h^+ \) are transported from Si to the etchant solution. Under this condition, Si is positively biased against the etchant solution. The process resembles the well-known electrochemical etching of Si. The electrochemical etching could also be described by a Schottky junction model.\(^{31,32}\) Here a positive bias is a forward bias for P-Si but a reverse bias for N-Si. Thus, in the sidewall etching the transport of \( h^+ \) is favored on P-Si but suppressed on N-Si. To further confirm this point, electrochemical etching experiments were conducted to mimic the sidewall etching process. Bare Si were connected to a potentiostat as the working electrode and immersed in a 1.5 mol/L HF\(_2\)O\(_2\) solution. A linear-increasing voltage was applied to the bare Si and the corresponding current density value was recorded. Given the fact that the doping level of N-Si and P-Si are similar, this result is also consistent with the results above. However, when the voltage is scanned from \(-1.0\) V (vs. Pt counter electrode) toward +4.0 V, current density increases sharply after the voltage passes \(-0.2\) V. In contrast, for N-Si, no significant current density can be observed within the scan range. Given the fact that the doping level of N-Si and P-Si are similar, this result is also consistent with the results above.

### Table II. Concentration of fluoride species and corresponding etching depth.

| Test# | Additive   | Conc. (M)\(^a\) | \( \langle H^+ \rangle/M \) | \( \langle HF \rangle/M \) | \( \langle HF_2^- \rangle/M \) | \( \langle F^- \rangle/M \) | Depth (\( \mu \)m)\(^b\) | Std. Dev\(^c\) |
|-------|------------|-----------------|---------------------------|---------------------------|---------------------------|---------------------------|-----------------|------------|
| 1     | None       | 0.000           | 0.048                     | 1.506                     | 0.006                     | 0.041                     | 8.00            | 0.13       |
| 2     | H\(_2\)SO\(_4\) | 0.064           | 0.09                      | 1.531                     | 0.004                     | 0.022                     | 7.39            | 0.45       |
| 3     | H\(_2\)SO\(_4\) | 0.319           | 0.326                     | 1.552                     | 0.001                     | 0.006                     | 7.15            | 0.23       |
| 4     | H\(_2\)SO\(_4\) | 0.638           | 0.641                     | 1.556                     | 0.001                     | 0.003                     | 7.50            | 0.19       |
| 5     | NH\(_3\) H\(_2\)O | 0.232           | 0.008                     | 1.292                     | 0.028                     | 0.211                     | 10.01           | 0.29       |
| 6     | NH\(_3\) H\(_2\)O | 0.463           | 0.003                     | 1.048                     | 0.046                     | 0.421                     | 11.92           | 0.49       |
| 7     | NH\(_3\) H\(_2\)O | 1.390           | 1.40E-04                  | 0.149                     | 0.021                     | 1.369                     | 12.52           | 0.57       |
| 8     | NH\(_4\)F  | 0.134           | 0.015                     | 1.524                     | 0.02                      | 0.129                     | 9.01            | 0.34       |
| 9     | NH\(_4\)F  | 0.445           | 0.001                     | 1.498                     | 0.061                     | 0.385                     | 10.84           | 0.22       |
| 10    | NH\(_4\)F  | 0.890           | 0.002                     | 1.441                     | 0.116                     | 0.777                     | 12.95           | 0.34       |

\(^a\)The concentration of additive molecules. For H\(_2\)SO\(_4\) as the additive, the pK\(_{a2}\) for the second proton dissociation is 1.99, \(-10\) times higher than pK\(_{a1}\) of HF; thus it is assumed that the H\(_2\)SO\(_4\) molecules completely dissociate and provide two protons per molecules; for NH\(_3\) H\(_2\)O as the additive, the pK\(_{a}\) of NH\(_3\) is 4.75, it is assumed that all the NH\(_3\) H\(_2\)O molecules is bonded with protons in the solution; for NH\(_4\)F as the additives, it is assumed that all NH\(_4\)F dissociate into NH\(_4^+\) and F\(^-\) ions. The pK\(_{a}\) and pK\(_{a2}\) values mentioned above can be found in Ref. 37;\(^b\)Depth of etching profile averaged from 5 independent tests on N-Si under the same condition as those used in Figs. 2–4;\(^c\)Standard deviation of etching depth in \( \mu \)m.

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**Figure 8.** (a) Schematic charge transport process during MaCE. CT1: charge transport from Au to the Si beneath; CT2: charge transport from Si on the sidewall to the etchant solution; (b) current density-voltage curve of bare Si substrates as the working electrode in 1.5 mol/L HF aqueous solution.
the result supports the point that once a positive bias is applied, h^+ can be favorably transported from P-Si to HF solution, while h^+ transport from N-Si to HF solution is intrinsically suppressed. It is observed that the current density of U-Si is also low, which may be attributed to the low doping level of U-Si (Table 1). For P(+) and N(-)-Si, however, due to a high doping level, h^+ can easily tunnel through the Si-HF solution interface regardless of the dopant type, thus their current density increases faster than P-Si.39 During MaCE of the heavily doped Si, the tunneling process not only induces sidewall etching, but also makes the Si between trenches highly porous on both substrates (Figure 6), which is consistent with results from previous reports of electrochemical etching34 and nano-MaCE35–37 on heavily-doped Si.

Now that CT1 and CT2 have been discussed, we can further investigate the correlation between CT1 and CT2. As discussed above, h^+ in both CT1 and CT2 are originated from the reduction of H2O2 on Au surface. Under the steady state, c_b+ in CT1 is constant over time, which means Au can be regarded as a source that constantly emits h^+ into Si while moving along the z-axis at constant velocity (v):

\[ c_{b+} (x, z, t) = c_{b+} (x, z, 0) = \text{constant} \]

where \(c_{b+\text{ETCH}}(x, z, t)\) is the amount of h^+ that are consumed in the vertical etching, while \(c_{b+\text{EX}}(x, z, t)\) is the amount of excessive h^+. Since the vertical etching rate is constant, then \(c_{b+\text{ETCH}}(x, z, t)\) is constant, which makes \(c_{b+\text{EX}}(x, z, t)\) also constant:

\[ c_{b+\text{EX}}(x, z, t) = c_{b+\text{EX}} = \text{constant} \]

These excessive h^+ can be transported to the sidewall through diffusion or drift. Here the term “diffusion” refers to the movement of h^+ driven by the gradient of \(c_{b+}\), while “drift” refers to that driven by electric field. If we assume that the excessive h^+ is the only source of h^+ in CT2 and transported to the sidewall only through diffusion, then we can establish a diffusion model to calculate \(c_{b+}\) in Eq. 8 by Fick’s Second Law:

\[ \frac{\partial c_{b+}}{\partial t} = D \nabla^2 c_{b+} (x, z, t) \]

where \(D\) is the diffusion constant of h^+ in Si. Here \(D\) is set as constant over space and time. If we introduce a new variable \(r = \sqrt{x^2 + z^2}\), the boundary condition and initial condition can be written as:

\[ \frac{\partial c_{b+}}{\partial t} \bigg|_{r=\text{crit}} = c_{b+\text{EX}} (r, t) \delta (t) \]

\[ c_{b+} (r, t) \bigg|_{r\rightarrow\infty} = 0 \]

\[ c_{b+} (x, z, 0) = 0 \]

Assuming the total \(c_{b+}\) is the sum of the contribution of each Au lines in a \(w_0 \times n\@s\) block, we have:

\[ c_{b+} (x, z, t) = \sum_{n=1}^{n} \left( \int_{-w_0/2}^{w_0/2} d w \int_{t}^{\infty} \frac{c_{b+\text{EX}}}{4\pi D (t - \tau)} \times \exp \left( \frac{(x - w - n_i \times s + (z - \tau r)^2)}{4D (t - \tau)} \right) d \tau \right) \]

It has been reported that in the electrochemical etching process, Si is completely removed when \(c_{b+}\) exceeds a certain critical value \(c_{b+\text{crit}}\), while porous Si is formed when \(c_{b+}\) is below \(c_{b+\text{crit}}\).33 Then using the diffusion model, \(\Delta w_t\) can be calculated by Eq. 17 if we assume that \(\Delta w_t\) is only related to the \(c_{b+}\) on the Si top surface at \(z = 0 \) (referred as \(c_{b+}\)(x, 0, 10 min)). The \(c_{b+}\)(x, 0, 10 min) equals to \(c_{b+\text{crit}}\) at the position of \((\Delta w_t, 0)\). Figure 9a shows the calculated \(c_{b+}\)(x, 0, 10 min) in MaCE of 2 \(\mu m \times 1\), 5 \(\mu m \times 1\), and 10 \(\mu m \times 1\) blocks on U-Si along x-axis where the origin is set at the geometric center of Au lines. The \(c_{b+}\) is calculated by fitting Eq. 17 with \(\Delta w_t\) in Figure 5b and expressed in arbitrary unit (a.u.). The fitting gives nominal value of \(c_{b+\text{crit}} = 0.164\) and \(D = 0.008\) m^2/s. The boundaries are between the edge of Au and Si are indicated as the vertical dot lines at \(x = \pm w_0/2\). For example, the boundaries of 2 \(\mu m \times 1\) block locate at \(x = \pm 1\) \(\mu m\). As the \(w_0\) increases, \(c_{b+}\) within the boundary increases and the curve extends farther out of the boundary, which is consistent with results in Figure 5b. To calculate \(\Delta w_t\), the \(c_{b+}\) curve outside the boundaries is detailed in Figure 9b, where the x-axis is set to start at the boundary of Au in each curve of Figure 9a and extend out of the boundary. Then the curves in Figure 9b represent the \(c_{b+}\) in the sidewall, which is involved in CT2. Given \(c_{b+\text{crit}} = 0.164\), \(\Delta w_t\) of each curve in Figure 5 can be identified by locating the intersection point of the curves with the \(c_{b+} = 0.164\) line (horizontal black dash line). We name these \(\Delta w_t\) value as the modeled value. The modeled \(\Delta w_t\) for P-Si and U-Si are plotted in Figure 5a as solid lines and labeled as P(M) and U(M), which shows good consistence with the experimentally measured value. The same \(c_{b+\text{crit}}\) and \(D\) value are used to obtain the modeled \(\Delta w_t\) in MaCE of other blocks, which are plotted in Figure 5c to 5e. For U-Si, the modeled \(\Delta w_t\) are close to the measured value. For P-Si, \(c_{b+\text{crit}}\) and \(D\) are fit to be 0.340 and 0.003 m^2/s from Figure 5b. However, although the modeled \(\Delta w_t\) well match the measured value Figure 5b, they are far below the measured value in Figures 5c to 5e. The comparison between the modeled and measured \(\Delta w_t\) in Figure 5b to 5e indicates that for U-Si, h^+ transported from Au to the sidewall is likely to be a diffusion process mainly from the excessive h^+ around Au. For P-Si, in single line etching, h^+ is also transported from Au through diffusion; in multiple line etching, however, the actual h^+ concentration in the sidewall region is much higher than the amount.
that transported through diffusion. The sharp increase of $\Delta w_1$ with $n$ on P-Si has not been reported before. Considering the fact that a large amount of $h^+$ is transported from Au to Si, a strong electric field may be established around every Au lines. Based on the depth of etching as $\sim 6 \mu m$ on P-Si, the amount of Si etched per unit area $r_2$ in the etching of 10 min is:

$$r_2 = \frac{\rho V}{M_{Si}} = \frac{6 \mu m \times 1 \mu m \times 1 \mu m \times 2.329 \text{ g/cm}^3}{28.09 \text{ g/mol} \times 600 \text{ s}}$$

$$= 8.3 \times 10^{-16} \text{ mol/s}$$  \[18\]

Where $\rho$, $V$, $M_{Si}$ are the density, etched volume and molecular weight of Si.\(^{39}\) Assuming etching of each Si atom consumes 4 $h^+$, then the current density of $h^+$ is estimated to:

$I = \frac{4 \times r_2 \times N_A \times e^-}{S}$

$$= \frac{4 \times 8.3 \times 10^{-16} \text{ mol/s} \times 6.02 \times 10^{23} \text{ mol} \times 1.6 \times 10^{-19} \text{ C}}{1 \mu m \times 1 \mu m}$$

$$= 32.0 \text{ mA/cm}^2$$  \[19\]

According to Figure 8b, the current correspond to a bias over 3 Volts. In MaCE of multiple Au lines, the increase of $n$ may significantly increase the synergistic electric field from all Au lines, which resulted in an increased amount of intrinsic $h^+$ that are involved in CT2 and an accelerated movement of $h^+$ toward sidewall. Besides, in P-Si, a considerable amount of $h^+$ exist at the dopant atoms in Si as intrinsic $h^+$. These $h^+$ also have a chance to be transported to the sidewall under the electric field. Therefore, although in the single Au line etching, $\Delta w_1$ (U-Si) is larger than $\Delta w_1$ (P-Si) due to a higher amount of excessive $h^+$ in CT1 (Figure 5b), $\Delta w_1$ (P-Si) quickly exceeds $\Delta w_1$ (U-Si) as $n$ increases (Figures 5c–5e). However, further study is needed to figure out the spatial distribution of the electric field and its interaction with $h^+$ inside Si.

In order to investigate the MaCE results on Si with other crystalline orientation, we conducted MaCE on the P-Si with (111)-orientation under the same condition as that on P-Si with (100)-orientation. As shown in Figure 10, after MaCE vertical trenches were formed on the (111)-Si substrates, in consistence with previous results.\(^{21}\) Similar to the results from (100)-Si, here the $\Delta w_1$ also shows an increase when $n$ increases. The increase of $\Delta w_1$ support the aforementioned mechanism that the charge transport during MaCE can be described by the Schottky models, where the doping of the Si plays the major role. The etching depth is much lower than that on (100)-Si. The slower etching rate on (111)-Si may be explained by the fact that the back bonds density is higher along the (111) orientation than that along (100) orientation.

Conclusions

In conclusion, 3D profiles of MaCE using Au lines with different line width ($w_2$), number ($n$) and spacing distance ($\delta$) on P-Si, N-Si, USi, P(+)Si and N(+)Si have been presented. Uniform trenches were formed on P-Si, N-Si and U-Si, while the 3D profiles on P(+)Si and N(+)Si are non-uniform. The depth $d$ and lateral width variation $\Delta w_1$ of the 3D profiles on P-Si, N-Si and U-Si are measured and correlated to the CT1 and CT2, respectively. The depth follows the order of $d$(P-Si) < $d$(U-Si) < $d$(N-Si), while the $\Delta w_1$ of N-Si is lower than that of U-Si and P-Si. The variation of $d$ and $\Delta w_1$ over the dopant type of Si can be explained by Schottky junction model, which indicates that CT1 is favored on N-Si and CT2 is favored on P-Si. The variation of $\Delta w_1$ over $w_2$, $n$ and $\delta$ can be further explained by the correlation between CT1 and CT2: in U-Si, $h^+$ in CT2 are mainly originated from excessive $h^+$ in CT1 through diffusion; in P-Si, the actual $h^+$ concentration in CT2 is much higher than that calculated from the diffusion model, which may be attributed to the drift of $h^+$.

The fundamental aspects revealed by the present work will serve as a reference for future MaCE research. It is expected that by deeper study about the effect of electric bias, etchant composition and other parameters, a complete controllability of 3D profiles in MaCE can be achieved. The novel insight is also meaningful in general electrochemistry where charge transport process in micro- and nanoscale are concerned, such as microfluidics and MEMS. Practically, the results pave the way to the fabrication of high-density micro- and nanostuctures by MaCE: vertical HAR structures can be readily formed on N-Si; the sidewall of the etched structures will be tapered on P-Si and U-Si as the pattern number and density increase, where the effect of lateral geometry of the structures should also be considered.

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