The controlled electrochemical etching at room temperature of deep (up to 200 µm) silicon microstructures with aspect ratio ranging from 5 to 100 and etching rates from 10 to 3 µm/min, respectively, is here reported and discussed. This allows silicon microfabrication technology entering a region in the parameter space etching-rate vs. aspect-ratio that was so far unreachable for silicon microstructuring technologies both at commercial and research levels. Addition of an inert oxidant molecule, namely H$_2$O$_2$, to a standard aqueous hydrofluoric (HF) acid electrolyte is used to drop the valence (number of electrons required to dissolve a single silicon atom) of the dissolution process down to 1 (from the standard value of about 3) under anodic biasing. This makes the electrochemical etching of silicon more effective without losing control accuracy in microfabrication, on the one hand, and allows to increase the etching rate by opening a more efficient silicon dissolution path with respect to the well-known Gerischer mechanism, both at lower and higher aspect ratios, on the other hand.

**Introduction**

The widespread development of silicon microstructuring technologies arisen from Feynman’s inspiring speech in 1959 pushed silicon employment toward novel research topics and market opportunities beyond Moore’s law, a trend well known as More Than Moore (1,2). This has allowed silicon microoptoelectromechanical systems to enter everyday life. Nevertheless, emerging applications in different fields, among which through silicon vias for 3D chip stacking and 3D capacitors with dramatically enhanced value for unit area in microelectronics (3), and lab-on-chips for point-of-care clinical diagnostics and microneedles for transdermal drug delivery and biosensing in nanomedicine (4), represent new challenges that silicon microstructuring technologies are facing today. These applications require fabrication of microstructures with high-aspect-ratio values that are in most cases beyond those attainable by commercial technologies (aspect ratio AR<40). Moreover, state-of-the-art technologies able to control microfabrication at high aspect-ratios (up to 100) are restricted to etching rates below 2 µm/min when the aspect-ratio increases over 20 (5).

In this work we report on a microstructuring technology able to achieve results in terms of etching-rate Vs aspect-ratio that are currently inaccessible to other technologies, both at commercial and research levels, thus setting a novel record among the silicon microfabrication technologies. More in detail, we show that electrochemical etching
enables the fabrication at room temperature of high aspect-ratio (from 5 to 100) silicon microstructures at high etching rates (from 10 to 3 \( \mu \text{m/min} \)) without loss of etching control accuracy at the higher depths (up to 200 \( \mu \text{m} \)). Aqueous electrolytes with low HF concentration (from 5 to 8 vol\%) additioned with \( \text{H}_2\text{O}_2 \), an inert oxidant molecule, are used to both reduce the valence of the silicon dissolution process down to 1 (from a common value of about 3), thus rendering the electrochemical etching more effective, and increase the etching rate at both shorter and higher depths by opening a more efficient path for silicon dissolution with respect to the well-known Gerischer mechanism (6,7).

**Materials and Methods**

**Materials and Chemicals**

The starting material was a CZ-growth n-type silicon wafer with resistivity of 3–8 \( \Omega \) cm, (100) oriented, phosphorus doped, with a 298 nm thick silicon-dioxide layer on top, provided by ST Microelectronics.

HF 48 wt\%, Perdrogen \( \text{H}_2\text{O}_2 \) 30 wt\%, pentane 99 wt\%, acetone 99 wt\%, and 2-propanol 99.8 wt\% were purchased from Sigma-Aldrich. Sodium lauryl sulfate powder was purchased from Carlo Erba Reagents. Potassium hydroxide, pure powder at 85\%, and ethanol 99.8 wt\% were purchased from Fluka Analytical. Ammonium fluoride solution 40 wt\% was purchased from Riedel-De Haën (Aldrich).

**Preparation of Regular Macropores and Complex Microstructures by Anodic Etching of n-Type Silicon Electrodes in Aqueous HF–H\(_2\)O\(_2\) Electrolytes**

Two different patterns were used to carry out microfabrication experiments, namely a 2D lattice with triangular unit cell consisting of holes with side of 2 \( \mu \text{m} \) and spatial period of 3.5 \( \mu \text{m} \) along the (110) direction (single-holes 2D pattern) and a 2D lattice with square unit cell integrating a 2D array of larger holes with side of about 40 \( \mu \text{m} \) and spatial period of 70 \( \mu \text{m} \) together with a 2D array of smaller holes with side of about 4 \( \mu \text{m} \) and spatial period of 10 \( \mu \text{m} \) (multi-holes 2D pattern).

Each pattern was defined by standard UV lithography technology on a photoresist layer spun on top the silicon substrate. The pattern was transferred to silicon-dioxide layer by buffered hydrofluoric acid (BHF) etching and then to the silicon surface by KOH etching using the patterned photoresist and the silicon-dioxide layer as mask, respectively. BHF etching was performed at room temperature with a solution of HF:NH\(_4\)F (4:25, v/v). KOH etching was performed at 50 °C in a 20 wt\% KOH solution, saturated with 2-propanol to improve solution wettability and, in turn, to increase the etching uniformity. The silicon-dioxide layer was eventually removed by chemical etching in a solution of HF:ethanol (1:1, v/v), thus leaving the patterned silicon surface uncovered. The patterned silicon samples were loaded in a three-electrode electrochemical cell and electrochemically etched under backside illumination (8).

The single-holes pattern was etched at constant anodic voltage of 1.2 V in the presence of different aqueous electrolytes with a given HF concentration ([HF] ranging from 5 to 8 vol\%) additioned with different \( \text{H}_2\text{O}_2 \) concentrations ([\( \text{H}_2\text{O}_2 \)] varying from 0\% (control) to 5, 10, 15, 20, and 25 vol\%). Etching experiments were performed for an etching time of 65 min during which depth was marked over time at regular time intervals (5). In order to keep the macropore diameter constant with depth, the photo-
generated etching current density ($J_e$) was linearly decreased over time with respect to its initial value $J_{e,0}=36.49 \text{ mA/cm}^2$, which was maintained constant throughout different experiments regardless of the electrolyte composition. The etching current density decreasing rate values were set by properly reducing the lamp power over time to $-1.67 \mu\text{A/s}$ for the control solution, $-1.67 \mu\text{A/s}$ for the electrolyte with $[\text{H}_2\text{O}_2] = 5\%$, $-3.44 \mu\text{A/s}$ for the electrolyte with $[\text{H}_2\text{O}_2] = 10\%$, $-4.04 \mu\text{A/s}$ for the electrolyte with $[\text{H}_2\text{O}_2] = 20\%$, and $-4.04 \mu\text{A/s}$ for the electrolyte with $[\text{H}_2\text{O}_2] = 25\%$. The multi-holes pattern was etched at constant anodic voltage of 3 V for 10 min in an aqueous electrolyte with $[\text{HF}] = 5\%\text{ vol%}$ and $[\text{H}_2\text{O}_2] = 25\%\text{ vol%}$. The electrochemical etching consisted of a single step with an initial anisotropic phase and a final isotropic phase, both controlled by varying the $J_e$ over time as the etching progresses (8). During the anisotropic phase the $J_e$ value was set to 103.9 mA/cm$^2$ and linearly decreased over time with a slope of $-11.7 \mu\text{A/s}$ for the next 10 min to keep pore diameter constant over depth; during the isotropic phase the $J_e$ value was abruptly increased to 148.4 mA/cm$^2$ for 90 s so as to isotropically consume silicon at the bottom of etched structures, which was functional to fabrication of the larger holes (8).

After the electrochemical etching, the microstructured silicon samples were rinsed in deionized water, ethanol, and pentane, then dried on a hotplate at 100 °C. Morphological investigation of the microstructured samples was carried out using a scanning electron microscope (SEM - JEOL).

Results and Discussion

SEM cross-section images in Figure 1a,b show a typical regular array of macropores resulting from the electrochemically etching of single-hole patterns for 60 min under back-side illumination at anodic voltage of 1.2 V in two aqueous electrolytes containing $[\text{HF}] = 5\%$ with $[\text{H}_2\text{O}_2] = 25\%$ (Figure 1a) and without $\text{H}_2\text{O}_2$ (control) (Figure 1b). Macropores etched in the presence of $\text{H}_2\text{O}_2$ feature a mean AR (ratio between depth of pore and its width) of about 96 and a mean depth of 177.93 µm (standard deviation $\text{sd} = 0.37 \mu\text{m}$), which corresponds to an average etching rate (ratio between etch depth and etch time) of about 3 µm/min. The average etching rate with $[\text{H}_2\text{O}_2] = 25\%$ is about 2 times larger than that of the control electrolyte (without $\text{H}_2\text{O}_2$) for which shorter macropores with depth of only 90.38 µm ($\text{sd} = 0.25 \mu\text{m}$) and AR of about 26 are etched in the same time (about 1.5 µm/min), in agreement with the current literature (9). Experimental data highlight a significant enhancement of the silicon etching rate in a HF-based electrolyte containing $[\text{H}_2\text{O}_2] = 25\%$ with respect to the control electrolyte (without $\text{H}_2\text{O}_2$) that is commonly employed for the electrochemical etching of both regular macropores (10,11) and complex microstructure (12). No appreciable drawback of the increased etching rate on macropore quality, e.g. pore diameter control over depth, pore surface roughness, is apparent (compare insets of Figure 1a,b).

Figure 1c shows SEM bird-views of a typical silicon microstructure resulting from the electrochemical etching of multi-hole patterns and consisting of a 2D array of square holes with sides of about 40 µm and spatial periods of 70 µm together with a 2D array of square pores with sides of about 4 µm and spatial periods of 10 µm, all with depth of 50 µm. The microstructure has been obtained by anodic etching in a $[\text{HF}] = 5\%$ electrolyte with $[\text{H}_2\text{O}_2] = 25\%$ for 10 min. The larger square holes has been obtained through the use of sacrificial structures that are removed by switching the electrochemical etching from the anisotropic to the isotropic regime at the end of the etching process (8). Remarkably, this microstructure integrates both low (about 1) and high (about 10) AR holes etched at
an average rate of 5 µm/min that is 2.8 times larger than that of the control electrolyte. Quality of microfabrication and surface roughness are comparable to those obtained using the control electrolyte, for which an etching time of 35 min is required to achieve same depth (13).

Investigation of the effect of different H$_2$O$_2$ concentrations ([H$_2$O$_2$] = 0, 5, 10, 20, and 25%) has been also carried out. Experimental data highlight as for a given set of etching parameters, pore depth increases with etching time (Figure 1d, top), whereas etching rate decreases as a function of both etching time (Figure 1d, bottom), pore depth and aspect ratio (Figure 1e), regardless of the H$_2$O$_2$ concentration, thus clearly indicating that diffusion kinetics of active species, i.e. HF and H$_2$O$_2$, to the active site of reaction, i.e. macropore tip, still plays a major role in the electrochemical dissolution of silicon over depth (9,10). Nevertheless, the lowest etching rate recorded in the presence of H$_2$O$_2$ at the

Figure 1. (a,b) SEM cross-section of regular macropore arrays, and relative tip magnification (inset), etched under back-side illumination for 60 min at 1.2 V and $J_{e_0} = 36.49$ mA/cm$^2$ in the presence of [HF] = 5%-based electrolyte a) with [H$_2$O$_2$] = 25% and b) without H$_2$O$_2$ (control). (c) SEM bird-views of a silicon microstructure with depth of 50 µm and holes with different aspect ratios (namely, 1 and 10) on the same silicon die, fabricated in 10 min at 3 V and 103.9 mA/cm$^2$ in the presence of [HF] = 5%-based electrolyte with [H$_2$O$_2$] = 25%; inset shows a magnification of (c). (d,e) Experimental data (average value and sd) on d) depth and etching rate versus time and e) etching rate versus pore depth and aspect-ratio of regular macropore arrays etched at 1.2 V and $J_{e_0} = 36.49$ mA/cm$^2$ in the presence of [HF] = 5%-based electrolyte with different H$_2$O$_2$ concentrations (i.e., 0, 5, 10, 20, and 25%).
higher etching depths (about 2.3 µm/min with \([\text{H}_2\text{O}_2] = 5\%) is still higher than the higher etching rate value reached without \(\text{H}_2\text{O}_2\) in the electrolyte solution at the smaller etching depths (about 1.8 µm/min).

Remarkably, experimental data point out as increasing the \(\text{H}_2\text{O}_2\) concentration in the electrolyte the pore diameter decrease (Figure 2a, red circles), which means that \(\text{H}_2\text{O}_2\) enhances silicon dissolution in the out-of-plane direction with respect to the in-plane direction; on the other hand, as \(\text{H}_2\text{O}_2\) concentration increases the dissolution valence (number of charge carriers required for the dissolution of a single silicon atom) decreases (Figure 2a, blue squares) from an average value of 2.97 (sd=0.40) of the control electrolyte (9) down to an average value of 1.12 (sd=0.24) at \([\text{H}_2\text{O}_2] = 25\%\), thus suggesting that the presence of \(\text{H}_2\text{O}_2\) changes the stoichiometry of silicon dissolution process.

Further experiments have been carried out to investigate the effect on the etching rate of increasing HF concentrations in for a given \(\text{H}_2\text{O}_2\) concentration value. All experiments have been performed at room temperature on single-hole patterns for an etching time of 10 min using electrolytes with HF concentration ranging from 5% and 8% and \(\text{H}_2\text{O}_2\)}

Figure 2. (a,b) Experimental data (average value and sd) on regular macropore arrays etched at 1.2 V and \(J_{\text{e}_0} = 36.49\) mA/cm\(^2\): a) dissolution valence and pore diameter versus \(\text{H}_2\text{O}_2\) concentration for [HF] = 5%-based electrolytes with different \(\text{H}_2\text{O}_2\) concentrations (i.e., 0%, 5%, 10%, 20%, 25%); b) etching rate versus \(\text{H}_2\text{O}_2\) concentration for aqueous electrolytes at different HF concentrations (namely 5, 6, 7, and 8%) at constant etching time, namely 10 min. SEM cross-sections of regular macropore arrays etched under back-side illumination for 10 minutes at 1.2 V and \(J_{\text{e}_0} = 36.49\) mA/cm\(^2\) (c-f) in the presence of aqueous electrolytes with: (c, d) [HF]=6% and \([\text{H}_2\text{O}_2] = 0\) and 10%; (e) [HF]=7% and \([\text{H}_2\text{O}_2] = 10\%\); (f) [HF]=8% and \([\text{H}_2\text{O}_2] = 15\%\).
ranging from 0% and 15%. Figure 2b summarizes experimental results. For a given H$_2$O$_2$ concentration, etching rate increases as the HF concentration increases (10). For instance, for [H$_2$O$_2$]=15% and etching time of 10 minutes, regular macropore array with depth of 40 (4 µm/min) and 70 µm (7 µm/min) are etched increasing the HF concentration from 5 to 8%. The increase of HF in the presence of H$_2$O$_2$ does not negatively affect the quality of etched macropores in terms of surface roughness and diameter over depth, as shown in Figure 2c-f, which shows SEM cross-sections of macropore arrays electrochemically etched with different HF and H$_2$O$_2$ concentrations.

A parallel etching path introduced by the presence of H$_2$O$_2$ and triggered by the capture of a conduction band electron released during fluoride-induced etching (right hand column in Figure 3) has been proposed to explain the enhanced etching rate, with respect to the well-known Gerischer path (left hand column in Figure 3) (6). This liberates OH$^-$ at the surface, which induces further etching through base-catalyzed hydrolysis. This parallel pathway is responsible both for etching rate enhancement and for dissolution valence reduction in the presence of H$_2$O$_2$.

![Figure 3. A schematic representation of the standard Gerischer etching of silicon electrodes in a HF-based aqueous electrolyte with a parallel etching mechanism catalyzed by the presence of H$_2$O$_2$.](image)

**Conclusion**

We demonstrate that the etching rate of in-silicon microstructures electrochemically etched in HF-based aqueous electrolytes is dramatically enhanced by the addition of H$_2$O$_2$. Higher etching rate is maintained during the formation of high-aspect-ratio microstructures, thus enabling silicon microfabrication technology to enter a region in the parameter space etching-rate vs. aspect-ratio that was unreachable so far for silicon microstructuring technologies both at commercial and research levels. The
increase of etching rate is strictly connected to a drop of the dissolution valence from about 3 of the control electrolyte (no \( \text{H}_2\text{O}_2 \)) down to 1 at the higher \( \text{H}_2\text{O}_2 \) concentration. We propose that a parallel etching mechanism introduced by the addition of \( \text{H}_2\text{O}_2 \) is triggered by the capture of a conduction band electron released during fluoride-induced etching, thus enabling both etching rate enhancement and reduction in dissolution valence.

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References