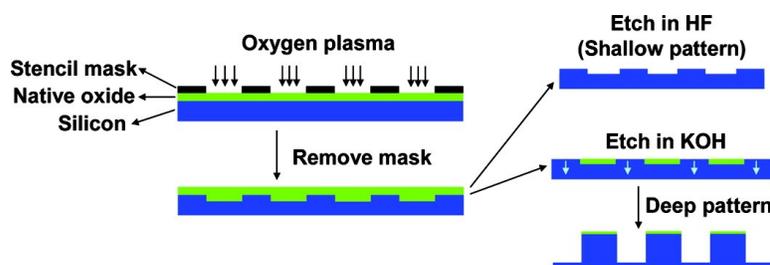


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## Subsurface Oxidation for Micropatterning Silicon (SOMS)

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Here we present a straightforward patterning technique for silicon: subsurface oxidation for micropatterning silicon (SOMS). In this method, a stencil mask is placed above a silicon surface. Radio-frequency plasma oxidation of the substrate creates a pattern of thicker oxide in the exposed regions. Etching with HF or KOH produces very shallow or much higher aspect ratio features on silicon, respectively, where patterning is confirmed by atomic force microscopy, scanning electron microscopy, and optical microscopy. The oxidation process itself is studied under a variety of reaction conditions, including higher and lower oxygen pressures (2 and 0.5 Torr), a variety of powers (50-400 W), different times and as a function of reagent purity (99.5 or 99.994% oxygen). SOMS can be easily executed in any normal chemistry laboratory with a plasma generator. Because of its simplicity, it may have industrial viability.

Surface patterning on silicon is critically important in research and industry. In silicon semiconductor manufacturing, it is central to microchip fabrication. For separation science, patterning can be used to make microchannels. There are a number of effective techniques for surface patterning and modification, such as lithography,<sup>1,2</sup> plasma etching,<sup>3-14</sup> plasma polymerization,<sup>15, 16</sup> microcontact printing,<sup>17, 18</sup> and the chemomechanical method,<sup>19</sup> that have been used in the laboratory and in industry.

Here, we add to this impressive set of known patterning methods and present a simple, straightforward tool for patterning silicon based on plasma oxidation through a stencil mask. We term this method subsurface oxidation for micropatterning silicon (SOMS).

The silicon dioxide pattern created during plasma oxidation can be removed by HF etching to reveal a pattern in silicon. Much deeper features are produced by etching with KOH. By adjusting the conditions of plasma oxidation and silicon etching, features with different aspect ratios and contrasts (polarity) can be made. To the best of our knowledge, this is the first report of substrate oxidation of silicon with a stencil mask for silicon patterning. SOMS can be easily executed in any normal chemistry laboratory with a plasma generator. Because of its simplicity, it may have industrial viability.

Plasma oxidation of silicon, especially at elevated temperatures, is a well-known technique in semiconductor processing, and the properties of the silicon dioxide grown in plasma oxidation are similar to those obtained from thermal oxidation.<sup>20</sup> Oxidation in this study is performed near room temperature, a convenient reaction condition, in a plasma chamber that contains three plates. The plasma density at the active plate is the highest. It is somewhat reduced on the ground plate and is much lower on the float plate. While there have been a number of reports of silicon oxidation, we are unaware of any publication that uses the oxidation conditions employed in our study.

We first report basic reaction conditions for oxide growth (effects of pressure and reagent purity). Our system (the YES 1224P) will be similar to many other home-built and commercial plasma systems, in addition to the fact that numerous YES 1224P instruments have been sold worldwide. First the effect of pressure was studied by performing oxidation at both 2 Torr and 0.5 Torr, where the resulting surface oxidation was evaluated on each of the active, ground, and float plates. Reagent purity was also studied. The second part of this letter describes the use of SOMS as a surface-patterning tool.

Surface oxidation at 2 Torr oxygen was performed from 100 to 250 W plasma power in 50 W increments, inclusively. In general, no increase in silicon oxide thickness was observed by spectroscopic ellipsometry from shards on the active, ground, or float plates in 14 experiments, where one silicon shard was present on each shelf in each experiment. However, in a few cases, film increases of up to 10 Å were found. This higher (2 Torr) pressure was eliminated as a viable reaction condition based on the irreproducibility of these results and/or lack of surface oxidation. After the treatments at 2 Torr O<sub>2</sub> and at lower pressure (vide infra), all surfaces were wetted by water.

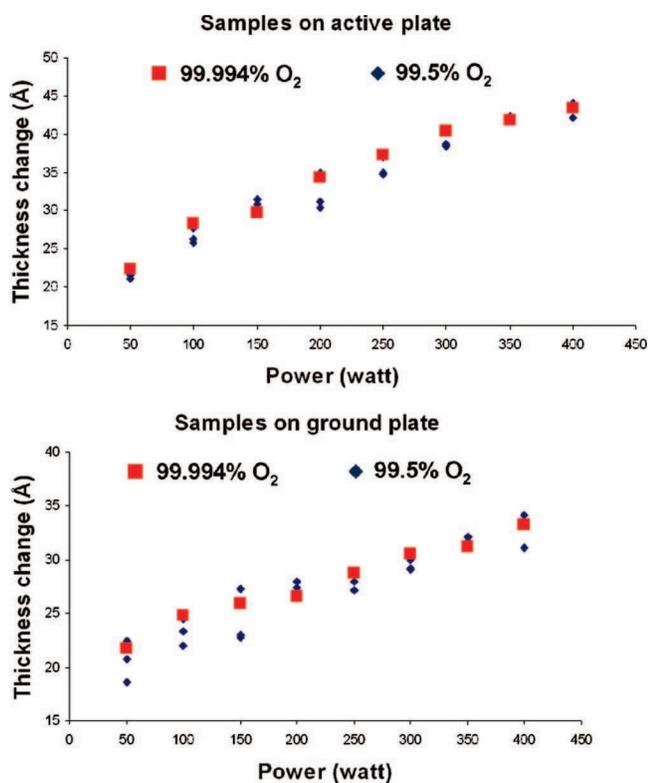
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**Figure 1.** Oxide growth as a function of gas purity and power.  $R^2$  values for linear fits to all data are 0.96 (99.5% O<sub>2</sub>) and 0.97 (99.994% O<sub>2</sub>) for the active plate and 0.91 (99.5% O<sub>2</sub>) and 0.98 (99.994% O<sub>2</sub>) for the ground plate. Each point represents a separate experiment of 5 min oxidation time.

Presumably because of longer mean free paths for reactive species<sup>21</sup> and therefore higher energies, stable, reproducible plasma oxidation was observed at 0.5 Torr O<sub>2</sub>. Linear increases in SiO<sub>2</sub> film thickness on the active and ground plates were observed as the plasma power increased from 50 to 400 W for a fixed time (Figure 1). Essentially no increase in film thickness took place on the float plate, and as expected, the film thickness increase on the active plate was somewhat higher than on the ground plate. Si 2p narrow scans in X-ray photoelectron spectroscopy (XPS) confirmed silicon oxide growth by the increase in the silicon oxide peak at ca. 103 eV compared to the bulk silicon signal at ca. 99 eV. Steady increases in oxide thickness were also observed as oxidation times were increased from 4 to 20 min at fixed power (250 W). Atomic force microscopy (AFM) confirmed the surface flatness. For example, after plasma oxidation at 250 W for 5 min, the rms surface roughness was 1.59 Å compared to 1.51 Å rms roughness prior to plasma oxidation.

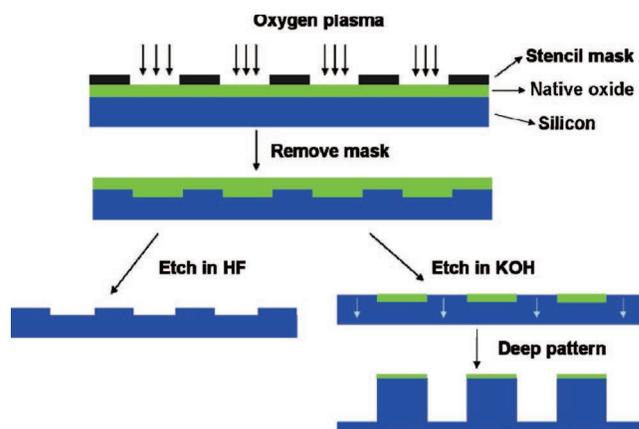
Increases in oxide thickness ( $\Delta t_{\text{oxide}}$ ) (from 4 to 20 min and from 50 to 400 W) could be well fit to an empirical model, giving  $\Delta t_{\text{oxide}}(\text{Å}) = 13.97(\text{Å}) + 0.05988(\text{Å/W}) \times \text{power(W)} + 1.281(\text{Å/min}) \times \text{time(min)}$  on the active plate and  $\Delta t_{\text{oxide}}(\text{Å}) = 14.22\text{Å} + 0.03415(\text{Å/W}) \times \text{power(W)} + 1.0515(\text{Å/min}) \times \text{time(min)}$  on the ground plate. The average absolute values of the errors from these

$$\frac{\sum |t_{\text{oxide}(\text{real})} - t_{\text{oxide}(\text{predicted})}|}{n}$$

(21) The mean free path,  $\lambda$ , is given by  $\lambda = kT/\sqrt{2}\sigma p$ , where  $\sigma$  is the collision cross section and  $p$  is pressure (upon going from 2 to 0.5 Torr,  $\lambda$  increases by a factor of 4, i.e.,  $\lambda \propto 1/p$ ).

models were 0.81 and 0.40 Å with mean square errors of 1.08 and 0.21 on the active and ground plates, respectively.

### Scheme 1. Process of Surface Patterning



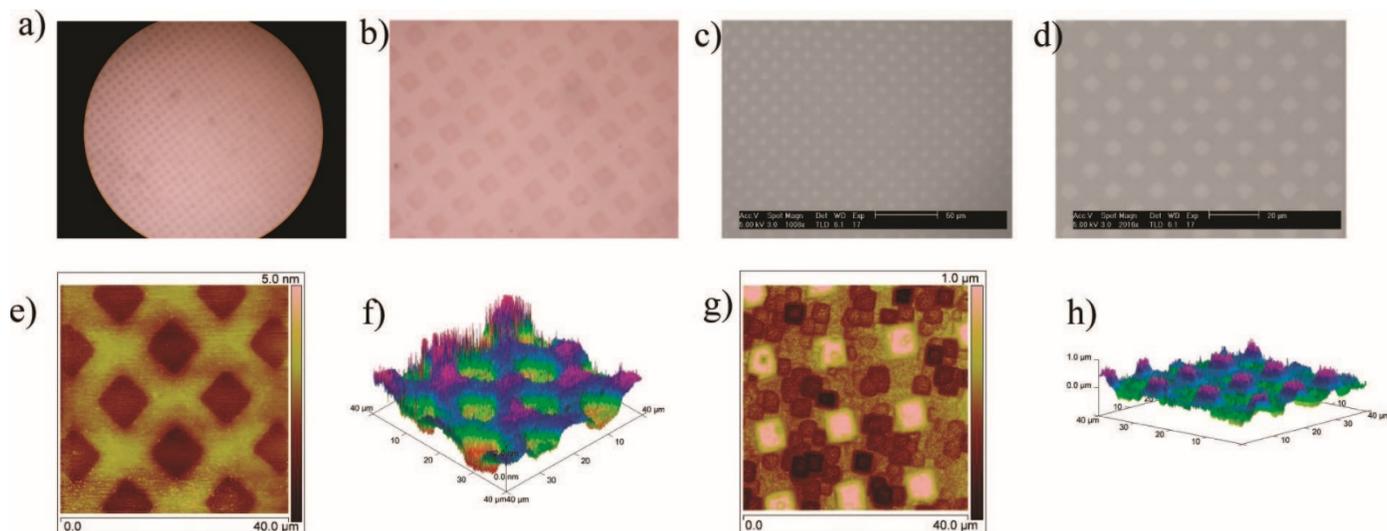
Reagent purity was also probed either 99.5 or 99.994% O<sub>2</sub>. After oxidizing silicon at 250 W for 5 min at 0.5 Torr with both O<sub>2</sub> sources, on the active and ground plates, the carbon content of the resulting films was evaluated by XPS, where this analysis included a gentle in situ cleaning of the surface to remove carbon contamination at the SiO<sub>2</sub>-vacuum interface using an Evactron C De-Contaminator from XEI Scientific, Inc. Although the carbon content is low on all of the surfaces, it is higher on the surfaces made with the less pure reagent gas. It is clear that higher-purity oxygen is preferred for silicon oxidation. The oxidation experiments in Figure 1 were repeated with the more pure O<sub>2</sub> gas, and the change in film thickness was essentially the same as before.

We wondered if it would be possible to use room-temperature plasma oxidation of silicon as a patterning method. A first proof-of-principle experiment involved plasma oxidation of a silicon shard that was half-covered with another silicon shard. After plasma oxidation, the ellipsometric thickness of the covered area did not change, but the thickness of the exposed area did increase.

A TEM grid (a square pattern of 5  $\mu\text{m}$  open squares separated by 7.5  $\mu\text{m}$  bars) was then employed as a more sophisticated stencil mask. A cartoon of this process (Scheme 1) illustrates the placement of the mask, oxygen plasma treatment of the surface, mask removal, and then etching in HF or KOH to reveal/create a 3D pattern. As suggested in this Scheme, HF etching (immersion in a 5% aqueous solution for 30 min) results in oxide removal to reveal shallow patterns of steps with lengths and widths of a few micrometers and heights of ca. 1 nm. Deep etching can be performed with KOH, which etches SiO<sub>2</sub> much more slowly than Si (1.44 nm/h vs 1.32  $\mu\text{m}/\text{h}$ , respectively, 20 °C).<sup>22</sup> Accordingly, the plasma-patterned surface was immersed in a KOH solution that slowly etches the oxide until it breaks through the thinner regions of the oxide layer (the masked regions). The thicker layers of oxide produced by plasma oxidation remain to mask regions of the substrate from deep etching.

Scanning electron microscopy (SEM), optical microscopy, and AFM confirm the patterning/etching process (Figure 2). SEM and optical micrographs show the expected pattern after plasma treatment. After HF etching, AFM reveals a pattern of squares ca. 1 nm lower than the background lines. The contrast is reversed a plasma-treated substrate is immersed in KOH (i.e., lines that are ca. 500 nm deep are observed next to raised squares (platforms)). Other stencil masks are available that should allow the creation

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**Figure 2.** Representative results for SOMS through a TEM grid. (a, b) Optical micrographs after etching. (c, d) SEM micrographs after etching. (e, f) AFM images after etching with HF, and (g, h) AFM images after etching with KOH.

of lines, dots, and other shapes with our method.

Plasma oxidation at ca. room temperature has been investigated as a function of plasma power, pressure, and time. Surface patterning using stencil masks is demonstrated. Patterns are revealed by HF or KOH etching. Future work in our group will focus on applying these techniques to make micro- and nanochannels for microfluidics.

### Experimental Details

**Instrumentation.** Plasma generator for subsurface oxidation: 1224P, Yield Engineering Systems, Livermore, CA, plasma generator for surface cleaning: PDC-32G, Harrick Plasma, Ithaca, NY, spectroscopic ellipsometer (M-2000D, J.A. Woollam Co., Lincoln, NE), X-ray photoelectron spectrometer (XPS) (Surface Science SSX100 instrument with a monochromatized Al KR source and a hemispherical analyzer), scanning electron microscopy (Philips XL30 S-FEG), atomic force microscopy (Veeco Dimension V scanning probe microscope), optical microscopy (Leica DM2000).

**Materials.** Silicon wafers (100), single polished, were obtained from Montco Silicon Technologies, Inc., SpringCity, PA. 2-Propanol (99.9%, Sigma), acetone (>99.5%, Sigma), potassium hydroxide (>90%, Sigma), hydrofluoric acid (49%, Ashland Inc.), and oxygen gas (99.5 and 99.994%, Airgas Inc.) were used as received.

**Surface Cleaning.** Native oxide terminated silicon wafers were washed with soap and water, 2-propanol, and acetone and dried under nitrogen. They were then cleaned in the Harrick plasma cleaner for ca. 3 min using air plasma.

**Surface Oxidation and Patterning.** A stencil mask was placed onto the silicon surfaces, and samples were transferred to the

plasma chamber. Plasma conditions of SOMS were 300 W, 0.5 Torr O<sub>2</sub>, and 10 min. The plasma generator is a 1224P instrument from Yield Engineering Systems (Livermore, CA). A large number of 1224P devices have been sold and are currently used for surface modification in industry by plasma and chemical vapor deposition (CVD). The 1224P can be configured with multiple shelves, including the three parallel active, ground, and float shelves (in this order) employed in this study. The distance between the plates in our study is 2 cm. The radio frequency in the 1224P is 40 KHz. Although the temperature in the 1224P can be raised to 200 °C, we worked near room temperature (i.e., the only heating came from the plasma itself, where the temperature in the chamber would typically rise to ca. 40 °C during oxidation studies).

**Surface Etching.** After surface patterning, samples were immersed in 5% aqueous HF or 35% w/w aqueous KOH for 30 min.

**Surface Characterization.** Surfaces were characterized by spectroscopic ellipsometry, AFM, and XPS. In the XPS measurement, a decontaminator (Evactron C RF plasma cleaner, XEI Scientific, Inc.) was used for in situ cleaning in the XPS antechamber.

**Acknowledgment.** We thank Yield Engineering Systems for financial support.

**Supporting Information Available:** Experimental details and a number of additional results, including details of silicon plasma oxidation and an AFM image of patterned surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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