

# Realization of atomic layer etching of silicon

Satish D. Athavale<sup>a)</sup> and Demetre J. Economou<sup>b)</sup>

Plasma Processing Laboratory, Department of Chemical Engineering, University of Houston,  
Houston, Texas 77204-4792

(Received 29 May 1996; accepted 17 August 1996)

An experimental system and methodology were developed to realize dry etching of single crystal silicon with monolayer accuracy. Atomic layer etching of silicon is a cyclic process composed of four consecutive steps: reactant adsorption, excess reactant evacuation, ion irradiation, and product evacuation. When successful, completion of one cycle results in removal of one monolayer of silicon. The process was *self-limiting* with respect to both reactant and ion dose. Control of the ion energy was the most important factor in realizing etching of one monolayer per cycle. © 1996 American Vacuum Society.

## I. INTRODUCTION

Control of device dimensions down to the atomic level is important in a number of emerging technologies including fabrication of abrupt heterostructure interfaces and extremely thin layers for optoelectronics, quantum devices, and nanostructures.<sup>1</sup> These technologies require film deposition and etching processes with the ability to control the film thickness with monolayer accuracy. Techniques to deposit solid materials one atomic layer at a time have been demonstrated successfully.<sup>2</sup> In contrast, etching a material surface one atomic layer at a time, has not hitherto met with the same degree of success.

Atomic layer etching of GaAs has been realized<sup>3-6</sup> by using Cl<sub>2</sub>/Cl gas and low-energy Ar<sup>+</sup> ion bombardment, energetic electron bombardment, or KrF excimer laser irradiation. In addition, by using chemical beam etching<sup>7</sup> (a reversal of molecular beam epitaxy), Tsang *et al.* have recently demonstrated atomic level control over etching of GaAs.

Although atomic layer etching of GaAs has been successful, that of silicon (the premier electronic material) has been an elusive goal. In their study of atomic layer etching of Si(100) using F atoms and Ar<sup>+</sup> ion bombardment,<sup>8</sup> Horiike *et al.* observed that a saturation etch rate can be achieved with respect to the Ar<sup>+</sup> ion dose; this etch rate, however, was found to be a function of the F atom percentage in the flow and also a function of the exposure time of silicon to F atoms, indicating that self-limiting etching was not achieved. An extension of the work by Horiike *et al.* was reported by Sakaue *et al.*, in which molecular chlorine was used as the adsorbate and Ar<sup>+</sup> ion bombardment was used to induce reaction.<sup>9</sup> Again, a saturation etch rate was observed as the Ar<sup>+</sup> ion irradiation time (ion dose) was increased. However, this etch rate was only 1/3 monolayer/cycle for Si(100). Matsuura *et al.*<sup>10,11</sup> and Suzue *et al.*<sup>12</sup> reported a study of layer-by-layer silicon etching by alternating adsorption of chlorine and Ar<sup>+</sup> ion irradiation. It was found that although a "saturation" etch rate with respect to the chlorine exposure could be obtained, the value of this etch rate was always <1 ML/

cycle, indicating that only "fractional atomic layer etching" was achieved. Based on the literature reports, atomic layer etching of Si with a self-limiting etch rate of 1 ML/cycle has not been realized to date.

In this work, an experimental system and a methodology were developed to etch single crystal silicon with monolayer accuracy.

### A. Atomic layer etching requirements

Atomic layer etching (ALET) of silicon is a cyclic process consisting of four consecutive steps:

(1) Exposure of a clean single crystal silicon surface to chlorine gas, and adsorption (chemisorption) of the gas onto the surface to form a monolayer;

(2) Evacuation of the chamber, so that only the chemisorbed layer of chlorine can subsequently react. This step is necessary to avoid etching by gas-phase species in step (3);

(3) Exposure to an Ar<sup>+</sup> ion beam, to effect chemical reaction between the adsorbed gas and the underlying solid. In this step, a monolayer of the solid is removed;

(4) Evacuation of the chamber to exhaust the reaction products. Completion of one cycle can result in etching of one atomic layer of silicon. The cycle can be repeated to etch as many atomic layers as required.

To achieve etching with atomic layer control, the process must be *self-limiting* with respect to both gas dose in step (1) and ion dose in step (3). This implies that the gas used in step (1) must not react spontaneously with the surface, the ions in step (3) must be inert, and the energy of these ions must be chosen so that sputtering does not occur. Molecular chlorine does not etch silicon spontaneously at room temperature.<sup>13</sup> Chlorine does chemisorb on the silicon surface<sup>14</sup> to form a monolayer of Cl atoms<sup>15</sup> but surface reaction leading to volatile chlorides (SiCl<sub>x</sub>) does not occur. Chlorine is, therefore, a suitable gas for step (1). Exposure of a Cl-covered silicon surface to argon ions in step (3) can induce a chemical reaction.<sup>16</sup> However, the ion bombardment energy has to be below the threshold for sputtering; otherwise self-limiting etching is impossible.

<sup>a)</sup>Current address: Tegal Corp., Petaluma, CA 94953.

<sup>b)</sup>Author to whom correspondence should be addressed; Electronic mail: economou@uh.edu

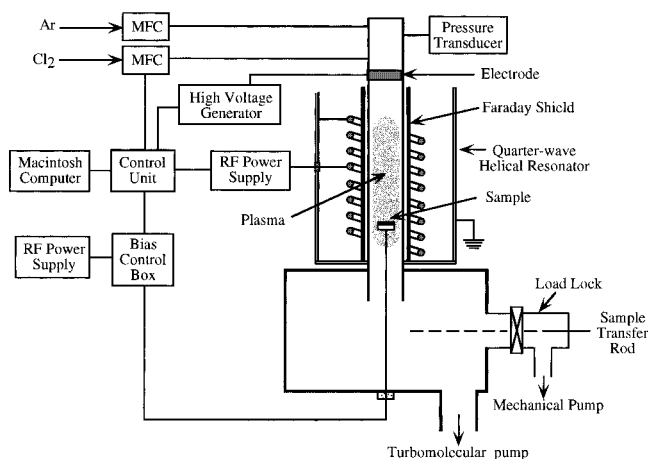


Fig. 1. A schematic of the experimental ALET system including the main vacuum chamber, the quarter-wave helical resonator plasma source, and the computer control system. The sample is shown immersed in the plasma. MFC=mass flow controller, RF=radio frequency.

## II. EXPERIMENT

Figure 1 shows a schematic of the ALET apparatus used in this work. A quarter-wave helical resonator was used to generate a high density plasma sustained in a 61.5 mm inside diameter quartz tube that was part of a turbomolecular-pumped high vacuum chamber. An electrostatic shield prevented any capacitive coupling to the plasma, resulting in a low plasma potential. This is thought to be important since the ion bombardment energy is determined by the difference between the plasma potential and the substrate potential. The plasma potential was not measured but it is expected to be a few tens of V. Separate radio frequency (13.56 MHz) power supplies (ENI, ACG-3) were used to generate the plasma and to bias the substrate holder. This way, the plasma (ion) density could be controlled essentially independently of the ion bombardment energy. A tesla coil was used to generate a high voltage pulse that was momentarily ( $<1$  s) applied to a copper band electrode outside the quartz tube to aid in plasma ignition. Megabit grade chlorine (Solkatronic, 99.998% minimum purity) and prepurified grade argon (Linde Specialty Gases, 99.998% minimum purity) were metered through mass flow controllers (Unit Instruments, UFC 100). The pressure in the plasma and the vacuum chamber underneath were measured using a pressure transducer (MKS Instruments, Baratron 622) and ionization gauge (Granville Phillips, 27006), respectively.

ALET experiments were conducted as follows: a continuous flow of argon (30 sccm) was maintained through the quartz tube for the duration of the experiment, resulting in a gas pressure (in the tube) of 15 mTorr. With the chlorine gas flow and the plasma OFF, a sample was introduced into the quartz tube. A chlorine gas pulse of variable duration and/or strength (partial pressure of chlorine) was then admitted into the tube [step (1)]. Excess chlorine from the sample atmosphere was evacuated [step (2), typical duration 12 s]. The plasma and the rf power to the substrate were then switched ON *simultaneously* and kept ON for a prescribed duration of

time [step (3)]. The forward and reflected power to the helical resonator was 140 and 25 W, respectively, as measured by an in line power meter (Bird), and was not changed for the experiments reported here. The dc bias developed on the substrate electrode was varied, however, by varying the power input to the substrate. Reaction products were finally evacuated [step (4), typically 2 s long] to complete an ALET cycle. The cycle was repeated a prescribed number of times; typically hundreds of cycles were used per sample. A microprocessor-controlled system was used to perform ON/OFF switching and timing of the chlorine gas flow, the rf power to the helical resonator and to the substrate, and the high voltage tesla coil. Control experiments were performed to ensure that physical sputtering or spontaneous chemical etching did not occur under the ALET conditions described herein.

Samples ( $\sim 1$  cm<sup>2</sup> area) were obtained from *p*-type (boron doped) Si(100) wafers with resistivity of 25.5–42.5  $\Omega$  cm. A 1000-Å-thick patterned chromium film was used as a mask. Just before an ALET experiment, the sample was dipped in buffered HF to remove the native oxide of silicon, followed by rinsing in deionized water. The sample was then blow dried using ultrafiltered pressurized nitrogen gas and was loaded immediately into the reactor through a load-lock chamber using a magnetically coupled transfer rod. After an experiment, the chromium mask was wet etched using a 1:1 mixture of HCl:glycerine. The resulting step height was measured using a surface profilometer (Tencor Instruments, Alpha Step 100). The step height divided by the total number of ALET cycles yielded the etch rate per cycle. An atomic force microscope (AFM, Omicron) was used to analyze the surface topography of selected samples. Both masked and etched areas of the sample were scanned to obtain information on the surface roughness before and after etching.

## III. RESULTS AND DISCUSSION

Figure 2 shows the silicon etch rate (in monolayers/cycle, ML/cycle) as a function of the duration of step (3) with the substrate dc bias as a parameter. With a constant plasma density and, hence, constant ion flux to the substrate, the duration of step (3) is proportional to the ion dose. The chlorine partial pressure during step (1) was 2.4 mTorr and the duration of step (1) was 9 s. It can be observed that, as the duration of step (3) is increased, the etch rate increases and reaches a saturation value. This indicates that self-limiting etching is achieved with respect to the ion dose; i.e., further irradiation of the substrate with Ar<sup>+</sup> ions does not lead to more etching. The value of this self-limiting etch rate depends strongly on the substrate dc bias and, hence, on the Ar<sup>+</sup> ion bombardment energy. It is important to note that in going from a dc bias of +3.0 to  $-1.0$  V, the energy of the Ar<sup>+</sup> ions bombarding the substrate increases. The corresponding self-limiting etch rate changes from  $\sim 0.5$  to  $\sim 1.3$  ML/cycle. At the dc bias value of +0.2 V a self-limiting etch rate of 1 ML/cycle is achieved. The behavior is extremely sensitive to the ion energy (applied bias voltage) indicating a near-threshold process.

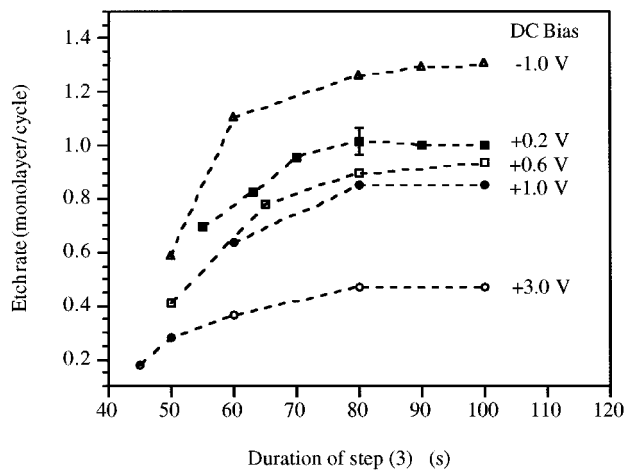


FIG. 2. ALET etch rate as a function of duration of step (3) at different substrate bias conditions (symbols). The dashed line serves as a guide to the eye. The experimental conditions were as follows: net plasma power=115 W, argon pressure=15 mTorr, duration of step (1)=9 s, chlorine partial pressure=2.4 mTorr.

A saturated silicon etch rate of more than 1 ML/cycle is obtained for a dc bias of  $-1.0$  V. At this dc bias, although no physical sputtering was observed, the  $\text{Ar}^+$  ions may still generate structural “damage” below the topmost silicon atomic layer.<sup>17</sup> Upon gas exposure during step (1), chlorine may adsorb on Si atoms beneath the topmost Si layer, and some  $\text{SiCl}_x$  products may be removed there from due to the  $\text{Ar}^+$  ion bombardment in step (3). As the duration of step (3) is increased, a steady-state (constant) thickness of this damaged layer is reached. Therefore, the  $\text{Ar}^+$  ions bombarding the substrate remove more than 1 ML per cycle, yet exhibit a self-limiting behavior. This would not be possible if there was any sputtering of the substrate taking place. Molecular dynamics studies are planned to elucidate these phenomena.

It is also interesting to note that at dc bias values of  $+0.6$  to  $+3.0$  V, less than 1 at. layer of silicon is removed per cycle, yet self-limiting behavior is observed. A plausible explanation for this behavior is that preferential removal of Cl atoms occurs from the surface at these dc bias values, in addition to  $\text{SiCl}$  product removal (which leads to etching). Once all the Cl atoms are removed from the surface, further exposure to  $\text{Ar}^+$  ions does not lead to etching, as physical sputtering by  $\text{Ar}^+$  ions does not occur under these conditions. The self-limiting etch rate of less than 1 ML/cycle achieved at  $+0.6$  to  $+3.0$  V dc bias seems consistent with the observation of “fractional atomic layer etching” by Matsuura *et al.*<sup>10,11</sup>

The variation of the silicon etch rate as a function of chlorine dose, i.e., the product of the chlorine partial pressure and the duration of step (1),  $P_1 \times t_1$ , is shown in Fig. 3. The duration of step (3) was fixed at 90 s. It can be observed that the etch rate increases and reaches a self-limiting value as the chlorine dose increases. The value of the self-limiting etch rate achieved is again strongly dependent on the dc bias of the substrate. In going from a dc bias of  $+1.0$  to  $-1.0$  V, the energy of the  $\text{Ar}^+$  ions bombarding the substrate increases.

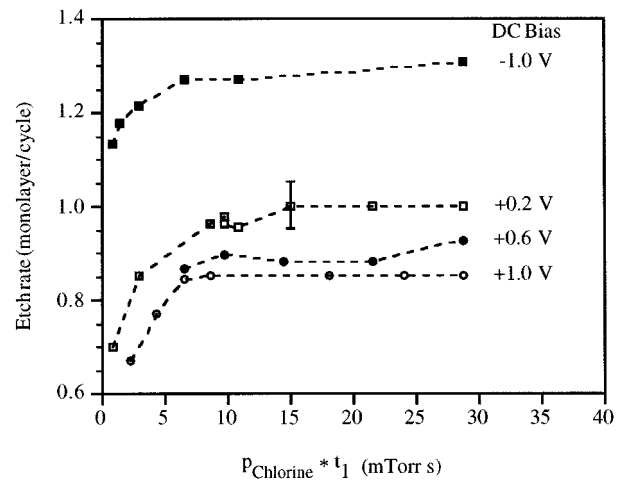


FIG. 3. ALET etch rate as a function of the product of chlorine partial pressure and duration of step (1) at different substrate bias conditions (symbols). The dashed line serves as a guide to the eye. The experimental conditions were as follows: net plasma power=115 W, argon pressure=15 mTorr, duration of step (3)=90 s.

The corresponding self-limiting etch rate changes from  $\sim 0.85$  to  $\sim 1.3$  ML/cycle. Again, at the dc bias value of  $+0.2$  V a self-limiting etch rate of 1 ML/cycle is achieved.

From Figs. 2 and 3 it is evident that the saturation etch rate of 1 ML/cycle, achieved at a substrate dc bias of  $+0.2$  V, is self-limiting with respect to both ion dose in step (3), and chlorine dose in step (1). This indicates that ALET of silicon has been achieved through careful control of the  $\text{Ar}^+$  ion bombardment energy.

The surface topography of the silicon samples before and after etching was studied using an atomic force microscope. Figure 4 shows AFM images of the sample surface showing (a) a masked area, and (b) an etched area of the sample after 280 ALET cycles at a 0.9 ML/cycle etch rate. The rms roughness ( $300 \text{ \AA} \times 300 \text{ \AA}$  scan area) of the masked area and the etched area is 4.13 and 4.94  $\text{\AA}$ , respectively. The rms roughness values were different at different locations on the sample; for example, the values were 2.36  $\text{\AA}$  (masked area) and 3.03  $\text{\AA}$  (etched area) at another location and they were 4.48  $\text{\AA}$  (masked area) and 3.06  $\text{\AA}$  (etched area) at still another location, which was 3 mm away from the previous one. Overall, the rms roughness of the etched area is very similar to that of the masked area. Hence, the surface roughness was not affected by ALET, another indication of a layer-by-layer process.

The importance of fine control of the  $\text{Ar}^+$  ion-bombardment energy in achieving ALET of silicon is clearly evident from this work. Attempts to achieve ALET of silicon, using chlorine and  $\text{Ar}^+$  ions, reported in the literature to date<sup>9–12</sup> seem to have lacked the ability to precisely control the  $\text{Ar}^+$  ion-bombardment energy. Apparently in these previous studies, the  $\text{Ar}^+$  ion-bombardment energy was not sufficiently high to remove a complete atomic layer of silicon per cycle. A self-limiting etch rate (with respect to chlorine exposure) of  $< 1$  ML/cycle (“fractional atomic-layer etch-

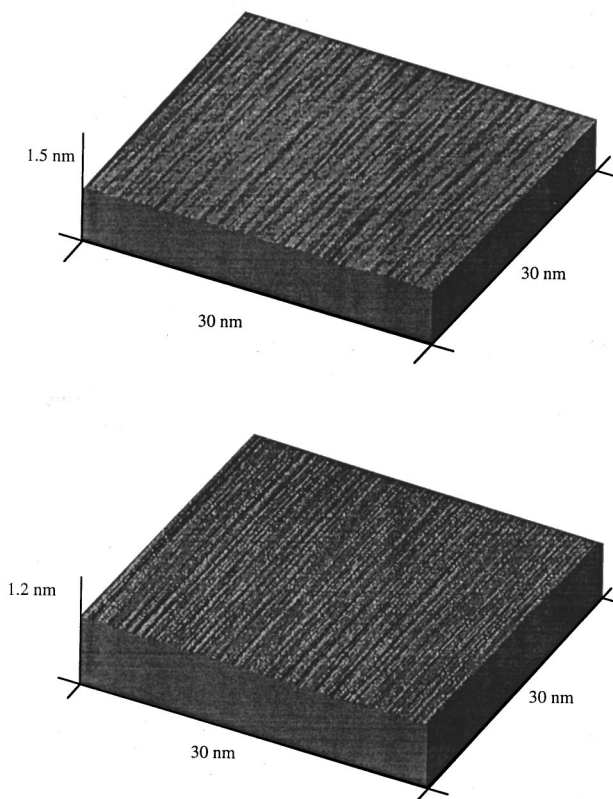


FIG. 4. AFM images of Si(100) surfaces (a) before and (b) after 280 ALET cycles at 1 ML/cycle.

ing<sup>7</sup>) was, therefore, achieved by these authors. It is clear from Figs. 2 and 3 that “fractional atomic-layer etching” can indeed be achieved if the Ar<sup>+</sup> ion-bombardment energy is not sufficiently high to remove a complete monolayer of silicon.

The experimental conditions reported in this paper are not optimized. For example, one can reduce the duration of step (3) by increasing the power input to the plasma, thereby increasing the ion flux to the substrate. In addition, the duration of steps (1) and (2) can be reduced by a better design of the chlorine gas “puffing” system that avoids unnecessarily long dead times.

#### IV. SUMMARY AND CONCLUSION

In summary, an experimental system and methodology were developed to etch single crystal silicon with monolayer

accuracy. It was found that the process was self-limiting with respect to both the chlorine dose in step (1) and the ion dose in step (3). The self-limiting etch rate was found to be a strong function of the dc bias on the substrate and, hence, the ion-bombardment energy. The ion-bombardment energy was the single most important factor in realizing etching of 1 ML per cycle. By controlling this variable, self-limiting etch rates of less or more than a monolayer/cycle could also be achieved. Atomic force microscope images of the silicon surface before and after etching showed that the surface roughness was not affected significantly by ALET.

#### ACKNOWLEDGMENTS

The authors are grateful to the State of Texas for financial support of this work through the Texas Advanced Technology Program and the Texas Center for Superconductivity at the University of Houston (TCSUH). Special thanks are due to Professor S. Perry and H. Kim of the Chemistry Department, University of Houston, for taking the AFM images.

- <sup>1</sup>*Atomic Layer Growth and Processing*, edited by T. F. Kuech, P. D. Dapkus, and Y. Aoyagi [Mater. Res. Soc. Symp. Proc. **222**, 115 (1991)].
- <sup>2</sup>T. Yao, Z. Zhu, K. Uesugi, S. Kamiyama, and M. Fujimoto, J. Vac. Sci. Technol. A **8**, 996 (1990).
- <sup>3</sup>T. Meguro, M. Ishii, K. Kodama, Y. Yamamoto, K. Gamo, and Y. Aoyagi, Thin Solid Films **225**, 136 (1993).
- <sup>4</sup>K. K. Ko and S. W. Pang, J. Vac. Sci. Technol. B **11**, 2275 (1993).
- <sup>5</sup>M. Ishii, T. Meguro, K. Gamo, T. Sugano, and Y. Aoyagi, Jpn. J. Appl. Phys. **1** **32**, 6178 (1993).
- <sup>6</sup>O. L. Bourne, D. Hart, D. M. Rayner, and P. Hackett, J. Vac. Sci. Technol. B **11**, 556 (1993).
- <sup>7</sup>W. T. Tsang, T. H. Chiu, and R. M. Kapre, Appl. Phys. Lett. **63**, 3500 (1993).
- <sup>8</sup>Y. Horiike *et al.*, J. Vac. Sci. Technol. A **8**, 1844 (1990).
- <sup>9</sup>H. Sakuae, K. Asami, T. Ichihara, S. Ishizuka, K. Kawamura, and Y. Horiike, Mater. Res. Soc. Symp. Proc. **222**, 195 (1991).
- <sup>10</sup>T. Matsuura, K. Suzue, J. Murota, Y. Sawada, and T. Ohmi, Appl. Phys. Lett. **63**, 2803 (1993).
- <sup>11</sup>T. Matsuura, K. Suzue, J. Murota, Y. Sawada, and T. Ohmi, *Self-Limited Fractional Atomic-Layer Etching of Si*, Extended Abstracts Vol. 95-1, Abstract No. 314, Paper presented at the Spring meeting of the Electrochemical Society, Reno, Nevada, May 21–26, 1995.
- <sup>12</sup>K. Suzue, T. Matsuura, J. Murota, Y. Sawada, and T. Ohmi, Appl. Surf. Sci. **82-83**, 422 (1994).
- <sup>13</sup>E. A. Ogryzlo, D. L. Flamm, D. E. Ibbotson, and J. A. Mucha, J. Appl. Phys. **64**, 6510 (1988).
- <sup>14</sup>Q. Gao, C. C. Cheng, P. J. Chen, W. J. Choyke, and T. J. Yates Jr., J. Chem. Phys. **98**, 8303 (1993).
- <sup>15</sup>M. Chander, D. A. Goetsch, C. M. Aldao, and J. H. Weaver, Phys. Rev. Lett. **74**, 2014 (1995).
- <sup>16</sup>J. W. Coburn, J. Vac. Sci. Technol. A **12**, 1417 (1994).
- <sup>17</sup>S. D. Athavale and D. J. Economou, J. Vac. Sci. Technol. A **13**, 966 (1995).