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# Atomic layer etching of SiO<sub>2</sub> by alternating an O<sub>2</sub> plasma with fluorocarbon film deposition

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This work demonstrated a process for the atomic-scale etching of SiO<sub>2</sub> films, consisting of alternating nanometer-thick fluorocarbon film deposition with O<sub>2</sub> plasma irradiation in a capacitively coupled plasma reactor. Ar plasma etching after fluorocarbon film deposition tends to suffer from nanometer- or subnanometer-thick carbon films deposited on the SiO<sub>2</sub> surface and chamber walls. These carbon films cause various problems, such as reductions in the etching rate per cycle and degradation of the SiO<sub>2</sub> quality. In contrast, in our two-step process, O<sub>2</sub> plasma removes carbon atoms in such fluorocarbon films. This process therefore allows the atomic scale etching of SiO<sub>2</sub> films without any residue or surface contamination. Additionally, since the etching rate per cycle plateaus as both the etching time and deposition time are extended, it is unnecessary to uniformly deposit a fluorocarbon film over the wafer. © 2016 American Vacuum Society.

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## I. INTRODUCTION

Atomic scale deposition and etching processes are necessary technologies for the fabrication of nanoscale devices such as fin-field effect transistors, nanowires, 3D NAND-type flash memory units, and others 3D devices. To improve the performance of such nanoscale devices, the continuous development of manufacturing processes is important. Atomic layer etching (ALE)<sup>1–3</sup> and atomic layer deposition (ALD)<sup>4–7</sup> are expected to allow this continuous improvement, since these result in a more precise, atomic layer-level process compared to conventional plasma etching.

ALE is a cyclic process consisting of two steps: adsorption of an etchant gas<sup>8–16</sup> or deposition of an etchant film<sup>16–20</sup> on a target material, followed by a reaction between the etchant species and the target material promoted by energetic particles (typically accelerated ions in a plasma). Horiike *et al.*<sup>17</sup> performed ALE of silicon by alternating subnanometer-scale fluorocarbon film deposition and Ar<sup>+</sup> ion etching in two different chambers, and reported self-limiting, layer-by-layer etching via controlling the thickness of the fluorocarbon film on the angstrom scale. The anisotropic etching was achieved by irradiated Ar<sup>+</sup> ion. Metzler *et al.*<sup>20</sup> investigated changes in surface chemistry throughout one cycle and monitored changes in the etched SiO<sub>2</sub> thickness over repeated cycles during ALE of SiO<sub>2</sub> using an Ar/C<sub>4</sub>F<sub>8</sub> plasma.

Fluorine atoms in the fluorocarbon film are known to produce SiFx products by reacting with Si atoms in the SiO<sub>2</sub> during Ar<sup>+</sup> ion etching, while carbon atoms will react with oxygen atoms in the SiO<sub>2</sub> to generate gas phase CO<sub>x</sub> molecules. The unreacted carbon atoms will form a carbon-rich film on the SiO<sub>2</sub> surface, and the thickness of this film increases with the number of cycles, eventually disturbing the etching reaction between the fluorocarbon and the SiO<sub>2</sub>.

Consequently, the ion energy required for the reaction changes with the number of cycles. To avoid an excess of carbon atoms in the fluorocarbon film within any given cycle, careful control of the ion energy, fluorocarbon film thickness (on the angstrom scale), and the carbon-to-fluorine ratio in the deposited fluorocarbon film is required. Tuning these parameters enhances the controllability of the ALE process when using Ar<sup>+</sup> ion etching in conjunction with fluorocarbon deposition.

In industrial applications, the ALE process is expected to allow both deposition and etching in the same chamber, and so the effects of fluorocarbons deposited on the chamber walls must be considered when attempting to achieve a highly repeatable etch rate per cycle (EPC). The residual fluorocarbon film on the chamber walls induces changes in the plasma condition and also causes variations in the EPC as it enters the gas phase.<sup>20–24</sup>

The carbon-rich film formed on the SiO<sub>2</sub> surface and the residual fluorocarbon film on the chamber walls result in difficulty in controlling the process and affect the repeatability of the EPC during the ALE of SiO<sub>2</sub>. The goal of the present study was therefore to develop an ALE process for SiO<sub>2</sub> with high controllability and repeatability. Our suggested method involves a cyclic process composed of two steps: a deposition step which forms a fluorocarbon film as the etchant material using an Ar/C<sub>4</sub>F<sub>8</sub> plasma, followed by an O<sub>2</sub> plasma etching step that induces the etching reaction between the fluorocarbon and the SiO<sub>2</sub>. Simultaneously, the excess carbon film is evaporated by producing CO<sub>x</sub>, such that the O<sub>2</sub> plasma prevents the formation of a carbon-rich film on the SiO<sub>2</sub> surface and maintains the original chamber conditions by removing the fluorocarbon on the chamber walls. Variation in the surface chemistry and etched thickness of SiO<sub>2</sub> during this ALE process were investigated to establish the improvement of the controllability of the process and the repeatability of the EPC.

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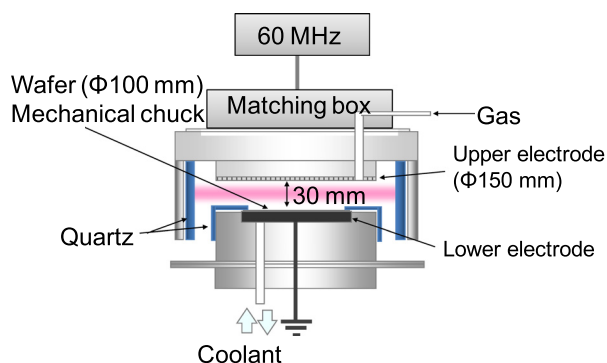


Fig. 1. (Color online) Diagram of the experimental apparatus serving as the dual frequency CCP reactor.

## II. EXPERIMENT

Figure 1 shows a schematic diagram of the experimental apparatus, incorporating a 60 MHz capacitively coupled plasma (CCP) reactor. The lower electrode has a mechanically chucked 100 mm diameter Si wafer attached and is maintained at 20 °C by a circulating coolant. The gap between the upper and lower electrode is fixed at 30 mm, and the pressure in the apparatus is kept constant at 2.0 Pa. The 60 MHz power supply to the upper electrode, with an attached shower head, is maintained at 100 W.

Figure 2 presents a typical sequence and processing times during ALE. In step 1, a C<sub>4</sub>F<sub>8</sub>/Ar gas mixture is employed to form a fluorocarbon film on the SiO<sub>2</sub> surface as the etchant source. A mixture of C<sub>4</sub>F<sub>8</sub> and Ar gases is used, with flow rates of 10 and 90 sccm, respectively. The reactant gas is allowed to flow through the apparatus for 2 min prior to plasma irradiation so as to purge any residual gases from previous trials and to obtain a stable internal pressure. In step 2, O<sub>2</sub> gas is introduced at a flow rate of 50 sccm. The reaction between the SiO<sub>2</sub> and the fluorocarbon film is induced by irradiating pure O<sub>2</sub> plasma.

A 24 nm-thick SiO<sub>2</sub> film deposited on a Si substrate using the ALD process was prepared as the etching sample and characterized by x-ray photoelectron spectroscopy (XPS) and ellipsometry.

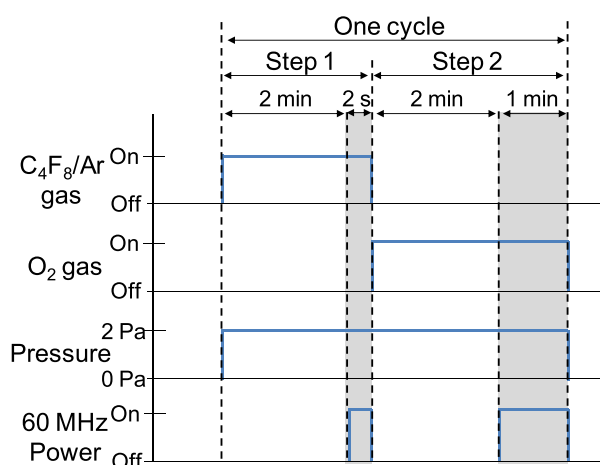


Fig. 2. (Color online) Typical sequences in the ALE process.

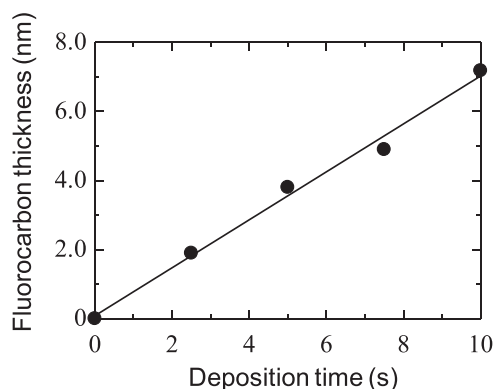


Fig. 3. Deposition thicknesses of fluorocarbons film on SiO<sub>2</sub> during step 1.

## III. RESULTS AND DISCUSSION

Variations in the thickness of the fluorocarbon film on the SiO<sub>2</sub> surface were observed by ellipsometry, and the fluorocarbon thickness and deposition time were found to have a linear relationship. The film thickness increased by 6.9 Å/s in the absence of any changes in the SiO<sub>2</sub> thickness, as shown in Fig. 3. The high deposition rate of the fluorocarbon film prevented etching of the SiO<sub>2</sub> by the C<sub>4</sub>F<sub>8</sub>/Ar plasma. In these experimental trials, the deposition time ranged from 1 to 5 s and these times resulted in film thicknesses from 6.9 to 34.5 Å. These films were relatively thick compared to those reported by other research groups using ALE.<sup>20</sup>

To investigate the surface modification over one cycle, XPS was performed following fluorocarbon deposition, Ar plasma etching, O<sub>2</sub> plasma etching, and O<sub>2</sub> plasma irradiation of the initial SiO<sub>2</sub> film and the initial SiO<sub>2</sub> film. The plasma etching and irradiation times during these trials were 1 min each. The C 1s spectra obtained after these processes are shown in Fig. 4. The C 1s spectrum after the deposition process exhibits C-C, C-CF<sub>x</sub>, CF, CF<sub>2</sub>, and CF<sub>3</sub> peaks. After Ar plasma etching, the spectrum shows a reduction in carbon-bonded fluorine and an increase in the C-C peak. Some carbon atoms close to the interaction sites evidently reacted with oxygen atoms and were desorbed as CO or CO<sub>2</sub> molecules, while the excess carbon atoms remaining after etching would have remained on the SiO<sub>2</sub> surface. This behavior would be expected to occur both on the chamber wall and the upper electrodes. Therefore, the remaining carbon film could lead to low reproducibility of the ALE process, such as changes in the EPC and plasma conditions.<sup>17</sup> In contrast, application of the O<sub>2</sub> plasma resulted in a chemical reaction between the oxygen atoms and the excess carbon. All peaks in the C 1s spectrum, excluding the peak from surface contamination, are seen to have disappeared after the O<sub>2</sub> plasma etching.

Following a deposition time of 2.0 s, Fig. 5 plots the SiO<sub>2</sub> thickness changes as a function of the O<sub>2</sub> plasma etching time. The etched thickness is seen to begin to level off at approximately 40 s and eventually plateaus. These results confirm that this process exhibits self-limiting ALE of SiO<sub>2</sub> regardless of the etching time.

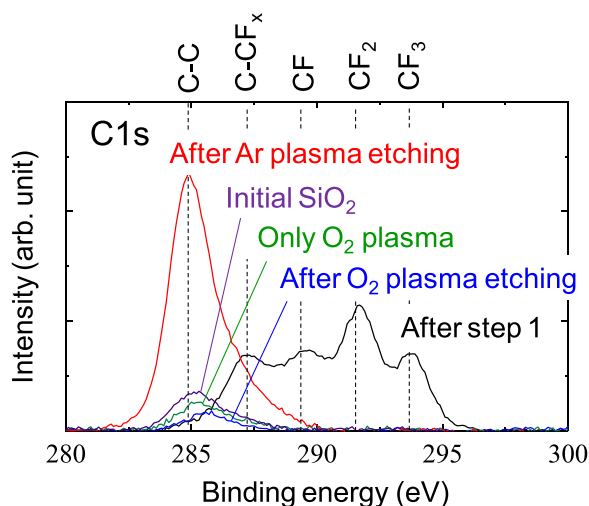


FIG. 4. (Color online) C 1s XPS spectra after various steps of a single cycle.

To investigate the relationship between the deposition time and the EPC, the deposition time was varied from 1.0 to 5.0 s, using an O<sub>2</sub> plasma etching time span of 60 s. Figure 6 shows the etched thickness of the SiO<sub>2</sub> at different deposition times as a function of cycle number. These results indicate that the etched thickness exhibits a linear relation with the cycle number and the EPC remains constant. Since the excess carbon atoms on the SiO<sub>2</sub> surface and chamber wall surface were removed by producing gaseous products such as CO<sub>x</sub>, the O<sub>2</sub> plasma maintained the surface condition of the SiO<sub>2</sub> and chamber wall. To clarify the effect from fluorocarbon film deposition on the chamber wall and the upper electrode on the etched thickness of SiO<sub>2</sub>, O<sub>2</sub> plasma irradiated the SiO<sub>2</sub> without the fluorocarbon film for 60 s, while the fluorocarbon film deposited on the chamber wall surface and the upper electrode surface for 7.5 s. The SiO<sub>2</sub> thickness decreased slightly by 1.1 Å before and after O<sub>2</sub> plasma irradiation. The amount of change is equivalent to thickness change due to O<sub>2</sub> plasma irradiation. Therefore, this ALE process consisting of alternating O<sub>2</sub> plasma etching with fluorocarbon film deposition is able to mitigate various problems, such as changes in the EPC due to residual surface carbon and deterioration of the chamber conditions with repeated cycles.

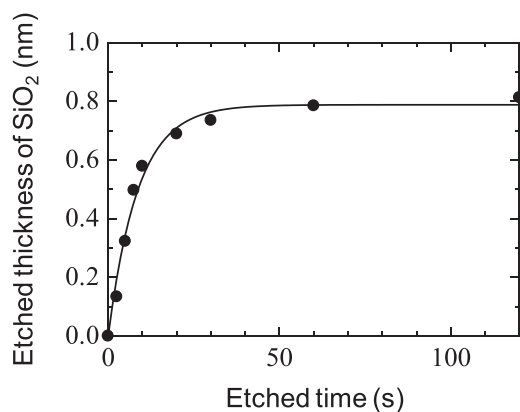


FIG. 5. SiO<sub>2</sub> thickness changes over O<sub>2</sub> plasma etching time during a single cycle following fluorocarbon deposition for 2.0 s.

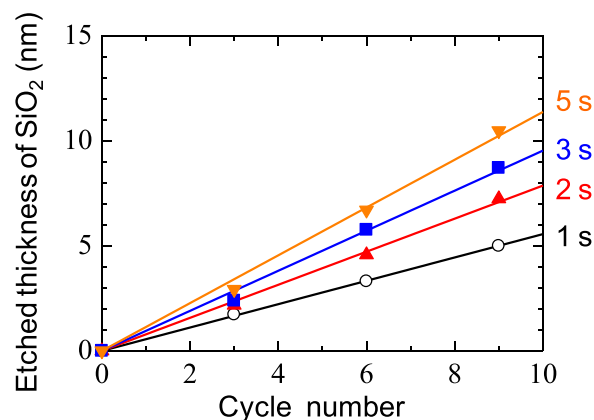


FIG. 6. (Color online) SiO<sub>2</sub> thickness changes as function of number of cycles for various deposition times following O<sub>2</sub> plasma etching for 60 s.

Figure 7 plots the relationship between EPC and deposition time. The EPC values for deposition times of 1.0, 2.0, 3.0, and 5.0 s were 5.6, 7.9, 9.5, and 11.4 Å/cycle, respectively. It is evident that the EPC increases with increasing deposition time, equivalent to increasing thickness of the fluorocarbon film. It can also be seen that the EPC value gradually reach the plateau region. This occurs because the etching reaction takes place only at the interface between the deposited fluorocarbon film and the SiO<sub>2</sub> film. Once the fluorocarbon film deposited on the SiO<sub>2</sub> surface reaches a critical thickness, the fluorocarbon reaction with SiO<sub>2</sub> will no longer increase with deposited fluorocarbon film thickness.<sup>20,25</sup> The critical fluorocarbon thickness depends strongly on the applied ion energy, because it is the ions reaching the interface that etch the SiO<sub>2</sub>.

During ALE of SiO<sub>2</sub> by an Ar plasma, fluorine atoms in the fluorocarbon film are evaporated as fluorine molecules and carbon atoms form a carbon-rich film, as shown in Fig. 4. This film disturbs the SiO<sub>2</sub> etching process by increasing the ion energy required to reach the interface between the fluorocarbon and the SiO<sub>2</sub>. Consequently, controlling the thickness of the deposited fluorocarbon film on the atomic-scale is required in order to achieve an adequate reaction of carbon with oxygen in the SiO<sub>2</sub> film. In contrast, the O<sub>2</sub> plasma removes the excess carbon by producing CO or CO<sub>2</sub>,

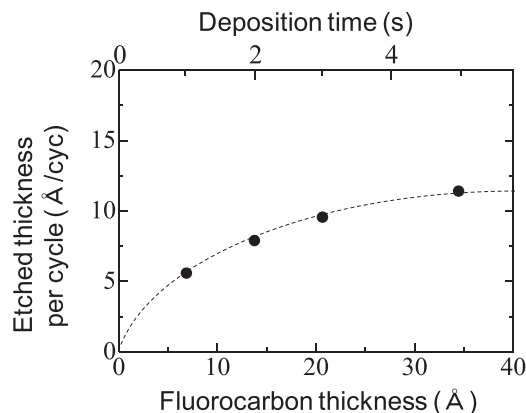


FIG. 7. Relationship between the EPC and the deposition time per cycle.

and allows the ALE process to proceed without forming a carbon film. Therefore, this new technique consisting of alternating an O<sub>2</sub> plasma with fluorocarbon film deposition makes it unnecessary to uniformly deposit a fluorocarbon film on the SiO<sub>2</sub>. Additionally, ions are able to reach the interface even when the ion energy contributing to the etching reaction is relatively low. We therefore expect that this ALE process will be well-suited to large-scale production in conjunction with reduced damage to the SiO<sub>2</sub>.

#### IV. SUMMARY AND CONCLUSIONS

We performed ALE of SiO<sub>2</sub> by alternating O<sub>2</sub> plasma etching with fluorocarbon film deposition. This process achieved constant and uniform EPC values because the O<sub>2</sub> plasma maintained the surface condition of the SiO<sub>2</sub>, such that excess carbon atoms in the fluorocarbon film deposited on the SiO<sub>2</sub> surface were removed in the form of gaseous products such as CO<sub>x</sub>. The O<sub>2</sub> plasma also preserved the initial chamber conditions by essentially cleaning the chamber interior. Additionally, the ALE process was found to be self-limiting as both the O<sub>2</sub> plasma etching time and the fluorocarbon deposition time were extended. This behavior suggests that the etching process ceased after depleting the fluorocarbon film on the SiO<sub>2</sub> surface and that the application of excess fluorocarbon film does not contribute to etching of the SiO<sub>2</sub>. This work has demonstrated that our new ALE process for SiO<sub>2</sub> exhibits high reproducibility and has the potential to allow uniform EPC values over large wafer surfaces.

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