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Fluorocarbon assisted atomic layer etching of SiO$_2$ using cyclic Ar/C$_4$F$_8$ plasma

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The authors demonstrate atomic layer etching of SiO$_2$ using a steady-state Ar plasma, periodic injection of a defined number of C$_4$F$_8$ molecules, and synchronized plasma-based Ar$^+$ ion bombardment. C$_4$F$_8$ injection enables control of the deposited fluorocarbon (FC) layer thickness in the one to several Ångstrom range and chemical modification of the SiO$_2$ surface. For low energy Ar$^+$ ion bombardment conditions, the physical sputter rate of SiO$_2$ vanishes, whereas SiO$_2$ can be etched when FC reactants are present at the surface. The authors have measured for the first time the temporal variation of the chemically enhanced etch rate of SiO$_2$ for Ar$^+$ ion energies below 30 eV as a function of fluorocarbon surface coverage. This approach enables controlled removal of Ångstrom-thick SiO$_2$ layers. Our results demonstrate that development of atomic layer etching processes even for complex materials is feasible. © 2014 American Vacuum Society.

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I. INTRODUCTION

The ability to precisely add and/or remove Ångstrom-thick layers from a surface is required for advanced semiconductor manufacturing and related technologies that increasingly demand atomistic surface engineering.\textsuperscript{1–3} While atomic layer deposition has been tremendously successful, the development of a corresponding atomic layer etching (ALE) method has lagged. In atomic layer deposition, control of deposited film thickness near one atomic monolayer is based on careful choice of chemical precursors which, once adsorbed at one monolayer on the substrate, passivate the surface and prevent multilayer adsorption. A subsequent reaction step transforms the precursor into the desired material. Experimental and computational efforts aimed at realizing a corresponding ALE approach using cyclic surface passivation followed by removal of weakly bound chemical reaction products resulting from interaction of the passivation layer with the surface started in the 1990s (see Refs. 3–11 for selected studies). These efforts have shown that a key obstacle toward realizing ALE is achieving self-limited etching, in particular, for situations when ion bombardment to remove the reacted material and precise control of surface coverage by the chemical precursor is required. Self-limited etching requires both negligible spontaneous chemical etching by the precursor used to passivate the surface and insignificant physical sputtering of the unmodified material after etch product removal.\textsuperscript{3} Minimizing physical sputtering has been difficult to realize consistently, and additional factors, e.g. photon-induced etching for plasma environments,\textsuperscript{12} have also been invoked to explain persistent etching for certain conditions. On the other hand, recent computational studies have demonstrated the feasibility of ALE for certain systems. For instance, Agarwal and Kushner described a computational investigation of ALE of silicon and SiO$_2$ using conventional plasma etching tools.\textsuperscript{3} They showed that self-limited etching can be achieved by careful control of chemistry and ion energies during the passivation and etching step, respectively. Raufl et al. applied molecular dynamics (MD) simulations to examine the possibility of realizing ALE using nanometer-scale fluorocarbon (FC) passivation of SiO$_2$ and silicon followed by Ar$^+$ ion etching.\textsuperscript{13} They observed self-limited etching of SiO$_2$ and Si for Ar$^+$ energies smaller than 40 eV. No experimental validation of these computational studies has been reported to the best of our knowledge.

It is the goal of the present study to evaluate these ideas using cyclic Ar/C$_4$F$_8$ plasma interacting with SiO$_2$ and to explore for what conditions controlled removal of SiO$_2$ layers approaching one atomic layer thickness per cycle can be achieved. We use time-resolved surface characterization to confirm ALE. In our approach, we deposit Ångstrom thick FC layers to form a modified SiO$_2$ surface layer. Subsequently, low energy Ar$^+$ ion bombardment is used to remove both the FC layer and a thin reacted SiO$_2$ layer. Material etching stops once the reacted SiO$_2$ surface layer has been removed,\textsuperscript{13} resulting in a self-limited process. To realize FC layer deposition on the order of Ångstroms, we use pulsed C$_4$F$_8$ injection into a low power Ar plasma. For an unbiased substrate, precise FC film thickness control in the one to several Ångstrom range is possible by adjusting...
the total number $N_{C_4F_8}$ of $C_4F_8$ molecules entering the reactor by varying pulse duration and $C_4F_8$ gas flow rate appropriately. For these conditions, FC film thickness increases linearly with $N_{C_4F_8}$. Following FC deposition, a small RF self-bias voltage ($-5$, $-10$, and $-15$ V) is applied for 35 s in the cases described here, creating maximum ion energies of 20, 25, and 30 eV, respectively. For the lower ion energies, $Ar^+$ ion induced physical sputtering of unmodified SiO$_2$ is negligible. This was confirmed in this work. At the end of a cycle, the process sequence is repeated to achieve precise control over the total etched thickness.

II. EXPERIMENT

We used an inductively coupled plasma system excited at 13.56 MHz. The plasma was confined within a 195 mm diameter anodized Al confinement ring. A 125 mm diameter Si substrate is located 150 mm below the top electrode on an electrostatic chuck and can be biased at 3.7 MHz. The base pressure achieved before processing was in the $1 \times 10^{-6}$ Torr range and the temperature of the samples (25 $\times$ 25 mm$^2$) was stabilized by substrate cooling (10°C) during plasma processing. Details of the plasma system have been described previously. The materials studied were SiO$_2$-Si-SiO$_2$ stacks deposited on a Si substrate by PECVD techniques and studied by in-situ ellipsometry in real time.

III. RESULTS AND DISCUSSION

In Fig. 1, a typical thickness evolution for an SiO$_2$ layer is shown for multiple cycles, along with the process parameters of one cycle. At the beginning of each cycle a pulse of C$_4$F$_8$ is injected for 1.5 s into a continuous argon plasma, and deposits about 5 Å of FC film. A synchronized RF bias potential is applied to the substrate 8 s after the C$_4$F$_8$ pulse to increase Ar$^+$ ion bombardment energies. This initiates FC film etching, followed by strongly time-dependent SiO$_2$ etching. Figure 1 shows that the initially high SiO$_2$ etch rate continuously decreases and finally ceases. The ion-induced reaction of deposited FC with SiO$_2$ enables transient etching and controlled removal of an ultrathin SiO$_2$ layer. Each cycle shows a similar behavior, although there are small systematic differences which will be discussed below. Figure 1 shows that the present approach permits a high degree of control over total etched SiO$_2$ thickness. The observed behavior is consistent with both the MD simulations of Rauf et al. and computational simulations of Agarwal and Kushner. For instance, the MD work showed that for Ar$^+$ ion energies of 20 eV ion-induced removal of chemical reaction products dominates etching and unmodified SiO$_2$ etches at a negligible rate.

Etching of SiO$_2$ for the low energy ion conditions is completely dominated by the fluorocarbon reactants and results...
in an etch rate decrease with time until the initially deposited FC layer is depleted and etching ceases. This effect can be clearly seen in the expanded views of single etching cycles for two conditions in Fig. 2. In Fig. 2(a), after deposition of 5 Å of FC, a bias potential of ~10 V is applied. The low energy ions induce etching of the FC layer and additionally reaction of carbon and fluorine with the underlying SiO$_2$.\textsuperscript{13,18} The resulting modified SiO$_2$ surface layer is etched by low energy Ar$^+$ ion bombardment until the modified layer has been removed, upon which SiO$_2$ etching ceases. A similar change in etch rate over time can be observed upon deposition of a thicker FC layer (15 Å) on SiO$_2$ [see Fig. 2(b)]. The use of a longer C$_4$F$_8$ pulse not only produces a thicker FC layer on the SiO$_2$ surface but also increases FC on the chamber walls. Overall, there is a larger amount of FC in the system, and the additional FC increases the etch rate during the second half of the cycle. A steady-state is not reached within the period the RF bias was applied for in this case. Therefore, even at the end of the etching cycle, FC material is still present at the SiO$_2$ surface and enables a finite etch rate. This can be minimized by using shorter C$_4$F$_8$ pulses.

Since one crucial factor of this approach is precise admission of chemical reactants to the system, we expect that residual FC deposited on the chamber walls will interfere with the management of chemical reactant supply at the substrate surface and reduce control over the etching process. Figure 1 shows that the time-dependent etch rate during the second half of each cycle increases slightly from cycle to cycle. Residual FC entering the gas phase from the chamber walls between C$_4$F$_8$ pulses can redeposit on the exposed, unmodified SiO$_2$ and increase SiO$_2$ etching for FC reactant-starved process conditions in the later part of a cycle. One key requirement for achieving ALE processes in a plasma reactor is to maintain well-defined clean process chamber conditions to control supply of chemical reactants.

To obtain insights on changes in surface chemistry throughout one cycle, x-ray photoelectron spectroscopy (XPS) has been performed after the FC deposition step, during the SiO$_2$ etch step, and after completion of a cycle. To study steady-state conditions, these experiments were performed for the 10th cycle of a sequence. The results are displayed in Fig. 3, which summarizes the different binding energy regions of interest (Si 2p, C 1s, O 1s, and F 1s). Data are shown for 15 Å and 5 Å thick FC films in Figs. 3(a) and 3(b), respectively. Si 2p and O 1s spectra were fit using SiO$_2$ and SiOF at 103.9 eV, 104.1 eV, 533.2 eV, and 533.4 eV, respectively. C 1s spectra were fit using C-C/H, C-CFx, CF, CF$_2$, and CF$_3$ peaks at 285 eV, 287 eV, 289.1 eV, 291.2 eV, and 293.4 eV, respectively. F 1s spectra were fit using SiF$_x$, CF, and CF$_2$ at 687.8 eV, 686.9 eV, and 689 eV, respectively.\textsuperscript{19} A more detailed description of this analysis has been given in previous publications.\textsuperscript{20–22} A clear reduction in F content is seen throughout the etch step for a deposited film of 15 Å as seen in Fig. 3(a). The C 1s spectra show a reduction in carbon-bonded fluorine. The Si 2p and O 1s signals increase correspondingly since they originate from the SiO$_2$ underneath the FC film. An SiO$_2$ surface covered with
a thin FC film [5 Å, Fig. 3(b)] shows little of the characteristic fluorocarbon bonding signature in the C 1s spectrum and only a slight F 1s signal reduction after etching in contrast to samples covered with a thick FC film. Since the C 1s spectrum shows the same reduction of carbon bonded to fluorine as the thicker films, the remaining fluorine must be associated with SiO₂. Bonding of fluorine with SiO₂ is shown by a slight shift of the Si 2p and O 1s spectra toward higher binding energy, consistent with the more electronegative environment. The MD simulations of Rauf et al. also show residual fluorine on the SiO₂ surface after the etch rate ceases for low energy ion bombardment conditions.¹³

The FC layer plays a critical role in enabling SiO₂ etching for the low energy ion bombardment conditions used here. Figure 4 summarizes the variation of FC etching rate [(a)–(c)], SiO₂ etching rate [(d)–(i)], and SiO₂ thickness removal [(g)–(i)] with FC layer thickness and maximum ion energy. The time dependent etch rate within one cycle increases with FC film thickness and maximum Ar⁺ ion energy. We expect that once a critical FC layer thickness on SiO₂ is reached, the FC reaction with SiO₂ will no longer increase with FC film thickness, and SiO₂ etched per cycle will saturate.¹⁸ If the FC layer thickness exceeds this critical thickness, on the order of the projected range of Ar⁺ ions in the FC material, the additional FC deposited will be etched by Ar⁺ bombardment with little interaction with the SiO₂ underneath. The impact of FC film thickness on SiO₂ etch rate is clearly seen in Figs. 4(d)–4(f), which shows an increase with both FC layer thickness and maximum ion energy. The maximum SiO₂ etch rate is not a strong function of total FC film thickness above 5 Å, but the minimum SiO₂ etch rate (achieved at the end of the cycle), depends strongly on FC film thickness. A deposited FC film thickness of 4 Å or less is required to achieve minimal SiO₂ etching at the end of the cycle at the low ion energies used in this study. Figure 4 shows that the SiO₂ etch rate and SiO₂ thickness removed per etching cycle increase with maximum Ar⁺ ion energy for a given FC layer thickness.

IV. SUMMARY

In summary, we have shown that using a steady-state Ar plasma, periodic injection of a defined number of C₄F₈ molecules and synchronized plasma-based Ar⁺ ion bombardment, atomic layer etching of SiO₂ is possible. The thickness of a deposited FC layer in the range of one to several Ångström and Ar⁺ ion bombardment are used to control the chemical modification of SiO₂, thus enabling etching of SiO₂ for low energy ion bombardment conditions for which the physical sputter rate of SiO₂ is negligible. We have measured for the first time the enhancement of the SiO₂ etch rate relative to the physical sputter rate at Ar⁺ ion energies below 30 eV as a function of fluorocarbon surface coverage. Our results are consistent with computational simulations that first suggested the feasibility to achieve ALE for the fluorocarbon/Ar⁺/SiO₂ system.

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