Surface chemical changes of aluminum during NF₃-based plasma processing used for in situ chamber cleaning

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During plasma-based in situ chamber cleaning of deposited dielectric films using NF₃ , a transformation of aluminum chamber parts into AlFₙ can take place. We studied the roles of fluorine atoms and ion bombardment in this process by employing NF₃ discharges mixed with He, Ne, or Ar interacting with or without ion bombardment with sputter-deposited Al films on silicon. Aluminum oxide erosion rates and surface chemistry changes, and information on the species that evolve from the surfaces during the process, were obtained by real-time ellipsometry and mass spectrometry, respectively. Characterization of processed Al surfaces was also performed using x-ray photoelectron spectroscopy. We find that Al oxide is rapidly removed/transformed in NF₃ discharges and also for C₂F₆/O₂ rf powered discharges. We observe a complex interactive role of fluorine atoms and ion bombardment that leads to the formation of thick fluorinated Al reaction layers during exposure of Al to NF₃-containing rf plasmas. For NF₃-rich rf discharges, the Al fluoride layer thickness continues to grow as a function of time, without saturation. The Al fluoride layer formation can be prevented if NF₃/noble gas mixtures containing a high noble gas proportion are employed instead. An increasingly thicker Al fluoride layer is produced with a greater proportion of NF₃ in He/NF₃ , Ne/NF₃ , and Ar/NF₃.

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I. INTRODUCTION

Discharges fed with NF₃ or fluorocarbon gases like C₂F₆ are widely used for plasma-based in situ chamber cleaning of deposited dielectric films after plasma-enhanced chemical vapor deposition processes. NF₃ enables high cleaning rates, has a shorter atmospheric lifetime than fluorocarbon gases and avoids fluorocarbon contamination. 1–3 Because the nitrogen–fluorine bond of NF₃ (59 kcal/mole) is weaker than the carbon–fluorine bond in C₂F₆ (127 kcal/mole), the dissociation of NF₃ is very effective relative to fluorocarbon gases. However, fluorine-rich cleaning discharges can transform chamber interior components made from aluminum into aluminum fluoride. NF₃ may be mixed with noble gases to enhance the dissociation of the electronegative gas. 4 Noble gases like helium, neon, and argon can stabilize the discharge, enhance source gas dissociation, and improve the uniformity of the etched species concentration. 5 High Si₃N₄ and SiO₂ etching rates have been achieved for NF₃ rf excited discharges when mixed with He and Ar additives. 6 Questions that need to be answered are: (1) “What are the most important factors that control the chemical transformation kinetics of the surface of Al films during fluorine-based in situ chamber wall cleaning into AlFₙ ?” and (2) “Which plasma operating conditions minimize changes in Al surface condition?”

In this work, we have found several critical factors that determine the kinetics of transformation of aluminum into AlFₙ in fluorine-based discharges. In particular, the relative roles of fluorine precursor gas (NF₃ versus C₂F₆/O₂), gas mixture (NF₃ mixed with He, Ne, and Ar), and ion bombardment (comparison of rf bias power produced plasmas with remote microwave excited discharges) in controlling the kinetics of this process was investigated. We used in situ real-time ellipsometry to monitor the state of sputtered Al films during the cleaning process. This approach enabled us to establish in situ the kinetics of removal of the native Al oxide layer and the formation of a fluorinated Al surface layer. The variation of the Al surface chemistry as a function of process parameters was also investigated using x-ray photoelectron spectroscopy (XPS). Mass spectrometry was employed to study the evolution of several Al-related products above the Al sample. rf discharge impedance analysis allowed us to establish the transition of the rf discharges from a capacitive mode to a resistive mode. This work clarifies the respective roles of fluorine atom density and ion bombardment in this transformation, and enables us to identify industrially useful conditions. We observe that rf bias power and the fluorine density are key factors that control the kinetics of the chemical transformation of the aluminum surface of Al films into AlFₙ during fluorine-based in situ chamber wall cleaning.

II. EXPERIMENTAL SETUP AND PROCEDURES

A. Experimental setup

Figure 1 shows a schematic of the experimental apparatus used for the present study. 6 The reactor walls are made of stainless steel. The experimental setup allows production of a

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discharge using either a capacitively coupled electrode fed with an rf power supply, or via a remote microwave applicator. In this work, the rf power level (~13.56 MHz) fed using an L matching network to the substrate electrode was varied from 190 to 350 W. Because rf power was supplied directly to the wafer chuck, a self-bias voltage is produced for rf plasma operating conditions at the wafer, resulting in ion bombardment of the Al surface. For instance, the measured self-bias and peak-to-peak voltages were 222 V and 462 V at 250 W rf power for a 1 Torr NF3 discharge, respectively. The self-bias voltage provides an upper limit of the ion energy especially considering the 1 Torr pressure for which the sheath is highly collisional. Alternatively, an Astex 2.45 GHz microwave applicator with a sapphire coupling tube is connected to the chamber and was used to produce a remote microwave plasma. In this case, the dissociated NF3 or C2F6/O2 gases travel downstream and the wafer is exposed to a flux of long-lived fluorine atoms but no ion bombardment. Al-coated Si wafers sputter-deposited Al films, 20 to 1000 nm thick, on Si(100) substrates or Al alloy coupons were located on a wafer holder that was cooled to 10 °C.

We investigated pure NF3, mixtures of NF3 with He, Ne or Ar, and C2F6/O2 in this work. The total gas flow was 300 sccm in all cases. Although we studied a range of pressures (~500 mTorr up to 2 Torr), most of the work was performed using 1 Torr operating pressure, and all data reported here were obtained at that pressure.

B. Diagnostic techniques

The Al surface modifications induced by the plasma processes were monitored using an in situ He–Ne (632.8 nm) rotating compensator ellipsometer operated in a polarizer-compensator-sample-analyzer configuration.7 The application of this technique was crucial to obtaining insights on the changes of the Al surface as a function of process conditions. The Al surfaces at the end of the fluorine-based process are highly reactive, and rapid changes in the Al surface conditions in the process chamber occur once the plasma was extinguished, but the gas still present in the reactor. These changes are evident in the ellipsometric data (e.g., see Fig. 2, end of plasma exposure).

A quadrupole mass spectrometer (MS) (Inficon Transpector) was mounted on top of the reaction chamber and used to detect products evolving from the Al surface during the plasma process. This mass spectrometer has a ceramic sampling cone with a 50 µm diameter orifice that is located above the Al surface. The distance between the sample surface and the MS orifice is 20 mm.

The electrical measurements were taken with a LeCroy LT 364 digital oscilloscope. Current and voltage wave forms were measured outside the reactor. Voltage and current wave forms were measured using a LeCroy PPE 4kV voltage probe and a Pearson 2877 current transformer in reactor characterization, and in-house built dV/dt and dI/dt probes. Both sets of probes had been calibrated prior to use.

Surface chemical information of processed Al samples was obtained using XPS. The Al thin films and polished coupons of Al 6061 alloys were transferred in air to the surface analysis chamber. Photoelectrons were excited using a nonmonochromatized Mg Kα x-ray source (1253.6 eV). Survey spectra and high-resolution spectra of Al 2p and O 1s, F 1s and C 1s electron emission were measured using an emission angle of 90° relative to the wafer surface. The spectra presented in this article were obtained at 20 eV pass energy.

III. RESULTS AND DISCUSSION

A. Comparison of NF3 and C2F6/O2 discharges produced using either a capacitively coupled rf electrode or remote microwave excitation

1. Ellipsometry results

Initially, either a microwave plasma or an rf plasma were employed to study the interaction of NF3 and C2F6/20% O2
discharges with Al thin films. The remote microwave plasma and the rf plasma were maintained at 1000 W and 250 W source power, respectively. The microwave plasma region is located about 50 cm upstream from the wafer and produces a high density of fluorine atoms that stream over the wafer surface, but the wafer is not exposed to energetic ion bombardment. Alternatively, rf power was capacitively coupled to the electrode, and produced ion bombardment of the Al surface simultaneously exposed to a flux of fluorine atoms.

Figure 2 shows the ellipsometric variables delta and psi as a function of treatment time. We focus initially on the changes of delta with treatment time in Fig. 2(a). In the portion of the delta–psi plane shown in Fig. 2, an increase (decrease) of delta corresponds to the removal (formation) of a transparent overlayer on the Al substrate. Curve (1) in Fig. 2 shows the attack of the Al surface in a C2F6/20% O2 rf discharge. We observe an increase of delta as a function of time. This increase corresponds to the removal of the native Al oxide layer. This removal takes place within the first 200 s of plasma exposure, and subsequently delta remains unchanged. This result indicates that a C2F6/20% O2 rf discharge is effective in removing the native Al oxide layer, but no growth of a transparent overlayer or other transformation of the Al surface simultaneously exposed to a flux of fluorine atoms.

The data of Fig. 2 can be explained by the processes of removal of the native Al oxide (discharge type and feed gas dependent), followed by the formation of a fluorinated surface layer (only for a NF3 rf discharge). Consistent with this result are the following observations made in separate experiments. We observed that Al films after Ar precleaning showed only growth of a modified surface layer for the NF3 rf discharge treatment. No saturation of the fluorinated-thickness layer was observed for the NF3 rf treatment. In the case of NF3 microwave plasmas, a very thin modified Al surface layer was produced with Ar precleaned Al films.

2. X-ray induced photoelectron spectroscopy analysis

XPS was used to analyze the modified Al surface layers. The XPS data obtained with the Al films used for the experiments shown in Fig. 2 are displayed in Fig. 3. Figure 3 summarizes high-resolution Al2p [Fig. 3(a)], O1s [Fig. 3(b)], F1s [Fig. 3(c)], and C1s [Fig. 3(d)] core-level spectra. Data were obtained with untreated Al films, and Al films after 10 min of rf or microwave discharge treatments using either pure NF3 or C2F6/20% O2. For the untreated Al, the native oxide layer is apparent in both the Al 2p and the O 1s data. This sample also shows the typical hydrocarbon contamination. Aluminum films after plasma exposure show that the native Al oxide film is reduced in thickness for all discharge treatments. However, rf discharges are found to be most effective, and the microwave discharge treatment employing C2F6/20% O2 is the least effective, consistent with the data of Fig. 2. In this case, we find that a very thin fluorocarbon surface layer is produced on the Al surface, which apparently protects the native Al oxide from further attack. For the NF3 microwave discharge treatment, more of the native oxide layer is removed by the plasma exposure, and significantly more fluorination of the Al surface takes place. This is evident in both the Al 2p and F 1s data. Consistent with the ellipsometric data shown in Fig. 2, the Al 2p, O 1s, and F 1s data of Fig. 3 show that rf discharges are more effective in removing the native Al oxide layer. In addition, in the case of NF3 rf discharges, a thicker reacted Al fluoride layer is produced. Different amounts of oxygen are found after all discharge treatments. Part of this is due to postplasma processes, which are apparent in the ellipsometric data, e.g., see curve (2) in Fig. 2 where changes of delta are apparent after the plasma has been extinguished. No fluorocarbon components are found for the rf discharge treatments, consistent with the low-energy threshold that exists for fluorocarbon etching in fluorine-containing plasmas.

The thicker reacted fluorinated Al surface layer that is produced for the NF3 rf discharge treatment is most apparent in the F 1s data of Fig. 3(c) and the metallic Al 2p data of Fig. 3(a). The F 1s peak component that is characteristic of Al fluoride is highest for the NF3 rf discharge. In Fig. 3(c), the CF3 peak component of the F 1s signal seen for the microwave plasma is due to the protecting fluorocarbon film deposited on the Al surface in the C2F6/O2 experiments or by interaction of hydrocarbons with fluorine for NF3. In addition, a comparison of the metallic Al 2p components in Fig. 3(a) for the different treatments shows that this component has the lowest intensity after the NF3 rf discharge treat-
ment, consistent with the thickest AlF$_3$O$_y$ reacted overlayer. Comparable metallic Al 2p intensities are found for samples exposed to the NF$_3$ microwave and the C$_2$F$_6$/20% O$_2$ rf discharges.

B. Further studies of NF$_3$ rf excited discharges

1. rf power dependence

For NF$_3$-based rf discharges, the rf power level is of overriding importance in determining the extent of the Al surface modifications. At high rf power levels, the Al surface is quickly modified. This is understandable since, for our capacitively coupled electrode, an increase of the rf power produces a higher plasma density and a higher sheath voltage, and thus more energetic ion bombardment of the Al surface. Figure 4 shows the ellipsometric variables delta [Fig. 4(a)] and psi [Fig. 4(b)] as a function of time using different rf power levels. A gas flow of 300 sccm NF$_3$ at 1 Torr pressure was used. The plasma is ignited at 150 W and maintained for a certain time, and then increased in steps up to 350 W. The ellipsometric data indicate that a threshold rf power exists in our reactor, below which the attack of the native Al oxide layer is slow and a thick reacted Al–fluoride layer is not produced. This critical power level appears to be about 250 W for our reactor (2.1 W/cm$^2$). When Al is exposed to an NF$_3$ rf discharge at this power level and above, significant changes in the Al surface characteristics are observed, and a thick reacted Al–fluoride layer that continues to grow in thickness is produced. On the other hand, if the rf discharge is sustained using a rf power level below this value, the Al
surface modifications are minimized. At 250 W rf power, the peak-to-peak and self-bias voltages were 462 V and 22 V, respectively. Because of the characteristic of the very electronegative NF₃ plasma, the dc self-bias voltage is very small in NF₃ rf produced discharges.

2. Noble gas/NF₃ rf discharges

We also studied He/NF₃, Ar/NF₃ and Ne/NF₃ discharges since such gas mixtures can be used for very rapid etching of SiO₂ and Si₃N₄. For instance, in the case of Ar/NF₃ discharges, it has been found that the etching rates of these materials during chamber cleaning are greatest when about 20% of NF₃ in NF₃/Ar were employed. Figure 5 displays the ellipsometric variables delta and psi as a function of time for He/NF₃ gas mixtures of varying compositions. Qualitatively similar results were obtained with Ne/NF₃ and Ar/NF₃ discharges. The discharge is ignited with only the noble gas, and the percentage of NF₃ is subsequently increased in 10% steps. A constant rf power level of 250 W and a pressure of 1 Torr were employed, and the total gas flow rate was kept constant at 300 sccm.

The behavior of the ellipsometric variables in Fig. 5 indicates that the Al surface modifications can be minimized as long as the NF₃ concentration in He/NF₃ is less than 40%. If the NF₃ concentration is increased to 40% and higher, the formation of a thick reacted Al–fluoride layer commences. The Al–fluoride layer becomes increasingly thicker as the percentage of NF₃ is increased. From the slope of the curve as a function of time, we can learn that the formation rate of the Al–fluoride layer increases as the amount of NF₃ in the He/NF₃ discharge is raised to 100%. These measurements imply that if He/NF₃ rf discharges are used for in situ chamber cleaning, the Al surface modifications can be minimized for a 250 W rf discharge as long as the NF₃ concentration is maintained at a value of less than 40%. The simplest interpretation of this observation is that the formation of the modified Al surface layer requires a high flux of fluorine atoms at the Al surface, which is not available in NF₃ deficient NF₃/He discharges. It is, of course, possible that the Al fluoride is formed in this case but immediately removed by the noble gas ion bombardment. However, the associated Al etching rates were so small, that we were unable to measure them in this work.

Figure 6 shows the behavior of the AlF₃ and AlOF mass spectrometer signals as a function of time for 50% NF₃/He, 50% NF₃/Ar and 50% NF₃/Ne rf discharges. The operating conditions were 250 W rf power, 1 Torr pressure, and 300 sccm total gas flow. The data show that AlF₃ is produced for all rf discharges and, that after an initial transient, the rate of formation is approximately constant as a function of time. Figure 6(b) indicates a much higher formation rate of AlOF in the Ar/NF₃ discharge than that seen for He/NF₃ or Ne/NF₃. This product must be produced by the removal of the oxidized Al in the Ar/NF₃ discharge. The ion enhancement effect of AlOF formation is expected to be lower for He/NF₃ and Ne/NF₃ than for Ar/NF₃ and likely responsible for the fact that no AlOF signal was measured for the He/NF₃ and Ne/NF₃ discharges.

C. Impedance measurements

We performed analysis of the impedance of the noble gas/NF₃ discharges similar to studies published previously. Figure 7 shows the impedance as a function of NF₃ addition to He, Ar, and Ne discharges. At about 20% of NF₃ in the NF₃/noble gas mixtures, a local minimum of the impedance is seen. If the NF₃ percentage is increased above that to 100%, the impedance magnitude increases monotonically with NF₃ concentration. Figure 8 shows the...
corresponding impedance phase angle as a function of percentage NF3 added. For the noble gas discharges, the phase angle is near 90°, consistent with capacitive discharge behavior. As the NF3 percentage is increased to 50% at 190 W and to 60% at 250 W, the impedance phase angle becomes 0° for all noble gases. The plasma changes from a highly capacitive state (≈90°) at 0% NF3 to a resistive/inductive state (≈0°) at around 50% added NF3. This transition appears to correlate with the change in the ellipsometry data measured for He/NF3 discharges. These data imply the following behavior: Without NF3, rf power is primarily absorbed in the sheath and ion bombardment of the Al surface takes place (capacitive discharge). The ion bombardment results in the removal of the native Al oxide layer, and this is most effective for Ar discharges. Since there is no fluorine available, no Al–fluoride formation can take place. Once NF3 is added to the discharge, the discharge impedance changes to the resistive/inductive state, where rf power is absorbed by the discharge bulk. This results in high dissociation of the NF3 gas, and production of free fluorine. The atomic fluorine density results in Al–fluoride formation. For He/NF3 discharges, this is the case once 50% or more NF3 has been added.

D. Discussion

The data presented above demonstrate that the removal of the native Al oxide surface layer in fluorine discharges takes place rapidly. This is the case even for NF3 microwave discharge treatments where ion bombardment of the Al surface occurs at much lower ion energies than in C2F6/O2 or NF3/noble gas mixtures. The ellipsometric data of Fig. 2 are consistent with this, since they show a much slower rate of removal of the native oxide in NF3 rf discharges than for C2F6/O2 rf discharges.

The XPS data indicate surface conditions as schematically displayed in Fig. 9. A thicker reacted Al–fluoride layer is formed for 10 min of exposure to the NF3 rf discharge than for any of the other treatments. Most important, the thickness of the Al–fluoride layer continues to grow with time and does not saturate, as is evident in the ellipsometry data. For the NF3 microwave discharge, a thinner reacted Al–fluoride is produced, and the thickness of this layer rapidly saturates. In addition, microwave discharges are much less effective in removing fluorocarbon groups from the Al surface, which may form either directly by the discharge if a fluorocarbon precursor gas is used, or by the interaction of fluorine with carbon contamination existing on the Al surface.

The present data also show that the formation of a thick heavily fluorinated Al surface region requires both a high gas phase fluorine density, e.g., as produced in pure NF3 discharges, but not in He-rich NF3/He discharges or C2F6/O2 discharges, and low-energy ion bombardment of the Al surface. The latter is most clearly demonstrated by the difference between NF3 discharges produced using either direct rf excitation or remote microwave plasma production. The observation that in the case of rf discharges a rf bias power threshold exists below which the formation of thick Al–fluoride layers does not take place (or cannot be observed in the time scale of the experiments conducted here), is also
consistent with this. The role of the low-energy ion bombardment appears to be very subtle since, for noble gas-rich discharges (capacitive character), little surface aluminum–fluoride is produced. The AlFx, even if formed in this case, is likely removed by the ion bombardment (see Fig. 6).

IV. SUMMARY AND CONCLUSION

The data presented in this work provide evidence of a complex interplay of fluorine atoms and low-energy ion bombardment in the formation of thick fluorinated Al surface layers during exposure of Al to NF3-containing plasmas. Little surface Al–fluoride is produced for C2F6/O2 discharges (rf or microwave) or remote microwave excited NF3 discharges. These comparisons imply that both ion bombardment of the Al surface and a high density of free fluorine are required to produce thick fluorinated Al surface layers. For NF3 discharges produced by direct rf excitation, an apparent threshold rf power exists below which formation of a thicker reacted Al–fluoride layer is either absent, or the formation rate is very slow. The threshold rf value is about 2.1 W/cm² in our reactor. When Al is exposed to an NF3 rf discharge at and above this power level, a thick reacted Al–fluoride layer is produced. If instead a He/NF3 discharge is used, the Al surface modifications are minimized at high rf power as long as the NF3 concentration is less than 40%, but an increasingly thicker Al–fluoride layer is produced with a greater proportion of NF3 in He/NF3. The real-time ellipsometry data also show that the Al–fluoride layer thickness continues to grow as a function of time when NF3-rich rf discharges were employed and that saturation is not observed.

Although actual chamber parts are often made of Al alloys, e.g., Al 6061, we used sputtered Al thin films on silicon substrates in this work since this enabled us to monitor the Al surface modifications using real-time ellipsometry. XPS surface analysis performed with sputtered Al thin films and 6061 Al alloy coupons after identical plasma exposures showed that the Al thin films and the 6061 Al alloy coupons exhibited very similar surface transformations. The insights reported here are, therefore, to a significant extent also relevant to the transformation of 6061 Al alloys in fluorine-containing plasmas.

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