I. INTRODUCTION

Halogen based plasmas have been utilized extensively to produce reactive atomic species for the etching of silicon and certain dielectrics. Of these systems, CF₄ and CF₄/O₂ plasmas are the best understood. In our previous work, we have investigated the role of N₂ addition to these discharges. Here, we will build upon this work and compare this system with the mechanisms of Si etching in the downstream effluent of a NF₃/O₂ microwave plasma.

In comparison to CF₄, the use of NF₃ as a substitute source of reactive fluorine is attractive in three ways: (1) the enhanced dissociation of the parent molecule, (2) the elimination of carbonaceous residues on the etched surface, and (3) as an alternate source of fluorine due to the increasing demands for more environmentally compatible process gases. It is primarily as this alternate fluorine source and specifically for its development into a reliable chamber cleaning process for amorphous silicon deposition that NF₃ has been studied.

It is well known that the addition of small amounts of O₂ to a CF₄ plasma enhances the atomic fluorine concentration by limiting recombination through oxidation of CF₄ radicals.

The resulting maximum in the fluorine concentration correlates with the etching behavior of Si. Adding O₂ to a low density NF₃ discharge can similarly enhance the fluorine density. In this work we used high flows (300 sccm NF₃) and high microwave powers (600–1400 W) and saw no enhancement in fluorine densities, but rather a reduction due to a dilution effect. The etch rates, however, still displayed a maximum after O₂ addition.

There has been a previous study of the dissociation levels of NF₃ as compared to CF₄. In a rf discharge, NF₃ has been shown to dissociate much more efficiently than CF₄ (by more than an order of magnitude). In our microwave discharge, we observed near complete dissociation of the NF₃, even at our lowest power setting.

Due to the strong evidence for a nitric oxide assisted etch mechanism, and the role that both O₂ addition into a NF₃ discharge and N₂ addition into a CF₄/O₂ discharge play in the formation of NO, we sought to support our conclusions by the direct downstream injection of NO into the processing chamber with both NF₃ and CF₄/O₂ gas mixtures fed into the discharge. Similar experiments performed while etching Si₃N₄ have shown the NO molecule to be central to a mechanism for nitrogen removal. When a low flow of NO is injected downstream from a NF₃ discharge (NO/NF₃=0.17), mass spectrometry results indicate that surface oxides are
removed which leads to enhanced Si etching. When CF$_4$/O$_2$ chemistries are used and when high levels of fluorine are available for the Si etch (e.g., O$_2$/CF$_4$=0.15), injection of NO (NO/CF$_4$=0.125) into the effluent of a CF$_4$/O$_2$ discharge results in a strong enhancement in the poly-Si etch rate. Again, we attribute this to the removal of the SiF$_x$O$_y$ reaction layer formed without NO. If a high O$_2$/CF$_4$ ratio is used, the NO has both the effect of increasing the poly-Si etch rate and the thickness of the modified surface layer. We postulate that this effect is possibly due to the formation of a highly dynamic (liquid-like) reaction layer on the etching surface. Even though at any instant, this layer is quite thick, in its steady state composition, this layer is highly reactive, allowing for the rapid attack of the Si by fluorine and the desorption of the etch products.

II. EXPERIMENTAL SETUP

In Fig. 1, the ultrahigh vacuum-compatible microwave based etching reactor used in this work is shown. A microwave plasma is produced in a modified ASTeX DPA-38 microwave plasma applicator. This device is equipped with a 38-mm-o.d. wall water cooled sapphire tube to which the process gases are fed. The plasma is separated from the processing chamber by tubing of variable length and lining material. For the current work, this lining material was polytetrafluoroethylene (PTFE) and the lengths studied were 0 and 75 cm. A gas line connected directly to the processing chamber allows for the direct injection of process gases, bypassing the plasma excitation region.

The etching experiments were performed in a stainless steel cylindrical processing chamber (inner diameter 27 cm, height 30 cm) with water cooled walls. The system is pumped using a Balzers 2200 l/s corrosive service turbomolecular pump backed by a roots blower and vane pump. The pressure was measured with a MKS Baratron capacitance manometer. For the experiments described here, the pressure was kept at 1.0 mTorr. A throttle valve in the bypass line was used to control the pumping speed and maintain this pressure in the chamber. Although, in general, the poly-Si etch rate is independent of the microwave power, a 1400 W discharge was maintained which provided the best window for a stable NF$_3$ discharge across a varying pressure range.

For the etching and surface analysis experiments, 2.5 cm by 2.5 cm square samples were prepared from 125 mm wafers covered with 580 nm polysilicon on 1000 nm SiO$_2$ on Si and 125-mm-diam single-crystal silicon wafers. These samples were HF dipped to remove the native oxide layer and were then mounted on 125 mm silicon carrier wafers using thermal glue. The mounted samples were then placed on an electrostatic chuck (dc bias of 600 V) with a helium backside pressure of 5 Torr. The electrostatic chuck temperature was set to 10 °C. The wafer temperature was measured with a fluoroptic probe which contacts the backside of the wafer. During processing, the silicon wafers heated up by approximately 2 °C.

In situ ellipsometry using a rotating compensator ellipsometer in the polarizer-compensator-sample-analyzer (PCSA) configuration with a 632.8 nm He/Ne laser source beam was employed to monitor real time film etching and deposition. Optical emission spectroscopy (OES) and mass spectrometry were used for real-time plasma and chamber gas phase diagnostics. The etching chamber is also connected via an ultrahigh vacuum (UHV) central wafer handler to both a load-lock and a multi-technique surface analysis chamber. Processed specimens were transported under vacuum to the multitechnique surface analysis system for x-ray photoelectron spectroscopy (XPS) measurements.

III. RESULTS

A. Etch rates

The silicon etch rate versus flow for a pure NF$_3$ discharge is shown in Fig. 2. These rates display a linear enhancement with increasing NF$_3$ flow. This is explained by the near complete dissociation of the NF$_3$ in the microwave discharge. Figure 3 shows this in terms of two sample mass spectrometry analog spectra. Panel (a) representing the plasma off condition and panel (b) with a 1400 W microwave discharge. When the discharge is ignited, we observe the complete loss of the 71 amu NF$_3$ peak, the 52 amu NF$_2$ peak and the 33 amu NF peak as well as the formation of the 38 amu F$_2$ signal and the 19 amu F peak. Also, the nitrogen signal is
dramatically increased beyond the residual magnitude seen in panel (a). We proceeded in spite of the background N\textsubscript{2} contamination, justifying that in these chemistries N\textsubscript{2} will always exist in a concentration several orders above the more reactive species. Blain, Jarecki, and Simonson\textsuperscript{13} have observed, through Cl titration experiments, that the transfer of the atomic fluorine from the discharge to the reactor can be almost 100\% efficient. We suspect that a substantial amount of fluorine recombines to F\textsubscript{2}, on our reactor walls. There was little dependence of the etch rate on the microwave power used. In fact, for the range of 600–1400 W, both the etch rates and the complete dissociation of the NF\textsubscript{3} remain unchanged. When small amounts of O\textsubscript{2} were added to the feed gas, an increase of the etch rate was observed. This increase quickly reached its maximum at an O\textsubscript{2}:NF\textsubscript{3} ratio of 0.1. These results are presented in Fig. 4. As the O\textsubscript{2} concentration is further increased, the etch rate is suppressed to a magnitude below that observed for the pure NF\textsubscript{3} discharge. This suppression of the etch rate is easily accounted for by the passivation of the reactive surface by an oxide-like film. The mechanism behind the initial increase is not as clear. The SiO\textsubscript{2} chamber viewport acts as an oxygen source, however the NO formation takes place only when the oxygen source is in the discharge region. This viewport-born oxygen serves to passivate the sample surface, while the NO is unavailable to compete for the removal of this oxygen. XPS data presented later will show that the surface is slightly oxidized in the ‘‘zero oxygen’’ experiments. The gas phase data of Fig. 5 show that there is a high level of N\textsubscript{2}O at this zero oxygen level. It is known that N\textsubscript{2}O is a good oxidizer of Si. Only when O\textsubscript{2} is injected into the discharge does the NO signal appear, and then at a local maximum.

We also acknowledge that nitrosyl fluoride species should be present when O\textsubscript{2} is added to the feed gas.\textsuperscript{14} One might speculate that these species are a more reactive fluorine source for the etching reaction. Without O\textsubscript{2} addition, the efficiency of the heterogeneous recombination of atomic fluorine on the reactor walls results in a high density of F\textsubscript{2}, presumably a less efficient source.\textsuperscript{14} This may account for the initial etch rate enhancement. In any case, we were not able to detect these species with our mass spectrometer, as it dissociates before ionization.

B. Surface analysis

After processing, specimens were transported under UHV conditions to the surface analysis chamber for XPS measurements. Figures 6(a) and 6(b) present these results for the samples processed with pure NF\textsubscript{3} discharges of varying flows. Panel (a) shows the Si 2\textit{p} and O 1\textit{s} spectra, while (b) shows the N 1\textit{s} and F 1\textit{s} core levels. From these spectra, one can see that the modified silicon surface contains silicon, fluorine, oxygen, and nitrogen after processing. Our previous work has shown that after CF\textsubscript{4}/O\textsubscript{2}/N\textsubscript{2} processing, the modified surface layers contain only silicon, fluorine and oxygen, while the nitrogen and carbon signals are not present. As the flow of NF\textsubscript{3} is increased from 100 to 300 sccm, both the F 1\textit{s} and the N 1\textit{s} peak areas decrease. When the flow is further increased to 500 sccm, however, this decrease is less pronounced. Also apparent in Fig. 6 are the asymmetric peak shapes in the F 1\textit{s}, O 1\textit{s}, and N 1\textit{s} spectra. Again, we attribute the oxygen contamination to the SiO\textsubscript{2} chamber viewport.

The Si 2\textit{p} peaks of Fig. 6 were fitted and the results were used to determine the apparent overlayer thickness by a method described elsewhere.\textsuperscript{15,16} These results are presented in Fig. 7.

XPS spectra were also taken in response to varying O\textsubscript{2} flows added to the NF\textsubscript{3} feed gas. In Fig. 8(a), the Si 2\textit{p} and O 1\textit{s} core levels are shown. As the panels progress from left to right, from an untreated reference sample to one treated at

**Fig. 3.** Analog mass spectra illustrating the complete dissociation of NF\textsubscript{3} in our discharge.

**Fig. 4.** Poly-Si etch rates vs O\textsubscript{2} content in a NF\textsubscript{3} discharge.

**Fig. 5.** Mass spectral data for NO and N\textsubscript{2}O vs O\textsubscript{2} content in the feed gas.
an O : NF ratio of 2:1, the level of oxidized Si monotonically increases. The O 1s spectra of the upper panels do not correspond to this change. As the O 2 content increases from 10% to 50%, the O 1s peak area remains constant, while in the Si 2p spectra, the bulk is no longer visible. In Fig. 8(b), where the N 1s and F 1s spectra are shown, there is a strong maximum in the N 1s signal at 10% O 2 addition. These trends suggest that the NO molecule may account for a significant portion of the oxygen signal coming from the sample surface.

During processing, the sample surface was monitored in real time with a He–Ne ellipsometer. This allowed us to determine the film thickness in situ. These film thicknesses versus O 2 content in the feed gas are shown in Fig. 9. Thicknesses range from 1 nm for pure NF 3 processing to above 12 nm when a high portion of O 2 is injected. The apparent thickness obtained from the Si 2p core levels of the XPS spectra was used to obtain the film thickness corresponding to 10% O 2, because surface roughening makes the ellipsometrically determined thickness unreliable. In the case of pure NF 3 processing, the surface modifications are due to the development of a thin overlayer. In the case of NF 3 with 10% O 2 addition, the sample surface is roughened, rather than modified by the growth of a film. This roughening is characteristic of small oxide islands left on the Si surface which serve as micro-etch masks. When higher flows of O 2 are added, roughening is not an issue and thick layers form on the sample surface.

C. Downstream NO injection

1. NF 3 plasma

The surface analysis of NF 3/O 2 treated samples and the mass spectral results have suggested that a NO assisted mechanism, where NO reacts with the surface to remove the
passivating oxide, plays a large role in the etching reaction. The importance of NO in the etching of Si₃N₄ in similar chemistries has been established. In the case of Si₃N₄, the NO acts to remove nitrogen from the surface.\(^{10-12}\) We sought to determine the products of such a reaction with Si by using a Leybold Transpector mass spectrometer modified so that the orifice could sample the gas phase immediately above the sample surface. The entire unit is mounted on a vertical linear motion drive so that the orifice can be lifted without changing the orifice-ionization chamber distance. More information on this apparatus can be found elsewhere.\(^{17}\) The results of a sampling taken during the Si etch are presented in Figs. 10 and 11. For these experiments, the microwave power was 900 W and the transport tube was set adjacent to the processing region (0 cm setting). A total of 300 sccm of NF₃ was fed into the discharge, while 30 sccm of NO was injected directly into the processing chamber, bypassing the discharge region. For the first 40 scans, the orifice was just 0.5 mm from the sample surface. After the fortieth scan, the orifice-sample distance was quickly increased to 20 cm. In this way, the products of the etching reaction are clearly distinguishable from the etchant reactants. In Fig. 10, these products are displayed on the left while the reactants are displayed on the right. As one would expect, the dominant product is SiF₄ as indicated by the 78% drop in the 85 amu SiF₄ peak after scan number 40. The loss of fluorine to the etch reaction is clearly visible in the 5% increase of the signals when the orifice is moved away from the surface. This same behavior was observed for low intensity NF₃ etching. This can explain the slight increase in the O₂ signal at the etch rate maximum. We postulate that this corresponds to reaction III, except where the main product is O₂. In the surface region, a lot of oxygen is lost to oxidation reactions. Even in conditions where nearly all of the oxidation is then removed, a significant portion is not in the same form as when it reacted (e.g., NO₂ instead of O₂). Under such consideration, one would expect that the “orifice down” O₂ signal would be higher, even though O₂ is coming off as a product of the passivation layer etching. This can explain the slight increase in the O₂ signal of Fig. 11, after the orifice has been lifted from the sample surface.

2. CF₄/O₂ plasmas

We also investigated direct NO injection in conjunction with the effluent from a CF₄/O₂ discharge. Some changes in experimental conditions must be noted for these experiments, namely the applicator to which the microwave power is applied was quartz, not sapphire. Again, the 75 cm PTFE transport tubing was removed, and the discharge was located adjacent to the processing chamber, i.e., the discharge edge to sample distance was 15 cm.

When the NO was injected into the effluent of a pure CF₄ discharge, there is an increase in the silicon etch rate. This increase is more pronounced when nitrogen alone is injected into the discharge.\(^{1}\) When the discharge also contains admixed oxygen, so that the effluent is fluorine rich
(O$_2$:CF$_4$=0.15), the etch rates are much greater. These results are shown in Fig. 13. When the NO is passed into the effluent of an oxygen rich discharge, both the etch rate and the overlayer thickness increase. This fast etching through thick overlayers is presented in Fig. 14 and suggests a very reactive and highly dynamic film. Mass spectrometry loading experiments were performed where the chamber was loaded with a 125 mm silicon wafer or a 125 mm fluorocarbon film coated wafer. Figure 15 shows these results for fluorine rich processing for the 85 amu SiF$_3$, the 46 amu NO$_2$, and the 32 amu O$_2$ signals. “Loaded intensity” refers to the plasma on minus plasma off intensities for the silicon loaded chamber minus the CF$_4$ loaded chamber. If we focus on the fluorine rich regime of the CF$_4$/O$_2$ discharge at a ratio of O$_2$:CF$_4$=0.15, we find a strong correlation between the “loaded” SiF$_3$ signal of Fig. 15 and the loaded NO$_2$ and O$_2$ signals. This indicates that both of these species are products of the etching reaction. We attribute the initial negative value in the O$_2$ signal to the oxidation of the Si surface. Such a correlation suggests that the etch rate enhancement with NO addition is due to the removal of oxygen from the Si surface, freeing bonds for fluorine attack. Such a mechanism is consistent with the data presented for CF$_4$/O$_2$/N$_2$ processing and also the NF$_3$/O$_2$ processing presented earlier. A return to the XPS spectra of Fig. 8(b) shows the N 1s intensity maximum coincides with that of the etch rate. This supports the evidence that a fraction of the NO arrives at the Si surface, donates its oxygen to the removal of a surface oxygen in the form of O$_2$, and leaves the nitrogen atom behind.

Real-time ellipsometry measurements taken while 50 sccm NO is injected, and then removed from this processing recipe are shown in Fig. 16. The top panel displays the ellipsometric variable delta versus time, while the bottom panel shows the evolution of psi. At event marker (a) is the ignition and stabilization of the CF$_4$/O$_2$ discharge, after which a thick reaction layer is formed. At event marker (b), 50 sccm of NO is injected directly into the processing chamber. This results in the removal of the overlayer back to the bare silicon point. A similar effect has been seen with the injection of nitrogen directly into the discharge. When the NO is removed, the modified surface layer again begins to grow. This process is repeated and the removal of the overlayer is again observed. The mirror image of psi in the bottom panel for the first growth/removal stage is indicative of the growth and removal of a smooth film. As the second growth and removal stage proceeds, the psi evolution becomes less pronounced, and in some instances follows the
delta evolution in trend. This is due to the formation of a rough surface. Such roughness is consistent with the removal of the overlayer in the first NO treatment. Although this first injection was efficient at oxygen removal, some islands remained, and these islands served as micro-etch masks leading to roughening. At event marker (c), the plasma is extinguished, and silicon overlayer quickly increases in thickness; without the source of fluorine, the etching component of the steady state film dynamics dies. NO serves to enhance the Si reaction component of the steady state film dynamics by opening bonding sites through the removal of oxygen. In chemistries with abundant fluorine, an etch rate enhancement will occur.

IV. CONCLUSIONS

We have discussed the role of nitrogen in Si etching, when using chemistries including fluorine and oxygen.

NO, and possibly one of the nitrosyl fluoride isomers, serves to enhance the Si reaction component of the steady state film dynamics by opening bonding sites through the removal of oxygen. The gas phase is rich in fluorine, the etch rate will increase. If the gas phase is oxygen rich, it will not. An exception to this was observed at high NO densities, where both the reaction layer thickness and the etch rate increased. In fact, fast etching was observed through 20-nm-thick overlayers.

In particular, NO reacts with the oxygen on the surface to form NO₂ or O₂ which escape. In the latter reaction, nitrogen can be left behind on the silicon surface. This mechanism has appeared in both CF₃/O₂/N₂ chemistries and NF₃/O₂ chemistries. This notion is supported by several observations: (1) the fluorine densities alone cannot explain the etching behavior (i.e., nonfluorine limited etching). (2) There is a correlation of etch rates and NO densities for both chemistries. (3) In the presence of fluorine, Si etch rates are higher in the presence of NO. (4) Reaction layers composed of SiOₓFₙ species are thinned in the presence of NO. (5) NO₂ and O₂ are observed as a product of the Si etching reaction, while NO is lost in the surface region.

ACKNOWLEDGMENTS

The authors would like to thank M. G. Blain for helpful discussions. They also thank R. E. Ellefson and L. C. Frees for their mass spectrometry assistance.