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Citation: Journal of Vacuum Science & Technology A 21, 461 (2003); doi: 10.1116/1.1547703
View online: http://dx.doi.org/10.1116/1.1547703
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Silicon nitride etching in high- and low-density plasmas using SF$_6$/O$_2$/N$_2$ mixtures

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(Received 30 August 2002; accepted 23 December 2002; published 10 February 2003)

Results of a comparative study of SiN$_x$, SiO$_2$ and Si etching in high- and low-density O$_2$–N$_2$ based plasmas with small additions of SF$_6$ are presented. Higher selectivities of SiN$_x$ etching over both SiO$_2$ (up to 50–70) and Si (up to 20) are obtained in a high-density reactor as compared with low-density reactive ion etching. Plasma and surface processes responsible for etching are analyzed. Kinetics of NO molecules responsible for enhanced nitride etching is shown to be distinctly different for low- and high-density plasma conditions. Possible ways of further optimization of the process are discussed. © 2003 American Vacuum Society. [DOI: 10.1116/1.1547703]

I. INTRODUCTION

Silicon nitride is one of the primary materials used in various microfabrication processes as a dielectric material, masking and passivation layer. In a complementary metal-oxide-semiconductor (CMOS) technology, silicon nitride is used as a hard mask in local oxidation and other isolation processes such as shallow trench isolation. The removal of silicon nitride film is one of the critical steps in a CMOS technology as possible overetch during a nitride layer processing may result in damages of an underlying oxide film. Furthermore, etchants can strongly damage the silicon substrate through imperfections of the oxide, as many plasma processes currently used for nitride stripping etch silicon much faster than SiN. Hence high selectivity of SiN etching over both Si and SiO$_2$ is strongly desired.

For plasma etching of silicon nitride, carbon containing gases such as CF$_4$, C$_2$F$_6$ and CHF$_3$ are widely used, in many cases with addition of gases promoting polymerization on the etched surfaces (CO, H$_2$). Polymer formation plays an important role in achieving selective and anisotropic etching. However, carbon rich plasmas may create damage due to implantation and postprocess diffusion of carbon into the silicon substrate. Another concern in using fluorocarbon gases is related to their environmental impact. To minimize the latter, various approaches are currently being explored, including process optimization and alternative chemistries.

One of the alternatives for the nitride processing is a recently introduced chemical dry etching (CDE) where remote plasmas containing fluorine and nitric oxide are used. In contrast to conventional reactive ion etching (RIE), in the CDE method the synergistic effect of ion bombardment, which is known to strongly enhance the etch rate, is not available. Instead, material removal occurs through purely chemical interactions taking place at the processed surface. In this case, the etching selectivity may be improved considerably by a proper choice of etching gases and reaction intermediates. Furthermore, in the lack of ion bombardment, etching of certain materials may be suppressed as many surface reactions require high activation energies. In particular, one can expect that absence (or reduction) of ion bombardment will favor higher SiN to SiO$_2$ etch selectivity as the strength of a Si–O chemical bond (8.3 eV) is considerably higher than that for a Si–N bond (4.6 eV). Note that the strength of a Si–F bond has an intermediate value of 5.7 eV. Therefore, ion bombardment is essential to promote faster SiO$_2$ etching using fluorine chemistry, while etching of SiN must be less sensitive to ion bombardment. It has been shown that addition of N$_2$ and O$_2$ or NO to fluorine containing gases may considerably improve the process selectivity as nitrogen atoms or NO molecules can accelerate the removal of nitrogen from the silicon nitride surface. Moreover, the oxide etch rate was shown to be reduced by NO injection in the discharge. In first experiments, mixtures rich in CF$_4$ and O$_2$ with small additions of nitrogen were used. In the further development of the method, mixtures composed basically of O$_2$ and N$_2$ with only small additions of fluorine containing gases (CF$_3$ or NF$_3$) have been shown to etch the nitride with higher selectivity over silicon and silicon dioxide.

Mechanisms responsible for highly selective nitride etching in O$_2$/N$_2$ rich plasmas were analyzed in Refs. 9–11 and 13, with emphasis on the surface chemistry. Still, a little is known on the corresponding plasma processes. In Refs. 10,11 chemical dry etching (CDE) of SiN using downstream O$_2$/N$_2$ plasmas with smaller additions of NF$_3$ or CF$_4$ was investigated. The role of NO molecules (either produced in the plasma or injected into the gas mixture) in the surface chemistry was shown to be important for significant improvement of SiN to SiO$_2$ etching selectivity. This was attributed to a highly exothermic reaction $\text{N}_{\text{surface}} + \text{NO}_{\text{gas}} \rightarrow \text{O}_{\text{surface}} + \text{N}_{2\text{gas}}$ (the energy released in the reaction is $\sim 7$ eV), which promotes the enhanced removal of nitrogen atoms from the nitride surface and thus...
accelerates the overall reaction rate. Oxygen atoms left on the surface by this reaction are believed to desorb promptly, most likely as O₂. Forma\[tion of an oxidized reactive layer on the top of Si surface, reducing the silicon etch rate to a level comparable to that of SiO₂, was detected by \textit{in situ} ellipsometry.

The main disadvantage of CDE is that, due to absence of ion bombardment, it is likely to produce isotropic etch profiles. In contrast, highly anisotropic etching is possible using RIE, which may be a critical advantage for some applications.

In this work, the results of a comparative study of silicon nitride etching in carbon-free SF₆/O₂/N₂ mixtures using a high-density electron cyclotron resonance (ECR) plasma source and a conventional low-density RIE etcher are presented. The ECR configuration proves to be more versatile than the CDE and RIE ones, allowing both downstream plasma processing and independent electrode biasing to control the energy of ions bombarding substrate at a relatively low level. In the ECR experiments, Si₃N₄ etch rates of 20–30 nm/min have been achieved with high selectivity over both SiO₂ and Si (up to 50–70 and 5–20, respectively). Lower selectivities to SiO₂ were found for the RIE process. For plasma diagnostics, optical emission spectroscopy was employed. Mechanisms of NO generation in the two plasma sources have been analyzed and shown to be different.

II. EXPERIMENT

The ECR plasma source of Plasma Therm SLR770 used here consists of two parts: a plasma chamber where a dense plasma is generated and a process chamber where the plasma flows downstream to a lower electrode used as a sample holder. An additional rf source is used to control the electrode bias and thus, the energy of ions bombarding the sample surface. A parallel-plate capacitively coupled rf-driven (13.56 MHz) asymmetric plasma source was used for RIE experiments. Radio frequency power was applied to a smaller Al electrode (12 cm in diameter) usually covered with a Si wafer (100 mm in diameter). Maximum gas pressures are 80 and 200 mTorr for the ECR and RIE reactors, respectively.

Experiments were carried out with three kinds of samples: (i) monocrystalline (100) Si, (ii) SiO₂ films (1 μm thick) produced by thermal oxidation of silicon substrates, and (iii) Si₃N₄ films (0.1 or 0.5 μm thick) deposited by a low pressure chemical vapor deposition (LPCVD) process over thin oxide films using silicon substrates. Samples were patterned by a AZ 5214 photoresist mask, with an open area exceeding 50% of the total area of samples. Mixtures of gases containing N₂, O₂, and SF₆ in different compositions were used. In most experiments, etching time was 2 min, to avoid a complete resist removal during the process. Etch depths were measured by a DEKTAK profiler. For diagnostic of optical emission from plasmas in a 200–900 nm spectral range, a scanning spectrometer was used. Plasma emission was collected through quartz windows.

III. RESULTS AND DISCUSSION

A. Etch rates

1. RIE

In order to have higher Si₃N₄ etch selectivity over SiO₂, most of the RIE experiments were carried out at a high pressure (150 mTorr) where the dc bias is lower. In Fig. 1, the effect of small SF₆ additions to O₂/N₂ plasma on the etch rates is shown. Flows of both gases were fixed at 30 sccm. As the SF₆ content rises, the dc bias falls and etch rates change in different ways: (i) rises gradually for silicon nitride, (ii) almost no changes are observed for oxide, and (iii) a sharp (~20-fold) rise of the silicon etch rate is observed when the SF₆ content increases from 5 to 7.5 sccm. In
Fig. 2, power dependence of etch rates is shown. At lower powers, etching for all materials including silicon is suppressed, likely due to oxidation of the surfaces. Under these conditions, the etching regime is essentially ion induced, and the dc bias threshold for the etching process is apparently lower than 100 V. The maximum nitride etch selectivity over oxide obtained with the SF$_6$/O$_2$/N$_2$ plasma was close to 2, with the SiN$_x$ etch rates being less than 30 nm/min. The maximum selectivity over silicon was only slightly higher (~2.5), and was not obtained at the highest nitride etch rates.

The effect of small additions of nitrogen on etching is shown in Fig. 3. The SF$_6$/O$_2$ mixture rich in oxygen (SF$_6$/O$_2$ = 5/50 sccm) was used, with small admixtures of N$_2$ and Ar. Nitrogen was gradually substituted by argon, keeping constant the total gas flow at 65 sccm. In contrast to what could be expected, the SiN$_x$ etch rate reduces with nitrogen addition. Note that the etch rates of SiO$_2$ and especially of Si drop, too. At the same time, considerable reduction of the dc bias is observed, therefore the etch rate reduction may be explained as a consequence of decreasing ion bombardment. In other words, surface processes involving NO molecules play a minor (if any) role in SiN$_x$ etching under the present RIE conditions. Under such conditions (high ratio of the ion energy flux to the NO flux), a reactive oxinitride layer which favors the nitride-to-oxide etching selectivity$^{13}$ apparently cannot be formed on the nitride surface.

2. ECR

Some results showing the etch rate dependencies on plasma parameters are shown in Figs. 4–8. As compared with the RIE results, two important points should be emphasized. First, the results obtained under the ECR conditions, where a dc bias between the downstream plasma and the electrode is quite low, show dramatic improvement in selectivity over oxide, in comparison with the RIE. In most cases, the oxide etch rate was very low or practically stopped. To measure the corresponding etch rates, longer etch times (up to 15 min) were used, giving in most cases SiO$_2$ etch rates as

![Fig. 3. Etch rates and dc bias vs N2 flow, RIE; SF$_6$/O$_2$/N$_2$ = 5/50/10 sccm, 150 mTorr, 75 W.](image)

![Fig. 4. Etch rates vs gas pressure, ECR; SF$_6$/O$_2$/N$_2$ = 10/30/30 sccm, ECR power 750 W, rf power 20 W. Silicon etch rate is divided by 10.](image)

![Fig. 5. Etch rates vs N2 flow, ECR; SF$_6$/O$_2$/N$_2$/Ar, total flow 65 sccm, SF$_6$ flow 5 sccm (a) and 7.5 sccm (b), O$_2$ flow 50 sccm, 50 mTorr, ECR power 750 W, rf power 0 W.](image)
low as 0.25–1 nm/min when no or low rf power was applied to the electrode. Under these conditions, the maximum SiN$_x$ to SiO$_2$ etch selectivity as high as 50–70 was obtained. With dc bias higher than 30–40 V (at rf power of 40–100 W), considerable rise of oxide etch rates to the level of 5–10 nm/min was observed. As the energy of ions bombarding the electrode is a sum of the dc bias and the plasma potential (usually about 15–25 eV), the threshold for the oxide etching can be estimated as $\sim$50–60 eV. Second, the ECR results show that considerable enhancement of the nitride etch rate occurs with small nitrogen additions presumably due to NO formation in an oxygen rich plasma. At the same time, the influence of ion bombardment proves to be of less importance.

The effect of the gas pressure on etching is shown in Fig. 4 for a SF$_6$/O$_2$/N$_2$ = 10/30/30 sccm mixture. As the pressure increases from 10 to 50 mTorr and higher, the oxide etch rate is practically stopped while the nitride etch rate rises considerably and then saturates. The silicon etch first rises and then drops. This etch rate behavior is evidently due to reduced role of ion bombardment in the downstream region occurring at higher pressures, as the ratio of radicals/ions arriving at
the electrode rises. In particular, at higher pressures a smaller fraction of fluorine reaches the electrode in an ionized form; this explains the oxide etching depression. Further experiments were performed with the pressure of 50 mTorr.

Figure 5 shows etch rate behavior as nitrogen is added instead of Ar for SF$_6$/O$_2$/N$_2$/Ar mixtures for different SF$_6$ contents. Note that oxide etch rate is negligible (not shown) as in most cases using ECR. Strong effect of nitrogen (NO) addition is clear, as a fast rise of the nitride etch rate as 3 sccm of N$_2$ (<5% of the total gas) is added to the mixtures instead of Ar. The effect of small nitrogen addition is especially strong at lower SF$_6$ percentage. The silicon etch rate is low due to strong oxidation occurring in the plasma rich in oxygen. Therefore the rise of the silicon etch rate with N$_2$ is likely due to reduced surface oxidation as nitrogen competes with oxygen at the surface. This effect is more pronounced at higher SF$_6$ content [compare Figs. 5(a) and 5(b)].

The etch rate dependence on the SF$_6$/O$_2$/N$_2$ mixture composition is shown in Fig. 6 for SF$_6$ fluxes of 5 and 7.5 sccm, with varying oxygen flux and the total O$_2$ + N$_2$ flux fixed at 60 sccm. As the oxygen content rises, the silicon etching slows down (faster for lower SF$_6$ percentage), due to increasing silicon surface oxidation. The nitride etch rates are lower for oxygen-deficient plasmas, with maximum being observed at intermediate oxygen levels.

In Fig. 7, the etch rate dependencies on the SF$_6$ content for mixtures containing O$_2$/N$_2$ = 50/10 sccm are shown. As the SF$_6$ flow rises from 2.5 to 13 sccm, the nitride etch rate rise is threefold, while the silicon etch rate growth is ~40-fold. At lower SF$_6$ content (~5 sccm), the highest SiN$_x$/Si selectivities (varying from 4 to 20) were obtained, however at higher nitride etch rates (>20 nm/min) the selectivity achieved was at most ~2. For some mixtures, nitrogen was substituted by the same amount of argon. The corresponding nitride etch rate ratio is also shown in Fig. 7. It can be seen that the enhancement of nitride etching due to NO effect is threefold for low SF$_6$ content and drops abruptly to ~1 (i.e., the etch rate is determined solely by the fluorine flux) as the SF$_6$ flow exceeds ~8 sccm. Note that at the same time, the nitride etch rate saturates at a level slightly lower than the maximum (~28 nm/min), while the silicon etch rate starts to rise rapidly. This indicates that: (i) formation of stable reaction layers, which enhance the nitride etching and slow down the silicon etching, is possible only at a relatively low flux of fluorine radicals, (ii) the change of the etching regime has a threshold behavior.

Figure 8 shows the effect of rf power on etching. Etch rates for all three materials grow with rf power (dc bias). The measurable oxide etching is observed at 40 W (dc bias of ~40–50 V). At lower SF$_6$ content [5 sccm, see Fig. 8(a)], the nitride etch rate increases three times as rf power rises, while at the higher content [10 sccm, Fig. 8(b)] the growth is much slower. At the lower SF$_6$ flow (5 sccm), the silicon etching grows much faster and from a lower level than at the higher SF$_6$ flow (10 sccm).

B. Optical emission spectra

Comparison of spectra emitted from the rf and ECR plasma sources shows significant difference in plasma chemistry for low- and high-density conditions.

1. O$_2$/N$_2$ plasmas

Characteristic band emission identified as a NO $\gamma$ system$^{12}$ was observed in a spectral region below 285 nm in both ECR and rf sources, see Fig. 9. The emission is much stronger for the ECR plasma [Fig. 9(a)], being comparable in intensity with N$_2$ emission in a 310–360 nm range (the sec-
ond positive system). A number of unidentified weaker bands, possibly belonging to NO, was also observed in a 465–525 nm range. Stronger O and N atomic emissions are also characteristic of the ECR plasma, while \( N_2 \) first negative system emission (391.4 nm) is relatively stronger in the rf plasma.

Along with more intense NO emission, higher vibrational \( N_2 \) excitation apparently occurs in the ECR \( O_2/N_2 \) plasma, as an intense emission of the \( N_2 \) first positive system (e.g., a \( \Delta v = 4 \) sequence in a 570–610 nm range) is observed. This emission corresponds to high vibrational numbers of the upper molecular state (\( v' \approx 10 \)). In contrast, in the rf driven plasma the emission of this \( N_2 \) system is much weaker [Fig. 9(c)], evidently due to lower electron density. Vibrational excitation of \( N_2 \) by electron impact is known to occur at a high rate, with maximum cross sections observed at energies of a few electron volts.\(^{18} \) This indicates that for the present high-density plasma conditions, the main mechanism of NO generation is likely to be

\[
N_2(v \geq 13) + O \rightarrow NO + N, \tag{1}
\]

where only vibrationally “hot” nitrogen molecules are involved. This mechanism was shown to be a principal source of NO generation in a medium-pressure (1–2 Torr) \( O_2/N_2 \) stationary dc discharge in Refs. 19 and 20, where discharge kinetics was analyzed both experimentally and theoretically. The electron density was measured to be in the range \( n_e = (0.5–2) \times 10^{10} \ \text{cm}^{-3} \) depending on the discharge current.\(^{20} \) Note that for ECR sources, an electron density is usually higher (\( \sim 10^{11} \ \text{cm}^{-3} \)), while for rf-driven capacitively coupled discharges, a lower density (\( \sim 10^9 \ \text{cm}^{-3} \)) is typical. Another two reactions were shown to be of less importance for the conditions of a dc discharge, except for oxygen-rich plasmas:\(^{19,20} \)

\[
N + O_2 \rightarrow NO + O, \tag{2}
\]

\[
N_2(A^3\Sigma_u^+ + O) \rightarrow NO + N, \tag{3}
\]

where \( A^3\Sigma_u^+ \) is a \( N_2 \) metastable state. A reaction of recombination

\[
N + O + N_2 \rightarrow NO^* + N_2, \tag{4}
\]

where excited NO molecules are generated, was shown to be negligible for the conditions analyzed.\(^{19,20} \) As in our experiments the gas pressure is much smaller (50–150 mTorr compared with 1–2 Torr), we can neglect the contribution of the last reaction to production and excitation of NO molecules. Recombination of ionic species, for example,

\[
NO^+ + O^- \rightarrow NO^{**} + O, \tag{5}
\]

where highly excited NO molecules can be produced, was not analyzed in Refs. 19 and 20. Then, in cascade transitions following Eq. (R5), optical emission of various NO systems could be observed (possibly including unidentified bands observed in the 465–525 nm range, see above). To our knowledge, no relevant data are available in the literature on this reaction. It might be significant for high-density plasmas with a high content of negative oxygen ions.

Based on available data, it is reasonable to assume that electronic impact is the main mechanism of NO optical excitation, at least for low and medium plasma densities. In this case, the actinometry technique with small amounts of an inert gas (Ar) added to the mixture can be used to characterize the NO relative concentration in the plasma. The general actinometry formula is

\[
N_X = \frac{I_X}{I_{Ar}}N_{Ar},
\]

where \( I_X \) and \( I_{Ar} \) are intensities of optical emission from \( X \) species (molecular or atomic) and Ar atoms, \( N_X \) and \( N_{Ar} \) are their number densities in the plasma. For actinometry, a 750 nm Ar line emission is widely used.\(^{21} \) Actinometry is also routinely employed for characterization of atomic fluorine, and with less accuracy, of atomic oxygen and some other molecular and atomic species. The basic condition for actinometry is that both species are excited in the same way, i.e., by a single-step electron impact.

The dependence of NO \( \gamma \) band emission at 259 nm on the \( O_2 \) flow is shown in Fig. 10. The data corrected for variation of Ar emission using the actinometry equation, with \( \sim 3\% \) of argon added for diagnostic purposes (previously, we have checked that this small Ar addition does not alter the main species emission), are also plotted in Fig. 10 (the right axis). It is seen that the NO generation is stronger at intermediate \( O_2 \) flows, with the maximum being slightly shifted to higher oxygen contents. The same trend can also be seen in Fig. 6 for the SiN\(_x\) etch rate.

To analyze changes occurring as the plasma flows downstream, we compared spectra taken in two regions: (A) just below the plasma chamber and (B) 10 cm downstream (above the electrode), see Table I. This comparison shows that NO emission intensity falls downstream considerably faster than that of Ar, \( N_2 \) and other main species. This indicates that NO is produced mostly in the upper (high-density)

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**Reyes-Betanzo et al.: Silicon nitride etching**

plasma region and its regeneration in the downstream (low-density) plasma does not compensate losses occurring mainly due to a rapid reaction \(^{(3,19)}\)

\[
\text{NO} + \text{N} \rightarrow \text{N}_2(\nu) + \text{O}
\]  

(6)

and to a lesser extent, due to a three-body reaction \(^{(3,20)}\) which is more important for high-pressure conditions

\[
\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M},
\]  

(7)

where \(\text{M} = \text{N}_2\) or \(\text{O}_2\). For the reaction (6) to occur, high \(\text{N}_2\) dissociation degree (i.e., high plasma density) is essential. Therefore, in low-density low-pressure plasmas with low atomic nitrogen content (e.g., as in the rf plasma source), diffusion to walls will be the main mechanism of NO losses.

Note that in the reaction (6), the vibrational level \(\nu = 3\) of the \(\text{N}_2\) ground state is predominantly populated with smaller contributions to the neighboring levels \(\nu = 2\) and \(4\). Moreover, due to a Frank–Condon principle, an electronic impact produces mainly “vertical excitation.” \(^{(19)}\) Therefore, vibrational distributions of excited electronic states will reproduce to some extent that of the ground state. Thus the corresponding molecular emission (from the upper level \(\nu' = 3\), e.g., the \(\nu' = 3 \rightarrow \nu'' = 6\) transition at 389.5 nm) may be useful for monitoring of NO losses due to the reaction (6) in a high-density ECR plasma. In the rf driven \(\text{O}_2/\text{N}_2\) plasma, the 389.5 nm band is much weaker than for the ECR case, due to lower N content.

### 2. \(\text{O}_2/\text{N}_2/\text{SF}_6\) plasmas

Addition of \(\text{SF}_6\) to the \(\text{O}_2/\text{N}_2\) mixture has a very strong impact on the emission spectra from the ECR plasma. Addition of 2.5 sccm of SF\(_6\) to the \(\text{O}_2/\text{N}_2/\text{Ar}=50/50/2\) sccm plasma results in a sevenfold drop of NO emission (the normalized intensity, \(I^* = I(\text{NO})/I(\text{Ar})\), reduced ten times), see Table I and Fig. 11. At the same time, other spectral features change in different ways:

(1) the Ar line emission falls \(~30\%\), and the first positive \(\text{N}_2\) system emission (high vibrational numbers) reduces \(~35\%\);

(2) the most intense bands of the second positive \(\text{N}_2\) system corresponding to \(\nu' = 0\) and \(1\) (e.g., \(337.1\) nm) rises \(~10\%\), while the weaker bands starting from \(\nu' = 3\) (e.g., the \(\nu' = 3 \rightarrow \nu'' = 6\) transition at 389.5 nm) reduce \(~15\%\);

(3) the first negative \(\text{N}_2^+\) system emission increases strongly (\(~1.6\) times), as well as both nitrogen (747 nm) and oxygen (777 nm) atomic lines (growth of \(~1.5\) times).

The changes of the species intensities normalized to that of Ar are shown in Table I. After abrupt transformation of spectra at small SF\(_6\) additions, further rise of SF\(_6\) content results in only gradual minor changes of plasma emission, see Fig. 11. These spectral changes basically can be attributed to the fall of the plasma electron density with SF\(_6\) addition due to attachment, as this molecule and its radicals are known to have much higher electron affinity than O and \(\text{O}_2\). A smaller electron density results in reduced emission of Ar, weaker vibrational excitation of \(\text{N}_2\) and, hence, reduced generation of NO in the reaction (1). In turn, emission of O and N atoms gets stronger because their losses in reactions with NO \([(16), (7)]\) become smaller. While the reasons for the \(\text{N}_2^+\) emission growth are not completely clear, it is probably due to reduced \(\text{N}_2^+\) losses in reactions with negative oxygen ions the population of which in the plasma should be much lower in the presence of SF\(_6\). The fact that the \(\text{N}_2\) second positive system emission (transitions from \(\nu' = 3\)) reduces notably, gives further evidence that the reaction with N atoms (6) is the dominant channel of NO losses in high density \(\text{O}_2/\text{N}_2\) plasmas. Comparison of spectra taken in spatial points A and B (Table I) shows that for the \(\text{O}_2/\text{N}_2/\text{SF}_6\) plasma, the NO concentration reduces downstream only slightly, in contrast to the \(\text{O}_2/\text{N}_2\) case. This indicates that NO regeneration

![Fig. 11. NO emission intensity vs SF\(_6\) flow; ECR and RIE reactors, SF\(_6\)/O\(_2\)/N\(_2\).](image)

<table>
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<th>Gas mixture, SF(_6)/O(_2)/N(_2)/Ar), sccm</th>
<th>Position</th>
<th>(I(\text{Ar})) (\text{arb. units})</th>
<th>(I^*(\text{NO}))</th>
<th>(I^*(\text{N}_2))</th>
<th>(I^*(\text{N}_2^+)</th>
<th>(I^*(\text{O}))</th>
<th>(I^*(\text{N}))</th>
<th>(I^*(\text{F}))</th>
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<tr>
<td></td>
<td>B</td>
<td>4.4</td>
<td>1.8</td>
<td>8.4</td>
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<td>1.1</td>
<td>…</td>
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downstream may be relatively more important for the O₂/N₂/SF₆ plasma. This regeneration probably involves long-living N₂ metastable molecules (reaction (3)) produced in a hotter plasma region. Note that in the presence of SF₆, formation of excited NO (A) molecules followed by γ band emission is possible through the nondissociative ion–ion neutralization reaction

\[ \text{NO}^+ + \text{SF}_6 \rightarrow \text{NO(A)} + \text{SF}_6. \]

In part, this may be also responsible for the very slight downstream reduction of the NO emission intensity observed in this case. On the other hand, the presence of SF₆ molecules and F atoms apparently does not result in enhanced losses of NO molecules, e.g., in a three-body reaction³

\[ \text{NO} + \text{F} + \text{M} \rightarrow \text{NOF} + \text{M}. \]

Analyzing the data presented, it is reasonable to conclude that

1. the reaction (1) between vibrationally hot N₂ molecules and O atoms is the main NO source in a high-density O₂/N₂ ECR plasma;
2. the reaction (3) involving metastable N₂ molecules is the main source of NO generation in the ECR plasma in the presence of SF₆ (i.e., at a reduced electron density). The same mechanism (3) seems to be dominant for the low-density rf plasma (whether or not SF₆ is present in the gas mixture, see below).

For rf-driven plasma, the character of spectral changes with SF₆ addition is distinctly different. As noted previously, for neat O₂/N₂ mixtures the normalized NO emission intensity is significantly (3–5 times) weaker than that from the ECR plasma. In striking contrast to the ECR plasma, the NO emission grows significantly with SF₆ addition, see Fig. 11. The same is valid for the main plasma species as N₂ and Ar. Emission intensities of other species such as O and N₂⁺ grow slower. As a result, the NO and N₂ intensities normalized to that of Ar change only slightly, while those of O and N₂⁺ fall and that of F rises as SF₆ is added (Table II). At the same time, a self-bias voltage \( U_{sb} \) reduces significantly with SF₆ addition indicating that strong redistribution of rf power occurs in the discharge.

The observed changes can be attributed to redistribution of rf power between the two main plasma regions in a capacitively coupled rf-driven discharge: the bulk plasma and the sheath. Studies of the power balance in an asymmetric rf discharge²³,²⁴ have shown that the distribution depends critically on the gases used, more specifically, on the losses of electron energy during lifetime of electrons in the bulk plasma. Two groups of gases may be distinguished. For simpler gases like Ar, O₂, N₂, etc., these energy losses are relatively low, and a dc self-bias built up between the plasma and the powered electrode is high. In this case, the main fraction of rf power is deposited in the sheath, and it is expended in acceleration of ions bombarding the electrode. For strongly electronegative gases like SF₆ and SiCl₄, the losses in the bulk plasma are much higher, the dc bias is low, and the main fraction of rf power is dissipated in the bulk plasma. When SF₆ is added to O₂/N₂ based plasma, an abrupt redistribution of rf power occurs with the fall of the dc bias, the ion current to the electrode and the power fraction deposited in the sheath, while the fraction dissipated in the bulk plasma increases significantly. The important point is that maximum attachment occurs at low electron energies so that the density of “cold” electrons, which represent the main body of plasma electrons, decreases strongly with the addition of an electronegative gas. About 2.5-fold reduction of electron density was detected by microwave measurements with the addition of 1% of strongly electronegative gas Cl₂ to Ar in a similar rf discharge, while the addition of less electronegative gases like O₂ had only a weak effect.²⁵ At the same time, the density of medium- and high-energy electrons in the bulk plasma may even increase, giving rise to the observed growth of emission from the main plasma species.

Actinometry data show that atomic fluorine production is an order of magnitude stronger in the high-density ECR plasma (for example, compare data in Tables I and II). However, Si and SiNx etch rates are usually higher for the RIE reactor. Therefore, etching of these materials in the ECR reactor is not limited by a fluorine supply, and SiNx etching is in fact limited by a NO supply. The fluorine radical flux can be estimated from the Si etch rate in oxygen-free plasmas, as silicon etching by fluorine is known to be spontaneous with the main volatile etch product being SiF₄. The Si etch rate achieved in the ECR reactor is ~30 nm/min. Thus, the potential of the technique is not fully realized, and at higher NO fluxes the nitride etch rate could rise significantly, possibly reaching the level of ~100 nm/min. The spectroscopy study has shown that even though the NO production in ECR O₂/N₂ plasmas is relatively high, it is strongly suppressed when SF₆ is added. As a result, NO production in O₂/N₂/SF₆ plasmas is comparable for the two reactors. The basic difference between them, which favors

### Table II. Spectroscopy data for the rf plasma, pressure 100 mTorr, 75 W, emission intensities \( I^* \) of NO, N₂, N₂⁺, O and F are normalized to that of Ar, wavelengths are the same as in Table I.

<table>
<thead>
<tr>
<th>Gas mixture</th>
<th>( U_{sb} ) (V)</th>
<th>( I(\text{Ar}) ) (arb. units)</th>
<th>( I^*(\text{NO}) )</th>
<th>( I^*(\text{N}_2) )</th>
<th>( I^*(\text{N}_2^+) )</th>
<th>( I^*(\text{O}) )</th>
<th>( I^*(\text{F}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₆/O₂/N₂/Ar, sccm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0/50/50/3</td>
<td>510</td>
<td>1.0</td>
<td>2.4</td>
<td>61</td>
<td>38</td>
<td>2.9</td>
<td>...</td>
</tr>
<tr>
<td>2/50/50/3</td>
<td>400</td>
<td>1.4</td>
<td>3.1</td>
<td>70</td>
<td>17</td>
<td>1.5</td>
<td>0.03</td>
</tr>
<tr>
<td>5/50/50/3</td>
<td>330</td>
<td>2.2</td>
<td>2.4</td>
<td>59</td>
<td>10</td>
<td>1.1</td>
<td>0.08</td>
</tr>
<tr>
<td>10/50/50/3</td>
<td>250</td>
<td>2.0</td>
<td>2.7</td>
<td>78</td>
<td>25</td>
<td>1.5</td>
<td>0.17</td>
</tr>
</tbody>
</table>
higher SiN\textsubscript{x} etch selectivities over both SiO\textsubscript{2} and Si in the ECR reactor, is associated with ion bombardment of the surfaces. Lower SiN\textsubscript{x} etching selectivity in the RIE case is due to stronger bombardment (higher ion energies) which apparently inhibits formation of reaction layers on the nitride and silicon surfaces and promotes faster ion-induced oxide etching. The ion energy threshold for the SiO\textsubscript{2} etching can be estimated from our data as \(\sim 40–50\) eV.

Based on the present results, it seems promising to use in the ECR reactor other fluorine-containing gases such as NF\textsubscript{3} which possibly has different impact on the NO kinetics in the plasma. In addition, a fluorine-containing gas may be injected directly into the downstream region closer to the target. In the present setup, SF\textsubscript{6} is injected together with a \(\text{O}_2/\text{N}_2\) mixture in the high-density plasma region. This evidently results in strong losses of NO molecules as plasma flows downstream. With these changes, it will be possible to reduce NO losses, enhance the nitride etch rate and further improve the etching selectivity.

IV. CONCLUSIONS

The results of comparative study of etching of SiN\textsubscript{x}, SiO\textsubscript{2}, and Si in \(\text{O}_2/\text{N}_2\) gas mixtures with small additions of SF\textsubscript{6} using high- and low-density plasmas (ECR and rf driven plasma sources, respectively) are presented. In \(\text{O}_2/\text{N}_2\) rich plasmas, the nitride etching by fluorine can be enhanced by NO molecules produced in various gas phase reactions. In our experiments, considerable enhancement of nitride etching could be obtained only for the ECR plasma, with maximum selectivities over silicon oxide and silicon reaching 50–70 and 4–20, respectively. Lower selectivities were obtained using the capacitive coupled rf plasma source, in a conventional RIE mode. This can be attributed to specific RIE conditions, where reaction layers promoting enhanced SiN\textsubscript{x} etching and reduced Si etching are apparently not formed on the top of the surfaces likely due to strong ion bombardment. The kinetics of formation of NO molecules, responsible for enhanced nitride etching, was analyzed using optical emission spectroscopy. Higher NO generation was found in a high-density ECR plasma, while using a \(\text{O}_2/\text{N}_2\) mixture.

In the downstream region, considerable losses of NO have been observed. Moreover, small additions of SF\textsubscript{6} resulted in a strong reduction of NO emission. Possible mechanisms of NO generation and losses in the plasma have been discussed. In a high-density plasma, the main NO generation mechanism is likely to involve vibrationally hot N\textsubscript{2} molecules, while in lower density plasmas, metastable N\textsubscript{2} molecules may play a more important role.

Further optimization of the ECR nitride selective etching technology is a subject of a future work. In particular, it is proposed to use other fluorine-containing gases such as NF\textsubscript{3} and inject a fluorine-containing gas directly into the downstream region. This could help to avoid strong losses of NO molecules, enhance the nitride etch rate and further improve the etching selectivity.

ACKNOWLEDGMENTS

The authors thank Dr. Luis da Silva Zambom (LSI-EPUSP) for providing samples of SiN\textsubscript{x}. The work was financially supported by CNPq, FAPESP, and CAPES.

17. J. Reece Roth, Industrial Plasma Engineering (Institute of Physics, Bristol, 1995), Vol. 1.