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Silicon nitride etching in high- and low-density plasmas using SF₆/O₂/N₂ mixtures

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Results of a comparative study of SiN_x, SiO₂ and Si etching in high- and low-density O₂–N₂ based plasmas with small additions of SF₆ are presented. Higher selectivities of SiN_x etching over both SiO₂ (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 thin oxide film.^{1–3} Furthermore, etchants can strongly damage the silicon substrate through imperfections of the oxide, as many plasma processes currently used for nitride stripping etch Si much faster than SiN_x. Hence high selectivity of SiN_x etching over both Si and SiO₂ is strongly desired.

For plasma etching of silicon nitride, carbon containing gases such as CF₄, C₂F₆ and CHF₃ are widely used, in many cases with addition of gases promoting polymerization on the etched surfaces (CO, H₂).^{1,4–6} 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.⁶ Another concern in using fluorocarbon gases is related to their environmental impact.^{7,8} 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.^{2,3,9–13} 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 consid-

erably 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_x to SiO₂ 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).¹⁴ 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 SiO₂ etching using fluorine chemistry, while etching of SiN_x must be less sensitive to ion bombardment. It has been shown^{2,3,9} that addition of N₂ and O₂ 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 CF₄ and O₂ with small additions of nitrogen were used.^{2,3} In the further development of the method, mixtures composed basically of O₂ and N₂ with only small additions of fluorine containing gases (CF₄ or NF₃) have been shown to etch the nitride with higher selectivity over silicon and silicon dioxide.⁹

Mechanisms responsible for highly selective nitride etching in O₂/N₂ 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_x using downstream O₂/N₂ plasmas with smaller additions of NF₃ or CF₄ 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_x to SiO₂ etching selectivity. This was attributed to a highly exothermic reaction $N_{(surface)} + NO_{(gas)} \rightarrow O_{(surface)} + N_{2(gas)}$ (the energy released in the reaction is ~ 7 eV), which promotes the enhanced removal of nitrogen atoms from the nitride surface and thus

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accelerates the overall reaction rate. Oxygen atoms left on the surface by this reaction are believed to desorb promptly, most likely as O_2 .¹¹ Formation of an oxidized reactive layer on the top of Si surface, reducing the silicon etch rate to a level comparable to that of SiO_2 , was detected by *in situ* ellipsometry.¹⁰

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 $SF_6/O_2/N_2$ 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, SiN_x etch rates of 20–30 nm/min have been achieved with high selectivity over both SiO_2 and Si (up to 50–70 and 5–20, respectively). Lower selectivities to SiO_2 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 here¹⁵ 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) SiO_2 films (1 μm thick) produced by thermal oxidation of silicon substrates, and (iii) SiN_x 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 N_2 , O_2 and SF_6 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.

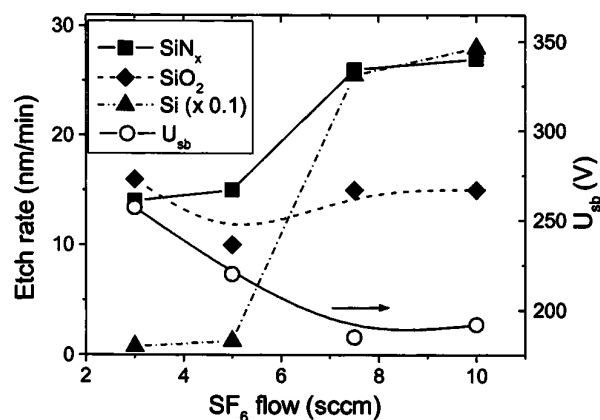


FIG. 1. Etch rates and dc bias vs SF_6 flow, RIE; gas flows $O_2/N_2=30/30$ sccm, 150 mTorr, 75 W. Silicon etch rate is divided by 10.

In the ECR source, two windows were used for diagnostics, being located in different parts of the process chamber: (A) near the exit from the plasma chamber (the area of a dense plasma), (B) 10 cm lower, above the electrode (downstream region of a lower density plasma). Most spectra were taken from the dense plasma region (window A), except where noted.

III. RESULTS AND DISCUSSION

A. Etch rates

1. RIE

In order to have higher SiN_x etch selectivity over SiO_2 , most of the RIE experiments¹⁶ were carried out at a high pressure (150 mTorr) where the dc bias is lower. In Fig. 1, the effect of small SF_6 additions to O_2/N_2 plasma on the etch rates is shown. Flows of both gases were fixed at 30 sccm. As the SF_6 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 SF_6 content increases from 5 to 7.5 sccm. In

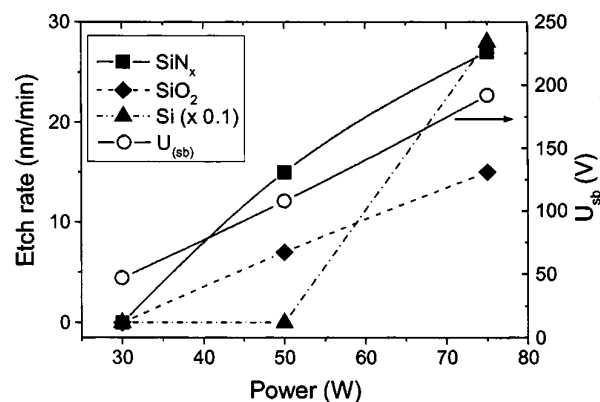


FIG. 2. Etch rates and dc bias vs rf power, RIE; $SF_6/O_2/N_2=10/30/30$ sccm, 150 mTorr. Silicon etch rate is divided by 10.

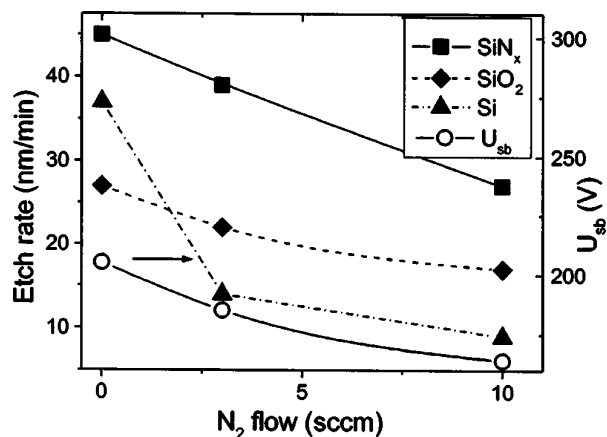


FIG. 3. Etch rates and dc bias vs N₂ flow, RIE; SF₆/O₂/N₂=5/50/10 sccm, 150 mTorr, 75 W.

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 SF₆/O₂/N₂ 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 SF₆/O₂ mixture rich in oxygen (SF₆/O₂=5/50 sccm) was used, with small admixtures of N₂ 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 SiO₂ 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

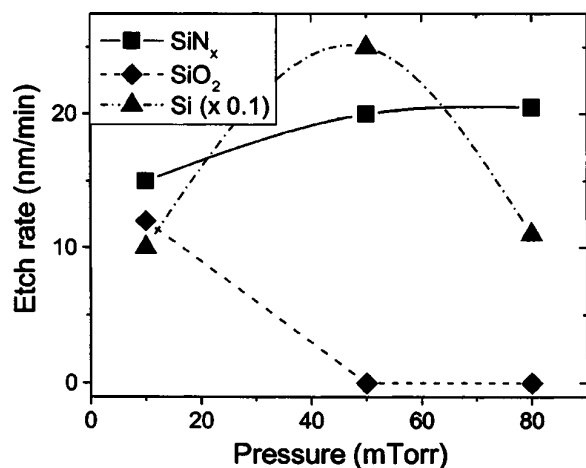


FIG. 4. Etch rates vs gas pressure, ECR; SF₆/O₂/N₂=10/30/30 sccm, ECR power 750 W, rf power 20 W. Silicon etch rate is divided by 10.

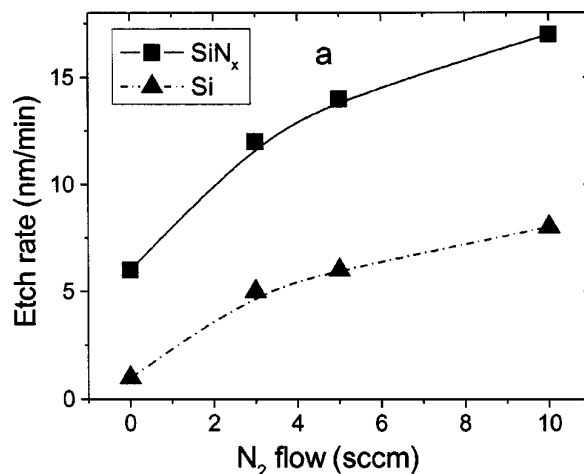
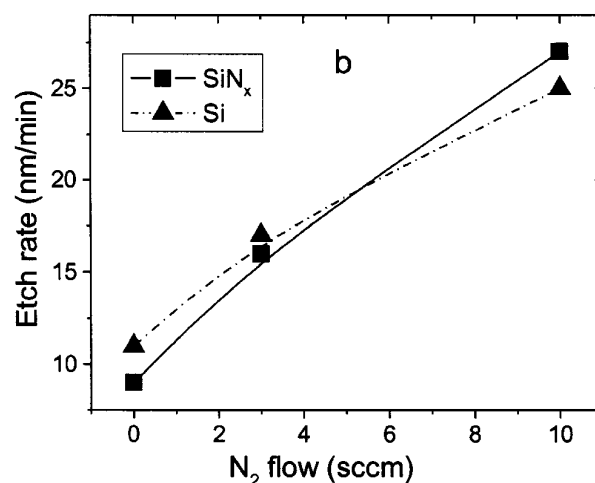


FIG. 5. Etch rates vs N₂ flow, ECR; SF₆/O₂/N₂/Ar, total flow 65 sccm, SF₆ flow 5 sccm (a) and 7.5 sccm (b), O₂ flow 50 sccm, 50 mTorr, ECR power 750 W, rf power 0 W.

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 selectivity¹³ 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 SiO₂ etch rates as

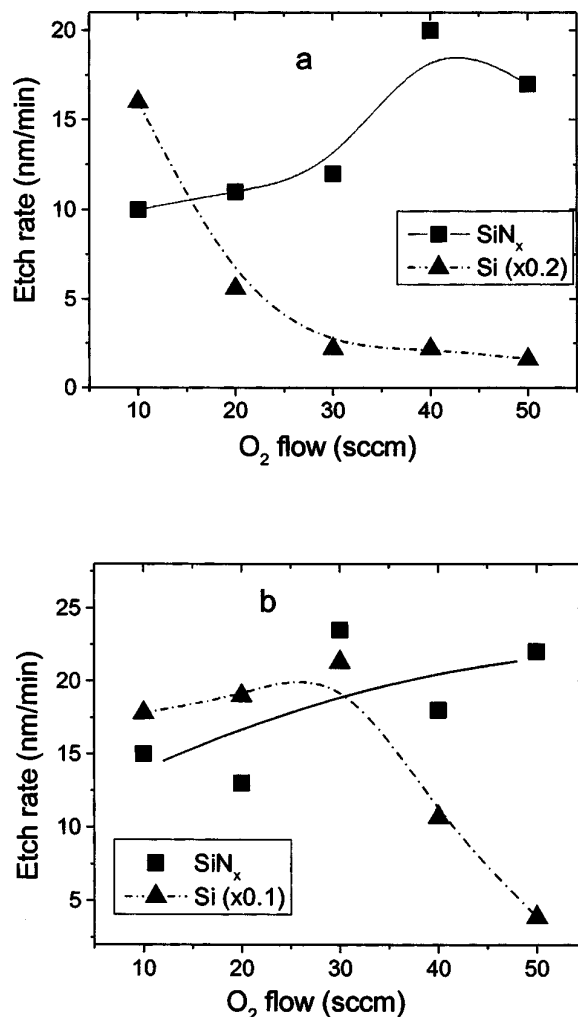


Fig. 6. Etch rates vs O_2 flow, ECR; $SF_6/O_2/N_2$, SF_6 flow 5 sccm (a) and 10 sccm (b), O_2+N_2 total flow 60 sccm, 50 mTorr, ECR power 750 W, rf power 0 W. Silicon etch rate is divided by 5 (a) and 10 (b).

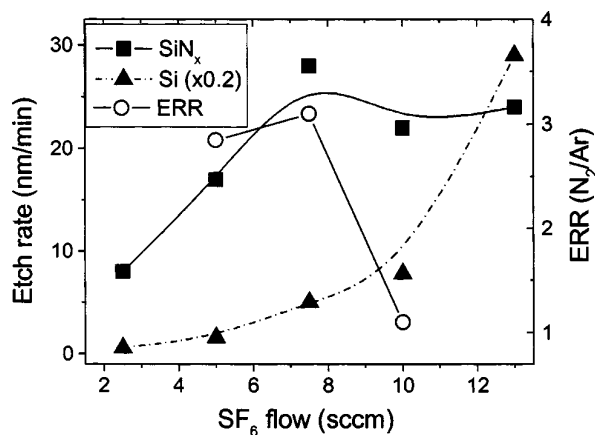


Fig. 7. Etch rates vs SF_6 flow, ECR; $SF_6/O_2/N_2$, $O_2/N_2=50/10$ sccm, 50 mTorr, ECR power 750 W, rf power 0 W. Right scale—etch rate ratios for $SF_6/O_2/N_2$ and $SF_6/O_2/Ar$ plasmas under the same conditions. Silicon etch rate is divided by 5.

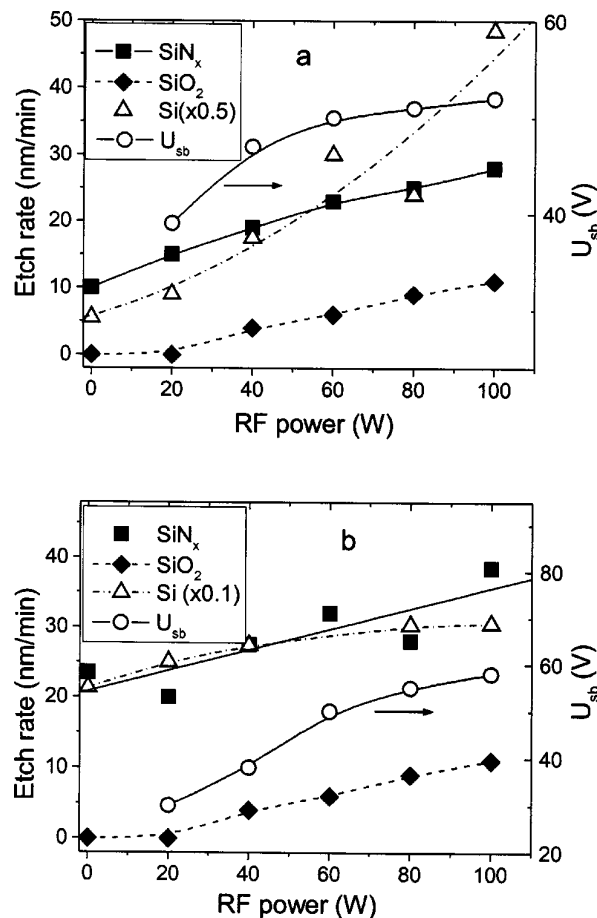


Fig. 8. Etch rates and dc bias vs rf power, ECR; SF_6 flow 5 sccm (a) and 10 sccm (b), $O_2/N_2=30/30$ sccm, 50 mTorr, ECR power 750 W. Silicon etch rate is divided by 2 (a) and 10 (b).

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),¹⁷ the threshold for the oxide etching can be estimated as ~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 $\text{SF}_6/\text{O}_2/\text{N}_2/\text{Ar}$ 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 ($\sim 5\%$ 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 $\text{SF}_6/\text{O}_2/\text{N}_2$ mixture composition is shown in Fig. 6 for SF_6 fluxes of 5 and 7.5 sccm, with varying oxygen flux and the total $\text{O}_2 + \text{N}_2$ 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 $\text{O}_2/\text{N}_2 = 50/10$ 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).

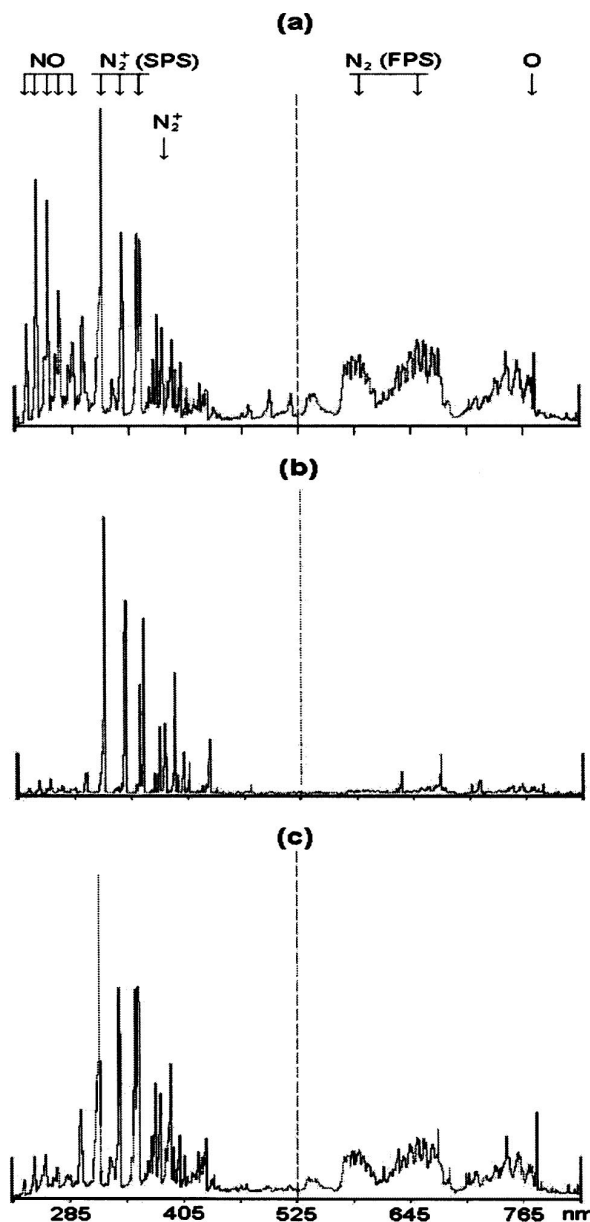


FIG. 9. Plasma emission spectra in 225–825 nm spectral range for ECR [(a),(c)] and rf (b) plasmas. Plasma composition: O_2/N_2 [(a),(b)], $\text{SF}_6/\text{O}_2/\text{N}_2$ (c). FPS and SPS– N_2 first and second positive system, respectively.

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 $\text{NO } \gamma$ system¹² 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 ($v' \geq 10$). 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



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 $n_e = (0.5\text{--}2) \times 10^{10} \text{ cm}^{-3}$ 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}



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



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,



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 knowl-

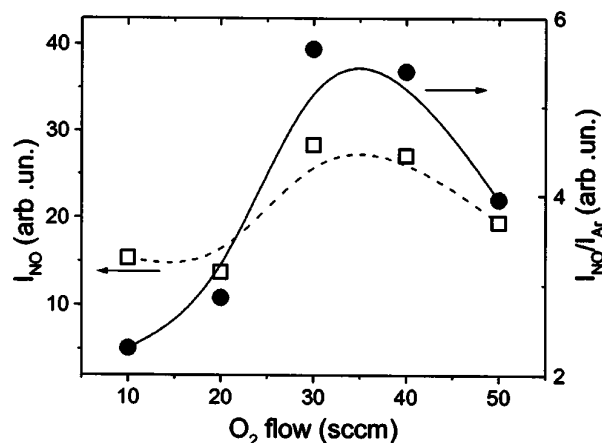


FIG. 10. NO emission intensity (as measured—left scale, and normalized to that of Ar—right scale) vs O_2 flow, ECR, conditions the same as for Fig. 6.

edge, 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

$$N_X = K(I_X/I_{Ar})N_{Ar},$$

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 γ 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)

TABLE I. Spectroscopy data for the ECR plasma; emission intensities I^* of NO (259 nm), N_2 (337 nm), N_2^+ (391 nm), O (777 nm), N (747 nm), and F (703 nm) are normalized to that of Ar (750 nm), 50 mTorr.

Gas mixture, $SF_6/O_2/N_2/Ar$, sccm	Position	$I(Ar)$ arb.units	$I^*(NO)$	$I^*(N_2)$	$I(N_2^+)$	$I^*(O)$	$I^*(N)$	$I^*(F)$
0/50/50/2	A	7.4	7.9	11.4	3.5	6.6	0.7	...
	B	4.4	1.8	8.4	3.0	8.7	1.1	...
2.5/50/50/2	A	5.3	0.80	17.5	6.5	14.4	1.2	0.81
	B	3.6	0.75	10.1	5.1	16.5	1.8	0.80

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



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



where $M = N_2$ or O_2 . For the reaction (6) to occur, high 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 $v = 3$ of the N_2 ground state is predominantly populated with smaller contributions to the neighboring levels $v = 2$ 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 $v' = 3$, e.g., the $v' = 3 \rightarrow v'' = 6$ 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 O_2/N_2 plasma, the 389.5 nm band is much weaker than for the ECR case, due to lower N content.

2. $O_2/N_2/SF_6$ plasmas

Addition of SF_6 to the O_2/N_2 mixture has a very strong impact on the emission spectra from the ECR plasma. Admixture of 2.5 sccm of SF_6 to the $O_2/N_2/Ar = 50/50/2$ sccm plasma results in a sevenfold drop of NO emission (the normalized intensity, $I^*(NO) = I(NO)/I(Ar)$, 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 $\sim 30\%$, and the first positive N_2 system emission (high vibrational numbers) reduces $\sim 35\%$;
- (2) the most intense bands of the second positive N_2 system corresponding to $v' = 0$ and 1 (e.g., 337.1 nm) rises $\sim 10\%$, while the weaker bands starting from $v' = 3$ (e.g., the $v' = 3 \rightarrow v'' = 6$ transition at 389.5 nm) reduce $\sim 15\%$;

- (3) the first negative 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 O_2 . A smaller electron density results in reduced emission of Ar, weaker vibrational excitation of 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 [(6, 7)] become smaller. While the reasons for the N_2^+ emission growth are not completely clear, it is probably due to reduced 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 N_2 second positive system emission (transitions from $v' = 3$) reduces notably, gives further evidence that the reaction with N atoms (6) is the dominant channel of NO losses in high density O_2/N_2 plasmas. Comparison of spectra taken in spatial points A and B (Table I) shows that for the $O_2/N_2/SF_6$ plasma, the NO concentration reduces downstream only slightly, in contrast to the O_2/N_2 case. This indicates that NO regeneration

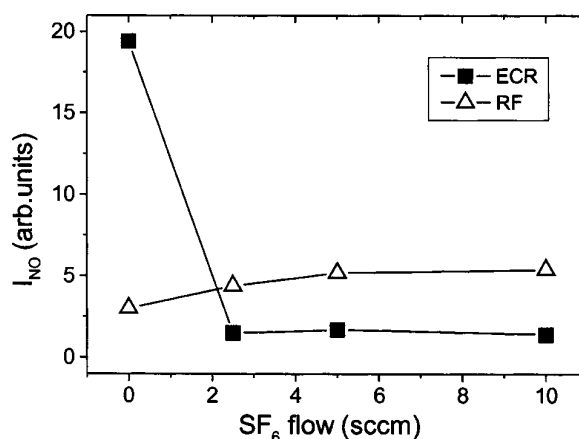


FIG. 11. NO emission intensity vs SF_6 flow; ECR and RIE reactors, $SF_6/O_2/N_2$.

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

Gas mixture SF ₆ /O ₂ /N ₂ /Ar, sccm	U_{sb} , V	$I(\text{Ar})$ arb.units	$I^*(\text{NO})$	$I^*(\text{N}_2)$	$I^*(\text{N}_2^+)$	$I^*(\text{O})$	$I^*(\text{F})$
0/50/50/3	510	1.0	2.4	61	38	2.9	...
2/50/50/3	400	1.4	3.1	70	17	1.5	0.03
5/50/50/3	330	2.2	2.4	59	10	1.1	0.08
10/50/50/3	250	2.0	2.7	78	25	1.5	0.17

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 reaction²²



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



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 discharge^{23,24} have shown that the distribution depends criti-

cally 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 SiN_x 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 SiN_x 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 under these conditions can be as high as 500 nm/min while the maximum SiN_x 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

higher SiN_x etch selectivities over both SiO_2 and Si in the ECR reactor, is associated with ion bombardment of the surfaces. Lower SiN_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_2 etching can be estimated from our data as $\sim 40\text{--}50$ eV.

Based on the present results, it seems promising to use in the ECR reactor other fluorine-containing gases such as NF_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_6 is injected together with a O_2/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_x , SiO_2 and Si in O_2/N_2 gas mixtures with small additions of SF_6 using high- and low-density plasmas (ECR and rf driven plasma sources, respectively) are presented. In O_2/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 capacitively coupled rf plasma source, in a conventional RIE mode. This can be attributed to specific RIE conditions, where reaction layers promoting enhanced SiN_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 O_2/N_2 mixture. In the downstream region, considerable losses of NO have been observed. Moreover, small additions of SF_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_2 molecules, while in lower density plasmas, metastable N_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_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.

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