

**СОСТАВ ПЛАЗМЫ И КИНЕТИКА ТРАВЛЕНИЯ SiO_2 В СМЕСИ $\text{CF}_4/\text{C}_4\text{F}_8/\text{Ar}/\text{He}$:
ВЛИЯНИЕ СООТНОШЕНИЯ $\text{CF}_4/\text{C}_4\text{F}_8$ И МОЩНОСТИ СМЕЩЕНИЯ****А.М. Ефремов, К.-Н. Kwon**

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Исследованы характеристики газовой фазы и кинетика реактивно-ионного травления диоксида кремния в плазме $\text{CF}_4/\text{C}_4\text{F}_8/\text{Ar}/\text{He}$ при варьировании соотношения $\text{CF}_4/\text{C}_4\text{F}_8$ и потенциала смещения в режиме малой ($\sim 0,05 \text{ Вт/см}^3$) вкладываемой мощности. Интерес к такому режиму обусловлен возможностью получения высокой анизотропии травления при малых радиационных повреждениях поверхности. Схема исследования включала диагностику плазмы с помощью зондов Ленгмюра и оптической эмиссионной спектроскопии в варианте внутренней (без использования стандартной добавки) актинометрии. Показано, что замещение C_4F_8 на CF_4 не приводит к существенным изменениям параметров электронной и ионной компонент плазмы, но сопровождается незначительным ростом концентрации атомов фтора. Напротив, увеличение мощности (а, следовательно, и потенциала) смещения не возмущает состава плазмы, но характеризуется пропорциональным изменением энергии бомбардирующих ионов. Таким образом, выбранные варьируемые параметры представляют классические «химический» и «физический» механизмы воздействия на кинетику гетерогенных стадий процесса травления. Установлено, что основной вклад в процесс травления SiO_2 вносит химическая составляющая, при этом при мощностях смещения выше 400 Вт вероятность химической реакции $\text{Si}(s.) + x\text{F} \rightarrow \text{SiF}_x$ (где индекс (s.) отвечает частице, локализованной на поверхности) не зависит от эффективности образования центров адсорбции для атомов фтора под действием ионной бомбардировки $\text{SiO}_x(s.) \rightarrow \text{Si}(s.) + x\text{O}$. В условиях малых мощностей смещения наличие такой зависимости подтверждается симбатным поведением эффективной вероятности взаимодействия и интенсивности ионной бомбардировки, характеризующейся произведением плотности потока ионов на корень квадратный из их энергии. Сделаны предположения об особенностях кинетики объемных и гетерогенных процессов в условиях низкой плотности плазмы.

Ключевые слова: C_4F_8 , CF_4 , плазма, параметры, активные частицы, ионизация, диссоциация, травление

**PLASMA COMPOSITION AND SiO_2 ETCHING KINETICS IN $\text{CF}_4/\text{C}_4\text{F}_8/\text{Ar}/\text{He}$ MIXTURE:
EFFECTS OF $\text{CF}_4/\text{C}_4\text{F}_8$ MIXING RATIO AND BIAS POWER****A.M. Efremov, K.-H. Kwon**

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Gas-phase characteristics as well as reactive-ion etching kinetics of silicon dioxide in CF₄/C₄F₈/Ar/He plasma with variable CF₄/C₄F₈ mixing ratio and bias potential were investigated under conditions of low (~ 0.05 W/cm³) input power regime. The interest to such regime is due to the possibility to obtain higher etching anisotropy with lower surface damages. The research scheme included plasma diagnostics by Langmuir probes and optical emission spectroscopy in the internal (with no use of standard additives) actinometry approach. It was shown that the substitution of C₄F₈ for CF₄ does not produce sufficient changes in both electrons- and ions-related plasma parameters, but causes a weak increase in fluorine atom density. On the contrary, an increase in the bias power (and thus, in the bias potential) does not disturb plasma composition, but is characterized by proportional changes in the ion bombardment energy. As such, selected variable parameters represent somewhat classical “chemical” and “physical” factors influencing heterogeneous stages of the etching process. It was found that the dominant contribution to the SiO₂ etching process belongs to its chemical component while bias powers above 400 W provide no dependence of Si(s.) + xF → SiF_x (where index (s.) points out the particle situated on the surface) reaction probability on the efficiency of ion-induced production of adsorption sites for fluorine atoms, as SiO_x(s.) → Si(s.) + xO. At lower bias powers, the presence of such dependence is confirmed by similar changes of effective reaction probability and ion bombardment intensity, traced by the multiplication of ion flux on square root of ion energy. Some suggestions concerning peculiarities of both gas-phase and heterogeneous process kinetics at low plasma densities were made.

Key words: C₄F₈, CF₄, plasma, parameters, active species, ionization, dissociation, etching

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INTRODUCTION

Fluorocarbon gases with a general formula of C_xF_y play a remarkable role in modern electronic device technology being used for dry (plasma-assisted) patterning of silicon family compounds [1-3]. The most effective tool to obtain nano-scale feature sizes is the reactive-ion etching (RIE) process which combines physical (physical sputtering) and chemical (ion-assisted heterogeneous reactions) etching pathways. Accordingly, the adjustment of these two components in most of cases provides the desirable balance between various output RIE characteristics, such as etching rate, etching selectivity in respect to the mask material as well as the degree of anisotropy which controls shapes of etching profiles. From many published works (see, for example, Refs. [4-6]), it is known also that the etching performance for the given fluorocarbon gas strongly depends on the y/x ratio that pre-determines densities of F atoms and polymerizing CF_x (x ≤ 2) radicals [5, 6]. In particular, the CF₄ plasma (y/x = 4) represents the system with low polymerizing ability and thus, provides the domination of etching over the surface polymerization. The fea-

tures of such plasmas are high etching rates and surface cleanness, nearly-isotropic etching profiles and bad SiO₂/Si etching selectivity [6, 7]. Oppositely, the C₄F₈ plasma (y/x = 2) is the case of high polymerizing gas systems. Accordingly, it is characterized by lower etching rates, but provides the decent etching anisotropy (due to the protection of sidewalls by the deposited polymer layer) and SiO₂/Si selectivity (due to the thinner polymer film on the oxygen-containing surface) [3, 4, 8].

The overall trend in the modern RIE technology is the use of multi-component gas mixtures combining one or several fluorocarbon components with noble and/or molecular additives. The reason is that the variation of gas mixing ratio offers the additional tool to optimize output RIE characteristics through changes in both gas-phase and heterogeneous reaction kinetics. In our previous works [9-13], we carried out detailed investigations of gas mixing effects in binary and ternary gas systems composed by CF₄, C₄F₈ and Ar under conventional RIE conditions (gas pressures below 50 mtorr, input power densities of 0.5-0.1 W/cm³ that correspond to the plasma density of ~ 10¹⁰-10¹¹ cm⁻³, and ion bombardment energies above

200 eV). Corresponding results may briefly be summarized as follows:

1) An increase in Ar fraction in both $\text{CF}_4 + \text{Ar}$ and $\text{C}_4\text{F}_8 + \text{Ar}$ plasmas changes electrons- and ions-related plasma parameters and thus, influences both gas-phase and heterogeneous reaction kinetics. Most principal effect here are a) the elevation of electron temperature and plasma density; b) the increasing efficiency of electron-impact processes that results in slower decrease of F atoms density [9, 10]; and c) the growth of ion bombardment intensity that accelerates ion-driven heterogeneous processes, such as surface bond breaking, the desorption of low volatile reaction products and the destruction of fluorocarbon polymer film. As such, the change in the effective probability of ion-assisted chemical reaction represents the superposition of all above effects [11, 12].

2) The substitution of C_4F_8 for CF_4 in the $\text{C}_4\text{F}_8 + \text{CF}_4 + \text{Ar}$ plasma exhibits much weaker effect on both electron temperature and plasma density, but directly influences densities of F atoms and CF_x radicals through corresponding source species. In this case, the ion-assisted chemical reaction occurs at the nearly constant ion bombardment intensity while the effective reaction probability traces the polymer film thickness.

Unfortunately, the existing data cannot be applied directly to explain plasma chemical phenomena in more complicated gas systems and/or under different processing conditions. The reason is that the introduction of new component as well as the change in discharge excitation regime disturbs both electron energy distribution and charged species balance. This causes the mandatory response from chemical kinetics of all gas-phase components and thus, results in the multi-channel influence on densities of plasma active species. Therefore, the study of plasma parameters and composition in new gas systems and/or processing regimes is the mandatory thing to understand the performance and the technological potential for given RIE process.

The subject of this work was the $\text{CF}_4 + \text{C}_4\text{F}_8 + \text{Ar} + \text{He}$ plasma excited in the low ($\sim 0.05 \text{ W/cm}^3$) input power mode. The interest to such regime is due to the possibility to obtain higher etching anisotropy with lower surface damages [14-16]. As variable parameters, we selected the $\text{CF}_4/\text{C}_4\text{F}_8$ mixing ratio and the bias power that directly influence the negative bias potential. According to previously published data, it can be expected that these ones represent somewhat classical "chemical" and "physical" factors influencing heterogeneous stages of the etching process. The silicon dioxide, as the etched material, was a kind

of test object with the well-known etching mechanism under conventional RIE conditions. Therefore, the analysis of corresponding etching kinetics allows one better understanding the features of the low-power RIE process.

EXPERIMENTAL DETAILS

Experiments were carried out in the inductively coupled plasma (ICP) reactor known from our previous works [10-13]. Plasma was excited using the 13.56 MHz power supply connected to the flat copper coil on the top side of reactor chamber. Another 13.56 MHz RF generator powered the bottom electrode to produce the negative bias potential, $-U_{dc}$. Constant processing parameters were gas pressure ($p = 10 \text{ mtorr}$, or 1.33 Pa), input power ($W = 50 \text{ W}$ that corresponded to $\sim 0.05 \text{ W/cm}^3$) and total gas flow rate ($q = 114 \text{ sccm}$). Accordingly, variable inputs were represented by bias power ($W_{dc} = 200\text{--}500 \text{ W}$) and initial composition of $\text{CF}_4 + \text{C}_4\text{F}_8 + \text{Ar} + \text{He}$ gas mixture. The latter was set by partial flow rates for CF_4 and C_4F_8 within the total value of 14 sccm at constant $q(\text{Ar}) = 25 \text{ sccm}$ and $q(\text{He}) = 75 \text{ sccm}$. Therefore, an increase in $q(\text{CF}_4)$ in the range of $0\text{--}14 \text{ sccm}$ corresponded to the full substitution of C_4F_8 for CF_4 , and the fraction of CF_4 in a feed gas $y(\text{CF}_4) = q(\text{CF}_4)/q$ was changed as $0\text{--}12\%$.

Gas-phase plasma parameters were measured using the double Langmuir probe tool (DLP2000, Plasmart Inc.). The treatment of raw I-V curves with accounting for well-known statements of Langmuir probe theory in low pressure plasmas [17, 18] yielded data on electron temperature (T_e) and ion current density (J_+). In order to reduce experimental errors due to the deposition of fluorocarbon polymer on probe tips, these were conditioned in $50\% \text{ Ar} + 50\% \text{ O}_2$ plasma for $\sim 5 \text{ min}$ before and after each experiment.

The negative bias potential, $-U_{dc}$, was monitored using the high-voltage probe (AMN-CTR, Youngsin Eng.).

Steady-state densities of F atoms were determined using plasma diagnostics by the optical emission spectroscopy (OES) (AvaSpec-3648, JinYoung Tech). For this purpose, we measured emission intensities of well-known actinometrical lines F 703.8 nm and Ar 750.4 nm which are featured by a) direct electron impact excitation mechanisms with known process cross-sections [19]; and b) low radiational lifetimes. Taking into account the constant and known density of Ar atoms in both feed gas and under plasma conditions, one can apply the standard actinometrical approach in a form of

$$I(\text{F})/I(\text{Ar}) = C_{\text{F,Ar}}[\text{F}]/[\text{Ar}], \quad (1)$$

where I is the measured emission intensity, and $C_{\text{F,Ar}}$

is the coefficient combining corresponding excitation rate coefficients $k_{ex} = f(T_e)$ and transition probabilities [19]. The last work demonstrated also that a) $C_{F,Ar} \approx \text{const}$ at $T_e = 3\text{-}4$ eV; and b) the F atoms density determined from Eq. (1) has a good agreement with mass-spectrometry experiments.

Etching kinetics of SiO_2 was studied using fragments of thermally oxidized Si (111) wafers. Treated samples with an average size of $\sim 2 \times 2$ cm were placed in the middle part of the bottom electrode. The bottom electrode has the built-in water-flow cooling system which allows one to stabilize its

temperature at the nearly constant value of ~ 17 °C. In order to determine SiO_2 etching rates, we covered a part of sample surface by the photoresist mask as well as measured the height of the step Δh between masked and non-masked areas using the surface profiler Alpha-Step 500 (Tencor). In preliminary experiments, it was found that all kinetic curves $\Delta h = f(\tau)$ exhibited nearly linear shapes within processing times τ up to 5 min. Since this surely points out on the steady-state etching regime, etching rates were simply calculated as $R = \Delta h/\tau$.

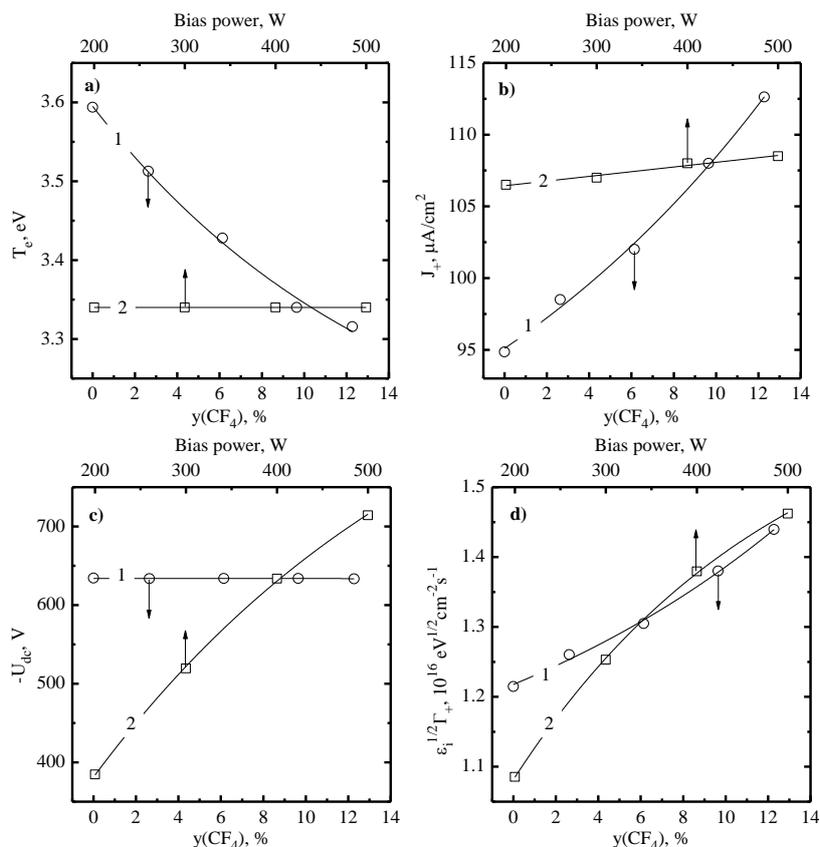


Fig. 1. Electrons- and ions-related plasma characteristics as functions of CF_4 fraction in a feed gas (at $W_{dc} = 400$ W, curve 1) and bias power (at $y(\text{CF}_4) = 10\%$, curve 2): a) electron temperature; b) ion current density; c) negative bias potential; and d) parameter $\epsilon_i^{1/2}\Gamma_+$, characterizing the ion bombardment intensity

Рис. 1. Характеристики электронной и ионной компонент плазмы в зависимости от доли CF_4 в плазмообразующем газе (при $W_{dc} = 400$ Вт, кривая 1) и мощности смещения (при $y(\text{CF}_4) = 10\%$, кривая 2): а) температура электронов; б) плотность ионного тока; в) отрицательный потенциал смещения; и д) параметр $\epsilon_i^{1/2}\Gamma_+$, характеризующий интенсивность ионной бомбардировки

RESULTS AND DISCUSSION

Fig. 1 represents effects of $\text{CF}_4/\text{C}_4\text{F}_8$ mixing ratio and bias power on electrons- and ions-related gas-phase characteristics. The analysis of these data with accounting for the previous research experience of $\text{CF}_4 + \text{Ar}$ [9, 13], $\text{C}_4\text{F}_8 + \text{Ar}$ [9-11, 13] and $\text{CF}_4 + \text{C}_4\text{F}_8 + \text{Ar}$ [10-12] plasmas allows one to formulate several important features which may be useful for

the optimization of corresponding RIE process. These are as follows:

1) Similarly to conventional RIE conditions [10, 11], an increase in CF_4 fraction in a feed gas causes rather weak changes in both electron temperature (Fig. 1(a)) and ion current density (Fig. 1(b)). Perhaps, the general reason is that the substitution of C_4F_8 for CF_4 does not results in global changes in the electron energy loss channels (and thus, in the

electron energy distribution function) as well as does not disturb formation/decay balances for both ion and electrons. On this background, the weak decrease in T_e may be associated with increasing fractions of more saturated and bigger-sized CF_x species (for instance, CF_4 and CF_3 , instead of CF_2 and CF which dominate in C_4F_8 -based plasmas [10-12]) characterized by higher cross-sections and lower threshold energies for electron-impact excitation and ionization processes. Accordingly, this also causes the growth of total ionization rate, densities of charged species and the parameter J_+ , as mentioned in Fig. 1(b). It can be seen also, that the combination of nearly constant bias potential (Fig. 1(c)) and increasing ion flux $\Gamma_+ \approx J_+/e$ provide the similar monotonic change in the parameter $\varepsilon_i^{1/2}\Gamma_+$ (Fig. 1(d)), where $\varepsilon_i = e(-U_{dc}-U_f)$ is the ion bombardment energy, and $U_f = f(T_e)$ [4] is the floating potential. As the sputtering yield is generally proportional to the momentum transferred from the incident ion to the surface atom [4], the multiplication of $\varepsilon_i^{1/2}\Gamma_+$ traces the ion bombardment intensity [9, 10]. Therefore, the somewhat activation of ion-driven heterogeneous processes also takes place.

2) An increase in bias power does not disturb both electron temperature and plasma density (as it follows from the change of J_+) that surely suggests no influence on densities of neutral species. At the same time, it results in the nearly proportional growth of negative bias potential (Fig. 1(c)), so that one can obtain the enforcement of the ion bombardment (Fig. 1(d)) even under the condition of $\Gamma_+ \approx \text{const}$. It is important to note that the corresponding change in $\varepsilon_i^{1/2}\Gamma_+$ value (and thus, in the effect on ion-driven heterogeneous processes) exceeds that for the CF_4/C_4F_8 mixing ratio.

From plasma emission spectra, it was found that emission intensities for F 703.8 nm and Ar 750.4 nm remain to be nearly constant vs. W_{dc} , but demonstrate the monotonic increase with increasing $y(CF_4)$ (Fig. 2(a)). In particular, the $I_{Ar} = f(W_{dc})$ curve surely means the constancy of corresponding excitation function $k_{ex}n_e$, as it would be expected from mentioned changes in T_e and J_+ . Accordingly, the same behavior of I_F , as well as the condition $I_F/I_{Ar} = \text{const}$ allow one to assume no effect of bias power on the F atom density. Obviously, such situation results from the nearly constant F atom formation rate in R1: $CF_x + e \rightarrow CF_{x-1} + F + e$ due to the quite close k_1 values for various CF_x species. It should be noted that the weak increase in $[F]$ toward higher bias powers, as shown in Fig. 2(b), is within the standard experimental error. However, the physical reason may be the slightly increasing electron density, as follows

from the behavior of J_+ . On the contrary, the $I_F = f(y(CF_4))$ curve reflects the overall effect from both F atom density and excitation function. The real $[F]$ value extracted from Eq. (1) demonstrates the non-linear growth toward CF_4 -rich plasmas as well as tends to be saturated at maximum $y(CF_4)$. The identical behavior of F atom density have been obtained by plasma modeling of $CF_4 + C_4F_8 + Ar$ gas system under conventional RIE conditions [11, 12]. In fact, this suggests the similarity of general plasma chemical phenomena in high- and low- input power modes as well as assumes the same explanation for the change in $[F]$. According to Refs. [11-13], this is a combination of the nearly constant F atom formation rate in R1 and the decreasing F atom loss frequency in R2: $C_2F_4 + F \rightarrow CF_2 + CF_3$ which dominates over the heterogeneous loss in C_4F_8 -rich plasmas. Therefore, the main feature of the low input power mode is only the lower F atom density.

From etching experiments, it was found that the SiO_2 etching rate increases slightly vs. $y(CF_4)$ as well as demonstrates the rapid growth toward higher bias powers (Fig. 2(c)). From Refs. [12, 20], it can be understood that the total rate of RIE process may be represented in a form of two summands, $R_{phys} + R_{chem}$. These components characterize parallel etching pathways, such as physical sputtering and ion-assisted chemical reaction. The evaluation of $R_{phys} \approx Y_S\Gamma_+$ using the experimental data on SiO_2 sputtering yields ($Y_S \approx 0.4$ atom/ion for 0-12% CF_4 and 0.3-0.45 atom/ion for $W_{dc} = 200-500$ W [21, 22]) indicated that the main contribution to the measured etching rate belongs to R_{chem} (Fig. 2(c)). The effective probability of ion-assisted chemical reaction $\gamma_R = R_{chem}/\Gamma_F$ (Fig. 2(d)), where Γ_F is the flux of fluorine atoms, exhibits no correlation with the fluorocarbon film thickness, as the latter decreases toward CF_4 -rich plasmas. The last fact evidently follows from decreasing polymer deposition rate (due to much lower polymerizing ability of CF_4 compared with C_4F_8 [4, 5, 9]) and increasing polymer destruction rate (due to increasing ion bombardment intensity). Therefore, the obtained situation contradicts with the general rule "the thinner film, the higher reaction probability" mentioned by both experiment and modeling for many fluorocarbon gas plasmas, including $C_4F_8 + Ar$ [10, 12] and $C_4F_8 + CF_4 + Ar$ [11, 12] gas systems. In our opinion, the reason is not the feature of low-power plasma excitation mode, but simply the low content of fluorocarbon components in the gas mixture. Accordingly, this produces the very thin or even the non-continuous polymer film which does not influence the SiO_2 etching kinetics. Another remarkable fact is that the

change of γ_R does not correlate with the ion bombardment intensity at $W_{dc} \geq 400$ W. In fact, this means that the ion-induced production of adsorption sites for F atoms R3: $\text{SiO}_x(\text{s.}) \rightarrow \text{Si}(\text{s.}) + x\text{O}$ (where index (s.) points out the particle situated on the surface) does not limit the rate of chemical reaction R4: $\text{Si}(\text{s.}) + x\text{F} \rightarrow \text{SiF}_x$. Perhaps, the latter occurs in the F-atom-deficient regime due to high ion bombardment intensity and low F atom flux, as a result of low plasma density in a low input power mode. Accordingly, the small decrease in γ_R toward higher $y(\text{CF}_4)$ values may be due to the ion-induced desorption of F atoms prior their interaction with silicon in R4. Therefore, the low input power RIE mode somewhat equal-

ized etching mechanisms for Si and SiO_2 . At the same time, at bias powers below 400 W, the effective reaction probability follows the ion bombardment intensity (Fig. 2(d)). Such situation is quite typical for conventional SiO_2 RIE process in low polymerizing plasmas. It was found also that the parameter $\Gamma_F/\varepsilon_i^{1/2}\Gamma_+$ (the so-called neutral/charged ratio) characterizing the etching anisotropy exhibits the weak sensitivity to $y(\text{CF}_4)$ (1.4-1.6 for 0-12% CF_4 at $W_{dc} = 400$ W), but decreases by ~ 1.5 times with increasing bias power. As such, similarly to conventional RIE conditions, W_{dc} represents the most effective tool to increase the “directional” component of the etching process and thus, to adjust the shape of etching profile.

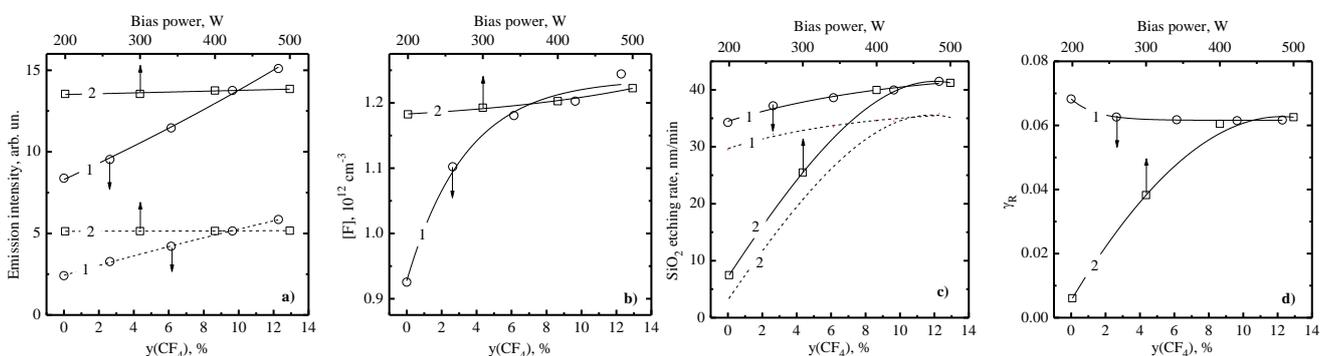


Fig. 2. Densities of F atoms and SiO_2 etching kinetics as functions of CF_4 fraction in a feed gas (at $W_{dc} = 400$ W, curve 1) and bias power (at $y(\text{CF}_4) = 10\%$, curve 2): a) emission intensities for Ar 750.4 nm (solid lines) and F 703.8 nm (dashed lines) maxima; b) F atom density; c) SiO_2 etching rate (dashed satellite curves represent R_{chem}); and d) effective reaction probability

Рис. 2. Концентрации атомов фтора и кинетика травления SiO_2 в зависимости от доли CF_4 в плазмообразующем газе (при $W_{dc} = 400$ Вт, кривая 1) и мощности смещения (при $y(\text{CF}_4) = 10\%$, кривая 2): а) интенсивности эмиссионных максимумов Ar 750,4 нм (сплошные линии) и F 703,8 нм (пунктир); б) концентрации атомов F; в) скорость травления SiO_2 (пунктирные кривые-спутники представляют R_{chem}); и г) эффективная вероятность взаимодействия

CONCLUSIONS

In this work, we investigated gas-phase characteristics and reactive-ion etching (RIE) kinetics of SiO_2 in $\text{CF}_4/\text{C}_4\text{F}_8/\text{Ar}/\text{He}$ plasma with variable $\text{CF}_4/\text{C}_4\text{F}_8$ mixing ratio and bias power in the low (~ 0.05 W/cm³) input power mode. It was found that the substitution of C_4F_8 for CF_4 does not produce sufficient changes in both electrons- and ions-related plasma parameters, but causes a weak increase in fluorine atom density. The last effect is the same with that obtained for conventional RIE conditions and probably results from decreasing loss frequency for F atoms in $\text{C}_2\text{F}_4 + \text{F} \rightarrow \text{CF}_2 + \text{CF}_3$. The increasing bias power has no influence on gas-phase plasma characteristics, but enforces the ion bombardment due to the change in the negative bias potential. From etching experiments, it can be understood that a) the measured SiO_2 etching rate is mainly composed by its chemical component; b) the thin or even the non-continuous fluorocarbon polymer film does not limit

the access of F atoms to the etched surface; and c) the condition $W_{dc} > 400$ W sufficiently reduces the influence of ion-induced process $\text{SiO}_x(\text{s.}) \rightarrow \text{Si}(\text{s.}) + x\text{O}$ on the $\text{Si}(\text{s.}) + x\text{F} \rightarrow \text{SiF}_x$ reaction kinetics. Perhaps, the last feature is due to the combination of high ion bombardment intensity and low F atom flux, as a result of low plasma density in a low input power mode. On the contrary, at lower bias powers, the effective reaction probability correlates with the ion bombardment intensity.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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