ПАРАМЕТРЫ ПЛАЗМЫ И КИНЕТИКА АКТИВНЫХ ЧАСТИЦ В СМЕСИ CF$_4$+C$_4$F$_8$+Ar

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В данной работе обсуждаются взаимосвязи между начальным составом смеси CF$_4$ + C$_4$F$_8$ + Ar, характеристиками газовой фазы и кинетикой гетерогенных процессов в условиях плазмы индукционного разряда пониженного давления. Целью работы являлось исследование зависимостей внутренних параметров плазмы (температура электронов, концентрация электронов, энергия ионной бомбардировки) и кинетики активных частиц от соотношения компонентов CF$_4$/C$_4$F$_8$ в плазмообразующей смеси, а также выявление механизмов влияния указанных параметров на такие характеристики «сухого» травления, как скорость травления и селективность. Исследования проводились методами диагностики плазмы двойным зондом Лангмюра и моделирования плазмы в условиях планарного индукционного плазмохимического реактора. Эксперименты и расчеты проводились при постоянном давлении газа (10 мтор), вкладываемой мощности (800 Вт) и мощности смещения (150 Вт), при этом отношение CF$_4$/C$_4$F$_8$ варьировалось изменением парциальных скоростей потока этих газов. Было найдено, что замещение CF$_4$ на C$_4$F$_8$ в плазмообразующем газе CF$_4$ + C$_4$F$_8$ + Ar приводит к снижению скорости генерации атомов фтора и плотности их потока на обрабатываемую поверхность из-за снижения концентрации в объеме плазмы. Предположено, что рост концентрации и плотности потока ненасыщенных радикалов CF$_x$ (x=1,2) в смесях с большим содержанием C$_4$F$_8$ при близких к постоянным значениях плотности потока энергии ионов (т.е. близкой к постоянной эффективности ионной бомбардировки) способствует снижению эффективной вероятности взаимодействия атомов фтора за счет увеличения толщины фторуглеродной полимерной пленки на обрабатываемой поверхности.

Ключевые слова: CF$_4$, C$_4$F$_8$, скорость реакции, энергия ионов, концентрация, поток, травление, полимеризация

PLASMA PARAMETERS AND ACTIVE SPECIES KINETICS IN CF₄+C₄F₈+Ar GAS MIXTURE

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This work discusses the relationships between the initial composition of the CF₄ + C₄F₈ + Ar gas mixture, gas-phase characteristics and heterogeneous process kinetics under the condition of low-pressure inductively coupled plasma. The goals were to investigate how the CF₄/C₄F₈ mixing ratio influences internal plasma parameters (electron temperature, electron density and ion bombardment energy) and kinetics of plasma active species as well as to analyze how the changes in above parameters may influence the dry etching characteristics, such as etching rates and selectivities. The investigation was carried out using the combination of plasma diagnostics by double Langmuir probes and 0-dimensional plasma modeling. Both experiments and calculations were carried out at constant gas pressure (10 mTorr), input power (800 W) and bias power (150 W) while the CF₄/C₄F₈ mixing ratio was varied through the partial flow rates for corresponding gases. It was shown that the substitution of CF₄ for C₄F₈ in the CF₄+C₄F₈+Ar feed gas lowers F atom formation rates and causes the decreasing F atom flux to the treated surface due to decreasing their volume density. It was proposed that an increase in the densities and fluxes of unsaturated CFx (x=1,2) radicals toward C₄F₈-rich plasmas at the nearly constant ion energy flux (i.e. at the nearly constant efficiency of ion bombardment) causes a decrease in the effective reaction probability for F atoms through the increasing thickness of the fluorocarbon polymer film on the treated surface.

Key words: CF₄, C₄F₈, reaction rate, ion energy, density, flux, etching, polymerization

INTRODUCTION

Fluorocarbon gases are widely used in the microelectronic industry for dry patterning of silicon wafers and dielectric (SiO_2, Si_3N_4) thin films [1,2]. Among these, the CF_4 is characterized by the highest F/C ratio and provides the domination of etching over the surface polymerization process under the typical reactive ion etching conditions [3, 4]. The more polymerizing fluorocarbons (C_4F_6, C_4F_8, CHF_3 and CH_2F_2) are normally used for the etching processes which require as much as possible SiO_2/Si etching selectivity. When both Si and SiO_2 etching mechanisms are sufficiently affected by the solid-state diffusion of etchant species through the fluorocarbon polymer film, the etching rates are rather sensitive to the film thickness than to the flux of F atoms coming from bulk plasma. Accordingly, since the thickness of the polymer film on the SiO_2 appears to be lower (due to the destruction of polymer in the reactions with surface oxygen atoms [2,5]), the SiO_2 etching rate exceeds that for Si. At the same time, together with increasing SiO_2/Si etching selectivity, the decrease in absolute Si and SiO_2 etching rates as well as an increase in etching residues take place [3-5]. These facts make difficulties for etching process optimization.

One can expect that the reasonable balance between SiO_2/Si etching selectivity, absolute etching rates and etching residues may be achieved by the use of two fluorocarbon gases in one gas mixture. In such gas system, the less polymerizing component (for example, CF_4) provides the effective generation of etchant species while the more polymerizing component creates the favorable conditions for obtaining high SiO_2/Si etching selectivity. From the other side, the mixing of CF_4 with other fluorocarbon gas mandatory results in more

complicated reaction scheme, changes plasma parameters as well as influences the formation/decay kinetics and fluxes for all types of plasma active species. Therefore, an understanding of plasma chemistry in the gas systems with two fluorocarbon components is the important tasks for the correct determination of etching mechanisms and optimal choice of gas chemistry for the given etching process.

The goals of current work were 1) to investigate how the CF_4/C_4F_8 mixing ratio in $CF_4+C_4F_8+Ar$ inductively coupled plasma influences internal plasma characteristics (electron temperature, electron density and ion bombardment energy) as well as the kinetics of plasma active species, their densities and fluxes; and 2) to analyze how the changes in above parameters may influence the dry etching characteristics, such as etching rates and selectivities.

EXPERIMENTAL AND MODELING DETAILS

Plasma diagnostics experiments were performed in a planar inductively coupled plasma (ICP) reactor described in our previous works [6,7]. The experiments were performed at a fixed total gas flow rate ($q = 60$ sccm), gas pressure ($p = 10$ mTorr), input power ($W = 800$ W) and bias power ($W_{dc} = 150$ W). The initial compositions of $CF_4+C_4F_8+Ar$ gas mixture were set by adjusting the flow rates of the corresponding gases. Particularly, the Ar flow rate q_{Ar} was fixed at 20 sccm, so that the fraction of Ar in the feed gas $y_{Ar} = q_{Ar}/q$ was always 33%. The fluorocarbon gases were mixed at various ratios within $q_{CF_4} + q_{C_4F_8} = 40$ sccm while the maximum flow rate for C_4F_8 did not exceed 15 sccm. Accordingly, the maximum fraction of C_4F_8 in the $CF_4+C_4F_8+Ar$ gas mixture reached 25%.

Plasma parameters were measured by double Langmuir probe (DLP2000, Plasmart Inc., Korea). The treatment of $I - V$ curves aimed at obtaining electron temperature (T_e) and ion saturated current density (j_+) was carried out using the software supplied by the equipment manufacturer. The calculations were based on the Johnson & Malter's double probes theory [8] with the one-Maxwellian approximation for the electron energy distribution function (EEDF). The total positive ion density (n_+) was extracted from the measured j_+ using the Allen-Boyd-Reynolds (ABR) approximation [9].

In order to obtain the densities of neutral species, we developed a simplified zero-dimensional kinetic model [6, 10, 11] with using the data of T_e and n_+ as input parameters. The set of chemical reactions was taken from our previous work [6]. Since the latter provides the detailed discussion on both kinetic schemes and sources of chemical kinetics data, these issues were not the subjects of current study. The model used following assumptions: 1) The electron energy distribution function

(EEDF) is close to Maxwellian one. The applicability of Maxwellian EEDFs for the description of the electron-impact kinetics for CF_4-based low-pressure ($p < 50$ mTorr) ICPs has been confirmed by the reasonable agreement between the diagnostic results and modeling [11,12]; 2) Under the given set of process conditions, the electronegativity of $CF_4+C_4F_8+Ar$ plasma with more than 30% fraction of electropositive components is low enough to assume $n_- \ll n_e \approx n_+$. The reasonability of such approach for the CF_4- and C_4F_8-based ICPs was confirmed in several works by both modeling and experiment [6, 12, 13]; 3) The heterogeneous chemistry of atoms and radicals can be described in terms of the conventional first-order recombination kinetics [6,11]; and 4) The temperature of the neutral ground-state species (T_{gas}) is independent on the feed gas composition. Since the experimental data on gas temperature were not available in this study, we took $T_{gas} = 600$ K as the typical value for the ICP etching reactors with similar geometry under the close range of experimental conditions [11, 13]. At least, our previous works [6, 7, 11] made with the same set of experimental equipment showed the reasonable agreement between measured and model-predicted plasma parameters for $T_{gas} = 600$ K. Also, the test model runs indicated no principal differences in gas-phase densities of neutral species obtained from the calculations within the T_{gas} uncertainty ~ 100 K. Such result looks quite reasonable since the dominant decay channels for atoms and radicals under the low pressure conditions are the heterogeneous processes.

For the analysis of heterogeneous chemistry, the fluxes for each king of neutral species with the volume density n were calculates as $\Gamma \approx 0.25 n v_T$, where $v_T = \left(8k_B T_{gas}/\pi m\right)^{1/2}$. The total flux of positive ions was simply evaluated as $\Gamma_+ \approx j_+/e$.

RESULTS AND DISCUSSION

The substitution of CF_4 for C_4F_8 at p, W and W_{dc}= const results in slightly increasing T_e (3.7-3.9 eV 0-25% C_4F_8), but suppresses the values of both j_+ (1.11-0.97 mA/cm^2 for 0-25% C_4F_8) and $n_+ \approx n_e$ (4.5·10^{10}–3.8·10^{10} cm^{-3} for 0-25% C_4F_8). The corresponding data are shown in Fig. 1. The behavior of electron temperature is probably connected with the decrease in electron energy loss for the electronic excitation and ionization of the dominant neutral species. As for the decreasing tendencies for n$_+$ and j$_+$, it may be caused by the combination of following reasons. First, since the addition of C_4F_8 results in only weak change of T$_e$, the ionization rate coefficients, k$_{iz}$, for all types of neutral species may be assumed to be independent on CF_4/C_4F_8 mixing ratio. According to Ref. [14], the absolute values of k$_{iz}$ for CF_4, CF_2, CF_2 and C_2F_4, which are the dominant neutral species in CF_4

and C_4F_8 plasmas, are rather close. That is why, one cannot expect an increase in the effective ionization frequency toward increasing C_4F_8 content in a feed gas. And secondly, under one and the same operating conditions the electronegativity of the C_4F_8 plasma is lower than that for CF_4 one [12,14]. Therefore, the substitution of CF_4 for C_4F_8 in the $CF_4+C_4F_8+Ar$ gas mixture leads to increasing electron diffusion coefficient and thus, to increasing electron decay rate on the reactor walls. Accordingly, the decreasing n_e results in the same behavior of n_+ in order to keep the plasma quasi-neutrality. Physically, the last effect is supported by the decreasing ionization rate.

It was found that, under the given set of operating conditions, the main sources of F atoms in 67% CF_4 + 33% Ar plasma are the electron-impact dissociations of CF_4 (R1: $CF_4 + e \rightarrow CF_3 + F + e$, R2: $CF_4 + e \rightarrow CF_3^+ + F + 2e$) and CF_3 (R3: $CF_3 + e \rightarrow CF_2 + F + e$).
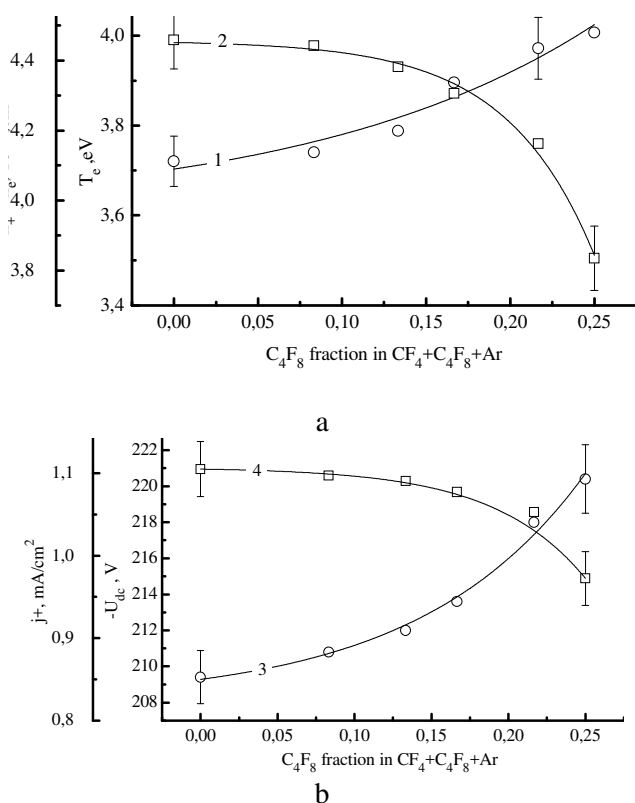

Fig. 1. Measured plasma parameters: a) – electron temperature (1), total positive ion and electron density (2), б – negative dc bias (3), ion current density (4) as functions of C_4F_8 fraction in $CF_4+C_4F_8+Ar$ gas mixture

Рис. 1. Измеренные параметры плазмы: а) – температура электронов (1), суммарная концентрация положительных ионов и электронов (2), б – напряжение отрицательного смещения (3), плотность ионного тока (4) как функции доли C_4F_8 в плазмообразующей смеси $CF_4+C_4F_8+Ar$

These processes constitute approximately 85% of the total F atom formation rate while the contribution from the CF_2 and CF radicals through R4: $CF_2 + e \rightarrow$

CF + F + e, R5: $CF_2 + e \rightarrow C + 2F + e$ and R6: $CF + e \rightarrow C + F + e$ does not exceed 5% due to the much lower densities of corresponding species. The remaining 10% comes from R7: $F_2 + e \rightarrow 2F + e$, which is supported by the high $F \rightarrow F_2$ recombination rate on the reactor walls. Accordingly, the decay of F atoms is mainly caused by their heterogeneous recombination while the rate of the fastest bulk process R8: $CF_3 + F \rightarrow CF_4$ is ~ 10 times less. As can be seen from Fig. 2, the substitution of CF_4 for C_4F_8 in the $CF_4+C_4F_8+Ar$ gas mixture results in rapidly increasing densities of both C_2F_4 ($n_{C_2F_4} = 2.1 \cdot 10^{11} - 3.4 \cdot 10^{13}$ cm^{-3}, or by ~ 160 times for 0-25% C_4F_8) and CF_2 ($n_{CF_2} = 2.8 \cdot 10^{12} - 4.1 \cdot 10^{13}$ cm^{-3}, or by ~ 15 times for 0–25% C_4F_8) radicals. The reason is that the C_2F_4 directly appears from C_4F_8 through R9: $C_4F_8 + e \rightarrow 2C_2F_4 + e$ while the CF_2 is the main dissociation product of C_2F_4 in R10: $C_2F_4 + e \rightarrow 2CF_2 + e$. The increasing density of CF_2 radicals lifts up the density of CF_3 ($n_{CF_3} = 1.3 \cdot 10^{13} - 2.9 \cdot 10^{13}$ cm^{-3}, or by ~ 2.2 times for 0-25% C_4F_8) mainly due to the increasing $CF_2 + F \rightarrow CF_3$ recombination rate both in bulk plasma and on reactors walls. As a result, the contributions of R3 and R4 to the total F atom formation rate exceeds the level of R1 and R2 after 20% C_4F_8 in $CF_4+C_4F_8+Ar$ gas mixture. Thought the rate coefficients for R3 ($8.9 \cdot 10^{-10} - 1.1 \cdot 10^{-9}$ cm^3/s for 0-25% C_4F_8) and R4 ($1.2 \cdot 10^{-9} - 1.6 \cdot 10^{-9}$ cm^3/s for 0-25% C_4F_8) exceed the sum of $(k_1 + k_2) = 5.8 \cdot 10^{-10} - 8.3 \cdot 10^{-10}$ cm^3/s, an increase in C_4F_8 fraction in a feed gas does no lead to increasing F atom formation rate. The reason is that a weak increase in the F atom formation efficiency toward C_4F_8-rich plasmas is overcome-pensated by decreasing n_e. Simultaneously, the substitution of CF_4 for C_4F_8 accelerated the decay of fluorine atoms through $CF_x + F \rightarrow CF_{x+1}$ (x = 1, 2) as well as introduces the new effective decay channel in R11: $C_2F_4 + F \rightarrow CF_2 + CF_3$ (k_{11} ~ $4.0 \cdot 10^{-11}$ cm^3/s). That is why the F atom density decreases monotonically ($n_F = 1.6 \cdot 10^{13} - 2.5 \cdot 10^{12}$ cm^{-3}, or by ~ 6 times) toward higher contents of C_4F_8 in $CF_4+C_4F_8+Ar$ gas mixture.

It was found that under the given set of operating conditions the main sources of F atoms in 67% CF_4 + 33% Ar plasma are the electron-impact dissociations of CF_4 (R1: $CF_4 + e \rightarrow CF_3 + F + e$, R2: $CF_4 + e \rightarrow CF_3^+ + F + 2e$) and CF_3 (R3: $CF_3 + e \rightarrow CF_2 + F + e$). These processes constitute approximately 85% of the total F atom formation rate while the contribution from the CF_2 and CF radicals through R4: $CF_2 + e \rightarrow CF + F + e$, R5: $CF_2 + e \rightarrow C + 2F + e$ and R6: $CF + e \rightarrow C + F + e$ does not exceed 5% due to the much lower densities of corresponding species. The remaining 10% comes from R7: $F_2 + e \rightarrow 2F + e$, which is supported by the high $F \rightarrow F_2$ recombination rate on the reactor walls.

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The changes in plasma parameters and composition described above allow one to make some approaches concerning the changes in etching rates, selectivities and etching residues. According to Refs. [6,15], the rate of chemical etching pathway in the fluorine-containing plasmas can be expressed through the flux of F atoms as $\gamma_R \Gamma_F$, where γ_R is the effective reaction probability. The data of Tab. 1 indicate that the flux of F atoms follows the behaviors of n_F and show the same decreasing tendency toward C_4F_8-rich plasmas ($3.5 \cdot 10^{17}$-$5.6 \cdot 10^{16}$ cm^{-2}s^{-1} for 0-25% C_4F_8). Assuming $\gamma_R \approx$ const at constant surface temperature, this fact obviously points out on the depletion of the chemical etching pathway. However, the above conclusion is valid only when the etching rate is not limited by the transport of F atoms from the fluorocarbon polymer film. In most of cases, the fluorocarbon polymer film is thick enough to reduce the amount of F atoms on the "film-etched surface" interface compared with that coming from bulk plasma [4,5]. In such situation, the etching kinetics should be described in the terms of the film-thickness-dependent reaction probability which is determined by the balance between polymer deposition and destruction rates [5].
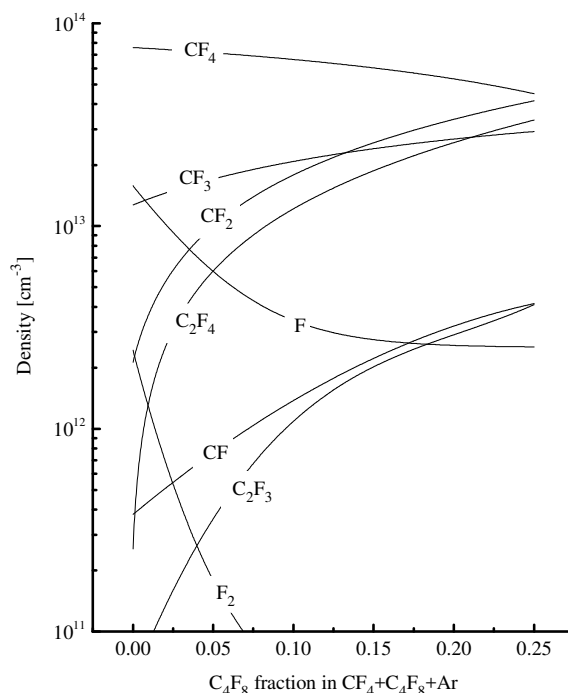

Fig. 2. Model-predicted densities of neutral species as functions of C_4F_8 fraction in $CF_4+C_4F_8+Ar$ gas mixture

Рис. 2. Расчетные концентрации нейтральных частиц как функции доли C_4F_8 в плазмообразующей смеси $CF_4+C_4F_8+Ar$

From Refs. [3-5, 16], it can be understood that 1 the formation of the fluorocarbon polymer films on the etched surface is mainly provided by the radicals with more than one free bonds; and 2) the polymer film growths better in the fluorine-poor plasmas where the polymer surface is composed by the less saturated fluorocarbon groups and thus, appears to be more reactive for radicals coming from bulk plasma. Accordingly, one can expect that the change in the polymer deposition rate may be adequately characterized by the Γ_{pol}/Γ_F ratio, where Γ_{pol} is the total flux of CF_2 and CF radicals. From Table, it can be seen that the substitution of CF_4 for C_4F_8 lifts up both Γ_{pol} ($3.1 \cdot 10^{16}$-$6.3 \cdot 10^{17}$ cm^{-2}s^{-1} for 0-25% C_4F_8) and Γ_{pol}/Γ_F (0.1-11.3 for 0-25% C_4F_8). Therefore, an evident increase in the polymer deposition rate takes place. The destruction of the fluorocarbon polymer film in the non-oxygenized plasmas is mainly provided by the physical etching pathway due to the ion bombardment [4,5]. This process has the rate of $Y_S \Gamma_+$ where Y_S is the ion-type-averages sputtering yield. Since Y_S is determined by the

momentum transferred from the incident ion to the surface atom in a single collision [5], one can assume $Y_S \sim \sqrt{M_i \varepsilon_i}$, where $\varepsilon_i \approx e|-U_f - U_{dc}|$ is the ion bombardment energy, M_i is the effective ion molar mass, $-U_f \approx 0.5T_e \ln(m_e/2.3m_i)$ is the floating potential and $-U_{dc}$ is the negative bias provided by W_{dc}. The data of Fig. 1 show that $-U_{dc}$ = 209-220 V for 0–25% C_4F_8 that results in $\varepsilon_i \approx$ 232-245 eV. The weak changes in ε_i together with $m_i \approx$ const allow one to apply the linear correlation for $Y_S = f(\varepsilon_i)$ and use the

parameter $\varepsilon_i \Gamma_+$, the so-called ion energy flux, to characterize the rate of the physical etching pathway for the fluorocarbon polymer film. From Tab. 1, it can be seen that the opposite changes of ε_i and Γ_+ maintain the ion energy flux on the near-to-constant level up to 22% C_4F_8 in a feed gas while the overall decrease in $\varepsilon_i \Gamma_+$ for 0–25% C_4F_8 does not exceed 10%. Accordingly, the parameter $\Gamma_{pol}/\varepsilon_i \Gamma_+ \Gamma_F$ characterizing the amount of deposited polymer exhibits the sufficient increase toward C_4F_8-rich plasmas and occupies that range of $6.0\cdot10^{-20}$-$7.6\cdot10^{-18}$ eV^{-1}cm^{2}s for 0-25% C_4F_8.

Table

Model-predicted fluxes and flux-to-flux ratios as functions of C_4F_8 fraction in $CF_4+C_4F_8+Ar$ gas mixture
Таблица. **Расчетные потоки частиц и их отношения как функции доли C_4F_8 в плазмообразующей смеси $CF_4+C_4F_8+Ar$**

Fractions in a feed gas			Γ_F, 10^{17} cm^{-2}s^{-1}	Γ_{pol}, 10^{17} cm^{-2}s^{-1}	$\varepsilon_i\Gamma_+$, 10^{18} eVcm^{-2}s^{-1}	$\dfrac{\Gamma_{pol}}{\Gamma_F}$	$\dfrac{\Gamma_{pol}}{\varepsilon_i\Gamma_+\Gamma_F}$ 10^{-18} eV^{-1}cm^{2}s^1
CF$_4$	C$_4$F$_8$	Ar					
0.67	0.00	0.33	3.49	0.31	1.61	0.09	0.06
0.58	0.08	0.33	0.69	2.81	1.60	4.27	2.66
0.53	0.13	0.33	0.62	3.41	1.59	5.61	3.49
0.50	0.17	0.33	0.59	4.36	1.57	7.36	4.60
0.45	0.22	0.33	0.58	5.70	1.55	9.74	6.10
0.42	0.25	0.33	0.56	6.28	1.49	11.3	7.59

The results described above allow one to formulate some conclusions concerning the features of the etching kinetics in the given gas system. First, the substitution of CF_4 for C_4F_8 in the $CF_4+C_4F_8+Ar$ gas mixture suppresses the chemical etching pathway not only due to the decrease in F atom flux, but also through the change in effective reaction probability because of the increasing thickness of the fluorocarbon polymer film on the etched surface. Therefore, one can expect the decreasing absolute etching rates. And secondly, the addition of C_4F_8 probably provides the film-thickness-limited etching regime and thus, creates the favorable conditions for obtaining higher SiO_2/Si etching selectivity. Accordingly, the reasonable balance between etching rate and selectivity may be effectively adjusted by the CF_4/C_4F_8 mixing ratio.

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