

## ОСОБЕННОСТИ КИНЕТИКИ РЕАКТИВНО-ИОННОГО ТРАВЛЕНИЯ $\text{SiO}_2$ В СМЕСЯХ $\text{CF}_4 + \text{Ar} + \text{O}_2$ И $\text{C}_4\text{F}_8 + \text{Ar} + \text{O}_2$

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*Проведено исследование влияния соотношения  $\text{Ar}/\text{O}_2$  на характеристики газовой фазы и кинетику травления  $\text{SiO}_2$  в плазме смесей  $\text{CF}_4 + \text{Ar} + \text{O}_2$  и  $\text{C}_4\text{F}_8 + \text{Ar} + \text{O}_2$  в условиях индукционного ВЧ 13,56 МГц разряда. В качестве постоянных внешних параметров выступали доля фторуглеродного компонента в плазмообразующей смеси (50%), общее давление газа (6 мтор), вкладываемая мощность (700 Вт) и мощность смещения (200 Вт). Было найдено, что полное замещение аргона на кислород в обеих смесях характеризуется немо-  
нотонным изменением (с максимумом при  $\sim 25\% \text{Ar} + 25\% \text{O}_2$ ) скорости травления  $\text{SiO}_2$  и монотонным ростом скорости травления фоторезиста при более высоких абсолютных значениях скоростей в плазме на основе  $\text{CF}_4$ . Стационарные концентрации активных частиц определялись при совместном использовании диагностики плазмы зондами Лангмюра и  $\theta$ -мерном (глобальном) моделировании кинетики плазмохимических процессов. Соответствующие результаты показали, что обе газовые системы характеризуются близкими параметрами электронной и ионной компонент плазмы, но существенно различаются по кинетике нейтральных частиц, особенно в присутствии  $\text{O}_2$ . Последняя особенность обуславливает противоположные изменения как концентрации атомов F, так и эффективной вероятности ионно-стимулированной химической реакции в зависимости от параметра  $\text{Ar}/\text{O}_2$ . Взаимосвязи между видом фторуглеродного компонента и кинетикой гетерогенных процессов анализировались с помощью набора параметров, характеризующих газовую фазу (плотностей потоков частиц и их отношений). На основании этого анализа предположено, что рост содержания  $\text{O}_2$  в смеси  $\text{CF}_4 + \text{Ar} + \text{O}_2$  со слабой полимеризационной нагрузкой на обрабатываемую поверхность снижает вероятность реакции  $\text{SiO}_2 + \text{F}$  через снижение эффективности деструкции оксидных связей и десорбции продуктов травления из-за снижения плотности потока энергии ионов. Напротив, рост содержания  $\text{O}_2$  в смеси  $\text{C}_4\text{F}_8 + \text{Ar} + \text{O}_2$  с высокой полимеризационной нагрузкой способствует росту эффективной вероятности взаимодействия за счет снижения толщины фторуглеродной полимерной пленки и облегчения доступа атомов F к обрабатываемой поверхности.*

**Ключевые слова:**  $\text{SiO}_2$ , травление, полимеризация, поток атомов фтора, поток энергии ионов, эффективная вероятность взаимодействия

## FEATURES OF $\text{SiO}_2$ REACTIVE-ION ETCHING KINETICS IN $\text{CF}_4 + \text{Ar} + \text{O}_2$ AND $\text{C}_4\text{F}_8 + \text{Ar} + \text{O}_2$ GAS MIXTURES

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*The effect of Ar/O<sub>2</sub> mixing ratio on gas-phase characteristics and SiO<sub>2</sub> etching kinetics in CF<sub>4</sub> + Ar + O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> plasmas was studied under conditions of 13.56 MHz inductive RF discharge. The constant processing parameters were fraction of fluorocarbon component in a feed gas (50%) total gas pressure (6 mTorr), input power (700 W) and bias power (200 W). It was found that the full substitution of Ar for O<sub>2</sub> in both gas systems results in non-monotonic (with a maximum at ~ 25% Ar + 25% O<sub>2</sub>) SiO<sub>2</sub> etching rates as well as in monotonically increasing photoresist etching rate with higher absolute values for CF<sub>4</sub>-containing mixture. The steady-state densities of active species were determined using a combination of plasma diagnostics by Langmuir probes and 0-dimensional (global) plasma modeling. Corresponding results indicated that both gas systems are characterized by quite close parameters of electron and ion components while exhibit sufficient differences in the kinetics of neutral species, especially in the presence of O<sub>2</sub>. The latter produces opposite changes in F atom density as well as in effective probability of ion-assisted chemical reaction vs. Ar/O<sub>2</sub> mixing ratio. Relationships between type of fluorocarbon component and heterogeneous process kinetics were analyzed through the set of gas-phase-related parameters (fluxes, flux-to-flux ratios) characterizing chemical etching pathways for SiO<sub>2</sub> and formation/destruction balance for the fluorocarbon polymer film. It was suggested that the transition toward O<sub>2</sub>-rich plasma in the low-polymerizing CF<sub>4</sub> + Ar + O<sub>2</sub> plasma suppresses the effective probability for SiO<sub>2</sub> + F reaction through decreasing efficiency for oxide bond breaking and desorption of etching products due to decreasing ion energy flux. Oppositely, an increase in O<sub>2</sub> content in the high-polymerizing C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> mixture lifts up the effective reaction probability by decreasing fluorocarbon film thickness and providing better access of F atoms to the etched surface.*

**Key words:** SiO<sub>2</sub>, etching, polymerization, fluorine atom flux, ion energy flux, effective reaction probability

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## INTRODUCTION

Recently, silicon and silicon-based materials (SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiC) still keep the leading position in modern electronic device technology. Particularly, SiO<sub>2</sub> is widely used as the gate dielectric in field-effect structures as well as frequently plays the roles of inter-element insulation or final passivation [1-3]. Since most of these applications assume the precise patterning of SiO<sub>2</sub> layers in fluorocarbon (C<sub>x</sub>F<sub>y</sub>) gas plasmas [3, 4], the optimization of corresponding dry etching processes is a key problem for achieving advanced device characteristics. For this purpose, one must clearly understand the interconnections between processing conditions, plasma chemistry and heterogeneous kinetics.

Until now, there were enough works reported on etching characteristics and mechanisms for SiO<sub>2</sub> in fluorocarbon gas plasmas [3-13]. Results of these works allow one to conclude that:

1) In all fluorocarbon-based gas chemistries, the dominant contribution to the chemical etching of SiO<sub>2</sub> is provided by F atoms [5-7]. The much weaker chemical effect from CF<sub>x</sub> radicals due to the ion-induced dissociation of their adsorbed states has no principal influence on the overall etching kinetics [13].

2) The patterning of SiO<sub>2</sub> is possible under the conditions of reactive-ion etching process and requires the ion bombardment energy of ~ 200-300 eV. The reason is that the spontaneous reaction SiO<sub>2</sub> + F is thermodynamically prohibited, as follows from the comparison of Si-O (~ 799 kJ/mol) and Si-F (~ 552 kJ/mol) bond dissociation energies [14]. Therefore, the role of ion bombardment includes a) the destruction of Si-O bonds to produce the chemisorption sites for F atoms; and b) the desorption heterogeneous reaction products which appear in a form of the non-saturated low volatile SiF<sub>x</sub> layer [5, 6, 8].

3) In high-polymerizing fluorocarbon gases ( $y/x < 3$  in the  $C_xF_y$  molecule), the  $SiO_2$  etching process is affected by the fluorocarbon (FC) polymer film grown at the plasma/etched surface interface [5-7]. Since the thick ( $> 10$  nm) FC film limits the transport of F atoms to the target material as well as reduces the effective ion bombardment energy, the  $SiO_2$  etching kinetics strongly depends on the film thickness and thus, on the polymer deposition/decomposition dynamics [6-8].

The problem is that the most of existing works have the pure experimental nature and thus, did not analyze the relationships between heterogeneous effects and gas-phase plasma characteristics. That is why the basic principles to control the  $SiO_2$  etching process by plasma-related operating parameters are still not clear enough. Another negative issue is that studies of different gas systems were performed for different processing conditions and reactor types. Such situation limits the possibility to compare corresponding results and thus, to select the gas mixture for achieving the desirable combination of etching rate, anisotropy and selectivity in the given etching process.

In our previous work, we have performed the comparative study of plasma chemistry in  $CF_4 + Ar + O_2$  and  $C_4F_8 + Ar + O_2$  gas systems [15]. Though some reasonable data on steady-state plasma parameters and gas-phase composition were obtained, these were not applied for the analysis of Si and/or  $SiO_2$  etching process. Therefore, since interconnections between gas-phase plasma parameters and heterogeneous kinetics in given gas systems are not still clear, differences in Si and  $SiO_2$  etching mechanisms are not completely understood. Such situation retards the optimization of plasma etching technology for silicon-based materials. From the others side, results of Refs. [10, 15, 16] clearly indicated that Ar/ $O_2$  mixing ratio at constant fraction of fluorocarbon component is a powerful tool to adjust densities of F atoms and polymerizing radicals. Accordingly, the idea of current work was to perform the comparative study of  $SiO_2$  etching kinetics in  $CF_4 + Ar + O_2$  and  $C_4F_8 + Ar + O_2$  plasmas with various Ar/ $O_2$  mixing ratios as well as to analyze the relationships between gas-phase plasma parameters and heterogeneous reaction pathways determining the features of  $SiO_2$  etching mechanisms.

#### EXPERIMENTAL AND MODELING DETAILS

Experiments with both  $CF_4 + Ar + O_2$  and  $C_4F_8 + Ar + O_2$  gas mixtures were performed in the planar inductively coupled plasma (ICP) reactor described in our previous works [15, 16]. Plasma was excited using a 13.56 MHz radio-frequency (RF)

power supply. Another RF power supply was connected to the chuck electrode in order to control the ion bombardment energy ( $\epsilon_i$ ) through the negative DC bias voltage ( $-U_{dc}$ ). The chuck electrode was equipped by the water-flow cooling system that allowed one to maintain its temperature at  $\sim 17$  °C. In all experimental series, the constant parameters were gas pressure ( $p = 6$  mTorr), total gas flow rate ( $q = 40$  sccm), input power ( $W = 900$  W) and bias power ( $W_{dc} = 200$  W). The variable parameter was the Ar/ $O_2$  mixing ratio. The initial composition of each gas mixture was set by adjusting partial flow rates for corresponding gases. Particularly, content of  $CF_4$  or  $C_4F_8$  was always 50% while the remaining half was represented by various fractions of Ar and  $O_2$ . Accordingly, an increase in  $O_2$  fraction  $y(O_2)$  from 0-50% corresponded to the full substitution of Ar for  $O_2$ .

Etched samples (parts of Si wafer with the 500 nm-thick  $SiO_2$  layer) had the size of about  $2 \times 2$  cm and was partially masked by the photoresist AZ1512 (positive). The etching rates for  $SiO_2$  and photoresist (PR) were determined as  $R = \Delta h / \tau$ , where  $\Delta h$  is the etched depth determined using surface profiler Alpha-Step 500 (Tencor), and  $\tau = 2$  min is the processing time. In preliminary experiments, it was found that, under the given set of processing conditions, both etching processes are featured by the steady-state kinetic regime with the negligible influence of reaction products on gas-phase plasma parameters.

Plasma diagnostic was performed by double Langmuir probe (DLP2000, Plasmart Inc.). The probe setup had the built-in tip cleaning system for measurements in polymerizing plasmas. The treatment of voltage-current curves with using the well-known statements of probe theory [5, 17] provided information on electron temperature ( $T_e$ ) and ion current density ( $J_+$ ). In order to minimize the effect of fluorocarbon polymer film on diagnostics results, the probe tip was additionally cleaned in 50% Ar + 50%  $O_2$  plasma for 1 min before and after each measurement. As a result, there were no sufficient differences between data points recorded under one and the same experimental conditions.

Plasma modeling was represented by 0-dimensional (global) kinetic model operated with volume-averaged plasma characteristics. Kinetic schemes (reaction sets with corresponding rate coefficients), modeling approaches and algorithm were taken from our previous works [15, 16, 18]. Input model parameters were experimental data on  $T_e$  and  $J_+$ . As output parameters, the model yielded steady-state densities of plasma active species and their fluxes on the etched surface.

Basic assumptions for the analysis of heterogeneous kinetics were also the same with those used in our previous works [15, 16, 19-21]:

1) Any chemical etching pathway (interactions of F atoms with the SiO<sub>2</sub> surface as well as O atoms with the fluorocarbon polymer film) has the rate of  $\gamma_{R,X}\Gamma_X$  [5, 20-23], where  $\Gamma_X$  (X = F or O) is the flux of corresponding atomic species with the gas-phase density [X], and  $\gamma_{R,X}$  is the effective reaction probability. Generally, the constant surface temperature allows one to assume  $\gamma_{R,X} \approx \text{const}$  [5] as well as to associate changes in the chemical etching pathway with changes in  $\Gamma_X$  only.

2) Any physical etching pathway (the breaking of Si-O bonds, the destruction of the fluorocarbon polymer film as well as the ion-stimulated desorption of reaction products) has the rate of  $Y_S\Gamma_+$  [21-24], where  $Y_S$  is the ion-type-averaged sputtering yield, and  $\Gamma_+ \approx J_+/e$  is the ion flux. According to Refs. [15, 16], one can suggest  $Y_S \sim (M_i\varepsilon_i)^{1/2}$ , where  $M_i$  is the effective ion molar mass,  $\varepsilon_i = e(-U_f - U_{dc})$  is the ion bombardment energy, and  $U_f$  is the floating potential. As such, the change in the physical etching pathway may be traced by the parameter  $(M_i\varepsilon_i)^{1/2}\Gamma_+$ , characterizing the ion energy flux.

3) The formation of the fluorocarbon polymer film is provided by CF<sub>x</sub> (x = 1, 2) radicals as well as appears to be slower in fluorine-rich plasmas [6-9]. As such, the polymer deposition rate is characterized by the  $\Gamma_{pol}/\Gamma_F$  ratio, where  $\Gamma_{pol}$  is the total flux of polymerizing radicals. Accordingly, the change in fluorocarbon polymer film thickness due to destruction by ion bombardment and etching by oxygen atoms may be traced by the parameters  $\Gamma_{pol}/(M_i\varepsilon_i)^{1/2}\Gamma_+\Gamma_F$  and  $\Gamma_{pol}/\Gamma_O\Gamma_F$ , respectively.

## RESULTS AND DISCUSSION

From Fig. 1(a), it can be seen that SiO<sub>2</sub> etching rates in oxygen-free CF<sub>4</sub> + Ar and C<sub>4</sub>F<sub>8</sub> + Ar plasmas are quite close with typical values ~ 100 nm/min. An increase in O<sub>2</sub> fraction in both gas systems (i.e. the substitution of Ar for O<sub>2</sub>) results in similar non-monotonic  $R = f(y(O_2))$  functions which exhibit maximums at ~ 25% O<sub>2</sub>. The main differences between two gas systems are only in quantitative scale and may be summarized as follows. First, under the condition of  $y(O_2) > 0$  the CF<sub>4</sub>-based gas system provides the systematically higher SiO<sub>2</sub> etching rates compared with the C<sub>4</sub>F<sub>8</sub>-based one. And secondly, the substitution of Ar with O<sub>2</sub> has the noticeably stronger effect on the SiO<sub>2</sub> etching process in CF<sub>4</sub> + Ar + O<sub>2</sub> plasma. Particularly, the change in  $y(O_2)$  from 0-25% causes the almost twofold (102-200 nm/min) increase in SiO<sub>2</sub> etching rate in CF<sub>4</sub> + Ar + O<sub>2</sub> plasma while the corresponding effect in C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> plasma is only 1.3 times (97-124 nm/min). As such, the principal

questions for understanding of SiO<sub>2</sub> etching mechanism in given gas systems are: 1) what mechanism does produce the maximum on SiO<sub>2</sub> etching rate as function of  $y(O_2)$  and 2) what are the reasons providing the quantitative differences in SiO<sub>2</sub> etching rates for CF<sub>4</sub>- and C<sub>4</sub>F<sub>8</sub>-based gas chemistries under one and the same operating conditions?

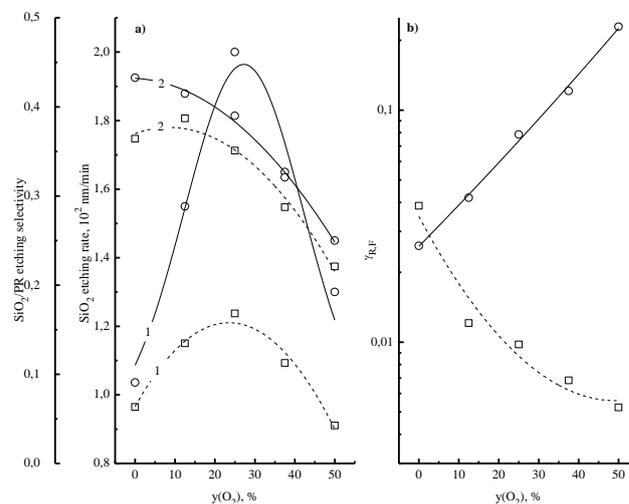


Fig. 1. Parameters characterizing the SiO<sub>2</sub> etching kinetics in CF<sub>4</sub> + Ar + O<sub>2</sub> (solid lines) and C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> (dashed lines) plasmas. In Fig. a): 1 – SiO<sub>2</sub> etching rate; 2 – etching selectivity over the photoresist. In Fig. b): effective reaction probability ( $\gamma_{R,F}$ ).  
Рис. 1. Параметры, характеризующие кинетику травления SiO<sub>2</sub> в плазме CF<sub>4</sub> + Ar + O<sub>2</sub> (сплошная линия) и C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> (пунктир). На рис. а): 1 – скорость травления SiO<sub>2</sub>; 2 – селективность травления по отношению к фоторезисту. На рис. б): эффективная вероятность взаимодействия ( $\gamma_{R,F}$ ).

From previously published works, it can be understood that SiO<sub>2</sub> etching rates shown in Fig. 1(a) may be expressed as  $R_{phys} + R_{chem}$  [21-23], where  $R_{phys}$  is the rate of physical sputtering and  $R_{chem}$  is the rate of ion-assisted chemical reaction between SiO<sub>2</sub> and F atoms. The experiments showed that, under conditions of given study, the SiO<sub>2</sub> etching rate in Ar plasma is ~ 5 nm/min. As such, the condition  $R_{phys} \ll R_{chem} \approx R$  takes place for both gas mixtures. Then, taking in mind that  $R_{chem} = \gamma_{R,F}\Gamma_F$ , one can suggest that the quantitative differences in SiO<sub>2</sub> etching rates for CF<sub>4</sub>- and C<sub>4</sub>F<sub>8</sub>-based gas mixtures mentioned in Fig. 1(a) may be connected with differences in both gas-phase plasma characteristics (through [F] and  $\Gamma_F$ ) and the heterogeneous kinetics (through  $\gamma_{R,F}$ ). Accordingly, the reasons which may cause the non-monotonic changes of SiO<sub>2</sub> etching rate vs. the O<sub>2</sub> fraction in a feed gas are: 1) the maximum on the  $\Gamma_F = f(y(O_2))$  curve due to the change in formation/decay balance for F atoms in the presence of oxygen; and 2) monotonic, but opposite tendencies for both  $\Gamma_F$  and  $\gamma_{R,F}$ . Particularly, even at constant surface temperature,  $\gamma_{R,F}$  may be dependent on the fraction of “active” surface which provides the chemisorption of F atoms. Obviously, the latter is sensitive to the intensity of ion

bombardment (through the Si-O bond breaking, desorption of reaction products and physical destruction of fluorocarbon polymer film) and O atom flux (through the chemical destruction of fluorocarbon polymer film). Therefore, the adequate interpretation of SiO<sub>2</sub> etching mechanism in CF<sub>4</sub> + Ar + O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> plasmas requires the study of plasma parameters and gas phase composition.

The basic properties of CF<sub>4</sub> + Ar + O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> plasmas have been discussed in detail in Refs. [15, 16]. As such, it seems to be reasonable just to summarize their principal features which are important for the purpose of given study at given process conditions. Particularly, one must underline several effects taking place during the substitution of Ar with O<sub>2</sub> at constant fraction of fluorocarbon component:

1) Both gas mixtures demonstrate similar effect of y(O<sub>2</sub>) on electron temperature and ion current density (Tab. 1). A decrease in T<sub>e</sub> (3.6-3.4 eV for CF<sub>4</sub> + O<sub>2</sub> + Ar and 4.8-3.1 eV for C<sub>4</sub>F<sub>8</sub> + O<sub>2</sub> + Ar at 0-50% O<sub>2</sub>) is connected with increasing electron energy loss in low-threshold excitations (vibrational, electronic) for O<sub>2</sub> itself and molecular products of plasma chemical reactions. The decreasing tendency for J<sub>+</sub> is produced by corresponding changes in ion densities n<sub>+</sub> (4.2·10<sup>10</sup>-3.2·10<sup>10</sup> cm<sup>-3</sup> for CF<sub>4</sub> + O<sub>2</sub> + Ar and 4.2·10<sup>10</sup>-3.7·10<sup>10</sup> cm<sup>-3</sup> for C<sub>4</sub>F<sub>8</sub> + O<sub>2</sub> + Ar at 0-50% O<sub>2</sub>). The reasons are that a) decreasing T<sub>e</sub> lowers ionization rate coefficients for all types of neutral species; and b) an increase in y(O<sub>2</sub>) enriches the gas phase by oxygen-containing electronegative species that accelerate decay for both positive ions and electrons through the ion-ion recombination and dissociative attachment, respectively.

Table

**Electro-physical plasma parameters**

**Таблица. Электрофизические параметры плазмы**

y(O <sub>2</sub> ), %	CF <sub>4</sub> + Ar + O <sub>2</sub>			C <sub>4</sub> F <sub>8</sub> + Ar + O <sub>2</sub>		
	T <sub>e</sub> , eV	J <sub>+</sub> , mA/cm <sup>2</sup>	-U <sub>dc</sub> , V	T <sub>e</sub> , eV	J <sub>+</sub> , mA/cm <sup>2</sup>	-U <sub>dc</sub> , V
0	3.60	1.10	137	4.81	1.21	145
25	3.53	1.01	149	4.01	1.08	167
50	3.40	0.95	153	3.12	0.91	177

2) Both gas mixtures exhibit quite similar changes in ion flux and ion bombardment energy (Fig. 2a). A weak increase in negative dc bias at constant W<sub>dc</sub> (-U<sub>dc</sub> = 137-153 V for CF<sub>4</sub> + O<sub>2</sub> + Ar and 145-177 V for C<sub>4</sub>F<sub>8</sub> + O<sub>2</sub> + Ar at 0-50% O<sub>2</sub>) and thus, in ion bombardment energy (ε<sub>i</sub> = 159-173 eV and 175-196 eV for CF<sub>4</sub>- and C<sub>4</sub>F<sub>8</sub>-based gas mixtures, respectively) does not compensate the decrease in Γ<sub>+</sub>. Accordingly, the monotonic decrease in the parameter (M<sub>i</sub>ε<sub>i</sub>)<sup>1/2</sup>Γ<sub>+</sub> (6.1·10<sup>17</sup>-4.9·10<sup>17</sup> eV<sup>1/2</sup>cm<sup>-2</sup>s<sup>-1</sup> for CF<sub>4</sub> + O<sub>2</sub> + Ar and 7.3·10<sup>17</sup>-5.4·10<sup>17</sup> eV<sup>1/2</sup>cm<sup>-2</sup>s<sup>-1</sup> for C<sub>4</sub>F<sub>8</sub> + O<sub>2</sub> + Ar at 0-50% O<sub>2</sub>) suggests that the substitution of Ar for O<sub>2</sub> suppresses the physical etching pathway.

3) Both gas mixtures are characterized by similar decreasing trends for densities and fluxes of

polymerizing radicals CF<sub>x</sub> (x = 1, 2), but by opposite changes in corresponding values for F atoms (Fig. 2b). The monotonic increase in F atom density in CF<sub>4</sub> + O<sub>2</sub> + Ar plasma ([F] = 5.6·10<sup>12</sup>-5.4·10<sup>13</sup> cm<sup>-3</sup> at 0-50% O<sub>2</sub>) is provided by the effective formation of these species in R1: CF<sub>x</sub> + O → CF<sub>x-1</sub>O + F, R2: CF<sub>x</sub> + O(<sup>1</sup>D) → CF<sub>x-1</sub>O + F and R3: F<sub>2</sub> + O → FO + F (with a consequent electron-impact dissociation of fluorine-containing reaction products) that overcompensate the decreasing rate of R4: CF<sub>x</sub> + e → CF<sub>x-1</sub> + F + e. The monotonic decrease in F atom density in C<sub>4</sub>F<sub>8</sub> + O<sub>2</sub> + Ar plasma ([F] = 8.0·10<sup>12</sup>-8.6·10<sup>11</sup> cm<sup>-3</sup> at 0-50% O<sub>2</sub>) results from the same change in the rate of R4 with the almost negligible contribution from the side of R1-R3. The reason is that the formation rates for both O and O(<sup>1</sup>D) in R5: O<sub>2</sub> + e → 2O + e, R6: O<sub>2</sub> + e → O + O(<sup>1</sup>D) + e and R7: O + e → O(<sup>1</sup>D) + e are sufficiently limited by the decay of O<sub>2</sub> molecules through R8: C + O<sub>2</sub> → CO + O. In addition, the low efficiency of R1-R3 provides also the much weaker fall in the density of polymerizing radicals compared with CF<sub>4</sub>-based gas system.

4) The oxygen-free C<sub>4</sub>F<sub>8</sub> + Ar gas system provides the much thicker FC polymer film compared with CF<sub>4</sub> + Ar one [6, 7]. Such situation results from the sufficient difference in polymer deposition rates (Γ<sub>pol</sub>/Γ<sub>F</sub> = 6.4 for C<sub>4</sub>F<sub>8</sub> + Ar vs. 0.1 for CF<sub>4</sub> + Ar) at quite close polymer destruction rates by ion bombardment ((M<sub>i</sub>ε<sub>i</sub>)<sup>1/2</sup>Γ<sub>+</sub> = 7.2·10<sup>17</sup> eV<sup>1/2</sup>cm<sup>-2</sup>s<sup>-1</sup> for C<sub>4</sub>F<sub>8</sub> + Ar vs. 6.1·10<sup>17</sup> eV<sup>1/2</sup>cm<sup>-2</sup>s<sup>-1</sup>). An increase in y(O<sub>2</sub>) reduces the thickness of the FC polymer film in both gas mixtures, as follows from the rapidly decreasing Γ<sub>pol</sub>/Γ<sub>O</sub>Γ<sub>F</sub> ratios (2.8·10<sup>-18</sup> cm<sup>2</sup>s for C<sub>4</sub>F<sub>8</sub> + Ar and 1.9·10<sup>-18</sup> cm<sup>2</sup>s at 5-50% O<sub>2</sub>). The latter implies also that the 50% C<sub>4</sub>F<sub>8</sub> + 50% O<sub>2</sub> plasma keeps the much higher polymerization ability compared with corresponding CF<sub>4</sub>-based gas mixture.

The comparison of Figs. 1(a) and 2 allows one to formulate two principal features of the SiO<sub>2</sub> etching mechanisms in CF<sub>4</sub> + Ar + O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> plasmas. First, in both gas mixtures, the non-monotonic etching rates contradict with monotonic changes of both Γ<sub>F</sub> and (M<sub>i</sub>ε<sub>i</sub>)<sup>1/2</sup>Γ<sub>+</sub>. And secondly, the similar changes in etching rates correspond to opposite behaviors of Γ<sub>F</sub>. Obviously, the last fact also provides the opposite changes in effective reaction probabilities γ<sub>R,F</sub> = R/Γ<sub>F</sub>, as shown in Fig. 1(b). Particularly, it can be seen that the substitution of Ar for O<sub>2</sub> in CF<sub>4</sub> + Ar + O<sub>2</sub> gas mixture results in monotonically decreasing γ<sub>R,F</sub> in the range of (3.9-0.52)·10<sup>-2</sup> for 0-50% O<sub>2</sub>. When neglecting the influence of FC polymer film on the SiO<sub>2</sub> etching kinetics in the low-polymerizing CF<sub>4</sub>-based gas system (that assumes, in fact, the case of non-continuous of very thin continuous FC film), the behavior of γ<sub>R,F</sub> may be associated with the decrease in ion energy flux (Fig. 3). Obviously, this effect appears through decreasing rates of

both oxide bonds breaking and ion-stimulated desorption of reaction products that lowers the fraction of free adsorption sites for F atoms. At the same time, the substitution of Ar with O<sub>2</sub> in C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> gas mixture causes monotonically increasing  $\gamma_{R,F}$  in the range of  $(2.0-20) \cdot 10^{-2}$  for 0-50% O<sub>2</sub>. This contradicts with the change in ion energy flux, but shows an agreement with the behavior of  $\Gamma_{pol}/\Gamma_O\Gamma_F$  ratio (Fig. 3) which traces the change in the FC film thickness. As the polymer layer retards the access of F atoms to the etched surface, one should reasonably assume that the decreasing FC film thickness accelerates the etching process through increasing effective F atom flux on the FC film/etched surface interface. In addition, it is important to mention that the shape of the  $\gamma_{R,F} = f(\Gamma_{pol}/\Gamma_O\Gamma_F)$  curve shown in Fig. 3 as well as the tendency itself are very close to those obtained for reaction probabilities and etching yields of Si and SiO<sub>2</sub> in high-polymerizing fluorocarbon gas plasmas [6, 8]. Therefore, based on above data, one can conclude that 1) the SiO<sub>2</sub> etching mechanism in both gas systems is represented by ion-assisted chemical reaction in the neutral-flux-limited regime; and 2) in both cases, the non-monotonic SiO<sub>2</sub> etching rate as a function of O<sub>2</sub> fraction in a feed gas results from opposite changes in fluorine atom flux and the effective probability of their reaction with the SiO<sub>2</sub> surface. However, the mechanisms influencing the effective reaction probabilities are different and depend, in general, on the polymerizing ability of the fluorocarbon component.

Finally, we would like to comment the SiO<sub>2</sub>/PR selectivity issue which seems to be important for etching process optimization. It was found that the etching rate of PR in both gas systems increases monotonically toward O<sub>2</sub>-rich plasmas (260-412 nm/min for C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> and 240-520 nm/min for CF<sub>4</sub> + Ar + O<sub>2</sub> at 0-50% O<sub>2</sub>). All these are in good agreements with both tendencies and quantitative differences for oxygen atom fluxes, as shown in Fig. 2b. The ratios of SiO<sub>2</sub>-to-PR etching rate have the quite close values (0.37-0.22 for C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> and 0.43-0.25 for CF<sub>4</sub> + Ar + O<sub>2</sub> at 0-50% O<sub>2</sub>) and exhibit the only weak decrease in the range of 0-25% O<sub>2</sub> (Fig. 1a). As such, the obtaining of maximum SiO<sub>2</sub> etching rates in 25% O<sub>2</sub> + 25% Ar gas mixtures is not escorted by principal losses in SiO<sub>2</sub>/PR etching selectivity.

### CONCLUSIONS

In this work, we investigated the possibility of Ar/O<sub>2</sub> mixing ratio in CF<sub>4</sub> + Ar + O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> gas mixtures to adjust steady-state plasma parameters and SiO<sub>2</sub> etching kinetics. It was found that the CF<sub>4</sub>-based gas system provides higher etching rates for both SiO<sub>2</sub> and photoresist, and the substitution of Ar with O<sub>2</sub> at constant fraction of any fluorocarbon component results in the non-monotonic (with a maximum at ~ 25% Ar + 25% O<sub>2</sub>) SiO<sub>2</sub> etching rates.

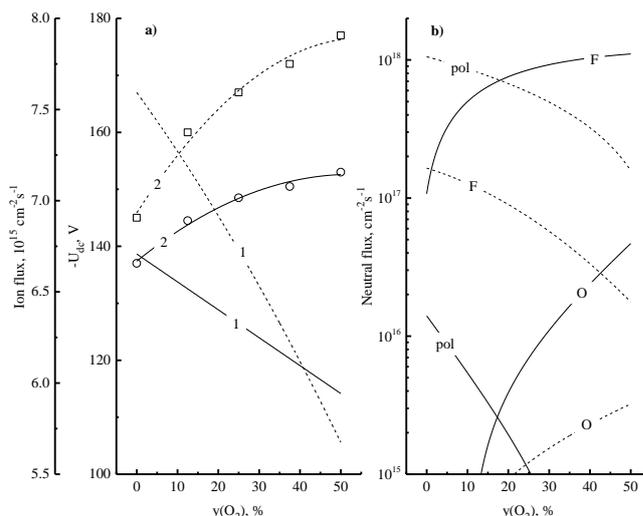


Fig. 2. Fluxes of active species on the etched surface in CF<sub>4</sub> + Ar + O<sub>2</sub> (solid lines) and C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> (dashed lines) plasmas. In Fig. a): 1 – total positive ion flux; 2 – negative dc bias. In Fig. b): “F” – fluorine atoms; “pol” – polymerizing radicals (CF<sub>2</sub> + CF); “O” – oxygen atoms

Рис. 2. Плотности потоков активных частиц на обрабатываемую поверхность в плазме CF<sub>4</sub> + Ar + O<sub>2</sub> (сплошная линия) и C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> (пунктир). На рис. а): 1 – суммарная плотность потока положительных ионов; 2 – отрицательное смещение. На рис. б): “F” – атомы фтора; “pol” – полимеробразующие радикалы (CF<sub>2</sub> + CF); “O” – атомы кислорода

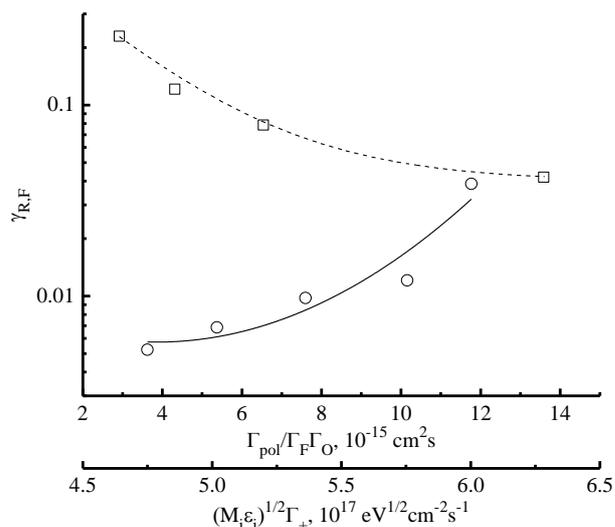


Fig. 3. Effective SiO<sub>2</sub> + F reaction probability in CF<sub>4</sub> + Ar + O<sub>2</sub> plasma (solid line) as a function of the parameter  $(M_i\epsilon_i)^{1/2}\Gamma_+$  characterizing the ion energy flux on the etched surface. Effective SiO<sub>2</sub> + F reaction probability in C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> plasma (dashed line) as a function of  $\Gamma_{pol}/\Gamma_F\Gamma_O$  flux ratio characterizing the fluorocarbon polymer film thickness

Рис. 3. Эффективная вероятность взаимодействия SiO<sub>2</sub> + F в плазме CF<sub>4</sub> + Ar + O<sub>2</sub> (сплошная линия) как функция параметра  $(M_i\epsilon_i)^{1/2}\Gamma_+$ , характеризующего плотность потока энергии ионов на обрабатываемую поверхность. Эффективная вероятность взаимодействия SiO<sub>2</sub> + F в плазме C<sub>4</sub>F<sub>8</sub> + Ar + O<sub>2</sub> (пунктир) как функция отношения плотностей потоков  $\Gamma_{pol}/\Gamma_F\Gamma_O$ , характеризующего толщину фторуглеродной полимерной пленки на обрабатываемой поверхности

The comparative study of gas-phase plasma characteristics indicated such principal features as 1) quite

close parameters of electron and ion components in both gas systems; 2) the much higher polymerizing ability for  $C_4F_8$ -based plasma due to higher formation rates and densities of  $CF_x$  ( $x = 1, 2$ ) radicals; and 3) opposite behaviors of F atom density with increasing  $O_2$  content in a feed gas. The last phenomenon is produced by differences in  $CF_x + O \rightarrow CF_{x-1}O + F$  reaction kinetics due to various loss rates and densities of oxygen atoms. The model-based analysis of  $SiO_2$  etching mechanism in a framework of ion-assisted chemical reaction yielded also the opposite behaviors for effective probabilities for the heterogeneous  $SiO_2 + F$  reaction. It was suggested that the transition toward  $O_2$ -rich plasma in the low-polymerizing  $CF_4 + Ar + O_2$  plasma reduces the effective reaction through decreasing efficiency for oxide bond breaking and desorption of etching products due to decreasing ion energy flux. In spite of this, the substitution of Ar with  $O_2$  in the high-polymerizing  $C_4F_8 + Ar + O_2$  mixture increases the effective reaction probability by lowering the fluorocarbon film thickness and providing better access of F atoms to the etched surface. The last suggestion is confirmed by the typical correlation (the shape of the curve and the tendency itself) between effective reaction probability and the fluorocarbon film thickness traced by the flux-to-flux ratio for polymerizing radicals, F atoms and O atoms.

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