

О МЕХАНИЗМАХ ВЛИЯНИЯ КИСЛОРОДА НА ПАРАМЕТРЫ ГАЗОВОЙ ФАЗЫ И КИНЕТИКУ РЕАКТИВНО-ИОННОГО ТРАВЛЕНИЯ КРЕМНИЯ В ПЛАЗМЕ $HBr + Cl_2 + O_2$

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Проведено исследование влияния соотношений компонентов HBr/O_2 и Cl_2/O_2 в плазмообразующей смеси $HBr+Cl_2+O_2$ на параметры плазмы, стационарные концентрации активных частиц и кинетику травления Si в условиях, характерных для процессов реактивно-ионного травления: давление плазмообразующего газа ($p = 10$ мтор), вкладываемая мощность ($W = 500$ Вт) и мощность смещения ($W_{dc} = 200$ Вт). Данные по внутренним параметрам плазмы и кинетике плазмохимических процессов были получены при совместном использовании диагностики плазмы зондами Лангмюра и θ -мерной (глобальной) модели плазмы. Было найдено, что варьирование соотношения HBr/O_2 при постоянном содержании Cl_2 в газовой смеси характеризуется более сильным влиянием на стационарный состав плазмы через реакции под действием электронного удара и процессы атомно-молекулярного взаимодействия, а также обеспечивает более широкое изменение суммарной концентрации атомов галогенов в газовой фазе. Было показано также, что варьирование соотношений HBr/O_2 и Cl_2/O_2 в сторону увеличения концентрации кислорода сопровождается снижением скорости травления кремния, которое не коррелирует с изменениями плотностей потоков атомов галогенов и энергии ионов. Модельный анализ кинетики травления позволил заключить, что эффективная вероятность гетерогенной реакции $Si + Cl/Br$ зависит от плотности потока окислительных частиц – атомов кислорода и радикалов OH . Причинами такой зависимости могут являть: 1) окисление кремния, приводящее к увеличению пороговой энергии взаимодействия; и 2) окисление галогенидов кремния в менее летучие соединения вида $SiBr_xO_y$ и $SiCl_xO_y$, которое обуславливает снижение скорости ионно-стимулированной десорбции продуктов и доли свободных центров адсорбции для атомов Cl/Br .

Ключевые слова: ионизация, диссоциация, поток атомов галогенов, поток атомов кислорода, поток энергии ионов, скорость травления, эффективная вероятность взаимодействия

Для цитирования:

Ефремов А.М., Рыбкин В.В., Бетелин В.Б., Kwon К.-Н. О механизмах влияния кислорода на параметры газовой фазы и кинетику реактивно-ионного травления кремния в плазме $HBr + Cl_2 + O_2$. *Изв. вузов. Химия и хим. технология*. 2019. Т. 62. Вып. 10. С. 76–83

For citation:

Efremov A.M., Rybkin V.V., Betelin V.B., Kwon K.-N. On mechanisms of oxygen influence on gas-phase parameters and silicon reactive-ion etching kinetics in $HBr + Cl_2 + O_2$ plasma. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2019. V. 62. N 10. P. 76–83

ON MECHANISMS OF OXYGEN INFLUENCE ON GAS-PHASE PARAMETERS AND SILICON REACTIVE-ION ETCHING KINETICS IN HBr + Cl₂ + O₂ PLASMA

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The effects of both HBr/O₂ and Cl₂/O₂ mixing ratios in HBr+Cl₂+O₂ gas mixture on plasma parameters, steady-state densities of active species and Si etching kinetics were studied under the typical conditions of reactive ion etching process: total gas pressure ($p = 10$ mTorr), input power ($W = 500$ W), bias power ($W_{dc} = 200$ W). The data on internal plasma parameters and plasma chemistry were obtained using a combination of Langmuir probe diagnostics and 0-dimensional (global) plasma modeling. It was found that the variation in HBr/O₂ mixing ratio at constant Cl₂ fraction in a feed gas is characterized by the stronger impact on the steady-state plasma composition through both electron-impact and atom-molecular reaction kinetics as well as allows one to obtain the wider change in the total halogen atom density. It was shown that changes in both HBr/O₂ and Cl₂/O₂ mixing ratios toward O₂-rich plasmas lowers the Si etching rate that exhibits no evident correlations with total halogen atom flux and ion energy flux. The model-based analysis of Si etching kinetics allowed one to conclude that the effective reaction probability for Si + Cl/Br heterogeneous reaction depends on the flux of oxidative species – oxygen atoms and OH radicals. The reasons may be 1) the oxidation of silicon resulting in higher reaction threshold energy; and 2) the decreasing fraction of free adsorption sites for Cl/Br atoms due to the oxidation of reaction products into the lower volatile SiBr_xO_y and SiCl_xO_y compounds.

Key words: ionization, dissociation, halogen atom flux, oxygen atom flux, ion energy flux, etching rate, effective reaction probability

INTRODUCTION

Chlorine- and bromine-containing gases (and namely, Cl₂ and HBr) play the remarkable role in modern micro- and nano-electronics technology being used for the dry (plasma-assisted) etching of various inorganic materials. The main application fields for Cl₂- and HBr-based plasmas are 1) the patterning of semiconductors, metals and metal oxides which form non- or very low-volatile reaction products being treated in the fluorine-containing environments [1-3]; and 2) the highly-anisotropic etching of both mono- and poly-Si [3-5]. The last phenomenon is caused by the much lower probability of spontaneous chemical reaction in the Si + Cl/Br system compared with that for Si + F [6, 7] due to the worse penetration of Cl/Br atoms inside the lattice. That is why, the etching of Si in Cl₂- and HBr-containing plasmas is accompanied by the formation of non-saturated SiCl_x and SiBr_x compounds which may

be desorbed only by ion bombardment. Another positive feature of HBr-containing plasmas is the obtaining of higher etching selectivity for Si and organic photoresist mask. This effects probably follows from the graphitization and the cross-linking of polymer surface due to the ultra-violet irradiation from excited HBr molecules [8].

Until now, there were several studies devoted to investigations of Si etching characteristics and mechanisms in Cl₂- and HBr-based plasmas. The results of these works may be summarized as follows:

- Effective probabilities for Si + Cl and Si + Br reactions have no principal difference under the typical reactive-ion etching conditions. Such conclusion is supported by several experimental facts, and namely by that: 1) differences in the halogenation degrees for Si in Cl₂ and HBr plasmas correlate with differences in corresponding atom size [9]; 2) silicon etching yields for Cl⁺, Br⁺ and HBr⁺ ions are quite close [10]; and 3)

the variation of Cl_2/HBr mixing ratio at constant ion bombardment energy leads to the neatly constant Si etching yield [6].

- Silicon etching rates in HBr plasma are lower than those in Cl_2 plasma under one and the same processing conditions [5]. Such difference is in agreement with differences in volume densities and fluxes of halogen atoms in corresponding gas systems [9, 11, 12]. Also, the addition of O_2 to HBr or Cl_2 slows Si etching rate, but allows one to obtain the more anisotropic etching [13, 14]. The last effect is normally associated with the passivation of sidewalls by low volatile oxy-chlorides and bromides.

In our previous works [15, 16], we have performed the combined (experimental and model-based) study to analyze plasma chemistry and Si etching kinetics in the ternary $\text{HBr}+\text{Cl}_2+\text{O}_2$ gas mixture. The most principal results were that 1) the composition of a feed gas influences the steady-state densities of neutral species through both electron-impact kinetics and gas-phase processes involving O, $\text{O}(\text{I}D)$ and OH species; and 2) under the typical conditions of reactive-ion etching process, the silicon etching kinetics corresponds to the neutral-flux-limited regime as well as is affected by the oxidation of SiCl_x and SiBr_x into lower volatile compounds. These findings clearly indicate that the O_2 content in a feed gas represent an additional factor to adjust both gas-phase and heterogeneous chemistries in order to optimize output process characteristics. In this work, we attempted to compare the effects of HBr/O_2 and Cl_2/O_2 mixing ratios on plasma parameters, steady-state densities of active specie and silicon etching kinetics. The main idea was to demonstrate the ability of $\text{HBr}+\text{Cl}_2+\text{O}_2$ gas system to control both gas-phase and heterogeneous chemistries by the gas mixing ratios only.

EXPERIMENTAL AND MODELING DETAILS

Experiments were performed in the planar inductively coupled plasma (ICP) reactor [15, 16]. Plasma was excited using a 13.56 MHz RF power supply connected to a flat copper coil on the top side of the chamber. Another 12.56 MHz RF generator powered the bottom electrode in order to produce the negative dc bias voltage ($-U_{\text{dc}}$) and to control the ion bombardment energy. The experiments were carried out at constant gas pressure ($p = 10$ mTorr), total gas flow rate ($q = 40$ sccm), input power ($W = 500$ W), bias power ($W_{\text{dc}} = 200$ W) while the variable parameter was the composition of feed gas. In one experimental series, the Cl_2 flow rate $q(\text{Cl}_2)$ was fixed at 20 sccm while HBr and O_2 flow rates were variably set to a combined total

of $q(\text{O}_2) + q(\text{HBr}) = 20$ sccm. Therefore the fraction of Cl_2 $y(\text{Cl}_2)$ was always 50%, and an increase in $q(\text{O}_2)$ from 0-10 sccm corresponded to the transition from 50% $\text{Cl}_2 + 50\%$ HBr to 50% $\text{Cl}_2 + 25\%$ HBr + 25% O_2 gas mixture. Another experimental series assumed the constant $q(\text{HBr}) = 20$ sccm as well as the variable flow rates for Cl_2 and O_2 within $q(\text{O}_2) + q(\text{Cl}_2) = 20$ sccm. In this case, the fraction of HBr in a feed gas was always 50% while an increase in $q(\text{O}_2)$ from 0-10 sccm corresponded to the transition from 50% $\text{Cl}_2 + 50\%$ HBr to 50% HBr + 25% $\text{Cl}_2 + 25\%$ O_2 gas mixture. Plasma diagnostic provided the data on electron temperature (T_e) and ion current density (J_+). The latter were extracted from voltage-current curves using the well-known statements of the double Langmuir probe theory [17, 18].

In etching experiments, samples of Si with dimensions of $\sim 2 \times 2$ cm were located in the middle part of the bottom electrode. The bottom electrode had a built-in water-flow cooling system that allowed one to maintain its temperatures at ~ 17 °C. Accordingly, we assumed constant sample temperatures (T_s) in all experimental series as well as ignored the temperature-related effects when analyzing the etching kinetics. The Si etching rates were calculated as $R = \Delta h/\tau$, where Δh is the etched depth measured by the surface profiler Alpha-Step 500 (Tencor), and $\tau = 2$ min is the processing time. In order to supply the measurements of Δh , we developed a partial surface masking by the photoresist AZ1512. The thickness of the photoresist layer was ~ 1.5 μm . Preliminary experiments showed that the presence of etched samples in the reactor chamber does not influence the Langmuir probe diagnostics results within the standard experimental error. This allows one to neglect the influence of reaction products on bulk plasma characteristics and thus, to match bulk and heterogeneous subsystems only through fluxes of active species from gas-phase to sample surface.

In order to analyze the influence of HBr/O_2 and Cl_2/O_2 mixing ratios on kinetics and densities of plasma active species, we developed a simplified 0-dimensional (global) kinetic model operated with volume-averaged plasma parameters. Similar to our previous works [11, 12], the model was based on the simultaneous solution of steady-state kinetic equations with using the experimental data on T_e and J_+ as the input parameters. The set of chemical reactions was taken from Refs. [15, 16]. Corresponding kinetic schemes have demonstrated an acceptable agreement between model-predicted and measured plasma parameters for pure HBr, Cl_2 and O_2 plasmas [19-21].

RESULTS AND DISCUSSION

Fig. 1 illustrates the influence of HBr/O₂ and Cl₂/O₂ mixing ratios on silicon etching rate (R_{Si}). It can be seen that in increased in y(O₂) in both cases lowers the R_{Si} value with different quantitative effects. Particularly, the substitution of HBr for O₂ at y(Cl₂) = const suppresses Si etching rate by ~ 14 times, in the range of 64.2-4.5 nm/min for 0-25% O₂. The influence of Cl₂/O₂ mixing ratio appears to be much weaker and slightly exceeds ~ 5 times (64.2-12.2 nm/min for 0-25% O₂). The above data clearly demonstrate that the higher O₂ content in a feed gas provides the stronger differences in the silicon etching kinetics within one and the same etching mechanism. Previously, several works have mentioned that the quantitative differences in Si etching rates in non-oxygenated Cl₂- and HBr-based plasmas are in general agreement with the fluxes of corresponding halogen atoms. In order to understand how this rule works for HBr+Cl₂+O₂ plasma as well as to figure out the features of Si etching mechanism in the given gas system, the information on plasma parameters and the steady-state plasma composition is mandatory required.

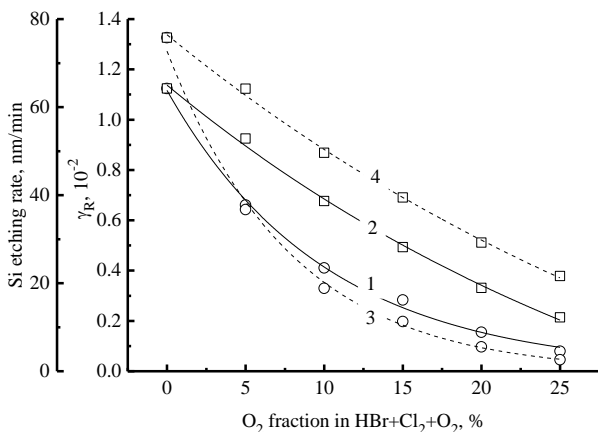


Fig. 1. Silicon etching rates (1, 2) and effective reaction probabilities for Si + Cl/Br reaction (3, 4) as functions of O₂ fraction in a feed gas at y(Cl₂) = const (1, 3) and y(HBr) = const (2, 4)
 Рис. 1. Скорость травления кремния (1, 2) и эффективная вероятность взаимодействия в реакции Si + Cl/Br (3, 4) как функции доли O₂ в плазмообразующей смеси при y(Cl₂) = const (1, 3) и y(HBr) = const (2, 4)

Fig. 2 represents experimental and model-predicted data plasma parameters and densities of charges species. It was found that electron temperature (mean electron energy) exhibits the similar decreasing tendency toward O₂-rich plasmas (T_e = 2.9-3.3 eV for 0-25% O₂ at y(Cl₂) = const and 2.9-3.4 eV for 0-25% O₂ at y(HBr) = const) due to similar shifts in electron energy losses. Particularly, the substitution of HBr for O₂ at y(Cl₂) = const changes dominant gas-phase components from HCl to Cl₂, Cl and O₂ (Fig. 3(a)) and causes

a decrease in electron energy losses for vibrational excitation, electronic excitation and ionization. The reasons are 1) higher threshold energies and cross-sections for vibrational excitation of HCl compared with those for Cl₂ and O₂ [22, 23]; and 2) increasing fraction of atomic species. The substitution of Cl₂ for O₂ at y(HBr) = const produces similar changes in the densities of both HCl and O₂ (Fig. 3(b)) as well as suppresses the density of Cl₂ molecules which are characterized by higher electronic excitation and ionization cross-sections (and thus, by higher electron energy losses for corresponding processes) compared with those for O₂ [23]. Therefore, an increase in y(O₂) in both cases lowers the overall electron energy loss and thus, enriches EEDF by the high-energy electrons.

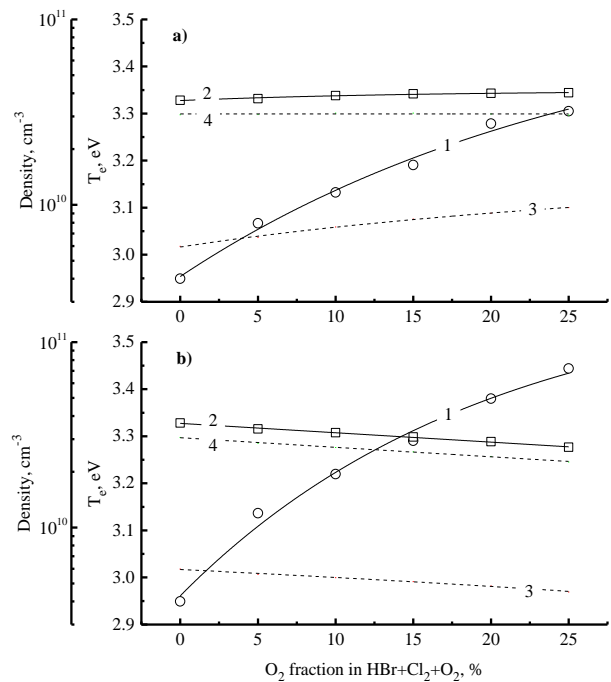


Fig. 2. Electron temperature (1) and densities of charged species (2 – positive ions; 3 – electrons; 4 – negative ions) as functions of O₂ fraction in a feed gas at y(Cl₂) = const (a) and y(HBr) = const (b)
 Рис. 2. Температура электронов (1) и концентрации заряженных частиц (2 – положительные ионы; 3 – электроны; 4 – отрицательные ионы) как функции доли O₂ в плазмообразующей смеси при y(Cl₂) = const (a) и y(HBr) = const (b)

Another important feature of HBr/O₂ and Cl₂/O₂ mixing ratios is the different effect on densities of charged species. Particularly, the substitution of HBr for O₂ at y(Cl₂) = const lowers the density of HCl molecules under the condition of [Cl₂] + [Cl] > [HCl] for y(O₂) > 8% (Fig. 3(a)). Such situation provides an increase in total ionization frequency due to 1) higher ionization rate coefficients for both Cl₂ and Cl compared with HCl [22]; and 2) an increase in all ionization rate coefficients together with increasing T_e. This reasonably causes an increase in n₊ and n_e. Simultaneously, one can obtain the nearly proportional increase

in both total attachment rate (because of higher attachment rate coefficient for Cl_2 compared with HCl [22]) and ion-ion recombination frequency for negative ions (because of increasing n_+). This results in the nearly constant n as well as in decreasing plasma electronegativity ($n/n_e = 5.1\text{--}3.1$ for 0-25% O_2). Oppositely, the substitution of Cl_2 for O_2 at $y(\text{HBr}) = \text{const}$ provides the continuous domination of HCl over other neutral components (Fig. 3(b)) while a decrease in $[\text{HCl}]$ (by ~ 2.5 times for 0-25% O_2) appears to be stronger than the growth in corresponding ionization rate coefficient (by ~ 1.6 times for 0-25% O_2). As such, an increase in O_2 fraction in a feed gas leads to monotonically decreasing formation rates for electrons and positive ions as well as causes similar decreasing tendencies for n_+ and n_e . In addition, the dominant contribution of HCl to the total attachment rate slows the formation of negative ions due to the simultaneous decrease in $[\text{HCl}]$ and n_e . This leads to a decrease in n as well as to the nearly constant $n/n_e \sim 5$.

From Fig. 3, one can conclude that the non-oxygenated 50% $\text{HBr} + 50\%$ Cl_2 plasma is characterized by 1) the domination of HCl and BrCl over other gas-phase components; and 2) the condition $[\text{Br}] \gg [\text{Cl}]$. When analyzing the kinetics of neutral species, it can be concluded that both phenomena result from the stepwise dissociation of HBr and Br_2 through their interaction with Cl atoms in R1: $\text{HBr} + \text{Cl} \rightarrow \text{HCl} + \text{Br}$ ($k_1 \sim 1.9 \times 10^{-11} \text{ cm}^3/\text{s}$) and R2: $\text{Br}_2 + \text{Cl} \rightarrow \text{Br} + \text{BrCl}$ ($k_1 \sim 1.5 \times 10^{-10} \text{ cm}^3/\text{s}$). The frequencies of these processes ($k_1[\text{Cl}] = 75 \text{ s}^{-1}$ and $k_2[\text{Cl}] = 595 \text{ s}^{-1}$) exceed the corresponding values for R3: $\text{HBr} + e \rightarrow \text{H} + \text{Br} + e$ ($k_3 n_e = 10 \text{ s}^{-1}$) and R4: $\text{Br}_2 + e \rightarrow 2\text{Br} + e$ ($k_4 n_e = 100 \text{ s}^{-1}$). Therefore, the mixing of HBr and Cl_2 accelerates the consumption of HBr , Br_2 and Cl as well as promotes the formation of Br , HCl and BrCl .

The substitution of HBr for O_2 at $y(\text{Cl}_2) = \text{const}$ rapidly suppresses densities of HBr , Br_2 and BrCl molecules (Fig. 3(a)). The reasons are the acceleration of R3, R4 and R5: $\text{BrCl} + e \rightarrow \text{Br} + \text{Cl} + e$ (due to an increase in T_e and n_e , see Fig. 2(a)) as well as the stepwise dissociation of above species in reactions involving O and OH . Among the latter, most effective ones are R6: $\text{HBr} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Br}$ ($k_6 \sim 8.0 \times 10^{-12} \text{ cm}^3/\text{s}$), R7: $\text{Br}_2 + \text{O} \rightarrow \text{BrO} + \text{Br}$ ($k_7 \sim 1.3 \times 10^{-11} \text{ cm}^3/\text{s}$), R8: $\text{Br}_2 + \text{OH} \rightarrow \text{HOBr} + \text{Br}$ ($k_8 \sim 3.1 \times 10^{-11} \text{ cm}^3/\text{s}$) and R9: $\text{BrCl} + \text{O} \rightarrow \text{BrO} + \text{Cl}$ ($k_9 \sim 2.0 \times 10^{-11} \text{ cm}^3/\text{s}$). The density of HCl also shows a decrease toward O_2 -rich plasmas, but exhibits the weaker change compared with

bromine-containing species. The first effect is provided by several factors, such as 1) an increase in HCl dissociation frequency through R10: $\text{HCl} + e \rightarrow \text{H} + \text{Cl} + e$, R11: $\text{HCl} + \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{Cl}$ ($k_{11} \sim 1.0 \times 10^{-10} \text{ cm}^3/\text{s}$) and R12: $\text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl}$ ($k_{12} \sim 1.5 \times 10^{-12} \text{ cm}^3/\text{s}$); and 2) a decrease HCl formation rate in R1 and R2. The slower change in $[\text{HCl}]$ results from an increase in HCl formation rates in R13: $\text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl}$ ($k_{13} \sim 4.0 \times 10^{-11} \text{ cm}^3/\text{s}$) and heterogeneous recombination of H and Cl atoms. The density of Cl atoms increases by about an order of magnitude due to the simultaneous increase in their formation rate and a decrease in decay frequency. The mentioned change in Cl atom formation rate is mainly provided by R14: $\text{Cl}_2 + e \rightarrow 2\text{Cl} + e$ due to the growth of $[\text{Cl}_2]$. The latter is connected with an increase in formation rate for Cl_2 molecules through R15: $\text{BrCl} + \text{Cl} \rightarrow \text{Cl}_2 + \text{Br}$ ($k_{15} \sim 1.5 \times 10^{-11} \text{ cm}^3/\text{s}$) and heterogeneous recombination. A decrease in Cl atom decay frequency is mainly connected with R2 and R15 due to decreasing densities of Br_2 and BrCl species. The weakly decreasing density of Br atoms is completely associated with the corresponding change in their total formation rate. The latter is produced by the opposite behaviors of R2 and R5 from one side and R15 from the other side.

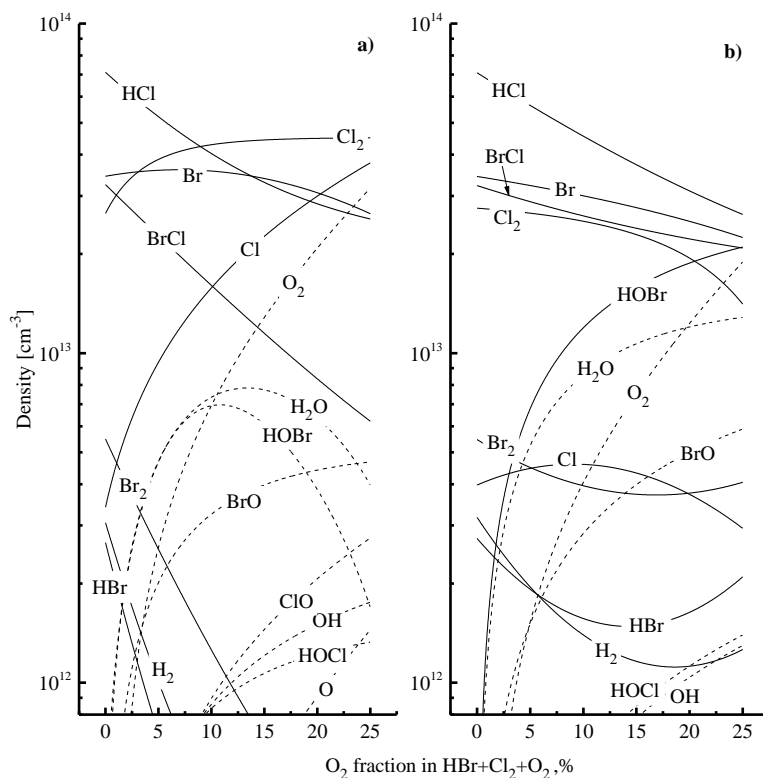


Fig. 3. Steady-state densities of neutral species in $\text{HBr} + \text{Cl}_2 + \text{O}_2$ plasmas with variable HBr/O_2 (a) and Cl_2/O_2 (b) mixing ratios
Рис. 3. Стационарные концентрации нейтральных частиц в плазме $\text{HBr} + \text{Cl}_2 + \text{O}_2$ с переменными соотношениями компонентов HBr/O_2 (a) и Cl_2/O_2 (b)

The substitution of Cl₂ for O₂ at y(HBr) = const provides the nearly constants electron-impact dissociation frequencies for molecular species due to an opposite change in Te and ne (Fig. 2(b)). As such, the weakly decreasing densities of HBr, Br₂, BrCl and HCl toward O₂-rich plasmas (Fig. 3(b)) result only from the effects of gas-phase atom-molecular processes R6–R9, R11 and R12. In contrast to the previous case, the relative contributions of stepwise dissociation processes to total dissociation rates for above species appear to be much weaker. The reasons are 1) the weaker influence of Cl₂/O₂ mixing ratio on the electron-impact kinetics of R16: O₂ + e → 2O + e and R17: O₂ + e → O + O(¹D) + e that limits the formation rates for O atoms and OH radicals; and 2) the lower rate coefficients for Cl₂ + O/OH reactions compared with those for HBr + O/OH and Br₂ + O/OH [23]. The last feature means also the gas system with y(HBr) = const provides higher conversion rates of O and OH into HOBr and BrO and thus, is characterized by lower densities of oxidant species compared with the case of y(Cl₂) = const. The density of Cl atoms shows the weak decrease toward O₂-rich plasmas due to a decrease in their formation rates in R5 and R14. The evident reason for such effect is the decreasing densities of source species. The similar behavior of [Br] is also caused by the change in Br atom formation kinetics. Particularly, one can obtain a decrease in Br atom formation rates through R2, R5 and R15 due to the corresponding changes in [Br₂] and [BrCl].

The above data allow one to conclude that that change in HBr/O₂ and Cl₂/O₂ mixing ratios leads to quite similar change in [Br] as well as exhibits the different effect on [Cl]. As a result, the gas system with y(Cl₂) = const provides the wider adjustment for the total density of chemically active species. In previous works [6, 9, 10], one can find enough arguments that partial probabilities for heterogeneous reactions Si + Cl and Si + Br are quite close. Therefore, the measured Si etching rate may be represented as R_{Si} = γ_R(Γ_{Cl} + Γ_{Br}), where γ_R is the effective reaction probability, and Γ_{Cl} + Γ_{Br} is the total flux of halogen atoms to the etched surface. The substitution of HBr for O₂ at y(Cl₂) = const provides an increase in Γ_{Cl} + Γ_{Br} (4.0×10¹⁷–8.2×10¹⁷ cm⁻²s⁻¹, or by ~ 2 times for 0-25% O₂) due to the rapid increase in Γ_{Cl}. Accordingly, the combination of decreasing etching rate and increasing flux of chemically active species corresponds to the rapidly decreasing γ_R toward O₂-rich plasmas (1.3×10⁻²–4.6×10⁻⁴, or by ~ 30 times for 0-25% O₂, see Fig. 1). The substitution of Cl₂ for O₂ at y(HBr) = const lowers the Γ_{Cl} + Γ_{Br} value (4.0×10¹⁷–2.7×10¹⁷ cm⁻²s⁻¹, or by ~ 1.5 times for 0-25%

O₂) due to the corresponding changes in partial densities and fluxes. However, the faster change in R_{Si} compared with Γ_{Cl} + Γ_{Br} toward O₂-rich plasmas also corresponds to decreasing γ_R (1.3×10⁻²–3.8×10⁻³, or by ~ 4 times for 0–25% O₂, see Fig. 1). From Refs. [5, 18], it can be understood that the effective probability of ion-assisted chemical reaction at nearly constant surface temperature normally correlates with the ion bombardment intensity. The latter may be characterized by the parameter (M_iε_i)^{1/2}Γ₊ [24–26], where M_i is the effective ion mass, ε_i = -e(U_{dc} + U_f) is the ion bombardment energy, -U_f ≈ 0.5T_eln(m_e/2.3m₊) is the floating potential, and Γ₊ is the flux of positive ions. It was found that the substitution of HBr for O₂ at y(Cl₂) = const decreases both -U_{dc} (453-429 V for 0-25% O₂, see Fig. 4) and ion bombardment energy because of eU_{dc} >> eU_f. However, this change is overcompensated by increasing Γ₊ (4.6×10¹⁵–6.1×10¹⁵ cm⁻²s⁻¹ for 0-25% O₂), so that the parameter (M_iε_i)^{1/2}Γ₊ indicates the intensification of ion bombardment toward O₂-rich plasmas (Fig. 4). The substitution of Cl₂ for O₂ at y(HBr) = const causes very similar change in -U_{dc} (453-425 V for 0-25% O₂) but results in slightly decreasing ion flux in the range of 4.6×10¹⁵–4.1×10¹⁵ cm⁻²s⁻¹. Accordingly, the monotonic decrease in (M_iε_i)^{1/2}Γ₊ takes place (Fig. 4).

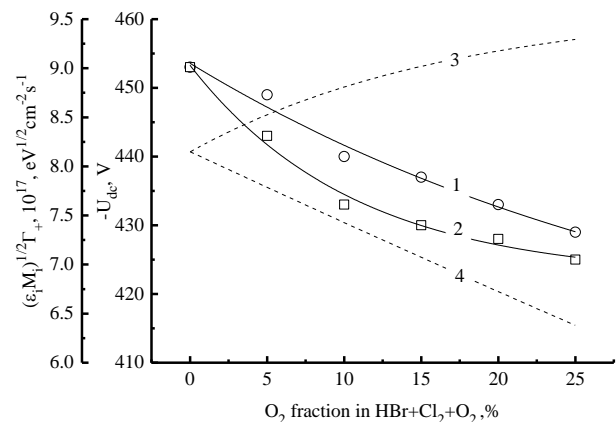


Fig. 4. Negative dc bias at W_{dc} = const (1, 2) and the parameter (M_iε_i)^{1/2}Γ₊ characterizing ion energy flux (3, 4) in HBr+Cl₂+O₂ plasmas with variable HBr/O₂ (1, 3) and Cl₂/O₂ (2, 4) mixing ratios
Рис. 4. Отрицательное смещение при W_{dc} = const (1, 2) и параметр (M_iε_i)^{1/2}Γ₊, характеризующий плотность потока энергии ионов (3, 4), в плазме HBr+Cl₂+O₂ с переменными соотношениями компонентов HBr/O₂ (1, 3) и Cl₂/O₂ (2, 4)

The absence of qualitative (in the case of y(Cl₂) = const) and quantitative (in the case of y(HBr) = const) correlation between the changes of γ_R and (M_iε_i)^{1/2}Γ₊ allows one to assume that the effective reaction probability is influenced by an additional factor connected with the chemistry of neutral species. Ac-

According to previously published works [13-16], this really may be the increasing flux of oxidative species $\Gamma_{\text{O}} + \Gamma_{\text{OH}}$ (2.5×10^{15} - 6.8×10^{16} $\text{cm}^{-2}\text{s}^{-1}$ for $y(\text{Cl}_2) = \text{const}$ and 1.3×10^{15} - 3.4×10^{16} $\text{cm}^{-2}\text{s}^{-1}$ for $y(\text{HBr}) = \text{const}$ at 1–25% O_2) that influences the heterogeneous stages of the etching process through suppressing γ_{R} . The mechanisms for such influence may be connected with 1) the direct oxidation of Si atoms into SiO_x through surface defects (broken Si-Si bonds) produced by ion bombardment; and 2) the oxidation of Si + Cl/Br reaction products into lower volatile SiBr_xO_y and SiCl_xO_y compounds. Obviously, the first pathway lowers γ_{R} through increasing reaction threshold for halogen atoms while the second one retards the chemical reaction through decreasing fraction of free adsorption sites for etchant species. For the case of $y(\text{Cl}_2) = \text{const}$, the last suggestion is confirmed by the fact that the growth of $\Gamma_{\text{O}} + \Gamma_{\text{OH}}$ appears to be faster compared with $(M_i \varepsilon_i)^{1/2} \Gamma_+$. This corresponds to an increase in surface fraction covered by reaction products.

CONCLUSIONS

In this work, we investigated the influence of O_2 on gas-phase parameters and Si etching kinetics in $\text{HBr} + \text{Cl}_2 + \text{O}_2$ inductively coupled plasma through the changes in HBr/O_2 and Cl_2/O_2 mixing ratios. The combination of plasma diagnostics by Langmuir probes and plasma modeling allowed one to conclude that the variation in HBr/O_2 mixing ratio 1) is characterized by the stronger impact on both electron-impact and atom-molecular reaction kinetics; 2) provides the wider change in the total halogen atom density and flux; and 3) results in increasing ion bombardment intensity toward O_2 -rich plasmas. The experiments showed that and increase in O_2 fraction in a feed gas in both cases lowers the Si etching rate and effective reaction probability for Si + Cl/Br heterogeneous reaction. The last effect may be related to 1) the oxidation of Si by O and OH species resulting in higher reaction threshold energy; and 2) the oxidation of reaction products into the lower volatile SiBr_xO_y and SiCl_xO_y compounds resulting in decreasing fraction of free adsorption sites for etchant species.

The publication was carried out as part of the state assignment of the Federal State Institution Scientific Center for Research and Development of the Russian Academy of Sciences (fundamental scientific research) on the topic No. 0065-2019-0006 "Fundamental and applied research in the field of subwave holographic lithography, physicochemical etching processes of 3D nanometer dielectric structures for the development of critical technologies for the production of electronic components".

Публикация выполнена в рамках государственного задания ФГУ ФНЦ НИИСИ РАН (проведение фундаментальных научных исследований) по теме № 0065-2019-0006 «Фундаментальные и прикладные исследования в области субволновой голографической литографии, физико-химических процессов травления 3D нанометровых диэлектрических структур для развития критических технологий производства ЭКБ».

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*Поступила в редакцию 16.03.2019
Принята к опубликованию 25.07.2019*

*Received 16.03.2019
Accepted 25.07.2019*