DOI: 10.6060/ivkkt.20226503.6463

УДК: 537.525

ПАРАМЕТРЫ ПЛАЗМЫ И КИНЕТИКА АКТИВНЫХ ЧАСТИЦ В СМЕСИ $Cl_2 + BCl_3 + Ar$

А.М. Ефремов, С.А. Смирнов, В.Б. Бетелин, K.-H. Kwon

Александр Михайлович Ефремов (ORCID 0000-0002-9125-0763)*, Сергей Александрович Смирнов (ORCID 0000-0002-0375-0494)

Ивановский государственный химико-технологический университет, Шереметевский просп., 7, Иваново, Российская Федерация, 153000
E-mail: amefremov@mail.ru*, sas@isuct.ru

Владимир Борисович Бетелин (ORCID 0000-0001-6646-2660)

ФГУ ФНЦ НИИСИ РАН, Нахимовский просп., 36, к.1, Москва, Российская Федерация, 117218
E-mail: betelin@niisi.msk.ru

Kwang-Ho Kwon (ORCID 0000-0003-2580-8842)

Korea University, 208 Seochang-Dong, Chochiwon, Korea, 339-800
E-mail: kwonkh@korea.ac.kr

Проведено исследование электрофизических параметров плазмы, стационарного состава газовой фазы и кинетики реактивно-ионного травления SiO_2 в смеси $Cl_2 + BCl_3 + Ar$ в условиях индукционного ВЧ 13,56 МГц разряда. Схема исследования включала диагностику плазмы зондами Лангмюра и 0-мерное (глобальное) моделирование кинетики плазмохимических процессов. В качестве неизменных параметров выступали: доля аргона в плазмообразующей смеси (20%), общее давление газа (6 мтор) и мощность смещения (300 Вт). Было найдено, что замещение Cl_2 на BCl_3 при постоянной вкладываемой мощности: а) оказывает влияние на параметры электронной и ионной компонент плазмы; б) приводит к снижению электроотрицательности плазмы; и в) сопровождается противоположными изменениями концентраций атомов хлора и радикалов BCl_x. Увеличение вкладываемой мощности при любом фиксированном составе смеси вызывает увеличение степени диссоциации исходных молекул и концентраций продуктов диссоциации. Показано, что зависимость скорости травления SiO_2 от соотношения Cl_2/BCl_3 имеет немонотонный характер (максимум ~ 120 нм/мин в смеси состава 40% Cl_2 + 40% BCl_3 + 20% Ar), при этом увеличение доли BCl_3 и вкладываемой мощности приводят к аналогичному изменению эффективной вероятности взаимодействия в системе SiO_2 + Cl. Это не согласуется с изменением плотности потока энергии ионов. Предположено, что в качестве химически активных частиц плазмы выступают также радикалы BCl_x, вовлеченные в гетерогенные реакции вида $SiO_y + BCl_x \rightarrow SiO_{y-1} + BCl_xO$. Протекание таких реакций способствует увеличению числа центров адсорбции атомов хлора.

Ключевые слова: Cl_2, BCl_3, плазма, параметры, активные частицы, ионизация, диссоциация, травление

PLASMA PARAMETERS AND ACTIVE SPECIES KINETICS IN $Cl_2 + BCl_3 + Ar$ GAS MIXTURE

A.M. Efremov, S.A. Smirnov, V.B. Betelin, K.-H. Kwon

Alexander M. Efremov (ORCID 0000-0002-9125-0763)*, Sergey A. Smirnov (ORCID 0000-0002-0375-0494)

Ivanovo State University of Chemistry and Technology, Sheremetevskiy ave., 7, Ivanovo, 153000, Russia
E-mail: amefremov@isuct.ru*, sas@isuct.ru

Vladimir B. Betelin (ORCID 0000-0001-6646-2660)

SRISA RAS, Nakhimovsky ave., 36, bld. 1, Moscow, 117218, Russia
E-mail: betelin@niisi.msk.ru

Kwang-Ho Kwon (ORCID 0000-0003-2580-8842)
Korea University, 208 Seochang-Dong, Chochiwon, Korea, 339-800
E-mail: kwonkh@korea.ac.kr

The investigation of electro-physical plasma parameters, steady-state gas phase composition and reactive-ion etching kinetics of silicon in Cl_2 + BCl_3 + Ar gas mixture under conditions of RF 13.56 MHz inductive discharge was carried out. The investigation procedure included plasma diagnostics by Langmuir probes as well as the 0-dimensional (global) modeling of plasma chemical kinetics. Fixed processing parameters were represented by the argon fraction in a feed gas (10%), total gas pressure (6 mTorr) and bias power (300 W). It was found that the substitution of Cl_2 for BCl_3 at constant input power a) does influence electrons- and ions-related plasma parameters; b) lowers plasma electronegativity; and c) causes opposite changes in densities of chlorine atoms and BCl_x radicals. An increase in input power at any fixed feed gas composition results in increasing both dissociation degrees for original molecules and densities of dissociation products. It was shown that the dependence of SiO_2 etching rate on the Cl_2/BCl_3 mixing ratio exhibits the non-monotonic shape (with a maximum of ~ 120 nm/min for Cl_2 + 40% BCl_3 + 20% Ar gas mixture), and an increase in both BCl_3 fraction and input power caused the same effect for the SiO_2 + Cl reaction probability. This contradicts with the change in ion energy flux. It was suggested that BCl_x radicals also play a role of chemically active species being involved in $SiO_y + BCl_x \rightarrow SiO_{y-1} + BCl_xO$ heterogeneous reactions. Such reactions provide an increase in the amount of adsorption sites for chlorine atoms.

Key words: Cl_2, BCl_3, plasma, parameters, active species, ionization, dissociation, etching

Для цитирования:
Ефремов А.М., Смирнов С.А., Бетелин В.Б., Kwon K.-H. Параметры плазмы и кинетика активных частиц в смеси Cl_2 + BCl_3 + Ar. *Изв. вузов. Химия и хим. технология*. 2022. Т. 65. Вып. 3. С. 14–21
For citation:
Efremov A.M., Smirnov S.A., Betelin V.B., Kwon K.-H. Plasma parameters and active species kinetics in Cl_2 + BCl_3 + Ar gas mixture. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*]. 2022. V. 65. N 3. P. 14–21

INTRODUCTION

Halogen-containing gases have found many applications in micro- and nano-electronics technology for the reactive-ion etching (RIE) of both silicon substrates and various functional layers [1, 2]. Among those, Cl_2 and BCl_3 are often used for the dry patterning of metals (Cu, Al, Mo), metal oxides (Al_2O_3, TiO_2, MgO) as well as semiconductor materials from A^2B^3 and A^3B^5 groups [2]. The general mechanism of all these process is the ion-assisted chemical reaction, where Cl atoms work as chemically active species while the ion bombardment provides the desorption of reaction products and/or the destruction of chemical bonds between surface atoms [3]. Accordingly, the study of interconnections between gas-phase plasma parameters and heterogeneous process kinetics is the mandatory condition for obtaining an optimal set of output process characteristic.

Until now, there are enough works dealt with both experimental and theoretical (model-based) investigations of Cl_2- and BCl_3-based plasmas [4-11]. Corresponding results may briefly be summarized as follows:

- Under typical RIE conditions (gas pressure below 10 mTorr and input power density ~ 0.1 W/cm^3 that yields plasma density above 10^{10} cm^{-3}), the Cl_2 plasma is characterized by high dissociation degrees for chlorine molecules [6, 12, 13] resulting in [Cl] > [Cl_2]. This produces high absolute etching rates but causes the nearly isotropic etching profiles due to high neutral/charged ratios. That is why one normally uses Cl_2 + Ar mixtures in order to reduce the density of Cl atoms;
- The BCl_3 plasma exhibits lower Cl atom densities [11] and thus, provides lower etching rates together with more anisotropic etch profiles. Another important feature is the effective etching of oxide materials due to their interaction with BCl_x radicals [2, 3]. The reason is that the B-O bond is stronger than that for many other metals and semiconductors. As such, BCl_x species easily extract the oxygen from the surface oxide in a form of gaseous BCl_xO compounds while the remaining non-oxidized material is etched by Cl atoms. The negative consequence is the re-deposition of boron oxides, especially if the feed gas contains O_2.

In our previous works [9-11, 14, 15], we applied a combination of plasma diagnostics and modeling techniques to study Cl_2 + Ar and BCl_3 + Ar plasmas in respect to RIE of several metal oxides. Results of these works allowed one a) to determine key chemical processes influencing steady-state densities of plasma active species; b) to understand how corresponding gas mixing ratios affect plasma chemistry through changes in both electron temperature and electron density; and c) to analyze etching mechanism in terms of effective reaction probability. The main idea of this work was to apply the same research scheme to the three-component Cl_2 + BCl_3 + Ar gas system with SiO_2 as the etched material. The motivation was that the Cl_2/BCl_3 mixing ratio may be an effective tool to adjust densities of plasma active species and thus, the overall etching result. The SiO_2 was selected as the test material with the well-studied etching mechanism. In our opinion, such situation provides the better understanding of side factors influencing etching kinetics.

EXPERIMENTAL AND MODELING DETAILS

EXPERIMENTAL SETUP AND CONDITIONS

All experiments (plasma diagnostics and etching rate measurements) were conducted in the planar inductively coupled plasma (ICP) reactor described in our previous works [9-11]. The low-pressure inductive discharge in the Cl_2 + BCl_3 + Ar gas mixture was produced using the rf 13.56 MHz power supply while the second 12.56 MHz rf generator was connected to the bottom electrode in order to control the ion bombardment energy through the negative dc bias voltage, $-U_{dc}$. Constant processing parameters were total gas flow rate (q = 50 sccm), gas pressure (p = 6 mTorr) and bias power (W_{dc} = 300 W). Variable parameters were input power (W = 500-800 W) and Cl_2/BCl_3 mixing ratio. The latter was adjusted by partial flow rates for Cl_2 and BCl_3 gases within $q(Cl_2) + q(BCl_3) = 40$ sccm at q(Ar) = 10 sccm. As such, the fraction of Ar in a feed gas was always 20% while an increase in $q(BCl_3)$ from 0-40 sccm corresponded to the full substitution of Cl_2 by BCl_3. Accordingly, the fraction of BCl_3 in a feed gas, $y(BCl_3)$, was varied from 0-80%. In fact, this range corresponded to the transition between 80% Cl_2 + 20% Ar and 80% BCl_3 + 20% Ar gas systems.

Electro-physical plasma parameters were examined by the double Langmuir probe tool DLP2000 (Plasmart Inc.). Data on electron temperature (T_e) and ion current density (J_+) were extracted from measured voltage-current curves using well-known statements of the double Langmuir probe theory [16].

Etched samples were fragments of the thermally oxidized Si(100) wafer with an average size of 2×2 cm. The thickness of oxide layer was ~ 2 μm. Samples were placed in the middle part of the bottom electrode, and their temperature was stabilized at ~ 17 °C using the built-in water-flow cooling system. The small sample size allowed one to neglect the loading effect as well as to provide the etching regime controlled by heterogeneous process kinetics. Etching rates, R, were determined from corresponding etched depths Δh. These values were measured using the surface profiler Alpha-step 500 (Tencor) for the processing time $\tau = 1$ min. As preliminary experiments indicated quasi-linear shapes for $\Delta h = f(\tau)$ curves, we simply accounted for $R = \Delta h/\tau$.

PLASMA MODELING

In order to obtain volume-averaged densities of plasma active species, we used the global (0-dimensional) model [4]. Input model parameters were experimental data on T_e and J_+. The kinetic scheme (the list of plasma chemical reactions with corresponding kinetic coefficients) was composed according to our previous works dealt with the modeling of BCl_3 + Ar [9, 10] and Cl_2+Ar [4, 5] plasmas. The computational procedure accounted for following assumptions:

- The electron energy distribution function (EEDF) has the nearly Maxwellian shape [7, 8]. This allows one to obtain rate coefficients for electron-impact processes using Arrhenius-like fitting expressions $k = f(T_e)$ [8].

- The loss of atoms and radicals on chamber walls can be described by the first-order (Eley-Redeal) recombination kinetics [9, 10]. Corresponding rate coefficients are $k \approx \gamma \upsilon_T/2r$, where γ is the recombination probability, $\upsilon_T = (8RT_{gas}/\pi M)^{1/2}$ is the thermal velocity for the given particle with the molar mass of M, and r is the inner radius of reactor chamber. Recombination probabilities for Cl atoms and BCl_x (x = 1, 2) radicals were taken from published works [8-10]. Corresponding values were either determined by experiments or adjusted using the plasma modeling procedure according to the agreement between measured and model-predicted densities of corresponding species.

- Gas temperature, T_{gas}, was assumed to be a) independent on Cl_2/BCl_3 mixing ratio; and b) the linear function of input power. Based on previous works [4-6], we suggested T_{gas} = 650-750 K for W = 500–800 W. Preliminary model runs indicated that the uncertainity in T_{gas} of ± 50 K has no principal impact on modeling results.

- The electronegativity of Cl_2 + BCl_3 + Ar plasma under the given set of processing conditions is high enough to assume $n_-/n_e > 1$ and $n_e < n_+$, where low-case indexes "+", "-" and "e" relate to positive ions, negative ions and electrons, respectively. As such, after the extraction of n_+ from measured J_+ [4], we solved the kinetic equation for negative ions together with the plasma quasi-neutrality equation [4, 9] in order to obtain the electron density.

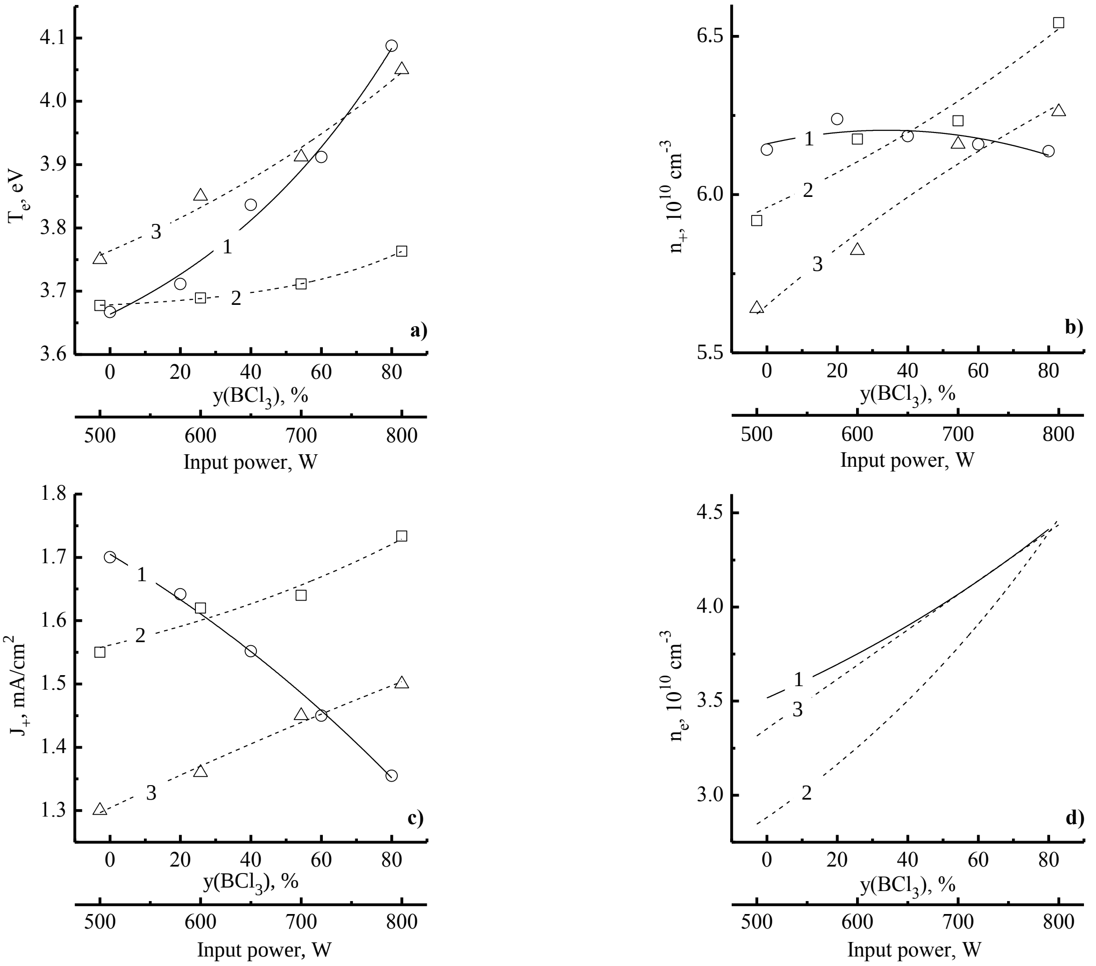

Fig. 1. Electrons- and ions-related plasma parameters as functions of Cl_2/BCl_3 mixing ratio (1, at 700 W) and input power (2 at 20% BCl_3 and 3 at 60% BCl_3): a) electron temperature; b) total positive ion density; c) ion current density; and d) electron density

Рис. 1. Параметры электронной и ионной компонент плазмы в зависимости от соотношения Cl_2/BCl_3 (1, при 700 Вт) и вкладываемой мощности (2 при 20% BCl_3 и 3 при 60% BCl_3): a) температура электронов; b) суммарная концентрация положительных ионов; c) плотность ионного тока; d) концентрация электронов

RESULTS AND DISCUSSION

Fig. 1 illustrates the influence of Cl_2/BCl_3 mixing ratio and input power on electrons- and ions-related plasma parameters. Corresponding results may briefly be commented as follows:

- Electron temperature (Fig. 1(a)) shows an increase with increasing both BCl_3 fraction in a feed gas and input power. The effect of Cl_2/BCl_3 mixing ratio results from lower electron energy losses for the electronic excitation of BCl_x species compared with those for Cl_2. Corresponding cross-section for chlorine molecules cover the wider energy range (due to lower threshold energies, as follows from Ref. [8]) as well as appear to be higher at electron energies below 20 eV [17]. As such, the substitution of Cl_2 for BCl_3 increases the fraction of "fast" electrons in the EEDF and shifts mean electron energy toward higher values. The effect of input power is surely connected with increasing dissociation degrees for Cl_2 and BCl_3 molecules that produce higher fractions of atomic species at higher input powers. This also results in decreasing electron energy losses, since Cl atoms are characterized by higher excitation thresholds and lower cross-sections compared with parent molecules [17].

- Total density of positive ions (Fig. 1(b)) keeps the nearly constant value vs. Cl_2/BCl_3 mixing ratio as well as shows the monotonic growth with increasing input power. The first phenomenon is due to the nearly constant total ionization frequency. The reason is that a bit lower rate coefficients for R1: BCl_x +

+e $\rightarrow$ BCl_{x-1}^+ + Cl + 2e (max. $k_1 = 2.2\cdot10^{-9}$ cm^3/s for x = 3 at 4 eV) and R2: BCl_x + e $\rightarrow$ BCl_x^+ + 2e (max. $k_2 = 1.8\cdot10^{-9}$ cm^3/s for x = 3 at 4 eV) compared with R3: Cl_2 + e $\rightarrow$ Cl_2^+ + 2e ($k_3 = 3.7\cdot10^{-9}$ cm^3/s at 4 eV) and R4: Cl + e $\rightarrow$ Cl^+ + 2e ($k_4 = 2.4\cdot10^{-9}$ cm^3/s at 4 eV) are compensated by an increase in T_e. Accordingly, an increase in W accelerates the ionization through an increase in both T_e and n_e.

- Ion current density (Fig. 1(c)) (and thus, the ion flux, since $\Gamma_+ \approx J_+/e$) decreases with increasing BCl_3 fraction in a feed gas as well as increases with input power. The formal disagreement between n_+ and J_+ vs. Cl_2/BCl_3 mixing ratio is due to sufficiently increasing effective ion mass that traces the change of the dominant positive ion from Cl^+ to BCl_2^+.

- Electron density (Fig. 1(d)) demonstrates the nearly linear increase with both BCl_3 fraction in a feed gas and input power. In the case of Cl_2/BCl_3 mixing ratio, the reason is a decrease in the total attachment frequency due to k_5 (~ $2.4\cdot10^{-10}$ cm^3/s at 4 eV) >> k_6 (~ $7.3\cdot10^{-11}$ cm^3/s at 4 eV), where R5: Cl_2 + e $\rightarrow$ Cl + Cl^- and R6: BCl_x + e $\rightarrow$ BCl_{x-1}+ Cl^-. That is why, an increase in y(BCl_3) also causes the fall in both relative (n_-/n_e = 0.76-0.38 for 0-80% BCl_3) and absolute ($n_- = 2.7\cdot10^{10}$-$1.7\cdot10^{10}$ cm^{-3} for 0-80% BCl_3) density of negative ions. The effect of input power directly follows from the power balance equation, as shown in Refs. [3, 5].

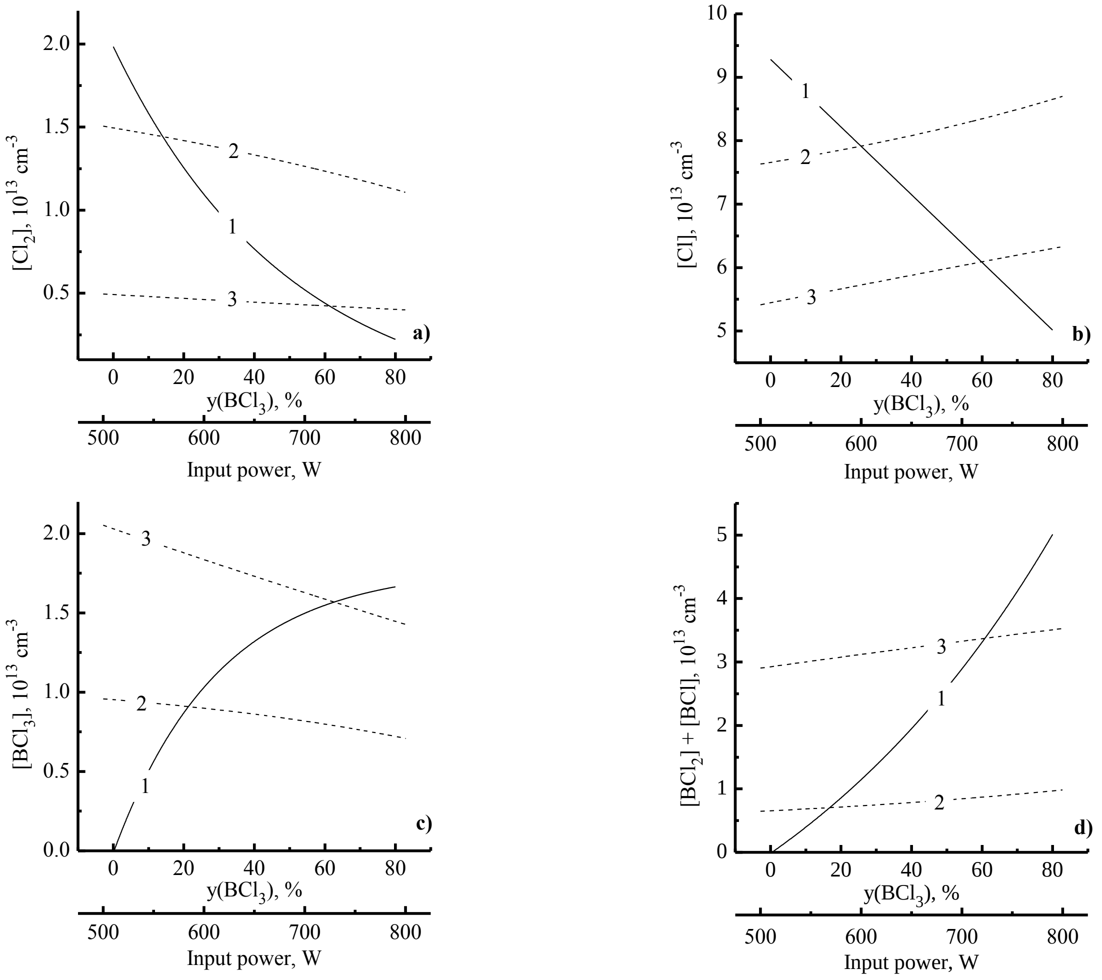

Fig. 2. Densities of neutral species as functions of Cl_2/BCl_3 mixing ratio (1, at 700 W) and input power (2 at 20% BCl_3 and 3 at 60% BCl_3)

Рис. 2. Концентрации нейтральных частиц в зависимости от соотношения Cl_2/BCl_3 (1, при 700 Вт) и вкладываемой мощности (2 при 20% BCl_3 и 3 при 60% BCl_3)

From plasma modeling, it was found that, under the given set of processing conditions, 80% Cl_2 + 20% Ar plasma surely exhibits the condition of [Cl] >> [Cl_2] (Figs. 3(a, b)). Such situation results from high rate coefficient for R7: Cl_2 + e $\rightarrow$ 2Cl + e (k_7 ~ $3.8\cdot10^{-8}$ cm^3/s at 4 eV) due to the low dissociation threshold of about 3 eV. The substitution of Cl_2 for BCl_3 lowers the rate of R7, but introduces new formation pathways for chlorine atoms, such as R1 and R8: BCl_x + e $\rightarrow$ BCl_{x-1} + Cl + e ($k_8 = 1.6\cdot10^{-9}$ cm^3/s for x = 2, 3 and $7.3\cdot10^{-10}$ cm^3/s for

$x = 1$ at 4 eV). The condition k_1, $k_8 << k_7$ limits the total Cl atom formation rate toward BCl_3-rich plasmas and causes the monotonic decrease in the Cl atom density, as shown in Fig. 3(b). The 80% BCl_3 + 20% Ar gas system is characterized by nearly equal densities of Cl atoms and BCl_x radicals as well as by the essential amount of Cl_2. The last feature is provided by R9: $2Cl \rightarrow Cl_2$ on chamber walls. The domination of BCl_2 over BCl ($[BCl_2]/[BCl]$ = 19.2–9.3 for 20-80% BCl_3) is because of their stepwise formation in R8 as well as due to R10: $BCl + Cl_2 \rightarrow BCl_2 + Cl$ ($k_{10} \sim 1.0\cdot10^{-10}$ cm^3/s). Accordingly, since the last process is more effective in Cl_2-rich plasmas, the $[BCl_2]/[BCl]$ ratio shows a decrease with increasing BCl_3 fraction in a feed gas. From Fig. 3, it can be seen also that an increase in input power always lowers densities of original molecules as well as increases densities of dissociation products. This phenomenon simply follows from increasing rates for R1, R7 and R8 due to the same change in n_e. In Cl_2-rich plasmas, the effect of input power on the Cl atom density (by ~ 1.1 times for 500–800 W) is weaker compared with those for BCl_2 (by ~ 1.4 times) and BCl (by ~ 1.7 times). This is because the acceleration of R7 (which is the dominant formation pathway for Cl atoms) is devaluated by the condition $[Cl] >> [Cl_2]$. In BCl_3-rich plasmas, the effect of input power is quantitatively similar for Cl and BCl_2 (by ~ 1.2 times for 500–800 W) but appears to be stronger for BCl (by ~ 1.5 times). Such situation reflects the multi-step formation process for BCl radicals in R8.

Etching experiments indicated that SiO_2 etching rates in pure Ar plasma (in fact, rates of physical sputtering) for input powers of 500-800 W do not exceed 5 nm/min. As can be seen from Fig. 3(a), corresponding values obtained in Cl_2- and BCl_3- containing plasmas occupy the range of 50-120 nm/min. Therefore, it can be assumed that the overall etching mechanism is the ion-assisted chemical reaction with a domination of the chemical etching pathway. Another important feature is that the transition toward BCl_3-rich plasmas causes the non-monotonic (with a maximum of ~ 120 nm/min at 40% BCl_3) change in the SiO_2 etching rate. This contradicts with the monotonic change in Cl atom flux, Γ_{Cl} (as follows from the change in the Cl atom density) as well as corresponds to increasing effective reaction probability $\gamma_R = R/\Gamma_{Cl}$ in the SiO_2 + Cl system (Fig. 3(b)). The change of SiO_2 etching rates with input power in both Cl_2-rich and BCl_3-rich plasmas formally corresponds with that for Γ_{Cl}, but appears to be faster in the quantitative scale. Such situation also corresponds to increasing γ_R values, as shown in Fig. 3(b). Normally, the behavior of γ_R follows the change of ion bombardment intensity through the fraction of free adsorption sites for main etchant species. Corresponding mechanisms are connected with the ion-stimulated desorption (sputtering) of reaction products and/or the destruction of chemical bonds between surface atoms [3]. According to Figs. 3(c), an increase in $y(BCl_3)$ results in increasing negative dc bias voltage at W_{dc} = const and thus, causes the same change in the ion bombardment energy (ε_i = 311-404 eV at 0-80% BCl_3). Together with increasing effective ion molar mass M_i, this overcompensates the decreasing tendency for Γ_+ and produces a growth of the parameter $(M_i\varepsilon_i)^{1/2}\Gamma_+$ (Fig. 3(d)) characterizing the ion bombardment intensity [5, 9-11, 19]. An increase in input power causes either the weak growth (in the case of Cl_2-rich plasma) or the weak fall (in the case of BCl_3-rich plasma) of $(M_i\varepsilon_i)^{1/2}\Gamma_+$ values. Such situation is because an increase in ion flux meets the opposite tendency of ion bombardment energy, as follows from the change in $-U_{dc}$ (Fig. 3(c)). Therefore, when making a comparison between Figs. 3(b) and 3(d), following conclusions can be made:

- In cases of Cl_2/BCl_3 mixing ratio and input power in the Cl_2-rich plasma, an increase in γ_R formally correspond to that for $(M_i\varepsilon_i)^{1/2}\Gamma_+$. At the same time, the last parameter always changes much weaker compared with the first one.
- In the case of input power in the BCl_3-rich plasma, an increase in γ_R contradict with the change in $(M_i\varepsilon_i)^{1/2}\Gamma_+$.

In our opinion, all these suggest that the ion bombardment is not only one and not the main factor influencing the effective reaction probability. Probably, the formation of adsorption sites for Cl atoms is provided by both ion-driven process R11: $SiO_x \rightarrow SiO_{x-1} + O$ and chemical reaction R12: $SiO_x + BCl_x \rightarrow SiO_{x-1} + BCl_xO$. Since the Si-O bond (~ 800 kJ/mol) is a bit weaker compared with the B-O one (~ 810 kJ/mol) [20], R12 has no energy threshold and can occur spontaneously even at nearly room temperatures. As such, it seems to be more effective compared with R11 due to the higher radical flux compared with the ion flux. One should mention also that a) the rule the more BCl_x radical flux, the higher γ_R does work in all investigated range of processing condition; and b) the stronger sensitivity of γ_R to input power takes place in the BCl_3-rich plasma which is characterized by the stronger change in the BCl_x radical density. All these confirm the reasonability of suggested etching mechanism. At the same time, an exact conclusion requires the additional study with including surface diagnostics methods. These are to check the correlation between BCl_x flux and oxygen content on the etched surface.

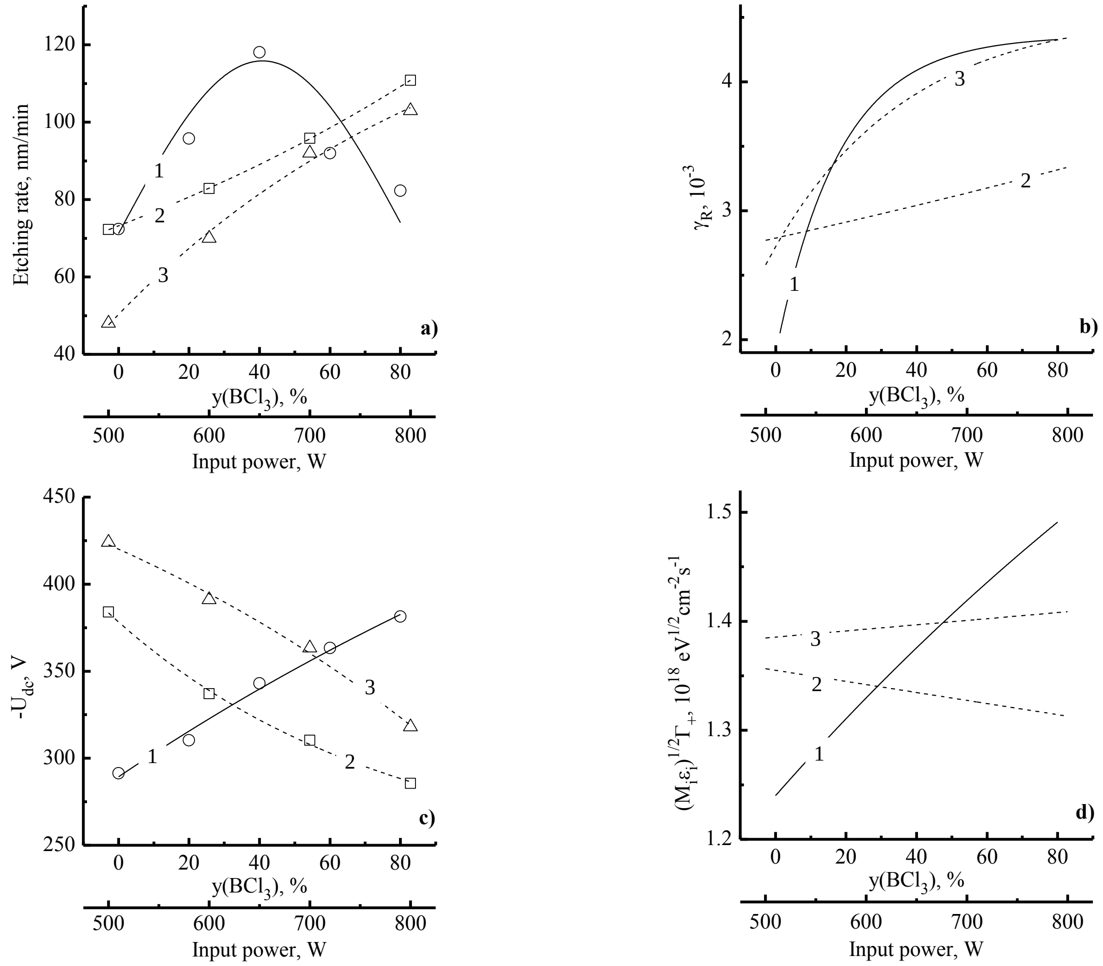

Fig. 3. Parameters characterizing plasma-surface interaction kinetics as functions of Cl_2/BCl_3 mixing ratio (1, at 700 W) and input power (2 at 20% BCl_3 and 3 at 60% BCl_3): a) SiO_2 etching rate; b) effective reaction probability; c) negative dc bias; and d) parameter $(M_i\varepsilon_i)^{1/2}\Gamma_+$ characterizing the ion bombardment intensity

Рис. 3. Параметры, характеризующие кинетику взаимодействия плазмы с поверхностью в зависимости от соотношения Cl_2/BCl_3 (1, при 700 Вт) и вкладываемой мощности (2 при 20% BCl_3 и 3 при 60% BCl_3): a) скорость травления SiO_2; b) эффективная вероятность взаимодействия; c) отрицательное смещение на нижнем электроде; d) параметр $(M_i\varepsilon_i)^{1/2}\Gamma_+$, характеризующий интенсивность ионной бомбардировки

CONCLUSIONS

In this work, we investigated plasma chemistry and SiO_2 etching kinetics in the $Cl_2 + BCl_3 + Ar$ gas mixture. Variable processing parameters were Cl_2/BCl_3 mixing ratio and input power. It was found that the substitution of Cl_2 for BCl_3 increases electron density, reduces plasma electronegativity, enforces ion bombardment as well as lowers both formation rate and density of Cl atoms. A growth of input power leads to the nearly constant ion bombardment intensity (due to opposite changes in ion flux and ion energy), but increases densities of both Cl atoms and BCl_x radicals. It was shown that the change in Cl_2/BCl_3 mixing ratio causes the non-monotonic behavior of SiO_2 etching rate while an increase in both BCl_3 fraction in a feed gas and input power enlarges the effective probability for the SiO_2 + Cl reaction. It was suggested that the last phenomenon is mainly contributed by heterogeneous reactions $SiO_y + BCl_x \rightarrow SiO_{y-1} + BCl_xO$ which increase the amount of adsorption sites for chlorine atoms.

The publication was carried out within the framework of the state assignment of the Federal State Institution «Scientific Research Institute for System Analysis of the Russian Academy of Sciences» (fundamental research) on subject No. 0580-2021-0006 “Fundamental and applied research in the field of lithography limits in semiconductor technologies as well as physical and chemical etching processes for 3D nanometer dielectric structures for the development of critical technologies for the production of ECB. Investigations and developments of both models and constructions for microelectronic elements in the extended temperature range (from -60C to +300C)”.

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

Публикация выполнена в рамках государственного задания ФГУ ФНЦ НИИСИ РАН (проведение фундаментальных научных исследований) по теме № 0580-2021-0006 «Фундаментальные и прикладные исследования в области литографических пределов полупроводниковых технологий и физико-химических процессов травления 3D нанометровых диэлектрических структур для развития критических технологий производства ЭКБ. Исследование и построение моделей и конструкций элементов микроэлектроники в расширенном диапазоне температур (от -60С до +300С)».

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

REFERENCES
ЛИТЕРАТУРА

1. **Nojiri K.** Dry etching technology for semiconductors. Tokyo: Springer Internat. Publ. 2015. 116 p.
2. Advanced plasma processing technology. New York: John Wiley & Sons Inc. 2008. 479 p.
3. **Lieberman M.A., Lichtenberg A.J.** Principles of plasma discharges and materials processing. New York: John Wiley & Sons Inc. 2005. 757 p.
4. **Efremov A., Min N.K., Choi B.G., Baek K., Kwon K.-H.** Model-Based Analysis of Plasma Parameters and Active Species Kinetics in Cl2/X (X = Ar, He, N_2) Inductively Coupled Plasmas. *J. Electrochem. Soc.* 2008. V. 155. N 12. P. D777-D782. DOI: 10.1149/1.2993160.
5. **Efremov A.M., Kim G.H., Kim J.G., Bogomolov A.V., Kim C.I.** Applicability of self-consistent global model for characterization of inductively coupled Cl_2 plasma. *Vaccum*. 2007. V. 81. N 5. P. 669-675. DOI: 10.1016/j.vacuum.2006.09.017.
6. **Corr C.S., Despiau-Pujo E., Chabert P., Graham W.G., Marro F.G., Graves D.B.** Comparison between fluid simulations and experiments in inductively coupled argon/chlorine plasmas. *J. Phys. D. Appl. Phys.* 2008. V. 41. N 18. P. 185202. DOI: 10.1088/0022-3727/41/18/185202.
7. **Tinck S., Boullart W., Bogaerts A.** Simulation of an Ar/Cl_2 inductively coupled plasma: study of the effect of bias, power and pressure and comparison with experiments. *J. Phys. D. Appl. Phys.* 2008. V. 41. N 18. P. 065207. DOI: 10.1088/0022-3727/41/6/065207.
8. **Meeks E., Ho P., Ting A., Buss R.J.** Simulations of BCl_3/Cl_2/Ar plasmas with comparisons to diagnostic data. *J. Vac. Sci. Technol. A.* 1998. V. 16. P. 2227-2239. DOI: 10.1116/1.581332.
9. **Kim M., Min N.-K., Yun S. J., Lee H. W., Efremov A., Kwon K.-H.** On the etching mechanism of ZrO_2 thin films in inductively coupled BCl_3/Ar plasma. *Microelect. Eng.* 2008. V. 85. P. 348–354. DOI: 10.1016/j.mee.2007.07.009.
10. **Kim M., Min N.-K., Yun S.J., Lee H. W., Efremov A., Kwon K.-H.** Effect of gas mixing ratio on etch behavior of ZrO_2 thin films in BCl3/He inductively coupled plasma. *J. Vac. Sci. Technol. A.* 2008. V. 26. N 3. P. 344-351. DOI: 10.1116/1.2891255.
11. **Kim M., Efremov A., Hong M. P., Min N. K., Park H.-H., Baek K.-H., Kwon K.-H.** Effect of gas mixing ratio on etch behavior of Y2O3 thin films in Cl2/Ar and BCl3/Ar inductively coupled plasmas. *Japan. J. Appl. Phys.* 2010. V. 49. P. 08JB04. DOI: 10.1143/JJAP.49.08JB04.
12. **Malyshev M.V., Donnelly V.M., Kornblit A., Ciampa N.A.** Percent dissociation of Cl_2 in inductively coupled chlorine-containing plasmas. *J. Appl. Phys.* 1998. V. 84. N 1. P. 137-146. DOI: 10.1063/1.368010.
13. **Malyshev M.V., Donnelly V.M.** Diagnostics of inductively coupled chlorine plasmas: Measurement of Cl_2 and Cl number densities. *J. Appl. Phys.* 2000. V. 88. N 11. P. 6207-6215. DOI: 10.1063/1.1321777.
14. **Lee J., Efremov A., Lee B. J., Kwon K.-H.** Etching Characteristics and Mechanisms of TiO_2 Thin Films in CF_4 + Ar, Cl_2 + Ar and HBr + Ar Inductively Coupled Plasmas. *Plasma Chem. Plasma Proc.* 2016. V. 36. N 6. P. 1571-1588. DOI: 10.1007/s11090-016-9737-y.
15. **Kim M., Efremov A., Lee H. W., Park H.-H., Hong M.P., Min N.K., Kwon K.-H.** HfO_2 etching mechanism in inductively-coupled Cl_2/Ar plasma. *Thin Solid Films*. 2011. V. 519. P. 6708-6711. DOI: 10.1016/j.tsf.2011.04.059.
16. **Shun'ko E.V.** Langmuir probe in theory and practice. Boca Raton: Universal Publ. 2008. 245 p.
17. **Raju G.G.** Gaseous electronics. Tables, Atoms and Molecules. Boca Raton: CRC Press. 2012. 790 p.
18. **Christophorou L.G., Olthoff J.K.** Fundamental electron interactions with plasma processing gases. New York: Springer Science+Business Media LLC. 2004. 776 p.
19. **Efremov A., Murin D., Kwon K.-H.** Plasma parameters, densities of active species and etching kinetics in C_4F_8+Ar gas mixture. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2019. V. 62. N 2. P. 31-37. DOI: 10.6060/ivkkt.20196202.5791.

    Ефремов А.М., Мурин Д.Б., Квон К.Х. Параметры плазмы, концентрации активных частиц и кинетика травления в смеси C_4F_8+Ar. *Изв. вузов. Химия и хим. технология*. 2019. Т. 62. Вып. 2. С. 31-37. DOI: 10.6060/ivkkt.20196202.5791.
20. CRC Handbook of Chemistry and Physics. New York: CRC Press. 2010. 2760 p.

Поступила в редакцию 10.06.2021
Принята к опубликованию 17.01.2022

Received 10.06.2021
Accepted 17.01.2022