

# NUMERICAL MODELING OF HEAT-MASS TRANSFER IN RADIAL FLOW PLASMA-CHEMICAL REACTOR WITH MULTICOMPONENT KINETICS $CF_4/O_2$

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## Introduction

The binary gas mixture  $CF_4/O_2$  is widely used in industrial production of semiconductor devices to increase the etching rate of silicon wafers. The number of papers devoted to mathematical modeling of silicon etching in  $CF_4/O_2$  plasma is relatively small. Moreover, the numerical modeling of silicon etching with simplifying kinetics of the gas phase and heterogeneous chemical reactions predicts a maximum of the etching rate near the 50% fraction of  $O_2$  in the parent gas mixture [1]. This is inconsistent with experimental data where the maximum etching rate detected was at the 15-30% range of  $O_2$ .

In this paper, the results of numerical optimization of a radial flow plasma-chemical reactor depending on the binary gas composition  $CF_4/O_2$  are presented. Quantitative estimations of oxygen chemisorption and adsorption of  $CF_2$ ,  $CF_3$  contributions to the etching rate are obtained.

## Mathematical model of radial flow plasma-chemical reactor

The authenticity of received numerical results depends on the choice of chemical kinetics of plasma etching. Using comparison with experimental data for plasma  $CF_4/O_2$  in [2] the minimum set of chemical reactions was derived which satisfactorily predicted the concentrations of stable reaction products  $COF_2$ ,  $CO_2$ ,  $CO$  and  $F$ . In [3] this basic set of reactions was added by heterogeneous reactions of species  $F$ ,  $CF_2$ ,  $CF_3$ ,  $CF_4$ ,  $O$  to describe the adsorption of  $CF_2$ ,  $CF_3$ . The improved chemical kinetic model [3] including 12 components –  $F$ ,  $F_2$ ,  $CF_2$ ,  $CF_3$ ,  $CF_4$ ,  $C_2F_6$ ,  $O$ ,  $O_2$ ,  $CO$ ,  $CO_2$ ,  $COF$ ,  $COF_2$  was used in present calculations. The heat-mass transfer in the reactor was calculated on the base of two-dimensional mathematical model of nonisothermal reactor [4] with taking into account the chosen multicomponent chemical kinetics. The heat radiation in the gas mixture was determined in optical thin layer approximation. To evaluate the emissivity of gas mixture the exponential model of band adsorption [5] describing the spectral adsorption of multiatomic molecule was employed. The experimental data shown that the radicals  $CF_2$ ,  $CF_3$ ,  $C_2F_4$ ,  $C_2F_5$  adsorbed on silicon surface form the recombination sites acting as a barrier preventing an etching. The quantitative estimations for silicon etching in pure  $CF_4$  presented in [4] have shown that the effect of  $CF_3$  adsorption on etching rate does not exceed 5%. In  $CF_4/O_2$  plasma the oxygen reacts with  $CF_x$  radicals preventing their recombination with  $F$  and reducing their concentrations. Nevertheless it is of interest to estimate the influence of adsorption layers on the etching rate also in this case. It is of great significance during silicon etching a formation of active centers of fluorine and oxygen atoms on silicon surface. This process was described in approach represented in [6]. The governing equations were numerically solved on the base of iterative finite-difference splitting-up schemes with stabilizing correction.

## Results and discussion

The calculations of loaded reactor have been completed for several values of gas flow rate  $Q$  and wafer temperature  $T_s$  presented in Table 1. The pressure in etching chamber of reactor was equal to  $p = 0.5$  torr. The average electron density was assumed equal to  $n_e = 6 \times 10^9$ ,  $cm^{-3}$ . The temperature of reactor walls –  $T_w = 300$  K. The  $O_2$  percentage fraction in  $CF_4/O_2$  feed gas

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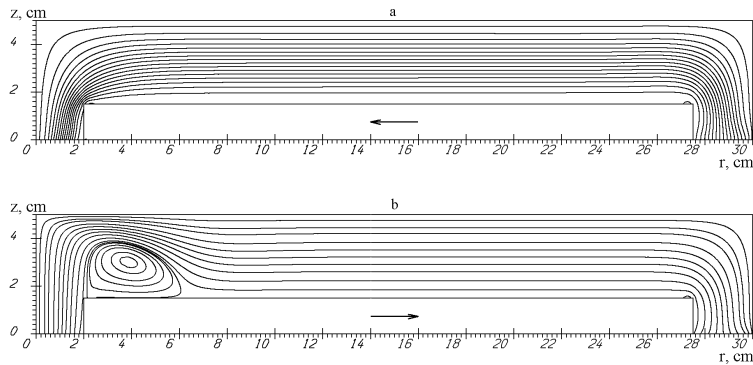


Fig. 1. Isolines of stream function in the radial flow reactor. The arrowed line shows the directions of gas flow in the reactor: a – “inflow”, b – “outflow”. Processing regime:  $p = 0.5$  torr,  $Q = 800$  cm<sup>3</sup>/min,  $T_s = 300$  K, 30% fraction of O<sub>2</sub> in CF<sub>4</sub>/O<sub>2</sub> input gas mixture.

mixture varied in the range 10-90%. In order to compare the results of our calculations with the results [3] the constructive dimensions and operating regimes were taken as in [3]. The wafer temperatures coincided with data [7]. Two gas flow directions were examined: “inflow”, when the gas flow was directed to the center of reactor, and “outflow” - with reversed direction.

**Flow structure and heat transfer.** The isolines of stream function in radial flow reactor are presented on Figure 1. The direction of feed gas flow determined a peculiarities of flow structure in the reactor. In the “inflow” case the flow structure in the etching chamber has no large vortices. The velocity distribution in the reactor is weakly dependent on gas flow rate and wafer temperature. Under “outflow” direction a vigorous gas stream is injected to the etching chamber and then is spreaded out along the RF-electrodes. Near the inlet tube arranged in the centre of lower electrode the recirculating vortical zone is formed. The radial dimension of vortical zone is increased with rising of gas flow rate or decreasing of O<sub>2</sub> percentage fraction in mixture. The ratio of characteristic velocities  $w_i$  to  $w_0$  at inner and outer reactor edges approximately consists of  $w_i / w_0 \sim 10^2$ .

For both feed gas flows the temperature of gas mixture monotonically rises along the flow direction. The maximum gas temperature localizes near the wafer. For “inflow” direction it lo-

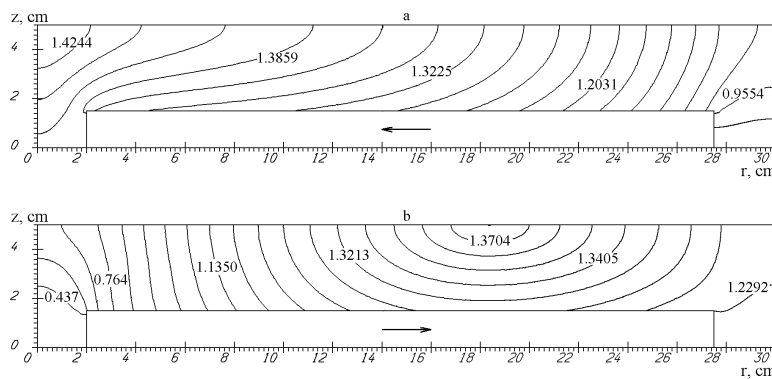


Fig. 2. Isolines of fluorine concentration,  $C_F \times 10^{-8}$  Mol/cm<sup>3</sup>. Processing regime:  $p = 0.5$  torr,  $Q = 200$  cm<sup>3</sup>/min,  $T_s = 300$  K, 40% fraction of O<sub>2</sub> in CF<sub>4</sub>/O<sub>2</sub> input mixture.

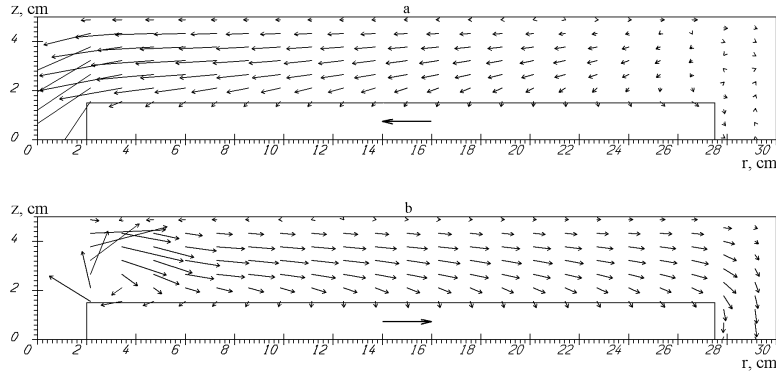


Fig. 3. Distribution of full flow of active species. Processing regime: see Fig.2.

cates in the range  $r = 2.9-11.8$  cm (Fig. 1,a). In opposite case it correspondingly falls within the range  $r = 15.0-21.4$  cm (Fig. 1,b). The typical differences of gas temperature in the reactor are found in interval 42-177 K. The rise of  $O_2$  fraction of in the range 10-90% in gas mixture reduces the gas temperature on 9-40 K, that is explained by the decreasing of emissivity of gas mixture. With the rising of wafer temperature the radial temperature gradients are increased that brings down an etching wafer uniformity. The distribution of full heat flow for the most part of reactor coincides with the direction of convective transfer. Over the wafer the axial component in the full heat flow is defined by the heat conduction and heat radiation flows. The contributions of heat conduction and heat radiation flows in the full heat flow are relatively small.

**Mass transfer.** The distribution of fluorine concentration in the reactor depends on many factors: operating regime of reactor, gas composition, direction of feed gas flow and etc. Figure 2 illustrates typical distribution of fluorine concentration in the reactor. If the feed gas flows to the center of reactor the fluorine concentration monotonically rises along the flow direction owing to the convective transfer (Fig. 2,a). The maximum of concentration is located near the upper electrode at  $r = 0-2.1$  cm. If the feed gas flows from a center of reactor the distribution of fluorine concentration is also monotone (Fig. 2,b). However at any fixed cross section by the height of reactor the fluorine concentration has the local minimum in the range  $r = 16.9-20.0$  cm. The position of concentration maximum is removed along the upper electrode with variation in the operating regime. Figure 3 illustrates the distribution of full flow of active species. The direction of fluorine mass transfer in middle part of reactor height, where  $|\mathbf{v}| \gg w_0$ , coincides with the direction of gas flow ( $\mathbf{v}$  – velocity vector). Near the RF-electrodes, where the velocity of gas flow is small, the fluorine mass transfer is realized by a concentration diffusion. Owing to intensive forced convection the nonuniform distribution of full flow of active species on the wafer is arised. Because of that the full flow of active species deviates from the normal to the wafer. Finally as one can see from Fig. 3, the mass transfer of fluorine atoms to the wafer surface depends strongly on the convective transfer in the reactor.

**Etching rate and uniformity.** The local spontaneous etching rate, its average value and uniformity index were calculated by the formulas [7, 8]:

$$V_s = 1.81 \cdot 10^{10} (1 - \vartheta_{O} - \vartheta_{CF_2} - \vartheta_{CF_3}) k_s x_F C_t, \quad (1)$$

$$\bar{V}_s = \frac{2}{R_o^2 - R_i^2} \int_{R_i}^{R_o} V_s r dr, \quad I_n = \frac{V_{s2} - V_{s1}}{2\bar{V}_s},$$

where  $V_s, V_{s1}, V_{s2}$  – local, minimum and maximum spontaneous etching rates;  $\vartheta_O$  – fraction of silicon surface covered by oxygen atoms,  $\vartheta_{CF_2}, \vartheta_{CF_3}$  – fractions of silicon surface covered by adsorbed radicals  $CF_2$  and  $CF_3$  correspondingly,  $k_s$  – etching rate constant. To simplify a representation of  $\vartheta_O$  it is assumed that  $C_F \gg C_{CF_2}, C_{CF_3}$ . Thus  $\vartheta_O$  can be represented as

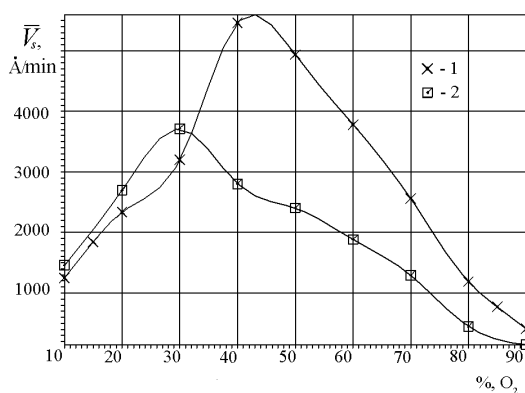
$$\vartheta_O \approx \frac{\nu_O \alpha_O}{\nu_O \alpha_O + \nu_F \alpha_F},$$

where  $\nu_F, \nu_O$  – molar flux of fluorine and oxygen atoms to the wafer;  $\alpha_F = 0.7, \alpha_O = 0.2$  – sticking coefficients of oxygen and fluorine atoms on silicon [6], and the denominator shows a competition of chemisorption of oxygen and fluorine atoms on silicon. The explicit expressions for  $\vartheta_{CF_2}, \vartheta_{CF_3}$  are not presented here because of its awkwardness. They are similar to used in [3], but here in addition we take into account an oxygen chemisorption.

The average etching rate dependence on percentage fraction of  $O_2$  in parent gas mixture has the maximum near 40% of  $O_2$  in the range of gas flow rate 100-400  $cm^3/min$  (Fig. 4, curve 1). With increasing of gas flow rate up to 800  $cm^3/min$  the maximum of etching rate moves to 30% of  $O_2$  (Fig. 4, curve 2). The location of extremum is independent of the feed gas flow direction and the gas temperature.

With increasing  $O_2$  percentage in  $CF_4/O_2$  gas mixture the fluorine concentration rises and has the maximum at 40%  $O_2$ . Decreasing  $CF_2, CF_3, CF_4, COF$  concentrations accompanies by the growth of fluorine concentration. The substances  $F_2, CO, CO_2, COF_2$  are formed as the products of reactions. It corresponds to one of channels of etching intensification by oxygen addition, which consists in replacement of fluorine by oxygen in fluorine-containing radicals. With oxygen addition more than 40% the fluorine concentration falls owing to decreasing total number of  $CF_2, CF_3$  radicals (depletion of mixture). Thus the calculation shows that the presence of etching rate maximum connects with chemical reactions of oxygen atoms with  $CF_2, CF_3$  radicals where the additional fluorine atoms set free. The maxima of etching rate and fluorine concentration coincide with respect to  $O_2$  addition in  $CF_4/O_2$  gas mixture.

The etching rate dependence on fluorine concentration with different fractions of  $O_2$  in  $CF_4/O_2$  mixture obtained in calculations has a hysteresis character (Fig. 5, curve 1). Because of the passivation of wafer surface by oxygen atoms (increasing  $\vartheta_O$ ) in the range of  $O_2$  concentration more than 40% the silicon etching rate falls more quickly than fluorine concentration (see formula (1)). At the same time the hysteresis is not observed under the absence of oxygen chemisorption. It is illustrated by the linear dependence of  $\bar{V}_s$  on  $\bar{C}_F$  (curve 2 at Fig. 5) obtained for  $\vartheta_O = 0$  and any fraction of  $O_2$  in mixture.



This fact corroborates with the results [9] where the hysteresis was experimentally detected and the assumption about its connection with oxygen chemisorption have been made. The influence of

Fig. 4. Average etching rate as a function of percentage fraction of  $O_2$  in  $CF_4/O_2$  input mixture. 1 –  $Q = 200 \text{ cm}^3/min$ , 2 –  $Q = 800 \text{ cm}^3/min$ . Processing regime:  $p = 0.5 \text{ torr}$ ,  $T_s = 300 \text{ K}$ . “Inflow” direction was examined. Numerical results were marked by points, solid lines – spline approximation.

CF<sub>2</sub>, CF<sub>3</sub> adsorption layers on the etching rate beginning from 5% O<sub>2</sub> concentration composes less 1% of nominal value.

The high etching uniformity may be achieved by controlling the processing regimes of reactor (gas flow rate, temperature, gas composition and etc.). As in [3] it is found that the minimum etching nonuniformity is realized at the small gas flow rates (Table 1, gas flow rate 100 cm<sup>3</sup>/min). Here it is possible the effective control of etching rate by changing the ratio CF<sub>4</sub>/O<sub>2</sub>. The rise of gas flow rate causes the increase of etching nonuniformity independently of feed gas flow direction. Note that at the gas flow rates larger then 200 cm<sup>3</sup>/min the quality of silicon etching does not correspond to requirements for semiconductor wafers. Table 1 shows that the “inflow”

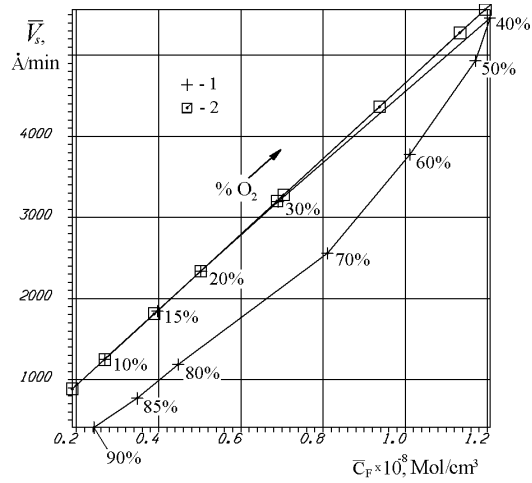


Fig. 5. Average etching rate as a function of average fluorine concentration on silicon with different fractions of O<sub>2</sub> in CF<sub>4</sub>/O<sub>2</sub> mixture. 1 –  $\mathcal{G}_O \neq 0$ ; 2 –  $\mathcal{G}_O = 0$ . Processing regimes:  $p = 0.5$  torr,  $Q = 200$  cm<sup>3</sup>/min,  $T_s = 300$  K. “Inflow” direction was examined.

Table 1. Uniformity index as a function of gas flow rate and wafer temperature. 30% fraction of O<sub>2</sub> in CF<sub>4</sub>/O<sub>2</sub> input mixture. “Inflow” and “outflow” directions were examined.

$Q$ , cm <sup>3</sup> /min	$T_s$ , K	$I_n$ , (Inflow)	$I_n$ , (Outflow)
100	300	0.05928	0.05385
200	300	0.09776	0.29991
200	373	0.07574	0.26711
200	473	0.05121	0.26986
200	573	0.03737	0.27081
400	300	0.20619	0.46885
800	300	0.39062	0.58001

direction is more preferable because of uniformity index decreases with rising of gas temperature. The dependence of etching nonuniformity on percentage fraction of O<sub>2</sub> has not pronounced tendency. But its high value at percentage fraction of O<sub>2</sub> more then 80% is common for all operating regimes. At this feed gas composition even if the gas flow rate is 100 cm<sup>3</sup>/min the large gradients of fluorine concentration are appeared. The influence of oxygen chemisorption on silicon surface on uniformity index is weak.

### Conclusions

The obtained results allow to make the following conclusions.

1. The oxygen addition allows to increase the etching rate in several times and it is an effective factor for controlling the process regime. The appearing etching rate maximum connects with chemical reactions of oxygen atoms with CF<sub>2</sub>, CF<sub>3</sub> radicals in which the additional fluorine atoms set free.

2. The fluorine and oxygen chemisorption on silicon leads to hysteresis on the diagram of etching rate with respect to fluorine concentration. Under the absence of oxygen chemisorption the hysteresis is absent too. The influence of  $CF_2$ ,  $CF_3$  adsorption layers on the etching rate composes less 1% of nominal value.

3. The fluorine transfer in the radial flow reactor to the wafer essentially depends on convective transfer. The minimum etching nonuniformity is realized at the small gas flow rates ( $100 \text{ cm}^3/\text{min}$ ) where fluorine transfer is determined by a concentration diffusion to the wafer. Here it is possible the effective control of etching rate by changing the ratio  $CF_4/O_2$ . The "inflow" direction of feed gas mixture provides the best etching uniformity and it is more preferable. At the gas flow rates larger than  $200 \text{ cm}^3/\text{min}$  the quality of silicon etching does not correspond to requirements for semiconductor wafers.

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