# MASS SPECTROMETRIC DETERMINATION OF REACTION RATES DURING PLASMA PROCESSING OF LAYERS

J.Trnovec[1], V.Martišovitš[1], G.Cicala[2], P.Capezzuto[2], G.Bruno[2], R. Jurani[1]

[1]Komensky University, Mlynska dolina F2, 84215 Bratislava, Slovakia
[2]Centro di Studio per la Chimica dei Plasmi, Dipartimento di Chimica, Università di Bari, Via Orabona 4, 70126 Bari, Italy

The mass spectrometry (MS) of stable species and determination of the rates of chemical reactions occurring in gas phase and on treated surfaces are discussed. The presented approach deals with basic equations of chemical kinetics, gas flow analysis and calibration of the mass spectrometer. To verify this approach, experimental data obtained during etching of amorphous silicon in $NF_3$ plasma have been evaluated.

## I. Formulation of the Problem

### *Kinetics of volume and surface processes*

The occurrence of chemical reactions in a discharge plasma leads to the variation of fluxes of stable molecules (reactants and products). The mass balance equation of each stable species gives a relationship between the difference of outlet and inlet flux and the rates of the overall reaction. Let $J$ types of stable molecules take part in $K$ independent chemical reactions which occur with rates $R_k$. The flux difference $\Delta I_j$ due to reactions occurring in the gas phase and on treated surface is given by the sum of contributions of all reaction rates [1]:

$$\Delta I_j = \sum_{k=1}^{K} a_{jk} R_k . \qquad (1)$$

The proportionality factors $a_{jk}$ represent the stoichiometric coefficients in the overall reactions. The reaction rates can be evaluated from (1) when the values of flux differences $\Delta I_j$ can be experimentally determined (e.g. from MS measurements). The number of independent equations in the set (1) is always lower than the number of chemical compounds. Therefore the reaction rates could be determined from the flux differences of such species where mass spectrometric measurements can be performed. The simultaneous measurement of the total rate of conversion of key reactant and the rates of reactions producing new stable molecules enables to evaluate the relative importance of the gas phase and surface processes [2].

*Determination of fluxes of molecules and mass spectrometer calibration*

The flux difference of molecules in a flow reactor due to the presence of the chemical reactions in discharge plasma could be written as:

$$\Delta I_j = I_j - I_{j0} \tag{2}$$

where $I_j$ is the outlet flux when plasma is ignited, $I_{j0}$ is the inlet flux of molecules (assumed the same in the states plasma off and on). The values of $I_{j0}$ can be measured by a flowmeter and fluxes $I_j$ should be determined by the MS measurements.
In ref.[3] the use of partial pressure calibration is recommended for the determination of flow rate of the specific species $Q_j$ (in torr.ls$^{-1}$) according to the expression:

$$Q_j = S_j^{(r)} \xi_j p_j^{(s)} \tag{3}$$

where $S_j^{(r)}$ is the effective reactor pumping speed for species $j$, $\xi_j$ is the ratio of the reactor pressure and mass spectrometer pressure $p_j^{(s)}$. If the flux of molecules into the mass spectrometer is negligible then the flux of molecules entering reactor pump can be identified with the flux leaving reactor $I_j$. Then the flux of molecules $I_j$ (in s$^{-1}$) obtained from (3) is:

$$I_j = S_j^{(r)} \xi_j p_j^{(s)} / (kT) \tag{4}$$

where $k$ and $T$ are Boltzmann constant and absolute temperature, respectively. The ion peak intensity $i_j$ of ion with mass $m$ originated from the fragmentation of molecule of mass $m_j$ in ion source is related to the partial pressure in spectrometer $p_j^{(s)}$ [4]:

$$p_j^{(s)} = \frac{i_j}{\sigma_j(m) F(m)} \tag{5}$$

where $\sigma_j(m)$ is the partial ionisation cross section of the molecule of mass $m_j$ for ion of mass $m$, $F(m)$ is the product of ion transmission efficiency of the spectrometer and the detector sensitivity for specified ion. $S_j^{(r)}$ can be expressed by pumping speed at pump inlet $S^{(n)}$ and the conductance $C_j^{(r)}$ of connection of plasma reactor and vacuum pump.

Using substitution for $p_j^{(s)}$ and $S_j^{(r)}$ in Eq. (4) the flux of molecules leaving the reactor is:

$$I_j = \frac{S^{(n)} C_j^{(r)}}{S^{(n)} + C_j^{(r)}} \frac{\xi_j}{\sigma_j(m)\ F(m)\ kT}\ i_j . \tag{6}$$

Generally, the vacuum conductance is a function of the fluxes of all species and (6) represents a set of non-linear equations for unknown fluxes.
The introducing of the overall calibration factor $K_j$ including all quantities except $i_j$ leads to:

$$I_j = K_j(S^{(n)}, C_j^{(r)}, \sigma_j, F, \xi_j)\ i_j . \tag{7}$$

The equation (7) provides the possibility to calibrate the mass spectrometer output for known values of fluxes i.e. to evaluate the calibration factors by means of relation:

$$K_{jCal} = \frac{I_{jCal}}{i_{jCal}}. \tag{8}$$

The flux difference $\Delta I_j$ (2) can be rewritten using the measured ion peak intensity $i_j$ as:

$$\Delta I_j = K_j\, i_j \; - \; I_{j0}. \tag{9}$$

According to the mentioned dependence of $C_j^{(r)}$ on all partial fluxes, the calibration factor is a complicated function of molar fractions $x_j = I_j / \sum_i I_i$. Therefore the values of $K_j$ in the state "plasma on" differ from those values $K_{jCal}$ obtained in the calibration procedure performed usually at different conditions. The extension of the direct partial flux calibration to the state "plasma on" depends on the kinetic flow regime in the apparatus. Two extreme cases of flow are analysed from point of view of mass spectrometer calibration .

**Molecular flow.** As the vacuum conductance is a function of mass of molecules $m_j$, the value of conductance $C_j^{(r)}$ differs for various species. The flows of single species can be considered to be independent and values of coefficients $K_{jCal}$ can be determined by calibration procedure using Eq. (8) for all components of the gas mixture of reactants and products. The coefficients $K_{jCal}$ obtained by this calibration procedure can be used during etching (i.e. plasma on). The flux difference in the state "plasma on" and "plasma off" is $\Delta I_j = K_{jCal}\ (i_j - i_{j0})$ or $\Delta I_j = K_{jCal}\ \Delta i_j$.

**Viscous flow.** The effective pumping speed is the same for all species (as relation $C_j^{(r)} = C^{(r)}$ is valid) but it depends on the total gas pressure and gas mixture composition. The set of values of $K_{jCal}$ ($K_{jCal}$ differ each other due to molecular flow at the mass spectrometer) can be obtained for mixture of reactants and products with known values of gas flow rates. Because of dependence of the calibration coefficient on gas mixture composition and total pressure, these coefficients $K_j$ are different in the plasma mixture. Therefore, the set of $K_{jCal}$ enables to calculate only the estimation of gas fluxes of molecules:

$$I_{jEstimate} = K_{jCal}\, i_j. \tag{10}$$

The following step is the correction of the value of the gas mixture viscosity $\eta$. As the value of $S^{(r)}$ is the same for all species, the relative distribution of fluxes given by equation (10) is correct and suitable for calculation of accurate value of coefficient of viscosity $\eta$ using formula [5]:

$$\eta = \sum_j \frac{x_j\, \eta_j}{\sum_k x_k \Phi_{jk}} \tag{11}$$

where function $\Phi_{jk}$ is taken from ref. [5]. New values of conductance $C^{(r)}$ can be calculated using value $\eta$. The corrected values of the coefficients $K_j$ can be obtained from relation:

$$K_j = K_{jCal} \frac{C^{(r)}}{C^{(r)}_{Cal}} \frac{S^{(n)} + C^{(r)}_{Cal}}{S^{(n)} + C^{(r)}}. \tag{12}$$

The correct values of the flux differences can be obtained from (9) using coefficients given by equation (12).

**Experimental procedure of the determination of the flux difference.** Usually the flow regime varies along the vacuum system of the plasma chemical reactor. Owing to this effect the value $K_j$ can not be calculated by any explicit formula and must be experimentally determined.

One possibility is an extrapolation of the calibration data for the state "plasma on". For this purpose the calibration procedure (in accordance with Eq. 8) should be carried out using a mixture of reactants and products at the total pressure near to a value measured in discharge plasma. If the significant changes of the gas mixture composition induce a small variation of the calibration coefficient (caused by small variation of the viscous coefficient, see Fig. 1), then its value can be expressed by Taylor's linear approximation

$$K_j = K_{jCal} + \sum_{i=1}^{J} \frac{\partial K_j}{\partial I_i} \Delta I_i. \tag{13}$$

The derivatives in (13) should be experimentally determined in the calibration mode. If the derivatives differ a little from each other, then the calibration factor is a function of total flux only.

Another way how to obtain directly the values $\Delta I_j$ consists in a calibration procedure using a simulation of gas mixture (consisting of reactants and products). In the first step, the mass spectrum of discharge plasma should be recorded. In the next step, a simulation of a mixture consisting of reactants and products is supposed. This simulation can be done by the variation of flow rates of reactants and by addition of a controlled amount of products to obtain a mass spectrum similar to situation when the plasma is present. The observed variation in the flow rates corresponds to flux differences $\Delta I_j$ due to the chemical reactions running in the plasma. The major drawback of this method is that the simulation represents a remarkably tedious work especially if number of species increases. An advantage of interpolation is to be taken to reduce the extend of this procedure.

## II. Application to Si etching by $NF_3$ plasma

### *Chemical reactions in $NF_3$ plasma*

The overview of chemical reactions occurring in gas phase and on etched surface can be found in [6]. The presence of electron impact dissociation of $NF_3$ molecules

in discharge plasma and the following recombination of radicals leads to the new stable molecules. First conversion reaction of $NF_3$ molecules produces molecules $N_2$ and $F_2$:

$$NF_3 \rightarrow 1/2\, N_2 + 3/2\, F_2. \qquad (14)$$

The rate of reaction (14) will be denoted as $R_1$. In paper [6] the occurrence of the additional association channel producing molecules $N_2F_4$ is presented. This reaction can be described in the following way:

$$NF_3 \rightarrow 1/2\, N_2F_4 + 1/2\, F_2 \qquad (15)$$

whose reaction rate is $R_2$. The reaction (15) produces the new stable molecules $N_2F_4$, its stoichiometry is different from the reaction (14). Generally, both reaction channels (14), (15) occur simultaneously in the gas phase of $NF_3$ plasma.
The influence of the a-Si etching on plasma kinetics was included in similar way. The fast dissociation processes of $NF_3$ molecules occurring in plasma volume produce free F atoms that are etchants for a-Si. We have considered a production of three F atoms from one $NF_3$ molecule. Then the etching reaction can be expressed :

$$NF_3 + 3/4\, Si \rightarrow 3/4\, SiF_4 + 1/2\, N_2. \qquad (16)$$

A comparison of Eq. (16) with equations characterizing the volume processes shows that the etching of a-Si layer can strongly affect the measured stoichiometry of the overall reaction. During etching of a-Si layer in $NF_3$ plasma, the conversion of $NF_3$ molecules occurs through all mentioned channels. In this case the set of Eqs. (1) reduces to three linear independent equations that provide the determination of the reaction rates of all the above mentioned reactions:

$$\Delta I(NF_3) = -(R_1 + R_2 + R_3) = -R \qquad (17a)$$
$$\Delta I(N_2) = 1/2\, R_1 + 1/2\, R_3 \qquad (17b)$$
$$\Delta I(SiF_4) = 3/4\, R_3. \qquad (17c)$$

*Experimental*

Experiments have been carried out in a parallel-plate plasma reactor developed for deposition of high quality a-Si films [7]. The plasma etching of inner surfaces was used as a standard cleaning procedure. The $NF_3$ flow rate was 7 sccm, the total gas pressure was in the range 200-300 mtorr. The electrode area was 100 $cm^2$, the electrode gap 3.5 cm. The discharge was driven by a 13.56 MHz generator. Mass spectra have been measured by Balzers QMA 311 quadrupole mass spectrometer connected to the reactor outlet by stainless steel tube about 1 m long with 6 mm of inner diameter. Gas flow rates were measured by means of MKS mass flow controllers.

The mass spectra have been taken during a-Si etching in $NF_3$ plasma. A calibration gas mixture consisting of $NF_3$, $N_2$ and $SiF_4$ was used for the calibration of mass spectrometer. As the differences of the viscous coefficients of the gas mixture

components in the plasma reactor are small ($\eta(NF_3) = 190$ μP, $\eta(N_2) = 177$ μP, $\eta(SiF_4) = 180$ μP), the calibration coefficient has been corrected taking into account only the gas pressure dependence. Fig. 2 shows the measured dependence of the effective pumping speed versus pressure in the plasma reactor for $NF_3$ molecules. The monitoring of the flux differences of $NF_3$, $N_2$ and $SiF_4$ by the corresponding ion peak intensities yields all three reaction rates.

The relative contribution of a-Si etching in $NF_3$ plasma kinetics depends on magnitude of the etched area. The ratio of a-Si etching rate to the total rate of $NF_3$ conversion has varied from 30%, when a sample with area of 86 $cm^2$ was used, to the value 95 %, when the whole inner surface (about 400 $cm^2$) was etched. In the last case nearly all reactive species originated within plasma volume are consumed due to etching, i.e. etching can be considered as a gas flow limited process.

The proposed method enables to check the relative importance of the gas phase and surface processes. This approach can be easily applied to a variety of plasma chemical reactors.

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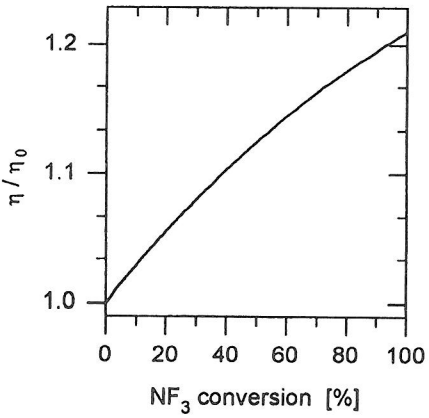


Fig. 1 The calculated relative viscosity of gas mixture as a function of $NF_3$ conversion due to plasma decomposition.

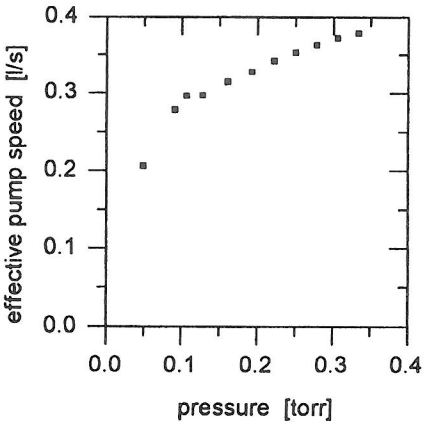


Fig. 2 The determinated effective pumping speed for $NF_3$ versus the reactor pressure.