

THEORETICAL STUDY OF HETEROGENEOUS REACTIONS DURING PLASMA ETCHING AND DEPOSITION BY MASS SPECTROMETRY OF STABLE SPECIES

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An analysis of reaction kinetics and calibration procedure for evaluating rates of single reaction channels is described. In this way it is possible to distinguish contributions of gas phase and surface processes. The details are discussed in the case of etching of a-Si layer in NF_3 plasma and deposition of a-Si in the mixture SiF_4/H_2 .

1. Introduction

Mass spectrometry is widely used tool for characterization of the discharge plasma during etching and deposition. The aim of many mass spectrometric studies is to estimate stable reaction products originated in the gas phase and at the surfaces. A number of problems complicates the investigation of reaction mechanisms in a plasmachemical reactor by means of mass spectrometry. Common feature of papers devoted to the study of various gas mixtures [1, 2, 3] is the application of the calibration procedure of a mass spectrometer developed by Turban for molecular flow and described in detail in [4]. The partial pressures of gases in plasmachemical reactor can be determined from ion intensities when the ionization cross sections from literature [5, 6, 7] and the transmission coefficients of mass spectrometer and vacuum system are used. In Turban's procedure these coefficients have been directly measured only for reactants and extrapolated for other species (reaction products) by means of results obtained for a mixture of inert gases. This calibration can be checked by summing of partial pressures of all species in the effluent and comparing this value with the total pressure. The another method involves performing of the atomic balance for each of atomic species in the system [8]. Because of the problems with quantitative measurements of the relative abundance of

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some species (F_2 , HF) [8] the possibility to use these methods is very limited. The accuracy of the mentioned calibration depends on the experimental arrangement used, flow conditions and on the nature of used gases. As a result, the mass spectrometric data cannot be used immediately to the study of the reaction kinetics in the discharge plasma.

Mass spectrometry of neutral molecules and positive ions extracted from the plasma zone through an orifice in the substrate electrode enables to measure the flow of particles moving towards the substrate and kinetic energy of impinging ions [9]. The discussion of neutral and ionic plasma chemistry has been done only on qualitative basis, too.

Systematic studies of mechanism of plasma induced deposition of amorphous silicon from silane were performed in [10, 11] by time resolved mass spectrometric method in specially designed discharge tube with dc discharge. A good correlation between concentration of di- and trisilane and deposition rate of a-Si was shown in the contrary with many authors preferring SiH_3 radicals as precursor of a-Si deposition.

This paper is devoted to a theoretical analysis of monitoring the dominant rates and mechanisms in the plasma by mass spectrometry of stable neutral species. A great deal of attention has been paid to the following items:

- to elaborate procedures of determining the relative rates of simultaneous reactions
- to find methods which distinguish between reactions in the volume and at the surfaces
- to obtain information on the unknown stoichiometric and constitution coefficients.

The results are illustrated using examples of plasma etching and deposition.

2. Description of kinetics of volume and surface processes

A variety of elementary processes and chemical reactions occurs in the discharge plasma excited in a gas mixture for etching and deposition applications. Let I is the number of chemical species in the mixture participating in J simultaneous reactions. Each of them (specified by subscript j) can be expressed in the form

$$\sum_i a_{ij} A_i = 0 \quad (1)$$

where a_{ij} are stoichiometric coefficients of species A_i in the j -th reaction. According to [12] the rate of the j -th reaction can be expressed for an arbitrary component of the gas mixture as

$$R_j = \frac{1}{a_{ij}} \frac{\delta N_{ij}}{\delta t} \quad (2)$$

where $\delta N_{ij}/\delta t$ represents a total number of i -th molecules taking part in the j -th reaction per time unit throughout the entire volume of the reactor. An approach to the calculation of the term $\delta N_{ij}/\delta t$ depends on a type of plasmachemical reactor. In a flow

reactor this quantity can be obtained by integrating the continuity equation over all reactor volume as

$$\frac{\delta N_{ij}}{\delta t} = \int_V \text{div } j_{ij} dV = \int_S j_{ij} \cdot dS = \Delta I_{ij} \quad (3)$$

where j_{ij} is the flux density and ΔI_{ij} is a difference between the flux of the i -th species at the reactor outlet and inlet due to the j -th reaction. We have supposed that stable neutral species do not react with the inner surfaces with exception of substrate. Then diffusion losses can be neglected. By substitution of Eq.(3) in Eq.(2) we obtain

$$\Delta I_{ij} = a_{ij} R_j \quad (4)$$

Eq.(4) shows that the contribution of chemical reaction to the difference of the gas molecule flux of each species is proportional to its stoichiometric coefficient.

When J simultaneous reactions occur in the plasmachemical reactor, the total flux difference of i -th species is given by the sum of the contributions of individual reactions

$$\Delta I_i = \sum_j a_{ij} R_j \quad (5)$$

A set of linear algebraic equations (5) can be solved to find the rates of individual chemical reactions when values of ΔI_i are known. This offers a possibility how to obtain a method which distinguish between the surface and volume processes.

If we introduce a relative rate of the individual reaction as $f_j = R_j/R$ (where $R = \sum_j R_j$), we can write the following expression

$$\sum_j f_j \sum_i a_{ij} A_i = \sum_i A_i \sum_j a_{ij} f_j = \sum_i A_i a_i = 0 \quad (6)$$

where we have introduced effective stoichiometric coefficients $a_i = \sum_j f_j a_{ij}$. According to Eq.(6), the sum of all equations (1) multiplied by the factors f_j gives the equation for the overall chemical reaction with the effective stoichiometric coefficients a_i . Then the Eq.(5) can be written

$$\Delta I_i = a_i R$$

The differences in the gas molecule fluxes can be evaluated from mass spectrometric measurements by means of a procedure described below.

The ratio

$$\frac{\Delta I_i}{\Delta I_k} = \frac{a_i}{a_k}$$

enables to study the mechanism of a single reaction channel as a function of discharge parameters. When only one reaction is present ($J = 1$), this ratio has a constant value in a case when the reaction mechanism does not vary with the discharge parameters. On the other hand, the variation of this ratio can offer information about a change in the reaction mechanism.

An application of the results described above requires to measure the differences in the molecule fluxes by mass spectrometry. A sampling of effluent from plasma chemical

reactor through vacuum pipe (downstream sampling technique) could be used. Measurements can be carried out alternately without the plasma and when the plasma is excited. As the next step a simulation of a mixture consisting of reactants and products is supposed. The simulation can be done by variation of the flow rates of reactants and by addition of a controlled amount of the product to obtain a mass spectrum similar to the situation when the discharge plasma is present. The observed variation in the flow rates corresponds to the flux differences due to the chemical reactions running in the plasma. As an independent check of the values obtained, the change in the total gas pressure can be used [13]. When a discrepancy occurs, it can be explained by the significant production of unstable species in the plasma. There is a difficulty associated with the use of the simulation as the unstable species cannot be mixed with the gas flow of the reactants. There is a problem of existence and uniqueness of this solution of the simulation procedure. A standard software currently used for identification of the mass spectra can be applied to this purpose.

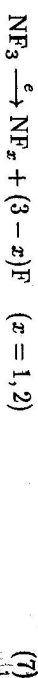
As an example etching and deposition of a-Si layer will be studied. The stable species N_2 , F_2 and SiF_4 are expected to be formed in a NF_3 plasma during the etching process. The species SiF_2H_2 and HF will be present in a SiF_4/H_2 plasma used in deposition process.

3. Influence of volume and surface processes on plasma composition

3.1. Kinetics of NF_3 discharge plasma

3.1.1. Volume processes in NF_3 plasma

Kinetics of NF_3 discharge plasma was studied with regard to a-Si etching in papers [3, 9, 14, 15]. Fluorine atoms which are Si etchants, should be directly produced by electron impact dissociation of NF_3 molecules, according to the following reactions



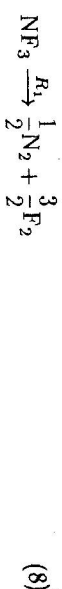
Simultaneously, fast recombination processes of radicals occur in the plasma volume. Recombination of two different radicals like NF_x ($x=1,2$) is described by the equation



Occurrence of electron impact dissociation of NF_3 molecules and following recombination of radicals leads to the new stable molecules N_2 and F_2 . It is impossible to distinguish individual reaction channels producing the same reaction products i.e. the channels with the same reaction stoichiometry. Therefore the following reaction sequence can be supposed



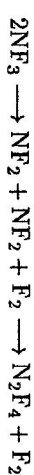
or



The rate of reaction (8) will be denoted as R_1 . The occurrence of an additional association channel producing molecules N_2F_4 is presented in [14]



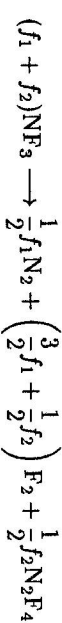
The chemical reactions include only such molecules which affect the balance of stable neutral species. Thus, such an approach does not describe the mechanism of running overall reactions. In this manner all following reactions will be written. The two step reaction (7), (9) produces molecules F_2 and N_2F_4 and can be written as



or as overall reaction



with the reaction rate R_2 . The reaction (10) produces new stable molecules N_2F_4 , with the stoichiometry different from that involved in reaction (8). Generally, both reaction channels (8, 10) occur simultaneously in NF_3 plasma. Then the conversion of NF_3 molecules to new stable species in absence of etching can be expressed as



where f_1 and f_2 are the relative rates of channels (8) and (10) respectively ($f_1 + f_2 = 1$). It is possible to evaluate the quantities f_1 , f_2 by mass spectrometry.

Applying Eq.(5) to both channels of NF_3 conversion we have received a set of linear equations for the total flux differences

$$\Delta I_{NF_3} = -(R_1 + R_2) = -R$$

$$\Delta I_{N_2} = \frac{1}{2}R_1$$

$$\Delta I_{F_2} = \frac{3}{2}R_1 + \frac{1}{2}R_2$$

$$\Delta I_{N_2F_4} = \frac{1}{2}R_2$$

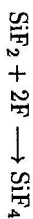
The difference in NF_3 and N_2 flux can be determined with a high accuracy by the simulation technique described above. Then, the quantity f_1 can be evaluated as $f_1 = R_1/R = -2\Delta I_{N_2}/\Delta I_{NF_3}$. The relative rate f_2 can be calculated as $f_2 = 1 - f_1$. When f_1 is close to unity the reaction channel (8) predominates. In case $f_1 < 1$ the production of N_2F_4 molecules cannot be neglected and the respective fragmentation products may be monitored by mass spectrometer to measure $\Delta I_{N_2F_4}$ [3].

3.1.2. Influence of a-Si etching on kinetics of NF₃ plasma

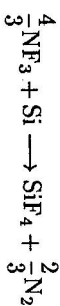
In NF₃ discharge plasma fluorine atoms are responsible for Si etching. Many authors have published an occurrence of the heterogeneous reaction



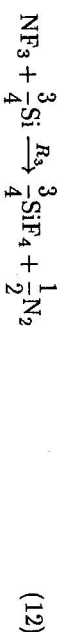
at Si surface. It is very difficult to recognize if etch products SiF₄ are formed directly on the Si surface or by subsequent homogeneous process



which occurs near the etched surface. We will discuss the influence of mentioned etch processes on kinetics of NF₃ plasma. According our previous considerations the fast dissociation process of NF₃ molecules (Eq. (7)) produces free F atoms. Therefore we will consider a production of three F atoms from one NF₃ molecule. Then Eq. (11) can be replaced by the equation



or



A comparison of Eq. (12) with equations characterizing the volume processes (8, 10) shows that the etching of a-Si layer can affect strongly the measured stoichiometry of resulting reaction. During etching of a-Si layer in NF₃ plasma the conversion of NF₃ molecules occurs through all mentioned channels. The sum of Eqs. (8, 10, 12) multiplied by the relative rates of individual channels, gives



where relative rates f_1, f_2, f_3 correspond to the two volume and to one surface processes ($f_1 + f_2 + f_3 = 1$). These rates can be evaluated by mass spectrometric measurements of the differences in the gas molecule fluxes. Now, it is possible to write a set of linear equations for the single channel rates

$$\Delta I_{NF_3} = -(R_1 + R_2 + R_3) = -R \quad (13)$$

$$\Delta I_{N_2} = \frac{1}{2}R_1 + \frac{1}{2}R_3 \quad (14)$$

$$\Delta I_{F_2} = \frac{3}{2}R_1 + \frac{1}{2}R_2 \quad (15)$$

$$\Delta I_{N_2F_4} = \frac{1}{2}R_2 \quad (16)$$

$$\Delta I_{SiF_4} = \frac{3}{4}R_3 \quad (17)$$

Only 3 equations are linearly independent in this set, the rest of them can be used to check the consistency of the measurement. The set of Eqs. (13-17) can be used to determine the total reaction rate R and the particular reaction rates of single channels. The measured flux difference of NF₃ molecules gives directly R (Eq. (13)). A value of R_3 can be obtained from the flux difference of SiF₄ molecules (Eq. (17)). Then a value of R_1 can be evaluated from Eq. (14) for measured flux difference of N₂ molecules. The simplest way for determining R_2 is given by $R_2 = R - (R_1 + R_3)$. The identification of mass spectra corresponding to NF₃ plasma free of etching products enables to calibrate the mass spectrometer for N₂F₄ molecules. There is also an independent way how to determine R_2 (see Eq. (16)). The above mentioned problems of F₂ detection complicate accurate measurements of F₂ flux difference by mass spectrometer. Therefore Eq. (15) was not used in our analysis.

Besides directly measured flux differences of the stable species, the equivalent flux of etched silicon atoms leaving the etched surface can be calculated using the etched area and etching rate. Then the mean etching rate can be determined and compared with a value obtained from the measured flux of SiF₄ molecules. If any discrepancies exist then the calibration procedure of the mass spectrometer must be checked or additional chemical reactions must be taken into account.

3.2. Kinetics of plasma deposition of a-Si:H layer from SiF₄/H₂ mixture

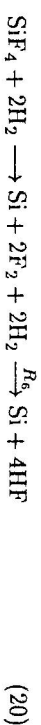
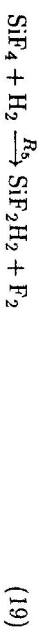
An experimental study of the plasma deposition process appears to be more difficult when compared with the plasma etching. This is partly because of the fact that the reactions of free radicals with the reactor walls play an important role in the loss of gas phase reactive species and cannot be ruled out as it can be done for the case of plasma etching (there is no etching process when the sample is not present). Therefore, the mass spectrometry is not capable of distinguishing between the stable reaction products originating in the gas phase and on the surfaces.

We will consider a deposition of hydrogenated amorphous silicon film in the SiF₄/H₂ plasma. An analysis of the gas phase and surface processes in a mixture containing SiF₄ can be found in [16] where principal differences are shown in comparison with the silane chemistry.

The dominant processes can be summarized as follows:

- molecules SiF₄ and H₂ are dissociated by electron impact, where radicals SiF_x ($x = 1 - 3$), F and H are formed
- free radicals disappear due to mutual recombination (backward reaction to the dissociation) and creation of new stable molecules.

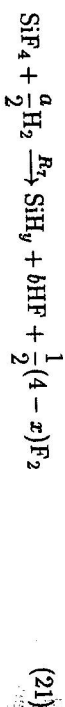
Occurrence of all gas phase reactions in the mixture SiF₄/H₂ can be summarized in the form



with the reaction rates R_4 , R_5 and R_6 , respectively. Surface a-Si:H deposition from precursors SiF_x (x is unknown) is described as



The SiF_x radical are produced by dissociation of SiF_4 molecules with $(4-x)\text{F}$ atoms appearing in each dissociation act. The deposition process can be described from point of view of stable molecules as follows



The rate of this reaction is R_7 .

As a first approximation, the set of Eqs. (18-20, 21) describes a conversion of SiF_4 molecules by the volume and surface processes.

Using Eq. (5) a set of linear equations for the rates of single reaction channels can be obtained

$$\Delta I_{\text{SiF}_4} = -(R_4 + R_5 + R_6 + R_7) = -R \quad (22)$$

$$\Delta I_{\text{Si}} = R_4 + R_6 \quad (23)$$

$$\Delta I_{\text{F}_2} = 2R_4 + R_5 + \frac{1}{2}(4-x)R_7 \quad (24)$$

$$\Delta I_{\text{SiF}_2\text{H}_2} = R_5 \quad (25)$$

$$\Delta I_{\text{H}_2} = -\left(R_5 + 2R_6 + \frac{1}{2}(y+x)R_7\right) \quad (26)$$

$$\Delta I_{\text{HF}} = 4R_6 + xR_7 \quad (27)$$

$$\Delta I_{\text{SiH}_4} = R_7 \quad (28)$$

where the laws of conservation of F and H atoms were used: $a = y + b$ and $x = b$.

This set of equations is linearly dependent and it has been found that three equations can be omitted. There is some uncertainty in the accuracy of the detection of unstable and reactive species (such as Si, HF and SiH_y) by the mass spectrometer, therefore the respective Eqs. (23), (27) and (28) were chosen to be deleted. Then a set of 4 equations in 6 unknowns is obtained. The unknown y characterizes the hydrogen content in a-Si layer that has to be determined by an independent technique (infrared spectrometry).

To measure $\Delta I_{\text{SiF}_2\text{H}_2}$, ΔI_{SiF_4} , ΔI_{H_2} and ΔI_{F_2} , the simulation procedure can be used, when the stable products F_2 and SiF_2H_2 are added to the reactants SiF_4 and H_2 to obtain a mass spectrum similar to the situation during the plasma deposition. Then the rates R_5 and $R_4 + R_6 + R_7$ can be estimated by Eq. (22 and 25). The following equation

$$y \frac{R_7}{2} = \Delta I_{\text{F}_2} - \Delta I_{\text{H}_2} + 2\Delta I_{\text{SiF}_4}$$

yields the value of R_7 .

Unfortunately, the unknown x cannot be calculated without knowledge R_4 or R_6 . A special case arises when $R_4 + R_6 \ll R_5$. Then x can be determined as

$$(y+x) \frac{R_7}{2} \approx -\Delta I_{\text{H}_2} - \Delta I_{\text{SiF}_2\text{H}_2}$$

or

$$\left(2 - \frac{x}{2}\right) R_7 \approx \Delta I_{\text{F}_2} - \Delta I_{\text{SiF}_2\text{H}_2}.$$

The relative rates f_5 , $f_4 + f_6$ and f_7 corresponding to the respective reaction rates can be calculated as

$$f_j = \frac{R_j}{\sum_j R_j} = \frac{R_j}{R}.$$

4. Conclusion

Mass spectrometry of stable neutral species originated in heterogeneous reactions during plasma etching and deposition is discussed in this paper. A simple theory using the basic equation of chemical kinetics is formulated to describe the plasmachemical processes occurred in the discharge plasma excited in a gas mixture. As a result, a simple relation between the difference in the gas molecule flux and the respective stoichiometric coefficient is obtained. It is assumed that the number densities of radicals can be neglected, so that their influence on particle balance (and on total gas pressure) is not taken into consideration. A special attention has been paid to the calibration procedure of a mass spectrometer using a simulation of the mixture consisting of reactants and products to avoid the known disadvantages of standard methods.

This procedure is illustrated in two cases: etching of a-Si layer in a NF_3 plasma and deposition of a-Si layer in a SiF_4/H_2 plasma. The NF_3 plasma is analyzed in two regimes: with and without etching of a-Si layer. The possible reaction channels and products are discussed with the stress laid upon differentiation of the reaction products originated in the gas phase and at the surfaces.

Special attention is devoted to mass spectrometry of discharge plasma used to the study of the deposition process including the simultaneous action of the volume and surface reactions. Three volume reactions together with the plasma deposition process are assumed to be present in the discharge plasma excited in the mixture SiF_4/H_2 . Under such conditions the stoichiometry of the precursor SiF_x has been studied in detail.

An experimental study is supposed to be done in future in order to apply the results obtained.

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