DIAGNOSTICS AND MODELLING OF PLASMAS USED FOR THE CVD
OF a-C:H, a-Si:H AND A-Si_xC_{1-x}:H FILMS

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ABSTRACT

In the plasmas of CH₄ and SiH₄ the dissociation degree and the dissociation rate of the parent gas molecules have been measured using a laser absorption technique, and the effects of the external parameters on the dissociation processes have been investigated. The measured results have been compared with a model calculation based on the rate equations.

1. INTRODUCTION

RF-discharges in CH₄, SiH₄ and their mixture have been successfully used in the chemical vapour deposition of a-C:H, a-Si:H and a-Si_xC_{1-x}:H films. However, for further improvements of the electrical and optical properties of the deposited films, it is important to understand the properties of the plasma based on the physico-chemical processes in the plasma and at the plasma-solid interfaces. Especially the dissociation processes of the parent gas molecules by electron collisions and by various secondary processes in the gas phase and at the solid surfaces are important for understanding the chemistry of the depositing plasma.

We report here in situ measurements of the dissociation degree of the parent gas molecules in the CH₄ and SiH₄ plasmas using a laser absorption technique. With the same technique the dissociation rate, which is a physical constant necessary in the plasma modelling, is also measured in a gas sealed-off system. For understanding the results the electron energy distribution in the plasma has been measured using an electrical probe. Conventional emission and absorption spectroscopy is also applied to the measurement of the densities of radicals in the plasma. Especially, from the absorption measurement the quenching rate constant for Si atom has been estimated.

On the other hand, a modelling of the plasma based on the rate equations for the densities of the species in the plasma has been tried under simplified conditions, and the results on the dissociation degree and the number density of Si atoms are compared with the experimental results measured as functions of the RF-power, the gas pressure and the gas flow rate.
2. PLASMA DIAGNOSTICS

2.1. Dissociation Processes of Parent Gas Molecules

Experimental setup for the measurement of the partial pressure of the parent gas in the plasma is shown schematically in Fig. 1. The light sources for the absorption technique are a He-Ne laser (3.39 μm) and a CO₂ laser (10.59 μm) of which the wavelengths coincide with the absorption lines of CH₄ and SiH₄, respectively. In order to increase the sensitivity a multiple-pass configuration has been used. The CVD chamber is equipped with two parallel electrodes of 8 cm diameter, separated by 2.5 cm.

Fig. 1 Scheme of the experimental setup.

For the measurement of the dissociation degree, the absorptions in the presence and in the absence of the plasma have been measured alternately. The results for CH₄ plasma have been reported previously. 2) Newly obtained results for SiH₄(10%) - H₂ plasma and SiH₄(5%) - Ar plasma are shown in Figs. 2 and 3, respectively, as functions of the RF-power at several values of the gas flow rate. (Solid curves show the calculated values. See Sec. 3.)

The dissociation degree increases as the RF-power increases mainly due to the increase in the electron density in the plasma. The dependence of the dissociation degree on the gas flow rate is due to the change in the residence time of parent gases in the plasma. It is seen from Figs. 2 and 3 that the dissociation degree in SiH₄ - Ar plasma is much higher than in SiH₄ - H₂ plasma at the same RF-power and gas flow rate.

Fig. 2 Dissociation degree of SiH₄ in SiH₄(10%) - H₂ plasma at a gas pressure of 0.5 Torr at several values of gas flow rate; (○) 10, (△) 20, (x) 30 and (□) 50 sccm (standard cubic centimeter per minute).
The effect of the carrier gas species will be discussed again later.

For the measurement of the dissociation rate, which means the product of dissociation rate constant $k_d$ and the electron density $n_e$, a sealed-off system has been used; the gas has been filled in the chamber at a constant pressure and the change in the absorption has been monitored after the start of the discharge at a fixed RF-power. The dissociation rate is deduced from the initial slope of the change in the partial pressure of parent gas. An example of the results for SiH$_4$ plasma is shown in Fig. 4 together with a result for CH$_4$ reported previously. 2) The rate for SiH$_4$ is much larger than for CH$_4$. This fact indicates that SiH$_4$ molecules can be dissociated by electron collisions more easily than CH$_4$ in consistent with the reported cross sections.3)

The dissociation rate in the SiH$_4$-Ar mixture is about ten times as large as that in the SiH$_4$-H$_2$ mixture. However, no systematic measurement has been possible in the SiH$_4$-Ar mixture by this method, since the dissociation rate is so large that it can no longer be assumed that the gas mixing by diffusion is much faster than the dissociation. 2) The large difference in these two kinds of mixtures is possibly due to the differences in the electron energy distributions and also in the electron densities in the two plasmas.

2.2. Measurement of Electron Energy Distribution

The electron energy distribution has been measured in the
plasmas of pure H₂ and Ar by an electrical probe (see ref. (2) for the apparatus and the technique). A typical result is shown in Fig. 5. The measured f(ε) for H₂ has smaller mean electron energy than that for Ar. However, the dissociation rate constants for SiH₄ calculated from these distributions do not differ with each other by more than a factor of 2 - 3. The rest of the contribution to the difference in the dissociation rates is possibly attributed to the difference in the electron densities in these two plasmas. Actually, the probe current in the Ar plasma was much larger than in the H₂ plasma. However, the electron density must be affected sensitively by mixing a small amount of SiH₄. At the moment we have not succeeded in the measurement of f(ε) and nₑ in SiH₄ mixtures.

2.3. Measurement of Radical Species

We have measured the absolute density of Si atoms in the SiH₄ plasma by a conventional absorption technique using a Si hollow-cathode lamp as a light source. We had to use the squarewave modulation method of the discharge as used previously in order to distinguish the absorption signal from the scattering and absorption by powders or clusters produced in the plasma.

A result for the SiH₄-Ar mixture is shown in Fig. 6 measured as a function of the RF-power at fixed gas pressure and flow rate. The emission intensity of Si atomic line (251.6 nm) measured at the same time is also shown in the figure for a comparison. Both the Si atom

Fig. 5 Electron energy distributions in H₂ and Ar plasmas at the same gas pressure of 0.5 Torr, gas flow rate of 10 sccm and RF-power of 5 W.

Fig. 6 Density of Si atoms and emission intensity of Si atomic line in SiH₄ (5%)-Ar plasma as functions of the RF-power at a gas pressure of 0.5 Torr and a gas flow rate of 10 sccm.
density and the emission intensity increase almost linearly with the RF-power. This fact suggests that the productions of both Si and Si* are due to one electron processes as discussed by Kampas.\textsuperscript{5)}

However, when the pressure has been changed at fixed RF-power and gas flow rate, Si atom density and the emission intensity have different functional dependences as shown in Fig.7. This is due to their different loss mechanisms. Densities of Si and Si* are given by

\begin{align}
[\text{Si}] &= k_d(Si)N_0n_e/(D/\Lambda^2N + k_qM), \\
[\text{Si}^*] &= k_d(Si^*)N_0n_e/\Lambda,
\end{align}

where \( k_d(Si) \) and \( k_d(Si^*) \) are the production rate constants for Si and Si* by dissociation of SiH\(_4\) in collisions with electrons, \( N_0 \) is the density of SiH\(_4\), \( D \) is the diffusion coefficient for Si, \( \Lambda \) is the diffusion length, \( N \) is the density of the buffer gas, \( k_q \) is the quenching rate constant for Si, \( M \) is the density of the quencher and \( \Lambda \) is the transition probability for the excited state. Then the ratio of [Si] to [Si*] becomes proportional to \( 1/(D/\Lambda^2N + k_qM) \). From the results given in Fig.6 the ratio becomes as shown by the broken curve in the figure. It can be seen that the diffusion term and the quenching term becomes comparable at a pressure of 0.25 Torr. Taking the density of the initial silane molecules as M, we obtain a value \( 7.4 \times 10^{-12} \text{ cm}^{-3}\text{sec}^{-1} \) for \( k_q \). However, this must be considered an effective value in a mixture of SiH\(_4\) and H\(_2\) since this has been measured in a real plasma. This value is slightly larger than the reported value \( 3.3 \times 10^{-12} \text{ cm}^{-3}\text{sec}^{-1} \) for the quenching of SiH radical by SiH\(_4\).\textsuperscript{6)}

3. PLASMA MODELLING

We have tried a modelling of the plasma based on the rate equations for the densities of species present in the plasma by assuming a spatially uniform plasma. The procedure of the
modelling and the reaction paths and the rate constants used in the model have been described elsewhere. The results for the dissociation degree calculated by the model are already shown in Figs.2 and 3 by solid lines, where the measured values of the dissociation rate have been used in the calculation. We have adjusted the rate constant for the following hydrogen abstraction reaction

$$\text{H} + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H}_2$$

(3)

to get better fits to the experimental values, since this reaction fairly contributes to the dissociation of SiH$_4$. Finally adopted value for the rate constant is $1 \times 10^{-12}$ cm$^{-3}$sec$^{-1}$. This is within the scatter of the reported values from $4.3 \times 10^{-13}$ to $8.5 \times 10^{-12}$ cm$^{-3}$sec$^{-1}$ but rather closer to the latest (the smallest) value.

An example of the calculated results for the number densities of the species in SiH$_4$-Ar plasma is shown in Fig.8 as functions of the RF-power at fixed gas pressure and flow rate. The calculated density of Si atoms is about two times as large as the measured results shown in Fig.4. This suggests that we have overestimated the fragmentation percentage for the production of Si from the dissociation of SiH$_4$ by electron collisions. According to the calculation, much higher densities of SiH$_3$ and SiH$_2$ are predicted in the plasma. In order to see whether this is true or not, we have to carefully check the validity of the reaction paths and the rate constants as well as to establish the method for the measurement of their densities in the plasma.

We have thus far studied the methane and silane plasmas used for the preparation of a-C:H and a-Si:H. we are extending the same kind of measurement to a plasma of the mixture of CH$_4$ and SiH$_4$ used for the preparation of a-Si$_x$C$_{1-x}$:H. Preliminary results will be shown at the conference.

REFERENCES