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# RADICAL MEASUREMENTS IN PROCESSING PLASMAS USING IR LASER ABSORPTION SPECTROSCOPIC TECHNIQUES

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In order to make quantitative investigations of plasmas for thin film processing, we need information on radicals in electronic ground states in plasmas which give important contribution to thin film processing.

Although a laser induced fluorescence method (LIF) has been used most widely among laser spectroscopic techniques, LIF cannot be applied to $SiH_3$, $CF_3$ and $CH_3$ which do not have visible spectra.

We developed a radical measurement method with combining IRLAS and a discharge modulation technique, and succeeded in measuring the $SiH_3$ and SiH radicals in DC pulsed, RF and ECR silane plasmas, the $CH_3$ radical in RF methane plasma, and the $CF_3$, $CF_2$ and CF radicals in RF and ECR $CHF_3$ plasmas for the first time [1]. Although the $SiH_3$, $CF_3$ and $CH_3$ radicals have been assumed to play important roles in plasma processing, their in situ measurements in plasmas have never been made. This IRLAS was shown to be a widely used spectroscopic method which is applicable to various radicals in plasmas.

The IRLAS is useful as a radical measurement method in plasma having the following merits.

(1) The disturbance of the system to be measured is very little because IR laser of low power is used as a light source.

(2) The radical density in plasma can be determined directly from the ratio of the laser intensities with and without absorption.

(3) Many kinds of radicals with IR spectra can be measured.

The radicals composed of two or more atoms have IR spectra generally, but do not always have visible spectra. The typical examples are $SiH_3$, $CH_3$ and $CF_3$. The IRLAS is only one measurement method of those radical densities in plasmas at present.

Table 1 shows the outline of the radical measurements in plasmas for thin film processing using IRLAS.

The measurement method of the $SiH_3$ and SiH radicals for amorphous Si thin film was established and their density measurements were already made in RF plasma and recently also in ECR plasma.

Table 1 Outline of radical measurements in plasmas for thin film processing using IRLAS.

| Molecule | Radical | Band($\mu$ m) | Plasma |
|---|---|---|---|
| $SiH_4$ | $SiH_3$ | $\nu_2$ (15)<br>$\nu_2$ (15) | P, RF<br>ECR |
| | SiH | v=0-1 ( 5) | P, RF |
| $CH_4$ | $CH_3$ | $\nu_2$ (16)<br>$\nu_2$ (i6) | RF<br>HF |
| $CF_4$ | $CF_2$ | $\nu_1$ (9) | RF |
| | CF | v=0-1 (8) | RF, P |
| $CHF_3$ | $CF_3$ | $\nu_3$ (8)<br>$\nu_3$ (8) | RF<br>ECR |
| | $CF_2$ | $\nu_1$ (9)<br>$\nu_1$ (9) | RF<br>ECR |
| | CF | v=0-1 (8)<br>v=0-1 (8) | RF<br>ECR |

P : DC pulsed plasma HF : 20 kHz plasma
RF : 13.56 MHz plasma
ECR : 2.45 GHz electron cyclotron resonance plasma

In the RF $CH_4$ plasma for diamond thin film, the measurements of the $CH_3$ radical density has been made. This $CH_3$ radical was also by other groups.

In the RF $CF_4$ plasma, the $CF_2$ and CF radicals were measured. In the $CHF_3$ plasma, the $CF_3$, $CF_2$ and CF radical densities were measured and their behaviors were investigated in the RF plasma and also in the ECR plasma.

The details of the radical measurement method by IRLAS and typical measured results will be given in the presentation.

[1] T. Goto: Oyo Buturi 62, 666 (1993).