PART I

Growth and Modification
MEASUREMENTS OF SIH3 AND SIH2 RADICAL DENSITIES IN RF SILANE PLASMAS USING LASER SPECTROSCOPIC TECHNIQUES

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ABSTRACT

In the RF (13.56 MHz) silane plasma, recently the SiH3 radical density was measured using infrared diode laser absorption spectroscopy, and the correlation between the SiH3 radical density and the growth rate of hydrogenated amorphous silicon thin film was investigated. The SiH2 radical density was also measured using modified laser induced fluorescence spectroscopy and intracavity laser absorption spectroscopy. Those measurement methods and main results are reviewed here.

1. INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) thin films are produced by RF discharge silane plasma usually. In that RF plasma, although ions, neutral radicals, molecules and electrons exist, the non-emissive neutral radicals in the electronic ground states are possibly the main precursors of the thin film. Especially among them, SiH3 and SiH2 radicals have been regarded as the important precursors, but there has been controversy about the contribution of the SiH3 and SiH2 radicals to the formation of a-Si:H thin film[1-3].

To clarify how the SiH3 and SiH2 radicals contribute to the thin film formation quantitatively, information on the densities of those radicals under actual CVD conditions has been demanded. However there have been no methods to measure the SiH3 and SiH2 radicals before.

With such a background, we developed the in-situ measurement method of the radical density in the plasma using infrared diode laser absorption spectroscopy (IRLAS) and succeeded in measuring the SiH3 radical density in the dc pulsed silane plasma[4-6] and also in the RF silane plasma[7,8] for the first time. On the basis of those results, the contribution of the SiH3 radical to the thin film formation was discussed[7,9].

Moreover we succeeded in detecting the SiH2 radical in the RF silane plasma using modified laser induced fluorescence spectroscopy (denoted by MLIF here) for the first time[10]. Since the SiH2 radical is reactive with the SiH4 molecule, its density is rather low (on the order of 10^9 cm^-3 or even lower). In addition, the SiH2 radical populated to the electronic excited state by laser irradiation is predissociated. Therefore the SiH2 radical has never been detected with LIF while it was measured with the intracavity laser absorption spectroscopy (ICLAS)[11].

In this review paper, the measurement method and main results of the SiH3 radical by IRLAS are described in Sec.2, and those of the SiH2 radical by MLIF and ICLAS are described in Sec.3. On the basis of those measured results, the contribution of the SiH3 and SiH2 radicals to the a-Si:H thin film formation are discussed briefly in each section. For the comparisons, the measured results on SiH and Si are also introduced briefly in Sec.4.
2. MEASUREMENT OF THE SiH₃ RADICAL BY IRLAS

2.1 Measurement method and experimental

Figure 1 shows the schematic diagram of the experimental arrangement of IRLAS used for the SiH₃ radical measurement.

The RF chamber of 40 cm diameter was used here. It had circular plane parallel electrodes of 20 cm diameter and 3 cm separation, and the on-off modulated RF (13.56 MHz) power was fed to the electrodes. The chamber was movable vertically so that the spatial distribution of the radical density between two electrodes could be measured. By using this discharge modulation technique, absorption signals of a good signal-to-noise ratio could be obtained.

The discharge cell was equipped with the White type multi-reflection system. It consisted of three mirrors of 200 cm curvature radius and 200 cm interval to obtain a larger absorption signal by increasing the absorption length. The laser beam was passed 60 times through the RF plasma.

The infrared diode laser was cooled down to few tens K and the wavenumber of the laser mode was coarsely selected by varying the cooling temperature and minutely by changing the laser current. The laser power was 0.1 mW or less. The laser linewidth was around 10 MHz, which is much smaller than the absorption linewidth of the radical.

The laser beam was split into three beams. The first beam was introduced into the reference gas cell for determining the absolute wavenumber of each rovibrational line of the radical. In the case of the SiH₃ radical, C₂H₂ gas was used. The second beam was introduced into an etalon for providing the relative scale of the wavenumber (1 fringe = 0.01 cm⁻¹). Those beams were measured with the HgCdTe detectors and phase sensitive detection systems. The third beam was introduced into the RF plasma generating the radicals to be measured and was absorbed partly there. The radical absorption signal was measured with the HgCdTe detector and transient wave memory.

Figure 2(a) shows one example of the observed absorption spectrum for Q branch lines of the ν₂ band of SiH₃. The infrared rovibrational lines in the ν₂ band are in the wavenumber region of 700 to 800 cm⁻¹ (≈ 15 μm). Figure 2(b) shows the transient

![Schematic diagram of the experimental arrangement of IRLAS](image)
The radical density in the electronic ground state is derived from the data shown in Fig. 2 in the following way[7].

The absorption coefficient $k(v)$ at the wavenumber $v$ of one rovibrational line belonging to the $v_2$ band is given by

$$k(v) = \frac{1}{L} \log \frac{I_0(v)}{I_A(v)}.$$  \hspace{1cm} (1)

Here $L$ is the absorption length in cm, $v$ is the wavenumber of the laser mode in cm$^{-1}$, $I_0(v)$ is the laser intensity without absorption, and $I_A(v)$ is the laser intensity absorbed in the RF plasma. The value of 1.8% shown in Fig.2(b) represents $I_A(v)/I_0(v)$. Measuring $k(v)$ by varying the laser wavenumber $v$ and integrating $k(v)$ over $v$, the radical density $N(J',K')$ of the lower state of one rovibrational line is obtained from the formula

$$N(J',K') = \frac{8\pi v^2}{g'_{J'K'} g_{J'K'}} \int k(v)dv .$$  \hspace{1cm} (2)

Here $g'_{J'K'}$ and $g_{J'K'}$ are the statistical weights of the lower and upper states, respectively, and $A_{11}(J'K',J''K'')$ is Einstein’s $A$ coefficient. The radical density of the upper state was neglected here.

Next determining the radical densities of the lower states (belonging to $v = 0$) of several $Q$ branch lines in the above way and taking the Boltzmann plot of those densities, all experimental points were located on one straight line as shown in Figure 3. From the slope of the straight line, the rotational temperature was determined to be 410 K under the conditions of Fig.2[7].

The total SiH3 radical density in the electronic ground state ($X^1A_1; v=0$) was determined by substituting the radical density in one rovibrational state and the rotational temperature obtained above into the rotational and vibrational partition functions[12].

2.2 Measured results

Figure 4 shows the spatial distributions between two electrodes of the SiH3 radical density and the emission intensity of the SiH+$^1(A-X)$ line measured for the SiH4/H2 (6.6/4 Pa) gas mixture and the RF on-power of 125 W.
The SiH₃ radical density increases gradually with the distance from the grounded electrode and shows the maximum near the RF electrode while the SiH* emission intensity changes more considerably. Since the upper state A' Δ of the SiH* emission line has a relatively short lifetime of about 0.5 μs, and also the SiH* and SiH₃ radicals can be assumed to be made mainly by the single electron impact on SiH₄ molecules, the spatial distribution of the SiH* emission intensity roughly reflects the generation rate of the SiH₃ radical. Therefore the spatial distribution of the SiH₃ radical density is smoothed out somewhat by the diffusion after the generation of the SiH₃ radical.

The flux density of the SiH₃ radical incident to the substrate was estimated to be about 6×10¹⁵ cm⁻² s⁻¹ from the slope of the curve near the grounded electrode. Using this flux density, the sticking coefficient (0.09), the mass density of a-Si:H (2.2 g/cm³) and the mass of Si₁.₀₀H₀.₂₅ (4.7×10²³ g), the growth rate of a-Si:H thin film through the SiH₃ radical was estimated to be 0.11 nm/s.

On the other hand, under the same conditions, the measured growth rate of a-Si:H thin film deposited actually on the substrate was about 0.18 nm/s. The growth rate estimated from SiH₃ explains a significant fraction of the measured value. It shows that the SiH₃ radical can be an important precursor of the thin film formation in the RF plasma.

Figure 5 shows the SiH₃ radical density as a function of H₂ partial pressure measured at the SiH₄ pressure of 6.6 Pa, the SiH₄ flow rate of 10 sccm, the RF on-power of 125 W and the distance of 1 cm from the grounded electrode. The SiH₃ radical density decreases with H₂ pressure.

Combining the result shown in Fig.5 with the relative spatial distributions of the SiH₃ radical measured in the H₂ pressure region of 0 to 60 Pa, the SiH₃ radical density at x=0 was obtained. Figure 6 shows the correlation of the SiH₃ radical density at x=0 and the growth rate of a-Si:H thin film measured when changing the H₂ pressure. It shows a linear relationship between the two quantities. Moreover the SiH₃ radical density at x=0 cm is
SiH4=6.6 Pa x=1.0 cm Fig. 5. SiH3 radical density as a function of H2 pressure measured at the SiH4 pressure of 6.6 Pa, the flow rate of 10 sccm, the RF on-power of 125 W and the distance of 1 cm from the grounded electrode in the RF SiH4/H2 plasma.

Fig. 5. SiH3 radical density as a function of H2 pressure measured at the SiH4 pressure of 6.6 Pa, the flow rate of 10 sccm, the RF on-power of 125 W and the distance of 1 cm from the grounded electrode in the RF SiH4/H2 plasma.

high enough to explain the growth rate of the thin film in the relatively low H2 pressure region. These results indicate that the SiH3 radical contributes considerably to the a-Si:H thin film formation.

In Fig. 6, the straight line does not cross the origin. Although the reason for this is under study, the contribution of radicals other than SiH3 may increase or the change of the surface condition of the substrate may influence the deviation from the origin of the straight line.

Fig. 6. Correlation of the growth rate of the a-Si:H thin film and SiH3 radical density near the substrate measured upon changing the H2 pressure. The SiH4 pressure is 6.6 Pa, the flow rate is 10 sccm and the RF on-power is 125 W.

3. MEASUREMENT OF THE SiH2 RADICAL BY MLIF AND ICLAS

3.1 MLIF (Modified laser induced fluorescence spectroscopy) [10]

Although the SiH2 radical in the silane plasma has never been detected using LIF, we could detect it by combining the common LIF method with the plasma modulation and photon counting technique.

Figure 7 shows the schematic diagram of the experimental arrangement. In this measurement, the RF chamber was equipped with plane parallel electrodes of 10 cm diameter and 3 cm separation.

A pulsed dye laser pumped with a YAG laser of 10 Hz repetition rate was used for this MLIF. The LIF emission was collected with a lens of 15 cm focus length in the direction perpendicular to the laser beam axis and was focussed on the entrance slit of a 20 cm monochromator. For Rayleigh scattering measurements, a polarizer was used to make the laser radiation linearly polarized in the vertical direction. The laser power was monitored.
either with a calorimetric power meter or with a biplanar phototube.

The LIF photons passing through the monochromator were detected with a photomultiplier and recorded with a fast digitizing oscilloscope with its input impedance of 50 Ω to obtain fast response. The LIF signal was averaged for several laser pulses in the digitizing oscilloscope and transferred to a computer for further averaging. In order to obtain the better signal-to-noise ratio of the very weak LIF intensity of SiH₂, the LIF signal was integrated by using a photon counting method.

A pulsed discharge was used at a low duty ratio to prevent the formation of particles which cause strong Mie scattering. The timing of laser excitation was set at 30 μs after the plasma turning-off, to avoid the background emission from the plasma. The laser wavelength was set at about 580 nm to excite the SiH₂ radical to the JKHJKC = 000 state in the A1Bi(viv2v3=020) electronic state which is non-predissociative and is expected to have strong LIF signal[13]. The observation wavelength was set at 618 nm to detect the induced fluorescence of the A(020)->X(010) transition.

Figure 8 shows the LIF spectrum of SiH₂ obtained thus in the SiH₄/Ar plasma. Photon pulses in the period of 50-490 ns after laser excitation were counted for 500 laser pulses at each excitation wavelength. Two observed peaks were 580.11 nm (000->110 transition) and 579.72 nm (100->110 transition).

In the RF SiH₄/Ar plasma, the behavior of the SiH₂ radical density was investigated at the excitation wavelength of 580.1 nm which is the absorption peak, the total gas pressure
of 5.3 Pa, the SiH₄ flow rate of 5 sccm and the distance of 0.65 cm from the RF electrode. To avoid the background emission, the discharge was turned off after a short period of about 10 µs. Since the measured lifetime of the SiH₂ radical in the afterglow of SiH₄ plasma was about 30 µs, all measurements on the parameter dependence of the SiH₂ radical were carried out at 5 µs after the discharge turning-off, when the observed LIF intensity was almost the same as that during the on-period of the plasma.

The absolute SiH₂ density was estimated by comparing the saturated LIF intensity with Rayleigh scattering by N₂ gas.

Figure 9 shows the SiH₂ density as a function of the SiH₄ mixing ratio at the total pressure of 5.3 Pa and the RF power of 40 W. It is of the order of 10⁹ cm⁻³ which is much lower than the SiH₃ radical density. This SiH₂ radical density is of the same order of magnitude as that by ref. 11 (described in Sec. 3.2). The SiH₂ radical density decreases with the increase in the SiH₄ mixing ratio. This relative variation agrees with that in ref. 11 qualitatively.

3.2 ICLAS (Intracavity laser absorption spectroscopy) [11]

The SiH₂ radical density in the actual RF silane plasma was measured quantitatively using ICLAS first [11]. This is the method to obtain the long absorption length by placing the plasma in the dye laser cavity and to determine the low SiH₂ radical density.

Figure 10 shows the experimental arrangement of ICLAS. The RF chamber equipped with Brewster windows was placed in the cavity of the cw dye laser pumped by an Ar⁺ ion laser. The plane parallel electrodes were 8 cm diameter and 2 cm separation. The chamber was mounted on the sliding stage for the spatial distribution measurement.

![Fig. 10. Schematic diagram of the experimental arrangement of ICLAS. AOM represents the acousto-optic modulator.](image)

The dye laser was operated with a spectral linewidth of about 0.5 nm and the laser wavelength was tuned by the angle of the intracavity pellicle. The laser beam passing the plasma was introduced into the 3.4 m spectrograph having the reciprocal line dispersion of 0.125 nm/mm in 4th order. The signal was detected with an image sensor and averaged with a digitizing oscilloscope.

In this ICLAS, the rotational lines belonging to the (020)-(000) band of the A-X electronic transition of SiH₂ were used for the absorption measurement. The procedure for deriving the SiH₂ radical density from the measured absorption coefficient is almost the same as in IRLAS.

Figure 11 shows the SiH₂ radical density as a function of the mixing ratio of SiH₄ in Ar and H₂ measured at the total pressure of 26.6 Pa, the flow rate of 10 sccm, and the RF
power of 15 W. Also in this measurement by ICLAS, the SiH₂ radical density was determined to be of the order of $10^9$ cm$^{-3}$. In this measurement, the SiH₂ radical density decreases in the high SiH₄ mixing ratio region, which is qualitatively in agreement with that in Fig. 9 obtained by MLIF. This is due to the fact that the reaction rate of SiH₂ with parent molecules increases with the increase in the SiH₄ pressure.

Figure 12 shows the spatial distribution of the SiH₂ radical density in the SiH₄/Ar plasma measured at the total pressures of 120 Pa and 26.6 Pa and the RF power of 15 W. In this CVD chamber, the SiH₂ spatial distributions are rather symmetric.

The SiH₂ flux densities to the substrate estimated from the slopes of the spatial distributions shown in Fig. 12 were $3 \times 10^{12}$ and $4 \times 10^{12}$ cm$^{-2}$s$^{-1}$ at 120 Pa and 26.6 Pa, respectively. These are much smaller than the flux density required from the deposition rate (about 0.1 nm/s) of a-Si:H thin film observed experimentally. This result implies that the direct contribution of SiH₂ to the thin film formation is negligibly small. However there is the possibility that SiH₂ plays an important role as a precursor of other radicals which may contribute to the thin film formation.

4. MEASUREMENTS OF THE SiH AND Si RADICALS

On the SiH and Si radicals, relatively many measurements have been made mainly by using LIF until recently. For the comparisons with the SiH₃ and SiH₂ radicals, here, the recent results on the SiH and Si radical measurements in ref. 14 are described briefly.

The behaviors of the SiH and Si radicals in the RF silane plasma were investigated using LIF in detail in ref. 14. Figure 13 shows the spatial distributions of the densities of those radicals and the emission profiles (solid curves) of the excited SiH and Si at the total pressure of 26.6 Pa and the RF power of 15 W in the SiH₄(10 %)/Ar plasma. Both of the SiH and Si radical densities are of the order of $10^9$ cm$^{-3}$. The spatial distributions of the SiH and Si radical densities are relatively close to those of the emission lines of SiH and Si, respectively. This is possibly due to the fact that the lifetimes of the SiH and Si radicals are relatively short because of their high reactivity with parent molecules and therefore the influences of the diffusion process on SiH and Si are little.

The Si radical density in the RF silane plasma was measured also with ring dye laser absorption spectroscopy by us[15]. In this method, because the ring dye laser with the very