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Description	

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Identification of Si and SiH in catalytic chemical vapor deposition of SiH_4 by laser induced fluorescence spectroscopy

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Radical species produced in catalytic chemical vapor deposition (CVD), often called hot-wire CVD, processes were identified by using a laser induced fluorescence technique. Ground state Si atoms could be detected at low pressures where collisional processes in the gas phase could be ignored. The electronic temperature of Si atoms just after the formation on the catalyzer (tungsten) surfaces was 1320 ± 490 K, when the catalyzer temperature was 2300 K. By the addition of 0.5 Pa of Ar, the electronic temperature was lowered down to 450 ± 30 K. The absolute density of Si atoms was $3 \pm 1\times 10^9\ cm^{-3}$ at 10 cm below the catalyzer when the flow rate and the pressure of SiH_4 were 0.5 sccm and 4 mPa, respectively. This density is just 0.3% of that of the parent SiH_4 molecules. However, since the decay rate of Si atoms is fast, it can be concluded that atomic silicon is one of the major products on the heated catalyzer surfaces. SiH radicals could also be detected, but the production rate of this species is two orders of magnitude less than that of Si atoms. It was also discovered that volatile SiH_4 molecules are produced by the atomic hydrogen attack on the amorphous silicon deposited on the chamber walls. © *2000 American Institute of Physics.*
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I. INTRODUCTION

The catalytic chemical vapor deposition (Cat-CVD), often called hot-wire CVD, technique to produce thin films has been developed in recent years.[1–5] It is known that device quality amorphous silicon, polycrystalline silicon, and silicon nitride films are easily obtained at low temperatures around 600 K. In this technique, gaseous materials, such as SiH_4 and H_2, are introduced into a vacuum chamber and are decomposed to radical species on heated catalyzer surfaces. The most widely used catalyzer material is tungsten. The relationship between the deposition conditions, such as the gas flow rate and the catalyzer temperature, and the properties of the deposited films has been examined extensively.[1,6,7] However, little information is available on what species are important in the film deposition. It is not clear what the primary decomposition product on the heated catalyzer surfaces is. The kinetic behavior of the radical species in the gas phase has just been speculated on. In order to control the film properties, such kinetic information is essential.

Doyle *et al.* have studied the Cat-CVD processes by using a mass spectrometric technique.[3] They employed a threshold ionization technique to ionize free radicals selectively. According to their results, the main products at the heated tungsten surfaces are Si and H atoms when SiH_4 was used as a reactant gas. Horbach *et al.* have also demonstrated that atomic silicon is the main precursor of the films by measuring the decomposition coefficients of SiH_4 at various filament temperatures.[8] However, the absolute scales of the radical densities have not been given in these studies.

In this article, a newly designed Cat-CVD chamber is described. With this chamber, radical species in the gas phase can be monitored by laser spectroscopic techniques such as laser induced fluorescence (LIF). Si atoms as well as SiH radicals could be identified and their absolute densities were measured under various conditions. It was also discovered that H atoms etch Si films deposited on the chamber walls to generate SiH_4 molecules, and that the densities of Si related species are strongly affected by the existence of H atoms.

II. EXPERIMENT

A schematic diagram of the Cat-CVD chamber is illustrated in Fig. 1. A showerhead to introduce gaseous species was attached to the top flange of the chamber. A ceramic frame with a tungsten wire was also installed at this top flange. The length and the diameter of the tungsten wire were 100 cm and 0.4 mm, respectively. A substrate holder was equipped at the bottom of the chamber. The chamber was evacuated with a turbomolecular pump (Osaka Vacuum TG1000), while the gas flow rates were controlled with mass flow controllers (STEC SEC-400MK3). The total pressure in

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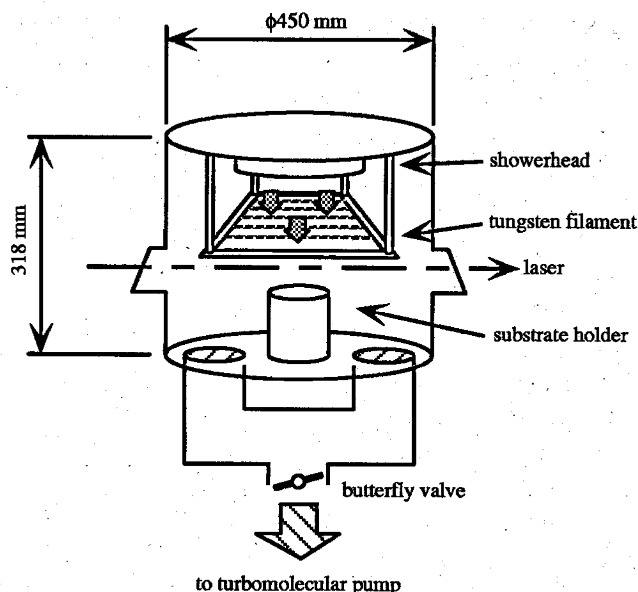

FIG. 1. Schematic diagram of the Cat-CVD chamber.

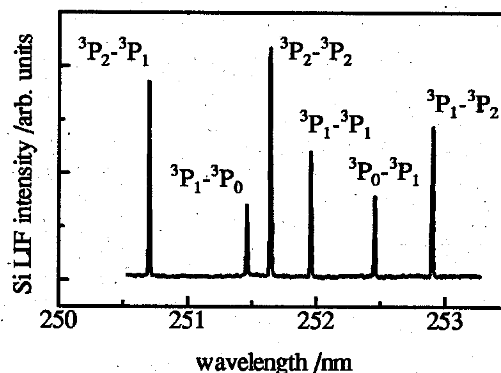

FIG. 2. LIF spectrum of Si atoms. The flow rate and the pressure of SiH_4 were 0.5 sccm and 4 mPa, respectively.

the chamber was monitored with a capacitance manometer (MKS 622). Pressures below 1 mPa were measured with an ionization gauge (Anelva MIG-061). The gas pressures could be controlled either by changing the flow rates or by throttling the butterfly valve to the pump. The laser beam was parallel to both the substrate holder and the tungsten filament. The distance between the filament and the detection zone was fixed at 10 cm, while the filament temperature was kept at 2300 K. The filament temperature was measured with a two-wavelength thermometer (Chino IR-AQ). This chamber can also be arranged for other detection methods, such as cavity ringdown spectroscopy and coherent anti-Stokes Raman scattering.[9,10] A quadrupole mass spectrometer (Anelva M-QA200TS) can also be attached to this chamber.

A pulsed dye laser (Lumonics HD-500) pumped with a *Q*-switched Nd:YAG laser (Spectra Physics PRO-190-10) was used to detect radical species such as Si and SiH. In the detection of Si, the output of the dye laser was doubled in frequency by using an angle-tuned β-BaB_2O_4 crystal. An autotracker (Inrad AT-III) was used when the wavelength was scanned. Coumarin 500 (Exciton) was used as a laser dye when Si was detected, while Furan 2 (Lambda Physik) was used when SiH was detected. The laser beam was introduced through a quartz window at the Brewster angle. The exit window was also tilted at the Brewster angle in order to reduce the reflection. The LIF was collected through a 350 mm focal length plano-convex collimating lens (Sigma Koki) and a 150 mm focal length bi-convex focusing lens (Sigma Koki) and detected with a photomultiplier tube (Hamamatsu Photonics R212UH). A slit was inserted between the focusing lens and the photomultiplier tube in order to reduce the stray light and the blackbody radiation from the catalyzer. A band-pass filter (Schott BG24 or Sigma Koki 410B) was also used to isolate the fluorescence. In the spectrum measurements, the photomultiplier signal was amplified and processed with a boxcar averager-gated integrator system (Stanford Research Systems SR240/SR250/SR280) and transferred to a computer (IBM PC300PL) via a general purpose interface bus. The temporal profiles of the fluorescence were recorded with a digital oscilloscope (LeCroy 9310CM). Both the laser and the detection systems were triggered with a delay/pulse generator (Stanford Research Systems DG535).

SiH_4 (Takachiho 99.9999%), H_2 (Takachiho 99.99995%), and Ar (Takachiho 99.9995%) were used from cylinders without further purification.

III. RESULTS

A. Detection of Si atoms

Figure 2 shows the LIF spectrum of Si atoms. The six spectral lines correspond to the $3p4s\,^3P_{J'}-3p^2\,^3P_{J''}$ transitions. In this measurement, the pressure was kept low enough to avoid secondary collisional processes among the gaseous species. The flow rate of SiH_4 was 0.5 sccm, while the pressure was 4 mPa. This pressure was determined by extrapolating the relationship between the flow rate and the pressure. Under such conditions, the detected Si atoms can be regarded as the primary decomposition products at the catalyzer surfaces since no collisions are expected during the transport from the catalyzer to the detection zone. The pulse energy of the laser was 120 μJ, which is intense enough to saturate the transitions.

The peak heights of the spectral lines in Fig. 2 can be converted to the relative populations of the $3p^2\,^3P_0$, $^3P_1$, and $^3P_2$ states if the relative detection sensitivities are known. However, the evaluation of the relative sensitivities is not straightforward. Since the lifetime of the upper $3p4s\,^3P_{J'}$ state is 5 ns and comparable to the duration time of the laser,[11] the excited atoms may decay radiatively during the irradiation of the laser pulse. The ground state atoms thus formed may reabsorb the laser light. The temporal profile of the laser pulse is not known precisely. Under such circumstances, it is difficult to estimate the number of this absorption–emission cycle; i.e., the degree of *pumpover*.[12] Then, the relative sensitivities were determined experimentally under thermal conditions. As will be discussed later, it is rather easy to determine the rotational state distributions of SiH, because the lifetime of the upper state is long enough not to decay during the laser pulse.[13,14] When the total pres-

sure of the system was 6.7 Pa, the rotational temperature of SiH was 390±40 K, which must be in near equilibrium with the temperature of the water-cooled inner walls of the chamber. The LIF intensities for $3p^2\,{}^3P_0$, ${}^3P_1$, and ${}^3P_2$ states were measured under the same conditions and the relative sensitivities were determined. Then, the populations of the $3p^2\,{}^3P_{J''}$ states under various conditions, including collision free conditions, were determined. From these relative populations, it is possible to evaluate the electronic temperature of Si atoms. It was 1320±490 K under the collision free conditions, at the total pressure of 4 mPa. By the addition of 0.5 Pa of Ar, this temperature was lowered down to 450±30 K. When the electronic temperature is high, the Si atoms must also be hot in the translational motion.

The absolute density of Si atoms was evaluated by comparing the LIF intensity I_{LIF} with the intensity of the Rayleigh scattering caused by Ar, I_R. The procedure is similar to that employed by Kono *et al.* for the absolute density measurement of SiH_2.[15] The $3p4s\,{}^3P_0-3p^2\,{}^3P_1$ transition at 252.4 nm was employed because the upper $3p4s\,{}^3P_0$ state can only decay back to the original $3p^2\,{}^3P_1$ state, and it is possible to regard this system as a complete two-level system. The differential cross section for Rayleigh scattering by Ar can be evaluated from the wavelength, the refractive index, and the density of the scattering gas.[16] The differential cross section at 252 nm is calculated to be $1.27\times10^{-26}\,cm^2$. The refractive index of Ar under standard conditions at 252 nm was estimated to be 1.000 31 from the refractive index at 590 nm, 1.000 28.[17] The time integrated LIF intensity was measured under completely saturated conditions. Under such conditions, the population ratio of the upper $3p4s\,{}^3P_0$ state to that of the lower $3p^2\,{}^3P_1$ state is 1/6 when the excitation laser is linearly polarized.[18] The collisional mixing among the Zeeman sublevels can be ignored because of the low pressure in the chamber. When $3p^2\,{}^3P_1-3p4s\,{}^3P_0-3p^2\,{}^3P_1$ transition cycle was employed, the emission from the $3p4s\,{}^3P_0$ state is isotropic since the corresponding depolarization coefficient is 0.[18] This isotropy was checked experimentally by rotating the plane of polarization of the laser with a double Fresnel rhomb (Sigma Koki). The laser beam diameter was 2.6 mm, while the pulse energy was 700 μJ. The intensity of the Rayleigh scattering was measured with the same setup. Since the output of the autotracker is horizontally polarized, the plane of polarization was rotated to be perpendicular to the observation direction with a double Fresnel rhomb after passing through a Glan-laser prism (Sigma Koki). The detection sensitivities for LIF and Rayleigh scattering can be assumed to be the same, since no polarization dependent detectors, such as a monochromator, were used. The I_{LIF}/I_R intensity ratio was 2.8 when the Ar density was $3.2\times10^{16}\,cm^{-3}$. Then, the absolute density of $3p^2\,{}^3P_1$ is determined to be 1.4×10^9 cm^{-3}. Since the electronic temperature of Si atoms is 1320 K, the total density of ground state Si atoms is calculated to be $4.2\times10^9\,cm^{-3}$. Here, one more correction is necessary; the correction for pumpover. Si atoms in the upper $3p4s\,{}^3P_0$ state may decay radiatively during the pulsed laser irradiation and may absorb laser light once again, as has been mentioned already. In such a case, the population of the Si atoms may be overestimated. If the temporal profile of the laser pulse is rectangular and the duration is the same as the radiative lifetime of the upper state, this overestimation should be a factor of 2. Since the laser pulse is not rectangular, the overestimation factor should be less than 2. In other words, the absolute density of Si atoms must be between 2.1 and $4.2\times10^9\,cm^{-3}$, or more compactly $3\pm1\times10^9\,cm^{-3}$. It should be noted that, under such low density conditions, radiation imprisonment can be ignored. This is important when the spin-orbit state distributions under various conditions are compared because the fluorescence is not, in general, isotropic and the anisotropy depends on the degree of radiation imprisonment.

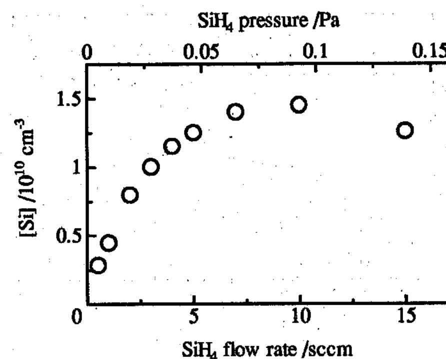

FIG. 3. SiH_4 flow rate (pressure) dependence of the Si atom density.

In order to check the validity of the present procedure for the density measurements, the absolute atomic density of Hg was measured. The $6s6p\,{}^3P_1-6s^2\,{}^1S_0$ resonance transition at 253.7 nm was employed for the LIF measurement, while the Rayleigh scattering by Ar was measured at 253.9 nm. A small reaction vessel made of stainless steel was used. A cold finger made of Pyrex glass was attached as a Hg reservoir. The temperature of the Hg reservoir was maintained at 255 K, while the other part of the vessel was kept at 293 K. Since the vapor pressure at 255 K is 3.1 mPa, the atomic density in the vessel should be $8.2\times10^{11}\,cm^{-3}$.[17,19] The measured density was $7\pm2\times10^{11}\,cm^{-3}$, which is consistent with the above value.

Figure 3 shows the SiH_4 flow rate (pressure) dependence of Si atom densities. It should be noted that the collisional mixing among the upper $3p4s\,{}^3P_{J'}$ states is still minor at these pressures. In this measurement, the butterfly valve to the pump was fixed, while the flow rate of SiH_4 was changed. The Si atom density increases at first and then decreases. The decrease should be attributed to the reaction between Si and SiH_4 in the gas phase. The bimolecular rate constant for this reaction has been reported to be as large as $4\times10^{-10}\,cm^3\,s^{-1}$.[20,21] The reaction of Si with SiH_4 must over-compensate the production of Si atoms on the catalyzer surfaces. The SiH_4 pressure dependence was also measured by fixing the flow rate at 10 sccm. The Si atom density decreased from 1.5×10^{10} to $0.9\times10^{10}\,cm^{-3}$, when the pressure was changed from 0.1 to 1.3 Pa by throttling the butterfly valve.

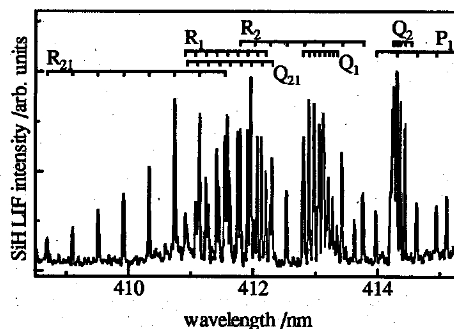

FIG. 4. LIF spectrum of SiH radicals. The flow rate and the pressure of SiH_4 were 10 sccm and 1.0 Pa, while those of H_2 were 150 sccm and 5.7 Pa, respectively.

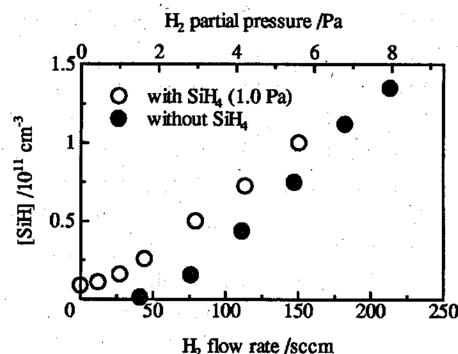

FIG. 6. H_2 flow rate (pressure) dependence of the SiH radical density in the presence and in the absence of 1.0 Pa of SiH_4.

B. Detection of SiH radicals

The LIF spectrum of SiH obtained in the presence of 1.0 Pa of SiH_4 and 5.7 Pa of H_2 is illustrated in Fig. 4. The flow rates were 10 and 150 sccm, respectively. SiH radicals could not be detected under collision free conditions as for Si atoms. Then, experiments were carried out at high pressures where secondary collisional processes cannot be ignored. All the spectral lines in Fig. 4 can be assigned to the (0,0) band of the $A\,^2\Delta - X\,^2\Pi$ system.[22] The (1,1) band was below the detection limit. In recording this spectrum, the pulse energy of the laser was reduced to 40 μJ in order not to saturate the transitions. The rotational population distribution was evaluated from the spectral peak heights and the Hönl–London factors.[23,24] The temporal profiles of the induced fluorescence were measured at $J''=2.5$, 4.5, and 7.5, where J'' is the total angular momentum quantum number of the lower state. The profiles were identical and the lifetime was 0.6 μs. This value agrees with the radiative lifetime reported recently, suggesting that collisional quenching is minor.[13,14] The radiative lifetime of the $A\,^2\Delta$ state is so long that it is not necessary to take into account any anisotropy in the radiative decay processes or the effect of pumpover.

Figure 5 shows the Boltzmann plot of the rotational populations of SiH in the vibrational ground state. A least squares analysis shows that the rotational temperature is 390 ± 40 K.

The absolute density of SiH was also evaluated. The procedure is similar to that employed for Si atoms. The R_{21} ($J''=4.5$) transition at 410.3 nm was utilized. The differential cross section for Rayleigh scattering by Ar at this wavelength is $1.62\times10^{-27}\,cm^2$. The ratio of the LIF signal intensity I_{LIF} in the presence of 1.0 Pa of SiH_4 and 5.7 Pa of H_2 to the Rayleigh scattering intensity I_R in the presence of 13.6 kPa of Ar was measured to be 4.1. The beam diameter was 5.0 mm, while the pulse energy of the laser was 1.3 mJ. Taking into account the Boltzmann distribution at 390 K, degeneracy of the upper and lower levels as well as the contribution of the Λ doublets, the ground state SiH density was evaluated to be $1.1\pm0.2\times10^{11}\,cm^{-3}$. A consistent result was obtained when the R_{22} ($J''=5.5$) transition at 412.5 nm was employed. The density was $0.8\pm0.2\times10^{11}\,cm^{-3}$. By averaging these values, the absolute density of SiH was determined to be $1.0\pm0.3\times10^{11}\,cm^{-3}$.

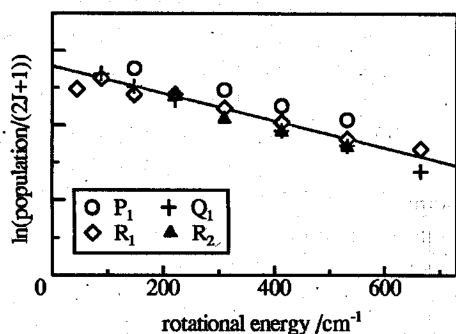

FIG. 5. Boltzmann plot of the rotational level populations of $SiH(X\,^2\Pi, v''=0)$.

The SiH density was found to increase with the partial pressure of H_2. This is why we measured the density by using a mixture of SiH_4 and H_2, instead of pure SiH_4, which we used in the density evaluation of Si atoms. During the measurements of the H_2 pressure dependence, a unique phenomenon concerned with H_2 inclusion was observed. SiH radicals could be detected even in the absence of SiH_4, if H_2 was introduced. No SiH signal was observed when Ar was introduced instead of H_2. Similarly, Si atoms could be detected in the presence of pure H_2. Figure 6 shows the H_2 flow rate (pressure) dependence of the SiH signal in the presence and in the absence of 1.0 Pa of SiH_4. The SiH signal increases nonlinearly, especially in the absence of SiH_4. One of the plausible explanations for the production of SiH in the absence of SiH_4 is as follows. The first step is the production of H atoms on the heated catalyzer surfaces.[25] The second step is the production of SiH_4 by the reaction of H atoms with the silicon compounds, possibly amorphous silicon, deposited on the chamber walls. As will be discussed later, the production of SiH_4 from H atoms was confirmed mass spectrometrically. The final step is the production of SiH by the following sequential abstraction reactions in the gas phase:

$$H+SiH_4 \rightarrow H_2+SiH_3+51\,kJ\,mol^{-1}, \tag{1}$$

$$H+SiH_3 \rightarrow H_2+SiH_2+144\,kJ\,mol^{-1}, \tag{2}$$

$$H+SiH_2 \rightarrow H_2+SiH+114\,kJ\,mol^{-1}, \tag{3}$$

or

$$Si+SiH_3 \rightarrow SiH+SiH_2+2\,kJ\,mol^{-1}. \tag{4}$$

Other reactions to produce SiH, such as $Si+SiH_4 \rightarrow SiH+SiH_3$, are all endothermic. The rate constants for reactions (1) and (2) have been reported to be 3×10^{-13} and $4 \times 10^{-11}\,cm^3\,s^{-1}$, respectively.[26–29] The nonlinear increase of the SiH signal against the H_2 pressure is consistent with the above mechanism. The decomposition of SiH_4 on the catalyzer surfaces cannot be the major source of SiH. The SiH signal in the presence of 1.0 Pa of SiH_4 is comparable to that in the presence of 2.0 Pa of pure H_2. If all the SiH radicals were formed from SiH_4 on the catalyzer surfaces, all the H_2 molecules introduced must have been converted to SiH_4, which cannot be true. The termolecular process to produce SiH, $Si+H+M \rightarrow SiH+M$, in the gas phase cannot be important, either, because the bimolecular insertion process, $Si+SiH_4 \rightarrow H_3SiSiH$, must be much faster under the present conditions. In general, the termolecular rate constants do not exceed $1 \times 10^{-30}\,cm^6\,s^{-1}$. The importance of the bimolecular reaction between Si and SiH_4 shall be discussed later.

The production of SiH in the absence of SiH_4 may suggest that, unless the wall conditions are specified, the absolute density measurements of SiH are meaningless. However, the extrapolated value to the zero pressure of H_2 must be independent of the wall conditions. The SiH density in the absence of H_2 is $9 \times 10^9\,cm^{-3}$ when the SiH_4 pressure is 1.0 Pa. The reaction of SiH with SiH_4 is termolecular and slow at low pressures.[30,31] Below 3 Pa, diffusional loss is more dominant than the reactive one.[30] In other words, the decay rate of SiH at 4 mPa must be faster than that at 1.0 Pa. Then, the SiH density at 4 mPa can be estimated to be less than $3 \times 10^7\,cm^{-3}$, which is two orders of magnitude smaller than that of Si atoms under the same conditions.

Detection of SiH_2 by an LIF technique was also tried, but we failed to observe any signals. The experimental conditions were the same as those employed for the SiH detection. The wavelength was scanned between 577 and 580 nm.[15,32,33] The lack of the signal should be attributed to the low transition probabilities as well as the predissociative nature of $SiH_2\,(\tilde{A}\,^1B_1)$.[33] It was also difficult to separate the LIF signal from the blackbody radiation from the catalyzer.

C. Mass spectrometric studies

Quadrupole mass spectrometric studies show that SiH_4 is produced in the reaction of atomic hydrogen with the Si compounds deposited on the chamber walls. Figures 7(a) and 7(b) show the mass spectra in the presence of 0.1 mPa of SiH_4, with and without heating the catalyzer. In these spectra, the background signals due to residual gases are subtracted. Shown in Fig. 8 is the difference spectrum with and without heating the catalyzer in the presence of 5 mPa of H_2. In these measurements, the mass spectrometer was attached to the chamber directly without using a sampling hole, in order to avoid any possible reduction of radical species at the hole. The mass peaks at 29, 30, and 31 in Fig. 7(a) are around 10% smaller than those in Fig. 7(b), while that at 28, which corresponds to Si^+, is 20% larger. This indicates that 10% of SiH_4 is decomposed at the catalyzer, and that Si is one of the main products. Si_2H_6 can also be identified as a minor product. The spectra shown in Figs. 7(a) and 8 are similar, suggesting that the main volatile species produced at the chamber walls is SiH_4. Si compounds were also observed when a virgin filament was used, showing that chamber walls are the only major sources of these species. Silicon deposition as well as silicification of the filaments is not a critical problem in Cat-CVD processes if the filament temperature is controlled higher than 1800 K during the deposition.[1] The production of SiH_4 from H and *a*-Si:H has been demonstrated by Perrin *et al.*, although the absolute yield has been reported to be low.[34,35] In Fig. 8, the mass peak at 28 is smaller than that in Fig. 7(a). This can be accounted for by considering that SiH_4 produced on the chamber walls may have less probability of being decomposed at the catalyzer surfaces.

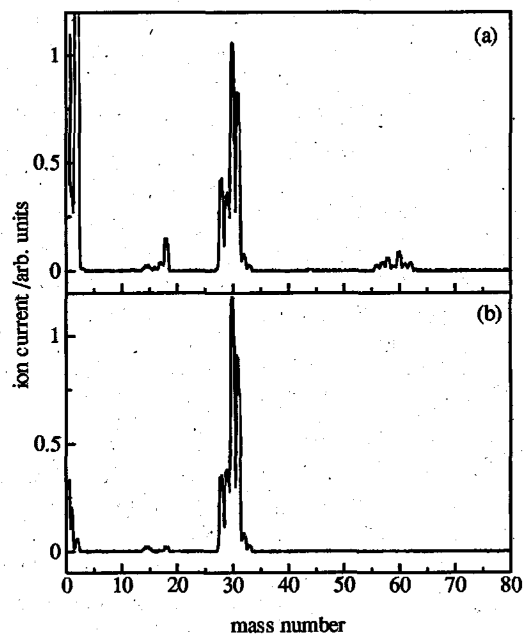

FIG. 7. Quadrupole mass spectra measured in the presence of 0.1 mPa of SiH_4 with (a) and without (b) heating the catalyzer. The background signal is subtracted.

IV. DISCUSSION

Steady state conditions can be assumed for all the intermediate species in the gas phase. In other words, the formation rate must be equal to the decay rate. The steady state

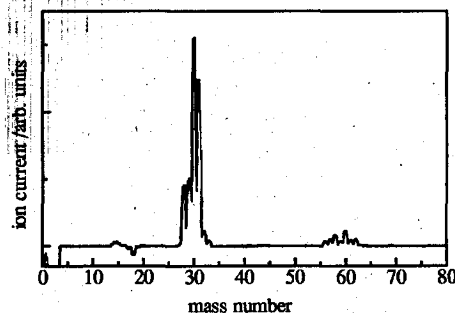

FIG. 8. Difference of the mass spectra measured with and without heating the catalyzer in the presence of 5 mPa of H_2.

density of Si atoms [Si] at 10 cm downstream from the catalyzer was 3×10^9 cm^{-3} when the SiH_4 pressure was 4 mPa. Under such conditions, since the mean free path is comparable to the geometry of the chamber, collisional decay processes in the gas phase may be ignored. The decay of Si atoms is controlled by the collisional processes with the chamber walls. The Si–wall collision rate k_w can be estimated from the surface/volume ratio of the chamber and the thermal velocity of Si atoms.[36] It is 4×10^3 s^{-1}. The surface loss coefficient β for Si atoms has not been reported but may be assumed to be around 0.5, judging from the loss coefficients for silicon hydride radicals.[31] If this value is much less than 0.5, the observed electronic temperature of Si should be much lower. Then, the decay rate per unit volume, $k_w\beta$ [Si], should be on the order of 6×10^{12} cm^{-3} s^{-1}. If the spatial distribution of Si atoms is uniform, from the chamber volume of 5×10^4 cm^3, the total decay rate of Si should be 3×10^{17} s^{-1} which must be equal to the total production rate. This value is too large because the flow rate of SiH_4 is only 0.5 sccm, which is equivalent to 2×10^{17} s^{-1}. This discrepancy strongly suggests that the Si atom density is not homogeneous. The Si atom density must decrease sharply with the distance from the catalyzer.

The above consideration suggests that the production of Si atoms is one of the major processes in the catalytic decomposition of SiH_4, although further quantitative analysis is difficult. Just for simplicity, let us assume that Si atoms are localized only at the space between the catalyzer and the substrate holder and that the density is uniform in this region. The volume is 3000 cm^3. Then, the total formation rate of Si should be 1.8×10^{16} s^{-1}. According to our mass spectrometric measurements, 10% of SiH_4 introduced into the chamber decomposes when the SiH_4 pressure is 0.1 mPa. If the efficiency is the same at 4 mPa, the total decomposition rate of SiH_4 is 2×10^{16} s^{-1}. The ratio of the formation rate to the decomposition rate 0.9 should represent the fraction of Si atoms among all the decomposed species. Of course, such a model is far from quantitative, but it may be concluded that Si atoms are important in the film deposition under low pressure conditions where gas phase reactions can be ignored. This conclusion is consistent with the observation by Doyle *et al.* who observed Si and H atoms as major initial products by employing a mass spectrometric technique.[3] Very recently, Koshi and his co-workers have also came to the same conclusion by observing Si atoms by using a photoionization mass spectrometer.[37,38] Of course, the above discussion is consistent with our own mass spectrometric measurements.

The direct production of SiH at the catalyzer surfaces is minor. The estimated density of SiH under collision free conditions is two orders of magnitude smaller than that of Si atoms. It is difficult to imagine that the decay rate of SiH is two orders of magnitude faster than that of Si.

In general, the primary products on the catalyzer surfaces are not necessarily the same as the deposition species. The primary products may change themselves by chemical reactions in the gas phase. Molenbroek *et al.* have shown that radical reactions in the gas phase improve the film quality.[6] Si atoms react with SiH_4 molecules rapidly.[20,21] In general, triplet atomic biradicals, such as $O(^3P)$ and $C(^3P)$, cannot insert into a single bond.[39–41] In the present $Si(^3P)$ system, hybridization must take place before inserting into an Si–H bond to produce silylsilylene, H_3SiSiH. After the insertion, the H_3SiSiH radicals may isomerize to form disilene $H_2Si{=}SiH_2$.[42,43] This species is stable and may reach the substrate or the chamber walls without reacting with SiH_4 or H_2 and may contribute to the film deposition.[6] Disilene is not a radical and may be less sticky. This unstickiness enhances its surface mobility and makes the film dense. Si_2H_4 may further decompose to Si_2H_2 and H_2.[44,45] However, according to very recent photoionization mass spectrometric measurements by Koshi and co-workers, Si_2H_2 has not been identified,[37,38] although they have succeeded in the detection of this species in the thermal decomposition of Si_2H_6.[46] SiH_3 radicals formed in the gas phase reaction, $H+SiH_4\rightarrow H_2+SiH_3$, is another candidate for the film precursor. It is now well established that SiH_3 is one of the major film precursors in plasma-enhanced CVD processes.[47]

V. CONCLUSIONS

By the use of a laser induced fluorescence technique, Si atoms and SiH radicals could be identified during the Cat-CVD processes of SiH_4. Si atoms are directly generated efficiently on the heated tungsten surfaces, while the direct production of SiH radicals is minor. SiH radicals are produced in the gas phase by secondary processes. Atomic silicon is one of the major species responsible for the silicon film growth at low pressures. However, at high pressures, gas phase reactions must become important and the direct precursor of the film must be different. Disilene, Si_2H_4, is one of the candidates.

Atomic hydrogen produced on the catalyzer surfaces plays important roles in Cat-CVD processes. It reacts with amorphous silicon deposited on the chamber walls to produce SiH_4. The absolute density measurement of H atoms is currently required. Atomic hydrogen should also contribute to the production of SiH_3 radicals in the gas phase by reacting with SiH_4. SiH_3 thus produced is another candidate for the Si film precursor. Detection of SiH_3 radicals by cavity ringdown spectroscopy is now in progress in our laboratory. The depletion of the SiH_4 density should also be measured. The coherent anti-Stokes Raman scattering technique should be useful for such measurements.

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