Transactions of the Materials Research Society of Japan. Vol. 20

Hydrogenated silicon clusters in SiH_4 plasma

A. Suzuki
Electrotechnical Laboratory, 1-1-4 Umezono
Tsukuba-shi, Ibaraki 305, Japan

Neutral hydrogenated silicon clusters (Si_nH_x) in radio frequency (RF, 13.56 MHz) glow-discharge SiH_4 plasma were investigated using photoionization mass spectroscopy (PIMS). Largest Si_nH_x of Si_4H_{10} was observed particularly at high pressure of 80 mTorr with 5 W of RF power. Dependence of neutral Si_4 density on plasma parameters (rf power, total pressure and cathode-anode distance) suggests that the growth of higher Si_nH_x is fairly minor under the optimized plasma conditions for a-Si:H film deposition.

1. INTRODUCTION

In silane (SiH_4) plasma, which is used for preparing hydrogenated amorphous silicon (a-Si:H) films, many kinds of radicals and ions are generated by collisions between electrons and SiH_4 molecules. These species result in a-Si:H films on substrates after gas-phase and surface reactions. Growth of hydrogenated silicon cluster ions ($Si_nH_x^+$) has been studied by several authors using traps. A magnetic trap with Fourier transform mass spectrometer was used by Mandich et al. to study clustering reactions of SiD_n^+ with SiD_4 systematically [1-4]. Kanayama et al. employed a quadrupole ion trap to grow $Si_nH_x^+$ and suggested detailed stable structures for $Si_nH_x^+$ (n=5, 6, and 10) [5]. Growth kinetics for $Si_nH_x^+$ in dc plasma was investigated by Weakleim et al. They presented that larger $Si_nH_x^+$ can be formed by sequential chain reactions of $Si_nH_x^+$ [6].

However, little information is reported on neutral Si_nH_x rather than ionic species of $Si_nH_x^+$ due to difficulties in detection. Concerning neutral Si_nH_x, their concentrations are 5-6 orders of magnitude higher than those of $Si_nH_x^+$ in SiH_4 plasma [7].

In this study, photoionization mass spectroscopy (PIMS) have been employed to detect neutral Si_nH_x in SiH_4 plasma. Although the SiH_4 plasma condition dependence of a-Si:H film quality is well known, that of Si_nH_x density is not. From this point of view, relative densities of Si_nH_x were studied by changing a total pressure, an applied radio-frequency power, and a distance between parallel electrodes in SiH_4 plasma.

2. EXPERIMENTAL

Fig. 1 shows schematic view of experimental setup used in this study, which consists of a conventional chamber for plasma enhanced chemical vapor deposition

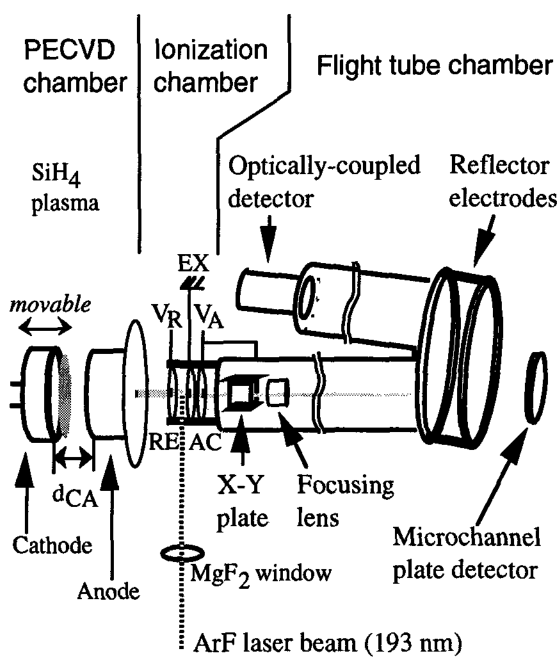

Figure 1. Schematic view of experimental apparatus used in this study. RE: repeller plate, EX: extraction plate, AC: acceleration plate

(PECVD) with a sampling orifice and a reflectron-type time-of-flight mass spectrometer (TOF-MS).

2.1. PECVD chamber

Before SiH_4 gas was introduced into PECVD chamber, it was evacuated down to the pressure of 4 X 10^{-7} Torr. Parameters on SiH_4 plasma were set to the optimal condition for preparing a-Si:H films. A flow rate of SiH_4 was 5 SCCM and a total pressure in the PECVD chamber was kept at 30-80 mTorr. 13.56 MHz radio frequency (rf) glow-discharge SiH_4 plasma was generated between parallel electrodes. In this chamber, a spacing between two electrodes can be varied from 30-80 mm by sliding the cathode electrode. 2-50 W of rf power was applied to the cathode electrode. Anode temperature was 250 °C which is also optimal as the substrate temperature for a-Si:H deposition.

2.2. TOF-MS

TOF-MS has two chambers. One is an ionization chamber and the other is a flight tube chamber. Each chamber has independent evacuation systems; the base pressures were almost same of 8×10^{-8} Torr. The ionization chamber has two MgF_2 windows. Si_nH_x species were extracted into the ionization chamber through a 2 mm diameter aperture located on the anode electrode by pressure difference. They are ionized at the middle of the two windows by ArF (193 nm) excimer laser (Lambda Physics EMG 103 MSC) which passes the center of the MgF_2 windows. During mass analysis, pressures in the ionization and the flight tube chamber reached to 1×10^{-4} and 3×10^{-6} Torr respectively.

Ions created in the ionization region were repelled by the repeller voltage (V_R = 200 V) and drawn through the extraction grid which is grounded to the earth. Under influence of an acceleration voltage (V_A = -2500 V), they were accelerated into the flight tube. While ions subsequently travel, they passed between the X-Y deflection plates, and the focusing ion lens steered the beam. These plates affected the ion flight line considerably but these voltages were adjusted to less than +10 V as compared to the voltage on the flight tube to maximize an ion current. Compensation of a transverse displacement due to the initial beam velocity is attained by voltages on the reflector.

3. RESULTS AND DISCUSSION

3. 1. Mass spectrum

A typical mass spectrum obtained from standard SiH_4 plasma mentioned above is shown in figure 2. Four groups of signal peaks related to $Si_nH_x^+$ (n=1-4), hydrogen atom and molecular ions by ArF laser were detected in this study. The group which appears at around 28 μs of TOF are assigned as to come from silane-related species (SiH_n^+, n=0-5) because these signals can be seen even when SiH_4 gas was introduced without plasma. Difference of these signal intensities from those in a plasma are quite small. A mass resolution (M/ΔM) at 28 μs was 320.

When discharge was turned on, three groups of mass signal peaks appeared at around 38, 46, and 54 μs of TOF. Calibration of mass for those signals was carried out based on the number of peaks in each group. For example, the peaks located around 38 μs consist of 7 peaks, thereby, these peaks are supposed to be come from $Si_2H_x^+$ (x=0-6). In the same way, the third mass group was assigned as $Si_3H_x^+$ (x=0-8). Finally, it is estimated that the peaks in the

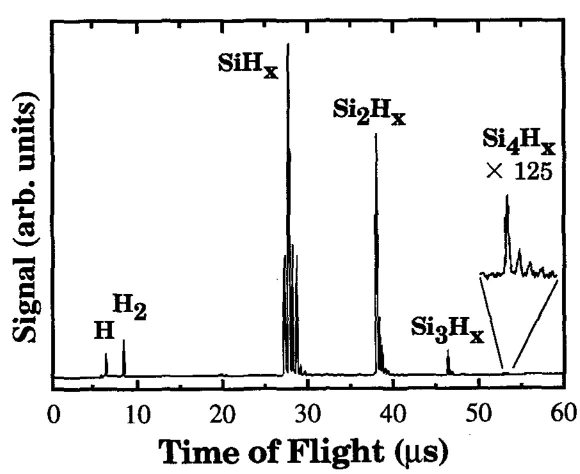

Figure 2. Mass spectrum obtained under total pressure of 30 mTorr and rf power of 5 W. ArF laser intensity was 87 mJ/cm^2.

fourth group come from Si_4H_x (x=0-10) by comparison to former three groups.

All Si_nH_x can be ionized through non-resonant two-photon ionization process by ArF laser (6.4 eV) since their ionization energy are in the range of 7.97-11.0 eV [8-9]. A photodissociation occurs together with a photoionization, thereby, all $Si_nH_x^+$ may not be arisen from the same mass of neutral Si_nH_x. However, as can be seen in fig. 2, the signal intensity is drastically depleted by the one order of magnitude with the number of silicon in $Si_nH_x^+$ increases by one. This means that the number of $Si_nH_x^+$ resulting from photodissociation of higher neutral Si_mH_x (m>n) is small. Therefore, in this paper, plasma condition dependence of the neutral Si_nH_x density is discussed under the assumption that the signal of each $Si_nH_x^+$ is primary originated from the neutral same mass of Si_nH_x.

Haller presented that relative densities of neutral Si_nH_x (n=2-4) over SiH_x are smaller than those of $Si_nH_x^+$ (n=2-4) over SiH_x^+ with ionizer on and off in a quadrupole mass spectrometer [10]. The ratio of $Si_nH_x^+$ (n=2-4) / SiH_x^+ obtained in this study quantitatively agrees with that of neutrals rather than ions.

3. 2. Pressure and RF power dependence of Si_4

The signal intensity originating from Si_4 is plotted against rf power and total pressure in fig. 3 since the signal intensity of Si_4 is the strongest in the heaviest group of Si_4H_x (x=0-10). The intensity of Si_4 increases with rf power up to 30 W and decreases up to at least 50 W. Though a deposition rate of a-Si:H films was not measured for each plasma condition, it is proportional to the flux density of film precursors of SiH_x (x=0-3) [11]. Present increase of Si_4 signal is quite similar to that of the deposition rate of a-Si:H film up to 30 W, which is explained by the increase of electron density [12].

As the total pressure increases, Si_4 signal increases almost linearly. It is reported that the electron density increases linearly for 13.56 MHz glow discharge plasma with total pressure in the range of 50-100 mTorr [13].

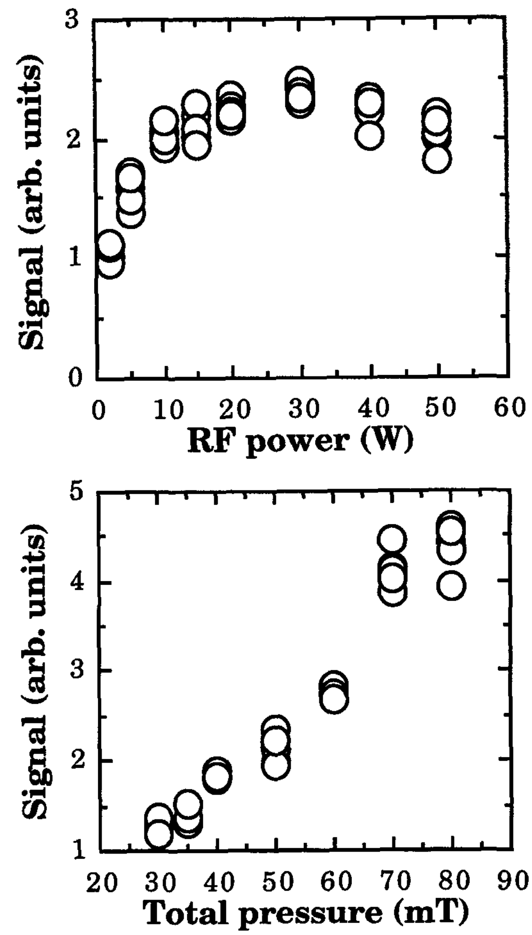

Figure 3. Relative Si_4 signal intensity plotted as a function of rf power and total pressure.

Enhancement of Si_4 signal by pressure is more effective rather than that by rf power. This can be explained by three-body reactions of SiH_2 with stable molecules, [14] in addition to the increase of electron density. However, these are still uncertain, because a variation of total pressure should modify many parameters in SiH_4 plasma. Finally, the Si_4 density is 3-4 orders of magnitude less the SiH_n (n=0-5) density.

3. 3. Dependence of Si_4 on the spacing of parallel electrodes

Weakleim et al. reported that $Si_nH_x^+$ (n≥2) tends to increase when a sampling orifice-to-cathode distance is increased with

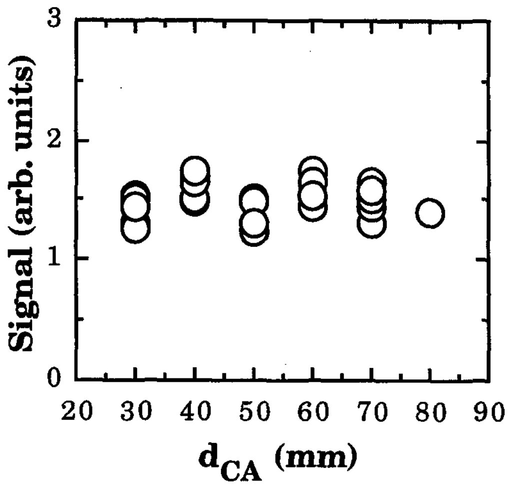

Figure 4. Cathode-anode spacing dependence of Si_4 signal.

keeping cathode-anode distance constant [6]. They suggested that $Si_nH_x^+$ (n≥2) are produced mainly via sequential reactions of $S_nH_x^+$ with SiH_4 in the gas-phase far away from negative glow in dc plasma.

For comparison, the cathode-to-anode (sampling orifice) distance was varied by shifting the cathode electrode. Figure 4 shows the intensity of Si_4 plotted as a function of the distance between the cathode and the sampling orifice, which corresponds to the cathode-to-anode distance (d_{CA}). As can be seen in fig. 4, Si_4 is almost constant against d_{CA}. $Si_nH_x^+$ (n≥2) production was not enhanced with d_{CA} in contradiction with the results by Weakleim et al. [6].

By taking a volume of chamber, a flow rate and a total pressure, residence time of SiH_4 in gas phase is calculated to be 0.2 s, which is about one order of magnitude shorter than that in the experiment by Weakleim et al. [6]. Therefore, a probability for chain reactions of $Si_nH_x^+$ with SiH_4 should be smaller. In a calculation reported, the relative Si_2H_6 density increases with a factor of 2 with the increase of residence time from 0.1 to several seconds [15].

4. SUMMARY

Si_nH_x (n=1-4) species were detected in SiH_4 plasma under the optimum condition for a-Si:H deposition and other modified conditions using PIMS. The heaviest Si_nH_x species observed in our PECVD chamber was Si_4H_{10}. It is found that the production of high Si_nH_x (x≥2) is not efficient under the optimized conditions for making device-quality a-Si:H films.

In terms of a source for higher size of hydrogenated silicon cluster (Si_nH_x, n>4), further investigations will be required, such as longer residence time for SiH_4 gas or "unstable" SiH_4 plasma which is not used for making device-quality a-Si:H films.

REFERENCES

1. M. L. Mandich, W. D. Reents, Jr. and M. F. Jarrold, J. Chem. Phys .88 (1988) 1703.
2. M. L. Mandich, W. D. Reents, Jr. and K. D. Kolenbrander, J. Vac. Sci. Technol. B 7 (1989) 1295.
3. M. L. Mandich, W. D. Reents, Jr. and K. D. Kolenbrander, J. Chem. Phys .92 (1990) 437.
4. M. L. Mandich, and W. D. Reents, Jr., J. Chem. Phys. 95 (1991) 7360.
5. H. Murakami, and T. Kanayama, Appl. Phys. Lett. 67 (1995) 2341.
6. H. A. Weakleim, R. D. Estes, and P. A. Longeway, J. Vac. Technol. A5 (1987) 29.
7. A. Matsuda, and K. Tanaka, Thin Solid Films 92 (1982) 171.
8. K. Fuke, K. Tsukamoto, F. Misaizu, and M. Sanetaka, J. Chem. Phys. 99 (1993) 7807.
9. J. Berkowitz, J. P. Green, H. Cho, and B. Ruscic, J. Chem. Phys. 86 (1987) 1235.
10. I. Haller, Appl. Phys. Lett. 37 (1980) 282.
11. A. Matsuda, T. Kaga, H. Tanaka, L. Malhotra, and K. Tanaka, Jpn. J. Appl. Phys. 22 (1983) L115.
12. J. C. Knights, Jpn. J. Appl. Phys. 18, Suppl. 1 (1979) 101.
13. S. Oda, J. Noda, and M. Matsumura,, Jpn. J. Appl. Phys. 29 (1990) 1889.
14. J. M. Jasinski, and J. O. Chu, J. Chem. Phys. 88 (1988) 1678.
15. J. P. Conde, K. K. Chan, J. M. Blum, M. Arienzo, and J. J. Cuomo, J. Appl. Phys. 71 (1992) 3981.