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Spatial distribution of $SiCl_n$ (n=0–2) in $SiCl_4$ plasma measured by mass spectroscopy*

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For a better understanding of the deposition mechanism of thin films in $SiCl_4$ source gas, we have measured the spatial distributions of $SiCl_n$ (n=0–2) radicals in $SiCl_4$ radio frequency glow discharge plasma utilizing a mass spectrometer equipped with a movable gas sampling apparatus. The experimental results demonstrate that the relative densities of $SiCl_n$ (n=0–2) radicals have peak values at the position of 10 mm above the powered electrode along the axial direction; the relative densities of the Si and $SiCl_n$ (n=1, 2) radicals have peak values at the positions of 27 mm and 7 mm away from the axis along the radial direction, respectively. Generally speaking, in the whole $SiCl_4$ plasma bulk region, the relative density of Si is one order of magnitude higher than that of SiCl, and the relative density of SiCl is several times higher than that of $SiCl_2$. This reveals that Si and SiCl may be the primary growth precursors in forming thin films.

Keywords: $SiCl_n$ (n=0–2) neutral radicals, spatial distribution, mass spectrometric diagnosis
PACC: 5275R, 0710, 0630E

1. Introduction

Silicon tetrachloride ($SiCl_4$), as one of the widely used gases, has been proved effective in the chemical vapour deposition (CVD) for polycrystalline silicon (poly-Si) and relevant thin films for manufacturing solar cells and thin film transistors, and patterning small structures such as Si-based metal-oxide-semiconductor (MOS) devices.[1−8] In previous work, we have deposited poly-Si films in $SiCl_4/H_2$ gases by using the plasma-enhanced chemical vapour deposition (PECVD) technique and obtained the poly-Si films with the deposition rate over 3.0 Å/s without deterioration of the optoelectronic properties.[9,10] To improve deposition rate and film quality, it is important to clarify the deposition mechanism of poly-Si films.

It is generally accepted that $SiCl_n$ (n=0–2) radicals are the dominant deposition precursors, and $SiCl_3$ is primary etching radical during deposition of poly-Si films in $SiCl_4$ source gas. So, measuring these radicals especially their spatial distributions is very important for clarifying the deposition mechanism of poly-Si films. In the last few years, some work has been carried out on the detecting of silicon chloride radicals in depositing and etching processes by using a number of plasma diagnostic techniques, such as mass spectroscopy (MS) and optical emission spectroscopy (OES).[6−8]

Optical spectroscopic diagnostic techniques, such as laser-induced fluorescence (LIF) spectroscopy and optical emission spectroscopy (OES), are powerful for measuring the neutral radicals in plasma with higher sensitivity and spatial resolution. However, the exciting and emitting spectra of these radicals always cover a very wide range, generally from ultraviolet to infrared, these spectra have to be measured by different spectrometers. In other words, it is difficult to use only one spectroscopic setup for detecting simultaneously all radicals in plasma.

Mass spectrometry is a simple and useful diagnostic technique and it can measure all radicals in plasma if their masses distribute in a large range. However, it must be operated under a high vacuum environment due to its particular conformation and operation principle. This makes it only detect those gas species sampled from a fixed position of plasma bulk, such as aperture of discharge chamber wall and

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discharge electrodes. Until now, no spatial distributions of $SiCl_n$ (n=0–2) radicals have been measured by means of mass spectroscopic analysis.

Recently, we have proposed and established a movable gas sampling apparatus that is suitable for mass spectroscopic sampling in our laboratory.[11,12] Using the movable apparatus, we can diagnose plasma states and analyse gas species properties at any sampling position in plasma. Utilizing the proposed straight-line fit method of deducing the depletion fraction of discharge plasma,[11,12] we have measured the spatial distributions of $SiCl_n$ (n=0–2) radicals in $SiCl_4$ radio frequency (rf) (13.56 MHz) glow discharge plasma.

2. Experiment and method

The experimental arrangement has been depicted in our previous papers.[11,12] It consists of a traditional PECVD system, a special sampling apparatus, a differentially pumping system and a residual gas analyser (RGA).

The discharge chamber was equipped with two parallel plate electrodes made of stainless steel. The glow discharge plasma in the chamber was generated by a capacitively coupled rf power source and confined in the space between the parallel electrodes with a gap of 30 mm. The flow rate of source gas was controlled by a mass flowmeter. The technical parameters were the chamber pressure (20 Pa), the substrate temperature (25 ^{o}C), the rf power (30 W, corresponding to a power density of 0.3Wcm^{-2}), and the $SiCl_4$ flow rate (5.8 SCCM). The mass spectrometric sampling position was fixed at the position of 2 mm under the substrate surface, and the radicals at this position could make a larger contribution to the film growth.

The sampled gas species from plasma region were introduced into the RGA ionization chamber via the above-mentioned movable gas sampling apparatus. Because the filament of RGA must operate in a high vacuum environment (10^{-2} Pa or less), it was important to keep the RGA ionization chamber at a stable pressure less than 10^{-2} Pa by using a differentially pumping system.

The mass spectroscopic signals of the sampled gas species from plasma region were detected by a residual gas analyser (SRS RGA-100) with a minimum detectable partial pressure of 6.7×10^{-12} Pa. The RGA-100 has a mass range from 1 to 100, and it consisted of a probe and electronic control unit (ECU). The ECU completely controlled the operation of the RGA, handled and transmitted its data to the computer for analysis and display.

In order to obtain the desired relative densities of $SiCl_n$ (n=0–2) radicals from the measured mass spectroscopic signals of the sampled gas species, it is necessary to deduce the depletion fraction (f) of the $SiCl_4$ plasma using the following equation:[11,12]

$$C_1^n = -S_0^n + f\,C_2^n, \tag{1}$$

where, $C_1^n = (S_{\rm off}^n(E_{\rm e}) - S_{\rm on}^n(E_{\rm e}))/\alpha_n(E_{\rm e})$, $C_2^n = S_{\rm off}^n(E_{\rm e})/\alpha_n(E_{\rm e})$, and $\alpha_n(E_{\rm e}) = \sigma_n(E_{\rm e})/\sigma_{n\,\max}(E_{\rm e\,m}^n)$. Both $S_{\rm off}^n(E_{\rm e})$ and $S_{\rm on}^n(E_{\rm e})$ are the mass spectroscopic signals of $SiCl_n^+$ (n=0–2) measured by RGA with discharge off and on at a certain electron energy ($E_{\rm e}$), respectively. $\sigma_n(E_{\rm e})$ and $\sigma_{n\ \max}(E_{\rm em}^n)$ are the ionization cross sections at the electron energy ($E_{\rm e}$) and the maximum ionization cross section corresponding to the certain electron energy ($E_{\rm em}^n$) for each $SiCl_n$ (n=1, 2), respectively. S_0^n is the mass spectroscopic signal of each sampled $SiCl_n$ (n=1, 2) radical and characterizes the relative density of each $SiCl_n$ (n=1, 2) radical in $SiCl_4$ plasma.

Corresponding to all the electron energy range of mass spectrometer, C_1^n versus C_2^n had a good linear relationship. According to Eq.(1), the slope of a straight line fit of C_1^n versus C_2^n is just the value of deflection fraction f.

In the process of deducing $SiCl_4$ depletion fraction, the values of ionization cross sections of $SiCl_n$ (n=1, 2) radicals are calculated using the theoretical models of Joshipura and are listed in Table 1.[13]

Table 1. The ionization cross-sections σ_n ($E_{\rm e}$) of $SiCl_n$ (n=1, 2) radicals.

Electron energy /eV	Ionization cross section (in 10^{-16} cm^2)	
	SiCl (IP*:10.93 eV)	$SiCl_2$ (IP*:10.93 eV)
15	0.33	0.46
20	1.63	1.88
25	2.74	3.59
30	3.54	5.06
35	4.19	5.99
40	4.66	6.76
45	5.03	7.54
50	5.36	8.13
60	5.82	9.03
70	6.14	9.59
80	6.37	9.86
90	6.52	10.08
100	6.63	10.22

*Assumed Ionization Potential (IP).

Define $S^n(E_{e0})$ as the S^n at a certain electron energy E_{e0} and $S^n(E_{e0})$ will be expressed as follows:[22]

$$S^n(E_{e0}) = S^n_{on}(E_{e0}) - (1-f)\,S^n_{off}(E_{e0})\,. \qquad (2)$$

Obviously, $S^n(E_{e0})$ characterizes the relative densities of the $SiCl_n$ (n=0–2) radicals in $SiCl_4$ plasma. We have calculated the relative densities of $SiCl_n$ (n=0–2) radicals by Eq.(2) using the average of depletion fraction deduced using the abovementioned method under different sampling positions at E_{e0}=40 eV.

3. Results and discussion

Figures 1(a) and (b) show the axial and radial distributions of $SiCl_4$ depletion fraction, respectively. The depletion fraction of $SiCl_4$ is deduced from the measured $SiCl^+$ and $SiCl_2^+$ signals by our newly proposed straight-line fit method. It is obvious that although the values of f are obtained from different mass spectroscopic signals of SiCl and $SiCl_2$, they are very close to each other within the deviation of the statistical fluctuation.

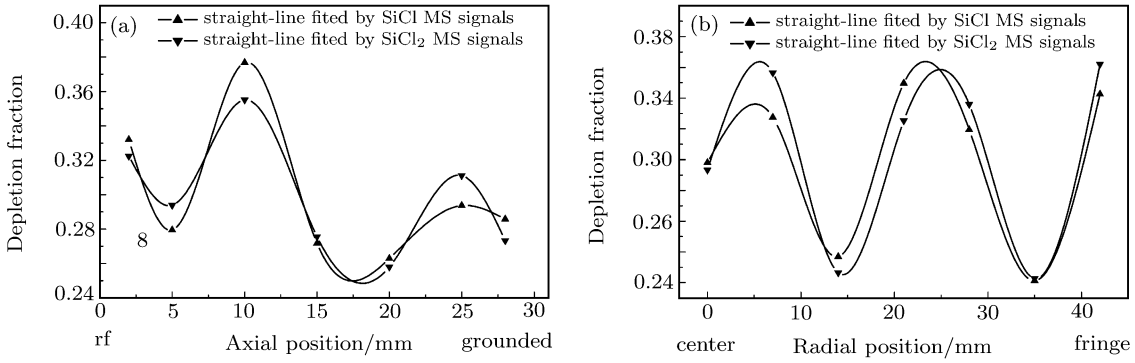


Fig.1. (a) The axial distribution of $SiCl_4$ depletion fraction; (b)The radical distribution of $SiCl_4$ depletion fraction.

From Figs.1 (a) and (b), we can also see that the axial and radial distributions of $SiCl_4$ depletion fraction look like cosine and sine waveforms, respectively. This may results from the distributions of electric field and the $SiCl_4$ plasma sheaths. More detailed studies are needed for analysing the axial and radial distributions of $SiCl_4$ depletion fraction.

Figures 2(a) and (b) show the axial and radial distributions of $SiCl_n$ (n=0–2) relative densities, respectively. It is obvious that the relative densities of the $SiCl_n$ (n=0–2) radicals have peak values along not only the axial direction but also the radial direction. The experimental results demonstrate that the relative densities of the $SiCl_n$ (n=0–2) radicals have peak values at the position of 10 mm above the rf-powered electrode along the axial direction; the relative densities of the Si and $SiCl_n$ (n=1, 2) radicals have peak values at the positions of 27 mm and 7 mm away from the axis along the radial direction, respectively.

From Figures 2(a) and (b), we can also see that Si is the most abundant radical in $SiCl_4$ plasma, SiCl is the second, and $SiCl_2$ is less than SiCl in number of radical. Generally speaking, in the whole $SiCl_4$ plasma space, the relative density of Si is one order of magnitude higher than that of SiCl, and the relative density of SiCl is several times higher than that of $SiCl_2$. This reveals that Si and SiCl may be the dominant precursors in forming the poly-Si film.

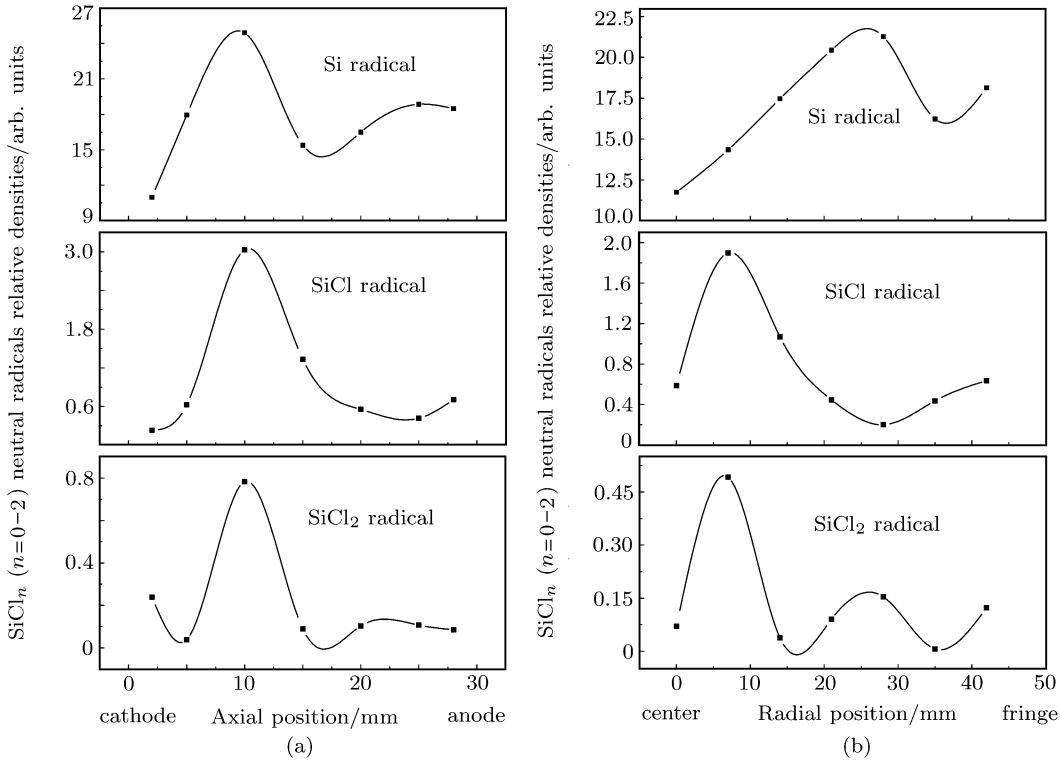


Fig.2. (a) The axial distribution of $SiCl_n$ (n=0–2)-radicals relative densities; (b) The radical distribution of $SiCl_n$ (n=0–2)-radicals relative densities.

These measured spatial distributions of $SiCl_n$ (n=0–2) radicals can provide useful data for researching the spatial reaction process in $SiCl_4$ plasma and understanding the deposition mechanism of poly-Si thin films. Moreover, further study of $SiCl_n$ (n=0–2) radial distribution for seeking a suitable deposition condition is beneficial to improving the uniformity of thin films.

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