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A new method of measuring the spatial distribution of depletion fraction of silane plasma by mass spectrometer*

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A newly established movable sampling apparatus of mass spectrometer is used to measure the spatial distribution of depletion fraction of silane plasma. A straight-line fit method of deducing the depletion fraction of silane is proposed. Theoretical analysis and test results demonstrate that the proposed new method is universal and more accurate than the existing one. There exist a largest peak near the middle of two electrodes and two peaks near the electrodes in the spatial distribution of silane depletion fraction, which are related to the distribution of electric field and the silane plasma sheaths.

Keywords: movable sampling apparatus of mass spectrometer, spatial distribution, straight-line fit, depletion fraction of radio frequency (rf) glow discharge

PACC: 5275R, 8280, 0710

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) film is an important semiconductor material and widely used in solar cells, thin film transistors for matrix liquid crystal displays and sensors. The a-Si:H film is usually prepared by plasma-enhanced chemical vapor deposition (PECVD) in silane (SiH_4) radio frequency (rf) glow discharge. However, the deposition mechanism of a-Si:H is still not well understood, and the fundamental reaction processes occurring on the substrate surface and in the space of plasma continue to be studied with interest experimentally and theoretically.[1−6] It is generally believed that the major precursors of a-Si:H film are SiH_n (n=0–3) neutral radicals. So it is important to measure systematically the densities of these neutral radicals for better understanding the film deposition mechanism and relevant chemical dynamics.

Some diagnostic techniques such as optical spectroscopy[7−9] and mass spectrometry[10−13] have been used to detect SiH_n (n=0–3) neutral radicals in silane discharge plasma. Optical spectrum analysis is a powerful tool for measuring the spatial distribution of the radicals. Due to the exciting and emitting spectra of the SiH_n (n=0–3) neutral radicals covering a very wide range, from the ultraviolet rays of Si, via the visible light of SiH and SiH_2, to the infrared rays of SiH_3, it is difficult to measure the spectra of all neutral radicals simultaneously by using only one piece of optical spectroscopy diagnostic equipment.

It can be realized to measure all SiH_n (n=0–3) neutral radicals in silane plasma using a mass spectrometer. No spatial distribution of the radicals is measured by mass spectrometer, because the sampling positions in all existing mass spectrometers each is fixed at a certain position.

The depletion fraction of silane is a key parameter for measuring the neutral radicals in silane plasma. Robertson *et al* have proposed a method to obtain the depletion fraction of silane, and we have measured the relative abundance of neutral radicals in silane plasma using the depletion fraction obtained by this method at a fixed sampling position.[10,11]

In this paper a new method, straight-line fit, of measuring the depletion fraction of silane is proposed

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based on the Robertson method. And the spatial distribution of depletion fraction of silane is measured for the first time using a newly established movable sampling apparatus of mass spectrometer. In this paper also described are basic theory of the straight-line fit method, the mechanics of the newly established movable gas-sampling apparatus of mass spectrometer, and characteristic analysis of the spatial distribution of depletion fraction of silane. The depletion fraction of silane deduced by the straight-line fit method is compared with that by the existing method. The test results show that the new method is universal and more accurate than the existing one.

2. Experiment apparatus

The experimental setup is shown schematically in Fig.1. The discharge chamber is equipped with two parallel electrodes made of stainless steel plates. The SiH_4 glow discharge in the chamber is generated by a capacitively coupled rf power source and confined in the space between the parallel electrodes with a gap of 30mm. The operation pressures are fixed at ~5Pa and ~10Pa corresponding to flow rate of 4.0 sccm and 7.5 sccm, respectively, controlled by a mass flowmeter. The mass spectroscopic signals of the SiH_n (n=0–3) are detected by a residual gas analyzer (SRS RGA 100) with a minimum detectable partial pressure of 6.66×10^{-12}Pa. A thin glass tube with an inner diameter of 1 mm is located in parallel with the electrodes. One end of the glass tube is used as a sampling aperture on the central symmetry axis of the parallel electrodes, the other is compactly inserted into the upper part of inner column of the coaxial polytetrafluoroethylene (PTFE) tube. The bottom part of the column is linked to the RGA chamber through a stainless steel tube with an inner diameter of 3mm. The inner column and its outer tube consisting of the coaxial PTFE tube are well matched and the inner column can slide smoothly in the outer tube. Thereby, the sampling position can be changed along the central symmetry axis from the bottom powered electrode to the upper grounded electrode which the substrate is hung beneath. Because the glass tube immersed in the plasma is so thin and the other parts of the sampling apparatus are close to the wall of the discharge chamber, outside the bulk plasma, the disturbance of sampling apparatus to the discharge plasma is negligible.

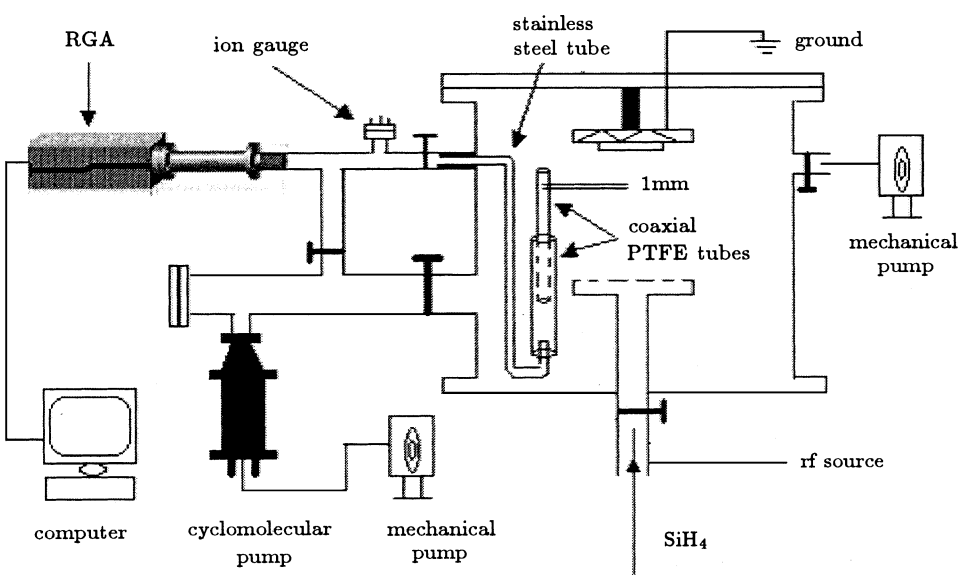


Fig.1. Schematic diagram of experimental apparatus for on-line mass spectroscopic analysis of SiH_4 plasma.

3. Theoretical analysis

The mass spectroscopic signals $S^n_{\rm off}(E_{\rm e})$ and $S^n_{\rm on}(E_{\rm e})$ of SiH^+_n (n=0–3) are measured by RGA with the discharge being off and on at a certain electron energy ($E_{\rm e}$), respectively. $S^n_{\rm on}(E_{\rm e})$ can be expressed as

$$S^n_{\rm on}(E_{\rm e}) = S^n_{\rm ion} + S^n(E_{\rm e}) + (1-f)S^n_{\rm off}(E_{\rm e}), \quad (1)$$

where $S^n(E_{\rm e})$ is the mass spectroscopic signals of SiH_n (n=0–3) radicals created and sampled from glow discharge chamber and ionized at $E_{\rm e}$ in RGA chamber,

$S^n_{\rm ion}$ is ion signals of SiH^+_n (n=0–3) created in the discharge chamber and leaked into the RGA, and f is defined as the depletion fraction of SiH_4.

The leakage ion signals are too weak to be detected even though the RGA is set at the maximum sensitivity because almost all of those leaked ions collide with the wall of long and thin gas sampling tube and are absorbed by the tube wall. Therefore, Eq.(1) can be simplified to the following form:

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

The contribution of $S^n(E_{\rm e})$ to $S^n_{\rm on}(E_{\rm e})$ can be neglected when the electron energy is several times the dissociate ionization threshold energy of SiH_4, which is because the ratio of $S^n_{\rm on}(E_{\rm e})/S^n_{\rm off}(E_{\rm e})$ is almost a constant no matter how the rf power or the pressure of discharge chamber is changed. Thus the depletion fraction of SiH_4 can be deduced by the following equation corresponding to a high electron energy:

$$f' = (S^n_{\rm off}(E_{\rm e}) - S^n_{\rm on}(E_{\rm e}))/S^n_{\rm off}(E_{\rm e}), \qquad (3)$$

where f' is defined as the depletion fraction of SiH_4 by the method of Robertson.[10]

Although the depletion fraction (f) of silane is a constant when the discharge condition and sampling position are fixed, all the signals of $S^n_{\rm off}(E_{\rm e})$, $S^n_{\rm on}(E_{\rm e})$ and $S^n(E_{\rm e})$ vary with electron energy because the ionization cross section of SiH_n (n=0–3) radicals and dissociation ionization cross section of silane are each a function of electron energy.

Considering the ionization cross sections of SiH_n (n=0–3) radicals at different electron energies, Eq.(2) can be changed into the following form:

$$S^n_{\rm on}(E_{\rm e}) = \alpha_n(E_{\rm e})\, S^n_0 + (1-f)\, S^n_{\rm off}(E_{\rm e}), \qquad (4)$$

where $\alpha_n(E_{\rm e})$ is defined as

$$\alpha_n(E_{\rm e}) = \sigma_n(E_{\rm e})/\sigma_{n\ \rm max}. \qquad (5)$$

$\sigma_n(E_{\rm e})$ and $\sigma_{n\ \rm max}$ are the ionization cross section at electron energy $E_{\rm e}$ and the maximum ionization cross section corresponding to a certain electron energy for each SiH_n (n=0–3), respectively. The values of $\sigma_n(E_{\rm e})$ and $\sigma_{n\ \rm max}$ of SiH_n (n=1-3) may be found in Refs.[14] and [15]. $S^n_{\rm o}$ is defined as the mass spectroscopic signal at the electron energy corresponding to the maximum ionization cross section for each SiH_n (n=0–3). Furthermore, Eq.(4) can be simplified as the following form:

$$C^n_1 = -S^n_0 + fC^n_2, \qquad (6)$$

where $C^n_1 = \dfrac{S^n_{\rm off}(E_{\rm e}) - S^n_{\rm on}(E_{\rm e})}{\alpha_n(E_{\rm e})}$, and $C^n_2 = \dfrac{S^n_{\rm off}(E_{\rm e})}{\alpha_n(E_{\rm e})}$.

According to Eq.(6), we propose a new method, straight-line fit of C^n_1 versus C^n_2 corresponding to all the electron energy ranges of mass spectrometer, to deduce the silane depletion fraction f; as a matter of fact, the slope of the line is right the value of f.

Because the straight-line fit of C^n_1 versus C^n_2 corresponds to all the electron energy ranges of mass spectrometer, this new method is universal compared with the existing method that is applicable only in a high electron energy range. Due to the contribution of $S^n(E_{\rm e})$ to $S^n_{\rm on}(E_{\rm e})$ not being neglected, the new method should be more accurate than the existing one. Moreover, the new method is suitable for measuring the depletion fraction of all AB_m-formed gas plasmas, such as SiH_4, GeH_4, CF_4, CH_4, SiF_4, $SiCl_4$ and SF_6 plasmas etc.

4. Results and discussion

Changing the discharge condition and sampling position, we obtain the spatial distribution of depletion fraction of silane by means of mass spectroscopic analysis. Figure 2 shows the straight-line fit of C^n_1 versus C^n_2 corresponding to SiH_2 under the discharge pressure P=5Pa and rf power $P_{\rm rf}$ =10W at the gas sampling position 28 mm away from the rf power electrode. A good linear relation of C^n_1 versus C^n_2 demonstrates that using the straight-line fit method to measure the depletion fraction of silane is feasible.

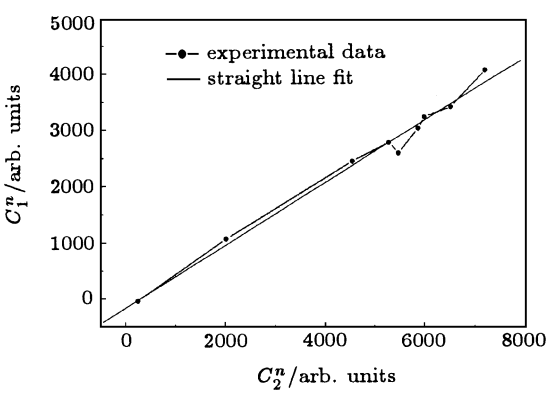


Fig.2. Straight line fit of C^n_1 versus C^n_2 corresponding to SiH_2 under the P=5Pa and $P_{\rm rf}$ =10W at the gas sampling position 28mm away from rf power electrode.

Figure 3 shows the silane depletion fraction versus sampling position measured by the new method and by the existing one, respectively, under the discharge pressure P and rf power $P_{\rm rf}$: 5Pa, 5W for (a) and 10Pa, 10W for (b).

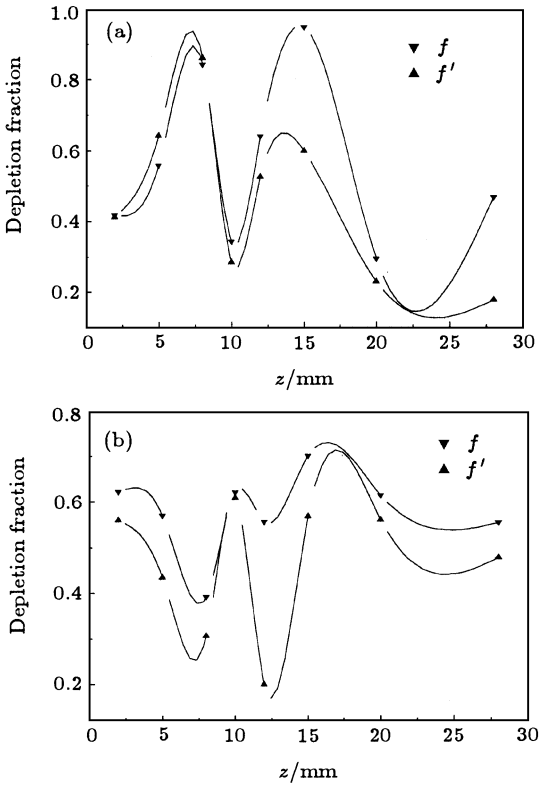


Fig.3. Depletion fraction versus sampling position under the pressure in discharge chamber P and rf power $P_{\rm rf}$: (a) 5Pa and 5W, (b) 10Pa and 10W respectively.

From Fig.3, we can see that both spatial distributions of f (by the straight-line fit method) and f' (by the existing method) are similar, and f is slightly larger than f' under the same discharge condition and at the same sampling position. Actually, f is obtained by using the following equation which is directly derived from the transformation of Eq.(2):

$$f = \frac{S^n_{\rm off}(E_{\rm e}) - S^n_{\rm on}(E_{\rm e}) + S^n(E_{\rm e})}{S^n_{\rm off}(E_{\rm e})}. \qquad (7)$$

The contribution of $S^n(E_{\rm e})$ to $S^n_{\rm on}(E_{\rm e})$ is not neglected in Eq.(7). Comparing Eqs.(3) and (7), f is larger than f', which is natural. This demonstrates that the new method is more accurate than the existing one.

A group of data for depletion fraction f of SiH_4 are obtained from the straight-line fit of the C^n_1 versus C^n_2 corresponding to radicals of SiH, SiH_2 and SiH_3 under different discharge pressures P and discharge powers $P_{\rm rf}$ at a series of sampling positions z. The curves of f versus z are shown respectively in Fig.4 (a) for P=5Pa and $P_{\rm rf}$=5W and (b) for P=10Pa and $P_{\rm rf}$=20W. It is obvious that although the curves of f versus z are obtained from different mass spectroscopic signals of radicals SiH, SiH_2 and SiH_3, respectively, they are almost the same in the deviation of the statistical fluctuation. It demonstrates that the depletion fraction f of SiH_4 depends on discharge condition and sampling position only. This is accordant with the qualitative analysis.

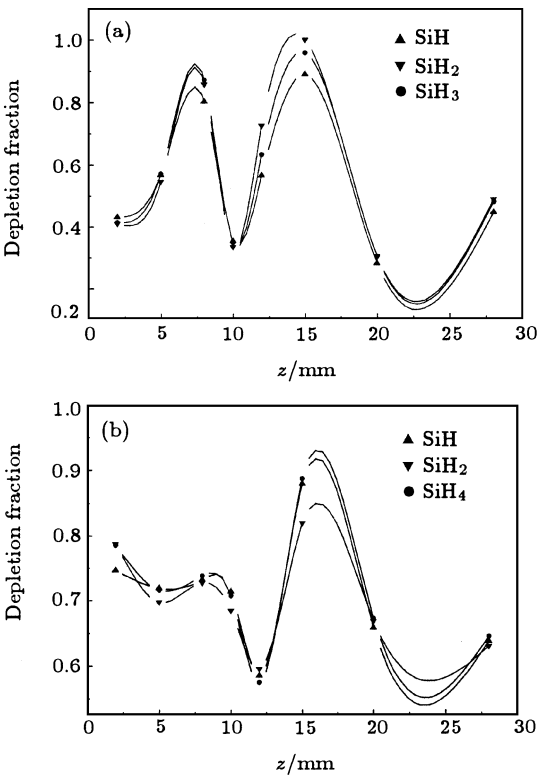


Fig.4. Depletion fraction of silane versus sampling position under the discharge pressures P and discharge powers $P_{\rm rf}$: (a) 5Pa and 5W, (b) 10Pa and 20W.

From Fig.4 it can be seen that the spatial distributions of depletion fraction of silane each has a largest peak near the middle of the two electrodes and two peaks at 7mm and 14mm under P=5Pa, $P_{\rm rf}$ =5W in Fig.4(a), and at 8mm and 16mm under P=10Pa and $P_{\rm rf}$ =20W in Fig.4(b). This is related to the distribution of electric field and the silane plasma sheaths generated near the two parallel plate electrodes of the rf glow discharge. It will be discussed in another paper.

5. Conclusions

From the above measurements and analyses, we can draw some conclusions as follows.

(1) The proposed new method of measuring silane depletion fraction in silane plasma is universal and more accurate than the existing one. This new method is suitable for all AB_m-formed gases.

(2) The spatial distribution of silane depletion fraction in silane rf glow discharge is measured for the first time by a newly established movable sampling

apparatus of mass spectrometer.

(3) The spatial distributions obtained from different mass spectroscopic signals of radicals SiH, SiH_2 and SiH_3, respectively, are almost the same in the deviation of the statistical fluctuation. It demonstrates that the depletion fraction f of SiH_4 depends on discharge condition and sampling position only.

(4) There exist a largest peak near the middle of two electrodes and two peaks near the electrodes, in the spatial distribution of silane depletion fraction, which may be related to the distribution of electric field and silane plasma sheaths. This will be discussed in another paper.

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