Vacuum ultraviolet absorption spectroscopy for absolute density measurements of fluorine atoms in fluorocarbon plasmas

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Absolute densities of fluorine (F) atoms at the ground state ($2p^5\ ^2P°$) were measured in helicon-wave excited high-density CF_4 plasmas by vacuum ultraviolet (VUV) absorption spectroscopy. By employing an electron cyclotron resonance CF_4 plasma as a light source in the VUV wavelength range, an absorption spectroscopy system with no vacuum windows was constructed. As a result, the density of F atoms was approximately $1\times10^{13}\ \mathrm{cm}^{-3}$ for an rf power of 1 kW and a CF_4 gas pressure of 2.5 mTorr, which was one-order higher than the density of CF_x radicals and was one-order lower than the density of the parent gas. © *1997 American Institute of Physics.* [S0003-6951(97)02711-3]

In the fabrication of ultralarge-scale integrated circuits (ULSI), fluorocarbon (CF_4, C_4F_8, etc.) plasmas are widely used for selective dry etching of silicon dioxide (SiO_2) over underlying silicon (Si) substrate. The principal problem in the SiO_2 etching using high-density, low-pressure plasma sources such as electron cyclotron resonance (ECR) plasmas, inductively coupled plasmas (ICP), and helicon-wave excited plasmas, is the low etching selectivity over Si, which is considered to be attributed mainly to the high fluorine (F) atom density in high-density plasmas. The etching selectivity is sensitive to the density ratio of CF_x radicals to F atoms, and the control of the composition of neutral species including F atoms is of great importance to obtain the high etching selectivity.[1]

The relative F atom density has been extensively measured by the actinometry technique,[2] which is in contrast to that of various methods such as laser-induced fluorescence (LIF) spectroscopy,[3] infrared laser absorption spectroscopy (IRLAS),[4] and appearance mass spectrometry (AMS),[5] which have been developed for the absolute density measurements of CF_x radicals. Estimation of the absolute F atom density is also possible with the actinometry by careful evaluations of excitation cross sections for FI (703.7 nm) and ArI (750.4 nm).[6] However, two primary assumptions have to be made for the actinometry: (1) all the excited F atoms contributing to the emission originate from the atomic ground state, (2) the excitation cross sections show the same energy dependence for both FI (703.7 nm) and ArI (750.4 nm). These assumptions seem to hardly be satisfied precisely in actual high-density plasmas.

In this letter, we have developed vacuum ultraviolet (VUV) absorption spectroscopy for the measurements of absolute F atom density. For detecting ground-state F atoms, the wavelength of the probe emission should be shorter than 100 nm. In this VUV wavelength range, both the light source and detector have to be installed in vacuum, and a windowless transmission line for the probe emission has to be constructed. To satisfy the above requirements, we used a compact ECR plasma device employing CF_4 gas as the light source. The absolute F atom density was measured with a satisfactory accuracy in helicon-wave excited high-density CF_4 plasmas.

The experimental apparatus is schematically shown in Fig. 1. The helicon-wave CF_4 plasmas were produced in a linear machine with a uniform magnetic field of 1 kG. An rf (13.56 MHz) power was applied to a $m=1$ helical antenna wound around a quartz glass tube of 3 cm in diameter and 25 cm in length.[7] The vacuum chamber was composed of a Pyrex glass tube (9 cm in diameter and 33 cm in length) and two stainless-steel observation chambers (20×20×10 cm). Pure CF_4 gas was employed for discharges with a fixed gas flow rate of 10 sccm. Plasmas were produced periodically with a repetition rate of 4 Hz and a discharge duration of 10 ms.

The measurements of F atom density were carried out in downstream plasmas at a distance of approximately 50 cm from the end of the helical antenna. The compact ECR plasma device was operated with a microwave (2.45 GHz) power of 0.1 kW and a CF_4 gas pressure of 1 mTorr. The length of the ECR plasma was approximately 40 cm. The emission from the ECR plasma was detected by a VUV monochromator (ARC, VM-502) with a wavelength resolution of 0.28 nm. The output signal from the monochromator was amplified by an electron multiplier tube and was recorded by a digital oscilloscope. The helicon-wave plasma source, the ECR plasma device, and the VUV monochromator were connected by vacuum tubes with no windows.

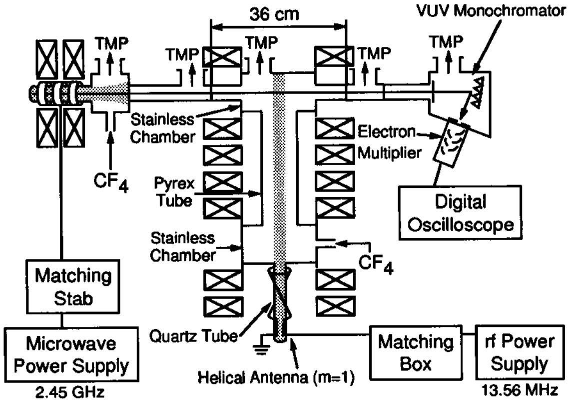

FIG. 1. Schematic of the experimental setup.

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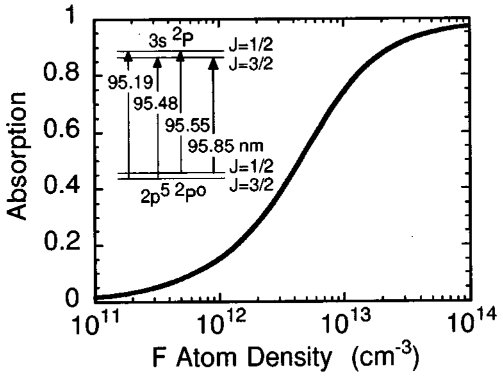

FIG. 2. Relation between the absorption A at 95.85 nm and the ground-state F atom density. The F atom temperatures in helicon and ECR plasmas are assumed to be 300 and 400 K, respectively. Partial energy level diagram of fluorine atom is also shown in the figure.

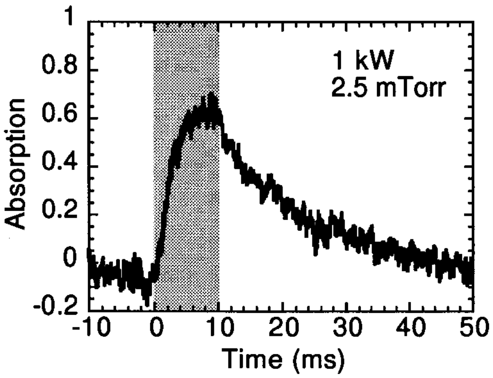

FIG. 3. Temporal variation of the absorption for an rf power of 1 kW and a CF_4 gas pressure of 2.5 mTorr.

Two connecting sections divided by four slits were differentially evacuated with turbomolecular pumps to prevent neutral species from passing through, so that the absorption length for the probe emission was determined to be 36 cm.

The relation between the absorption $A=1-I_t/I_0$ and the ground-state $(2p^5\ ^2P^{\circ}_{3/2,1/2,})$ F atom density is shown in Fig. 2 for the absorption length of 36 cm together with the partial energy level diagram of F atom, where I_0 and I_t are the incident and transmitted emission intensities, respectively. The resolution of the VUV monochromator was not sufficient to separate emissions at wavelengths of 95.48 and 95.55 nm. Accurate measurements were impossible with an emission at 95.19 nm since the absorption by the lower ground state $(2p^5\ ^2P^{\circ}_{3/2})$ became greater than 90%. Therefore, we chose a wavelength of 95.85 nm as the probe emission. The absorption by the parent gas and the other active species (CF_x radicals, C atoms, etc.) is negligible at this wavelength. With this emission, the density of the higher ground state $(2p^5\ ^2P^{\circ}_{1/2})$ can be obtained. The total density of F atoms at the ground state $(2p^5\ ^2P^{\circ}_{3/2,1/2})$ was evaluated by assuming the Boltzmann distribution at a temperature of 300 K for F atoms in the helicon chamber. Figure 2 was obtained with a conventional theory[8] by assuming the Doppler broadening at a temperature of 400 K for the spectral distribution of the probe emission. Since the lifetime of F atoms was longer than 5 ms, the uniform distribution can be assumed for the F atom density in the helicon chamber along the transmission line of the probe emission.

Figure 3 shows temporal variations of the absorption for an rf power of 1 kW and a CF_4 gas pressure of 2.5 mTorr. The rf power was applied to the helicon plasma during the hatched period (0–10 ms). The absorption was obtained by the following four-step measurements to subtract a background dark current and emission from the helicon plasma. First, only the ECR plasma was turned on and the emission intensity, including the dark current, was recorded (signal I_1). Second, both the helicon and ECR plasmas were turned on. The recorded data in this step (signal I_2) consisted of the dark current, the emission from the helicon plasma, and the emission from the ECR plasma with the absorption by F atoms in the helicon plasma. Third, the emission intensity from the helicon plasma was measured (signal I_3). Finally, the level of the dark current was recorded (signal I_4). Each of the four measurements was repeated 500 times to obtain a high signal-to-noise ratio. The incident emission intensity I_0 was obtained by subtracting the signal measured in the fourth step from that in the first step $(I_0=I_1-I_4)$, while the transmitted intensity I_t was obtained by subtracting the signal measured in the third step from that in the second step $(I_t=I_2-I_3)$. Referring to Fig. 2, the temporal variation of the absolute F atom density can be deduced easily from Fig. 3. The decay curve of the absorption contains interesting information about the reaction processes of F atoms. It is presently under the analysis, and the results, including the pressure dependence of the decay characteristics, will be reported elsewhere.

The F atom densities at a discharge time of 9.9 ms are plotted in Fig. 4 as a function of the rf power applied to the helicon plasma. In the figure, the averages of two measurements (on different days) for each rf power are indicated by solid circles and squares for CF_4 gas pressures of 2.5 and 10 mTorr, respectively. The error bars correspond to the results of the two measurements. The larger error bars for the 2.5 mTorr discharge than for the 10 mTorr one are mainly due to the poor reproducibility of the plasma production. In low-pressure discharges with high power, the plasma parameters were sensitive to the adjustment of the matching circuit, resulting in the greater scatter of the F atom density. As shown in Fig. 4, the absolute F atom density was obtained and was on the order of 10^{12}–10^{13} cm^{-3} for an rf power of 0.2–1.5

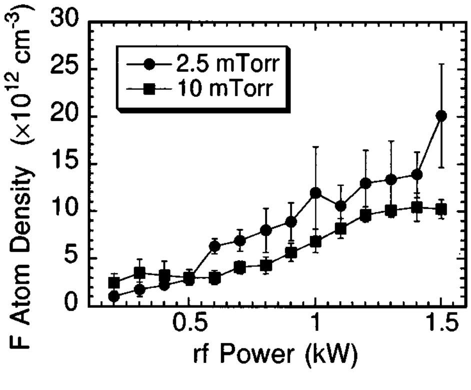

FIG. 4. Absolute F atom density as a function of the rf power for CF_4 gas pressures of 2.5 and 10 mTorr.

kW. For the same discharge condition, the electron density measured by a microwave interferometer was $5\times10^{11}-5\times10^{12}$ cm^{-3}, and the density of CF radicals measured by LIF was on the order of $10^{10}-10^{11}$ cm^{-3}. The density of CF_2 radicals would be approximately one-order higher than that of CF radicals. Hence the density ratio of CF_x/F is much smaller than unity in the high-density helicon plasmas. This small CF_x/F density ratio may be a reason for the low etching selectivity in high-density plasma sources. The increase of the F atom density with the rf power is due to the increase of the electron density. Since the predominant production process of F atoms in CF_4 plasmas is electron impact dissociation of the parent gas ($CF_4+e\rightarrow CF_3^++F+2e$, $CF_4+e\rightarrow CF_3+F+e$), a higher F atom density is obtainable for a higher electron density. The smaller F atom density for the 10 mTorr discharge than for the 2.5 mTorr discharge is attributed mainly to the lower electron density for the 10 mTorr discharge. In our helicon plasmas, a higher electron density is obtainable for a higher rf power and a lower gas pressure. This is probably because the excitation efficiency of the helicon wave decreases with the CF_4 gas pressure.[9] The present results imply that the F atom density is essentially determined by the product of the electron and parent gas densities; the detailed reaction kinetics of F atoms will be discussed in a separate paper.

The measurement error of the present experiment is attributed to the following uncertainties of several quantities. The transition probability used in calculating Fig. 2 is a source of the error, which has an uncertainty within 25%.[10] Fluorine atoms seeping from the helicon chamber to the connecting sections cause the overestimation of the F atom density. Considering the gas pressures in the helicon chamber and the connecting sections, it is possible that the F atom densities in the connecting sections are approximately one-fifth of that in the helicon chamber. If the absorption length in the connecting sections of the both sides is assumed to be 70 cm, the overestimation becomes approximately 40%. It is noted here that F atoms produced in the helicon plasma did not reach the ECR plasma, which was confirmed by measuring a visible emission from FI in the ECR plasma with and without the operation of the helicon plasma. The random noise in the emission intensities was suppressed by averaging the signals by 500 times, and corresponds to the uncertainty of the F atom density of ±10%.

In this letter, the F atom temperature in the helicon source was assumed to be 300 K, which may be a good approximation since most of the F atoms are outside of the plasma column (3 cm in diameter). On the other hand, the temperature of 400 K assumed for the emitting F atoms in the ECR plasma is the major source of the measurement error. The change of the temperature from 400 to 700 K corresponds to the change of the F atom density from 8.5×10^{12} cm^{-3} to 1.3×10^{13} cm^{-3} for an absorption of 0.7. Hence, if such a high F atom temperature is possible in the low-pressure ECR plasma, the F atom densities in this letter are underestimated by approximately 30%. In addition, the underestimation of the F atom density is also due to the self-absorption of the probe emission by ground-state F atoms in the ECR plasma. The self-absorption distorts the spectral distribution of the probe emission from the Gaussian profile, resulting in the error of Fig. 2.[11] In the present experiments, a low microwave power (0.1 kW) was used to avoid the self-absorption as much as possible. When we assume a F atom density of 5×10^{11} cm^{-3} (400–700 K) and a length of 40 cm for the self-absorption, the underestimation of 10% is added to the measurement error. The F atom density of 5×10^{11} cm^{-3} is fairly high for the 0.1 kW ECR discharge which produced an electron density of $\sim3\times10^{10}$ cm^{-3}. However, if the excited F atoms in the ECR plasma are produced by dissociative excitation of CF_4, the spectral distribution of the probe emission is distorted extremely, resulting in serious underestimation of the F atom density. This kind of spectral distortion has been observed in Lyman α transition of H atoms in a capillary hollow cathode discharge with H_2/He mixture.[12]

In conclusion, we have carried out the absolute density measurements of F atoms in helicon-wave CF_4 plasmas by vacuum ultraviolet absorption spectroscopy. The F atom density obtained was on the order of $10^{12}-10^{13}$ cm^{-3} for an rf power of 0.2–1.5 kW. The accuracy of the present measurements was estimated to be within a factor of 2 by considering the several sources of error.

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