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Lifetimes of active species in afterglow of inductively-coupled nitrogen plasma
誘導結合窒素プラズマのアフターグローにおける活性粒子の寿命

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We measured the lifetimes of active species in the afterglow of inductively-coupled nitrogen plasmas. The species we detected were molecular nitrogen at the metastable $A^3\Sigma_u^+$ state, atomic nitrogen at the ground (^4S) state, and atomic nitrogen at the metastable ^2D state. We measured the density of $N_2(A^3\Sigma_u^+)$ by cavity ringdown spectroscopy, and we measured the densities of $N(^4S)$ and $N(^2D)$ by vacuum ultraviolet absorption spectroscopy. The lifetimes of these species were evaluated from the temporal decays of their densities in the afterglow.

1. Introduction

One of most serious problems of plasma-aided dry etching is the formation of damaged layers. A simple way for avoiding plasma-induced damages is “remote plasma etching”, where the wafer to be etched is placed at a long distance from the active plasma zone. Recently, a new technology of remote plasma etching has been developed, in which a nitrogen plasma is produced in a remote plasma source and NF_3 is fed into the downstream region. It has been shown that this remote plasma system can etch silicon successfully with avoiding plasma-induced damages.

The successful etching of silicon suggests that NF_3 is dissociated into atomic fluorine in the downstream region of the N_2 plasma. However, chemical processes which dissociate NF_3 into F have not been identified yet. Electron impact dissociation is not expected in this system because of a long distance between the plasma zone and the downstream region where NF_3 is injected. Therefore, dissociation of NF_3 is considered to be induced by unknown radical species.

According to a molecular orbital calculation, candidate species which dissociate NF_3 are molecular nitrogen at the metastable $A^3\Sigma_u^+$ state and atomic nitrogen at the metastable ^2D state, while atomic nitrogen at the ground (^4S) state cannot dissociate NF_3. A problem here is the transport characteristics of $N_2(A^3\Sigma_u^+)$, $N(^4S)$, and $N(^2D)$. This is because the species which dissociate NF_3 should have a long transport length from the active plasma zone.

In this work, we investigated the lifetimes of $N_2(A^3\Sigma_u^+)$, $N(^4S)$, and $N(^2D)$ in the afterglow of inductively-coupled nitrogen plasmas. The direct objective is to understand destruction processes of $N_2(A^3\Sigma_u^+)$, $N(^4S)$, and $N(^2D)$. The knowledge on the destruction processes will be utilized for the estimation of most efficient species which dissociate NF_3 in the downstream region of the remote nitrogen plasma.

2. Experimental Setup

Inductively-coupled plasmas (ICPs) were

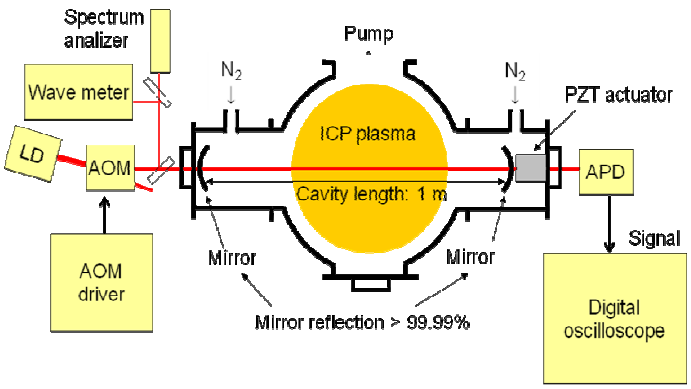

Fig. 1 Experimental setup for cavity ringdown spectroscopy.

produced in a cylindrical vacuum chamber with a diameter of 30 cm. A one-turn antenna placed on a quartz window at the top of the chamber was connected to an rf power supply at 13.56 MHz via a circuit for impedance matching.

The absorption of a diode laser beam by $N_2(A^3\Sigma_u^+)$ was measured by cavity ringdown spectroscopy (CRDS). The experimental apparatus is shown in Fig. 1. The ICP plasma was sandwiched by a stable cavity consisting of two mirrors with high reflectivities. A diode laser beam was injected into the cavity, and the transmitted laser beam was detected using an avalanche photo diode. The wavelength of the laser beam was 771.100 nm, which corresponded to the $Q_{33}(10)$ line of the N_2 first positive system. The cavity length was modulated slightly by holding one of the cavity mirrors using PZT. When the cavity length was resonant with the laser wavelength, the injection of the laser beam was switched off using an AOM device. We measured the exponential decay time constant (ringdown time) of the transmitted laser intensity after switching off the laser beam. We measured the ringdown time at various delay times after the termination of the rf power.

The densities of $N(^4S)$ and $N(^2D)$ were measured by vacuumed ultraviolet absorption spectroscopy (VUVAS) at wavelengths of 120.0 and 124.1 nm, respectively.

3. Results and Discussion

The absorbance of $N_2(A^3\Sigma_u^+)$ and the density of $N(^2D)$ in the afterglow are shown in Fig. 2. The nitrogen pressure and the rf power were 20 mTorr and 400 W, respectively. The absorbance of $N_2(A^3\Sigma_u^+)$ is expected to be roughly proportional to its density. As shown in the figures, we observed exponential decreases in the $N_2(A^3\Sigma_u^+)$ and $N(^2D)$ densities. The decay time constants of the $N_2(A^3\Sigma_u^+)$ and $N(^2D)$ densities were 2.0 and 3.0 ms, respectively. On the other hand, the decay of the $N(^4S)$ density was roughly linear with respect to the time after the termination of the rf power, as shown in Fig. 3. Although the mechanism of the linear decay has not been understood yet, it can be said that the lifetime of $N(^4S)$ is much longer than those of $N_2(A^3\Sigma_u^+)$ and $N(^2D)$.

Since the nitrogen plasma has no active species which have densities much higher than the densities of $N_2(A^3\Sigma_u^+)$ and $N(^2D)$, we should observe second-order kinetics for the temporal decays of the $N_2(A^3\Sigma_u^+)$ and $N(^2D)$ densities if their dominant loss processes are gas-phase quenching. Therefore, the exponential decays (the first-order kinetics) of the $N_2(A^3\Sigma_u^+)$ and $N(^2D)$ densities suggest that their dominant loss processes are diffusion. The validities of the dominant diffusion losses of $N_2(A^3\Sigma_u^+)$ and $N(^2D)$ will be examined by the relationships between their lifetimes and the discharge pressure. On the other hand, the much longer lifetime of $N(^4S)$ than $N_2(A^3\Sigma_u^+)$ and $N(^2D)$ indicates a small surface loss probability of $N(^4S)$. A small surface loss probability is suitable for efficient transport in a remote plasma source. Accordingly, the present experimental results suggest a longer transport length of $N(^4S)$ than $N_2(A^3\Sigma_u^+)$ and $N(^2D)$ in a remote nitrogen plasma. However, since dissociation of NF_3 due to collision with $N(^4S)$ is not expected according to a molecular orbital calculation, further investigations on detailed transport processes of $N_2(A^3\Sigma_u^+)$ and $N(^2D)$ are necessary.

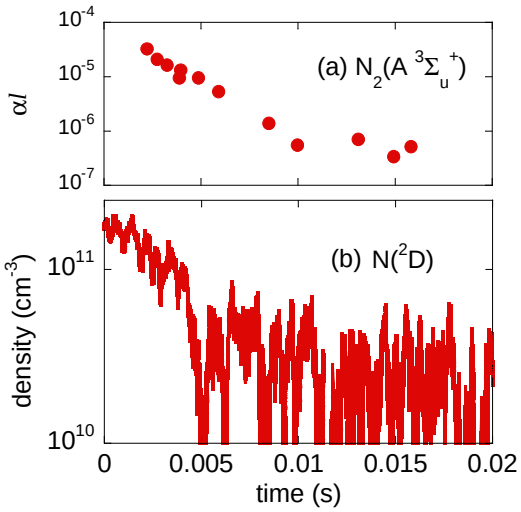

Fig. 2 Temporal decays of the (a) $N_2(A^3\Sigma_u^+)$ and (b) $N(^2D)$ densities in the afterglow. The nitrogen pressure and the rf power were 20 mTorr and 400 W, respectively.

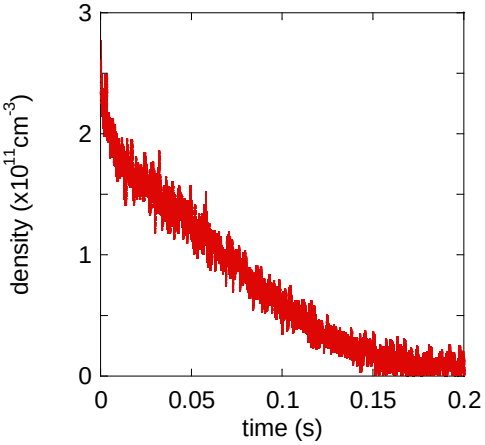

Fig. 3 Temporal decay of the $N(^4S)$ density in the afterglow. The nitrogen pressure and the rf power were 20 mTorr and 400 W, respectively.