Diode laser cavity-ringdown absorption spectroscopy for measuring \(N_2(A^3\Sigma_u^+)^{\text{density in plasmas}}\)

Y Horikawa\(^1\), K Kurihara\(^2\) and K Sasaki\(^3\)

\(^1\)Department of Electrical Engineering and Computer Science, Nagoya University, Nagoya 464-8603, Japan
\(^2\)Research and Development Center, Toshiba Corporation, Yokohama 235-8522, Japan
\(^3\)Plasma Nanotechnology Research Center, Nagoya University, Nagoya 464-8603, Japan

E-mail: sasaki@nuee.nagoya-u.ac.jp

Abstract. We developed a system of cavity-ringdown absorption spectroscopy employing a cw diode laser for measuring the absolute density of \(N_2(A^3\Sigma_u^+)\) in plasmas. We achieved a sensitive detection limit of \(10^{-7}\) for the absorbance. The saturation of absorption was avoided simply by switching off the laser beam when the cavity length was detuned slightly from the length corresponding to the perfect resonance. The absolute \(N_2(A^3\Sigma_u^+)\) density was deduced from the absorbance of the \(B^3\Pi_g(v' = 2) \rightarrow A^3\Sigma_u^+(v'' = 0)\) band by comparing the absorption spectrum with spectral simulation, where we assumed the same values for the translational and rotational temperatures.

1. Introduction

The metastable \(A^3\Sigma_u^+\) state of molecular nitrogen plays important roles in discharge kinetics as well as plasma-surface interaction in material processing. We are interested in plasma-aided nitriding of silicon for synthesizing silicon nitride films with high dielectric constants, which are necessary for gate-insulation films in metal-oxide-semiconductor field-effect transistors [1]. The active species which play the principal role for surface nitriding have not been identified yet, and \(N_2(A^3\Sigma_u^+)\) is a candidate for the nitriding precursor. The difficulty in the experimental investigation of the nitriding precursor is due to the difficulty in the measurement of the \(N_2(A^3\Sigma_u^+)\) density. Although the \(N_2(A^3\Sigma_u^+)\) density is measured by laser-induced fluorescence [2, 3], the calibration of the absolute density is not an easy task. On the other hand, the measurement by simple absorption spectroscopy is not sensitive because of the small transition probability of the first positive system. Although intracavity laser absorption spectroscopy is a sensitive absorption method [4], its applicability is limited by the geometry of the experimental apparatus. In this work, we developed a system of cavity-ringdown absorption spectroscopy (CRDS) [5, 6] for measuring the \(N_2(A^3\Sigma_u^+)\) density in an inductively-coupled plasma source.

2. Experimental apparatus

A schematic illustration of the experimental apparatus is shown in figure 1. Inductively-coupled plasmas (ICP) were produced in a cylindrical vacuum chamber with a diameter of 30 cm. The vacuum chamber had a quartz window at the top, and a one-turn antenna and a matching circuit were placed above the quartz window. An rf power supply at 13.56 MHz was connected
Figure 1. Schematic illustration of the system of cavity-ringdown absorption spectroscopy installed in an inductively-coupled plasma source.

Figure 2. Decay curves of the transmitted laser intensity with and without the plasma. The laser beam was switched off when the cavity length was tuned to the almost perfect resonance.

to the matching circuit. Two long tubes were attached to the vacuum chamber, and the plasma was placed inside a cavity consisting of two concave mirrors with high reflectivities. The cavity length was 1 m, and the radii of the cavity mirrors were 3 mm. The distance between the quartz window and the optical axis of the cavity was 15 cm. A piezo-electric transducer supported one of the cavity mirrors. All the optics including the mirror holders were installed inside the chamber. The mirror holders had motor-drive systems, and the angle of the mirrors were adjusted from the outside of the chamber.

The light source was a cw diode laser. The diode laser beam was diffracted using an acousto-optic modulator (AOM). The wavelength of the diffracted laser beam was tuned around 771.1 nm, which corresponded to the \( B^3\Pi_g (v' = 2) \rightarrow A^3\Sigma_u^+ (v'' = 0) \) absorption band of \( \text{N}_2 \) (the first positive system). The wavelength was monitored using a wave meter and a spectrum analyzer. The diffracted laser beam was injected into the cavity, and the intensity of the laser beam transmitted through the cavity was measured using an avalanche photo diode (APD). When the cavity length was modulated using the piezo-electric transducer, the signal from APD gave the transmission curve of the Fabry-Perot interferometer. The resonance between the cavity length and the wavelength of the laser beam was detected using a comparator with a reference voltage. The output of the comparator was used for stopping the laser beam by switching off the AOM device. The temporal decay of the transmitted laser intensity after the truncation was recorded in a digital oscilloscope. The absorption spectrum was obtained by repeating the measurement with sweeping the laser wavelength.

3. Results and discussion
The absorbance in CRDS is given by

\[
\alpha l = \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right) \frac{L}{c},
\]

where \( 1/\tau \) and \( 1/\tau_0 \) are the decay frequencies of the transmitted laser intensities with and without the plasma, respectively, \( \alpha \) is the absorption coefficient, \( l \) and \( L \) are the lengths of the plasma and the cavity, respectively, and \( c \) is the speed of light. Figure 2 shows an example of the temporal decay of the transmitted laser intensity observed in the empty cavity. This decay
Figure 3. Decay curves of the transmitted laser intensity with and without the plasma. The laser beam was switched off when the cavity length was slightly detuned from the perfect resonance.

Figure 4. Absorption spectrum observed in a nitrogen plasma at an rf power of 300 W and a pressure of 60 mTorr.

curve was obtained by switching off the diode laser beam when the cavity length was tuned to the almost perfect resonance (i.e., the transmitted laser intensity was almost the maximum). The laser wavelength was 771.1016 nm, which corresponded to the overlap of the $R_{21}(4)$ and $Q_{33}(9)$ absorption lines. The decay curve observed in the empty cavity was fitted well with an exponential function, and the decay frequency was evaluated to be $1/\tau_0 = 1.756 \times 10^4 \text{ s}^{-1}$, corresponding to 99.997% for the reflectivities of the mirrors. We repeated the measurement of the decay frequency in the empty cavity for 10 times. As a result, the scattering of the decay frequency, which was evaluated by the standard deviation of the 10 measurements, was 30 s$^{-1}$.

Therefore, the CRDS system developed in this work was compatible with a small absorbance of $10^{-7}$.

We must be careful about saturation of absorption in cw laser CRDS because of the strong laser field inside the cavity. A decay curve in the presence of a nitrogen plasma is also plotted in figure 2. The rf power and the gas pressure were 300 W and 20 mTorr, respectively. As shown in figure 2, the decay curve in the presence of the plasma was not fitted with an exponential function. The decay frequency was accelerated with time. The small decay frequency in the initial part is attributed to the saturation of absorption due to the strong laser field inside the cavity. Since the laser intensity decreased with time, the saturation of absorption was moderated in the latter half of the decay curve, resulting in the acceleration of the decay frequency.

We used a simple way for avoiding the saturation of absorption in this work. Figure 3 shows decay curves with and without the plasma, when the reference voltage to the comparator was 30% of that in figure 2. In this case, the cavity length at the truncation was detuned slightly from the perfect resonance. In the case of the slightly detuned truncation, as shown in figure 3, the decay curve in the presence of the plasma was roughly fitted with an exponential function because of the weak laser intensity inside the cavity. We operated the CRDS system by adjusting the reference voltage to the comparator in order to avoid the saturation of absorption.

Figure 4 shows an absorption spectrum observed in a nitrogen plasma at an rf power of 300 W and a pressure of 60 mTorr. The absorbance observed experimentally was below $10^{-4}$ as shown by the solid symbols in the figure. There were three absorption lines of $Q_{22}(14)$, $R_{21}(4)$, and $Q_{33}(9)$ in the wavelength range shown in figure 4. The locations of the absorption
4. Conclusions
We have developed a CRDS system employing a cw diode laser for measuring the absolute \(N_2(A^3\Sigma_u^+)\) density in plasmas. The system has a high sensitivity corresponding to an absorbance of \(10^{-7}\). We have succeeded in evaluating the absolute \(N_2(A^3\Sigma_u^+)\) density from the absorption spectrum of the \(B^3\Pi_g(v' = 2) - A^3\Sigma_u^+(v'' = 0)\) absorption band. We measured the absolute \(N_2(A^3\Sigma_u^+)\) densities in nitrogen-argon gas mixture plasmas and found that the \(N_2(A^3\Sigma_u^+)\) density increased significantly with the percentage of Ar. The significant increase is possibly attributed to the energy transfer from Ar metastable atoms to \(N_2\). Further investigations are necessary to understand the kinetics of \(N_2\) in nitrogen-argon mixtures.

Acknowledgments
The authors are grateful to Nader Sadeghi for his valuable advices about the CRDS system.

References
[1] Sekine M, Saito Y, Hirayama M and Ohmi T 1999 J. Vac. Sci. Technol. A 17 3129
[2] De Benedictis S, Dilecce G and Simek M 1993 Chem. Phys. 178 547
[3] Kramesa B, Glenewinkel-Meyer Th and Meichsner J 2001 J. Appl. Phys. 89 3115.
[4] Feissac C, Campargue A, Kachanov A, Supiot P, Weirauch G and Sadeghi N 2000 J. Phys. D: Appl. Phys. 33 2434
[5] Busch K W and Busch M A ed. 1999 Cavity Ringdown Spectroscopy (Washington, DC: American Chemical Society)
[6] Hancock G, Peverall R, Richie G A D and Thornton L J 2006 J. Phys. D: Appl. Phys. 39 1846
[7] Horikawa Y, Kurihara K and Sasaki K submitted to Jpn. J. Appl. Phys.