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Measurement for dissociation ratio of source gases in plasmas using a quartz sensor

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ABSTRACT

The dissociation ratio of source gas molecules is measured using a quartz sensor, for which the output depends on the average molecular weight and viscosity of gases. The change in the pressure and temperature-normalized quartz sensor output (NQO) by discharge correlates with changes of the signal intensity of the source gas of ammonia (NH_3), as measured by gas analysis using a quadrupole mass spectrometer. Thereby, the dissociation ratio is obtainable from the change in NQO by the discharge. The spatial distributions of the change in NQO in the plasma chamber show a larger change in NQO near the plasma electrode, indicating that the change in NQO correlates with the dissociation ratio of NH_3. Finally, the dissociation ratios of NH_3 near and between the plasma electrodes were obtained from the spatial distribution of the dissociation ratio of NH_3. Results show that the Q-sensor measurement is simple and useful to derive the dissociation ratio of the source gases for the plasmas of reactive gases.

1. Introduction

Dissociation of gas molecules occurring via collision with electrons is the initial reaction in the gas phase of plasmas. These dissociation reactions determine the initially generated active chemical species such as radicals and ions, and lead to secondary gas phase reactions in the plasmas.

Several reports have described dissociation ratios of gas molecules in environmental studies for which the dissociation ratio is crucial. Environmental studies typically use gas chromatography (GC) because measurements are done at atmospheric pressure [1,2]. Other techniques such as infrared absorption spectroscopy, ion chromatography, and emission spectroscopy are also useful to study the decomposition of toxic or gas molecules of key species related to global warming [3–5].

Few studies have addressed the dissociation of the source gases in plasmas, particularly for industrial plasma processes. Dissociation of hydrogen has been studied using laser-induced fluorescence for hydrogen atoms [6–9]. Coherent anti-Stokes Raman scattering method has been used to measure the dissociation of silane molecules used for preparation of amorphous silicon films [10].

However, the techniques in the works described above mainly require expensive lasers. For that reason, they are unsuitable for use with industrial plasma processes. Moreover, GC is only applicable to plasmas at high pressures because of the necessity for gas sampling. In contrast, gas analysis using quadrupole mass spectrometry (QMS) alone can measure the gas phase of the plasmas at low pressures; it is unsuitable for use at higher pressures [3,11]. Therefore, gas analysis is not applicable in high-pressure conditions like those used for plasma processing for thin silicon films. Furthermore, it is complicated to obtain information on the dissociation ratio of the source gas molecules.

Information related to the dissociation of the source gas molecules should be important because the degree of the dissociation ratio affects properties of the products processed by the plasma. Moreover, because one can know the consumption rate of the source gas molecules from information on the dissociation of the source gas molecules, information about the dissociation of the source gas molecules is expected to be important from an economic perspective. Therefore, simpler measurements of the dissociation ratio of the source gases are expected to be useful for industrial plasma processes such as those for silicon films: an important material used for thin film solar cells [12].

We have taken measurements using a quartz sensor, for which the output depends on pressure, molecular weight, and viscosity of gases measured [13–20]. Because the pressure and temperature-

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normalized quartz sensor output (NQO) depends only on the molecular weight and viscosity of the gases measured, our Q-sensor measurement can detect changes in chemical species in the gas phase of the plasmas [19]. This Q-sensor measurement can measure the dissociation ratio of the source gas molecules in the plasmas if this change in NQO induced by the plasma correlates to the dissociation ratio of the source gas molecules.

The size of quartz in the Q-sensor is less than 1 cm: it can be fixed easily anywhere in the plasma chamber. Its small size is also advantageous for measuring the spatial distributions of the dissociation ratio of the source gas molecules by sliding the Q-sensor in the plasma chamber. Application of the Q-sensor measurement for obtaining the dissociation ratio of the source gases is convenient because it is like a simple pressure measurement without sampling of the gas from the chamber, which would reduce the pressure. Moreover, it is applicable to highly reactive gases.

For this study, we attempted to use Q-sensor measurement to measure the dissociation ratio of the source gas in low-pressure radio frequency (rf) NH_3 plasmas. We used NH_3 to avoid chemical influences on the quartz in the Q-sensor such as deposition and etching because this is the first attempt of Q-sensor measurement of plasmas with reactive gases. The NH_3 plasma is used practically as a coating to reduce ashing damage, nitridation, and deposition [21–23]. Comparison by gas analysis using QMS revealed that the dissociation ratio of NH_3 by the plasmas can be derived from the change of the Q-sensor output.

2. Experimental

Details of the experimental setup are shown elsewhere [19,20]. Briefly, the rf 13.56 MHz glow discharge is generated between parallel plasma electrode plates. The diameter and spacing of the plasma electrodes are, respectively, 112 and 20 mm. The respective flow rate and pressure of NH_3 are 10 sccm and 20 Pa. The rf power was 20–250 W. The anode electrode temperature was set to 100 °C. The Q-sensor, installed near the plasma electrodes, can be slid and close to the plasma electrodes. Here, we define Z as the distance between the Q-sensor and the edge of the plasma electrodes [20].

The electric impedance of the quartz oscillator has been analyzed theoretically using a simple model in which the fork-shape quartz oscillator vibrates with a single frequency [13]. The Q-sensor output is the voltage output which is converted from the impedance of the quartz oscillator, depending on molecular weight and viscosity of the gas measured [13]. However, the total pressure and temperature also affect the Q-sensor output [13,24]. Thereby, we used the pressure and temperature-normalized Q-sensor output (NQO) to obtain information about the gas composition in the plasmas because NQO only depends on viscosity and molecular weight of the gases [19]. Details of the derivation for NQO from the Q-sensor output are described in Ref. [19].

For comparison to the Q-sensor measurement, the gas phase in the plasma was analyzed using QMS. In this study, etching or nitridation were not observed to affect the results from the Q-sensor measurement.

3. Results and discussion

3.1. Gas composition change measured using a Q-sensor

The Q-sensor measurement can measure the gas composition change in plasmas because the Q-sensor output depends on molecular weight and viscosity of the gases, which depends on the gas composition. Fig. 1 portrays temporal changes in the total pressure, the Q-sensor output, and NQO with and without plasmas. With the discharge turned on, the pressure and the Q-sensor output changed and reached constant outputs. After the discharge was turned off, they reverted to the output levels before the discharge. Then NQO was calculated from the pressure-normalized Q-sensor (PQO) output and its temperature dependence; PQO was calculated from the Q-sensor output and its pressure dependence [19]. Because NQO depends only on the molecular weight and viscosity of the gas measured, the change in NQO between with and without the discharge depicted in Fig. 1 means that the gas composition changes as a result of the discharge.

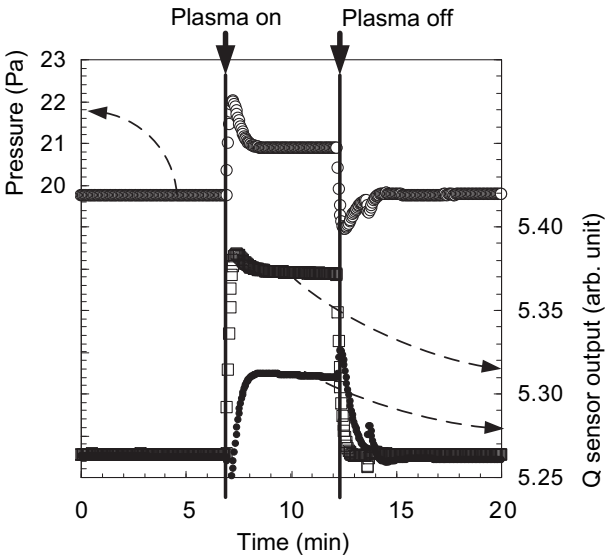

Fig. 1. Temporal changes in the total pressure (○), the Q-sensor output (●) and the pressure and temperature-normalized output (□) with and without plasmas measured at $Z = 70$ mm.

The rf power dependence of the change in NQO in Fig. 2 also supports that the change in NQO correlates to the gas composition change in the gas phase by the plasmas. As expected, the change in NQO increases with the rf power, indicating that the change in NQO reflects the gas composition change in the gas phase of the plasmas because they increase with rf power. These gas composition changes were attributed to dissociation of the source gas: NH_3. Therefore, the change in NQO is expected to correlate with the dissociation ratio of NH_3.

3.2. Working curve for the dissociation ratio of NH_3

Gas analysis using QMS was used to evaluate the dissociation ratio of NH_3. Fig. 3 depicts the mass spectrum measured using QMS

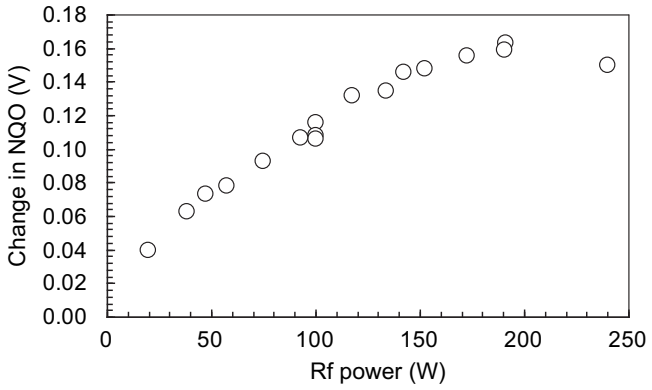

Fig. 2. Rf power dependence of the change in the pressure and temperature-normalized output measured at $Z = 70$ mm.