Emission spectroscopy of Ar + H₂ + C₇H₈ plasmas: C₇H₈ flow rate dependence and pressure dependence

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Abstract. We have studied toluene flow rate dependence and pressure dependence of Ar emission intensities at 425.9 nm, 750.4 nm and 811.5 nm for Ar + H₂ + C₇H₈ plasmas. Electron density and the electron impact excitation rate coefficients are nearly the same for Ar(100%) and Ar+H₂(33%) plasmas. Toluene addition leads to a decrease in the high energy electron density, whereas the effective electron temperature and low energy electron density remain almost the same. The effective electron temperature, and Ar metastable density and/or low energy electron density decrease significantly with increasing the total pressure from 0.1 to 5 Torr.

1. Introduction
Carbon films, due to their hardness, wear resistance, chemical inertness, and biological compatibility, have been widely used as protective coatings in areas of magnetic storage disk, car parts, micro-electromechanical systems (MEMS) [1-4]. Deposition profile control of carbon films on nano-patterned substrates is one of the concerns to realize such protective coatings.

So far, we have succeeded in controlling deposition profiles of copper films on trench substrates, and realized sub-conformal, conformal and anisotropic deposition profiles [5-10]. Then the methods of controlling deposition profiles have been applied to carbon films, and realized sub-conformal, conformal and anisotropic deposition profiles, for which carbon is deposited only to the top or without sidewall deposition [11-16]. One remaining issue of our study is the low deposition rate. To increase the deposition rate, it is important to obtain information on plasma parameters. For this purpose, we have carried out optical emission spectroscopy. In this paper, we report experimental results of toluene flow rate dependence and pressure dependence of Ar emission intensities for Ar + H₂ + C₇H₈ plasmas.

2. Experimental
Experiments were performed using the H-assisted plasma CVD reactor, in which a capacitively-coupled main discharge and an inductively-coupled discharge of H atom source were sustained as shown in figure 1 [5-16]. The main discharge, which was sustained between a mesh powered electrode of 85 mm in diameter and a plane substrate electrode of 85 mm in diameter at a distance of 33 mm,
was employed to produce carbon containing radicals as precursors. The excitation frequency of the main discharge was 28 MHz and the supplied voltage was 150 V. The discharge of H atom source, which was sustained using a radio frequency (RF) induction coil of 100 mm in diameter placed at 65 mm above the substrate electrode of main discharge, generated a high flux of H atoms toward the substrate. This reactor provided independent control of generation rates of carbon containing radicals and H atoms. The H atom source was separated from the main discharge using a grounded mesh (30 meshes/inch) of 160 mm in diameter placed at 2 mm above the mesh powered electrode of main discharge. In addition, an RF bias voltage of 400 kHz was applied to the substrate to control kinetic energy of incident ions. In this study, the H atom source and RF bias voltage were not applied.

Toluene (C\textsubscript{7}H\textsubscript{8}), Ar and H\textsubscript{2} were supplied at flow rates of 0.63 - 20 sccm, 60 sccm and 30 sccm, respectively. Toluene has a low ionization potential of 8.82 eV and a methyl group. The low ionization potential of toluene is expected to bring about a high deposition rate, because the deposition rate of carbon films tends to increase with decreasing the ionization potential of precursor gas [2]. The methyl group of toluene is expected to stabilize carbon films, because thermal stability of the deposited carbon films can be enhanced due to the methyl group [17]. C\textsubscript{7}H\textsubscript{8} was vaporized at 150 °C and introduced into the reactor with H\textsubscript{2}. The total pressure was set in a range of 0.1 - 5 Torr. The substrate temperature was 100 °C.

Optical emission intensities were measured at 11 mm above the center of substrate electrode with a miniature fiber optic spectrometer (Ocean Optics USB2000+).

3. Results and discussion
Figure 2 shows typical emission spectra for plasmas of (a) Ar(100%), (b) Ar+H\textsubscript{2}(33%) and (c) Ar+H\textsubscript{2}(32.4%)+C\textsubscript{7}H\textsubscript{8}(0.027%) plasmas at 0.1 Torr. The emission intensities for Ar+H\textsubscript{2}(33%) are a half of those for Ar(100%). The emission intensities for Ar+H\textsubscript{2}(33%) are a half of those for Ar(100%). The emission intensities for Ar+H\textsubscript{2}(33%) are a half of those for Ar(100%). The emission intensities for Ar+H\textsubscript{2}(33%) are a half of those for Ar(100%). The emission intensities for Ar+H\textsubscript{2}(33%) are a half of those for Ar(100%). Most Ar emission intensities are proportional to Ar partial pressure, electron density, and the rate coefficients for electron impact excitation from the Ar ground state. The emission intensities for Ar+H\textsubscript{2}(33%) are weak compared to those for Ar(100%) mainly due to the decrease in the Ar partial pressure. In other words, the electron density and the excitation rate coefficients (effective electron temperature) are nearly the same for Ar(100%) and Ar+H\textsubscript{2}(33%) plasmas. These results are consistent with the fact that Ar\textsuperscript{+} is the predominant ion in Ar(100%) plasmas, whereas Ar\textsuperscript{+}
and ArH⁺ are the main ions in Ar+H₂(33%) plasmas in the pressure range of 0.1 - 5 Torr [18, 19]. Because the Ar partial pressure of Ar + H₂(33%) and Ar + H₂(32.4%) + C₇H₈(0.027%) are nearly the same, the decrease in the emission intensities by adding C₇H₈ is caused by decreases in the high energy electron density (ε ≥ 13 eV) and/or the excitation rate coefficients, which depend on electron temperature.

To obtain insight into the mechanisms of the decrease in the emission intensities by adding C₇H₈, emission spectra were normalized by the intensity at 750.4 nm I₇50.4 in each subgraph of figure 2 as shown in figure 3. The normalized three spectra in figure 3 are similar with each other, indicating that effective electron temperature of these three plasmas is almost the same. Therefore, the decrease in the emission intensities by adding C₇H₈ is caused mainly by the decrease in the high energy electron density. Moreover, there exists Hα emission for Ar + H₂(33%) and Ar + H₂(32.4%) + C₇H₈(0.027%) in figure 3.

Figure 4 shows the toluene flow rate dependence of Ar emission intensities at (a) 750.4 nm, (b) 811.5 nm and (c) 425.9 nm. It can be seen a sudden drop in the I₄25.9, I₈11.5 and I₇50.4 after introducing C₇H₈, then all of them have a linear decrease with increasing the toluene flow rate from 0.63 to 20 sccm. Ar emissions at 425.9 nm and 750.4 nm have little influence of quenching and radiation trapping, and their upper levels of 2p₁ (excitation energy of 13.5 eV) and 3p₁ (excitation energy of 14.7 eV) have small cross section for electron impact excitation from metastable states [20, 21]. Therefore, the ratio of emission intensity of Ar I at 425.9 nm to that at 750.4 nm, I₄25.9/I₇50.4 is used to evaluate the effective electron temperature. The Ar emission at 811.5 nm is strongly influenced by the
The metastable state (excitation energy of 11.5 eV) that can provide an additional channel for Ar atom excitation by low energy electrons (1.5 ≤ e ≤ 3 eV). So the emission intensity ratio, $I_{811.5}/I_{750.4}$ is used to obtain information on the Ar metastable density and the low energy electron density [22, 23].

The Ar emission intensity ratios are shown in figure 5. Both the ratios are nearly constant irrespective of the toluene flow rate, showing that the effective electron temperature, Ar metastable density and low energy electron density remain almost the same. These results indicate that the high energy electron density decreases with increasing the toluene flow rate from 0 to 20 sccm. The total flow rate increases from 90 sccm to 110 sccm with increasing toluene flow rate from 0 to 20 sccm. The change of the total flow rate is small. In addition, the discharge voltage was kept constant in this study. Therefore the total flow rate and the discharge voltage have little influence on plasma parameters in this study.

Figure 6 shows the total pressure dependence of Ar emission intensities at 425.9 nm, 750.4 nm and 811.5 nm, normalized by each intensity for 0.1 Torr. To obtain information of plasma parameters in the bulk region, we have measured the emission intensities at 11 mm above the center of substrate. Though $I_{750.4}$ has a slight increase in the pressure range of 0.5 - 1.5 Torr, $I_{425.9}$ and $I_{811.5}$ decrease significantly with increasing the total pressure from 0.1 to 3 Torr.

The corresponding normalized Ar emission intensity ratios of figure 6 are shown in figure 7. $I_{425.9}/I_{750.4}$ and $I_{811.5}/I_{750.4}$ decrease by 84.3% and 55.6% with increasing the pressure from 0.1 to 3 Torr, and then they decrease by 24.6% and 4.8% with increasing the pressure from 3 to 5 Torr. These results indicate that the effective electron temperature, and Ar metastable density and/or low energy electron density decrease significantly with increasing the total pressure from 0.1 to 3 Torr, and then they decrease slightly with increasing the total pressure from 3 to 5 Torr.

**Figure 4.** Toluene flow rate dependence of Ar emission intensities at (a) 750.4nm, (b) 811.5 nm and (c) 425.9 nm. Total pressure is 0.1 Torr.

**Figure 5.** Toluene flow rate dependence of Ar emission intensity ratios. Total pressure is 0.1 Torr.
4. Conclusions
We studied the toluene flow rate and pressure dependence of emission intensities in Ar + H₂ + C₇H₈ plasmas. The following conclusions are obtained in this study.

1. Electron density and the electron impact excitation rate coefficients (effective electron temperature) are nearly the same for Ar(100%) and Ar+H₂(33%) plasmas.

2. Toluene addition leads to a decrease in the high energy electron density, whereas the effective electron temperature and low energy electron density remain almost the same.

3. The effective electron temperature, and Ar metastable density and/or low energy electron density decrease significantly with increasing the total pressure from 0.1 to 5 Torr.

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