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Measurement of radical densities in microwave plasma CVD employing carbon-containing gas mixture

炭素含有ガス混合を用いたマイクロ波プラズマCVD中のラジカル計測

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To realize high-performance plasma process, it is important to elucidate the specific species that contribute to the deposition. And then, it is necessary to control the process plasma to obtain carbon nanostructures with structure and morphology customized for a specific application on the basis of the knowledge of the species. In this study, carbon (C) atom density was measured using vacuum ultraviolet absorption spectroscopy (VUVAS) with micro-discharge hollow-cathode lamp (MHCL). It was found C atom density was to be 1.2×10^{12} cm^{-3} at $CH_4/(CH_4+H_2)$ flow rate of 2% below, while was below the detection limit ($\sim10^{11}$ cm^{-3}) over CH_4 flow rate of 3%. This suggests that background absorption by source gas molecules and species produced in plasma was dominant and the determination of C atom density could not be attained when the CH_4 concentration increased.

1. Introduction

Microwave plasma, which is one of high-density plasmas and is suitable for decomposing H_2 molecules to generate H atom effectively, has been used to fabricate carbon allotropes including diamond, nanocrystalline diamond (NCDs), and carbon nanotubes (CNTs). The main reaction mechanisms of deposition using plasmas are determined by the species produced in the plasma. To realize high-performance plasma process, it is important to first elucidate the specific species that contribute to the deposition. Second, on the basis of the knowledge of the species, it is necessary to control the process plasma to obtain carbon nanostructures with structure and morphology customized for a specific application.

Thus far, we measured C_2 radical density at the lowest excited state using white-light absorption spectroscopy with Xe lamp emitting a continuous spectrum as a light source and to be on the order of 10^{12} cm^{-3} at $CH_4/(CH_4+H_2)$ flow rate of 25-30% [1]. In this study, carbon (C) atom density was measured using vacuum ultraviolet absorption spectroscopy (VUVAS).

2. Experimental

Figure 1 shows a schematic of experimental set-up for C atom density measurement using VUVAS with high pressure CO_2 micro-discharge hollow-cathode lamp (C-MHCL) as a VUV light source for absorption spectroscopy [2,3]. The transition lines used for C atom density measurements were $2s^22p^2\ ^3P_1 - 2s^22p3s\ ^3P_2^o$ at 165.626 nm, $2s^22p^2\ ^3P_0 - 2s^22p3s\ ^3P_1^o$ at 165.692 nm, $2s^22p^2\ ^3P_2 - 2s^22p3s\ ^3P_2^o$ at 165.700 nm, $2s^22p^2\ ^3P_1 - 2s^22p3s\ ^3P_1^o$ at 165.737 nm, $2s^22p^2\ ^3P_3 - 2s^22p3s\ ^3P_1^o$ at 165.789 nm, and $2s^22p^2\ ^3P_5 - 2s^22p3s\ ^3P_3^o$ at 165.811 nm for the C atom. Since the wavelength resolution of the VUV monochromator was 0.4 nm, the total absorption intensity of six transition lines $2s^22p^2\ ^3P_J - 2s^22p3s\ 3P^o_J$ (J=0, 1, 2) at 165.7 nm was measured for the absolute C atom density. He line at 164.0 nm and Xe lamp emitting a continuous spectrum around 165.7 nm were used for the evaluation of background absorption.

Measurement was carried out employing CH_4/H_2 mixture at a total pressure of 55 Torr and a microwave power of 800 W. Total gas flow rate was kept at 200 sccm, and $CH_4/(CH_4+H_2)$ flow rate was changed.

3. Results and discussion

Figure 2 shows the absorption intensities measured at C atom resonance line and background absorption as a function of CH_4 flow rate ratio. C atom density was estimated to be 1.2×10^{12} cm^{-3} at $CH_4/(CH_4+H_2)$ flow rate below 2%. As the flow rate ratio increased above 2%, on the other hand, the behavior measured at C atom resonance line was almost the same as those of background absorption measured at 164.0 nm He line and 165.7 nm using Xe lamp emitting a continuous spectrum. This suggests that background absorption by source gas molecules and species produced in plasma was dominant and the determination of C atom density could not be attained when the CH_4 concentration increased. In the case of microwave CH_4/H_2 plasma sustained at relatively high pressures under the typical condition for the growth of aligned CNT and NCD films, C_2 radical density was on the order of 10^{12} cm^{-3}, while the C atom density was below the detection limit (~10^{11} cm^{-3}) over CH_4 flow rate of 3%. Moreover, emission from C resonance line at 165.7 nm was hardly observed in the microwave CH_4/H_2 plasma. In this case, a lot of by-product molecules such as acetylene were generated in the plasma and absorbed dominantly the VUV light including C resonance line. This background absorption deteriorated the sensitivity of C atom detection at large flow rate of CH_4 seriously.

It is likely in CH_4 plasmas that C atoms are generated in stepwise processes via CH_3, CH_2, and CH. On the other hand, C atoms would be removed due to the reactions with CH_x radicals to produce acetylene and higher-order hydrocarbons. It was reported that acetylene molecules on the order of 10^{13} cm^{-3} were generated in hot filament CVD employing CH_4/H_2 mixture at 20 Torr [4]. Moreover, C atoms can react with acetylene [5]. Therefore, in the case of microwave plasma employing CH_4/H_2 mixture at relatively high pressures, it is considered that the direct effect of C atoms by way of the surface reaction might be negligible for the growth of NCD and CNT films.

Now, we are going to investigate dominant molecular species in CH_4/H_2 plasma by mass spectrometry and discuss the growth mechanism of carbon nanostructures in more detail.

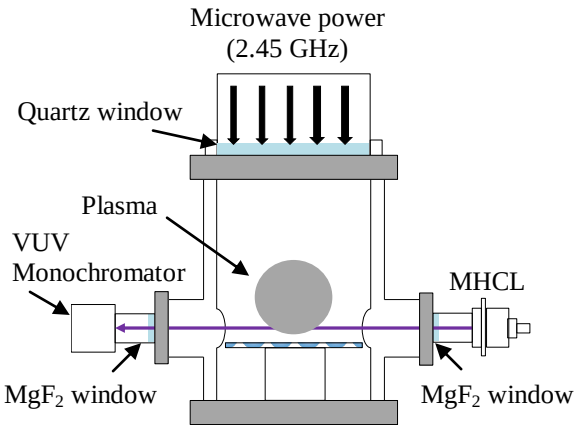

Fig. 1 Schematic of experimental set-up used for C atom density measurement with MHCL (micro-discharge hollow-cathode lamp) as a VUV light source.

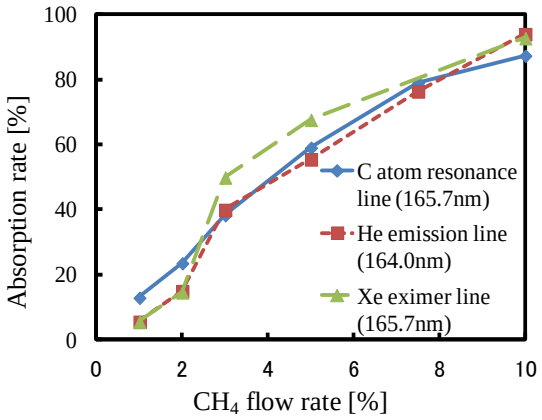

Fig. 2 Absorption rate of C atom line and background absorption as a function of CH_4 flow rate

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