DEPOSITION OF HARD CARBON FILM IN CH_4 RF DISCHARGES MIXED WITH Ar AND Xe

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The deposition of hydrogenated hard carbon film was carried out in planar rf (13.56MHz) CH_4-Ar and CH_4-Xe plasmas. The film deposition rate, mechanical and optical properties of deposited films, and plasma characteristics were examined in this work. These results describe the relationship between the plasma characteristics and the film properties. The results on mass spectrometry measurements suggest that the reaction of CH_3 radicals and hydrocarbon ions determines the carbon film deposition.

I. INTRODUCTION

Much interest has been increasing recently in the properties of hydrogenated amorphous hard carbon (a-C:H) films which is normally called as diamond-like carbon (DLC) [1]. The most common method used for the deposition of hard carbon film is the rf plasma induced chemical vapor deposition (CVD). These hard carbon films, which have high mechanical hardness, smooth surface, and high electrical resistance, have been used in several industrial applications [2]. Up to the present, many articles about the film deposition mechanism and the properties of the carbon film deposited in pure CH_4 plasma under the several conditions have been published. In this work, we carried out the deposition of hard carbon film in CH_4 rf discharges mixed with both Ar and Xe gases. We have investigated the relationship between the mixture gas plasma characteristics and the film properties. In view of the role of ions, the film deposition mechanism was also discussed using the results obtained in this work.

II. EXPERIMENT

A schematic diagram of an experimental apparatus for the plasma diagnostics and the deposition of hard carbon films is shown in Fig.1. A power supply is a 13.56 MHz rf generator. A plasma chamber consists of a stainless-steel cylinder 400 mm in diameter and 280 mm in height. Parallel electrodes consist of stainless-steel disks 153 mm in diameter, and are separated by 60 mm from each other. The lower cathode electrode was covered with a ground shield set. A flow rate of CH_4 gas was controlled with a mass flow controller (MFC), and flow rates of Ar and Xe gases were controlled with gas flow meters (GFM). An optical emission profile (OEP) between both electrodes and a sheath thickness at the cathode electrode were measured by a charge-coupled device (CCD) image sensor with a micro computer. In order to estimate kinetic energies of ions accelerated towards the cathode electrode, a dc self-bias voltage was measured. In the measurement of ion flux density, a quadrupole mass spectrometer was attached to upper anode electrode, and ions reaching the anode electrode were extracted through an orifice (200 $\mu m\phi$ in diameter) formed at the center of the electrode. The rf power input density was kept constant at 0.54 W/cm^2. The carbon films were deposited on Si substrates placed at a cathode electrode, and were examined by means of deposition rate, Fourier transform infrared (FTIR) absorption spectrum, and Knoop hardness.

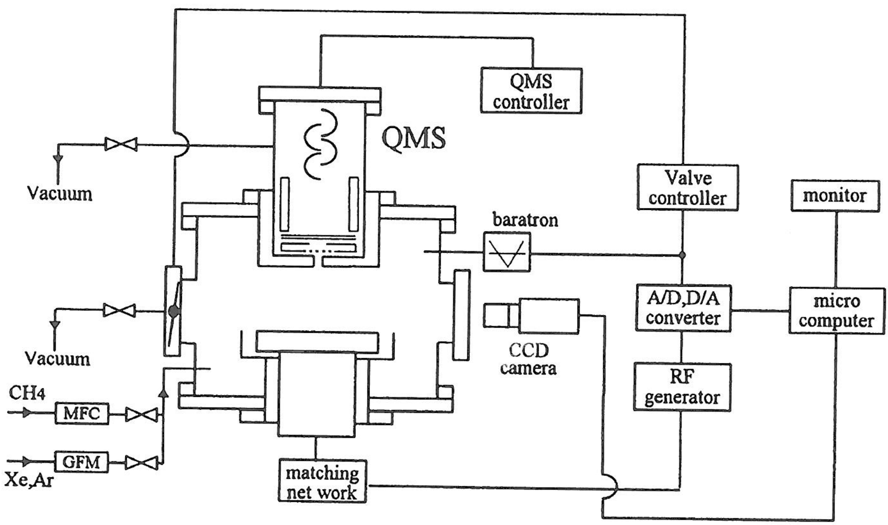

Fig.1 Schematic diagram of an experimental apparatus for plasma diagnostics and plasma processing in rf plasma.

III. RESULT AND DISCUSSION

A. Deposition of hard carbon films in CH_4-Ar plasma

To study the individual contributions of radicals and ions in the film deposition, the film deposition rates were measured. The deposition rate depending on CH_4 composition ratio is shown Fig. 2. It indicates a gradual decrease when the CH_4 content decreased, and decreased rapidly for less than 10% of CH_4. The results on FTIR absorption spectra of the deposited films indicated that the deposited films contained predominant sp^3-type carbon atoms for more than 10% of CH_4, and also contained considerable sp^2-type carbon atoms for other small amount of CH_4 ratios. The results on Knoop hardness shown in Fig. 3 indicated that the film changed from a mechanical hard film into a soft film at around 10% CH_4 when the CH_4 content decreased. Thus, the deposited film properties greatly changed at around 10% of CH_4.

The plasma diagnostics was carried out in order to examine a change in the plasma characteristics when the Ar composition ratio was changed. The ion sheath thickness and the dc self-bias voltage V_b were measured. The sheath thickness scarcely changed when the Ar content increased, because the difference between the sheath thickness in pure CH_4 plasma and that in pure Ar plasma was small. The voltage increased with the decrease of CH_4 ratio, and then decreased for less than 10% of CH_4. This phenomenon may be associated with the change of plasma characteristics at around 10% CH_4. These results suggest that the plasma characteristics considerably influence the film properties. Zou *et al.* reported that the hard carbon films can be produced for the conditions of $|-V_b| > 100$ V [4]. Although at the conditions of CH_4 ratio less than 10% the measured voltages were larger than 400 V, the deposited films became soft, much less than 2000 kgf/mm^2. The mass spectrometry measurements were carried out in order to measure the ionic species in the plasma. Figure 4(a) shows the sum of hydrocarbon ion currents depending on the CH_4 composition ratio. The hydrocarbon $C_mH_n^+$ ions diminished for a small amount of CH_4 ratios less than 10%. It has been reported that the ions maybe creating the adsorption sites (dangling bond) of neutral radicals were need for the deposition of hard carbon films [4]. The hydrocarbon ions indeed play a major role for the deposition of hard carbon film. But they will not be the main precursor for the film formation, because the behavior of hydrocarbon ions shown in Fig. 4(a), does not follow the deposition rate shown in Fig. 2. Considering the contribution of CH_3 radicals to the film formation, we calculated the product of the sum of hydrocarbon ions and CH_3 radical density. The CH_3 density is considered to be proportional to the CH_4 composition ratio. The result is shown Fig. 4(b). It qualitatively describes well the behavior of the deposition rates shown in Fig. 2. It suggests a following relationship

$$Dr \propto [\Phi_i] \bullet [\Phi_{CH_3}]$$

where, Dr is the deposition rate, Φ_i the sum of hydrocarbon ion current, and Φ_{CH_3} the CH_3 radical density. Thus, the hydrocarbon ions are not the main precursor for the film formation, and the reaction between hydrocarbon ions and predominant CH_3 radicals will determine the film formation.

B. Deposition of hard carbon films in CH_4-Xe plasma

The film deposition rate depending on the CH_4 composition ratio is shown in Fig. 5. The deposition rate indicated an anomalous behavior. This was characterized with three different regions when the CH_4 ratio decreased, which were (I)abrupt decrease for CH_4 ratios more than 80%, (Ⅱ) gradual decrease for 10 - 80% of CH_4, and (Ⅲ) great decrease again for CH_4 ratios less than 10%. The behavior was quite different from that in CH_4-Ar plasma especially in the region (I). We also measured the FTIR absorption spectra and the Knoop hardness of deposited films in order to examine the film properties in each region. The results of IR spectra indicated that an absorption peak at 2925 cm^{-1}, which is associated with sp^3 C-H_n components, appeared for the films deposited in regions (I) and (Ⅱ). For the films deposited in region (Ⅲ), an absorption peak associated with sp^2-type carbon was observed in addition to that of sp^3-type carbon. The Knoop hardness gradually increased with the decrease of CH_4 ratio, and a maximum hardness of about 4000 kgf/mm^2 was obtained at around 20% of CH_4, as shown in Fig. 6.

Figure 7(a) shows the sum of hydrocarbon ion currents in the plasma as a function of CH_4 volume. The behavior is quite different from that in CH_4-Ar plasma shown in Fig. 4(a). As an ionization energy of Ar atom (15.7 eV) is larger than that of CH_4 molecule (12.6 eV), the hydrocarbon ions flux density will be increased in CH_4-Ar plasma by the penning effect. However, an ionization (12.1 eV) and an excitation (9.45 eV) energy of Xe atoms are smaller than the ionization energy of CH_4 molecule, so that the CH_3 radical density will be increased rather than the hydrocarbon ions density in CH_4-Xe plasma [5]. This way be a reason why the hydrocarbon ions density is abruptly decreased by a small amount of Xe addition. Figure 7(b) shows the product of the sum of hydrocarbon ion currents and CH_3 radical density (CH_4 volume). It also qualitatively similar to the behavior of the deposition rate shown in Fig. 5, as well as in CH_4-Ar plasma. It suggests that the film deposition rate was determined by not only the hydrocarbon ion flux density but also the CH_3 radical density. Thus, it is tentatively concluded that the reactions of hydrocarbon ions having large kinetic energy and hydrocarbon radicals on the substrate surface induce the formation of the hard carbon film.

IV. CONCLUSION

We carried out the plasma diagnostics in both CH_4-Ar plasma and CH_4-Xe plasma, and the mechanical and the optical properties of carbon films were examined. When the characteristics of the mixture plasma changed, the film properties also changed. It was demonstrated that the deposition rate was qualitatively proportional to the product of the hydrocarbon ion flux density and the CH_3 radical density. The hard carbon films will be generated by the reaction of CH_3 radicals and hydrocarbon ions on the surface of depositing film.

References

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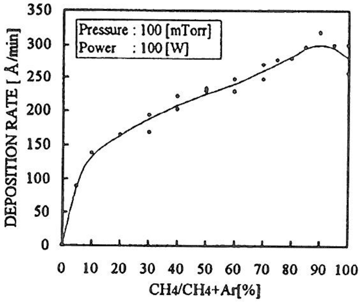

Fig.2 The film deposition rate as a function of CH_4 composition ratio in CH_4-Ar plasma.

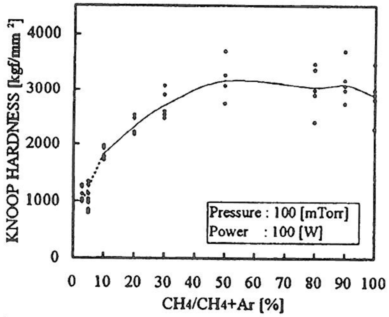

Fig.3 The Knoop hardness of the film deposited in CH_4-Ar plasma, depending on CH_4 composition ratio.

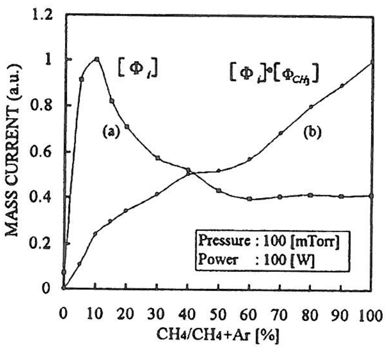

Fig.4 The sum of the hydrocarbon ions (a) in CH_4-Ar plasma, and the product of CH_3 radical density and the sum of the hydrocarbon ions (b), depending on CH_4 composition ratio.

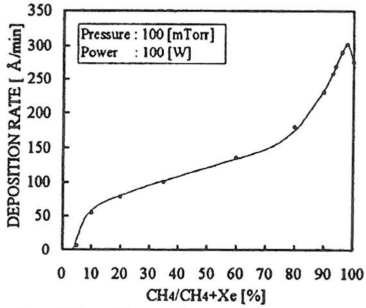

Fig.5 The film deposition rate as a function of CH_4 composition ratio in CH_4-Xe plasma.

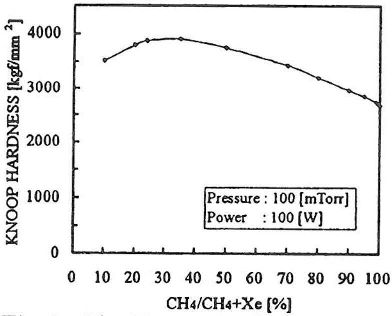

Fig.6 The Knoop hardness of the film deposited in CH_4-Xe plasma, depending on CH_4 composition ratio.

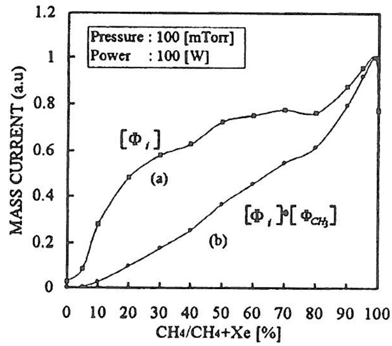

Fig.7 The sum of the hydrocarbon ions (a) in CH_4-Xe plasma, and the product of CH_3 radical density and the sum of the hydrocarbon ions (b), depending on CH_4 composition ratio.