Preparation of Amorphous Diamond-Like Carbon Films by ECR Plasma CVD

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Amorphous diamond-like carbon films were successfully prepared by plasma CVD with the aid of an additional negative bias to the substrate. In the present work, the effects of the additional bias and added gases (H_2 or Ar) to CH_4 on the formation of amorphous carbon films have been studied mainly as to the ECR plasma CVD method. The application of the negative bias of up to -300 V improved the deposition rate (from 6.3 to 55.3 nm/min) and Vickers microhardness (from 5.1 to 22.4 GPa) of the carbon films prepared. Moreover, H_2 gas was shown to be superior to Ar gas as an added gas relating to both the deposition rate and Vickers microhardness of the films.

[Introduction]

Amorphous hydrogenated carbon (a-C:H) films have been synthesized at low temperatures (200℃ or below) by plasma chemical vapor deposition (CVD) using RF[1-5] (Radio Frequency) or ECR[6] (Electron Cyclotron Resonance). It is also suggested that amorphous carbon films with diamond-like properties will be formed under high-energy impact.[4] Furthermore, some experimental results as to plasma CVD with an additional direct current (dc) bias were presented, and exemplified its effectiveness for the formation of hard amorphous carbon films.[7-10]

The plasma deposition apparatus used in this study allows the performance of high quality thin film deposition at low temperatures without the need for thermal reaction. A high-performance of this apparatus is achieved by enhancing the plasma excitation efficiency and by the acceleration effect of ions with high energies on the deposition reaction, using a microwave electron cyclotron resonance plasma and a plasma extraction by a divergent magnetic field method.[11] The present study is concerned with the effects of the additional dc bias and the added gases (H_2 or Ar) to CH_4 on the formation of amorphous carbon films by the ECR plasma CVD method.

【Experimental】

A schematic diagram of the ECR plasma CVD apparatus used in this experiment is shown in Fig.1. The chamber of the apparatus is divided into two parts, i.e., the plasma (the upper) and film formation (the lower) zone. A divergent magnetic field field method has been developed for plasma extraction from the plasma zone to the film formation zone. The intensity of the magnetic field in the film formation zone is gradually weakened from the plasma zone to the specimen holder, as shown in Fig.2.

Si(100) substrates were placed on the specimen holder which was electrically isolated from the chamber. Negative dc bias up to -300 V was applied to the specimen holder. Experimental conditions are summarized in Table 1. Microwave power (2.45 GHz) was conducted into the plasma zone through a fused quartz plate. The mixed gases between CH_4 and H_2 (or Ar) was introduced into the plasma zone of the chamber.

【Results and Discussion】

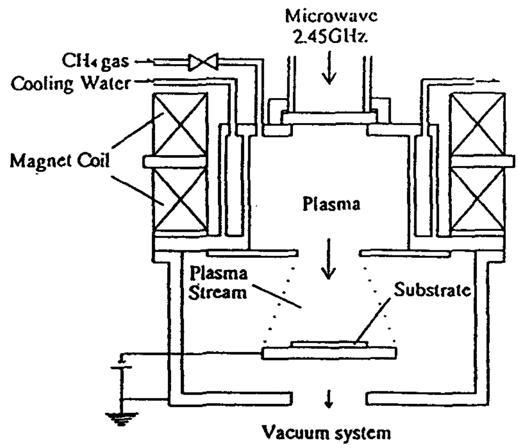

Fig. 1 Schematic diagram of ECR-plasma reactor.

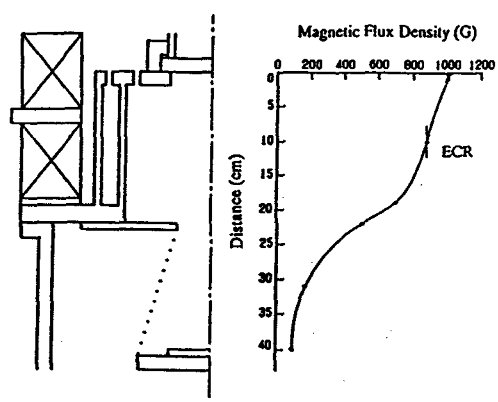

Fig. 2 Magnetic flux density of ECR-plasma reactor.

Table 1 Exprimental conditions

CH_4 gas flow rate	15 - 30	$cm^3 min^{-1}$
H_2 gas flow rate	0 - 30	$cm^3 min^{-1}$
Ar gas flow rate	0 - 30	$cm^3 min^{-1}$
Micro wave power	50 - 230	W
Bias voltage	0 - -300	V
Substrate temperature	200	℃
Substrate	Si	(100)

Yellow-brown carbon films of about 1 μm thick were prepared by the ECR plasma CVD system. All amorphous carbon films prepared had a considerably smooth surfaces which are the characteristic of amorphous materials. Similarly to the previous papers[9-12], the surfaces of the films were observed to become more smooth under additional the negative bias. This cause also as follows: the impact of high-energy ions accelerated by the additional bias to the substrate might promote the migration and rearrangement of particles on the substrate.

Figure 3 shows the relationship between the additional negative bias (V) and the deposition rate of the films on the Si substrates heated at 200℃. The deposition rate (6.3 nm/min at 0 V) of the carbon films was improved significantly by the application of the negative bias, increasing up to the maximum value of 55 nm/min at -300 V. This increase of the deposition rate is considered to originate from the applied bias which prevents the dispersion of positive ions from CH_4 and/or H_2, and increases the speed of cationic atoms and molecules in the gas phase with increasing bias. These bias effects should increase the supply of ions onto the substrate and, result in the increase of the deposition rate.

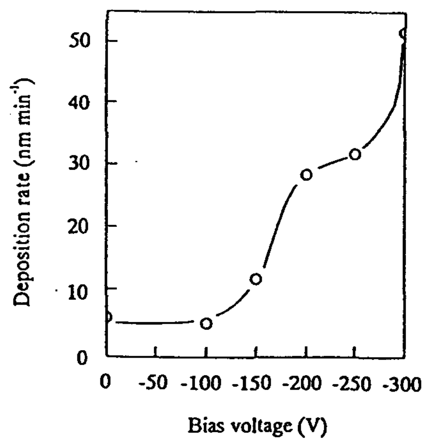

Fig. 3 Effect of bias voltage on deposition rate of carbon films obtained at CH_4 gas flow rate of 30 $cm^3 min^{-1}$, H_2 gas flow rate of 30 $cm^3 min^{-1}$ and microwave power of 200 W.

As shown in Figure 4, the microhardness (Hv) of the carbon films deposited on Si substrates was measured by a Vickers microhardness tester under the load of 0.098. The Vickers microhardness (5.1 GPa at 0 V) of the films increased steeply over -250 V, and reached 22.4 GPa at -300 V. It suggests that the impact of high energy ions accelerated by the

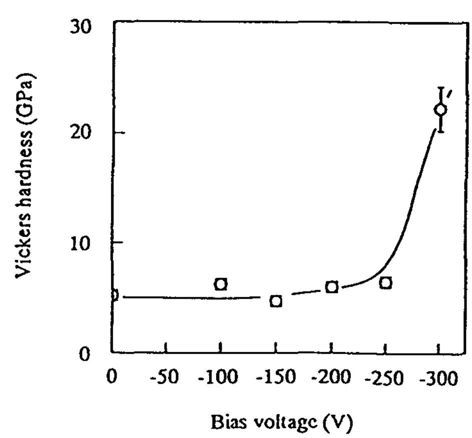

Fig. 4 Effect of bias voltage on Vickers hardness of carbon films obtained at CH_4 gas flow rate of 30 $cm^3 min^{-1}$, H_2 gas flow rate of 30 $cm^3 min^{-1}$ and microwave power of 200 W.

additional bias to the substrate might be promote the formation of dense and hard carbon films in the ECR plasma CVD process similarly to the RF plasma CVD process.[7]

The infrared spectra of these films revealed the decrease of C-H absorption (2962, 2926 and 2872cm $^{-1}$) with increasing bias, as shown in Fig.5. The peak height of C-H absorption became significantly small under the bias of -300 V. This proves that the film prepared under -300 V contains the lowest hydrogen content, because the decrease of C-H absorption in the infrared spectra corresponds to the decrease of the hydrogen content in the carbon films. It is well known that the decrease of the hydrogen content in the carbon films prepared in various plasma deposition processes results in the increment of the density (or refractive index) and microhardness of the films.[6,8,9] Consequently, an outstanding increase in the microhardness under -300 V can be attributable to the decrease of the hydrogen content in the films caused by cationic bombardments onto the substrates.

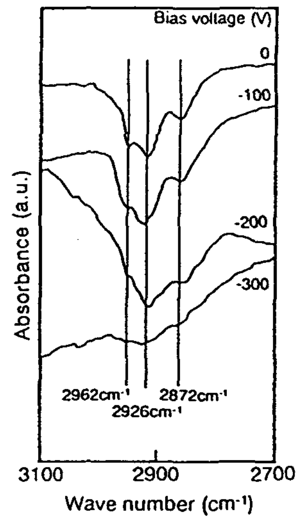

Fig. 5 IR spectra of carbon films.
Deposition conditions : flow rates CH_4=30 cc min^{-1} H_2=30 cc min^{-1}, microwave power =200W.

The Raman spectra of these films are also shown in the figure 6. It reveals that the Raman spectrum of the film under -300 V has the similar feature to that of the i-carbon film (named by Weissmantel[13]) which has a main peak at 1550 cm $^{-1}$ with a shoulder at 1400 cm $^{-1}$. As interpreted from the infrared and Raman spectrum measurements, the decrease of C-H bonds means the increase of C-C bonds, which leads to the rigid matrix structure constituted of SP^3 bonds and the

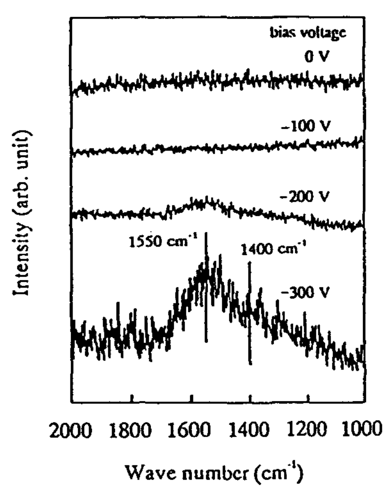

Fig. 6 Raman spectra of carbon films obtained at CH_4 gas flow rate of 30 cm^3 min^{-1}, H_2 gas flow rate of 30 cm^3 min^{-1} and microwave power of 200 W under various bias voltages of 0, 100, 200 and 300 V.

formation of hard carbon films. Thus, It was ascertained that the impact of high-energy ions accelerated by the additional bias to the substrate promoted the formation of hard carbon films and enhance its deposition rate.

In oder to investigate the effects of added gases, the carbon films were also prepared from the mixed gas between CH_4 and Ar. Figure 7 shows the relationship between the additional bias (V) and the deposition rate of the carbon films on the Si substrates heated at 200℃ from the mixed gas containing Ar. The improvement of the deposition rate (6.7 to about 15 nm/min) was also observed at -150 V or above, as shown in Figure 7. However, the maximum improved value (16.3 nm/min) of the deposition rate was significantly small in comparison with the case of H_2 (55.3 nm/min). This might be attributed to the sputtering effect of Ar ions because Ar has a large sputtering effect, which leads to suppression of the increase in the deposition rate through a etching effect.

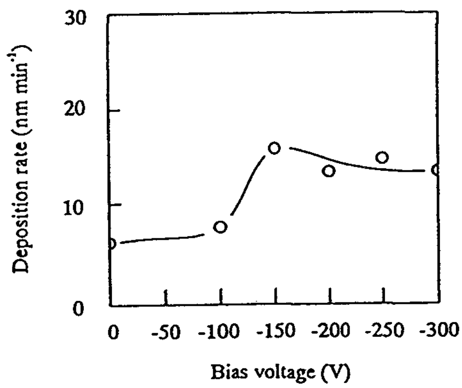

Fig. 7 Effect of bias voltage on deposition rate of carbon films obtained at CH_4 gas flow rate of 30 cm^3 min^{-1}, Ar gas flow rate of 30 cm^3 min^{-1} and microwave power of 200 W.

The Vickers microhardness of the carbon films prepared from the mixed gas containing Ar was improved up to about 20 GPa at above -100 V as shown in Figure 8. Figure 8 indicates that the effective negative bias (≧150 V) to improve the microhardness of the films is lower than that in the case of H_2 (≧300 V). As interpreted from Figure 7, i.e., the negative bias effect on the deposition rate of the films, the ion-bombardment became effective at the negative bias more than -150. Consequently, the cause for the formation of hard carbon films is considered as follows: the increase of C-C bonds, which leads to the rigid matrix structure, might be

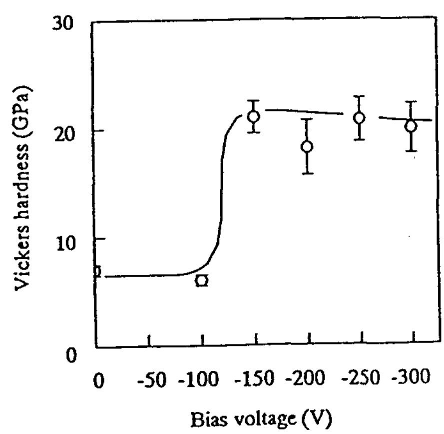

Fig. 8 Effect of bias voltage on Vickers hardness of carbon films obtained at CH_4 gas flow rate of 30 cm^3 min^{-1}, Ar gas flow rate of 30 cm^3 min^{-1} and microwave power of 200 W.

brought about at -150 V or above because Ar ions start to sputter and etch the weak part (containing C-H bonds) of the carbon films at -150 V. The Vickers microhardness of the carbon films should be improved at -150 V or above from the reason mentioned above.

Figure 9 shows the Raman spectra of the films prepared from the mixed gas containing Ar. It was observed that the similar structure to the i-carbon film was also realized at the negative bias of -200 and -300 V. Thus, Ar gas could improve the Vickers microhardness of the carbon films at the negative bias lower than that of H_2 gas. In conclusion, H_2 gas has turned out to be superior to Ar gas as the mixture gas with CH_4 relating to the improvement of both the deposition rate and microhardness of the carbon films by ECR plasma CVD.

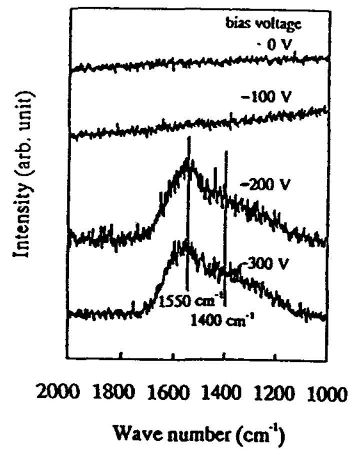

Fig. 9 Raman spectra of carbon films obtained at CH_4 gas flow rate of 30 cm^3 min^{-1}, Ar gas flow rate of 30 cm^3 min^{-1} and microwave power under various bias voltages of 0, 100, 200 and 300 V.

【Conclusion】

1. In the ECR plasma CVD method, the application of the negative bias of up to -300 V was ascertained to significantly improve the deposition rate (from 6.3 to 55.3 nm/min) and Vickers microhardness (from 5.1 to 22.4 GPa) of the carbon films.
2. H_2 gas was shown to be superior to Ar gas as an added gas to improve both the deposition rate and Vickers microhardness of the carbon films prepared in the present method.

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