PLASMA DIAGNOSTICS ON ECR PLASMA SPUTTERING FOR CARBON NITRIDE DEPOSITION

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Abstract

Carbon nitride films were deposited by reactive sputtering using electron cyclotron resonance (ECR) discharge. ECR discharge is very effective method for generating high density ions and highly reactive radicals. Maximum atomic composition ratio of N/C = 0.57 was obtained at N$_2$/Ar=1.0 and target bias voltage of -250 V. The sp$^3$ bonding ratio increased with target voltage by changing the sputtering plasma condition.

1. Introduction

Carbon nitride film has been very attractive material owing to its expected hardness of hypothetical compound $\bar{a}$-C$_x$N$_y$ [1-3]. The structure mainly consists of sp$^3$ bonding between carbon and nitrogen atoms. It is assumed that this C-N network with sp$^3$ bonding exhibit high hardness. Reactive sputter deposition by electron cyclotron resonance (ECR) plasma source or helicon plasma source achieved nearly stoichiometric value of N/C [4,5], although those films did not show high hardness. These plasma sources efficiently generate highly reactive species, such as atomic nitrogen. These species effectively react with carbon, and increase the nitrogen concentration of carbon nitride film. However, the deposition processes are not clear.

In this study, carbon nitride films were deposited by ECR plasma sputtering. The atomic composition of N/C and bonding state of the deposited film were estimated. Furthermore, sputtering plasma were diagnosed for investigating the deposition process. We employed optical emission spectroscopy for excited species in the plasma, quadrupole mass spectroscopy for sputtered species transported to the substrate. Especially, the effect of target bias voltage was investigated.

2. Experimental Apparatus

Figure 1 shows the experimental system of the ECR plasma sputtering for carbon nitride deposition. The chamber consists of a discharge chamber, a processing chamber and
an analyzing chamber. The discharge chamber (ø57 mm x 1.65 mm) has a rod antenna (ø10 mm x 1.30 mm) for 2.45GHz microwave radiation and ring cusp shaped magnetic field by permanent magnets. A mixture of nitrogen and argon is introduced into the discharge chamber for reactive sputtering. A ring shaped graphite target (ø35 mm x 1.10 mm) is placed within the discharge chamber exit and applied dc negative voltage for sputtering. The processing chamber is attached on the discharge chamber exit, and evacuated by pump to control the deposition pressure. A substrate is placed at 20 mm downstream from the target. The substrate holder is isolated from the chamber wall to bias the substrate. The substrate bias voltage controls ion bombadment energy to the deposited film. The deposited films were analyzed by X-ray photoelectron spectroscopy (XPS). Its properties were estimated with atomic composition ratio (N/C) and bonding states of deposited films.

Excited species within the discharge chamber were analyzed by optical emission spectroscopy. Plasma density and electron temperature were diagnosed by Langmuir probe method. The analyzing chamber with a quadrupole mass spectrometer (QMS) is placed next to the processing chamber. An orifice (ø0.1 mm) is set on the substrate position to analyze the transported species to the substrate. In the case of deposition condition (2 Pa), the analyzing chamber can be kept below $10^{-5}$ Pa by differential pumping. Only species through the orifice can be analyzed with QMS.

3. Experimental Results

Carbon nitride films were deposited with 2 Pa of discharge chamber pressure and 200 W of microwave power. Figure 2 shows the XPS spectra of deposited film. Each spectrum is decomposed into several bonding structures. Both C1s and N1s spectra have sp$^3$ and sp$^2$ bonding in it. Figure 3 shows the atomic composition ratio of deposited film dependence on gas mixture ratio and target bias voltage. Nitrogen content in the films is sensitive for mixture ratio of sputtering gas. Maximum atomic composition ratio of N/C = 0.57 was obtained at
N$_2$/Ar=1.0 and target bias of -250 V in this experiment. However, the atomic composition ratio of N/C decreases to 0.52 at target voltage of -500 V. Figure 4 shows the sp$^3$-bonding ratio within the film which decomposed from the narrow scan spectra, as shown in Fig.2. The sp$^3$ bonding between C and N is important for forming a-C$_x$N$_y$ structure. Hence, it is important to estimate bonding structures of C and N. The sp$^3$-bonding ratio both C and N increases with gas mixture ratio and target bias voltage. Though increase of target bias voltage decreases the atomic composition ratio, the sp$^3$-bonding ratio increases.

![Fig.2 XPS spectra of deposited film.](image)

![Fig.3 Atomic composition ratio with various gas mixture ratio.](image)

![Fig.4 sp$^3$-bonding ratio with various gas mixture ratio.](image)

Optical emission spectroscopy revealed that highly reactive species such as nitrogen ions and nitrogen atoms were existed in ECR plasma. Figure 5 shows the emission intensity of atomic nitrogen (416.8 nm) dependence on sputtering voltage. The intensity increases with sputtering voltage. Especially, the emission intensity at target position steadily increases with target voltage. Target bias voltage affected the plasma composition. Figure 6 shows the plasma parameter dependence on target bias voltage. Increasing target bias voltage decreases the plasma density. Also, electron temperature slightly increases with target bias voltage. An
increase of electron temperature enhances the dissociation of nitrogen, and increases the emission intensity of atomic nitrogen. It is considered that this increase of atomic nitrogen increases the sp³ bonding between carbon and nitrogen as shown in Fig. 4.

Fig. 5 Emission intensity of NI (746.8nm) with various target voltage.

Fig. 6 Plasma parameter dependence on target bias voltage.
Figure 7 and 8 show the mass spectra of sputtered species at the target voltage -200V and -700V. The number of heavy sputtered species (m/e>50) was increased with increasing the target voltage. The number of carbon nitride species \((\text{C}_n\text{N}_m)^+\), \((\text{C}_n\text{N}_m)^-\), \((\text{C}_n\text{N}_m)^0\), \((\text{C}_n\text{N}_m)^2\) was increased with increasing the mixture ratio (N\(_2\)/Ar). These species increase the atomic composition ratio N/C within the film. Also, it is assumed that some species enhance the deposition of sp\(^3\) bonding.

4. Conclusions

Deposition characteristics of carbon nitride by ECR plasma sputtering were studied. And the sputtering plasma was investigated by optical emission spectroscopy and quadrupole mass spectroscopy. Maximum atomic composition ratio of N/C = 0.57 was obtained at N\(_2\)/Ar = 1.0 and target bias of -250 V in this experiment. The sp\(^3\)-bonding ratio increased with target voltage by changing the sputtering plasma condition.

References
