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SYNTHESIS OF CARBON NITRIDE FILMS BY HIGH-DENSITY HELICON PLASMA SPUTTERING

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Abstract

Production of high-density nitrogen plasmas with excitation of the m=0 mode helicon wave has been studied for reactive plasma sputter synthesis of carbon nitride films. High-density nitrogen plasmas with densities of 4×10^{12} cm^{-3} were obtained in nitrogen at nitrogen pressure of ~0.1 Pa. Optical emission spectroscopy showed that the line emissions of atomic nitrogen (NI) and atomic-nitrogen ions (NII) were considerably enhanced in the helicon wave-excited high-density plasma, showing that a high concentration of atomic nitrogen was produced in the high-density plasmas. This is different from the spectra measured for the induction-mode (non-wave excitation) low-density plasma dominated by the molecular band emission associated with the first positive system of N_2, which is likely to be the case with conventional plasma sources. Carbon nitride films have been deposited on Si (100) substrates by reactive sputtering of carbon target with the helicon wave-excited high-density nitrogen plasmas. Compositional characterizations with Rutherford backscattering spectrometry (RBS) showed that the N/C ratio of ~1.3 was achieved by depositing the CN films at plasma densities as high as 1×10^{12} cm^{-3}, where the line emissions of atomic nitrogen were significantly higher than the molecular band emissions. The increase in the plasma density and/or in the ratio of the atomic nitrogen (NI) emission intensity to the molecular band in the vicinity of the substrate were found to directly affect the N/C ratio in the CN films.

1. Introduction

Studies on the synthesis of superhard nitride films in B-C-N atomic system (c-BN, CN and BCN) have attracted great interests due to their potentially- and/or theoretically-expected extreme properties similar or even superior to those of diamond [1,2]. Motivated by the desire to establish a nitridation environment with extremely high reactivity for the synthesis of these metastable covalent materials, we have developed a high-density helicon wave-excited plasma source designed for sputter deposition to supply high concentration of atomic nitrogen [3,4].

Helicon wave-excited plasma generation has attracted great interests as a means of obtaining high-density plasmas (10^{12}-10^{13} cm^{-3}) for materials processing [5-10]. Recently, increasing attentions have been focused on the studies of reactive helicon plasmas in dissociative molecular gases [3,4,11], which are important to apply these plasmas to the materials processing. In our previous study, we reported the results of investigations on the helicon-wave excited nitrogen plasmas generated using the helical antennas with m=0 mode and the properties of the CN films, where the wave magnetic field measurements confirmed the excitation of m=0 mode helicon wave [4].

This work presents the properties of the helicon wave-excited nitrogen plasmas especially regarding the axial distribution of plasma density and the optical emission spectra for investigation of the correlation between the reactivity during CN film deposition and film composition. Carbon nitride films have been deposited on Si (100) substrates using reactive sputtering of cylindrical carbon target with a high-density nitrogen plasmas sustained with excitation of the m=0 mode helicon wave.

2. Experimental

Experimental set-up for deposition of CN films with helicon plasma sputtering is schematically shown in Fig. 1. The plasma source consists of a helical antenna wound on a quartz discharge tube of 235 mm in length and 36 mm in internal diameter, which is connected to the stainless steel chamber. The vacuum chamber is pumped with a 300-l/s turbomolecular pump to attain a base pressure of 3×10^{-4} Pa. Plasmas were produced in N_2 of 0.1-0.8 Pa. An m=0 mode helical antenna (3-turn) is used for the plasma production. The helical antenna is coupled to a 3 kW RF power generator at 13.56 MHz via a matching box. The discharge tube is surrounded with two magnetic coils to apply the static magnetic field (~1000G). The axial distribution of the static magnetic field strength is also depicted in Fig. 1, where the z axis is taken along the discharge system so that the z=0 position lies at the end of the discharge tube and the positive z values are taken in the direction from the tube to the substrate.

Plasma density was measured using an axially movable Langmuir probe. Optical emission spectra from the plasmas in the

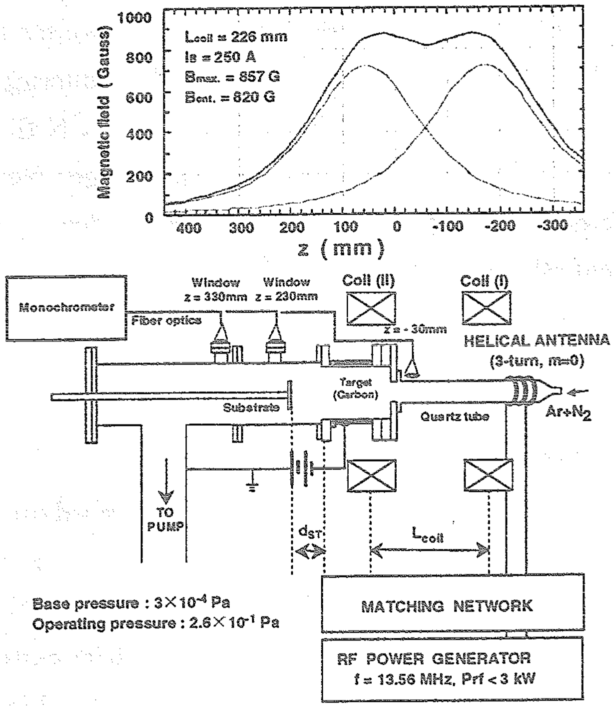

Fig. 1. Schematic diagram of experimental apparatus.

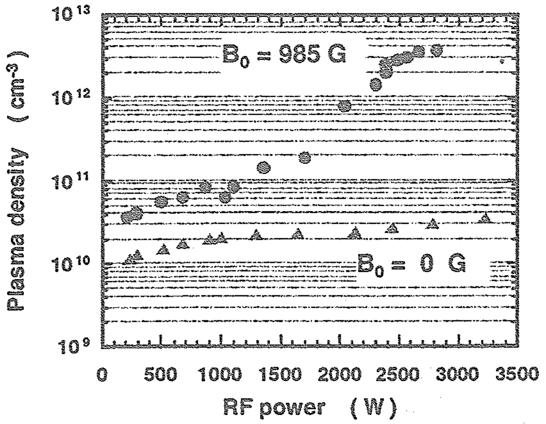

Fig. 2. Variation of nitrogen plasma density as a function of RF power.

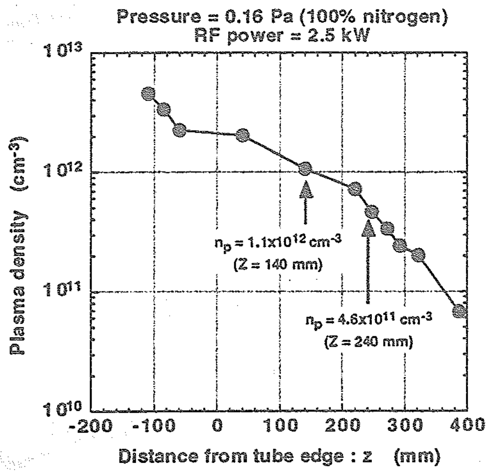

Fig. 3. Axial distribution of nitrogen plasma density in high-density mode.

discharge tube region were measured using a 35 cm monochromator with quartz fiber optics for light collection. For investigation of the axial variation of reactive species in the plasma, the optical emission spectra measurements were also preformed at two window positions (z=230 mm , 330 mm).

For deposition of CN films a hollow graphite cylinder of 60 mm in internal diameter and 80 mm in length was installed as a sputtering target which was biased to a negative DC voltage. The films were deposited on Si(100) wafers fixed on the axially movable substrate holder, which is kept at a plasma floating potential (measured to be approximately -50 V) and negative bias voltages of -100 and -300 V. Before deposition, the substrate was sputter-cleaned by Ar ions by negatively biasing the substrate in helicon wave-excited Ar plasma.

The elemental composition of the deposited films was analyzed using Rutherford backscattering spectrometry (RBS). The RBS measurements were performed using 2.281 MeV He2+ beam from a tandem accelerator and the backscattered ions were detected at a scattering angle of 165°. Chemical and structural analysis of the CN films was performed using x-ray photoelectron spectroscopy (XPS). Mechanical properties were evaluated using nanoindentation.

3. Results and discussion

3.1 Production of helicon wave-excited nitrogen plasmas

Figure 2 shows the variation of plasma density in 0.3 Pa nitrogen as a function of the RF power, which was measured at a position of z=50 mm. In absence of an external magnetic field (B0 =0 G), the plasma density is of the order of 10^{10} cm^{-3} even at an input RF power as high as 3 kW. The plasma density in presence of the external magnetic field (985 Gauss), however, dramatically enhanced with increasing RF power above 2-2.5kW to attain a density as high as

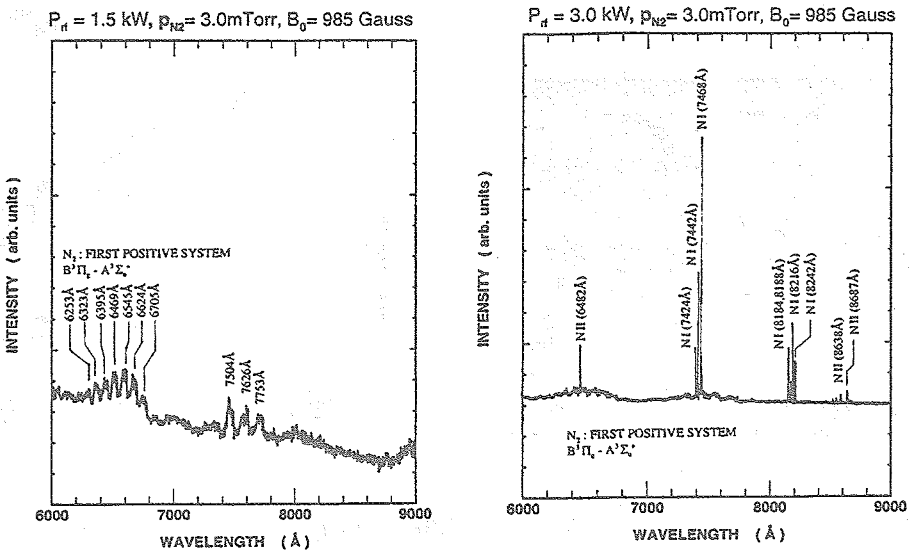

Fig. 4. Optical emission spectra from N2 plasmas in low-density mode (left) and in high-density mode (right).

4×10^{12} cm^{-3} (high-density mode), which was experimentally verified to be associated with the excitation and/or propagation of the m=0 helicon wave [4]. The "low-density mode" below the density with the onset of wave excitation was also verified to be sustained by the induction near field [4]. The density in the "low-density mode" is only fourfold higher than that obtained in the induction plasma without external magnetic field, whereas the density in the "high-density mode" is approximately two orders of magnitude higher than that obtained in the induction plasma produced without an external magnetic field.

Axial profile of the nitrogen plasma density is shown in Fig. 3, in which the discharge was sustained in 0.16 Pa pure nitrogen at an RF power of 2.5 kW ('high-density mode' with excitation of the m=0 mode helicon wave). The plasma density reached as high as $>2\times10^{12}$ cm^{-3} in the discharge tube region (z< 0 mm) due to the excitation and/or propagation of the helicon wave in a rather flat external magnetic field. With increasing distance from the discharge tube to the downstream region, the plasma density decreased gradually in the region z< 200 mm and more drastically in the region z>200 mm, which is considered to be associated with the divergence of the external magnetic field toward the downstream region.

Optical emission spectra from the plasma are shown in Fig. 4 for the low-density mode at 1.5 kW RF power and the high-density mode at 3.0 kW. Here it should be noted that the vertical scale for the spectrum in the low-density mode is magnified by 6 times to that in the high-density mode. The emission spectra from the low-density mode is dominated by the molecular band spectra from the first positive system of N_2, where the line emissions corresponding to the atomic nitrogen (NI) and the nitrogen ion (NII) are negligible. While in the high-density mode, significantly strong emissions of NI and NII lines were observed. Especially the line emissions at 7424, 7442 and 7468 Å from the atomic nitrogen are found to be significantly strong compared to the band emissions overlying with small intensity.

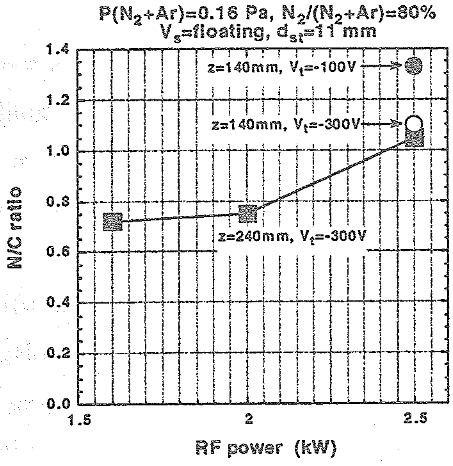

Fig. 5. N/C composition ratio in CN films.

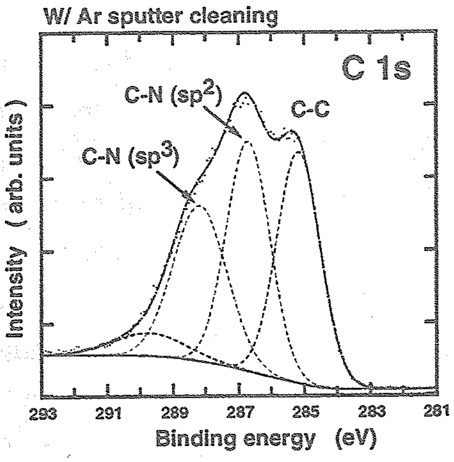

Fig. 6. XPS C1s spectrum of a CN film.

3.2 *Film characterizations*

Variation of elemental composition ratio N/C in the CN films is summarized in Fig. 5 as a function of RF power with the substrate position and target bias voltage as parameters. In a series of film depositions performed at the substrate position of z=240 mm, the N/C ratio was found to increase with increasing RF power and approached to ~1 at an RF power of 2.5 kW. Further increase in the N/C composition ratio was obtained by shortening the source-to-substrate distance and reducing target sputtering bias to achieve the highest N/C ratio of nearly stoichiometric value 1.3 at z=140 mm and the target bias of -100 V. Here it is noted in Fig. 3 that the plasma density at z=140 mm was measured to be ~$1\text{x}10^{12}$ cm^{-3}, which is twofold higher than that at z=240 mm. In addition to this, the axial variation of the emission spectra suggest that the relative concentration of the dissociated atomic species is lowered with increasing source-to-substrate distance. These results show that the increase in plasma density and/or the relative concentration of atomic species at substrate position may directly contribute to the N/C composition ratio in CN films, indicating that the excitation states of nitrogen and carbon atoms in the vicinity of the growing films are significant to enhance

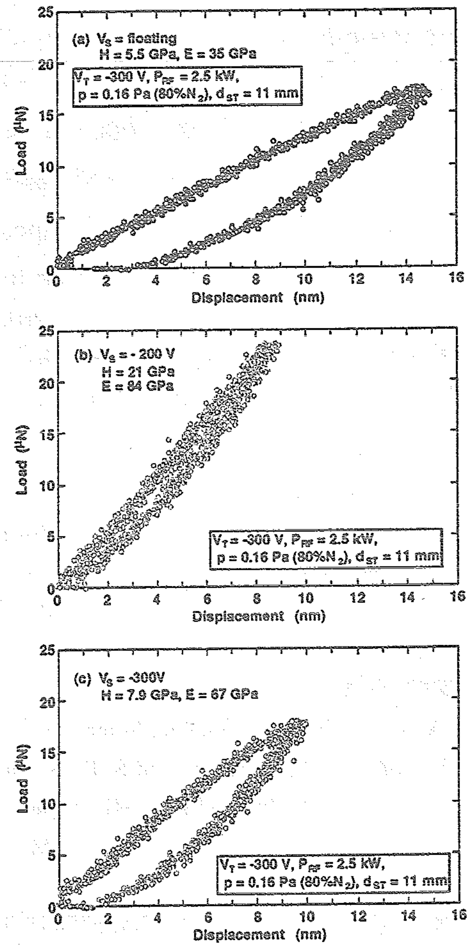

Fig. 7. Nanoindentation loading/unloading curve for CN films deposited on Si(100) substrates at substratebias of (a) floating, (b) -200V and (c) -300V.

reactivity to form the C-N bonding.

Fig. 6 shows a C1s spectrum from a CN film with a N/C ratio of 0.76. The C1s spectra were analyzed using the curve deconvolution fitting by Marton et al. [12]. Based on their analysis of the XPS spectra, two CN bonding states have been presented. The C1s spectrum was decomposed into four distinguishable peaks. The middle two peaks are assigned into two C-N bonds, where N is bonded to C atoms in sp^2- and sp^3-hybridized states, respectively.

Finally microhardness was also evaluated using nanoindentation. Typical loading / unloading curves obtained from nanoindentation measurements of CN films prepared at substrate bias of floating to -300V are shown in Fig. 7. The CN film prepared at the substrate bias of -200V showed the highest value among this series of deposited films, and further increase in the absolute value of the negative substrate bias voltage degraded the hardness value.

4. Summary

We performed investigations on the helicon-wave excited nitrogen plasmas generated using the m=0 mode helical antenna, which is designed for the reactive sputtering of carbon target. The achieved plasma density in 0.2 Pa nitrogen was 4×10^{12} cm^{-3} at an RF power of ~3 kW and a magnetic field strength of ~1000 Gauss. The optical emission spectroscopy showed that the line emissions of atomic nitrogen (NI) and nitrogen ions (NII) were significantly enhanced in the helicon-wave excited plasma. Compositional analysis using RBS showed that the N/C ratio in the CN films could be controlled up to nearly stoichiometric value 1.3. Chemical analysis by XPS also showed the existence of peaks indicating a C-C bond and two C-N bonds where N is bonded to C atoms in sp^2- and sp^3-hybridized states. Nanoindentation measurements showed taht hardness values as high as ~20 GPa were attained at substrate bias of -200V.

Acknowledgments

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