Trans. JWRI, Vol. 24 (1995), No. 2

Helicon Wave Plasma Enhanced Sputtering and Application to Synthesis of Carbon Nitride Films†

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Abstract

Production of RF plasma excited by helicon wave in Ar and (Ar+N_2) mixture gases was studied. A dense plasma of the order of 10^{12}~$10^{13}cm^{-3}$ was obtained through helicon wave excitation at an Ar pressure around 0.1Pa. The DC discharge was enhanced by the helicon wave plasma, and the dense plasma enhanced DC sputtering system was applied to synthesize the carbon nitride film. The bonding state and composition ratio N/C of the sputtered CN_x films were investigated by using x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The N/C radio of more than 0.5 in the sputtered film was achieved, and FTIR spectrum showed an absorption band near 2200cm^{-1} indicating the existence of C≡N covalent bonding.

KEY WORDS: (RF plasma) (Helicon wave) (Sputtering) (Carbon nitride film) (X-ray photoelectron spectroscopy)(Fourier transform infrared spectroscopy)

1. Introduction

In the sputtering process it is required that the mean free path for sputtered atoms in the gas is larger than the distance from source to substrate to achieve high quality deposition. Such conditions lead to the sputtered atoms arriving at the substrate surface with sufficient energies and modifying the growth of the films, while the mean free path of sputtered atoms will increase with decreasing the operating pressure. So it is necessary to keep the pressure as low as possible (≤0.1Pa)[1,2]. Recently plasma sputtering techniques with low-pressure and high-density have been required for less gas contamination and high sputtering rate[3]. As one of the possible plasma sources, electron cyclotron resonance (ECR)[4,5] and magnetron plasmas[6] have been studied by several researchers, since these plasmas can be generally characterized by high electron density under low pressures. However, it has been realized that it is difficult to generate a uniform and large diameter plasma in ECR or magnetron discharge[7].

Recently the plasma production based on RF excitation of helicon waves in an external magnetic field has attracted attention[8-11] because the high plasma density (10^{12}~$10^{13}cm^{-3}$) can be obtained at low pressures(around 0.1Pa). It is considered that helicon waves[12] are known to be right-handed circularly polarized electromagnetic waves, in the frequency range $\omega_{ci} \leq \omega \leq \omega_{ce}$[10] propagating parallel to the magnetic field. The phase velocity of the helicon wave that propagates along the line of the magnetic field is almost equal to the thermal velocity of the electron so that the energy of the helicon wave is transported to the electron by Landau damping which has been proposed by Chen[13]. The helicon wave plasma is characterized by various advantages[14,15] such as plasma production in the wide range of magnetic fields (a few tens of G to a few kG) corresponding to the same frequency (a few tens of MHz), so this type of plasma also has unusually high ionization efficiency and is finding wide applications in material processing[15,16] in competition with ECR plasmas and magnetron discharge. Present work was motivated to introduce such a high density plasma for sputtering at low pressures to improve the sputtering performance and obtain high quality film deposition.

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So far the helicon wave excited plasma production has been mainly performed in monotomic noble gases such as Ar[17,18]. However, reactive plasmas generated in polyatomic molecular gases such as Cl_2, N_2 and/or H_2 etc[7,19,20], are widely used in various materials processing, where the excitations of the deposited atoms are considered to be important in the formation of highly functional films in the metastable phases. One such a metastable material attracting great interest at present is carbon nitride, in which was theoretically predicted the existence of a covalently bound C-N solid with a hardness comparable with or greater than diamond (Liu and Cohen)[21]. The material identified by the empirical model and ab initio calculation was considered to be ß-C_3N_4, similar to ß-Si_3N_4 in structure. There have been numerous attempts to synthesize CN_x films. Torng et al.[22] prepared C:N films by RF sputtering of a graphite target in a mixed Ar-N_2 plasma. Niu et al.[23] claimed to have synthesized crystalline ß-C_3N_4 using laser ablation of graphite combined with an atomic nitrogen beam. More importantly, they have pointed out the importance of atomic nitrogen in the synthesis of carbon nitride. Song et al.[24] have successfully prepared carbon nitride thin films by NH_3-ion-beam-assisted deposition. They also emphasized that the chemical activities possessed by nitrogen atoms were crucial in the formation of ß-C_3N_4. From the various reports of CN_x film formation by the plasma sputtering methods, we consider it important to obtain a high concentration of atomic nitrogen via production of high density plasma for the growth of ß-C_3N_4.

The aim of the present work was to study the RF plasmas caused by helicon waves using helical antennas(2turn or 3turn) with azimuthal mode number of m=0. Such RF plasmas were introduced into a DC sputtering discharge with a cylindrical target to improve the sputtering performance. Sputtering characteristics of a graphite target in (Ar+N_2) mixture plasmas were investigated. The syntheses of carbon nitride films were carried out by sputtering the target in the plasma mixture. The chemical bond state and composition of the obtained films were characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy. The effect of the plasma mixture parameters on the composition ratio N/C in the films was described.

2. Experimental

The schematic diagram of the RF plasma-enhanced

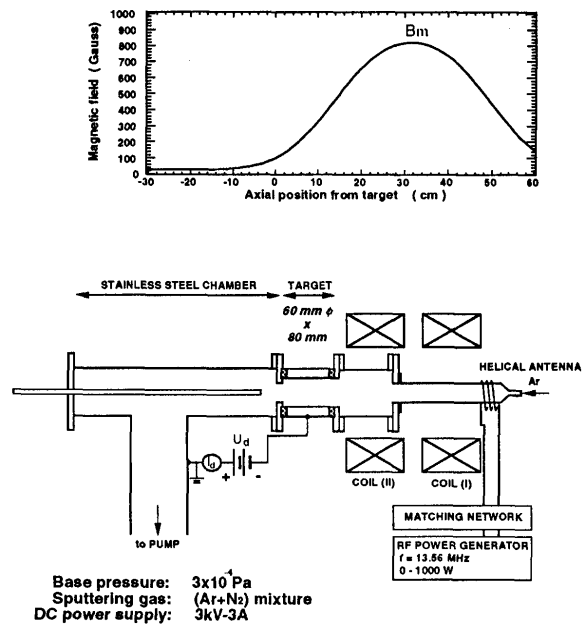

Fig. 1 Schematic diagram of RF Plasma enhanced DC sputtering

DC sputtering apparatus is shown in **Fig. 1**. The distribution of the magnetic field strength along the axis of the vacuum chamber is also shown in Fig. 1. The vacuum chamber is made of stainless steel and is pumped with a 150l/s turbomolecular pump. The base pressure was $3x10^{-4}$Pa. The RF plasmas were generated in Ar and (Ar+N_2) mixture in the range of 10^{-1}~1Pa.

Two types (2 turn and 3 turn) of helical antennas with azimuthal mode number of m=0 were employed for the RF plasma production. The helical antenna surrounded a quartz tube (235mm in length and 36mm in internal diameter) was coupled to an RF power generator at a frequency of 13.56MHz via a matching box. The RF power was varied in the range of 0~3kW, and it was measured at the output of the RF generator when the optimum matching conditions (zero reflected power) were achieved.

Plasma density was measured by using a Langmuir probe which was located at the center of the target that corresponded to the distance of 370mm downstream from the edge of the helical antenna. Substrates used are Si wafers placed at a distance of 20mm downstream from the end of the cylindrical target. The target installed in the chamber was made of a hollow graphite cylinder, 60mm in internal diameter and 80mm in length. A DC power supply of 3kV~3A was used to supply the target. The composition of the sputtered CN_x film was analyzed by

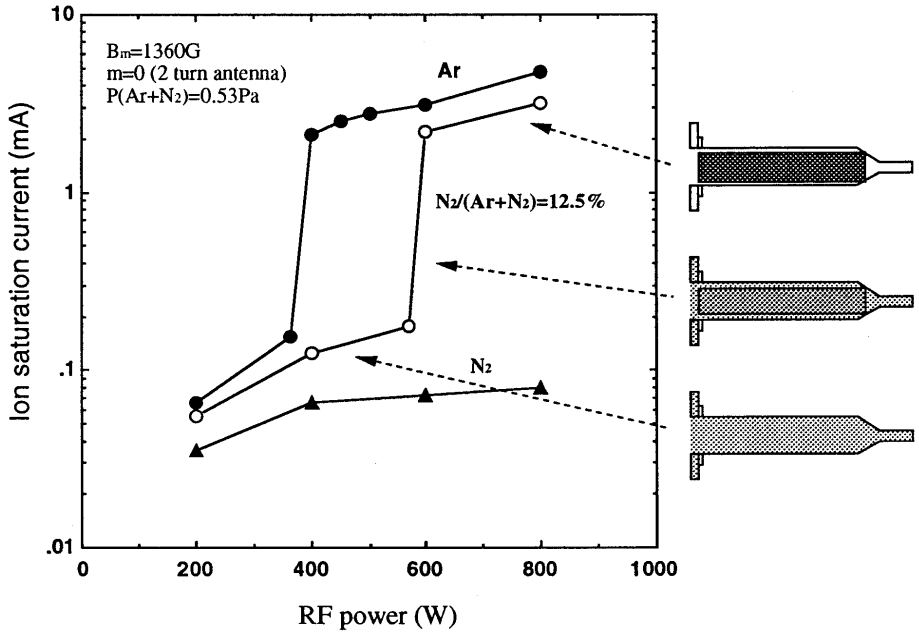

Fig. 2 Ion saturation current together with the plasma appearance as a function of RF power in ($Ar+N_2$) mixed gas

XPS, carried out with MgKα (1253.6 eV) X-ray radiation using a PHI Model 550 system. The FTIR was performed in the range of 4000~400cm^{-1} to study chemical bonding state.

3. Results and discussion

3.1 RF plasma characteristics in ($Ar+N_2$) mixed gases

Plasma densities for the ($Ar+N_2$) mixture were first investigated by using a 2 turn of m=0 mode antenna. **Fig. 2** shows the variation of ion saturation current together with the plasma appearance as a function of RF power at a total pressure of 0.53Pa. In the case of pure Ar, the saturation current corresponding to the plasma density increased with RF power, at low RF powers (below 400W), a glow discharge with a light pink color was observed, and the plasma looked like filling up the whole discharge tube. With increasing the RF power, a density jump was observed at 400W and the appearance of the discharge drastically changed into the blue one due to emission of ArII[17]. At 800W the electron density at the center of the cylindrical target was as high as $2.2x10^{12}cm^{-3}$, and was measured to be fourtimes less than that in the discharge tube($10^{13}cm^{-3}$).

In addition, experiments on the wave pattern in the plasma were also carried out by measuring the axial magnetic component of the RF wave field (B_θ) and the antenna current (I_{RF}). The results of the ratio and phase

Table 1. Conditions of syntheses of CN_x films

Antenna:	m=0 (3 turn)
Target:	Graphite
P(Ar+N2):	0.26Pa
N2/(Ar+N2):	30%~60%
Target voltage:	-100V
RF power:	0~3kW
Magnetic field:	1360G
Substrate:	Si (100)
Substrate bias:	-45V

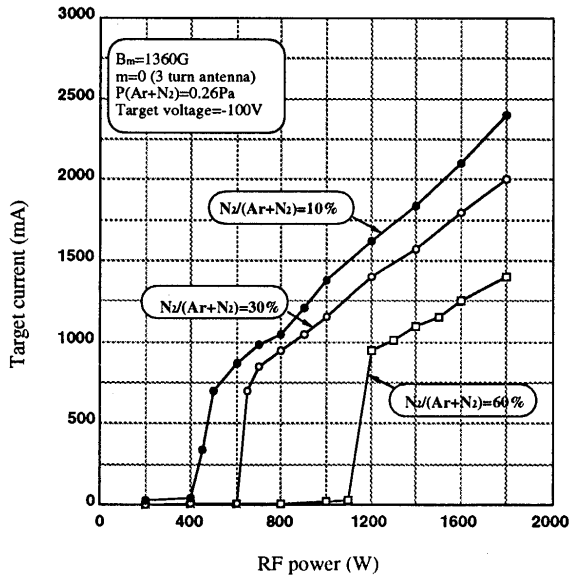

Fig. 3 Target current as a function of RF power

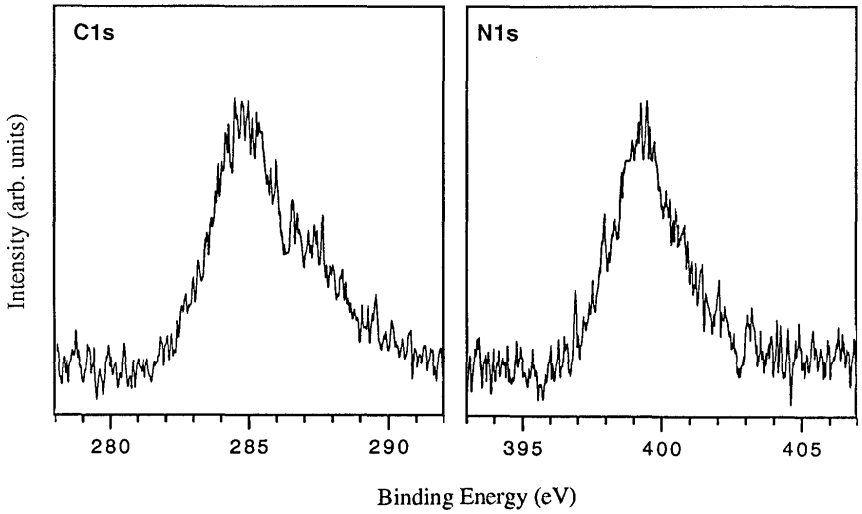

Fig. 4 XPS spectra for C1s and N1s state for the CN_x film prepared at 60% N_2 mixture

shift between the B_θ and I_{RF} indicated that the density jump was accompanied by helicon wave propagation in the plasma.

On the other hand, for pure N_2, no density jump was observed even at 1kW, possibly because the power dissipation in the plasma is dominated by the dissociation of N_2 molecules rather than the ionization processes. The saturation current gradually increased with RF power. Eventually the electron density was only $4x10^{10}cm^{-3}$ at 800W, which is lower by approximately two orders of magnitude than that for pure Ar. However, for the (Ar+N_2) mixture, the density jump was also observed up to 12.5% N_2 concentration, but the threshold RF power was as high as 600W. Other experiments have indicated that this density jump was also caused by the helicon wave excitation.

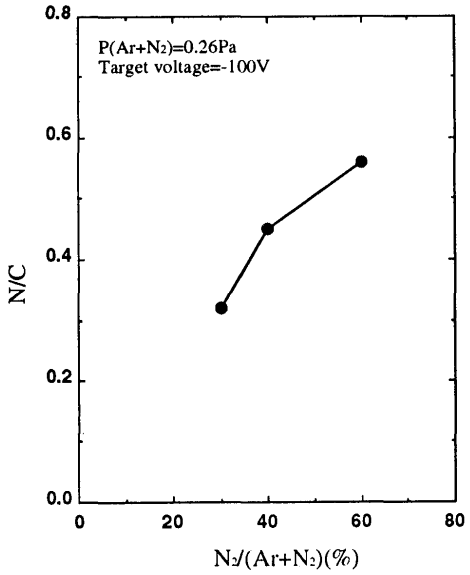

Fig. 5 Effect of nitrogen concentration in (Ar+N_2) mixture plasmas on the N/C ratio in the films

3.2 Application to the synthesis of carbon nitride films

3.2.1 Film preparation

Although the plasma density jump of (Ar+N_2) mixture could be achieved by using 2 turn antenna, the threshold (600W) for that jump was rather higher. For a 3 turn antenna, however, the threshold value was only 200W under the same conditions as that for the 2 turn antenna. The 3 turn antenna was therefore employed to produce RF plasma, and such plasmas were applied to synthesize the carbon nitride film by sputtering graphite in (Ar+N_2) mixture gases. **Fig. 3** shows the results of preliminary experiments for the target current as a function of RF power. The target current jump corresponding the density jump could be observed for 30% N_2 mixture when the input RF power was above 600W, but the input power needed was as high as 1200W for a 60% N_2 mixture. A series of films were prepared under various sputtering conditions, as given in **Table 1**.

3.2.2 Film characterization

The sputtered films were characterized for the chemical bonding state by XPS. **Fig. 4** shows the XPS spectra for C1s and N1s for the CN_x film prepared at 60% N_2

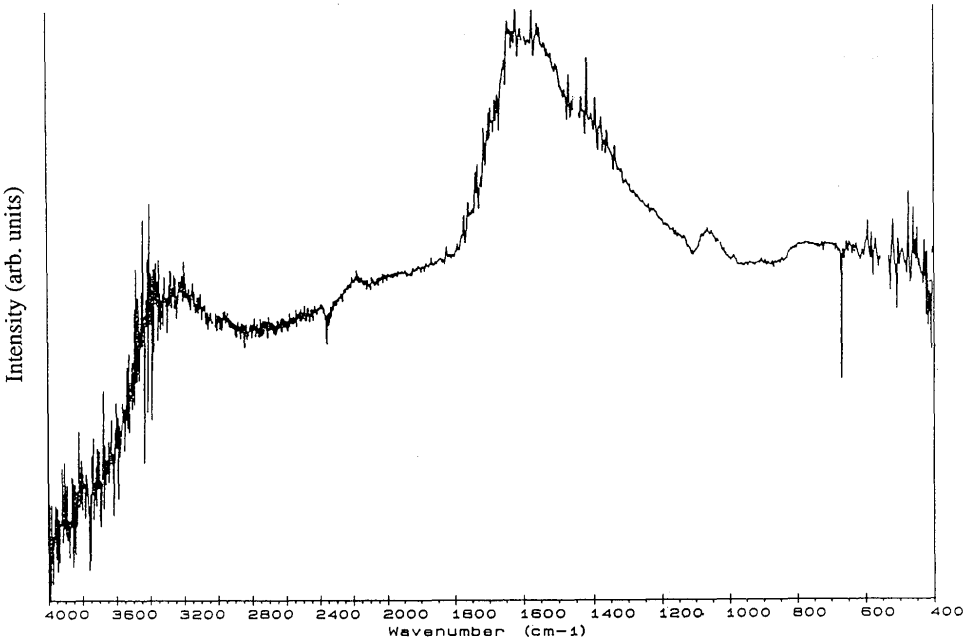

Fig. 6 FTIR spectrum of the film sputtered in 60% N_2 mixture

mixture. The XPS spectra of the films for the C1s showed a broad peak at 284.7eV that contained a tetrahedral phase, C_3N_4, and an sp^2 bonded structure, CN_x, proposed by Marton[25]. On the other hand, the bonding state of N1s indicated differently from that of nitrogen itself. Both spectra of C1s and N1s electrons show the existence of a bond between carbon and nitrogen in the sputtered films. An N/C ratios in the films were calculated from the area ratio of both C1s and N1s peaks in the XPS spectra. **Fig. 5** shows the effect of N_2 concentration in ($Ar+N_2$) mixture plasmas on the N/C ratio in the films. The N/C ratio of more than 0.5 was achieved for the 60% N_2 mixture. More importantly, this result confirms that the N concentration in the film will increase with increasing amounts of atomic N via the production of high density plasmas as mentioned above.

The FTIR spectrum of the film for 60% N_2 mixture is shown in **Fig. 6.** The absorption band at 1200~1700cm^{-1} is considered to correspond to the Raman active G and D bands which become infrared active due to the presence of nitrogen[26]. The band at 2200cm^{-1} can be attributed to a C≡N stretching mode that has been observed by earlier researchers[27,28]. These results indicate the obtained CN_x film is combination of graphite and the diamond-like, sp^2 and sp^3-bonded carbon, respectively, involving the presence of sp C∫N bonding. For 30%N_2 mixture, however, the bands at 2200cm^{-1} could not be observed.

4. Conclusions

On the basis of high density plasmas involving excitation of the helicon wave, an RF plasma enhanced DC sputtering system has been developed. The CN_x films sputtered by this system were analysed. The XPS and FTIR spectra indicated the existence of various C-N bonding states in these films. Although the N/C ratio of more than 0.5 has been achieved, it still does not reach at the stoichiometric amount of ß-C_3N_4(1.33). Further experiments will be designed to increase the concentration of atomic and ionic nitrogen through higher density plasma production under higher N_2 mixture or pure N_2 pressure.

Acknowledgment

The authors are grateful to Dr. R. Yuan, Dept. of Applied Chemistry of Osaka University, for his useful discussions.

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