Plasma Characterization of Facing Target Sputter System for Carbon Nitride Film Deposition

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The plasma properties in the facing target sputtering system during carbon nitride film deposition have been investigated. The ionized nitrogen species of the deposited films increased with increasing discharge current and were independent of the nitrogen pressure. The nitrogen content in the films did not vary significantly with the variation of nitrogen gas. The electron temperature was high close to that in the inter-cathode region, reduced as the electrons moved away from the most intense region of magnetic confinement and increased again outside this region. Calculations based on the film composition showed that the ion to carbon atom ratio at the substrate was about 50 and that the ratio between the ionized and neutral nitrogen molecules was about 0.25.

Keywords : Plasma, Facing target sputter, Carbon nitride film, Electron temperature

1. INTRODUCTION

The magnetron sputter technique has been used in laboratory and industry for thin film research, development and production. However, further development of thermal stable thin film media with high uniformity has been limited with the use of the normal magnetron sputter. Therefore, in addition to research on new materials and multilayer deposition, we must concentrate our attention on the development of various sputtering techniques. Facing target sputtering is one of the widely used techniques for magnetic materials coating[1,2], hard coating[3-5] and photochemical devices[6]. This technique consists of two targets placed opposite to each other, with the substrates held on a plane perpendicular to the surface of the targets.

Some investigators[7,8] have tried to grow carbon nitride or diamond films by conventional magnetron sputtering technique, but the nitrogen concentration of the films was very low and the film properties showed to be amorphous in nature. To increase the nitrogen content in the film, its effect on crystalline features in the C-N film was the motivation for using a Penning source[1]. Many factors should be considered in the production of successful continuous crystalline β-C_3N_4.: the degree of ionization of the reactive species(N_2^+/N_2), C/N_2^+ ratios, elimination of energetic electron bombardment and low deposition temperature. Considering these factors, the facing target sputtering technique was used for crystalline carbon nitride film deposition[3].

Although this system is new for thin film deposition, Naoe et al.[1] used the sources based on the facing target geometry. Their motivation was that they needed to achieve reasonable deposition rates from a ferromagnetic target material. With conventional magnetrons, it is necessary to use very strong magnets, which saturate the target and thereby reduce permeability and/or use a very thin target, to achieve adequate ferromagnetic deposition rate. In such case, a suitably strong transverse magnetic field component B_x must be established above the target surface. Naoe et al.[1] overcame this difficulty since the plasma discharge in this device depends solely on the perpendicular B_y component of the magnetic field for confinement.

In facing target sputter system using the Penning source, secondary electrons emitted during sputtering are constrained to reside within the volume between the cathodes; thus, an intense discharge sustainable down to low pressures can be ignited. We studied this kind of geometry because a higher degree of ionization in the plasma at low operating pressure ($<5x10^{-4}$ mbar) represents an advancement in magnetron sputtering technology for carbon nitride film deposition [9]. In this paper, we investigated the plasma properties in the facing target sputtering system during carbon nitride film deposition.

2. EXPERIMENT

The vacuum chamber with accessories is shown schematically in Fig. 1. The chamber was originally designed for running a conventional magnetron sputtering system. Thus the chamber still has four magnetron ports. The chamber has rotatable shutter ports, plasma emission spectrometer ports, thermocouple feedthrough flange, high vacuum port and backing line port. Penning type two magnetrons are inserted inside the chamber, one from the top and the other from the bottom. The clamping arrangements of various dimensions were employed to facilitate the sealing for various flanges and apparatus. The chamber was fabricated using non-magnetic AISI 304 stainless steel. It is a double skinned wall, which allows water circulation for heating or cooling. To avoid hydrogen contamination from water molecules on the chamber wall, the whole chamber was heated up to 150 °C before film deposition by the resistively-heated coil. The flow rates of both working and reactive gases were controlled by a mass flow controller (Edwards 825). The total pressure of the chamber was monitored by the use of Edwards Penning(type CP25-K, model D145-37-000) and Pirani (type PRL 10, model D021-58-000) gauges which were controlled by an Edward Pirani-Penning controller (type 1005).

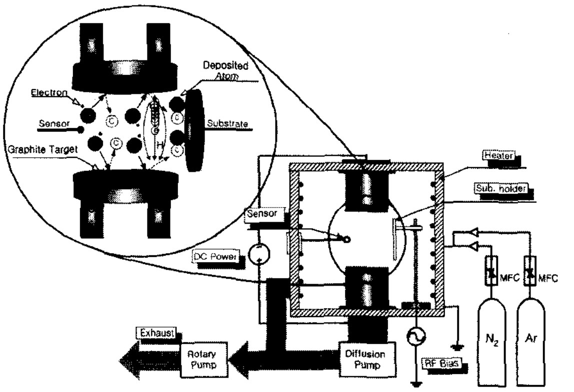

Fig. 1. A schematic of facing target sputtering system with the penning source.

Figure 1 also shows the schematic positioning of the source within the vacuum chamber and illustrates the resulting plasma. The Penning Sources can be moved independently of one another so that the inter target distance can be varied. An additional option is to change the magnetic field by either changing the target thickness, moving the magnets within the Penning Source, reducing the number of magnets behind each body, altering the inter magnet spacing, or using a combination of one or more of these techniques. The substrate holder is mounted to the side of the device and can be electrically biased.

Carbon nitride films were grown on polished n-type (100) silicon substrates. For these depositions, the inter-target distance was 10 cm and the target diameter was 10 cm. The substrate was placed parallel to the axis on the centre line between the targets and 10 - 15 away from it. Prior to deposition, the substrate was Ar^+ sputter etched in situ to remove the surface contamination for 20 minutes at a pressure of 1.5×10^{-4} mbar using a 13.56 MHz RF supply, which gave a substrate bias of -80 V. The sputtering targets were 99.99% graphite, and the sputter gas was a mixture of argon and nitrogen of varied composition. The gas purity was 99.999 % in each case.

3. RESULTS AND DISCUSSION

A "K" type thermocouple was used to measure the growth temperature. The measurements were taken in two ways. The first temperature was recorded after sputter cleaning by Ar at -80V bias for 20 min. At that time, the temperature was recorded 120 °C. Then, deposition was started and -50V bias voltage was applied during this time. The temperature effect due to -50V bias was very low as compared to the exposed plasma temperature. Because most of the samples were grown for 5 and 30 minutes, two separate temperature readings were taken for those deposition times. For 5-min grown samples, the temperature was 273 °C and for 30-min grown samples the temperature was 320 °C after deposition. The temperature profile was plotted in Fig. 2. during film growth for 30 minutes.

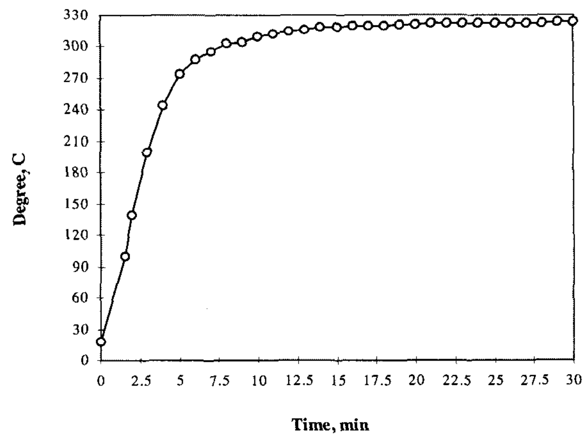

Fig. 2. Temperature profile during film growth. The deposition parameters are 3.0A current and -50 bias voltage. Deposition pressure was 1×10^{-3} mbar.

Optical emission spectroscopy (OES) measurements was performed using a Digitwin Sofie instrument. The detector scans emission spectra in the 200-900 nm range.

The light emitted from the plasma was transmitted to the spectrometer by means of an optical quartz fiber. The plasma emission intensities are measured directly from the spectrum by converting the height of the peak according to the gain of the system. The observed peak positions are compared with the reference peaks given by the instrumental data library.

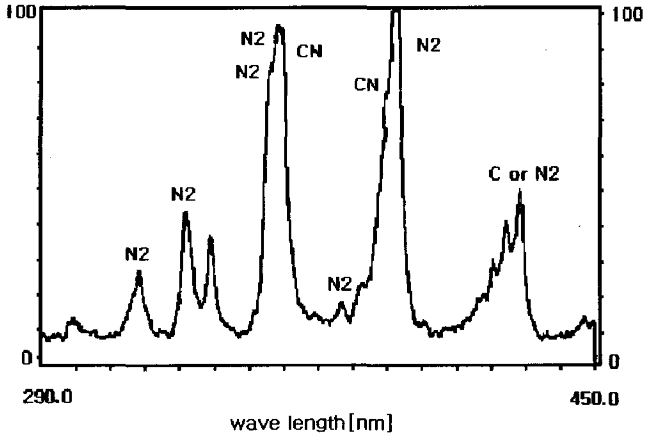

Fig. 3. An optical emission spectrum for the nitrogen plasma during carbon nitride film deposition.

Figure 3 shows the optical emission from the plasma during sputtering. Striking features include the high level of N_2^+ ions at 391.44 nm relative to the neutral nitrogen, and also the presence of CN radicals in the plasma. Table 1 summarizes the optical emission spectra from the plasma during sputtering shown in the Fig. 3. CN radicals appear to arise in the plasma which comes from nitrogen content in the target rather than chemical sputtering from the substrate or chamber walls. If argon replaces the nitrogen as the sputtering gas, then the emission due to CN does not immediately stop but slowly disappears over several minutes as fresh material is sputtered from the graphite target. This gradual disappearance is not due to the time required for the gas composition in the chamber to change because a slow reduction occurs even with a delay between sputtering in nitrogen and argon.

Figure 4 shows the N_2^+ ion (391.5 nm) intensity as a function of the discharge current. Interestingly, the number of ionized nitrogen species in a confined plasma increases with increasing discharge current and is independent of the nitrogen pressure. This statement can be validated by the analysis of the film deposited at different nitrogen pressures (low to high), while the other deposition parameters are kept constant. The nitrogen content in the films does not very significantly with the variation of nitrogen gas.

Table 1. Spectral assignments for emission from N_2 plasma.

λ_{obs}(nm)	λ_{ref} (nm)	Species
317	315.93	SPS of N_2
332	333	SPS of N_2
353.2	353.67	SPS of N_2
356	356.35	CN
358	357.69	SPS of N_2
376	375.54	SPS of N_2
388	388.5	CN
391.5	391.44	FNS of N_2^+
428.5	428.76	C^+
428.5	427.81	FNS of N_2^+

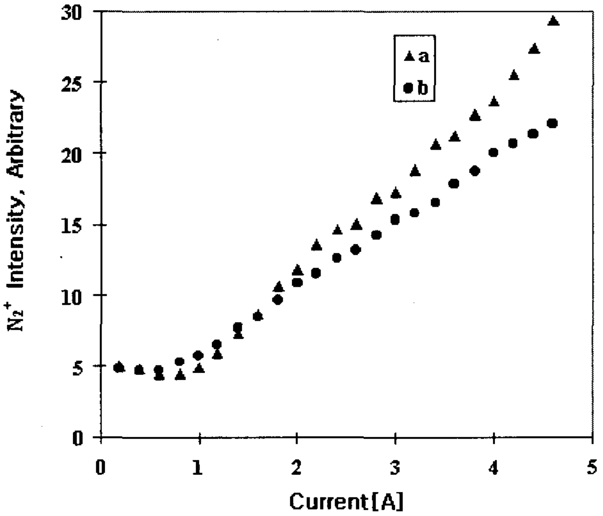

Fig. 4. N_2^+ ion intensity as a function of discharge current. (a) indicates higher pressure (1×10^{-3} mbar) and (b) indicates lower pressure (1.5×10^{-4} mbar).

For the lngmuir probe measurements[10], the deposition pressures were kept at 1.5×10^{-4} and 6×10^{-4} mbar and the substrate was biased at 0 or -50 V with a 13.56 MHz RF supply. The plasma characteristics did not change significantly when the substrate bias was changed. Therefore later on, only the results for -50 V bias are discussed. As shown in Fig. 1., the maximum insertion distance of the Langmuir probe (200 mm) corresponds to the outer edge of the cathodes. The plasma characteristics in the inter cathode space could not be read because the probe insertion into this region extinguished the plasma. In a conventional (unmagnetized) plasma, the plasma potential is slightly positive and remains approximately constant throughout the bulk of the plasma outside the electrode sheaths. As can be seen from Fig. 5., the plasma potential in this system behaves quite differently. It remains negative for a long distance away from the cathode sheath and only becomes positive near the chamber walls. This phenomenon occurs because of the magnetic confinement of the electrons between the opposed cathodes. This negative space charge in the magnetic confinement region gives rise to an electric field and an increase in potential with distance from the cathode axis as shown in Fig. 5.

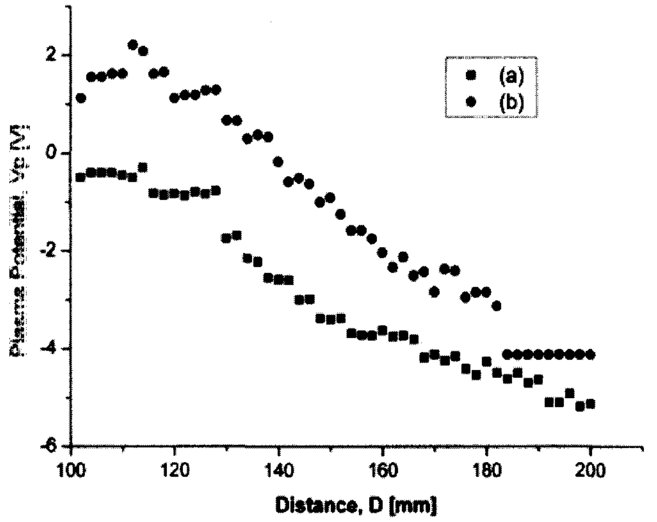

Fig. 5. Plasma potential as a function of distance of the probe (a) Bias -50V, 4.5A, 6×10^{-4} mbar and (b) Bias -50V, 3.0A, 1.5×10^{-4} mbar.

The floating potential which is the potential taken up by an isolated body in the plasma is related to the plasma potential and the electron temperature according to the equation[11]

$$V_f = V_p - (3.3 + 0.5\ln\mu)\frac{T_e}{e} \tag{1}$$

where, V_f is the floating potential (V), V_p is the plasma potential (V), T_e is the electron temperature (eV), e is the electron charge, and μ is the atomic mass (amu). The floating potential also shows the effects of magnetic confinement of the electrons in Fig. 6. According to the above equation, the electron temperature, T$_e$, will be minimum when V_p-V_f is minimum, that is, when V_f is maximum. By comparing Fig. 5. and Fig. 6., one can see that this phenomenon occurs at the probe position of ~150 mm. As plot of the electron temperature vs. probe position, Fig. 7. displays this phenomenon. The Fig. 7 shows that the electron temperature is high close to the inter-cathode region, reduces as the electrons move away from the most intense region of magnetic confinement, and increases again outside this region. This occurrence can be explained as follows. High density of hot electrons are present in the magnetic trap because of the intense plasma and the magnetic confinement. Very low energy electrons are able to drift and diffuse out of the trap, and thus, the average electron energy at the outer regions of the trap will be lower. However, at the edges of the trap, these cold electrons will still see an electric field, and therefore, they will start to accelerate again and hence, their average energy will rise. Once they leave the region influenced by the electric field, their energy will remain constant.

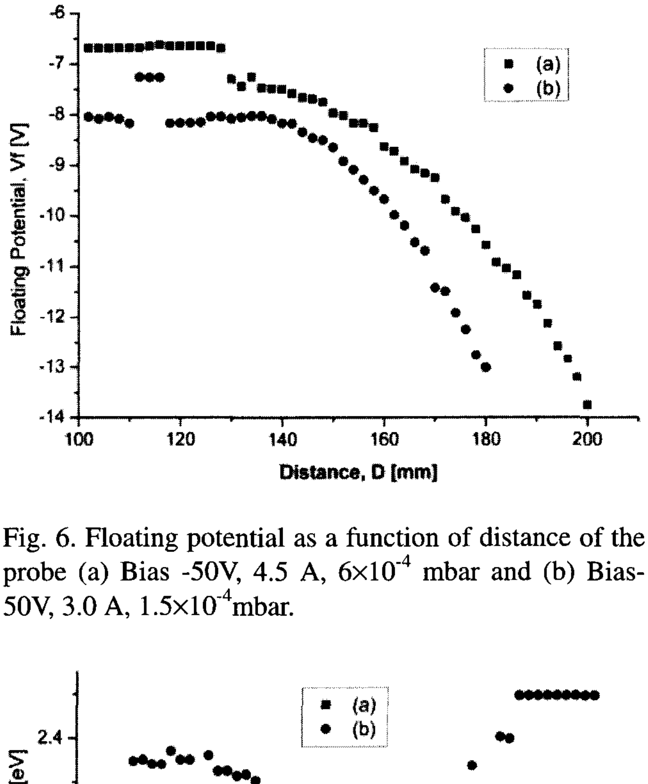

Fig. 6. Floating potential as a function of distance of the probe (a) Bias -50V, 4.5 A, 6×10^{-4} mbar and (b) Bias-50V, 3.0 A, 1.5×10^{-4}mbar.

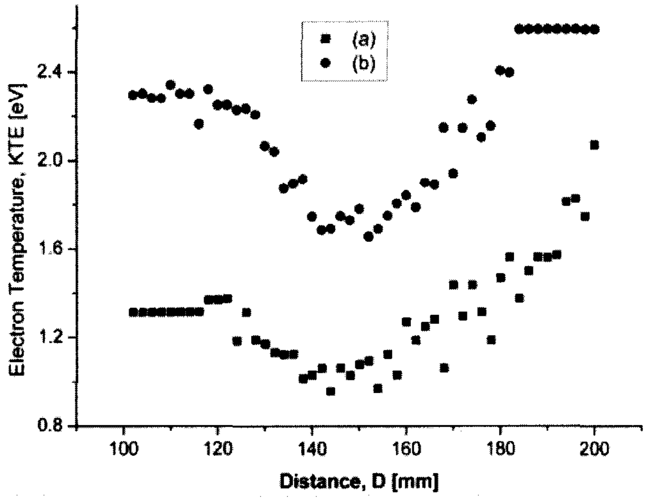

Fig. 7. Electron temperature as a function of distance of the probe (a) Bias -50V, 4.5A, 6×10^{-4} mbar and (b) Bias -50V, 3.0A, 1.5×10^{-4} mbar.

As shown in Fig. 8., the electron density at the edge of the inter-cathode space rises to >1.7×10^{11} at a pressure of 6×10^{-4} mbar and >7.5×10^{10} cm^{-3} at 1.5×10^{-4} mbar. It is expected to be considerably higher on the cathode axis. These high densities correspond to an ionization ratio of >1.1 % and 2 %, respectively. Thus, on the cathode axis, the ionization level will be very high, allowing intense activation of the molecules to occur.

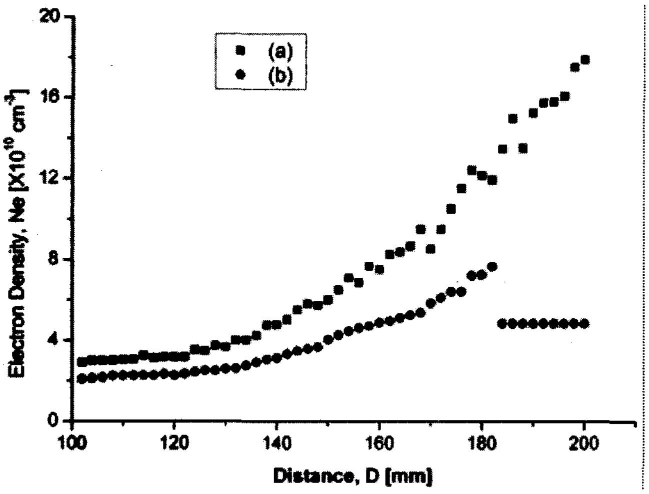

Fig. 8. Electron density as a function of distance of the probe (a) Bias –50 V, 4.5 A, 6×10^{-4} mbar and (b) Bias–50 V, 3.0 A, 1.5×10^{-4} mbar.

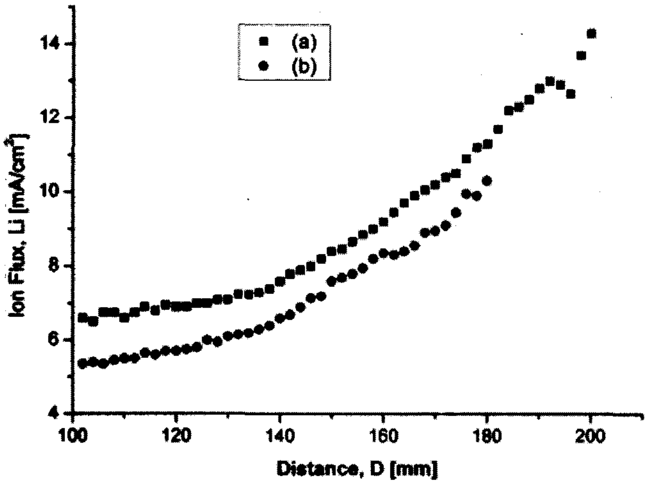

Fig. 9. Ion flux as a function of distance of the probe (a) Bias –50 V, 4.5 A, 6×10^{-4} mbar and (b) Bias –50 V, 3.0 A, 1.5×10^{-4}mbar.

Figure 9 shows the ion flux falling off with distance from the cathode as expected. For the normal deposition of carbon nitride used in this system, the substrate is held at a distance corresponding to the 150 mm point. At this point, for a pressure of 1.5×10^{-4} mbar, the current density due to ions at the substrate is ~7 mA.cm^{-2}. This corresponds to an ion flux of 4.4×10^{16} cm^{-2} s^{-1}. We can calculate the ion to neutral flux ratio at the substrate. The film growth rate is approximately 2 μm/hr, which is equivalent to 5.6×10^{-8} cm s^{-1}. If we assume the film structure is that of β-C_3N_4, the unit cell dimensions are a, b = 6.44 Å, c = 5.65 Å[12], and then, the volume of the unit cell is 2c(asin30°×bcos30°) = 203 Å^3, which is 2.03×10^{-22} cm^3. In conjunction with the growth rate this gives a C_3N_4 molecular deposition rate of 2.8×10^{14} cm^{-2} s^{-1}. Because each C_3N_4 molecule contains 3 carbon atoms, the carbon atom arrival rate at the substrate must be 8.4 $\times10^{14}$ cm^{-2} s^{-1}, if the sticking coefficient is assumed to be 1. Thus, the ratio of the incorporated carbon to the bombarding ions (which are predominantly nitrogen) is ~0.02. Also, the impingement rate of the neutral background nitrogen molecules is given approximately by[13]

$$r = 3.5\times10^{22}(MT)^{-0.5}\, p \ \text{cm}^{-2}\text{s}^{-1} \qquad (2)$$

where, M is the molar mass of the nitrogen molecule (g), T is the temperature (K) and p is the pressure (mbar). For nitrogen molecules at 300 K, this value is 2.3×10^{17} cm^{-2} s^{-1}. The ion to neutral arrival ratio at the substrate is then ~0.25. This result means that the film deposition process is highly active because of the high ion to neutral arrival ratio at the substrate.

4. CONCLUSION

Facing target magnetron sputter can be a good system for production of carbon nitride material. The electrons can be completely entrapped by changing the position of the sources. Thus, effective ion bombardment can be increased and thus, eventually, can increase nitrogen content in the film. The Langmuir probe measurements show that the source gives rise to magnetic confinement of the hot electrons in the inter-cathode space. They show that there is a high degree of ionization exceeding 2% in the intense plasma region and that an electric field exists outside the anode and cathode sheaths. Approximate calculations based on the film composition show that the ion to carbon atom ratio at the substrate is ~50 and that the ratio between the ionized and neutral nitrogen molecules at the substrate is ~0.25. Optical emission from the plasma shows that there are CN radicals present in the plasma which come from nitrogen content in the target rather than from chemical sputtering from the substrate.

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