Transactions of the Materials Research Society of Japan 33[4] 815-818 (2008)

Mechanical Properties, Thermal Properties and Microstructures of Amorphous Carbon-nitrogen Films

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We have investigated the relationship among thermal properties and mechanical properties of the amorphous carbon films containing nitrogen prepared by the RF plasma enhanced CVD. Thermal conductivity was measured by the 3ω method and related with I_D/I_G from the Raman spectroscopy, N/C and density from the RBS/ERDA and hardness from the nanoindentation method. The thermal conduction in the films was discussed in terms of the graphite cluster size L_a derived from the I_D/I_G and correlated with the mechanical properties and tribological properties.
Key words: RF plasma enhanced CVD, 3ω method, naoindentaiton method, ball on disk (BOD)method

1. INTRODUCTION

Diamond-like carbon (DLC) films or amorphous carbon films have been applied to the protective films of digital video tapes, hard disks and machining tools because of its hardness, low frictional coefficient and chemical stability [1]. Recently, the application of the gas permeation barrier films for PET bottles and the biological application of antithrombogenic coating for stents have been reported [2,3]. Many reports have been published for the study of the structure of amorphous carbon films, mechanical properties and tribological properties [4-6]. However, not so many reports on thermal properties that might affect tribological properties have been published so far. The thermal conductivity of crystal diamond which consists of sp^3 bonds of carbon reaches 2000 W/(m·K) because of phonetic lattice vibration and the thermal conductivity of hexagonal graphite reaches 1000 W/(m·K) . On the other hand, because amorphous carbon film consists of carbon and hydrogen mainly and has the mixed structure of sp^3 bonds and sp^2 bonds, phonetic distraction causes much lower thermal conductivity [7-9]. Chen reported 4.7 W/(m·K) for the thermal conductivity of ta-C by photo thermal analysis [7]. By the 3ω method, Bullen *et al.* reported 0.2 W/(m·K) for the thermal conductivity of amorphous carbon film from the remote plasma CVD and 2.2 W/(m·K) for amorphous carbon from the Filtered Arc method, concluding that the thermal conductivity of amorphous carbon film increased with its density [8]. The mechanical properties of amorphous carbon-nitrogen films have been studied so far [9], however, thermal properties have not been reported yet. In this paper, we discuss the thermal conductivity of amorphous carbon-nitrogen films in terms of the cluster size of graphite bonds, L_a the ratio of nitrogen to carbon, N/C and density as the properties of microstructure of amorphous carbon films. In addition, we correlate hardness, thermal conductivity and tribological properties.

2. Experimental

Amorphous carbon films were deposited on Si (100) substrates from acetylene and the mixtures of acetylene and nitrogen (C_2H_2:N_2=3:1, 2:1, 1:1, 1:2 and 1:3) as precursors by the capacitive coupling RF plasma enhanced CVD method. RF power for deposition was 500W at 13.56 MHz and deposition pressure was 1.1 Pa to 1.9 Pa depending on RF power. With Ar laser (ν= 514.5 nm), Raman spectroscopy measurements were conducted to calculate the ratio of the peak strength of the D-peak to G-peak, or I_D/I_G. Hydrogen, carbon and nitrogen content and density of films were measured by Rutherford Back Scattering/Elastic Recoil Detection Analysis (RBS/ERDA) with the incident ion, He^+ : 2.3 MeV, incident angle: 75.0°, scattering angle: 160° and recoil angle: 30°. Hardness was measured by the nanoindentation method with a Berkovich indenter [10]. Indenting force was 500μN and indenting depth was less than 1/10 of the thickness of DLC film. Thermal conductivity was measured by the 3ω method [11-13]. In Fig. 1, a block diagram of the measurement system of the 3ω method is shown. The measurement was conducted at 25℃ in vacuum. By supplying the alternating current of frequency ω (=2πf) to a sputtered Al thin film line (25 μm×3 mm×600 nm) patterned by photolithography on the DLC film, thermal conductivity was calculated from the temperature oscillation in the Al thin film line by detecting 3ω components in the AC voltage. Tribological measurements were conducted with the ball-on disk (BOD) method [14]. An alumina ball was attached to the bottom of load cell with the dead weight of 10 N. The radius of the rotating disk was 3 mm and the line speed was 10 cm/sec. The sliding tests were carried out for 600 m of sliding distance and the friction coefficient was measured. The Raman spectroscopy measurements were also carried out on the initial surface and the surface of the wear track to compare the change in properties after BOD tests .

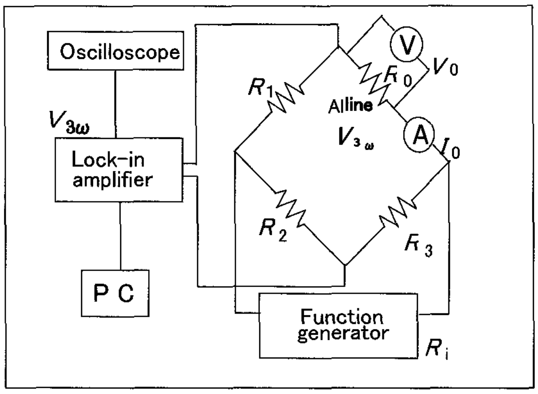

Fig.1. Block diagram of the measurement system of the 3ω method

3. Results and discussions

3.1 Characterization of DLC films

Figure 2 shows the Raman spectra of the DLC films deposited from acetylene and the mixture of acetylene and nitrogen. The intensity of D-peak (1300-1400 cm^{-1}) increased as the fraction of nitrogen in the feed gas increased. By deconvoluting the spectra into D-peak and G-peak, I_D/I_G, or the ratio of D-peak to G-peak was

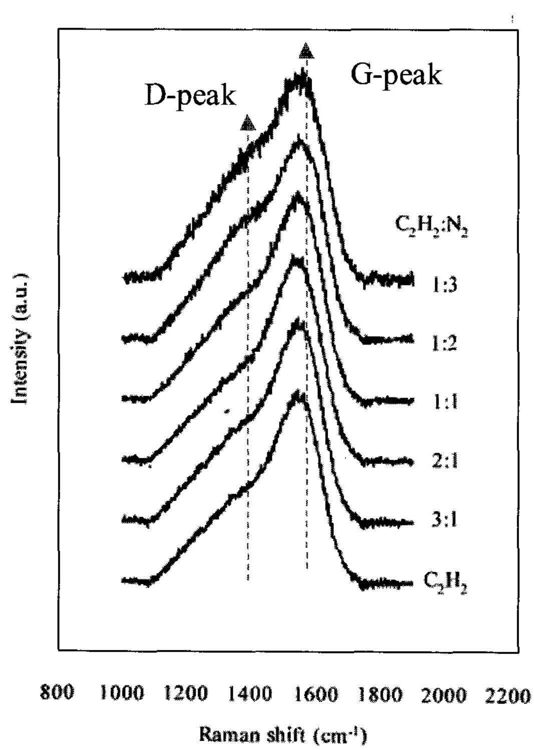

Fig.2. Raman spectra for DLC with different nitrogen fraction

In Fig. 3, I_D/I_G increased with the ratio of nitrogen to carbon, or N/C derived from the RBS/ERDA data. In this study, the content of nitrogen reached up to 25% in the amorphous carbon-nitrogen film. Since I_D/I_G is correlated with the graphite cluster size, L_a, ($I_D/I_G \propto cL_a^2$)[15], increase of I_D/I_G corresponds to the increase of L_a.

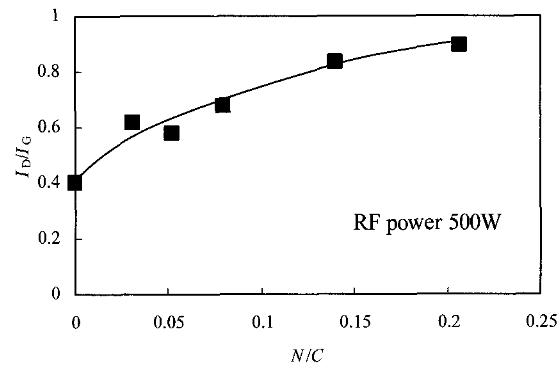

Fig. 3. Dependence of I_D/I_G on N/C

In Fig. 4, density obtained from the RBS/ERDA is shown against I_D/I_G. The density decreased with the increase of I_D/I_G, which corresponds to the increase of L_a.

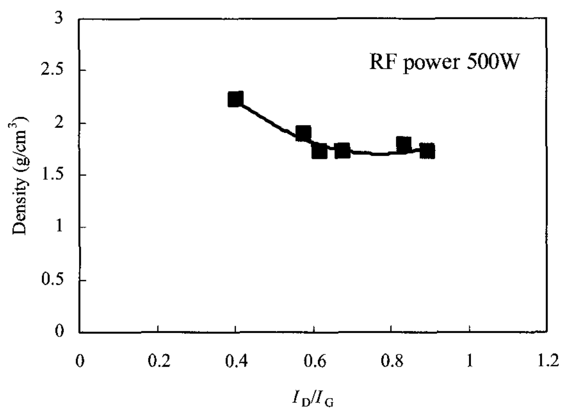

Fig. 4. Dependence of density on I_D/I_G

The bond length between carbon and nitrogen (C-N) is 0.147 nm, which is shorter than 1.53 nm between carbons (C-C). The atomic weight of nitrogen is 14 heavier than 12 of carbon. If the amount of nitrogen contained in the amorphous carbon-nitrogen film increased, the density of the film had the possibility of increase, but it did not. This is explained by the FT-IR spectra shown in Fig. 5. It can be seen with the increase of nitrogen content that the C=N bond at around 1500-1700 cm^{-1} and the C≡N bond at around 2300 cm^{-1} increased while the C-N bond at around 1100 cm^{-1} did not increase. The C≡N bond and C=N bond form dangling bonds, so the density decreased with the increase of such bonds instead of C-N bond which does not form dangling bond: namely, nitrogen bonds with three carbons. This also explains the decrease of hardness with the increase of I_D/I_G, or the increase of N/C obtained from the RBS/ERDA in Fig. 6. The increase of the content of nitrogen in the amorphous carbon-nitrogen film did not contribute to increase the bond strength, hence the hardness decreased.

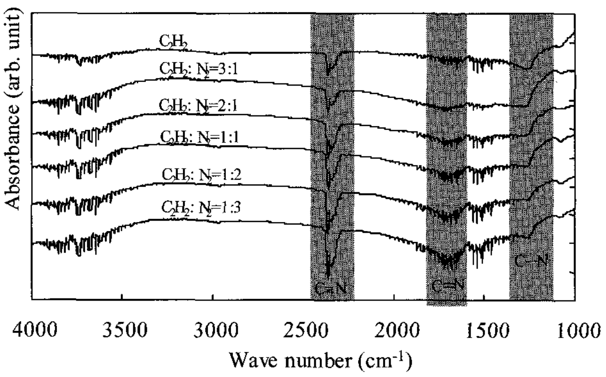

Fig. 5. FT-IR spectra of amorphous carbon-nitrogen films with different nitrogen content

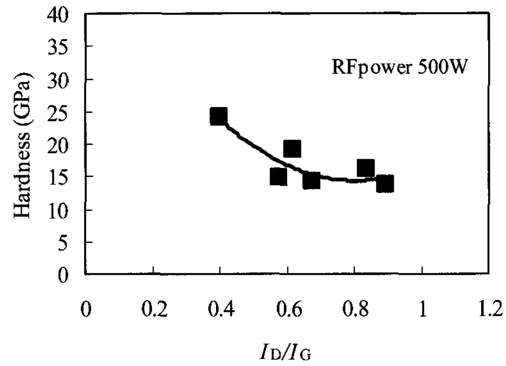

Fig. 6. Dependence of hardness on I_D/I_G

3.2 Thermal conductivity and the microstructure of amorphous carbon-nitrogen films

In Fig.7, thermal conductivity of amorphous carbon-nitrogen films decreased with the increase of I_D/I_G, which is the similar dependence of hardness. Increase of nitrogen atoms in the DLC films corresponds to the increase of L_a, hence, thermal conductivity decreased.

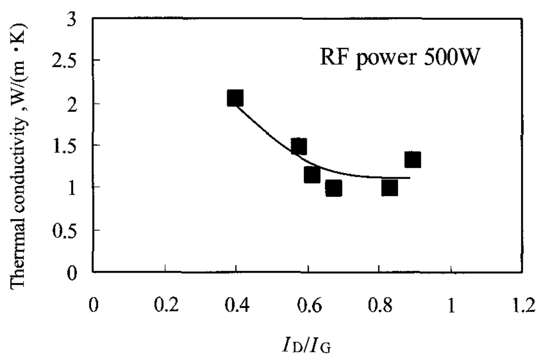

Fig. 7 Dependence of thermal conductivity on I_D/I_G

The mechanism of thermal conductivity in crystals is explained in terms of lattice vibrations and heat is transmitted by phonons. In amorphous materials, however, this does not holds because of phonetic diffraction by the disorder of atoms. In order to explain thermal conductivity in amorphous materials, Cahill *et al.* proposed a model based on the assumption of uncorrelated harmonic damping oscillators of the size of half the wave length of phonon to contain as many atoms in a oscillator [16]. He described the energy is exchanged between the oscillators and the heat is transmitted in a manner of random walk, so thermal conductivity is lower than crystalline materials and proposed the expression of thermal conductivity κ_{cp} expressed as equation (1).

$$\kappa_{CP}=\left(\frac{\pi}{6}\right)^{1/3}\kappa_B n^{2/3}\sum_{j=1}^{3}u_j\frac{T}{\theta_{Dj}}\int_0^{\theta_{Dj}/T}\frac{x^3}{(e^x-1)^2}dx \quad (1)$$

where, κ_B is Boltzmann constant, u_j is the velocity of phonon in j direction, n is the number of atoms in unit volume and θ_{Dj} is Debye temperature in j direction. According to this expression, thermal conductivity is affected by the number of atoms per unit volume *n*. Increase of I_D/I_G, or increase of L_a corresponds to the decrease of n, or decrease of density, hence thermal conductivity decreased.

3.3 Tribological properties.

In Fig. 8, dependence of coefficient of friction on sliding distance in BOD tests for is shown. The friction coefficient showed the maximum for both films at the initial sliding, then decreased to the minimum followed by the slight increasing. Amorphous carbon-nitrogen film showed higher friction coefficient than the amorphous carbon film without nitrogen. For amorphous-carbon nitrogen films, the existence of nitrogen on the wearing surface and larger L_a than the film without nitrogen might cause higher surface roughness and higher friction coefficient.

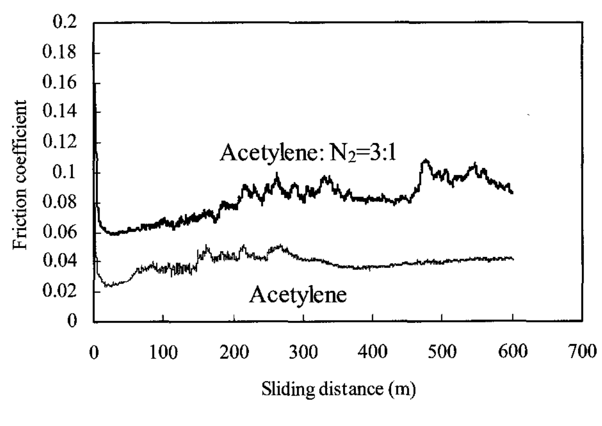

Fig. 8 Change in friction coefficient in BOD test

Rabinowicz [17] calculated the flash temperature rise at the contact point between the ball and the wearing surface in the ball-on disk test as in the equation (2). Zau applied it to calculate the flash temperature rise in BOD tests for DLC films [15] based on the assumed thermal conductivity of the DLC films.

$$\Delta T = \frac{1}{4}\frac{\mu P v}{(K_1 + K_2)a} \qquad (2)$$

$$a = \left(\frac{P}{\pi H}\right)^{1/2}$$

ΔT: Temperature rise, ℃
μ : Initial coefficient of friction
P: Normal load , N
v : Sliding speed, m/sec
K_1: Thermal conductivity of thin film, W/(m·K)
K_2: Thermal conductivity of the ball, W/(m·K)
a : Contact radius at the real contact area , μ m
H: Measured hardness of thin film , GPa

With the results of hardness, thermal conductivity and coefficient of friction above, the initial flash temperature rise was estimated and shown in Table Ⅰ. The flash temperature rise at the initial rotation was estimated as 148℃ for the feed gas of acetylene and 198℃for acetylene:N_2=3:1. Both were below the graphitization temperature of amorphous carbon films of 300-400℃.

In order to know if there is the change in properties of the amorphous carbon films tested, the Raman spectroscopy measurements were carried out on the initial surface and the center on the wear track. The results are shown in Table Ⅱ. After BOD tests, I_D/I_G for both amorphous carbon films decreased. It indicates that the properties of the films changed, although the initial temperature rise at the contact point was below graphitization temperature. This is ascribed to change in film properties mechanically, but not to change in film properties thermally. From the change in I_D/I_G or L_a for both films decreased on the wear track. The change in L_a is estimated from $I_D/I_G \propto cL_a^2$ (C=0.055 for the Ar laser of 514.5 nm), and 0.1 nm for amorphous carbon film without nitrogen and 0.06 nm for amorphous carbon-nitrogen film. This difference is ascribed to the presence of nitrogen atoms. The change in L_a was smaller for amorphous carbon-nitrogen film, because of larger atomic diameter and heavier atomic weight of nitrogen in the film than carbon.

Table Ⅰ Experimental properties to estimate the flash temperature rise at the contact point in BOD tests

Feed gas	P (N)	H, Gpa	K_1,W/(m·K)	K_2,W/(m·K)	μ initial	v, m/s	ΔT,℃
Acetylene	10	24.2	2.1	17.3	0.13	0.1	148
Acetylene:N_2=3:1	10	19.4	1.5	17.3	0.16	0.1	198

Table Ⅱ Property change in BOD tests

Feed gas	I_D/I_G on initial surface	I_D/I_G on wear track
Acetylene	0.44	0.39
Acetylene:N_2=3:1	0.54	0.52

4. Conclusion

Mechanical, thermal and tribological properties of the amorphous carbon-nitride films were investigated. Hardness, thermal conductivity decreased with the nitrogen content in the films and the decrease was correlated with the increase of the graphite cluster size L_a. The friction coefficient of amorphous carbon-nitrogen film was higher than that of the film without nitrogen because of existence of nitrogen on the wear track and the larger L_a cause the higher surface roughness and friction coefficient. The estimated flash temperature rise in BOD tests revealed that the L_a decreased by mechanical stress, not by thermal stress from. The I_D/I_G from Raman spectroscopy proved to be useful property to understand the relationship between the microstructure of amorphous carbon films and their mechanical, thermal and tribological properties.

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(Recieved January 0, 1900 ; Accepted November 26, 2008)