

Journal of Korean Institute of surface Engineering
Vol. 29, No. 5, Oct., 1996

STRUCTURE AND MACHANICAL PROPERTIES OF a-C:N MULTILAYER FILMS PREPARED BY ARC ION PLATING

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ABSTRACT

Amorphous carbon nitride (a-C:N) multilayerfilms are formed by using alternating conditions during film deposition in arc ion plating process. Because hard a-C:N films prepared with suitable negative bias voltages have large compressive stress, it is difficult to increase film thickness more than 200nm. Preparing multilayer films composed of hard layers and soft layers, we can grow thick multilayer films on Si and SKH steel substrate. The total thickness of multilayer films is more than 1 μ m. The multilayer films are several times thicker than the single layer films and almost equal in hardness and internal stress to the single layer ones. X-ray photoelectron spectroscopy(XPS) and Raman spectroscopy reveal that multilayer films equal to single layer films in structure, which is similar to the structure of DLC films.

INTRODUCTION

Carbon nitride, β -C₃N₄, which is a hypothetical material predicted by Liu and Cohen^[1], have a crystal structure similar to β -Si₃N₄. The calculated bulk modulus of this material was comparable to that of diamond. Since this theoretical study, many attempts to synthesize crystalline β -C₃N₄ have been done by various techniques such as sputtering^[2], electron resonance plasma assisted vapor deposition^[3] and laser ablation^[4]. However most of the films prepared by these techniques are amorphous. The clear difference between the experimentally obtained composition and theoretically predicted composition suggests that β -C₃N₄ may not be the most stable structure or stoichiometry for binary carbon nitride ph-

ases^[5]. Recent theoretical studies have demonstrated that two other hypothetical C₃N₄ structures, which resemble defect zinc-blende structure and rhombohedral graphite-like structure, should have a stability similar to that of β -C₃N₄^[6]. Moreover Guo et al.^[7] calculated that α -C₃N₄ was far more stable than β -C₃N₄.

We have prepared carbon nitride films by arc ion plating (AIP)^[8-10]. AIP method can achieve high deposition rate and high ionization compared to other plasma enhanced deposition processes. X-ray diffraction study showed that the films were amorphous. We prepared a-C:N films harder than TiN. However, the films had so large compressive stress that they could not grow thicker than 200nm because of peeling. The thickness

more than $1\mu\text{m}$ is necessary to use the films for cutting tool coating. In this study we report on the preparation of a-C:N multilayer films and the evaluation of the structure and mechanical properties of the films.

EXPERIMENTAL PROCEDURE

Deposition of a-C:N films was carried out in the AIP apparatus (Nissin Electric MAV-15.2N) shown in Figure 1. Si(100) wafers (size: $10\text{mm} \times 35\text{mm}$, thickness: 0.5mm) and SKH9 plates (size: $10\text{mm} \times 10\text{mm}$, thickness: 2mm) were used as substrates. The substrate holder was equipped with substrate biasing facilities. A high purity sintered graphite target (Toyo Tanso IG510, ash: 10ppm , $\phi 64\text{mm} \times 32\text{mm}$) was mounted on a cathode as a carbon source and the substrate was located in front of it. The target surface was vaporized by dc arc plasma. Carbon atoms and clusters evaporated from the target were ionized and reacted with nitrogen in the plasma and deposited onto the substrate. At the same time, melted

carbon particles with the size of micrometer order also deposited and decreased the hardness of the growing film. Avoiding carbon macroparticles, we inserted a shielding plate between the target and the substrate. Arc plasma was generated at 60A and the total pressure was fixed at 1 or 5Pa . N_2 was used as a reactant gas for film preparation. Varying the ion bombardment effect on the growing film, we applied the negative bias voltage of $0 \sim -1000\text{V}(\text{de})$ to the substrate.

Multilayer films were formed by stacking four kinds of film prepared at different film conditions (Film-1, -2, -3 and -4). The preparation conditions of Films 1-4 and the structure of Multilayer A-D are given in Table 1.

The substrate temperature was kept at $20 \sim 100^\circ\text{C}$ by water-cooling system.

The structure of the as-deposited films was characterized by XPS and Raman spectroscopy. We carried out the XPS analysis using Shimadzu-Kratos AXIS. $\text{MgK}\alpha$ radiation (1253.6eV) was used. We estimated both chemical composition and bonding states of the films. Raman spectroscopy system (Jasco NR-1800) with Ar laser at 514.5nm as an excitation source was used to investigate the carbon networks in the films.

In order to evaluate the mechanical properties of the films, analyses of hardness, internal stress and adhesion of the films were carried out. The microhardness of the films was measured with a dynamic ultra micro-hardness tester (Shimadzu DUH-200). A trigonal pyramidal diamond indenter with an edge angle of 115° was used at the load of 0.50gf . Recording load and displacement relation

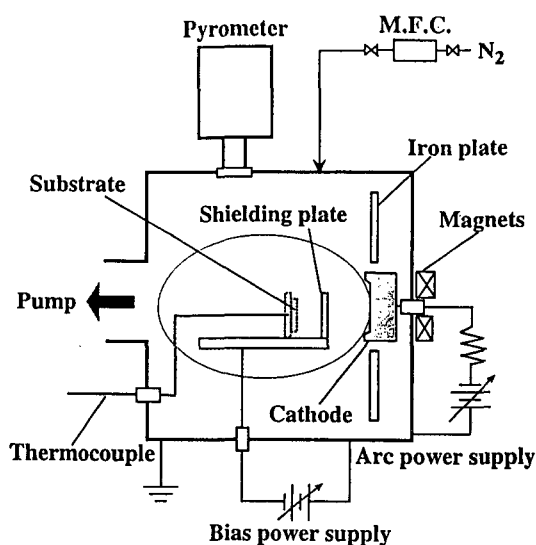


Fig. 1 Schematic diagram of the AIP apparatus.

Table 1 Preparation conditions of single layer, Films 1-4 and structure of Multilayers A-D.

Single layer film	Condition	Film-1	Film-2	Film-3	Film-4
	Total pressure(Pa)	1	5	5	1
	Bias voltage(V)	-300	0	-300	-1000
	Film thickness(nm)	100	400	100	50
Multilayer film	Film-1	Film-1	Film-1	Film-1	Film-4
	Film-2	Film-3	Film-2	Film-2	
	Film-1	Film-1	Film-1	Film-1	
	Film-2	Film-3	Film-2	Film-2	
	Film-1	Film-1	Film-1	Film-1	
	Si(100)	Si(100)	SKH9	SKH9	
	Multilayer-A	Multilayer-B	Multilayer-C	Multilayer-D	

during both loading and unloading, we obtain information about both elastic and plastic deformation of a sample. The hardness corresponding to the plastic deformation called "permanent depth hardness" is used as film hardness in this paper. Knoop microhardness was also obtained for thick films at the load of 10g.

When a film deposits onto a thin substrate, the internal stress in the film causes a spherical deformation of the substrate. From the sign of the curvature we know the kind of residual stress. Its magnitude is calculated from the following equation^[11]:

$$\delta = \frac{E_s}{6(1-\nu_s)} \frac{t_s}{t_f} \left(\frac{1}{R_f} - \frac{1}{R_s} \right), \tag{1}$$

where R_s and R_f are the radii of curvature of a naked substrate and a film-coated substrate, respectively. E_s and ν_s are Young modulus and Poisson's ratio for the substrate. t_s is the substrate thickness and t_f (with $t_f \ll t_s$) is the film thickness. The value of 1.8×10^4 Pa was for $E_s/(1-\nu_s)$ of biaxial modulus of the (100)-oriented Si substrate. The film thickness and the curvatures were determined with a stylus instrument (Mitutoyo SV-600).

The adhesion between a substrate and a film was investigated with a scratch tester(Resca CSR-02).

RESULT AND DISCUSSION

The structure and mechanical properties of the films depended markedly on preparation conditions. Figure 2 shows the variation of the permanent depth hardness and the compressive stress of the a-C:N films prepared at 1Pa as a function of bias voltage. The film hardness increases with bias voltage up to -300V. The stress increased up to -150V similarly. Excessive bias makes the hardness and the stress decrease gradually. The hardness and the stress can be controlled by changing the incoming energy of ions. Rossi et al.^[12] also found the optimum bias voltage for hardening the films and explained that the excessive ion bombardment induced graphitization of the films. The sign of the curvature indicates that the internal stress is compressive

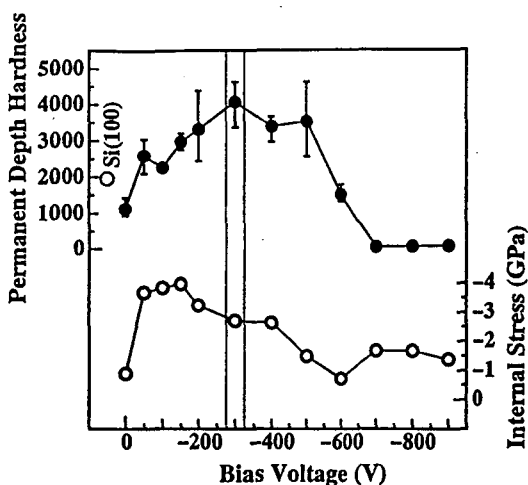


Fig. 2 Relations between the permanent depth hardness and the internal stress in the films prepared at 1 Pa and bias voltage.

sive in nature. The films prepared at 1Pa contain high compressive stresses of the order of GPa. It gave rise to peeling after a period of time(a few day~a few month) when the thickness of the film was beyond a critical one of 200nm. The maximum hardness obtained at a bias voltage of -300V was about twice as high as the hardness of Si. For reference, Knoop Hardness of Si is 1400. At this condition the film had a large stress(3GPa) and could not grow thicker than 200nm.

Table 2 shows the stress and hardness of Film-1, -2 and -3 and Multilayer-A, -B, -C and -D. The stress in the films prepared at 5 Pa is relatively low. Film-3 has only 37MPa but its the hardness is low. Therefore we decided that Film-2 and -3 were used as a interlayer to reduce stress. Multilayer-A has similar stress and hardness to Film-1 in spite of the thickness of 1.1 μ m. Hence the film stress can be relaxed by interlayer(Film-2) without decrease in hardness. To insert interlayer which has small stress is effective to increase film thickness. On the other hand, the stress and the hardness of Multilayer-B is very low(merely 0.87GPa and 100). Though the top layer of multilayer films is all the same, hardness is very different. The reason is as follows. The hardness of thin film is influenced by the hardness of substrate when the film is very thin. Despite of a hard layer (Film-1) at the surface, hardness of Multilayer-B is largely affected by the hardness of interlayer(Film-3) and becomes low. From this, interlayers must have suitable hardness (at least hardness of Film-2) to keep multilayer hard.

Multilayer-A and -B maintained thickness

Table 2 Mechanical properties of the single layer and multilayer

	Film-1	Film-2	Film-3	Multilayer-A	Multilayer-B	Multilayer-C	Multilayer-D
Stress (GPa)	2.72	1.26	0.04	2.94	0.87	-	-
Permanent Depth Hardness	4062	886	255	4096	866	-	4418
Knoop Hardness	-	-	-	3223	-	-	3276
Thickness (nm)	150	150	150	1100	1100	peel off	1100
Substrate	Si(100)	Si(100)	Si(100)	Si(100)	Si(100)	SKH9	SKH9

more than $1\mu\text{m}$, whereas Multilayer-C peeled off instantly. Peeling of the film from the substrate is due to the force produced at the Si/film interface by the large internal stress. It shows that the Si substrate has superior adherence to the a-C:N film to the SKH substrate. This is due to the difference in bonding state and strength at interface between Si-C and Fe-C. From our study, to increase the adhesion between the film and the substrate bias voltage is necessary to apply to the substrate. Then it becomes possible to prepare an a-C:N multilayer on a SKH substrate by means of pre-coating of Film-4 on the SKH substrate. Multilayer-D enables the thick hard coating on the SKH substrate.

Raman spectra of Film-1, -2 and -3 are shown in Figure 3. Two Raman active modes are observed at approximately $1580\text{-}1530\text{cm}^{-1}$ (G band) and 1360cm^{-1} (D band). The G band arises from a symmetric vibration observed in graphite and is known to broaden and shift to lower wavenumbers for disordered sp^2 bonded carbon atoms^[13]. The D

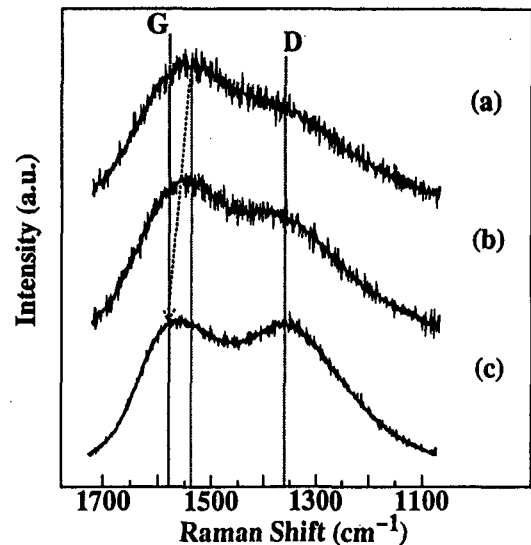


Fig. 3 Raman spectra of Film-1, Film-2 and Film-3; G: Graphitic band, D: Disorder band; (a) Film-1 (b) Film-2 and (c) Film-3.

band is attributed to a disordered mode which becomes Raman active as a result of the lack of long-range order in the sp^2 domains^[14] and the bond-angle disorder in the graphitic layers induced by the linking with sp^3 carbon atoms^[15]. Figure 3 shows that the structure of Film-1 and -2 is similar to that

of a typical DLC film, which consists of sp^2 and sp^3 carbon domains. It also shows that the G band of Film-1 shift to lower frequency than that of Film-2 and Film-2 shifted lower than Film-3. Generally, the G band of crystalline graphite and graphitic carbon composed of sp^2 carbon atoms only is appear at $1580-1575\text{cm}^{-1}$ ^[14]. The ratio of sp^2 domains to sp^3 dormains in Film-3 is larger than that in Film-1. Therefore Film-3 is softer than Film-1. This result corresponds well to the result in table1. Intensity of the D band becomes strong from Film-1 to Film-3.

Figure 4 shows the comparison of the Raman spectra between Film-1 and Multilayer-A and -B. Though the surface layer(Film-1) is all the same for these three films, the spectra are different. The spectrum of Multilayer-A is similar to that of Film-1, whereas,

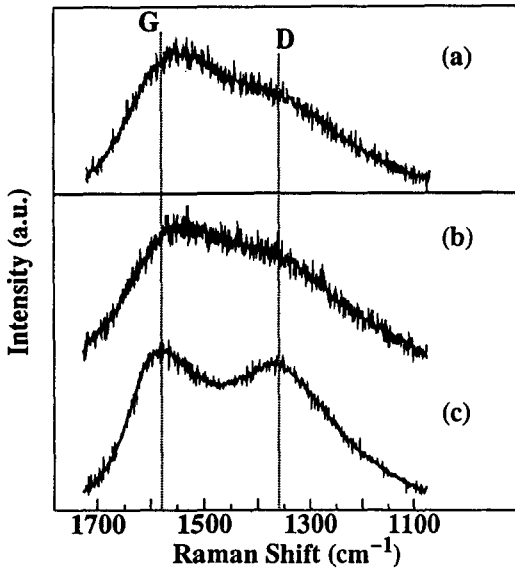


Fig. 4 Raman spectra of Film-1 and Multilayer-A and -B; G: Graphitic band and D: Disorder band. (a): Film-1, (b): Multilayer-A and (c): Multilayer-B.

the spectrum of Multilayer-B is similar rather to film-3(Figure 3) because the interlayer is Film-3, When the surface layer is thin, the surface structure (Film-1) is affected by the underlayer structure(Film-2 or -3) and this result agrees with hardness data.

Three films of Film-1 and Multilayer-A and -B were analyzed with XPS. Wide-scan spectra for these films revealed dominant C1s and N1s related peaks and a small O 1s peak. Detailed N 1s spectra for these films are shown in Figure 5. From our structural analysis, N atoms in the films mainly consist of two different N binding configurations ; one is N located in the aromatic rings in sp^2 -C (pyridine-like) and the other is N linked car

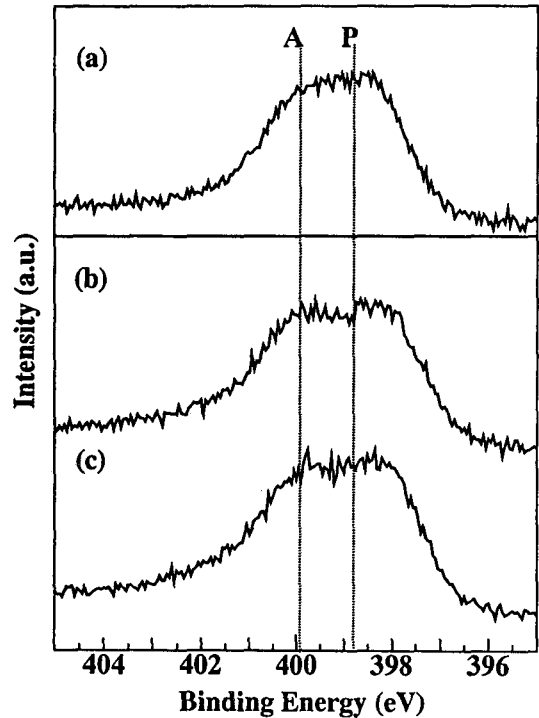


Fig. 5 XPS N1s spectra of Film-1 and Multilayer-A and -B; A: aniline-like, P: pyridine-like, (a): Film-1, (b): Multilayer-A and (c): Multilayer-B.

bon atoms constituting aromatic rings in graphitic(aniline-like)^[10]. We assign the peak at 399.92eV to pyridine-like N bonding and that at 398.8 to aniline-like N. No significant difference was found in binding energies between analyzed samples. The N/C ratio in the films was 0.3.

CONCLUSIONS

The a-C:N film which had maximum hardness which was about two times larger than hardness of Si was prepared by biasing substrates at -300V. By using this film as a top layer and inserting single layers which had small stress, we prepared a-C:N multilayer-A, -B, -C and -D, in order to reduce internal stress in the films and increase film thickness. Multilayer-A, -B and -D kept thickness more than 1 μm . Their mechanical properties and structure are similar to the hard single layer film. The film stress can be relaxed by inserting interlayers without decrease in hardness. By this technique we can grow thick hard films. Furthermore, Multilayer-D showed that preparing of the a-C:N multilayer film on the steel substrate was possible by means of carrying out pre-coating of the film deposited at high bias voltage. a-C:N multilayer films can be applied to tool coating by this present technique.

ACKNOWLEDGMENT

We wish to thank Research Center for Advanced Energy Conversion, Nagoya University for Raman spectroscopy.

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