Adhesive strength of DLC films prepared by ionization deposition

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Abstract

Diamond-like carbon (DLC) films are considered to be promising to develop extensively for practical applications owing to their good properties. Improvement of adhesive strength of DLC films to substrates is required to enhance their suitability and reliability. The purpose of this study is to investigate the influence of the preparation conditions of DLC films on the adhesion. DLC films were prepared from benzene gas by the ionization deposition method. Three different anode voltages of 50, 75 and 100 V were applied during deposition. The substrates used were WC-Co, austenitic 18Cr-8Ni stainless steel and Al-Mg alloy. The adhesive strength was measured by a tensile pull-off tester. We examined and discussed the adhesion of DLC films from the viewpoints of the internal stress in the films and the species in plasma during deposition. The main results obtained from this study are as follows: (1) The adhesive strength of DLC films to substrates can be enhanced by controlling the anode voltage. (2) For thicker films, the adhesive strength of DLC films increases with increasing internal stress. (3) At the anode voltage of 50 V, higher adhesive strength of DLC films can be attained than that prepared at other anode voltages, but the internal stress is much higher. It is presumed that DLC films prepared at an anode voltage of 50 V have large amounts of C_2, CH and C_5H_5 fragments against hydrogen in deposited films.

1 Introduction

Diamond-like carbon (DLC) films have powerful attraction due to good properties such as high hardness [1], low friction coefficient [2, 3] and excellent corrosion-resistance [4-7]. DLC films are, therefore, expected in coating field to progress among ceramic coatings by physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods. Since the adhesion is considered to play an important role to achieve limitless reliability, it is necessary to enhance the adhesion of films to substrates. However, little investigation has been reported on the adhesion of DLC films to metal substrates in detail [8].

In this paper, DLC films are prepared by the ionization deposition method which has some advantages compared to other coating methods for industrial use. To examine the adhesive strength of DLC films to substrates, DLC films were deposited on three kinds of metal substrates (WC-Co, austenitic 18Cr-8Ni stainless steel and Al-Mg alloy). The adhesion of the film was evaluated by pull-off tests. The internal stress in films was examined by the Stoney method [9], in which the film was deposited on a strip of Si (100) wafer. The species in plasma during deposition of DLC film were monitored by optical emission spectroscopy (OES). The effect of the deposition process of DLC films on the adhesion was discussed together with the result of the evaluated internal stress of films.

2 Experimental procedures

2.1 Preparation of DLC films by the ionization deposition method

DLC films were prepared by the ionization deposition method. The components in the chamber of apparatus are a filament, an anode and a reflector electrode. Electrons emitted from the hot filament are accelerated by the anode and reflected by the reflector electrode. Electrons move back and forth in the electrode system and collide with source molecules. Thus an ionization of the precursor molecules is achieved, and ionized species are extracted and accelerated towards the substrates by a negative bias voltage. Further details about the apparatus have already been described in elsewhere [1]. To investigate the effects of the anode voltage on the adhesion of DLC films to substrates, the anode voltage was changed at 50, 75 and 100 V.

The substrates used were WC-Co, austenitic stainless steel (JIS std. SUS304) and Al-Mg alloy (JIS std. 5052). The surfaces of substrates were mirror-polished and were ultrasonically cleaned in an acetone bath and a methanol bath. Being set into the chamber, the substrates were sputter-cleaned by Ar ions under the Ar gas pressure of 2.7×10^{-1} Pa for 1.2 ks, followed by switching to the deposition of DLC films by introducing benzene (C_6H_6) as source gas. Table 1 lists the detail of deposition conditions.

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Table 1. Preparation conditions of DLC films by the ionization deposition method.

Source gas	Benzene
Benzene flow rate, F / mol•s^{-1}	7.5×10^{-6}
Working pressure, P / Pa	2.7×10^{-1}
Bias voltage, V_b / kV	- 1.0
Anode voltage, V_a / V	50, 75, 100
Reflector voltage, V_c / V	20
Filament current, I_f / A	30
Distance between substrate and anode, D / mm	220
Revolution number of sub., N / rpm*	5
Film thickness, d / nm	79 - 993

* Revolutions per minute

2.2 Adhesion tests

The adhesive strength between the film and the substrate was measured by the tensile pull-off test using a Sebastian V Adherence Tester (Quad Group) [10]. An aluminum stud (2.7 mm in diameter) pre-coated with epoxy was bonded tightly and perpendicularly to the surface of the film. To make a stable glue, this arrangement was heated in a furnace at 423 K for 1 h. The tensile pull-off test was performed by pulling off the stud and by measuring the force required to remove the film from the substrate.

2.3 Evaluation of internal stress and species in plasma during deposition

The internal stress in DLC films was evaluated by the Stoney method [10], in which the DLC film was coated on a strip of Si (100) wafer (thickness: 0.5 mm) at the area of 5 mm ×50 mm. The displacement of the bending free edge caused by the internal stress by the film deposition was measured.

The species in plasma during deposition were monitored by using a photonic multi-channel analyzer system PMA-11 (Hamamatsu Photonics) which was equipped with a charged coupled device (CCD). The measurement was carried out at wavelength between 300 and 800 nm.

3 Results and discussion

Adhesive strength of DLC films prepared on three kinds of substrates under various anode voltages is shown in fig. 1 as a function of the film thickness. All

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values exhibit high adhesive strength and are 70 MPa or above.

For WC-Co substrates, the adhesive strength seems to scatter in the range from 80 to 100 MPa but tends to increase with decreasing film thickness, irrespective of the anode voltage. After the adhesion test, each surface of the specimens was observed and found to remain being covered with DLC films, indicating that the stud had not been removed from the interface between the film and substrate.

For SUS304 and Al-Mg alloy substrates, on the contrary, the adhesive strength is seen to increase with increasing film thickness in both cases of the anode voltage at 50 and 75 V. While, at the anode voltage of 100 V, the thinner the film thickness becomes, the higher the adhesive strength is.

In the case of thickness above 300 nm coated on these substrates, the adhesive strength of DLC films tends to be improved when the anode voltage was applied at 50 V. The findings above suggest that the adhesion of DLC films to substrates can be enhanced by controlling the anode voltage.

We also examine the internal stress in the films. The stress σ_s in the DLC films of thickness d was calculated from the Stoney's equation

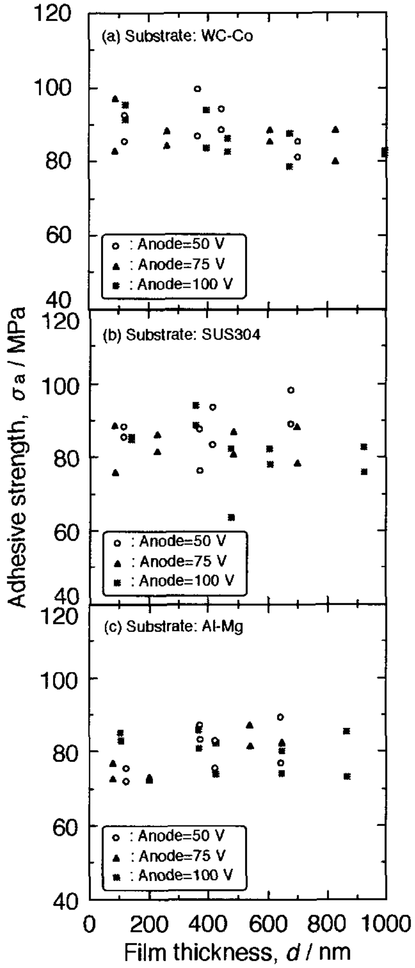

Figure 1: Adhesive strength of DLC films prepared at various anode voltages. The substrates used were (a) WC-Co, (b) SUS304 and (c) Al-Mg alloy.

$$\sigma_s = \frac{E_s \cdot D^2}{3(1-\nu_s)d \cdot l^2} \cdot \delta, \qquad (1)$$

where E_s, σ_s, D (» d), l and δ are Young's modulus, Poisson's ratio, thickness, length of the Si substrate and the displacement of the bending free edge of the Si substrate, respectively. When the internal stress becomes compressive, the value of σ_s in equation

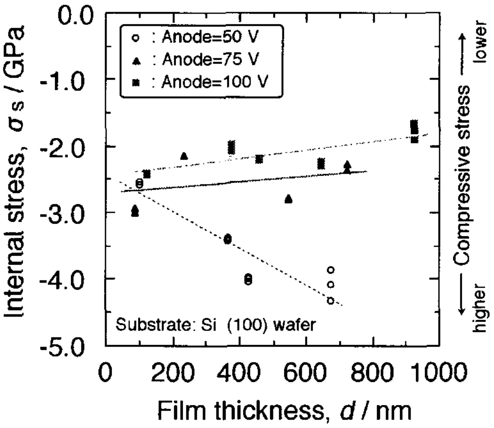

Figure 2: Influence of the anode voltage on the internal stress in DLC films.

(1) is negative. The value of $E_s/(1 - \sigma_s)$ adopted here is 181 GPa [11]. Fig. 2 shows the influence of the anode voltage on the internal stress in DLC films as a function of the film thickness. The internal stress of films deposited under the anode voltage of 50 V increases from about 2.5 GPa to the maximum value of about 4.1 GPa as the thickness changes from about 100 to 700 nm. In contrast with the case of 50 V, the internal stress of both cases of 75 and 100 V are inversely proportional to film thickness and is smaller than that obtained for the case of 50 V. The minimum value is about 1.7 GPa in the case of the anode voltage at 100V. These results indicate that DLC films prepared at the anode voltage of 100 V can repress the internal stress. The thermal stress σ_T of DLC films deposited on the strip of Si (100) wafer was estimated by the equation

$$\sigma_T = \frac{E_F}{1 - \nu_F}(\alpha_F - \alpha_S) \cdot \Delta T \quad , \qquad (2)$$

where E_F and α_F are Young's modulus, Poisson's ratio of the film, respectively. The symbols α_F and α_S are the thermal expansion coefficients of the film and substrate, respectively. The value of $E_F/(1 - \alpha_F)$ used is 174 GPa [12]. ΔT is the temperature difference between film deposition and the displacement measurement after deposition.

The change in temperature near the substrates during Ar ions bombardment and deposition of DLC is shown in fig. 3. In the figure, the deposition temperature for various anode voltages denotes the maximum temperature of each case and is used as the value of ΔT. The values calculated from eq. (2) for the thermal stress of DLC films deposited at the anode voltage of 50, 75 and 100 V were -29.8, -32.1 and -35.0 MPa, respectively. As these values are smaller by two orders of magnitude compared with the experimental values, the contribution of thermal stress to the internal stress in DLC films is considered to be negligible.

The dependence of the adhesive strength on the internal stress is shown in fig. 4 for four different thickness of DLC films. For thicker films than 100 nm, the adhesive strength reduces with decreasing internal stress, suggesting that the adhesion may be improved by the higher compressive internal stress in the films.

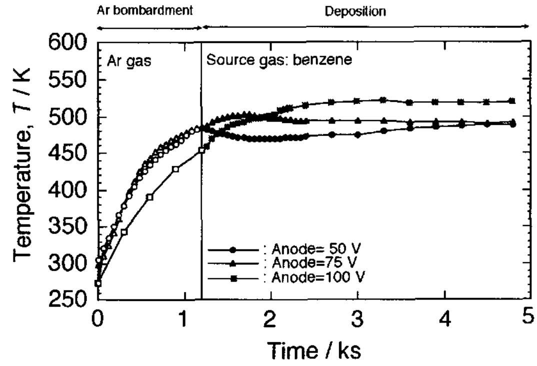

Figure 3: Change in temperature during the Ar bombardment and deposition. For the deposition, the applied anode voltage was 50, 75 and 100 V.

To investigate the effects of the anode voltage on the film p roperties, the benzene

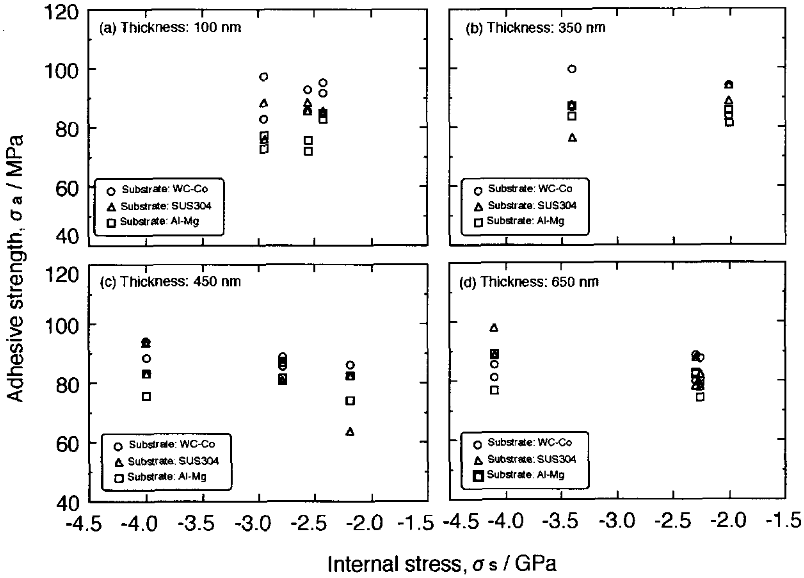

Figure 4: The adhesive strength of DLC films as a function of the internal stress in the films. The film thickness is (a) 100 nm, (b) 350 nm, (3) 450 nm and (d) 650 nm.

plasma characterization was carried out using optical emission spectroscopy (OES). Fig. 5 shows the optical emission spectra in benzene plasma by the ionization deposition. The peak spectra are identified as CH (314 nm), C_5H_5 (337.8 nm), C_2 (358.7 nm), CH^+ (380.6 nm), CH (390 nm), H_δ (410.1 nm), CH radical (430 nm), C_2 (467.8 nm), H_β (486.1 nm), $C_4H_2^+$ (506.7 nm), $C_4H_2^+$ (533 nm) and H_α (656.3 nm) [13, 14]. The peak intensity for the cases of anode voltage at 75 (fig. 5 (b)) and 100 V (fig. 5 (c)) is higher than that for the case of anode voltage at 50 V (fig. 5 (a)). Especially, CH radical 430.9 nm, H_δ 410.1 nm, H_β 486.1 nm and H_α 656.3 nm lines increase remarkably. The line of C_5H_5 (337.8 nm) which is bigger fragment for the anode voltage at 50 and 75V is on the decline for the anode voltage at 100 V. This means that benzene source gas is more completely decomposed under the anode voltage of 100 V. K. -R. Lee *et al.* [15] reported that the stress in DLC films prepared from benzene gas was inversely proportional to hydrogen concentration in the films. In this study, for both cases of anode voltage at 75 and 100 V, it is presumed that DLC films possess lower internal stress due to more hydrogen in the film in comparison with the case of anode voltage at 50 V. Contrary to the trend of the internal stress, the adhesion of DLC films prepared at the anode voltage of 50 V is better. We consider that the DLC films may be composed of many fragments, *i. e.* C_5H_5, C_2 and CH, against hydrogen content and their network structure may be more complete. At the anode voltage of 100 V, since many amounts of hydrogen may be included in deposited films, the adhesion of DLC film is poor.

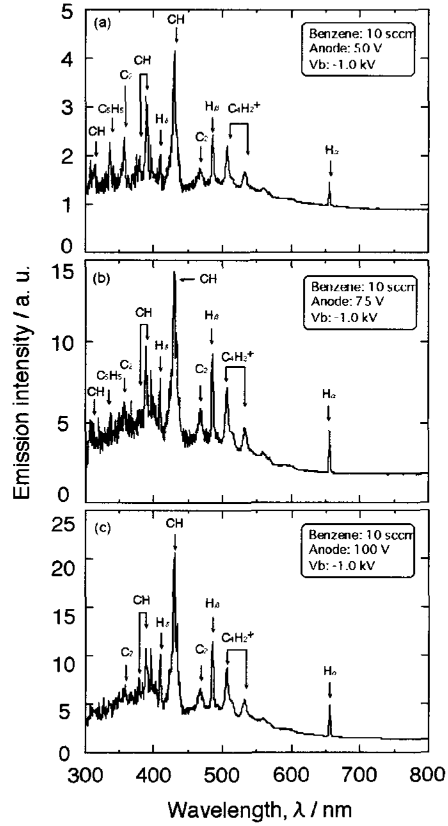

Figure 5: Optical emission spectra in benzene plasma by the ionization deposition method. The anode voltage was applied at (a) 50 V, (b) 75 V and (c) 100 V.

4 Conclusions

DLC films were prepared by the ionization deposition method. We examined the effect of the anode voltage on the adhesion, internal stress and species in plasma during deposition. The adhesive strength of DLC films to substrates is found to be influenced by the anode voltage. Anode voltage affects the adhesive strength of DLC films on the film thickness, showing the inverse relationship between the internal stress and the film thickness. For thicker films, the adhesive strength of DLC films increases with increasing internal stress. The adhesion of DLC films prepared at the anode voltage of 50 V is better than that prepared at other anode voltages but the internal stress is much higher. We consider that benzene source gas is more completely decomposed under the anode voltage of 100 V. It is presumed that since DLC films prepared at the anode voltage of 50 V have many amounts of C_2 and CH fragments against hydrogen in deposited films, their network structure might be more complete.

Acknowledgments

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