

Properties of Diamond-like Carbon Films Deposited on Polymer Substrates by Plasma Source Ion Implantation

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Abstract – Diamond-like carbon (DLC) films were prepared on polymer substrates and silicon wafer by a plasma source ion implantation (PSII) with superposed negative pulse. Glass-reinforced epoxy resin, silicon rubber were used as polymer substrates. Oxygen, argon, hydrogen and methane plasmas were used as the pretreatments for the substrates. A pulse voltage of -10 kV, 100 Hz, 100 μ s was applied to metal substrate holder. Acetylene gases were used as working gases for plasma for deposition of DLC films. A negative DC voltage of -2.0 kV and a negative pulse voltage of -10 kV, 100 Hz, 100 s were superposed and applied to the metal substrate holder. The surface morphology of the films and the film thickness were observed by scanning electron microscopy (SEM). The films structure was characterized by Raman spectroscopy. The pretreated surface of the polymer substrates was characterized by X-ray photoelectron spectroscopy (XPS). Adhesion of the films was estimated by a pull-off test and a scratch test. Furthermore, a ball-on-disc test and a reciprocal sliding test were employed to obtain information about friction properties and sliding wear resistance of the DLC films. The DLC films were deposited all substrates, and there was no clear dependence on ID/IG ratio of Raman spectroscopy. The surface of the DLC films was very smooth. Adhesive strength was improved by the oxygen implantation as pretreatment. Low friction coefficients around 0.2–0.3 were derived for all substrates.

1. Introduction

Diamond-like carbon (DLC) coatings exhibit a number of attractive mechanical and tribological properties such as low friction, high wear resistance, and high hardness. Much of work has been carried out on DLC films by a variety of methods, including physical vapor deposition (PVD) [1, 2] and chemical vapor deposition (CVD) [3, 4].

Ion implantation has been shown to be an effective technique for improving the wear, corrosion and fatigue properties of materials. It is easy to control energy of ions but difficult to use for three dimensional substrate and large area, because of line-of-sight process of ion beams. On the other hand, as the plasma process is a non-line-of-sight process, it is possible to treat over the entire surface of three dimensional substrate exposed to plasma. As the energy of ions in plasma

is lower than that of ion beam, the depth of treatment by plasma is restricted to top surface or thermal diffusion is necessary to treat deeper inside of materials.

Conrad et al. [5, 6] and Tendys et al. [7] developed plasma source ion implantation (PSII) and plasma immersion ion implantation (PIII). In these processes, the components to be treated are immersed in plasma and biased to a high negative voltage. This method has several advantages over conventional ion implantation, such as low cost, large area, multiple targets and non-line-of-sight process. Furthermore PSII has possibility to give high adhesion and good surface coverage for DLC films [8–10]. In the PSII, a high voltage negative pulse was applied to the substrate to extract the ions from surrounding plasma and implant into the substrate.

In this study, the DLC films were deposited on polymer and silicon substrates by the PSII method developed in our laboratory [11]. Plasma was generated by the superposed pulse voltage applied to the substrates without an additional plasma source. The surface of the pretreated polymer substrates by Oxygen (O_2), argon (Ar), hydrogen (H_2) and methane (CH_4) PSII were investigated by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The chemical structure of the DLC films was characterized by a Raman spectroscopy. The adhesion of the films was evaluated by a pull-off test. Wear property was estimated by a ball-on disc test and a reciprocal sliding test.

2. Experimental

Fig. 1 shows schematically the experimental equipment [11]. The vacuum chamber is made up of 304 stainless steel, 50 cm in diameter and 65 cm in length. The base pressure of $7 \cdot 10^{-5}$ Pa in the PSII chamber was obtained by a turbo molecular vacuum pumping system. The two types of power supplies were used in this study. The specification of the high voltage generator was maximum voltage of -25 kV, maximum current of 10 A, repetition of 10 Hz – 5 kHz and maximum duration of 2 % of a pulse period. And the specification of the low voltage generator was maximum voltage of -5 kV, maximum cur-

rent of 10 A and repetition of DC – 1 kHz. These two generators were connected in series to make superposed pulses. The implantation voltage and current was monitored using a voltage divider and a current transformer, which were connected to a digital oscilloscope. In this method, plasma was generated by the application of superposed bias voltage of DC and pulse to substrate without additional plasma source. Glass-reinforced epoxy resin, silicon rubber, and silicon wafer Si (100) were used as the substrates. O₂, Ar, H₂ and CH₄ plasmas were used for pretreatments of the substrates. Acetylene (C₂H₂) plasma was used for the deposition of DLC films. The pulse condition of –10 kV with the pulse frequency of 100 Hz and the pulse width of 100 μs was used for the pretreatment of the substrate and the pulse condition of –10 kV with the pulse frequency of 100 Hz and the pulse width of 100 s superposed with –2 kV DC was used for the deposition of DLC films. The vacuum pressure during the process was around 2 Pa.

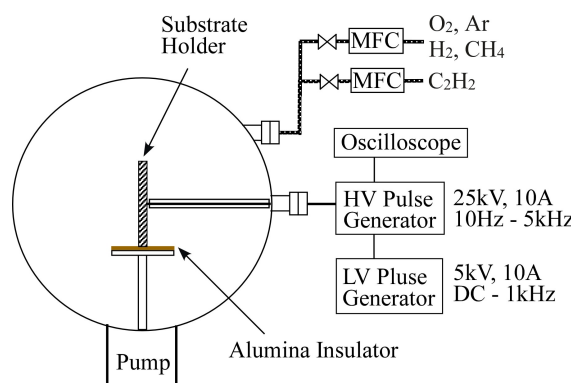


Fig. 1. Schematic diagram of the PSII system

The surface morphology and the thickness of the films were observed by SEM. The chemical structure and the composition of the pretreated surface were characterized by XPS under MgK_α X-ray irradiation. The film structure was characterized by Raman spectrometer at an excitation wavelength of 514 nm. Adhesion strength between the film and the substrate was estimated by a pull-off test. Furthermore, a ball-on-disc test was employed to obtain information about the friction coefficient and wear resistance of the films deposited on the epoxy resin. Six millimeter in diameter tungsten carbide ball was used as the ball. The sliding speed was 100 mm/sec and the normal load was 2 N. For silicon rubber, a reciprocal sliding test was employed with a 10 mm in diameter stainless steel ball at a sliding speed of 1 mm/s and the normal load of 0.245 N.

3. Results and discussion

The surface morphology of the pretreated substrates was observed by SEM. Fig. 2, a and b show the O₂ plasma treated and Ar plasma treated surface of epoxy resin. In the case of PSII with O₂, the surfa-

ce became very rough and fine granular structure was observed. On the other hand, in the case of PSII with Ar and other gases, the surface was not changed.

The surface structure of pretreated substrates was investigated by XPS. Fig. 3 shows C1s and O1s spectra of untreated and O implanted epoxy resin substrates. C1s photoelectron consists of two bonding states of major C-C bond and minor -C-O- and epoxy bonds [12]. And the peak of O1s spectrum was assigned to -C-O- bond [12]. For the O implanted substrate, the main peak of C1s photoelectron at a binding energy of 285.6 eV is attributed to C-C bond and photoelectrons from -C-O- and epoxy bonds were observed as weak shoulder [12]. And the peak of O1s photoelectron shifted to lower binding energy side and the major bonding states were assigned to C=O and epoxy bonds [12]. The composition ratios O/C derived from the peak area of C1s and O1s photoelectrons for untreated and O implanted epoxy resin were 0.22 and 0.35, respectively. The enrichment of oxygen content by O implantation was observed.

The surface of the DLC films deposited on Si wafer was very smooth and none of the special structure, such as grain, was observed by SEM. And the average roughness Ra estimated by AFM was 0.2 nm.

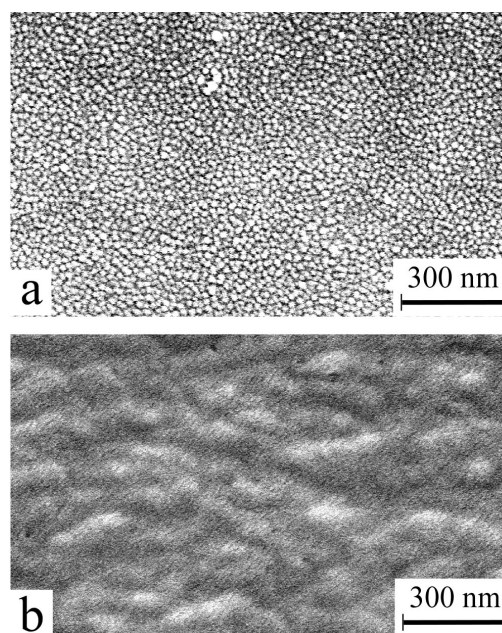


Fig. 2. SEM photographs of the surface of epoxy resin pretreated by (a) O₂ and (b) Ar plasma

In the PSII method employed in this study, plasma was generated by the application of the DC and pulse voltages to substrate holder. At the same time positive ions are extracted from the plasma and implanted into the substrates by the applied negative high voltage. Then the electrical conductivity of substrates was important. Fig. 4 shows the Raman spectra of the films deposited on epoxy resin substrate. The spectral profile is fitted by two Gaussian profiles

centered at 1378 cm^{-1} corresponding to the D-line and centered at 1551 cm^{-1} corresponding to the G-line [13, 14]. The integrated intensity ratio I_D/I_G is correlated to the sp^3/sp^2 bonding ratio and the graphite particle size [15]. The I_D/I_G ratio of 1.02 was derived for epoxy resin substrate. This value was common value for DLC films [16]. There was no clear difference on the I_D/I_G ratio for other substrates.

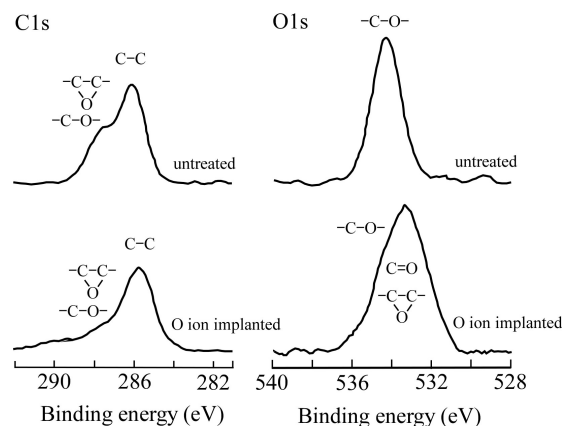


Fig. 3. C1s and O1s XPS spectra of untreated and O ion implanted epoxy resin

The adhesion between the DLC film and the substrate was estimated by a pull-off test. Epoxy glue was used to join the pull-stud to the film. Adhesion strength of 217 kgcm^{-2} for untreated epoxy resin and that of 348 kgcm^{-2} for O implanted epoxy resin were derived.

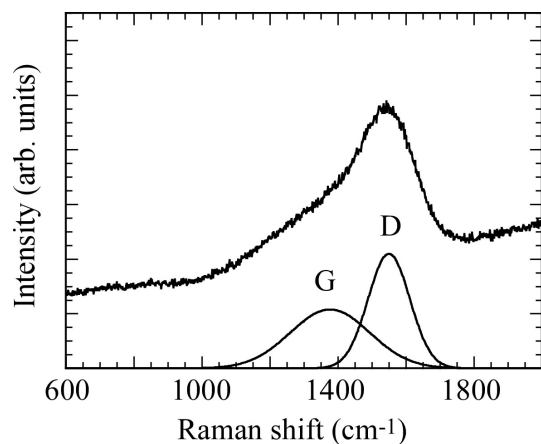


Fig. 4. Raman spectrum of DLC film prepared on epoxy resin substrate

From SEM observation and XPS results, it is concluded that the surface becomes rough by the treatments of PSII with oxygen plasma by a chemical and physical etching. These chemically and physically modified surface result in the high adhesion.

Tribological property of DLC films is one of the important properties of DLC films. Fig. 5 shows the friction coefficient of DLC films deposited on epoxy resin substrate estimated by a ball-on-disc test. The friction coefficient is around 0.2 at the early stage, then increased gradually with run of the tests. After

10,000 rotations the friction coefficient became 0.33. The friction coefficient of the DLC film deposited on silicon rubber estimated by a reciprocal sliding test was around 0.21 after 100 reciprocating cycles. No delamination was observed for the DLC films deposited on both polymer substrates.

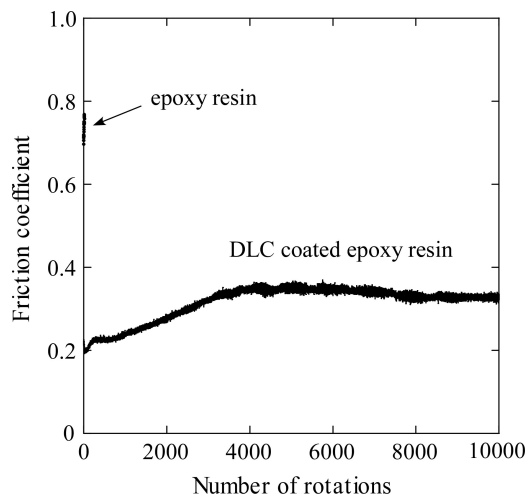


Fig. 5. Friction coefficient as a function of the number of rotations in the ball-on-disc tests for untreated and O ion implanted epoxy resin substrates

4. Conclusions

The DLC films were deposited by the PSII method on polymer and Si substrates. The effects of the pretreatments on adhesion of the films were investigated with respect to the source gas for plasma. The chemical structure of the DLC films revealed by Raman analysis was similar. The PSII pretreatment with O_2 gas was effective to improve the adhesion of DLC films for epoxy resin substrate. This enhancement was attributed to the formation of C-O and C-C chemical bonds and the physical etching at the surface of the substrates. The friction coefficient was around 0.3 for the DLC film coated epoxy resin and 0.21 for the DLC film coated silicon rubber.

References

- [1] K. Bewilogua, C.V. Cooper, C. Specht, J. Schroder, R. Wittorf, M. Grischke, *Surf. Coat. Technol.*, 127, 224 (2000).
- [2] D.P. Monaghan, D.G. Teer, P.A. Logan, I. Efeoglu, R.D. Arnell, *Surf. Coat. Technol.* 60, 525 (1993).
- [3] K. Oguri, T. Arai, *Surf. Coat. Technol.* 47, 710 (1991).
- [4] C. Zuiker, A.R. Krauss, D.M. Druen, X. Pan, J.C. Li, R. Csencsits, A. Erdemir, C. Bindal, G. Fenske, *Thin Solid Films*, 270, 154 (1995).
- [5] J.R. Conrad and T. Castagna, *Bull. Am. Phys. Soc.*, 31, 1479 (1986).

- [6] J.R. Conrad, *J. Appl. Phys.* 62, 777 (1987).
- [7] J. Tendys, I.J. Donnelly, M.J. Kenny, J.T.A. Pollock, *Appl. Phys. Lett.* 53, 2143 (1988).
- [8] C.P. Munson, R.J. Faehl, I. Henins, M. Nastasi, W.A. Reass, D.J. Rej, J.T. Scheuer, K.C. Walter and B. P. Wood, *Surf. Coat. Technol.*, 84, 528 (1996).
- [9] X.M. He, J.-F. Bardeau, K.C. Walter and Young, *J. Vac. Sci. Technol.*, A17, 2525 (1999).
- [10] K. Baba and R. Hatada, *New Diamond and Frontier Carbon Technology*, 9, 417 (1999).
- [11] K. Baba and R. Hatada, *Nucl. Instrum. Methods Phys. Res. B* 206, 708 (2003).
- [12] JEOL, *Handbook of X-ray Photoelectron Spectroscopy*, Japan, 1991.
- [13] O. Dillon, J.A. Woollam, V. Katkanant, *Phys. Rev. B* 29, 3482 (1984).
- [14] M. Ramsteiner, J. Wanger, *Appl. Phys. Lett.*, 51, 1355 (1987).
- [15] F. Tuinstra and J.L. Koenig, *J. Chem. Phys.*, 53, 1126 (1970).
- [16] M.A. Tamor, W.C. Vassell, *J. Appl. Phys.*, 76 (1994) 3823.