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Microstructure and Mechanical Properties of Si-DLC Films Deposited by PBII with Bipolar Pulses

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In the present study, Si incorporated diamond-like carbon (DLC) films were deposited on steel and silicon substrates using a plasma based ion implantation (PBII) with bipolar pulses, and the effect of the positive pulse power on the properties of DLC films was investigated. A mixture of tetramethylsilane (TMS, $Si(CH_3)_4$) and toluene was used for the deposition of the DLC films. The positive pulse voltage was varied from 2.0 to 6.3 kV while the negative pulse voltage was maintained at 5.0 kV. The surface temperature of the DLC films during deposition increases and the hydrogen contents in the DLC films decreases with applied positive pulse power. We obtained DLC films with very low internal stress and a relatively high hardness. The DLC film deposited at 4.0 kV showed the highest deposition rate due to the high plasma density and the lowest friction coefficient.
Key words: DLC films, PBII, positive pulse, friction

1. INTRODUCTION

It is possible to produce DLC films using a wide range of deposition methods, including ion beam assisted deposition, plasma-assisted chemical vapor deposition, pulsed laser deposition, filtered cathodic vacuum arc and sputter [1]. The plasma based ion implantation (PBII) technique is a relatively new method for DLC deposition [2]. PBII processing with bipolar pulses provides improved adhesion strength between the DLC film and target, and can treat 3-D workpieces having complex shapes [3]. The glow discharge plasma by a positive pulse applied to the target is omnidirectionally implanted into the target with a subsequent negative high voltage pulse. Although various reports have been published on DLC films deposited using PBII, there are no reports about the positive pulse effect on the properties of DLC films to the best of our knowledge. In the present study, we report the effect of positive pulses on the microstructure and mechanical properties of DLC films deposited by PBII.

2. EXPERIMENTS

The PBII system (Fig. 1) with bipolar pulses, which was described in details in a previous study [3], was used to deposit DLC films on steel (SKD 61) and Si substrates. The deposition process of the DLC films is as follows: (1) the substrate surfaces are sputter-cleaned with an Ar plasma to remove any organic contaminants and oxide layer, (2) the substrates are irradiated with nitrogen ions using N_2 plasma to harden the surfaces, (3) carbon ions using CH_4 plasma are implanted into the substrates, (4) SiC layer is deposited using TMS in order to improve adhesion between the substrate and DLC film, and then (5) the DLC films are deposited under the deposition conditions shown in Table I. The composition and microstructure of the DLC films were investigated using elastic recoil detection analysis (ERDA), x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

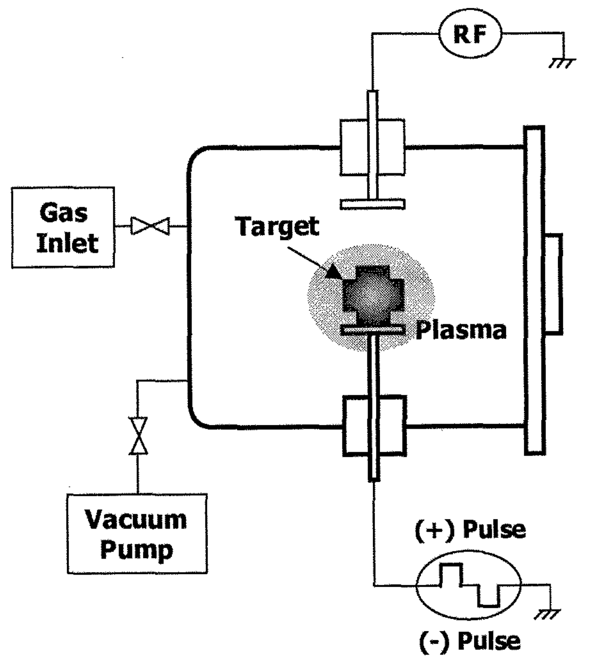

Fig. 1. Schematic diagram of experimental setup for the deposition of DLC films. RF plasma was used for surface cleaning and nitrogen treatment.

Table I. Deposition conditions for DLC films.

Precursor Gas	TMS/toluene mixture
Base Pressure	10^{-4} Pa
Deposition Pressure	10^{-1} Pa
Positive Pulse	2.0, 4.0, 6.3 kV
Negative Pulse	5.0 kV
Pulse Frequency	4 kHz
Pulse Duration	5 μs

The mechanical properties of the films were measured by a nanoindentor and a reciprocal friction tester. The applied load, the reciprocal sliding distance, the sliding speed, and diameter of the steel balls (SUJ2) were 0.98 N, 8 mm, 0.5 Hz, and 3 mm, respectively. The internal stress σ in the DLC films was calculated using Stoney equation (1) by measuring the curvature radii (r) of DLC-coated silicon substrates with a microstylus profilometer [4];

$$\sigma = \frac{E_s h_s^2}{6(1-\nu) r h_f} \quad (1)$$

where E_s and ν are the Young's modulus and the Poisson ratio of the silicon substrate, respectively, and h_s and h_f are the thickness of silicon substrate and DLC film, respectively.

The temperature of the steel surface during the DLC deposition was measured using an infrared thermometer.

3. RESULTS AND DISCUSSION

3.1 Surface temperature and film thickness

Figure 2 shows the surface temperature of the steel substrates during the DLC deposition, and the DLC film thickness as a function of the positive pulse. The surface temperature linearly increases with the positive pulses due to the enhanced electron bombardment. The film thickness (i.e., the deposition rate) increases with the increasing positive pulses up to 4 kV, but decreases as the positive pulse further increases to 6.3 kV. The deposition rate is dependent on the plasma density and the atomic mobility on the substrate. The increased positive pulse increases the plasma density on the surfaces of the substrate, resulting in a high deposition rate, whereas the high atomic mobility due to too high a temperature can lead to reflection of the atoms from the substrate and the deposition rate eventually decreases [5].

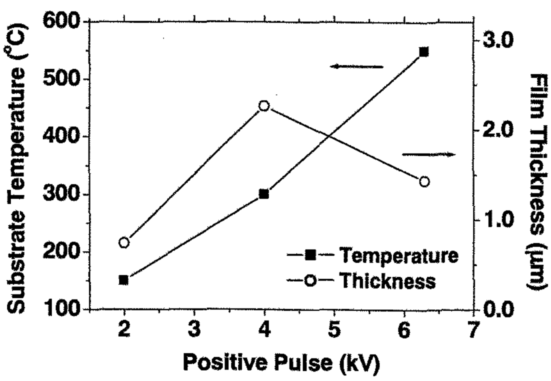

Fig. 2. The surface temperature of steel substrates during DLC deposition and the thickness of DLC films as a function of positive pulse.

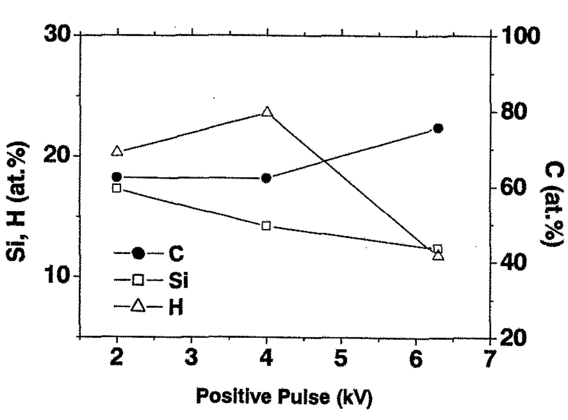

Fig. 3. The relative atomic concentration of C and Si in the DLC films.

3.2 Film composition

Figure 3 shows the relative atomic concentration of C, Si and H in the DLC films measured using XPS and ERDA. The XPS peaks were collected after the DLC surfaces were sputtering-cleaned with Ar plasma. The atomic concentration of O for all the DLC films was less than 2 %. Several authors have observed that the atomic concentration of C decreases with the increasing substrate temperature in the DLC films [4,6-8]. In this study, the atomic concentration of C linearly increases with the increasing positive pulse. It indicates that the substrate temperature induced by the electron bombardment is not the major factor that determines the composition of the DLC films. Increased positive pulses enhance the decomposition of TMS to several types of ions in the plasma [9] giving rise to a higher amount of SiHx gaseous species, which decreases the Si/C ratio of the films [8,10]. Another possible explanation is the difference in the dissociation energy of TMS and toluene, as described by Bhusari and Kshirsagar [6]. The concentration of H abruptly decreases as the positive pulse increases to 6.3 kV. It is related to the surface temperature induced by electron bombardment during the DLC deposition. It is known that hydrogen is evolved in the temperature range of 400 to 600 ℃ [11,12].

3.3 Raman spectra

The Raman spectra of the DLC films deposited under different positive pulses are shown in Fig. 4. The Raman

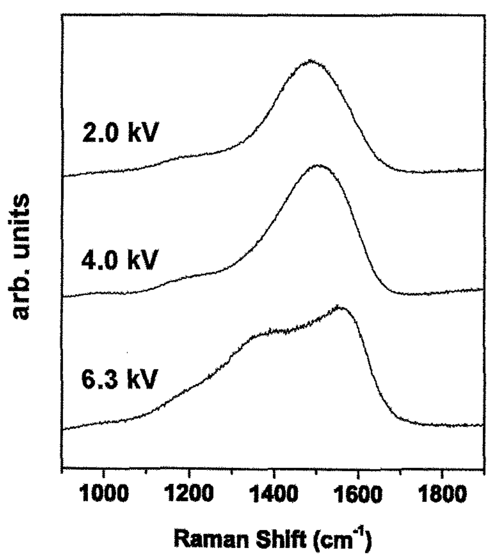

Fig. 4. Raman spectra of the DLC films deposited under different positive pulses.

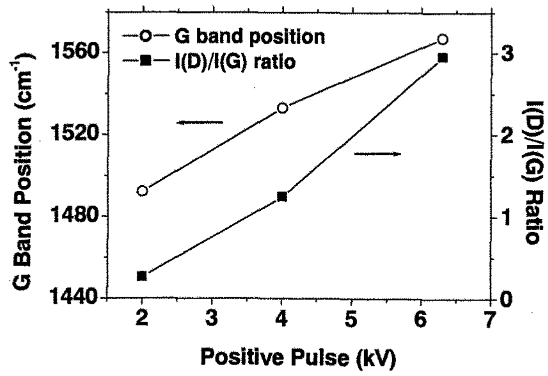

Fig. 5. The positions of G bands and I(D)/I(G) ratio of the DLC films deposited under different positive pulses.

Table II. The internal stress and hardness of the deposited Si-DLC films as a function of the positive pulse.

Positive Pulse (kV)	Hardness (GPa)	Internal Stress (GPa)
2.0	24.6	0.43
4.0	23.5	0.18
6.3	22.2	0.11

spectra for the DLC films deposited at 2.0 and 4.0 kV exhibit asymmetric single peaks, whereas the broad shoulder D band is enhanced as the positive pulse increases to 6.3 kV. Figure 5 shows the positions of the G bands and the I(D)/I(G) ratio of the DLC films, which were measured by fitting the Raman spectra with two Gaussian peaks, i.e., the G and D peaks. The results show graphitization of the DLC films as the positive pulse increases. It may be because the subplanted carbon atoms migrate to the surface due to the high deposition temperature induced by the electron bombardment, which results in the surface growth of graphitic films.

3.4 Hardness and internal stress

Table II shows the hardness and internal stress of the DLC films. We obtained DLC films with the very low internal stress of less than 0.5 GPa and a relatively high hardness greater than 22 GPa. The hardness and the internal stress gradually decrease with the increasing positive pulse, which are ascribed to the graphitization of the DLC films with the increasing positive pulse as shown in Figs. 4 and 5.

3.5 Friction and wear tests

Figure 6 shows (a) a typical friction profile, and (b) the friction coefficients of the DLC films as a function of the positive pulse. The friction coefficients shown in Fig. 6 were measured values after 300 cycles of sliding. We obtained DLC films with a friction coefficient lower than 0.1.

It is said that great involvement of hydrogen in the DLC film results in a weaker matrix against wear, causing a higher friction coefficient [13]. On the other hand, in the present study, the DLC film deposited at a positive pulse of 4.0 kV had the lowest friction

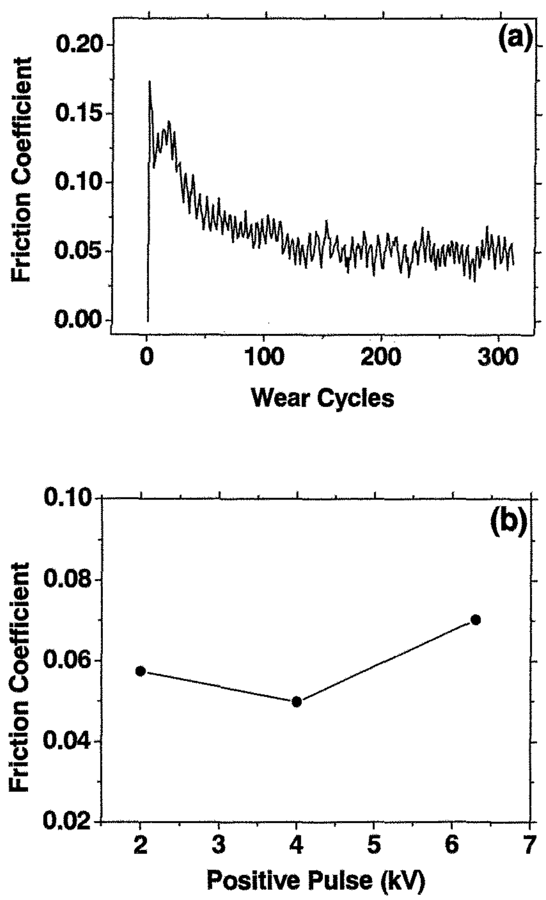

Fig. 6. (a) A typical friction profile of DLC film and (b) the friction coefficients of DLC films as a function of the positive pulse.

coefficient despite the film had greater hydrogen content than other films. It may be related to very low internal stress of DLC film deposited at 4.0 kV as shown in Table II. Another possible explanation is more graphitic nature of the DLC film deposited at 4.0 kV compared to that deposited at 2.0 kV. A certain graphitization contributes to lower friction due to formation of transferred layer on the steel ball surface. For 6.3 kV, the enhanced graphitization of the DLC film as shown in Fig. 4 leads to greater wear and friction. Figure 7 shows the wear surfaces of the DLC films and steel balls. It is apparent that the wear of the DLC film deposited at a positive pulse of 6.3 kV is greater than that deposited at 4.0 kV. The DLC film deposited at 4.0 kV showed the highest deposition rate due to the high plasma density, and had the lowest friction.

4. CONCLUSION

DLC films were deposited on the steel and silicon substrates using PBII with bipolar pulses, and the effect of the positive pulses on the properties of the DLC films was investigated. We obtained DLC films with the very low internal stress of less than 0.5 GPa and a relatively high hardness greater than 22 GPa. The DLC film deposited at 4.0 kV showed the highest deposition rate due to the high plasma density, and had the lowest friction.

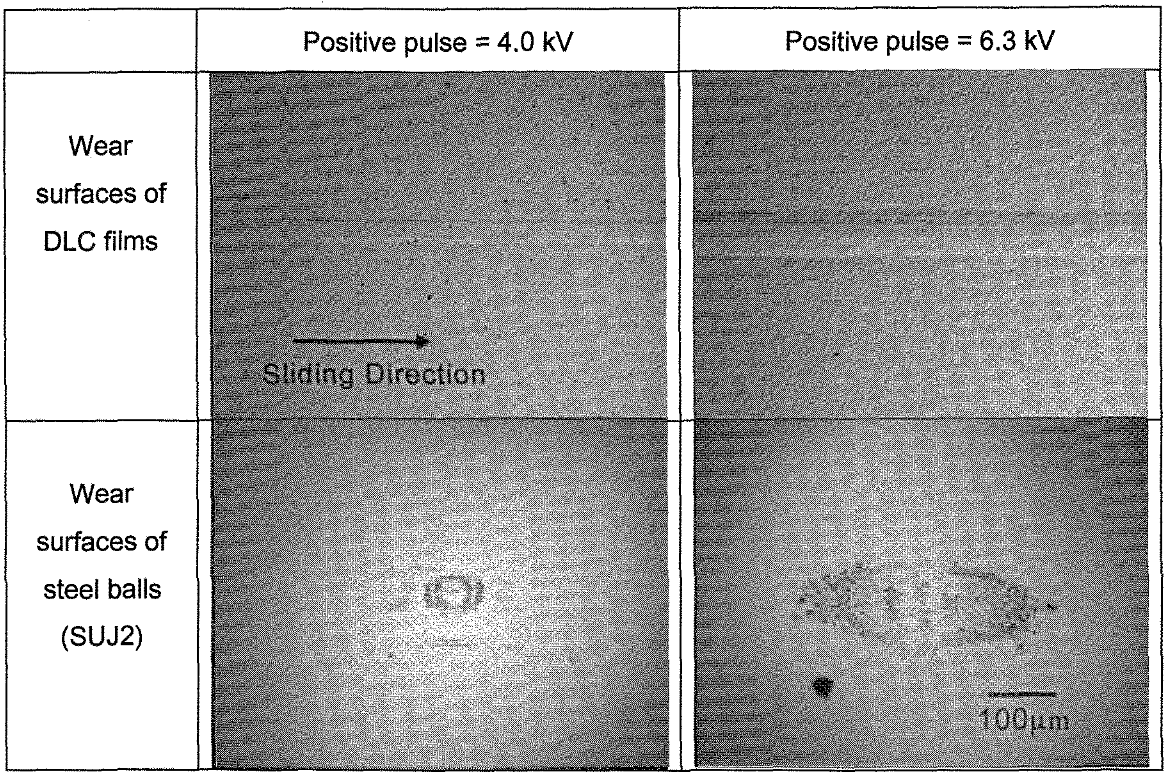

Fig. 7. Wear surfaces of the DLC films and steel balls.

REFERENCES

[1] J. Robertson, Mater. Sci. Eng. **R 37**, 129-281 (2002).
[2] J.R. Conrad, J.L. Radtke, R.A. Dodd, F.J. Worzala, N.C. Tran, J. Appl. Phys. **62**, 4591-4596 (1987).
[3] S. Miyagawa, S. Nakao, M. Ikeyama, Y. Miyagawa, Surf. Coat. Technol. **156**, 322-327 (2002).
[4] W. Wu, M. Hon, Thin Solid Film **307**, 1-5 (1997).
[5] S. Chowdhury, M.T. Laugier, I.Z. Rahman, Thin Solid Films **447-448**, 174-180 (2004).
[6] D.M. Bhusari, S.T. Kshirsagar, J. Appl. Phys. **73**, 1743-1749 (1993).
[7] W. Wu, M. Hon, Thin Solid Film **345**, 200-207 (1999).
[8] L. Thomas, L. Maille, J.M. Badie, M. Ducarroir, Surf. Coat. Technol. **142-144**, 829-834 (2001).
[9] L. Thomas, M. Ducarroir, R. Hillel, R. Berjoan, Surf. Coat. Technol. **142-144**, 314-320 (2001).
[10] Y.H.C. Cha, P.G. Kim, H.J. Doerr, R.F. Bunshah, Surf. Coat. Technol. **90**, 35-41 (1997).
[11] S.S. Camargo, A.L.B. Neto, R.A. Santos, F.L. Freire, R. Carius, F.Finger, Diamond Relat. Mater. **7**, 1155-1162 (1998).
[12] S. Bhargava, H.D. Bist, A.V. Narlikar, S.B. Samanta, J. Narayan, H.B. Tripathi, J. Appl. Phys. **79**, 1917-1925 (1996).
[13] J.H. Park, H.S. Kwon, J.Y. Lee, J. Appl. Phys. **72**, 5246-5252 (1992).

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