Tribology International 37 (2004) 907–912
TRIBOLOGY INTERNATIONAL
www.elsevier.com/locate/triboint

# Properties of flexible DLC film deposited by amplitude-modulated RF P-CVD

Takahiro Nakahigashi *, Yoshikazu Tanaka, Koji Miyake, Hisanori Oohara

*Nippon ITF, Inc., 575 Kuze Tonoshiro-Cyo, Minami-ku, Kyoto 601-8205, Japan*

**Abstract**

The flexible DLC film is one of the novel techniques to deposit the DLC film on polymer materials such as rubber and resin, which does not cause any peeling-off of the film even with the deformation of the substrates. It was found that the DLC film deposited by modulated RF plasma-CVD has the features of (1) small friction, (2) small wear (less than Teflon), (3) high water repellency (90° contact angle for pure water), (4) good insulation characteristic (surface resistance on the order of $10^{12}$ Ω cm), (5) less peeling-off due to expansion and contraction of the polymer material, and (6) deposition at lower temperatures (below 80°). This new DLC film is applied to the rubber seal ring (O-ring) for zoom lens system of 35 mm compact cameras. The flexible DLC technique is expected to expand itself and to create wider applications of DLC films.


*Keywords:* DLC; Plasma; CVD; Low friction; Polymer material

## 1. Introduction

As diamond-like carbon (DLC) has the lowest friction coefficient among various coating materials and its aggressiveness toward other materials is much less, its practical use has progressed in the field of sliding parts, etc. However, the DLC products so far developed are limited to polymer materials with high hardness such as metals and ceramics because of the high internal stress peculiar to DLC. In addition, because of recent environment issues, requirements have a risen from users for improvement in friction and wear of polymer materials such as resin and rubber with less oil and powder.

This paper reports the formation of a flexible DLC thin film, which is adherent even when polymer materials such as resin and rubber are deformed, its various characteristics, and its applications.

## 2. Characteristics of DLC

Among various thin film coating materials diamond-like carbon (DLC) has features such as the lowest friction coefficient, high hardness, superior wear resistance, and less damage in the counterparts. Because of these features, many types of DLCs have been developed and are easily available in the global market. The character of DLC is between diamond and graphite. Fig. 1 shows these structures. Historically, in the early 70s, amorphous pure carbon film deposited using ion

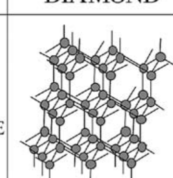
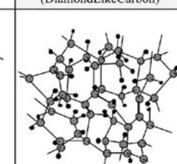
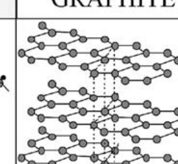
| | DIAMOND | DLC (DiamondLikeCarbon) | GRAPHITE |
|---|---|---|---|
| STRUCTURE |  Crystalline (sp3Bondings) |  Amorphous (sp3 and sp2 Bondings) |  Crystalline (sp2 Bondings) |
| CONSTITUTIVE ELEMENT | C | C·H | C |
| PROCESS | Plasma-Assisted Chemical VaporDeposition(CVD) (NonequilibriumPlasma) | Plasma-AssistedCVD IonPlatingetc. (NonequilibriumPlasma) | CVD (EquilibriumPlasma) |
| REACTIVEGAS | Cn Hm and H2 CH4:H2=1:100 | CnHm or CVapor CH4,C2H2,C6H6,etc. | CnHm |
| PROCESSING TEMPERATURE | ~700 °C | RT ~ 300 °C | >1500 °C |

Fig. 1. Comparison of carbon-containing materials structures and methods of forming.

* Corresponding author. Tel.: +81-75-931-6040; fax +81-75-931-6166.
*E-mail address:* nakahigashi@nippon-itf.co.jp (T. Nakahigashi).

0301-679X/$ - see front matter 
doi:10.1016/j.triboint.2004.07.007

beam deposition was the first DLC, which was called "i-C" [1]. After that, hydrogen-containing (hydrogenated) amorphous carbon film deposited using ionized beam of hydrocarbon gas was developed in the late 70s [2]. Radio frequency plasma assisted chemical vapor deposition (RF-PCVD) was also developed for hydrogenated amorphous carbon film. Non-hydrogenated amorphous carbon film is also deposited using cathodic arc physical vapor deposition (CA-PVD), cathode sputtering or laser ablation. In the middle 80s, metal containing amorphous carbon film was developed using simultaneous sputtering of metal and carbon targets [3]. In the 90s, plasma immersion ion implantation and deposition (PIII and D) method was developed for hydrogenated amorphous carbon film.

Thus, many types of amorphous carbon, which are classified as DLC, have been developed and have been put in practical use. However, each DLC shows different characteristics such as friction coefficient, electric conductivity, the degree of transparency, and so on, according to the hydrogen and/or metal content and sp3/sp2 ratio. Hence, today's DLC market is, so to speak, in a state of confusion. Generally, film properties are strongly depended on the film contents. Also, film contents are strongly depended on the source material and the principle of deposition process. So, we must use each DLC properly taking the essential information given above into consideration.

Many researchers have tried to clarify why DLC shows such low friction coefficient and good tribological properties. In the early stage of such research, it was reported that graphitization of DLC could have been the reason [4]. Graphite itself is a solid lubricant material. During friction, DLC is thought to be transformed or decomposed to generate thin graphite layer at the sliding surface of DLC. Recently, it was found that the highly hydrogenated DLC showed extremely low friction coefficient in ultra-high vacuum or in dry nitrogen [5–7]. These results indicate that hydrogen, which is contained in DLC, plays an important role during friction [8,9]. Fukui and his co-workers investigated the surface of DLC (a-C:H) after friction test in ambient air using the time-of-flight secondary ion mass spectroscopy, and they found the evidence of hydrocarbon material which was generated during friction [10]. This "friction polymer" or "transferred layer" is thought to act as the lubricant material during friction. Hydrogen in the DLC film also affects the film hardness and so on.

The content of diamond-like (sp3) C–C bonding state is also the essential parameter of DLC [11]. The higher the sp3/sp2 ratio in the DLC, the higher the hardness and transparency of DLC. Using CA-PVD, relatively high sp3/sp2 ratio can be obtained, and such DLC is called tetrahedral amorphous carbon (ta-C). On the other hand, graphite-like carbon film with relatively low sp3/sp2 ratio, which is called amorphous carbon (a-C), is obtained using conventional cathode sputtering. Recently, unbalanced magnetron sputtering (UBMS) has been widely used to deposit DLC [12]. Generally, graphite cathode and inert gas, such as argon, are used to deposit the a-C film. But, in many cases, some kind of hydrocarbon gas, such as acetylene, is simultaneously used to deposit the a-C:H film. Furthermore, metal carbide cathode, inert gas and hydrocarbon gas are used to deposit the metal containing a-C:H film. Therefore, UBMS is a useful technique to obtain the various kinds of DLCs including multi-layered or composite structured DLCs. Some kinds of metallic or non-metallic additives produce unique properties. Silicon containing a-C:H shows very low friction coefficient under dry (no-oil) condition [13]. Tungsten containing DLC, such as WC/C, shows lower internal stress, hence thick coating more than 3 μm can be obtained. But, also the film hardness is generally low, it is possible that the wear resistance property tends to fall down.

Attractive features of DLC film are (1) abrasion resistance (Vickers hardness is 1500–2500), (2) low friction coefficient. (without lubrication $\mu$ is 0.05–0.2), (3) lower aggressiveness to counterparts (damage to the other party polymer material is suppressed), (4) separability (decreased cohesion and fusion to soft metals as aluminum and copper), (5) super-smooth film (smoothness of polymer material is not degraded), (6) it is possible to use this film up to 250 °C in the stationary state. Because of these features, DLC film has been applied to (1) moldings of IC lead bending and fabrication to increase repairability, (2) machine parts such as video tape guide shafts, rotating axis parts, hot water tap mixture [14], etc. to increase slipping ability and wear resistance, (3) transport equipment parts such as transport rails, silicon wafer transport arms and guides, etc. to increase slipping ability, wear resistance, and to improve particle prevention. Such DLC features and these applications could help improve friction and wear of polymer materials such as resin and rubber.

## 3. Adjustment of flexible DLC to polymer material

Oil and fat are added to improve the surface lubricity of polymer materials such as rubber and resin. When oil and fat run dry, however, drawbacks such as gradual increase in the friction coefficient arise. For instance, car windshield wipers become noisy in 6 months. Components and products made of rubber also tend to cling to the other materials used in their construction. Elimination of such oil and fat additives that cause such bad effects would be benefited. Coating polymer materials such as rubber and resin make the best use of the features of DLC.

Three issues have to be resolved (1) low heat resistance of the polymer materials such as rubber and resin, (2) pollution of the polymer material surface by oil, fat, resin, and oxidation prevention agents, etc., and (3) transformation of the polymer materials. To resolve these possible problems: (1) a processing method is developed by using the amplitude-modulated radio frequency (RF) plasma chemical vapor deposition (CVD) method which enables coating at lower temperature (below 80 °C) and does not allow the processing temperature to rise any higher [15,16]. (2) To prevent the pollution, the polymer surface needs to be clean. However, lengthy washing by solvent causes extraction out of fat and oil that are contained in rubber in order to mix with carbon black. Cleaning in a short time cannot sufficiently remove the pollution. The polymer surface can be cleaned by plasma. (3) To prevent the transformation, the film should be flexible enough to absorb the polymer material transformation. We have modified the DLC film structure to permit expansion and contraction. Hardness of this film is lower than that of usual DLC films (1500 or higher Vickers hardness). Because of the above-mentioned characteristics of this film, it is named "Flexible DLC (Japanese trade mark)".

## 4. Deposition device and processing method

We used RF plasma-CVD method for this experiment. Use of the modulated RF plasma process enables a decrease of particles [15,16]. A frequency of 13.56 MHz was used. While the substrate is on the high frequency electrode, the electrode is water-cooled to suppress any temperature rise up in the polymer material. In the deposition process, the surface contamination is first removed by $H_2$ plasma cleaning at the basic vacuum level of the chamber and then a flexible DLC film is formed by an $CH_4$ plasma. The plasma cleaning is effective in removing oil and fat as well as parting agent on the substrate surface. However, it is necessary to fully consider possible damages given to the polymer material by cleaning before determining the gas to use and its conditions. In other words, depending upon the characteristics of each polymer material, it is necessary to properly use the spatter cleaning, which uses gases like Ar, generally used as plasma cleaning, and the chemical etching, which uses activated gases like F, O, H, etc. In general, surface of the polymer materials like resin and rubber easily changes when hit by high-energy ions. Occasionally, their original characteristics are deteriorated as a result. In order to minimize the damage to the polymer material, $H_2$ plasma cleaning was adopted which has larger chemical etching effect.

## 5. Evaluation of film characteristics

The film thickness was measured after masking the polymer material surface, by a surface difference meter (type Dekata3000st Sloan). For friction measurement, a round trip sliding type friction instrument was used (Type Heidon-14D manufactured by Shinto Science). The material of ball (diameter was 8 mm) was made from aluminum. The load weight was 0.1 N. Ball speed was 10 mm/s. For wear measurement, a pin on disk type friction instrument (Type FPD-2DE600HVG (S), Tokyo Testing Machine Mfg.) was used. The material of ball (diameter was 8 mm) was SUJ-2 (bearing steel). The load used was 0.5 N. Ball speed was 0.1 m/s. Sliding distance was 1.0 km.

For evaluation of insulation characteristics and water repellency, a voltage examination method (JIS K 6911) and a contact corner measurement device using pure water (manufactured by Kyowa Kaimen Kagaku) were used.

## 6. Results and discussion

### 6.1. Deposition rate

Fig. 2 shows the dependency of the deposition rate on polymer materials. We found that, while the deposition rate of general DLC was 0.5–1 μm/H on a metallic substrate such as silicon, the deposition rate became about two to three times faster when the flexible film was formed on polymer material. It was also found that, while a thick film greater than 1 μm on metal was likely to flake off due to the larger film stress, the internal stress became small and therefore

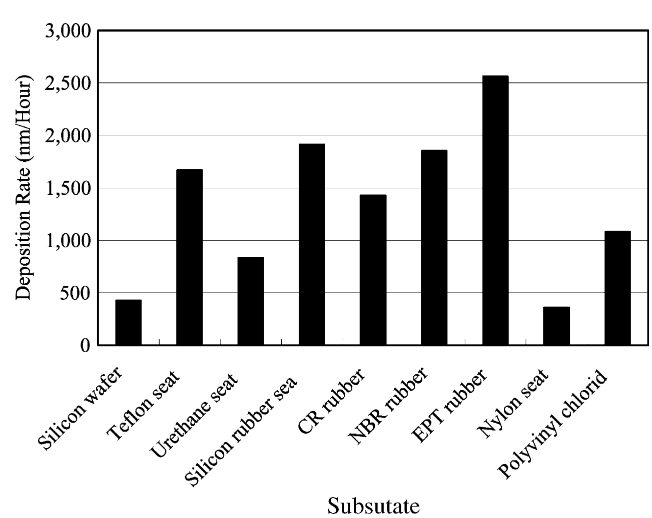



Fig. 2. Deposition rate of flexible DLC on polymer materials.

thicker film deposition up to some 5 μm could be made when flexible DLC was formed on polymer material.

### 6.2. Friction coefficient

Fig. 3 shows the dependency of the friction coefficient on polymer material. It is difficult to measure the friction coefficient of the soft surface of the polymer material such as rubber and resin. Here, the friction coefficient was measured with a light load of 0.1 N in order not to greatly distant the polymer material. To compare the friction coefficient of the polymer material with those of general polymer materials, a piece of glassy material was also measured beside the polymer materials. As a result, it was found that four of spindles used this time corresponded to one of the friction coefficients used in general.

The friction coefficient of the polymer material before the coating process indicated a value from 1 to 6 depending on the polymer materials. On the contrary, the friction coefficient measurements after the coating process showed one or less for all the polymer materials tested and all of them were virtually identical. It was found that this value was in the same range as Teflon, often used as a low friction polymer material.

### 6.3. Wear characteristic

PTFE is used to decrease the friction coefficient of sliding parts since its friction coefficient is as low as 0.2. For similar purpose, heat-resistant silicon and fluorine rubber are processed by print coating. However, Teflon is worn out very fast as its graphitized structure is the same as graphite. Fig. 4 shows the wear characteristics of Teflon material and Teflon material coated with flexible DLC film. The conditions for measurement

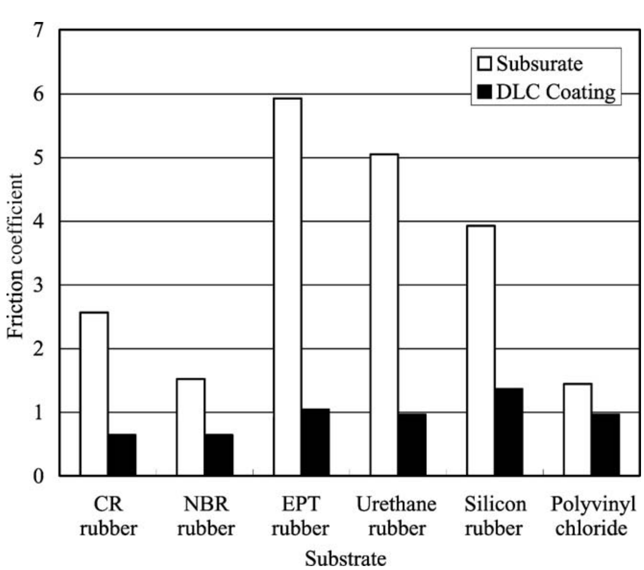



Fig. 3. Friction coefficient of flexible DLC on polymer materials.

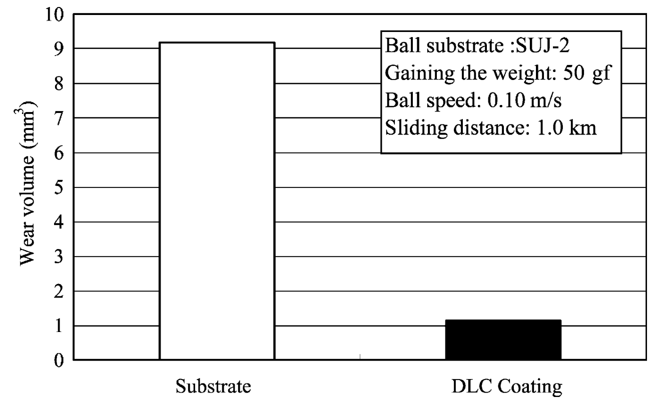



Fig. 4. Wear rate of flexible DLC on Teflon sheet.

included a ball of SUJ-2 (bearing steel), a load of 0.5 N, sliding speed of 0.1 m/s, and sliding distance of 1 km. The measurement showed that the wear out volume of the flexible DLC film coated Teflon polymer material was as low as 1 $mm^3$, which corresponds to about 1/9 of that of the unprocessed Teflon polymer material.

### 6.4. Film hardness

Measurement of the flexible DLC film hardness on the polymer materials is very difficult as the polymer material itself is deformed. Therefore, measurement was performed by using a super-minute hardness meter [17]. Head of the super precision diamond was pushed into 20 places of the center part of the grain of DLC, and the hardness of the average was evaluated. As a result, the value of 0.1GPa was obtained. It was a value that surpassed expectations, and this hardness value was not without regard to the influence of the radical material.

### 6.5. Surface morphology of flexible DLC

Two scanning electron microscopy (SEM) photographs, Fig. 5, show the surface of the flexible DLC deposited on silicon rubber sheets. "A" is a film thickness of 10 nm, and "B" is a film thickness of 1 μm. For the case of the 10 nm film thickness, grains of 10–20 μm are seen. This is the reason why the flexible DLC is not flaked off even if the polymer material does expand and contract. These cracks can be controlled by changing the deposition condition. The cross section photograph confirmed that thicker the film became, the edge side of the grain became more stressed.

### 6.6. Electrical resistance

Surface resistance of a flexible DLC film deposited on a silicon rubber sheet was measured. With a film thickness of 1 μm and an applied voltage of 500 V, the

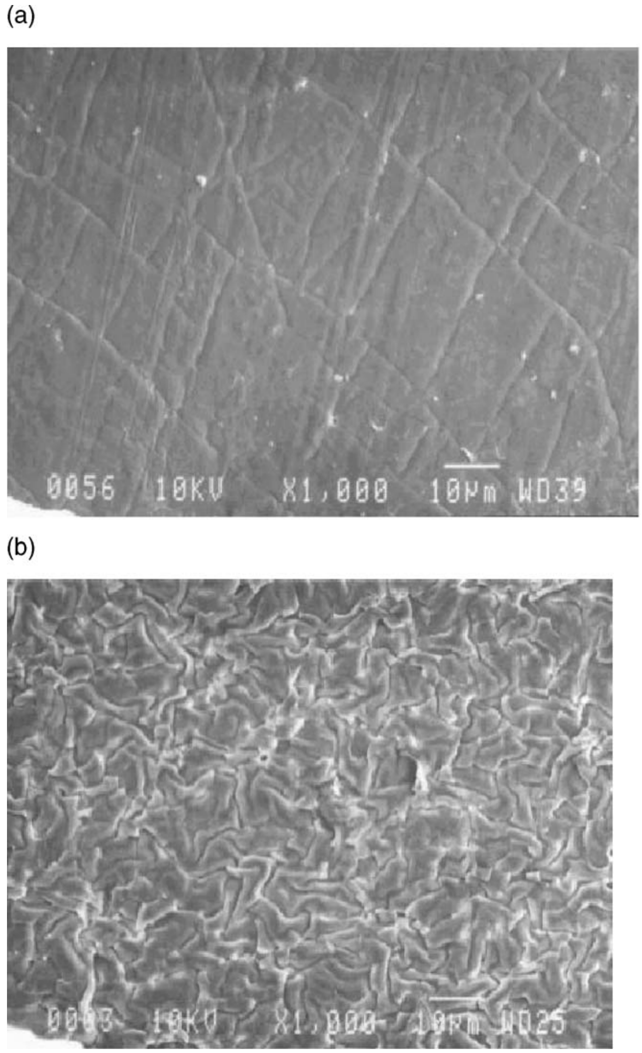



Fig. 5. Surface morphology of DLC films on silicon rubber determined by scanning electron microscopy: thickness is (a) 10 nm, (b) 1 μm.

insulation resistance was 1–2 × $10^{12}$ Ω cm. This shows that the films have excellent insulation characteristics.

### 6.7. Water repellency

Water repellency measurements were made on polyurethane rubber sheets, one unprocessed and the other was coated with flexible DLC film. While the unprocessed substrate showed a contact corner of about 80°, the DLC film coated sample showed a better repellency, 90°.

### 6.8. Gas permeability

Use of "polyvinyl chloride" is now prohibited because of its dioxin generation. Polyethylene is used as a substitute, however, its gas permeability characteristics are poor. Therefore, multi-layer coating is now being studied. Moreover, the practical use of the DLC

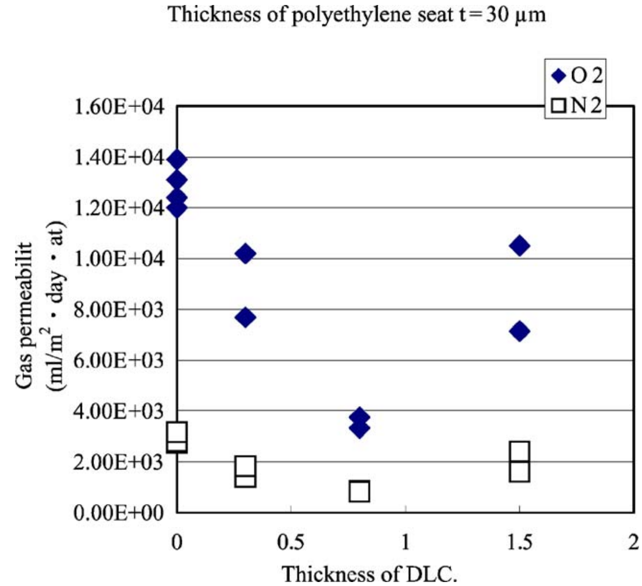



Fig. 6. $O_2$ and $N_2$ gas permeability of a flexible DLC film deposited on polyethylene.

coating over inside surface of containers is beginning for the following reasons: (1) to keep clean the inside surface of PET bottles like cans and glass bottles for the purpose of material recycling and (2) to improve the gas permeability characteristics. This process is used to introduce acetylene into the container and to deposit a DLC film inside of the container by using microwave radiation. Fig. 6 shows $O_2$ and $N_2$ gas permeability characteristics for the flexible DLC film that was deposited on polyethylene. Improvements on $O_2$ permeability by lowering permeability by 1/4 or less are obtained by choosing the optimum thickness of DLC film.

## 7. Conclusion

It was found that the DLC film has the features of (1) small friction, (2) small wear (less than Teflon), (3) high water repellency (90° contact angle for pure water), (4) good insulation characteristic (surface resistance on the order of $10^{12}$ Ω cm ), (5) less peeling-off due to expansion and contraction of the polymer material, and (6) deposition at lower temperature (below 80 °C).

The flexible DLC film applied to polymeric materials, enabled a concept by *clacking* DLC film, has expanded its applications to an area very familiar in our daily life such as "O" rings and gaskets of 35 mm cameras [18]. New applications to other fields other than sliding are also being developed. Coating the inside surface of PET bottles to lower gas permeability, and recycling of used materials are examples. Because of its superior characteristics in bio-compatibility and chemical stability, application of DLC to the medical area is being developed in Europe.

## Acknowledgements

We would like to thank Dr. S. Sasaki of the Agency of Industrial Science and Technology, Dr. K. Miyoshi of NASA and Dr. K. Ogata of Nissin Electric for many helpful discussions. I also wish to express my gratitude to Y. Murakami and J. Takeuchi who helped with experiments in this research. We acknowledge the cooperation given by Nissin Analytical Characterization Center for the SEM photographs.

## References

[1] Aisenberg S, Chabot R. Physics of ion plating and ion beam deposition. Journal of Applied Physics 1971;42(7):2953–8.

[2] Weissmantel C, Reisse G. Preparation of hard coatings by ion beam methods. Thin Solid films 1979;63:315–25.

[3] Dimigen H, Hubsch H, Memming R. Tribological and electrical proper-ties of metal-containing hydrogenated carbon films. Applied Physics Letter 1987;50:1056–8.

[4] Liu Y, Erdemir A, Meletis EI. An investigation of the relationship between graphitization and frictional behavior of DLC coatings. Surface and Coating Technology 1996;86–87:564–8.

[5] Donnet C, Fontaine J, Le Mogne T, Belin M, Heau C, Terrat JP, Vaux F, Pont G. Diamond-like carbon-based functionally gradient coatings for space tribology. Surface and Coating Technology 1999;120–121:548–54.

[6] Erdemir A, Eryilmaz OL, Nilufer IB, Fenske GR. Synthesis of diamond like carbon films with superlow friction and wear properties. Journal of Vaccuum Science and Technology 2000;18A(4):1987–92.

[7] Erdemir A, Eryilmaz OL, Nilufer IB, Fenske GR. Synthesis of superlow-friction carbon films from highly hydrogenated methane plasmas. Surface and Coating Technology 2000;133–134: 448–54.

[8] Fontaine JC, Donnet C. Tribochemistry between hydrogen and diamond-like carbon films. Surface and Coating Technology 2001;146–47:286–91.

[9] Erdemir A. The role of hydrogen in tribological properties of diamond-like carbon films. Surface and Coating Technology 2001;146–147:292–7.

[10] Fukui H, Irie M, Utsumi Y, Oda K, Ohara H. An investigation of the wear track on DLC (a-C:H) film by time-of-flight secondary ion mass spectorscopy. Surface and Coating Technology 2001;146–147:378–83.

[11] Ferrari AC, Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. Physical Review B 2000;61(20):14095–107.

[12] Monaghan DP, Teer DG, Logan PA, Efeoglu I, Arnell RD. Deposition of wear resistent coatings based on diamond-like carbon by unbalanced magnetron sputtering. Surface and Coating Technology 1993;60:525–30.

[13] Sugimoto I, Miyake S. Oriented hydrocarbons transferred from a high performance lubricative amorphous C:H:Si film during sliding in a vaccum. Applied Physics Letters 1990;56(19): 1868–70.

[14] Kuwayama K. Fiction of DLC/a SiC coated alumina in water. Synopses of International Tribology Conference, Nagasaki. 2000, p. 216–7.

[15] Kirimura H, Maeda H, Murakami H, Nakahigashi T, Ohtani S, Tabata T, Hayashi T, Kobayashi M, Mitsuda Y, Nakamura N, Kuwahara H, Doi A. Study of deposition process in modulated RF silane plasma. Japanese Jounal of Applied Physics 1994;33: 4389–94.

[16] Nakahigashi T, Hayashi T, lzumi Y, Kobayashi M, Kuwahara H, Nakabayashi M. Properties of a-Si:H film deposited by amplitude-modulated RF plasma chemical vapour deposition for thin film transistor. Japanese Journal of Applied Physics 1997;36:328–32.

[17] Sasaki S, Nakahigashi T. Evaluation of tribolodical properties of DLC coated on rubbers using nanoindentation and nano-scratch testing. Synopses of International Tribology Conference, Nagasaki. 2000, p. 435–6.

[18] Nakahigashi T, Iura S, Komamura H, Ishibashi Y. Application of flexible DLC coating to O-ring for zoom camera (in Japanese). Proceedings of JAST Tribology Conference Tokyo, May 2002, p. 109–10.