Deposition Technology and Applications of DLC Films

M. SUZUKI　K. YAMAKAWA　T. SAITO

Diamond-Like Carbon (DLC) films possess good properties such as low friction, high wear resistance, high hardness, smooth surfaces, and chemical stability. DLC films have been used widely in industrial applications as protective and lubricating films for sliding parts. However, the properties of DLC films are known to depend upon the deposition methods and conditions. The JTEKT Group supplies DLC films produced by the plasma enhanced chemical vapor deposition (PE-CVD) method, which has the advantage of making it possible to deposit on three-dimensional surfaces. This report introduces the deposition methods, properties and some application examples of DLC films.

Key Words: *diamond-like carbon (DLC), chemical vapor deposition (CVD), deposition method, application*

1. Introduction

Being superior in obtaining low friction coefficient, wear resistance, high hardness, surface smoothness, chemical stability, etc., DLC films are acknowledged to be such surface treatments that contribute to efficient utilization of natural resources and be environmentally friendly. For example, if they are applied to surfaces of low cost materials, material properties can be improved. This helps such low cost materials be more widely used and natural resources be more efficiently utilized. DLC films themselves are friendly to the global environment because they consist of carbon and hydrogen.

Recent research and development activities on DLC films are at a turning stage, from the phase of basic studies by universities or academic institutes to the phase of practical applications in industrial fields by companies. In industrial fields, technology for mass production is gradually but significantly being established, and general-purpose DLC films with little quality variance are appearing in the market. The JTEKT Group also mass-produces DLC films by the plasma CVD method, which is suitable for mass production. DLC films are able to induce various characteristics depending on deposition methods and processing conditions. In order to best utilize DLC films, it is important to understand deposition technology and film properties well. This report introduces deposition technology, film properties and application examples.

2. DLC Deposition Technology

In the early 1970s, Aisenberg and other engineers adopted an ion beam deposition method and succeeded in depositing carbon films showing properties very similar to those of diamonds, and they were the first to use the nomenclature "DLC"1). In recent years, the term "DLC" film is used as a general term for amorphous carbon films. DLC films are formed by the physical vapor deposition (PVD) method or chemical vapor deposition (CVD) method (**Fig. 1**). These deposition methods and processing conditions control film composition (sp^3 bonding component, sp^2 bonding component and amount of hydrogen, etc.) and have a significant influence on film properties. Because of this, it is important to understand such deposition technology (deposition methods and processing conditions) well in order to obtain a film suitable for each application.

In DLC deposition technology, many deposition methods are availabe2). For mass production in particular, the plasma CVD method, sputtering method, ionization deposition method and arc ion plating method are adopted in many cases. The JTEKT Group has adopted the plasma CVD method, which is better suited to mass production. Details of this method will be explained later in this report. On the other hand, other methods such as the sputtering method, ionization deposition method and arc ion plating method fall into the category of PVD methods. In these PVD methods, films have directional properties in deposition, and therefore processed materials need to be rotated. Each PVD method is detailed hereunder.

The sputtering method is deposition technology utilizing a sputtering phenomenon whereby ions are collided at high speed with the surface of a solid material.

In case of DLC films, with a carbon target as a cathode (a negative pole), a film is deposited by applying voltage between the cathode and the anode in the atmosphere of noble gas (**Fig. 2**(a)). During this processing, it is also possible to deposit element-added DLC films by combined use of a metal target and gas mixed with such reactive gases as methane, acetylene, or hydrogen. Also, in many cases, a sputtering apparatus additionally equipped with a non-equilibrium magnetic field is used for the purpose of increasing ion assist effect, adhesion strength and reactivity.

In the ionization deposition method, radicals and ions generated by the ionization source (thermion excited by a filament) are used to deposit a film (**Fig. 2**(b)). Applying negative bias voltage to a processed material accelerates the speed of collision of the generated radicals and ions with the processed material and forms films. Because of this, unlike other PVD methods, this method uses gas as a source instead of a solid source, and, by use of hydrocarbon type gas as a source, DLC films can be obtained.

Arc ion plating is a kind of ion plating method. A target is vaporized and ionized by arc discharge in order to deposit a film (**Fig. 2**(c)). In case of depositing DLC films, graphite is used as a target. In this method, it sometimes becomes a problem that agglomerate of source materials called droplets are taken in films. In recent years, this problem has been settled by grinding the film after deposition and deposition technology additionally using a magnetic field.

Besides the above-mentioned methods, deposition of DLC films has also been done by such new methods as combined PVD and CVD technology, plasma based ion implantation (PBII) technology using an ion implantation technology, atmospheric pressure plasma, etc.

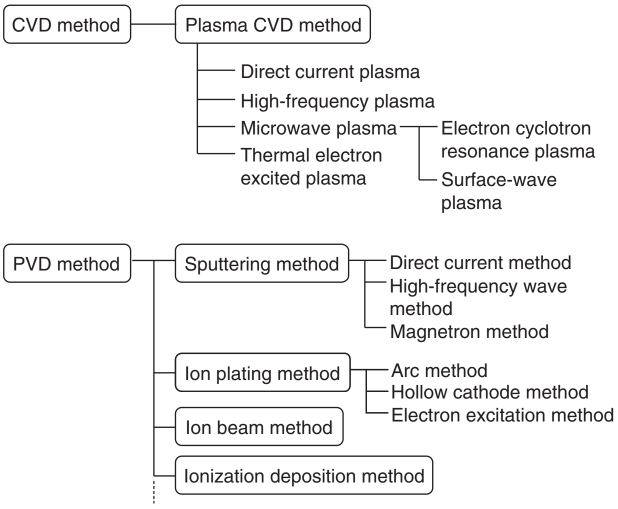
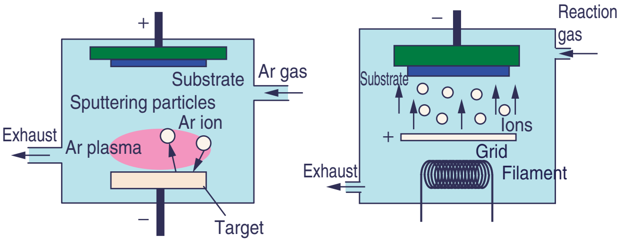
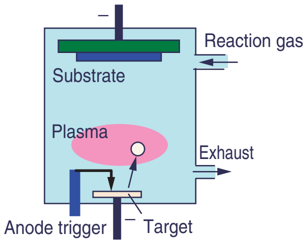


Fig. 1 Deposition methods using plasma



(a) Sputtering (b) Ionization deposition



(c) Arc ion plating

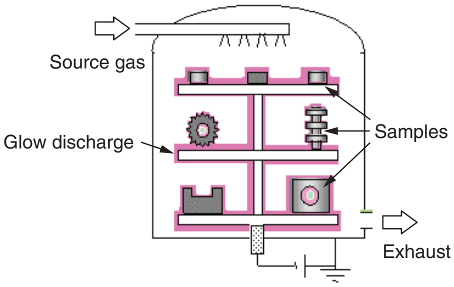
Fig. 2 Schematics of various deposition methods

3. Deposition by Plasma CVD Method

With the plasma CVD method using plasma, it is possible to deposit under lower temperature (500℃ or lower) than in the case of the thermal CVD method (1 000℃ or higher). This is due to deposition using various active particles existing in plasma. The generation of plasma requires a steady discharge of electricity between electrodes after gas is supplied in a vacuum. The plasma CVD method is classified into types such as direct current plasma, high frequency plasma and micro wave plasma depending on the power supply source applied for discharge3). The JTEKT Group has adopted the direct current plasma CVD method because of its superiority in coating 3-dimensional objects with complex shape and simple apparatus structure. The JTEKT Group has already mass-produced DLC-Si films that are Si-added DLC films.

Figure 3 shows the appearance and a schematic drawing of the direct current plasma CVD apparatus. With the direct current plasma CVD method, electrons generated in a cathode are accelerated by an electric field, collided with gaseous atoms or molecules while moving toward an anode, and then ionized into plasma. Generally, plasma generated by direct current power reaches a non-equilibrium state in which gas temperatures become as low as several 100℃, whereas the temperature of electrons increases to 10^4℃ level under the pressure of depositing DLC films (several - several 100 Pa). Electrons retain extremely high energy under this non-equilibrium plasma state and collide with atoms and molecules in the atmosphere to accelerate excitation (radicalization, ionization), resulting in the generation of many activated species. In this apparatus, a processed material is placed at an electrode and works as a cathode. The generation of plasma forms an area at the side of the cathode where ions are accelerated along with the configuration (plasma sheath), and film deposition progresses in line with the configuration. The film deposition can be done at the comparatively high speed of several μm/h thanks to many activated species being there. When it comes to actual mass-production, it becomes necessary to take many measures for uniformity of film thickness and film quality, stable deposition, gas flow, distribution of electric fields, processing conditions, etc.

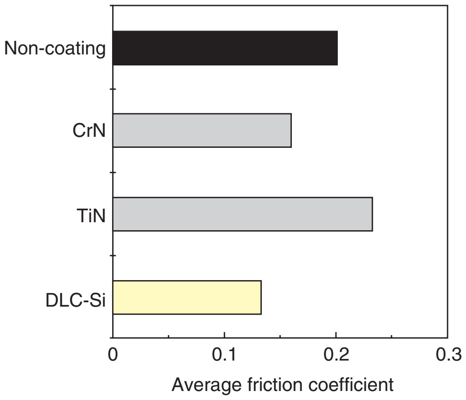
(a) Apparatus



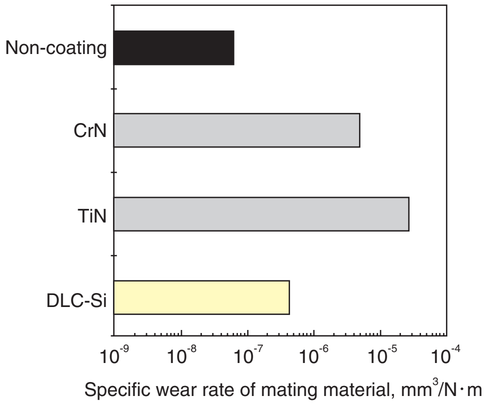
(b) Direct current plasma CVD

Fig. 3 Direct current plasma CVD apparatus

DLC-Si films that have been mass-produced in the JTEKT Group by the direct current plasma CVD method possess excellent tribological properties thanks to the addition of Si, and the adhesion strength of deposited films is ensured by a newly developed deposition technology for high adhesion strength4). **Figure 4** shows the results of friction and wear testing under oil lubrication by a ball-on-plate type rotating friction tester. The friction coefficient of general hard films such as CrN and TiN is nearly equivalent to that of a non-processed material which is 0.2. On the other hand, the DLC-Si films showed low friction coefficients of 0.1-0.13, displaying excellent friction characteristic even under boundary lubrication condition (**Fig. 4**(a)). The wear amount of these hard films was less than the measurement limit, demonstrating the excellent wear resistance of the films themselves. However with regard to the wear amount of the mating materials, differing results were observed depending on the film. In case of DLC-Si films, the specific wear rate of the mating material was 10^{-7}-10^{-8} $mm^3/N \cdot m$, by which it was confirmed that the DLC films attack the mating material very little (**Fig. 4**(b)). On the other hand, attacking by the CrN and TiN films was as heavy as 10^{-5}-10^{-6} $mm^3/N \cdot m$ in terms of specific wear rate of the mating material.



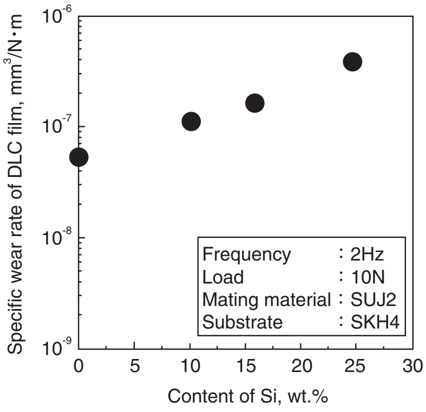
(a) Average friction coefficient



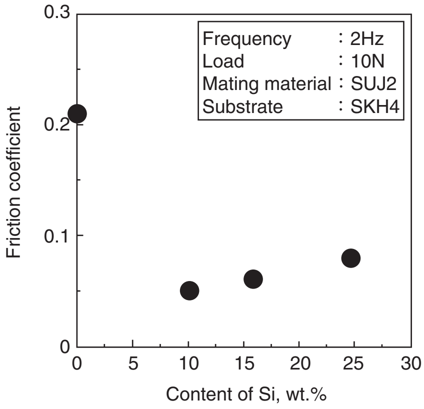
(b) Specific wear rate of mating materials

Fig. 4 Tribological properties of DLC-Si and hard films

While DLC-Si films deposited by the direct current plasma CVD method have superior film properties and are better suited to mass-production, there is a restriction in applied materials and application development because the temperature during deposition goes up to 500-600℃. In order to solve this problem, the JTEKT Group has striven to develop technology to enable depositing films even at 200℃ or lower while securing the same ease of coating of 3D objects and mass-production fitness of the plasma CVD method. The development of plasma state control, substrate interface control and a new intermediate layer have enabled deposition of DLC films at low temperatures by the plasma CVD method. With regard to DLC films deposited at 200℃, film properties can be controlled by adjusting the film composition. For example, super-hard films of HV1 500 or higher are superior in wear resistance (**Fig. 5**(a))[5]. And it also is possible to adjust properties depending on the application, for example, using low-friction films for lubrication whose friction coefficient is 0.05 (**Fig. 5**(b)). At present, the JTEKT Group is promoting the practical application of films based on advantages in properties as discussed in the next section and will further endeavor to improve properties.



(a) Wear resistance



(b) Frictional property

Fig. 5 Tribological properties of DLC films deposited at low temperatures

Table 1 DLC film properties

Properties	Contents
Low friction coefficient	Low friction coefficient in dry condition
Wear resistance	Hard and high wear resistance
Corrosion resistance	Superior in corrosion and chemical resistance
Anti-adhesion	Low adhesion with aluminum alloy
Water repellency	Low wettability and high water repellency
Antifouling property	Resistant to be fouled
Biocompatibility	Non-allergic due to carbonic material
Electrical characteristics	Electric insulation
Optical characteristics	Infrared ray permeable through
Acoustic characteristics	High elastic modulus and good sound transmission
Gas barrier characteristics	Gas permeation prevention

4. Application Examples

DLC films possess not only excellent tribological properties but also other properties such as high hardness and chemical stability (**Table 1**)[6]. These properties originate from diversity of DLC films having an amorphous structure and are influenced by deposition methods and processing conditions. Application examples by making use of particular properties of the DLC films are hereunder introduced.

4. 1 Friction and Wear Properties

The most outstanding feature of DLC films is their excellent tribological properties such as low friction coefficients, high wear resistance, and less attack to mating materials that are not available in other hard films. Low-temperature DLC films developed by JTEKT also possess excellent friction and wear resistance properties that can be optimized to best meet the required purpose by adjusting their film composition.

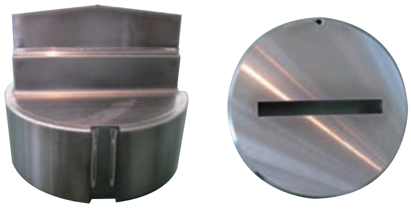
Currently, the application of DLC films to a wide range of sliding components is being pursued. Automotive components, hard disc components, cutting tools, etc. Are examples of applications for which DLC films have already been adopted. Moreover, the excellent properties of DLC films have begun to attract attention from industries involving parts used in fresh or sea water environments where lubrication does not work properly. It is expected that applications for sliding parts used in poor lubrication conditions and parts requiring anti-corrosion properties will expand.

4. 2 Corrosion Resistance

DLC films, whose components are carbon and hydrogen, are known to be chemically stable and therefore superior in corrosion resistance against chemicals, etc. For this reason, it is possible to replace expensive stainless steels with low-cost materials deposited with DLC films. Furthermore low-temperature DLC films of JTEKT are deposited at a temperature lower than the level at which stainless steels are sensitized, which makes it possible to further improve the anti-corrosion surface of stainless steels. Not only for parts used in water environments but also medical devices, chemical-related devices, chemical-distribution piping parts, etc., DLC films can be applied and are already in use. However, pin holes sometimes appear depending on deposition methods, and therefore careful attention should be paid to select the proper deposition method.

4. 3 Anti-Adhesion

DLC films are superior in anti-adhesion in comparison with ferrous materials and, especially, their adhesion property with aluminum materials is low. The chemical stability and surface smoothness of DLC films contribute to this property, which makes DLC films suitable for cutting tools for aluminum materials, especially for drilling deep holes under poor lubrication conditions. DLC films can be also applied to tools and dies involving sliding to prolong cleaning cycles thanks to this anti-adhesion property (**Fig. 6**)[7].



(a)Punch (b)Die

Fig. 6 Cutoff tools

4. 4 Wettability and Antifouling Property

Compared with metal surfaces, DLC film surfaces are not easily wetted or fouled due to their low surface energy. It is possible to control surface wettability by adding elements or exposing plasma to the surface, and a surface design to meet application requirements is possible. Regarding the low-temperature DLC films of JTEKT in particular, wettability against liquid can be adjusted by changing the film composition. This property originates from the top-surface condition of the DLC films. It is expected that it will find broad new applications for antifouling, control of friction property in the environment of fluid lubrication, etc.

4. 5 Biocompatibility

Carbon and hydrogen, of which DLC film are composed, possess excellent biological compatibility and antithrombogenicity (blood platelets hard to adhere or cohere). Efforts are underway to apply such films to medical instruments like stents and parts within organisms such as artificial vessels and joints. Application of DLC films to medical instruments is proceeding more quickly than applications to parts in organisms. Examples already showing good results are painless needles thanks to the biological compatibility and low frictional properties of DLC films and reusable surgical knife holders whose number of re-use times is increased thanks to biocompatibility and chemical stability. And, as there is no risk of metal allergy, DLC films have been successfully applied to commodities such as wristwatches, necklaces, etc.

4. 6 Electrical Characteristics

DLC films containing hydrogen have good insulation properties, and it is known that the electrical resistance of films correlates with the amount of hydrogen. Therefore, studies are underway to reduce electrical resistance by decreasing the amount of hydrogen in order to secure electrical conductivity and also provide electrical conductivity by adding metallic elements. In recent years, carbonic thin films have been studied as a low dielectric constant film for next-generation silicon integrated devices. Future research on this will be attracting attention in view of the increasing application of electronic parts.

4. 7 Optical Characteristics and Heat Radiation Capability

DLC films can let through light from visible regions to infrared region depending on the film thickness. Permeation capability in visible regions is lowered as film thickness increases, so super-thin films are considered suitable as protective films for sunglasses, glasses for bar code readers or optical glasses. When the film thickness is several μm, the color is black and thermal conduction is comparatively good, and such film can be used as a heat-radiation material.

4. 8 Acoustic Characteristics

Due to the high elastic modulus and superior sound transmission properties of DLC films, the application of DLC films for sound instrument parts is considered as well. Speaker vibration plates of ear phones are the first example of such application.

4. 9 Gas Barrier Characteristics

As far as gas barrier capability of DLC films is concerned, such films that contain comparatively large amounts of hydrogen atoms and small amounts of sp^3 bonding are known to be effective. For this reason, DLC films have already been applied to inner surfaces of PET bottles for drinks. In this application, the DLC films prevent oxygen from penetrating through to the PET bottle inside and contribute to keeping the flavor and taste of contents for a long time. DLC films for PET bottles are high molecular type soft films with the thickness of about several 10 - 100 nm.

5. Conclusion

In this report, the JTEKT Group's deposition technology of DLC films has been introduced together with its film properties and some application examples. In order to achieve the required properties for each application, it is necessary to study from the stage of deposition processes, and it is important to properly control and adjust DLC films. Production costs, which used to be a bottleneck in mass-production, are gradually lowering thanks to the progress of deposition technology and the spread of film applications. Especially, DLC films have begun to be applied to automotive parts which require high reliability and durability, and thereby DLC films are predicted to be rapidly and more widely used in various applications. It is our pleasure that this report will be of assistance for studying product development of DLC films for selecting the most suitable films for application.

References

1) S. Aisenberg and R. Chabot: Ion-Beam Deposition of Thin Films of Diamondlike Carbon, J. Appl. Phys., 42, (1971) 2953.
2) J. Robertson: Diamond-like amorphous carbon, Mat. Sci. & Eng., R37 (2002) 129.
3) K. Yukimura: Houden Pulazuma Kougaku, Ohmsha, Ltd. (2008) 25.
4) H. Mori: NEW DIAMOND, 26, 1 (2010) 50. (in Japanese)
5) K. Matsuo, M. Suzuki, T. Saito: Effect of Si Content in DLC Film on Friction and Wear Properties, JAST Tribology Conference, Tokyo, May 2010, 93.
6) H. Saito, N. Ootake, T. Nakahigashi: Handbook of diamond-like carbon films, NTS (2006) 80.
7) T. Saito, H. Fukami, T. Iseki, H. Tachikawa: Effect of DLC-Si coating on sheet metal forming tool life, JAST Tribology Conference, Tokyo, May 2004, 299.

M. SUZUKI*

K. YAMAKAWA**

T. SAITO*

* *Material Engineering R&D Dept., Research & Development Center, Doctor of Engineering*

** *Material Engineering R&D Dept., Research & Development Center*