CHAPTER 17

Applications in carbon-based film

17.1 Overview

Carbon-based film is a type of material with carbon as the main component that is obtained by physical vapor deposition (PVD) or chemical vapor deposition (CVD) technology. Because of its different composition and structure, it has a variety of special functions to meet the needs of aerospace, military industry, information, energy, medical, high-end manufacturing, and other fields.

17.1.1 Types of carbon-based films

Carbon exists in nature in two different forms, namely, diamond and graphite, because of the different combination modes between carbon atoms. The carbon atoms in diamond are combined in the form of sp^3 hybrid bonds, and the carbon atoms in graphite are combined in the form of sp^2 hybrid bonds. Owing to the different structures, their performances are very different.

In the process of preparing carbon-based films by PVD or CVD, hydrogen-containing gas is usually introduced. In heating or gas discharge plasma, different types of carbon-based films are formed; these can be diamond-like films with regular tetrahedral crystals and graphite-like films with layered crystals, or they can be amorphous films containing hybrid forms of the two bonds.

17.1.2 Ternary phase diagram of carbon-based film

Fig. 17.1 is a ternary phase diagram of carbon-based films [1], which is a three-dimensional cross-ring network structure composed of sp^3 hybrid carbon atoms, sp^2 hybrid carbon atoms, and hydrogen atoms. The ternary phase diagram shows that there are various carbon-based films with different percentages of sp^3-C, sp^2-C, and H. In addition to diamond films and graphite films, various types of amorphous carbon-based films can be obtained. The types are as follows:

1. Diamond-like carbon (DLC) film is a carbon-based film with manly a sp^3 structure.
2. Graphite-like carbon (GLC) film is a carbon-based film with mainly a sp^2 structure.
3. Polymer-like carbon (PLC) film is a carbon-based film with high hydrogen content and similar hydrocarbon polymer characteristics.

Modern Ion Plating Technology
DOI: https://doi.org/10.1016/B978-0-323-90833-7.00017-6

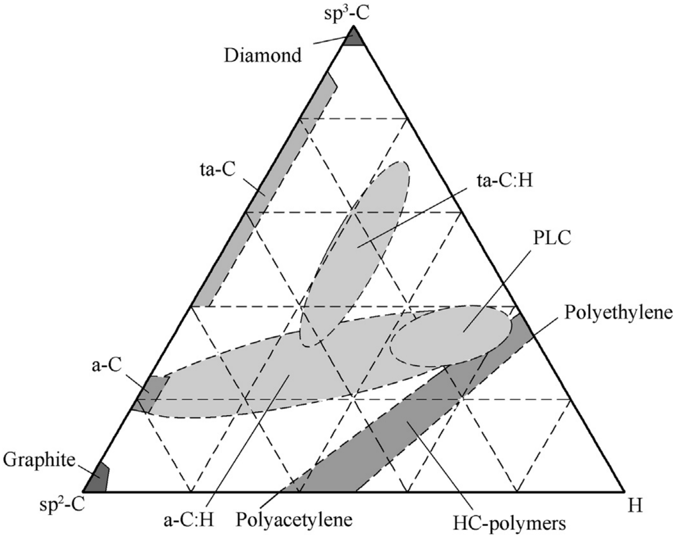

Figure 17.1 A ternary phase diagram of the hydrocarbon system in carbon-based film [1].

Table 17.1 Comparison of properties between diamond film and amorphous carbon-based film.

Properties at 300K	Diamond film	Amorphous carbon-based film
Carbon composition	100% sp^3	15%–85% sp^3
Percentage of Hydrogen (%)	0.1–1.0	1.0–60
Density (g/cm^3)	>3.5	1.5–1.8
Hardness (GPa)	100	5–80
Resistivity (Ω/cm)	10^{16}	10^{-1}–10^{13}
Optical energy gap (eV)	5.5	0.8–4.0

The upper left of the phase diagram contains hydrogen-free DLC film dominated by tetrahedral amorphous carbon, the lower left contains GLC film dominated by graphite-like amorphous carbon film, and the lower right contains PLC film dominated by high hydrogen content. In the middle region of the ternary phase diagram, DLC films with different hydrogen content can be obtained with different deposition processes.

Depending on the structural and performance requirements, carbon-based films can be doped with nonmetallic elements such as hydrogen and nitrogen and various metal elements (W, Ti, Mo, Al, etc.). The properties of carbon-based films with different compositions and structures vary greatly. Table 17.1 lists the properties of diamond films and amorphous carbon-based films.

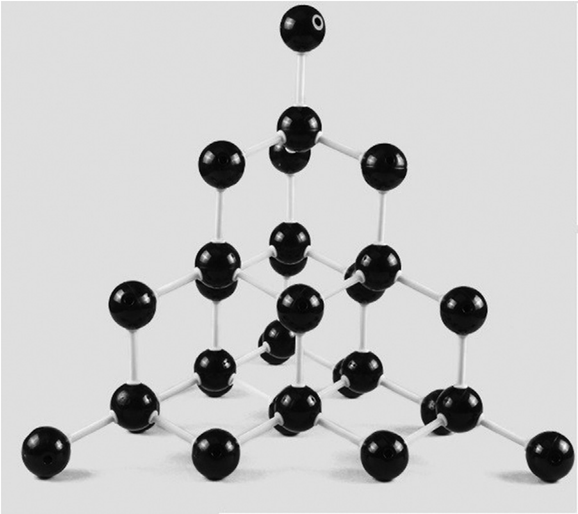

Figure 17.2 The three-dimensional structure of diamond.

17.2 Structure of carbon-based films

17.2.1 Structure of diamond film

Diamond film refers to a type of carbon-based film artificially synthesized by low pressure or atmospheric pressure CVD. Diamond is one of the allotropes of carbon. When carbon atoms form diamond, the 2s, $2p_x$, $2p_y$, and $2p_z$ orbits of carbon atoms will form four sp^3 hybrid orbits, and the symmetry axis points to the four corners of the tetrahedron to form a regular tetrahedral crystal structure, with a bond length of 0.154 nm and a bond angle of 109 degrees 28 minutes. As shown in Fig. 17.2, the four vertex directions of the tetrahedron are combined with the other four atoms by sp^3 hybrid bonds to form a three-dimensional grid.

17.2.2 Structure of diamond-like carbon films

DLC film is a kind of metastable amorphous material with a diamond bonded structure and a graphite bonded structure [2,3]. According to whether the film contains hydrogen, DLC films can be divided into hydrogen-containing DLC films and hydrogen-free DLC films:

1. Hydrogen-containing DLC film have a mainly sp^3 hybrid bond content less than 70% and a hydrogen content between 20−50 at.%, referred to as a-C:H film.
2. Hydrogen-free DLC film are mainly tetrahedral amorphous carbon with sp^3 hybrid bond content higher than 70%, referred to as tetrahedral amorphous carbon (ta-C) film.

Carbon atoms in DLC films can covalently bond to four other carbon atoms, and each carbon atom can interact with distant atoms through the van der Waals force to form a complex spatial network cross-structure. The bonding content of C—C and C—H sp3 is in the range of 15—85 at.%, while the hydrogen content can range from 1 at.% to more than 60 at.%. Therefore the properties of the films can vary widely.

17.2.3 Structure of graphite-like carbon films

The concept of GLC film was gradually put forward in 2000 [4—6]. Yang et al. [7] proposed that carbon-based films can be divided into GLC film and DLC film. DLC film has a mainly sp^3 structure with high hardness, and graphite-like film has a mainly sp^2 structure, but the hardness of graphite-like film can be equivalent to that of diamond-like film. The hardness of graphite-like film that was prepared by unbalanced magnetron sputtering technology can reach 4000 HV, showing excellent wear resistance.

17.2.4 Structure of polymer-like carbon films

PLC film is made of a kind of hydrogenated amorphous carbon (a-C:H) film with characteristics similar to those of hydrocarbon polymer, such as a hydrogen content higher than 35%, hardness lower than 10 GPa, and an optical band gap width of 1.7—4 eV [8,9]. In addition to hydrogen, PLC film has a higher content of sp^3 hybrid carbon atoms (most of which are bonded with hydrogen), so it is located far from sp^2 hybrid carbon atoms in the ternary phase diagram (as shown in Fig. 17.1). To distinguish PLC film from other a-C:H film with low hydrogen content and high hardness, PLC film is also called soft or highly hydrogenated a-C:H or DLC film.

17.3 Preparation technology and performance of carbon-based films

17.3.1 Preparation technology and performance of diamond films

17.3.1.1 Preparation technology of diamond films

Since researchers discovered in the 18th century that diamond is made of carbon atoms, they have carried out research on synthetic diamonds. Since the advancement of high-pressure deposition technology in the 1950s, breakthroughs have been achieved in the research into synthetic diamonds.

1. CVD

CVD technology employs a chemical vapor reaction to prepare diamond films. That is, the elements and reaction source gases (such as methane, hydrogen and argon) participating in the composition of diamond film compounds are decomposed, desorbed, and combined by high temperature or plasma, and finally a uniform diamond film is deposited on the substrate surface. The CVD method to prepare diamond films includes two categories: heat chemical vapor deposition (HCVD) [10,11] and plasma chemical vapor deposition (PCVD). The comparison of various methods for synthesizing diamond films is shown in Table 17.2.

Table 17.2 Comparison of vapor-phase synthesizes for diamond film.

Methods		Deposition rate (μm/h)	Maximum deposition area (cm^2)	Substrates	Advantages	Disadvantages
Heat chemical vapor deposition	Flame	30−100	<1	Si, Mo, TiN	Simple process	Small area, poor stability
	Hot wire	0.3−2	100	Si, Mo, SiO_2	Simple process, large area	Vulnerable to contamination
Plasma chemical vapor deposition	DC discharge (low pressure)	<0.12	70	Si, Mo, SiO_2	Simple process, large area	Poor quality, low rate
	DC discharge (medium pressure)	20−25	<2	Si, Mo	Fast rate, good quality	Very small area
	DC plasma jet	930	<2	Si, Mo	Fast rate, good quality	Small area, defective
	RF (low pressure)	<0.1	—	Si, Mo, BN, Ni, SiO_2	—	Low rate, poor quality
	RF (normal atmosphere)	180	3	Mo	Fast rate	Small area, poor stability
	Electron cyclotron resonance (0.9−2.45 GHz)	1 (low pressure), 30 (high pressure)	40	Si, Mo, WC, SiO_2	Good quality	Low rate, small area

2. Hot-filament CVD technology

Fig. 17.2 shows the working principle of hot-filament CVD technology. In this method the workpiece (Si, Mo, quartz glass sheet, etc.) is placed in the reaction chamber made of quartz glass tube, and the system is vacuumized to the predetermined value. The raw gas is then introduced to make the gas pressure in the reaction chamber reach 10^3-10^5 Pa, the external electric furnace is raised to the predetermined temperature, and the filament (tungsten or tantalum filament) is then heated to more than 2000°C [10,11]. The distance between the hot wire and the substrate ranges from 1 mm to tens of millimeters, and the workpiece temperature is 500°C–900°C. Under such reaction conditions, CH_4 and H_2 are pyrolyzed, and carbon is deposited on the workpiece in the form of diamond to obtain diamond film products. The advantages of the hot-wire method are its simple equipment and easy operation. The advantage is that the growth rate is slow (1–2 μm/h), and the chemical composition of the hot wire will pollute the diamond film. Fig. 17.3A is the schematic diagram of hot-wire CVD process, and Fig. 17.3B and C are the hot-wire arrangement diagrams [10].

3. Microwave plasma CVD technology

Plasma CVD technology includes three types: direct current (DC) plasma, high-frequency plasma, and microwave plasma. Fig. 17.4 is a schematic diagram of the microwave PCVD process [12]. The microwave that is generated by the microwave generator is coupled into the reactor through the waveguide, thereby generating a glow discharge. On the one hand, the microwave in the reactor ionizes the mixed gas of CH_4 and H_2 into plasma

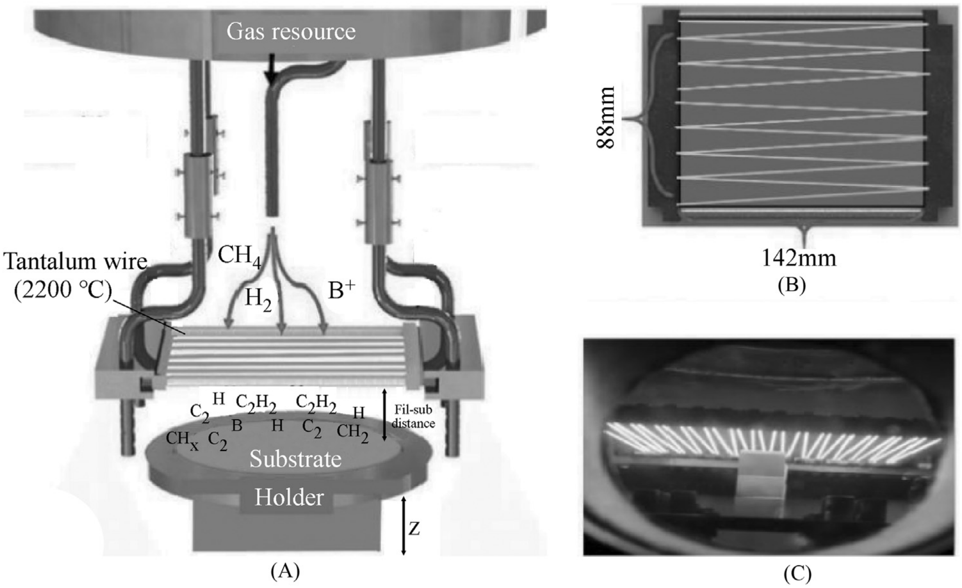

Figure 17.3 Schematic diagram of hot-filament chemical vapor deposition process [10].

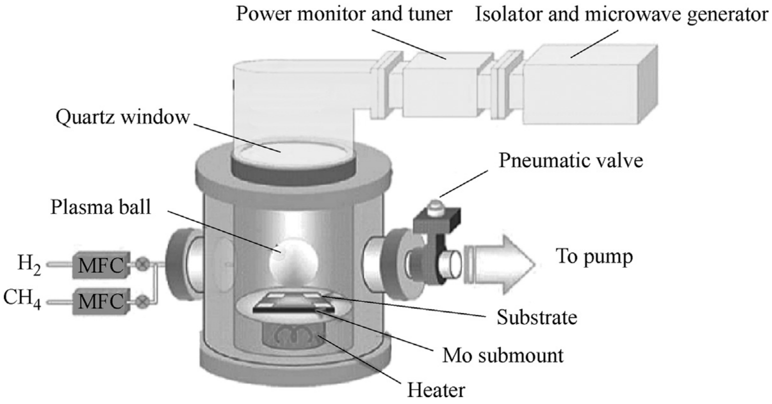

Figure 17.4 Schematic diagram of microwave plasma chemical vapor deposition [12].

state; on the other hand, it heats the substrate temperature to 700°C−900°C. Therefore the output power of the microwave plasma will affect not only the substrate temperature, but also the quality of the reactants [13,14]. When this method is used, the deposition rate of diamond is 3 μm/h. At present, the most popular devices for PCVD include the ring antenna type, cylindrical resonator type, quartz bell jar type, and ellipsoidal resonator type. Most of them have a frequency of 2.45 GHz and a power of 5−6 kW.

4. DC plasma jet arc CVD technology

In a DC plasma jet CVD device, the nozzle is composed of a cylindrical nozzle (anode) and a rod cathode in the cylinder; the cathode is made of nickel, and the anode material is red copper. The working principle is as follows. The CH_4 and H_2 gas that are introduced between the cathode and anode generate discharge and a variety of plasmas such as C, H, and H_2. Then, under the action of the pressure difference, the plasma is ejected from the nozzle at a high speed close to the velocity of sound to form a plasma jet, which collides with the water-cooled substrate and produces diamond films [15,16]. The advantage of this method is that it produces high-quality large-size diamond films at a very fast speed; the fastest growth rate can reach 930 μm/h. The disadvantage is that the equipment is complicated and expensive. The famous American Norton Company uses this method to produce high-quality diamond films for industrial use.

17.3.1.2 Properties of diamond films

The unique crystal structure of diamond determines its excellent physical and electrochemical properties.

1. Mechanical properties

The C−C covalent bond that is formed between two adjacent carbon atoms in the diamond unit cell gives diamond ultrahigh hardness and Young's modulus.

Because of their ultrahigh hardness (~90 GPa) and wear resistance, diamond films are widely used in the field of mechanical manufacturing [17–19], such as cutting tools and wear-resistant parts. The ultrahigh Young's modulus facilitates application of these films in surface pressure sensors.

2. Electrical properties

   The electrons in the C–C bond composed of adjacent carbon atoms in diamond are stable and difficult to be excited. The forbidden bandwidth is 5.5 eV, which is about five times that of silicon. The resistivity of diamond at room temperature is about 10^{12} Ω/cm, making it a good insulating material. However, the ion-doped diamond becomes a semiconductor, owing to its wide band gap and stable electrochemical properties. It can be used as an electrode material for high-temperature semiconductor current limiters, radiation detectors, transistors, integrated circuits, supercapacitor electrodes, and so on [20,21].

3. Optical properties

   In addition to the 1.8- to 2.5-μm wavelength in the infrared region, diamond has good optical transparency in the wavelength range from 225 nm in the ultraviolet region to 25 μm in the infrared region. This optical characteristic makes it a corrosion-resistant and wear-resistant material for infrared optical windows [22,23].

4. Thermal properties

   The thermal conductivity of diamond is the highest among all materials at present, and its thermal expansion coefficient is similar to that of the silicon materials that are commonly used to prepare electronic devices. It is an ideal heat dissipation material for microwave transmitters, high-performance chips, and mid- and far-infrared lasers [24].

5. Chemical properties

Diamond is a good corrosion-resistant material because of its very stable chemical properties at room temperature and pressure and excellent corrosion resistance to all acid and alkali solutions.

17.3.1.3 Application of diamond film

Diamond film has high hardness, good wear resistance, good insulation performance, and excellent thermal, electrical, optical, and acoustic properties. Therefore it has great application potential in the fields of high-speed computers, superlarge integrated circuits, high-temperature microelectronics, optoelectronics, space technology, laser technology, and modern communications [25–27]. Diamond film is mainly used for the following:

1. The heat sink of integrated circuits and laser devices
2. Infrared windows
3. Very large integrated circuit chips
4. Thin-film sensors

Table 17.3 Typical application fields of chemical vapor deposition diamond films.

Implemented application areas	Potentially important application areas (examples)
1. Superhard coating of cutting tools	Semiconductor power devices, antiradiation devices, high voltage devices, microwave power devices, and high-power millimeter wave amplifiers working at high temperature
2. Diaphragm coating of loudspeaker	Graphite fiber—reinforced composite material coated with diamond film can be used to manufacture substrates and components that are resistant to impact and heat stress
3. X-ray window	High-strength transparent material with thermal shock
4. Surface coating of optical substrates and components	Magnetic disk and optical disk coating and millimeter wave radome coating
5. Insulating heat dissipation substrate for semiconductor lasers and high-power integrated circuits	Boron-doped diamond film foam electrode for treatment of wastewater in enclosed spaces

5. High-fidelity speaker diaphragms
6. Wear-resistant surface layers of mechanical parts
7. The heat sink materials of transistor diodes and laser diodes
8. Thermistor sheets (temperature up to 600°C)
9. The surface layer of antichemical corrosion

The successful preparation of a three-dimensional boron-doped diamond foam electrode with uniform distribution and adjustable size is conducive to the promotion of the application in the fields of electrocatalysis, electrosynthesis, electrochemical sensing, supercapacitors, and so on. The typical application areas of CVD diamond film are shown in Table 17.3.

17.3.2 Deposition technology and properties of diamond-like carbon films

17.3.2.1 Deposition technology of diamond-like carbon films

Since Aisenberg and Chabot [28] first used ion beam deposition technology to prepare DLC films at room temperature in the 1970s, a variety of DLC film deposition technologies have been successfully developed, mainly divided into PVD and CVD. Fig. 17.5 shows the relationship between common DLC deposition technologies and their corresponding ion energy [29—31]. Generally speaking, DLC films that are prepared at an ion energy of 1—100 eV have dense structure and high content of sp^3 hybrid bond, showing good mechanical properties. DLC films that are prepared at

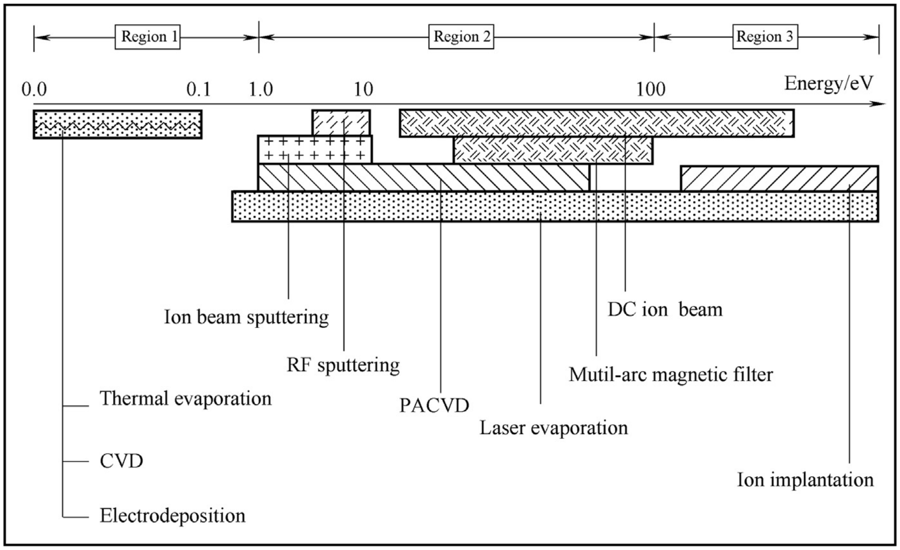

Figure 17.5 Ion energy distribution of diamond-like carbon film preparation technology [15].

an energy less than 1 eV are deposited mainly by thermal evaporation, CVD, and electrochemical deposition, showing loose structure and poor adhesion. DLC films that are prepared at an energy higher than 100 eV are produced mainly by high-energy ion implantation technology, showing compact structure, strong adhesive force, but low deposition rate. Therefore DLC films that are deposited in the middle energy of ions are more suitable for practical production. The following discussion briefly introduces DLC film deposition technology that is suitable for industrial-scale production.

1. PVD technology

DLC that is film prepared by PVD usually has high-purity graphite as a solid carbon source and uses evaporation or energetic ion bombardment sputtering to make carbon separate from the graphite target and deposit on the substrate surface. Hydrocarbon gases such as methane and acetylene are used as gas carbon sources. The common deposition methods of DLC films are ion beam deposition technology, sputtering deposition technology, vacuum cathode arc deposition technology, and pulsed laser deposition (PLD) technology.

1. Ion beam–assisted deposition (IBAD) technology

In the late 1970s, Weissmantel et al. [32] improved ion beam deposition technology and developed IBAD technology, which uses composite surface ions combined with evaporation or sputtering and ion implantation. This technology uses two sets of independent ion sources. One is used to sputter the graphite target to generate a carbon ion beam and then prepare thin films; the other is used to bombard growing DLC films. The comprehensive properties of DLC thin films that are obtained by this method are greatly improved. The ion sources that are generally used in IBAD technology are Kaufman ion source, cold cathode ion source, and End-Hall gateless ion source. IBAD technology has the advantages of a low deposition temperature; easy control of deposition conditions, such as independent control of ion energy and ion current density in a wide range; strong adhesive force; and low cost.

2. Sputtering deposition technology

   Magnetron sputtering technology is the most common deposition technology in the industrial production of DLC films. Usually, argon ions excited by a radio frequency (RF) power supply or magnetic field are used to bombard solid graphite to form sputtered carbon atoms, which are then ionized into carbon ions, thereby depositing DLC films on the substrate. On the one hand, this technology increases the sputtering rate of graphite; on the other hand, it also increases the density and control the sp^3 hybrid bond content in the film. Therefore magnetron sputtering technology is currently a major mainstream technology for preparing DLC films at low temperatures. At present, sputtering deposition technology of DLC film mainly includes ordinary magnetron sputtering technology and unbalanced magnetron sputtering technology. The closed magnetic field that is generated by the unbalanced magnetron sputtering technology can expand the plasma to the range of 200–300 mm in front of the sputtering target, which ensures that the surface of substrate is completely immersed in the plasma, and the sputtered ions and particles are deposited on the surface of substrate at the same time. High-density plasma bombarding the substrate with a certain energy plays the role of ion bombardment–assisted deposition, which significantly improves the quality of the film, makes it easy to obtain films with high adhesion and high density, and avoids excessive internal stress.

3. Cathodic vacuum arc deposition technology

   The power supply for maintaining arc discharge is characterized by low voltage (15–150 V) and high current (20–200 A). The current density is as high as 10^6–10^8 A/cm^2, the ionization rate of evaporated carbon atoms is 60%–80%, and the energy of the output carbon ions is 100 eV. This method was used to prepare ta-C film with high sp^3 hybrid bond content. However, the properties of the films are significantly reduced by the macroscopic particles generated by the graphite target under the action of the electric arc. Aksenov et al. developed the filtered cathodic vacuum arc deposition technology, which can significantly eliminate macroscopic carbon particles during the deposition process and improve the quality of DLC film. The prepared DLC film has high hardness (58 GPa), a low friction coefficient of 0.1, a high elastic modulus (350 GPa), high internal stress (9–10 GPa), and a strong adhesive force.

4. PLD technology

PLD technology uses high-power pulsed laser beam to evaporate a graphite target to produce high-temperature and high-pressure carbon plasma, which is directionally emitted and deposited on the substrate to form DLC film. a-C films with high sp^2 content (about 70%) with a hardness of only a few GPa can be prepared by PLD technology. The ta-C films with high sp^3 content (75%–90%) with a hardness of 80 GPa can also be prepared, and the friction coefficient and wear rate in atmospheric environment are as low as 0.1 and 1.6×10^{-8} $mm^3/(N \cdot m)$, respectively.

5. Plasma-enhanced CVD technology

Plasma-enhanced chemical vapor deposition (PECVD) technology uses glow plasma discharge to dissociate and excite hydrocarbon mixed gas sources to produce various ions, active atoms, and groups, which can prepare high-quality DLC films on a large area substrate. PECVD technology has the following advantages: low deposition temperature, deposition on complex surface and easy control of process parameters. It is one of the most common technologies for preparing DLC films.

6. Typical PECVD technology

PECVD technology mainly includes direct current glow discharge technology, RF glow discharge technology, electron cyclotron resonance (ECR) CVD technology, and so on. Among them the composite deposition technology of PECVD and in situ nitriding recoating is used to obtain the hard coating with an adhesive force of 69 N, high hardness, a low friction coefficient, and excellent wear resistance. This technology also incorporates metal elements into DLC films. For example, iron-doped DLC films have an ultralow friction coefficient (≤ 0.01) and long life (not worn through after 4×10^5 cycles). Moreover, the conditions of the ultralow friction coefficient in the atmosphere can be expanded from the previous high load and high velocity (≥ 15 N and ≥ 0.12 m/s, respectively) to medium load and medium velocity (5 N and 0.05 m/s, respectively) [33].

7. Plasma immersion ion implantation deposition technology

Wei Ronghua at the Southwest Research Institute in the United States developed special plasma immersion ion implantation deposition technology by adding a

Figure 17.6 Schematic diagram of plasma immersion ion implantation deposition technology [34].

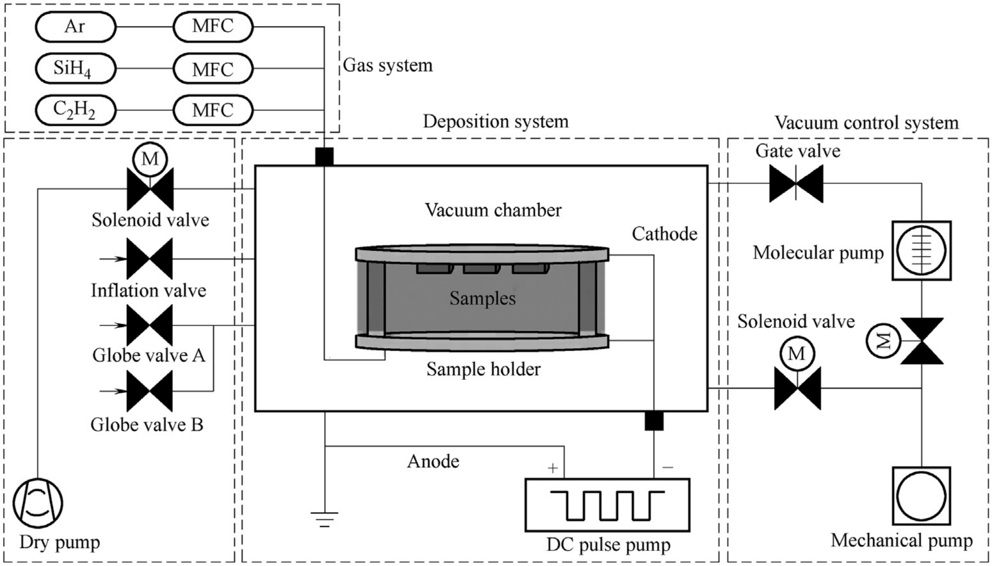

Figure 17.7 Schematic diagram of flat cathode plasma-enhanced chemical vapor deposition equipment to prepare ultrathick diamond-like carbon film [35].

metal mesh cage outside the plating parts, as shown in Fig. 17.6, to increase the density and intensity of the plasma. This deposition technology realizes the uniform deposition of DLC films with high adhesive force on the surface of large-size and supersize workpieces [34]. In addition, on the basis of the principle of hollow cathode discharge, Wei Ronghua have developed a set of unique coating technology for the inner wall of pipes, which can deposit DLC films on the inner surface of various pipes, such as slender pipes and curved pipes with a length of up to 10 m.

Xue Qunji and Zhang Guangan's team at Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, further combined in situ plasma immersion ion implantation technology and hollow cathode high-density plasma enhancement technology to realize rapid and large-area deposition of DLC films [35]. A schematic diagram of the equipment is shown in Fig. 17.7. The hollow cathode effect of the flat cathode, the external auxiliary cathode, and the tube are used to deposit uniform and dense DLC films with a thickness of more than 50 μm on the plane workpiece, piston ring functional surface, and pipe inner surface with different shapes (straight pipe, right angle pipe, and U-shaped pipe) and different metals (304 stainless steel, 6063 Al, and cast iron). A series of ultrathick DLC films containing fluorine, sulfur, silicon, and nitrogen have been successfully developed. Fig. 17.8 shows some superthick DLC products [35].

8. Ion beam CVD technology

Ion beam chemical vapor deposition technology uses various ion sources (e.g., anode layer ion source, Hall ion source) to ionize hydrocarbon gas to produce

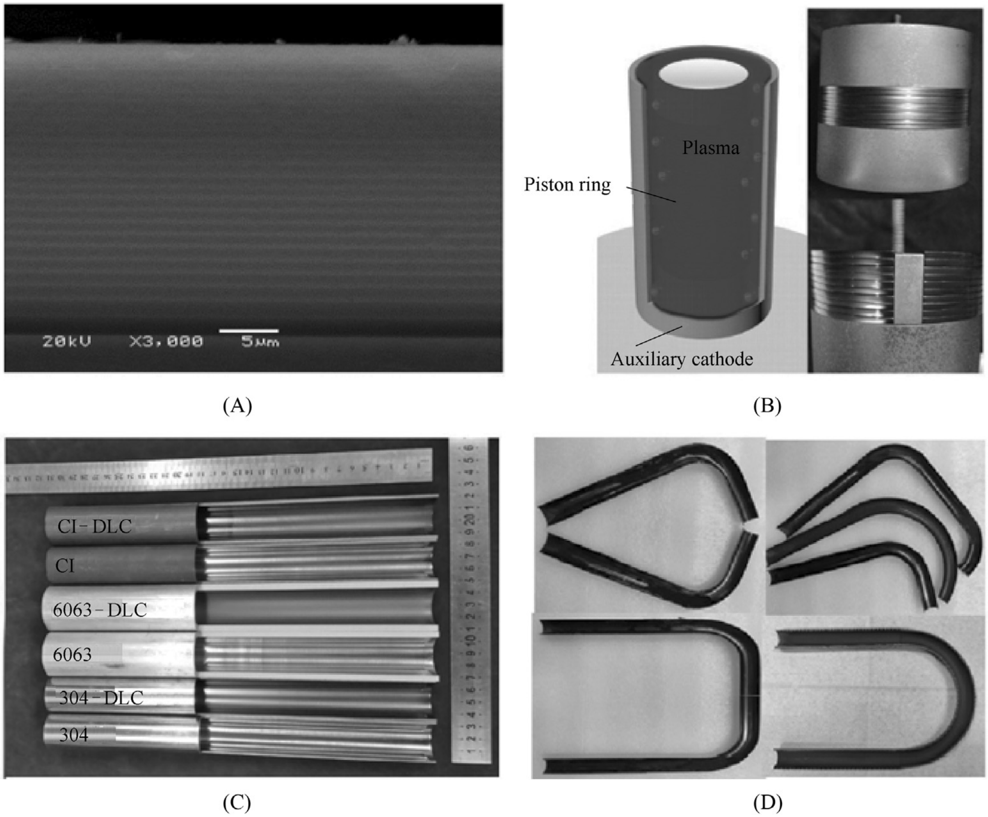

Figure 17.8 Deposition of ultrathick diamond-like carbon film on the plane, the outer surface of a piston, and the inner wall of a metal pipe.

carbon or hydrocarbon ions, and obtain energy under the acceleration of electric field to prepare DLC film on the substrate. Sun et al. [36] used the anode layer ion source (high ionization rate and stable long-term plasma operation) and magnetron sputtering composite technology to carry out the composition and structure design and process preparation of Cu/Cr-DLC thin films. The deposited metal-doped DLC film has a multilayer structure with a thickness of 1.73 μm, adhesive force greater than 45 N, hardness of 27.1 GPa, residual stress of 1.0 GPa, a friction coefficient of about 0.1, and an extremely low wear rate.

17.3.2.2 Properties of diamond-like carbon films

DLC film has many properties similar to diamond film, such as high hardness, high wear resistance, good chemical stability, thermal conductivity, electrical insulation, light permeability, corrosion resistance and biocompatibility. However, DLC film has many unique advantages compared with diamond film, such as a low deposition temperature, a large deposition area, simple deposition conditions, smooth surface, and so on. Therefore as a new functional film material, DLC film has great application prospects in many fields.

The structure and properties of DLC films are adjusted through the doping of heterogeneous elements, and the type and content of doped elements have an important impact on their structure and mechanical properties. Fig. 17.9 shows the effect of doped elements on the improvement of film properties.

Adjusting the bonding mode of doping elements and carbon atoms, the surface chemical state, the ratio of sp^3 and sp^2 hybrid bonds, and the number of active σ dangling bonds can effectively alleviate the accumulation of internal stress, reduce high brittleness, improve binding force, enhance the mechanical properties, and greatly enhance the antifriction and wear resistance, thereby improving the stability, durability, and adaptability of the DLC film under severe service conditions.

In addition, the synergistic use of the small size effect of metal nanocrystals and the high chemical stability and excellent mechanical tribological properties of DLC films can transform it from insulators to semiconductors, greatly expanding application in the fields of biomedicine, electricity, optics, and magnetism. The metal-doped DLC composite film is realized mainly by magnetron sputtering technology and multiarc ion plating technology.

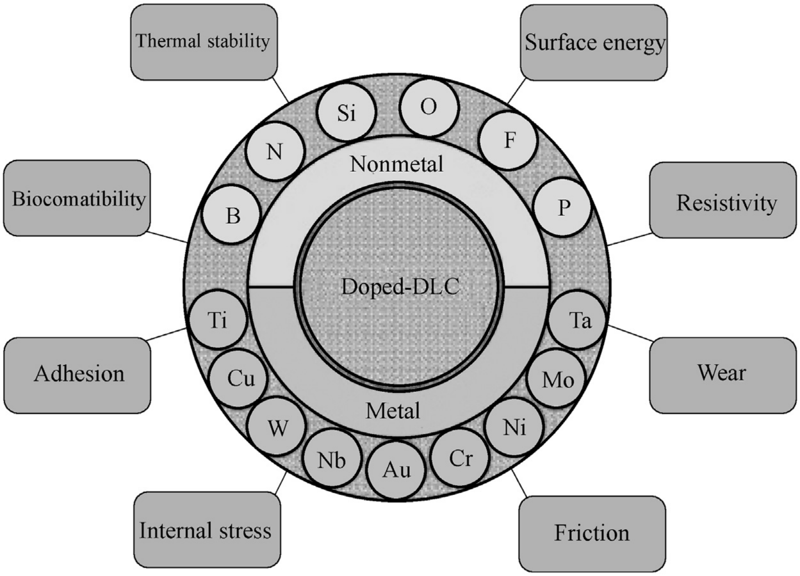

Figure 17.9 Schematic diagram of the effect of doping elements on improving the properties of diamond-like carbon films.

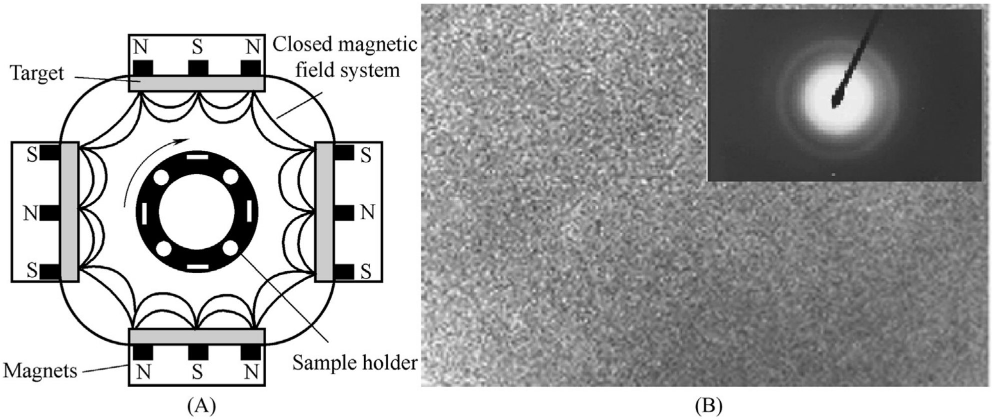

Figure 17.10 (A) A schematic diagram of an unbalanced closed-field magnetron sputtering device. (B) A selected area diffraction diagram of graphite-like carbon.

17.3.3 Preparation technology and properties of graphite-like carbon films

In 2000, Teer Coating Company used a closed-field unbalanced magnetron sputtering system (Fig. 17.10) to successfully prepare an amorphous carbon-based film in which sp^2 hybrid carbon is absolutely dominant; it was named graphite-like carbon based (GLC) film [4]. The technical technology of GLC films mainly include DC glow discharge technology [37], CVD technology [38], ion beam—assisted sputtering technology [39,40], and magnetron sputtering technology [5,6]. Among them, magnetron sputtering technology is widely used to prepare GLC films because of its advantages, such as a high deposition rate, low temperature, strong adhesion, a smooth surface, a compact structure, a wide selection of targets, a large working pressure range, process stability, and easy large-scale production. Because of its graphite-like structure, GLC film has good self-lubricating properties in both air and humid environments, and its high hardness provides higher load-bearing capacity and wear resistance. Therefore it has great potential in tribological applications in ambient air, wet environments, and water [4].

In China the research team of Xi'an Jiaotong University and Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, prepared graphite-like films with sp^2 content of 60%—80% and hardness of 25 GPa by magnetron sputtering deposition technology [41]. He Jiawen et al. prepared the GLC film with sp^2 structure as the main component, and its resistivity is about $10^{-4}—10^{-2}\ \Omega \cdot m$, which is obviously different from that of diamond-like film with sp^3 structure as the main component [42—44]. In addition, GLC has good wear resistance, good corrosion resistance, and excellent chemical stability in corrosive media, so it is expected to be used in the protection and functionalization of bipolar plates in fuel cells and diaphragms in lithium batteries. Fig. 17.11 shows the friction curves of GLC film in air and water [41].

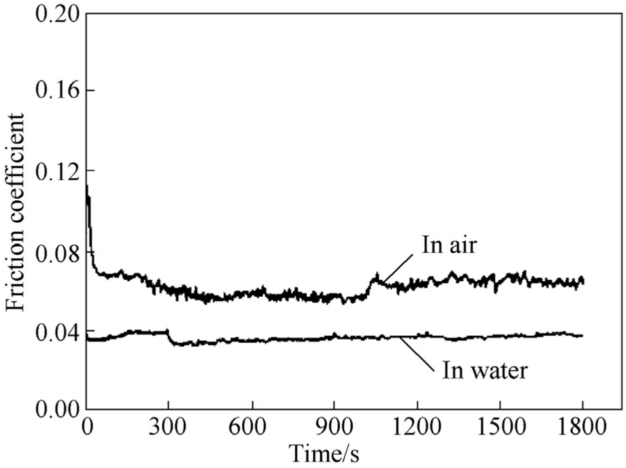

Figure 17.11 Friction curve of graphite-like carbon film in air and water [41].

17.3.4 Preparation technology and properties of polymer-like carbon films

PLC films are usually prepared by vacuum vapor deposition based on plasma discharge. The energy of neutral hydrocarbon molecules, free radicals, and atomic clusters in plasma is generally low (thermal movement), while the energy of $C_mH_n^+$ is regulated by negative bias voltage [8] to obtain the expected performance. Therefore negative bias voltage is the key experimental parameter affecting the hydrogen content of PLC film. The main preparation techniques of PLC films include magnetron sputtering deposition technology, inductively coupled PCVD technology [45], and microwave-assisted RF PCVD technology [46]. The deposition of PLC films by reactive magnetron sputtering technology not only requires low substrate negative bias, but also adjusts the contribution proportion of deposition by magnetron sputtering and plasma polymerization to the film growth. It is also necessary to reduce the sputtering rate of the target material (including graphite targets) and increase the flow rate of hydrocarbon gas; otherwise, the deposited film will be composed mainly of the target material. Liu et al. [47] deposited Si-PLC and SiAl-PLC films by magnetron sputtering graphite targets, silicon targets, and silicon-aluminum composite targets in CH_4 and Ar mixed gas without an external negative bias voltage. At present, the research on PLC film is still in its infancy. Researchers will need to carry out a lot of investigations and accumulate a lot of basic data in order to promote PLC film from basic research to engineering applications.

17.4 Application of amorphous carbon film

Although the structure and composition of amorphous carbon films are different, owing to different preparation processes, there are many similarities in their physical and chemical properties and applications. Therefore amorphous carbon films have a unique application value as a result of their different structures.

17.4.1 Application of diamond-like carbon films

The high hardness, low friction coefficient, and good antiwear performance of DLC film make it very suitable for use as a mechanical antifriction and wear-resistant protective film. DLC film, which has the following typical applications with special requirements for friction and wear, has reached the practical stage.

1. Application in cutting tools

   DLC films are used as a protective film on the surface of cutting tools, such as drill bits, milling cutters, and cemented carbide blades. DLC films not only improve the hardness of tool edges and their service life, but also has a very low friction coefficient, low adhesion, and excellent wear resistance. Therefore the performance of DLC film—coated tools far exceeds that of other hard-coated tools, which are used mainly for cutting graphite, various nonferrous metals (e.g., aluminum alloys, copper alloys), and nonmetallic hard materials (e.g., acrylic, glass fiber, PCB material), and so on.

   In the aluminum alloy cutting process, aluminum quickly adheres to the surface of the cutting tool, resulting in a decrease in the processed surface. DLC films can effectively reduce the adhesion of aluminum alloy. Therefore DLC films provide an effective solution for aluminum alloy processing, especially for the automobile manufacturing industry.

   If cutting tools that have been coated with TiN or TiAlN are used to process nonmetallic materials that have high hardness and lower melting points than metal materials, such as acrylic, glass fiber, and PCB materials, the cutting tools will melt or semimelt as a result of the increase in temperature. This leads to poor emission of cutting abrasive particles and ultimately to cutting tools failure. The DLC film with high hardness (HV: 3500) and an extremely low friction coefficient (~ 0.08) effectively solves these problems, mainly by greatly reducing the high temperature that is generated by friction and wear during the process and enhancement of the emission performance of the cutting abrasive particles. The average service life of the cutting tool is thus increased by three to four times. This feature is particularly prominent on cutting tools with a diameter of less than 10 mm, which are widely used in the field of microdrilling and micromilling cutters. Fig. 17.12 is a photo of microdrill cutters coated with ta-C film.

2. Application in the compression molding

   Molds that are made by traditional processes often suffer product scrap as a result of difficulty in demolding, and high production costs in the molding process have become a bottleneck in the production of semiconductors. DLC film coated on the surface of the mold effectively solves this problem. The deposition of DLC film on the surface of key parts of the mold can significantly reduce the demolding

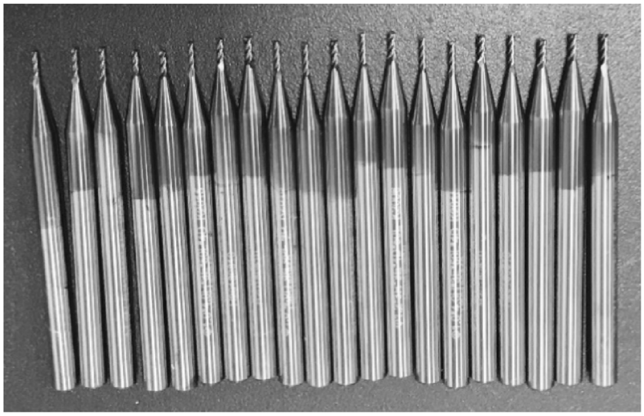

Figure 17.12 The ta-C film deposited on the surface of the microdrill.

force and prevent the phenomenon of product scrap resulting from excessive demolding force. The deposition of DLC film on the surface of the mold also greatly improves the production efficiency. Uncoated molds need to be repaired after producing fewer than 100 products, while coated molds need to be repaired after producing more than 1000 products.

3. Application in automobile engines

   DLC films deposited on engine parts can reduce friction and wear of engine sliding parts, reduce energy loss, and reduce fuel consumption. DLC films exhibit higher wear resistance because their hardness is two to three times that of ordinary electroplated chromium coatings or the surface of nitriding treatment. Furthermore, their low friction coefficient (<0.2) can significantly reduce the power consumption caused by friction. In addition, DLC films can effectively solve the early abnormal wear effect of friction parts. DLC films have been widely used on the surface of engine parts such as piston pins, common rail fuel injection systems, direct fuel injection systems, plunger pumps, rollers, tappets. and valve seats (Fig. 17.13).

   Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, and Yizheng Shuanghuan Piston Ring Co., Ltd. jointly developed a technology with independent intellectual property rights to deposit DLC film on the surface of piston rings. The developed technology can deposit DLC films with a thickness of 2−5 μm on the surface of nitriding, chromium plating, chrome ceramic coating, and PVD piston rings with a diameter of 65−126 mm. After the piston ring bench test, there was no significant wear on the surface of the piston ring with DLC film and the cylinder liner. The technology has been promoted and applied to original equipment manufacturing in China. Fig. 17.14 is a photo of a piston ring with DLC film.

4. Other mechanical parts

   To reduce the problems of friction, wear, vibration, impact, noise, poor reliability, and short life of mechanical parts caused by movement, the surface

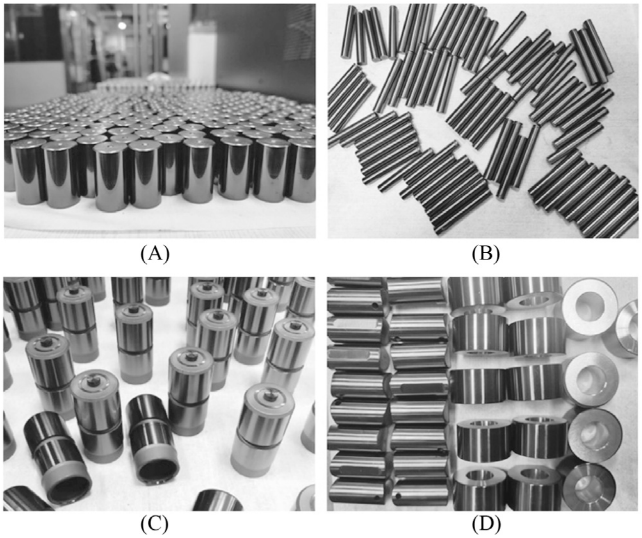

Figure 17.13 Engine parts deposited with diamond-like carbon film. (A) Piston pin. (B) Plunger. (C) Tappet. (D) Roller.

Figure 17.14 Piston with diamond-like carbon film deposited on its surface.

treatment of high hardness and low friction for the friction pair and the solid–liquid composite lubrication modification technology have become an important way to improve the service performances of bearing systems.

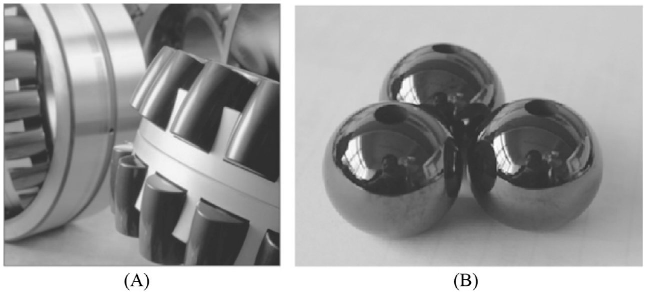
(A) (B)

Figure 17.15 Photographs of bearings with diamond-like carbon films. (A) Cylindrical bearings. (B) Ball bearings.

a. Bearings

The surface treatment of the bearing with ultrasmooth DLC film significantly reduces the friction and wear of the bearing system. A roller bearing without surface treatment has obvious scratches after running for 15 hours, while a roller bearing that has been coated with DLC film has no obvious scratches after running for more than 200 hours, and the wear depth is reduced from 1.85 to 0.68 μm. Fig. 17.15 shows photos of roller bearings and ball bearings coated with DLC film. DLC film, with its high hardness and toughness, has received extensive attention from bearing manufacturers and has been applied to the surface of various bearings.

b. Gears

Gears are power transmission parts of mechanical equipment that require excellent wear resistance, high contact fatigue strength, and bending fatigue strength as well as high impact resistance and overload resistance. NASA's Green Research Center, Boeing, Northwestern University, and some European coating service companies have all developed deposition technology on the surface of gears and the performances evaluation the gear with various coatings. They have introduced a variety of DLC films with excellent operation effects for high-load and high-speed gears. The antigluing load capacity of gears with WC/C and B_4C coatings are significantly improved. Compared with uncoated gears, the antigluing load capacity of coated gears is increased by more than two levels, the torque transmission capacity is increased by more than 50%, and the life factor is increased by two to three times. Fig. 17.16 shows gears with DLC film deposited on the surface.

5. Other applications

In recent years, deposition technology and equipment of DLC films have been continuously improved, and applications are expanding to areas other than tribological functions. The application range of DLC film involves corrosion protection, hard disk, disk protective film, acoustic components (e.g., tweeter diaphragms), optical components

Figure 17.16 Gears with diamond-like carbon film deposited on the surface.

(e.g., antireflection film, infrared transmission film, plastic transparent protective film), medical components (e.g., heart valves, artificial joints), electronic components (e.g., insulation resistance, plane transmitter, resistive electrodes), entertainment and fitness (e.g., golf equipment), decorative components (e.g., cell phones, high-end watches), and so on.

17.4.2 Application of graphite-like carbon films

GLC films show good physical and chemical properties, such as low internal stress, high adhesion, good thermal stability, high bearing capacity, excellent electrical conductivity, and good biocompatibility. In particular, the excellent tribological properties in atmospheric environments, humid environments, and water environments give it broad applications. Field et al. [4] compared the friction and wear behavior of GLC film and DLC film in deionized water. The results show that because GLC film has both high hardness and high graphite structure content, it shows better friction and wear characteristics in water lubrication. Guan Xiaoyan et al. deposited GLC film on the surface of titanium alloy through structural design and optimization. Compared with the original titanium alloy, the friction coefficient decreased significantly; in particular, the wear rate in a water environment decreased by approximately three orders of magnitude, and the wear rate in seawater environment decreased by approximately two orders of magnitude. The researchers concluded that the GLC film not only exhibits excellent tribological properties under dry friction conditions in an atmospheric environment, but also exhibits outstanding tribological properties in humid air, water, and seawater. This opens up a path for the development of environmentally adaptive carbon-based film to meet the development needs of water lubrication systems. Fig. 17.17 shows the wear rate of DLC deposited on the surface of titanium alloy in deionized water and seawater [4].

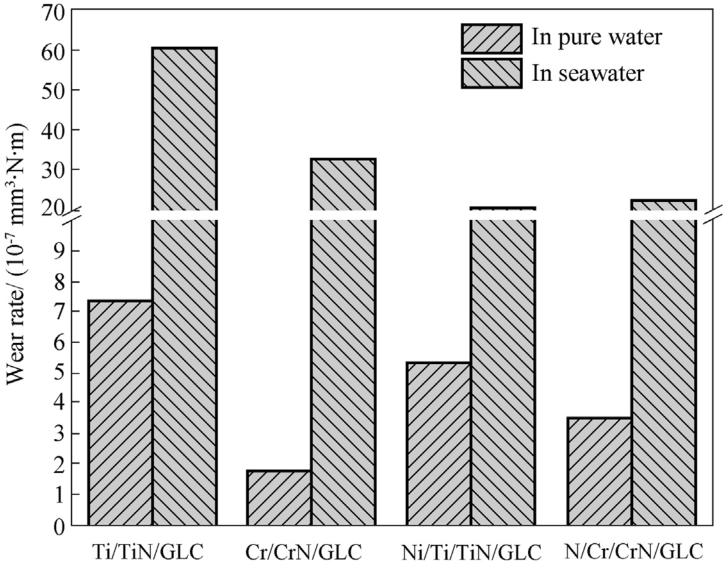

Figure 17.17 The wear rate of titanium alloy coated with graphite-like carbon film in pure water and seawater.

The research group led by Xue Qunji used magnetron sputtering technology to prepare GLC films and systematically studied their tribological properties in water environments. GLC film deposited on the surface of carbide ceramics (SiC), nitride ceramics (Si_3N_4), and tungsten carbide cemented carbide (WC) ensures the low friction operation of the friction pair in the case of insufficient lubrication, such as start-stop or instantaneous overload, and its good wear resistance effectively protects the surface of the friction pair. Therefore it provides an effective way to solve the problem of friction and wear of the friction parts in water with poor lubrication conditions. GLC film that is prepared on a SiC ceramic surface has a friction coefficient of 0.074 under dry friction conditions, which is 68.9% lower than that of the uncoated SiC ceramic (friction coefficient: ~0.238), and the wear rate is 5.2×10^{-7} $mm^3/N \cdot m$, which is two orders of magnitude lower than uncoated SiC ceramic (wear rate: 7.5×10^{-5} $mm^3/N \cdot m$). The friction coefficient of GLC film under water lubrication is 0.035, which is 67.0% lower than that of uncoated SiC ceramic (friction coefficient: 0.106), and the wear rate is 6.2×10^{-7} $mm^3/N \cdot m$, which is less than one order of magnitude lower of uncoated SiC ceramics (wear rate: 4.9×10^{-6} $mm^3/N \cdot m$).

GLC film exhibits good corrosion resistance and excellent chemical stability, and its resistivity can be adjusted within a larger range. Therefore it is expected to solve the bottleneck restricting the wide application of metal bipolar plates, that is, the contradiction between corrosion resistance and electrical conductivity. As shown in Fig. 17.18, Zhang Guangan's research team used a closed-field unbalanced magnetron sputtering system to

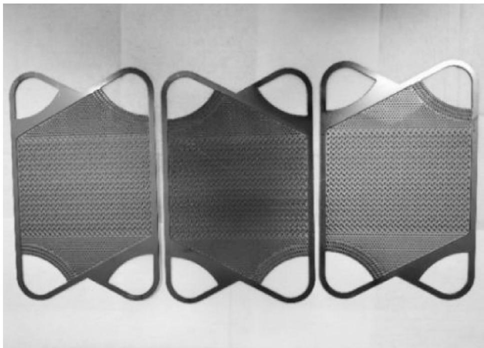

Figure 17.18 Electrochemical performance curve of graphite-like carbon film deposited on titanium alloy bipolar plate in concentrated phosphoric acid environment.

prepare a GLC film with excellent comprehensive properties on the surface of a titanium alloy bipolar plate. The thickness is about 2 μm, the hardness is about 14.7 GPa, the elastic modulus is about 191.1 Gpa, and the adhesive force is greater than 30 N. Under a pressure of 1.4 Mpa, the interface contact resistance of titanium alloy reaches 13.3 mΩ/cm^2, and the surface contact resistance of GLC film reaches 1.2 mΩ/cm^2. The potentiodynamic polarization curves in the H_2SO_4 and 0.1 ppm HF electrolyte (pH = 3) show that the corrosion potential of GLC film is about 0.11 V, and the corrosion current density is about 3.63×10^{-8} A/cm^2. The corrosion potential of the titanium alloy bipolar plate is about 0.01 V, and the corrosion current density is about 1.81×10^{-8} A/cm^2. Moreover, the potentiostatic (+0.6 V) polarization curves show that the corrosion current density of GLC film is stable at 3.5×10^{-9} A/cm^2, and the corrosion current density of titanium alloy reaches 8.3×10^{-9} A/cm^2. This clearly shows that GLC film significantly improves the corrosion resistance of the titanium alloy bipolar plate.

17.4.3 Application of polymer-like carbon film

PLC film has the largest band gap, the lowest density, and the lowest internal stress, which make it an excellent candidate dielectric material to obtain a breakdown strength close to that of diamond. Since the energy density of a capacitor is proportional to the square of the applied voltage (V^2) and inversely proportional to the thickness of the dielectric, it is reasonable to believe that capacitor films with high energy density can be made of very thin dielectrics with high breakdown strength. At present, PLC film with the highest energy density (Ue = 4.13 J/cm^3) and breakdown strength (7.2 MV/cm) have been successfully prepared on capacitors by RF PECVD.

PLC film shows long-life superlubrication performance in a space environment. It is regarded as a new space solid lubrication material with potential application value and has attracted the extensive attention of researchers around the world [9]. Compared with traditional lubrication technology, superlubrication means lower

Figure 17.19 Polymer-like carbon film deposited on the surface of a high-precision bearing.

friction power consumption, vibration, and noise and higher mechanical performance indicators. This is particularly important for space machinery developing toward ultralong life, ultrahigh precision, high stability, large torque, low power consumption, low vibration, low noise, miniaturization, and light weight. As shown in Fig. 17.19, PLC film was deposited on the surface of a high-precision bearing, which successfully solved the lubrication problem under 150°C helium [48].

This chapter has shown that carbon-based films have excellent and easy-to-control properties, and they are the ascendant films with wide application prospects. The deposition technology of carbon-based films will become a hotspot for scientific and technological workers. Carbon-based films will play a major role in the development of national economies and social development.

References

[1] Robertson J. Diamond-like amorphous carbon. Materials Science and Engineering: R: Reports 2002;37(4−6):129−281.

[2] Wang YH, Zhang X, Wu XY, et al. Superhard nanocomposite nc-TiC/a-C:H film fabricated by filtered cathodic vacuum arc technique. Applied Surface Science 2008;254(16):5085−8.

[3] Wang P. Study on the design, preparation and properties of nanocomposite carbon-based films (in Chinese). Lanzhou: Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences; 2008.

[4] Field SK, Jarratt M, Teer DG. Tribological properties of graphite-like and diamond-like carbon coatings. Tribology International 2004;37(11−12):949−56.

[5] Stallard J, Mercs D, Jarratt M, et al. A study of the tribological behaviour of three carbon-based coatings, tested in air, water and oil environments at high loads. Surface and Coatings Technology 2004;177:545−51.

[6] Stallard J, Teer DG. A study of the tribological behaviour of CrN, Graphit-iC and Dymon-iC coatings under oil lubrication. Surface and Coatings Technology 2004;188:525−9.

[7] Yang S, Camino D, Jones AHS, et al. Deposition and tribological behaviour of sputtered carbon hard coatings. Surface and Coatings Technology 2000;124(2−3):110−16.

[8] Cui LC, Wang JJ, Huang WJ. A survey on deposition and tribological study of polymer-like carbon films (in Chinese). Chinese Journal of Materials Research 2019;33(5):797−804.

[9] Nosaka M, Kusaba R, Morisaki Y, et al. Stability of friction fade-out at polymer-like carbon films slid by ZrO_2 pins under alcohol-vapored hydrogen gas environment. Proceedings of the Institution of Mechanical Engineers -- Part J -- Journal of Engineering Tribology 2016;230(11):1389−97.

[10] Ali M, UErgen M. Surface morphology, growth rate and quality of diamond films synthesized in hot filament CVD system under various methane concentrations. Applied Surface Science 2011;257(20):8420−6.

[11] Guo L, Chen GH. High-quality diamond film deposition on a titanium substrate using the hot-filament chemical vapor deposition method. Diamond & Related Materials 2007;16(8):1530−40.

[12] Zhang J. Study of preparation and supercapacitor property of boron doped diamond (BDD) film (in Chinese). Beijing: China University of Geosciences (Beijing); 2020.

[13] Fernandes A, Neto MA, Almeida FA, et al. Nano- and micro-crystalline diamond growth by MPCVD in extremely poor hydrogen uniform plasmas. Diamond and Related Materials 2007;16(4):757−61.

[14] Man WJ, Weng J, Wu YQ, et al. A novel method of fabricating a well-faceted large-crystal diamond through MPCVD. Plasma Science & Technology 2009;11(6):688−92.

[15] Bai YZ, Jin ZA, Lv XY, et al. Influence of cathode temperature on gas discharge and growth of diamond films in DC-PCVD processing. Diamond and Related Materials 2005;14(9):1494−7.

[16] Huang TB, Tang WZ, Lu FX, et al. Influence of plasma power over growth rate and grain size during diamond deposition using DC arc plasma jet CVD. Thin Solid Films 2003;429(1−2):108−13.

[17] Butler-Smith PW, Axinte DA, Daine M, et al. A study of an improved cutting mechanism of composite materials using novel design of diamond micro-core drills. International Journal of Machine Tools & Manufacture 2015;88(5):175−83.

[18] Dumpala R, Chandran M, Madhavan S, et al. High wear performance of the dual-layer graded composite diamond coated cutting tools. International Journal of Refractory Metals & Hard Materials 2015;48:24−30.

[19] Zhao YZ, Yue W, Lin F, et al. Friction and wear behaviors of polycrystalline diamond under vacuum conditions. International Journal of Refractory Metals & Hard Materials 2015;50:43−52.

[20] Aleksov A, Kubovic M, Schmid P, et al. Diamond-based electronics for RF applications. Diamond & Related Materials 2004;13(2):233−40.

[21] Kalish R. The search for donors in diamond. Diamond & Related Materials 2001;10(9−10):1749−55.

[22] Han JC, Zhu JQ, Li N, et al. Superexcellent infrared protective coatings: amorphous diamond films deposited by filtered cathodic vacuum arc technology. Surface & Coatings Technology 2007;201(9−11):5323−5.

[23] Pace E, Pini A, Corti G, et al. CVD diamond optics for ultraviolet. Diamond & Related Materials 2001;10(3−7):736−43.

[24] Moussa T, Garnier B, Peerhossaini H. Measurement and model on thermal properties of sintered diamond composites. Journal of Alloys and Compounds 2013;551(5):636−42.

[25] Li H. Study on the fabrication of boron doped diamond electrode and its application in the recycling process of wastewater in confined space (in Chinese). Hangzhou: Zhejiang University; 2016.

[26] Su QF. The research on CVD diamond films and radiation detectors (in Chinese). Shanghai: Shanghai University; 2006.

[27] Xu P. Development and performance of CVD diamond film radiation detectors (in Chinese). Hengyang: University of South China; 2020.

[28] Liebler V, Baumann H, Bethge K. Characterization of ion-beam-deposited diamond-like carbon films. Thin Solid Films 1993;270(2−4):584−9.

[29] Mei RQ, Wei QP, Zhu CW, et al. 3D macroporous boron-doped diamond electrode with interconnected liquid flow channels: a high-efficiency electrochemical degradation of RB-19 dye wastewater under low current. Applied Catalysis B: Environmental 2019;245:420−7.

[30] Zhang L, Zhou KC, Wei QP, et al. Thermal conductivity enhancement of phase change materials with 3D porous diamond foam for thermal energy storage. Applied Energy 2019;233−234:208−19.

[31] Xue QJ, Wang LP. Diamond-like carbon films (in Chinese). Beijing: Science Press; 2012.

[32] Weissmantel C, Bewilogua K, Dietrich D, et al. Structure and properties of quasi-amorphous films prepared by ion beam techniques. Thin Solid Films 1980;72(1):19−32.

[33] Wang YF. Study on design, control and superlubric application of special nanostructured carbon-based thin films (in Chinese). Lanzhou: Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences; 2018. p. 6.

[34] Wei YH, Li CM. Plasma immersion ion deposition (PIID) research at SwRI and its practical applications (in Chinese). China Surface Engineering 2012;25(1):1−10.

[35] Wei XB, Shang LL, et al. Rapid preparation of super thick diamond-like carbon Films by PECVD (in Chinese). Vacuum & Cryogenics 2020;26(5):402−9.

[36] Sun LL. Study on synthesis, structure and properties of copper/chromium Co-doped diamond-like carbon based films (in Chinese). Ningbo: Ningbo Institute of materials technology and engineering, Chinese Academy of Sciences 2017;.

[37] Jones DI, Stewart AD. Electrical and optical properties of hydrogenated amorphous carbon films. Le Journal De Physique Colloques 1981;42:147−58.

[38] Singh SV, Creatore M, Groenen R, et al. A hard graphitelike hydrogenated amorphous carbon grown at high deposition rate (> 15 nm/s). Applied Physics Letters 2008;92(22):129.

[39] Rossi F, André B, Van Veen A, et al. Effect of ion beam assistance on the microstructure of nonhydrogenated amorphous carbon. Journal of Applied Physics 1994;75(6):3121−9.

[40] Zeng XT, Zhang S, Ding XZ, et al. Comparison of three types of carbon composite coatings with exceptional load-bearing capacity and high wear resistance. Thin Solid Films 2002;420:366−70.

[41] Wang YX. Preparation and properties of the high performanced graphite-like carbon films in water (in Chinese). Lanzhou: Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences; 2011.

[42] Huang H, Wang X, He J. Synthesis and properties of graphite-like carbon by ion beam-assisted deposition. Materials Letters 2003;57(22−23):3431−6.

[43] Du J, He JW. The preparation of graphite-like-carbon film (GLC) and difference from diamond-like-carbon (DLC) Film (in Chinese). China Surface Engineering 2005;18(4):6−8.

[44] Fu YH, Zhu XD, He JW, et al. Tribological properties of graphite-like carbon coating prepared by unbalanced magnetron sputtering method (in Chinese). Tribology 2003;23(06):463−7.

[45] Dworschak W, Kleber R, Fuchs A, et al. Polymer-like and hard amorphous hydrogenated carbon films prepared in an inductively coupled RF glow discharge. Thin Solid Films 1990;189(2):257−67.

[46] Bouchet-Fabre B, Dixmier J, Heitz T, et al. X-ray diffraction investigation of polymer-like hydrogenated amorphous carbon films. Journal of Non-Crystalline Solids 2000;266−269:755−9.

[47] Liu XQ, Yang J, Hao JY, et al. Microstructure, mechanical and tribological properties of Si and Al co-doped hydrogenated amorphous carbon films deposited at various bias voltages. Surface & Coatings Technology 2012;206(19−20):4119−25.

[48] Tomastik C, Lackner JM, Pauschitz A, et al. Structural, chemical and nanomechanical investigations of SiC/polymeric a-C:H films deposited by reactive RF unbalanced magnetron sputtering. Solid State Sciences 2016;53:1−8.