



國立宜蘭大學工程學刊第五期, 131-167 頁, 2009 年 3 月

Bulletin of College of Engineering, National Ilan University, NO. 5, P. 131-167, Mar., 2009

# Mechanical and Tribological Investigations on Carbon Allotropes

**Chih-Kuo Fang**

Professor, Department of Mechanical and Electromechanical Engineering, National Ilan University.

## ABSTRACT

Carbon allotropes are of prime interest to the field of tribology because of their peculiar structures and properties. In this article, a review of recent development in the research on the properties of carbon allotropes (fullerenes, diamond, graphite, and diamond-like carbon) is presented. In particular, their mechanical and tribological characterization is investigated in detail. It is observed that their tribological properties and behaviors are closely related to the structures and the environments. Among carbon allotropes, diamond-like carbon (DLC) coatings show sublimed characteristics including high stiffness and mechanical strength, self-lubricating properties, low friction coefficient, high thermal conductivity, high wear and corrosion resistance etc. DLC protective coating is thus a good candidate for applications to tribological engineering. The crystal structures, hydrogen content, deposition techniques, and environmental factors related to the tribological behaviors of DLCs are studied. This paper also details the tribological mechanisms and phase transformation of DLC films during sliding.

**Keywords:** Tribology, Friction, Wear, Lubrication, Carbon allotropes, Diamond-like carbon.



# 同素異形碳機械性質與磨潤行為之探討

方治國

國立宜蘭大學機械與機電工程學系教授

## 摘要

由於同素異形碳特有之結構及性質，其在磨潤領域具有相當之研究價值。本文回顧關於富勒烯、鑽石、石墨、及類鑽碳等同素異形碳特性研究之進展。尤其針其機械及磨潤特性作較詳細之探討。研究顯示同素異形碳之機械性質及磨潤行為與其本身結構及其操作環境息息相關。在同素異形碳中，類鑽碳鍍膜具有相當傑出之特性，包括高勁度及機械強度、具自潤性、摩擦係數低、熱傳導性佳、良好的耐磨耗及耐腐蝕性等。因此類鑽碳膜在磨潤工程應用上是一極佳選擇。本文分析影響類鑽碳膜磨潤特性之結晶結構、氫含量、成膜技術、及環境因子。對於類鑽碳膜磨潤機制及表面滑移過程導致之相變化有較詳細之探討。

**關鍵詞：**磨潤、摩擦、磨耗、潤滑、同素異形碳、類鑽碳。

## I Introduction

Carbon is an unusual material in that it exhibits both metallic and nonmetallic characteristics. The electronic configuration of carbon is  $1s^2 2s^2 2p^2$ , i.e. with four valence electrons spread in the  $s$  and  $p$  orbitals. It is a very versatile element because of the different ways carbon atoms can bond to each other and to other elements. There are several allotropes of carbon of which the best known are graphite, diamond, and amorphous carbon. Carbon exists in both crystalline and amorphous forms. Crystalline carbon includes graphite, diamond and a family of fullerenes. The graphite and diamond are infinite periodic network solids, whereas the fullerenes are a molecular form of pure carbon with a finite network [Bushan, 1999a]. Diamond is among the hardest materials known, while graphite is soft. Under normal conditions, diamond has the highest thermal conductivity of all known materials. All the allotropic forms are solids under normal conditions but graphite is the most thermodynamically stable. The different structures and thus different properties of carbon allotropes result in significant different tribological behaviors.

## II. Tribology of Fullerene

Fullerenes are a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere (buckyballs), ellipsoid, tube (buckytubes or carbon nanotubes), or plane (graphene). One of the fullerene molecule is  $C_{60}$ , commonly known as buckyball. The tribological properties of buckyballs have been speculated since the time of its discovery because of its unique spherical shape with cage diameter of 0.71 nm, high load-bearing capacity, low surface energy, high chemical stability, weak intermolecular and strong intramolecular bonding

[Kratschmer et al., 1990; Kroto et al., 1985; Feng, 1997; Bhushan et al., 1993]. These sublimed properties offer potential for various mechanical and tribological applications.

C<sub>60</sub> molecules are expected to have low surface energy and low adhesion to the mating surface because they are very stable and do not require additional atoms to satisfy chemical bonding requirements. Similar to other layered-lattice structures, C<sub>60</sub> clusters get detached readily since C<sub>60</sub> molecules are weakly bonded to other molecules due to their perfect spherical symmetry. They are easily get transferred to the mating surface by mechanical compaction or are present as loose wear particle rolling like tiny ball bearings [Blau and Haberlin, 1992; Gupta et al., 1994] in a sliding contact, resulting in low friction and wear. Theoretical simulations found that C<sub>60</sub> molecule was able to roll between graphite sheets, as well as between hydrogen-terminated surfaces of diamond under relatively low load [White et al., 1993]. It should be noted that the wear particles are expected to be harder than as-deposited C<sub>60</sub> molecules because of their phase transformation at high asperity contact pressures present in a sliding interface.

The sublimed C<sub>60</sub> coatings and fullerene particles as an additive to mineral oils and greases have been reported to be good solid lubricants comparable with graphite and MoS<sub>2</sub> [Bhushan, et al., 1993; Gupta et al., 1994; Gupta and Bhushan, 1994]. The tribological properties of fullerene particles (in the form of molecular cluster) as an additive to liquid lubricants were studied by a few groups [Jiang and Zheng, 2005; Yan et al., 1993]. It was observed that the presence of fullerene was able to increase the load carrying ability and decrease the friction coefficient and wear. The lubrication characteristics of nanoparticle-added lubricating oil have been investigated in many other works. For example, Ginzburg et al. [2002] investigated the antiwear

effect of fullerene-added I-40A industrial oil. The fullerene-oil-made film was formed on the copper foil surface of a steel roller which exhibited outstanding antiwear properties. As a result, the bearing strength of the tribo-technical unit was enhanced and the operation was stabilized at a fairly low friction coefficient. However, fullerenes are only soluble in few solvents such as benzene, toluene, carbon disulfide, etc. Because of their poor solubility in common solvents, fullerene particles are normally dispersed in liquid lubricants by some physical and mechanical means (such as solid grinding, solvent evaporation, ultrasonic, etc.)

Fullerene-like carbon films have attracted significant attention recently due to the unique resilient behavior [Broitman, 2001] and thermal stability [Neidhardt et al., 2003]. The common characteristic of atom arrangement in these films is the presence of curvature in an all  $sp^2$  three-dimensional network, constituting closed cages in the case of fullerene molecules [Gago et al., 2005b]. Such an atom arrangement makes these films elastic and hard simultaneously, and the mechanical performance is significant improved [Gago et al., 2005a].

More recently, Wang et al. [2008] investigated the tribological behaviors of fullerene-like hydrogenated carbon (FL-C:H) film in different atmospheres ( $N_2$ ,  $O_2$  and air). It was observed that friction oxidation reaction occurred to the FL-C:H film surface at contact area in  $O_2$ . They found that the fullerene-like structure of the film surface was destroyed and oxidized polymeric layer containing carboxylic functional group was formed. The lowest friction coefficient (0.013) and the highest wear rate ( $2.46 \times 10^{-7} \text{mm}^3/\text{Nm}$ ) were obtained at the same time. This was because the layer easily yielded to sliding shear and produced a great deal of lubricating particle-like wear debris.

### III. Tribology of Diamond

Diamond is an allotropic form of the element carbon with cubic structure (space group). It is historically known as a gemstone, however, it is the physically hardest substance known and is now widely used as an abrasive in high productivity tools in industry. Diamond crystallizes in the modified face-centered cubic (fcc) structure with an interatomic distance of 0.154 nm. Its cubic lattice consists of two interpenetrating fcc lattices displaced by one-quarter of the cube diagonal. All the bonds are of the same length (1.54 Å), with the same bond angle (109.47°), and the bonding is strong in all directions. Each carbon atom is tetrahedrally coordinated, making strong  $\sigma$  (covalent) bonds to its four carbon neighbors using the hybrid  $sp^3$  atomic orbitals which accounts for its highest hardness (80 to 104 GPa) and thermal conductivity (900–2100  $Wm^{-1}K^{-1}$ , on the order of five times that of copper) of any known solid, and a high electrical resistivity, optical transmission (from the far ultra-violet to the far infra-red) and a large optical bandgap [Bhushan, 1999a]. In addition to hardness, several of its mechanical properties, such as bulk modulus and critical tensile stress for fracture, are also the highest known.

The tetrahedral structure, together with the highly directed charge density, give strength and stability to the bonds. Diamond is thermodynamically stable at pressures above 6 GPa at room temperature and metastable at atmospheric pressure. The diamond can be used to high temperatures and it starts to graphitize at about 1000°C in ambient air and at about 1400°C in vacuum. At low pressures it converts rapidly to graphite at temperatures above 1900K in an inert atmosphere.

Because of its high hardness, diamond is far more effective and efficient than other competing materials used for abrasive (e.g. grinding), cutting (e.g. sawing and drilling), shaping or finishing (e.g. lapping and polishing) tools and other extreme

wear applications. Consequently, diamond and its coatings find many industrial applications: optical applications (exceptional optical transmission, high abrasion resistance), thermal management or heat sink applications (high thermal conductivity), and tribological applications (low friction and wear) [Bhushan, 1999a].

Diamond is relatively chemically inert, and it exhibits poor adhesion with other solids with consequent low friction and wear. Its high thermal conductivity allows dissipation of frictional heat during sliding and protects the interface, and the dangling carbon bonds on the surface react with the environment to form hydrocarbons which act as good lubrication films. These are some of the reasons for low friction and wear of the diamond [Bhushan, 1999a].

The natural diamond particularly in large sizes is very expensive and its coatings, a low cost alternative, are attractive. In manufactured diamond, the process of forming diamond from carbon, either by high temperature/high pressure process (HPHT) or by high temperature/low pressure deposition process (such as Chemical Vapor Deposition, CVD), is commonly known as synthesis of diamond. In CVD process, the true diamond coatings are deposited at high substrate temperatures (on the order of 800-900°C). One advantage of CVD diamond technology over high-pressure technology is its low cost and its ability to coat on any shape. The diamond coatings adhere best on a silicon substrate and require an interlayer for other substrates. In the mid-1990s, several new mass-production technologies for producing diamond films emerged, including interactive laser technique and the technique using fullerenes in an argon microwave plasma to produce nanocrystalline diamond.

The measured hardness values are dependent on the crystal orientation of the face measured for both natural and synthetic single crystal diamond. They typically range from 57 GPa (for the (100) surface) to 104GPa (for the (111) surface) in Knoop

hardness value. The tribological behavior of a single crystal diamond thus varies with respect to its crystallographic plane and direction [Wilks et al., 1972; Seal, 1958; Tabor, 1979]. CVD diamond (which is polycrystalline) has no single crystal orientation and consequently no orientation dependence of its bulk hardness which has been measured as  $81\pm 18$  GPa.

A major roadblock to the widespread use of true diamond films in tribological, optical and thermal management applications is the surface roughness. Growth of the diamond phase on a non-diamond substrate is initiated by nucleation either at randomly seeded sites or at thermally favored sites due to statistical thermal fluctuation at the substrate surface. Based on growth temperature and pressure conditions, favored crystal orientations dominate the competitive growth process. As a result, the grown films are polycrystalline in nature with relatively large grain size ( $>1\mu\text{m}$ ), and terminate in very rough surfaces with rms roughnesses ranging from few tenths of a micron to tens of microns [Bhushan, 1999a]. Techniques for polishing these films have been developed. It has been reported that the laser polished films exhibit friction and wear properties almost comparable with that of bulk polished diamond [Bhushan et al., 1993, 1994]. Another problem in vacuum deposition of diamond films is that the optimum substrate temperature for coating is about  $900^\circ\text{C}$  which severely limits the range of substrates to which diamond can be applied.

It is well known that diamond behaves very differently when slide in different atmospheres [Bowden and Hanwell, 1966; Gardos, 1999]. The formation of strong carbon-carbon bonding across the clean interface formed between sliding diamond mating surfaces under vacuum is believed to be the cause of a high coefficient of friction [Field, 1991]. Although diamond is a “high-friction material” in dry air, dry argon and other dry and hydrogen free atmospheres, it behaves as a “low-friction

material” in humid air or water [Bowden and Tabor, 1964; Andersson et al., 2003]. A coefficient of friction of 0.05–0.1 has been obtained from a diamond stylus sliding over a polished diamond (001) face in air [Bowden and Hanwell, 1966], and it is believed that the adsorbed layers such as water, some other liquids and gases on the surface of diamond play an important role. On the contrary, Hayward et al. [1989] reported that the coefficient of friction of diamond is independent of humidity.

Covalent H-C bonds can terminate the surface in the presence of hydrogen in the surrounding atmosphere. Ideally, two H-terminated diamond surfaces make contact only through their H atoms. This leads to very weak H-H bonds across the interface and thus very low friction level in sliding these surfaces against each other. This was due to the weak bonds combined with a very small area of real contact offered by the extreme hardness of diamond. This was elucidated by Andersson [2004] through detailed studies of the influence of surrounding medium on the frictional behavior and wear of self-mated CVD diamond layers in sliding contact.

There is a constant supply of hydrogen to the diamond surface in humid air or water. However, the superficial hydrogen termination has very little influence on the friction as long as the surfaces are rough. This is because the contact situation is so severe that the adsorbed or reacted species cannot stick to the surface. Thus, the surfaces are initially worn by local mechanical fracture of the diamond grains. However, as soon as a set of plateaus are worn down to the same level to form a sliding surface, the local contact pressures fall dramatically. Accordingly, the stresses on the adsorbed or reacted species fall accordingly. These species may thus stick to the surfaces, offering weak adhesive bonds across the interface and increasingly masking the stronger carbon bonds. The remaining points of severe contact, where carbon bonds still dominates, are gradually smoothed during the continued wear. As

soon as the conditions become mild enough for the adsorbed species to stick, the local wear and friction becomes very low. Correspondingly, the friction drops with the sliding distance for the test in humid air. Here, some of the wear fragments accumulate between the plateaus. If the same experiment is performed in the inert argon atmosphere, the friction increases gradually despite the removal of the sharpest peaks. This is because of the missing of absorbing species and thus the strong carbon will now form over larger areas, although the formation of plateaus still reduces the normal pressures. [Jacobson and Hogmark, 2009]

Diamond material and its smooth coatings are used for very low wear and relatively low friction. However, major limitations of the true diamond coatings are that they need to be deposited at high temperatures, can only be deposited on selected substrates, and require surface finishing.

#### **IV. Tribology of Graphite**

Graphite is a soft, black (opaque), conducting, and low density substance which occurs naturally. It is also known as black lead - and when mixed with clay, forms the "lead" in pencils. There is a wide variety of graphite with difference in origin (synthetic and natural), purity, crystallinity, particle size, shape, thermal and electrical conductivity, etc. It is an allotropic form of the element carbon consisting of graphene layers with hexagonal rings of carbon atoms. Graphene layer is a single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size. These sheets or layers are stacked parallel to each other in a three-dimensional crystalline long-range order. These layers are stacked 0.34 nm apart with a 0.1415 nm interatomic distance between the carbon atoms in the

basal plane. The atoms lying in the basal planes are trigonally coordinated and closely packed with strong  $\sigma$  (covalent) bonds to its three carbon neighbors using the hybrid  $sp^2$  orbitals. The fourth electron lies in a  $p_z$  orbital lying normal to the bonding plane and forms a weak  $\pi$  bond by overlapping side to side with a  $p_z$  orbital of an adjacent atom to which carbon is attached by a  $\sigma$  bond.

Strong interatomic bonding and packing in each layer is thought to help reduce wear. The layers (basal planes) themselves are relatively far apart and the forces that bond them are weak van der Waals forces [Bushan, 1999a] resulting from the interactions between clouds of delocalized  $p$  electrons from each of the layers. These layers can align themselves parallel to the direction of the relative motion and slide over one another with relative ease because of the weak interlayer bonding forces in the crystalline lamellar structure. It thus provides low friction making graphite an effective solid lubricant. Since graphite exhibits a relatively low friction coefficient and a good wear resistance, it is used as a dry lubricant in its natural form. Because of the excellent lubrication properties, graphite lubricants are specialty items for use at very high or very low temperatures, as a wire die extrusion lubricant, an antiseize agent, a gear lubricant for mining machinery, and to lubricate locks.

Many parameters, experimental or intrinsic, play a role on the tribological behavior of graphite. Normal force or stress created between sliding surfaces of test pairs has a significant influence on the friction and wear properties of graphite [Jradi et al., 2009].

In addition to the strong bonding forces between the individual carbon atoms and the relatively weak bonding forces between the planes, the lubricity behavior of graphite is also ascribed to the presence of condensable vapors such as water [Chung, 2002; Bragg, 1928]. The environment in which friction occurs is thus one of the key

factors. The environmental influence has already been the subject of various studies [Jradi et al., 2009]. Under vacuum or inert atmosphere, the friction coefficient of graphite is very high (i.e., above 0.5) and fluctuated greatly (this is referred to as a dusting regime in [Yen, 1996]). The friction coefficient of graphite is however reduced markedly down to 0.1 level in the presence of water vapor or oxygen [Lancaster and Pritchard, 1980; 1981]. It was often attributed to the elimination of  $\pi-\pi^*$  attraction, and to the passivation of any dangling  $\sigma$ -bonds that may have become active during sliding [Yen, 1996]. It was noticed that significant reductions in the friction of graphite when using Highly Oriented Pyrolytic Graphite (HOPG) in the presence of helium or argon [Zaidi et al., 1995]. Such a variation was attributed to a self lubrication effect in the absence of passivation of the dangling bonds. They have also shown that the friction coefficient was low when the (002) basal planes turned towards a direction parallel to the contact surface, and are covered with a physisorbed layer [Zaidi et al., 1995].

Because the lubricity of graphite depends on the adsorbed moisture, the same graphite shows the drastic reduction in lubricity at higher temperatures and may perform as a mild abrasive [Clauss, 1972]. Graphite can thus be used in friction materials. Multiple ingredients (more than 10) are normally contained in the friction materials to achieve desired amalgam of performance properties [Bijwe, 1997]. To smoothen the unwanted fluctuations in the friction coefficient with operating parameters, graphite in general is added in friction composites. Significant quantities (typically 5–20 vol.%) of carbonaceous materials including different types of graphite, coke, carbon black, and carbon fibers were used when formulating sintered metallic brake linings [Kolluri et al., 2009].

## V. Tribology of Diamond-like carbon films

Since the true diamond coatings need to be deposited at high temperatures and require surface finishing, its application is limited. In the last few years a lot of research has proved that tribological properties attributed to diamond layers can also be achieved by hard amorphous carbon (a-C), commonly known as diamond-like carbon (DLC, implying high hardness), coatings which can be produced at or near room temperature. In addition, these coatings generally reproduce substrate topography and do not require any post-finishing.

DLC films are the tetrahedral amorphous carbons (ta-C) that contain a chaotic carbon mixture with  $sp^3$  and  $sp^2$  hybrid sites. They are hard, amorphous films with a significant fraction of  $sp^3$ -hybridized carbon atoms, i.e. a large proportion of the carbon atoms are bonded as in diamond and which resemble diamond in many ways – hence diamond-like carbon. As a result, DLC coatings exhibit mechanical, thermal and optical properties close to that of diamond. Since the early 1970s, DLCs have been produced for a variety of practical uses, and become the subject of intense research activity for tribological applications. DLC films can be deposited with a large range of thicknesses by using a variety of deposition processes, on variety of substrates [Bhushan, 1999a].

DLC coatings are mostly metastable amorphous materials but include a micro- or nanocrystalline phase. They can be fully amorphous or contain diamond crystallites, depending on the deposition conditions. Amorphous carbon has no long-range order and the short-range order of carbon atoms can have one or more of three bonding configurations —  $sp^3$  (diamond),  $sp^2$  (graphite) or  $sp^1$  (with two electrons forming strong  $\sigma$  bonds and the remaining two electrons left in orthogonal  $p_y$  and  $p_z$  orbitals to form weak  $\pi$  bonds). Short range order controls the properties of amorphous materials

and coatings [Bhushan, 1999a]. The films can also contain a significant amount of hydrogen (a-C:H). In brief, the coatings are a random network of covalently bonded carbon in hybridized tetragonal ( $sp^3$ ) and trigonal ( $sp^2$ ) local coordination, with some of the bonds terminated by hydrogen [Bhushan, 1999a].

DLC films catch people's eye recently because of their unique combination of desirable mechanical, electrical and optical properties. They have shown promising characteristics including high mechanical strength, high stiffness, low friction coefficient, self-lubricating properties, high wear resistance, high thermal conductivity, high corrosion resistance, chemical inertness (to both acids and alkalis [Bhushan, 1999a; Grill, 1997]), lack of magnetic response, and good insulation property (high electrical resistivity [Ham and Lou, 1989]) etc. In addition, they are optically transparent in the visible and infrared [Kaplan et al., 1985] with an optical band gap ranging from zero to a few eV, depending upon the deposition conditions.

Due to the low surface energy, DLC's reactivity with conventional oils and additives is limited and remain unsatisfactory. However, many excellent features of DLC protective films enable them to be used in a wide range of applications in the industrial domains like cutting tools, metallic molds, machine parts [Reisel et al., 2003; Robertson, 2002; Ban et al. 2003; Voevodin et al., 1997; Franceschini et al., 1992; Rinon et al., 2001], microelectronics, medical devices [Meunier et al., 2004; Meunier et al., 2006], and space applications [Litovchenko and Klyui, 2001; Vanhulsel et al., 2007]. More recently, their biocompatibility and low wettability [Yang et al., 2003] have opened new fields for applications in biology and medicine as protective coatings for implants, biosensors and biochips.

## **5-1 Types of DLC coatings**

DLC is an amorphous carbon with a significant fraction of C–C  $sp^3$  bonds. Hydrogen-free (a-C), hydrogenated (a-C:H), metal doped (Me-C:H) or nonmetal doped (x-C:H) are the most important types of DLC-layers. Different types of DLC coatings have different chemical structures and thus different mechanical and electrical properties, depending mainly on the deposition technique, which results in different hydrogen content and  $sp^2/sp^3$  ratio. Hydrogen-free DLCs with the highest  $sp^3$  content are called tetrahedral amorphous carbons (ta-C). Hydrogenated amorphous carbons (a-C:H) can be classified into four classes [Casiraghi, 2005; Shamsa et al., 2006]: (1) polymer-like a-C:H (PLCH), with  $\sim 35\text{--}60$  at. % H and up to 70%  $sp^3$  bonds; (2) diamond-like a-C:H (DLCH), with  $\sim 20\text{--}35\%$  H and  $sp^3$  content between 20% and 60%; (3) hydrogenated tetrahedral amorphous carbon (ta-C:H), with  $\sim 70\%$   $sp^3$  and  $\sim 25\text{--}30$  at. % H; and (4) graphite like a-C:H (GLCH), with less than 20%  $sp^3$ .

Fig.1 shows the Ternary phase diagram of  $sp^2$ ,  $sp^3$ , and H contents of various forms of DLC [Robertson, 1999]. As can be found in the lower left corner of diagram, the amorphous carbon (a-C) coatings contain mainly  $sp^2$  bonds and unsorted graphite structure. Soot, chars, glassy carbon and evaporated a-C belong to this group. (Glassy carbon is a non-graphitizing carbon which combines glassy and ceramic properties with those of graphite.) The type of carbon with predominantly  $sp^3$  bonds is called the tetrahedral amorphous carbon (ta-C) [McKenzie, 1996]. The sputtered amorphous hydrogenated carbon a-C:(H) is located in a separate field of the triangle, where  $sp^2$  bonds are extended to  $sp^3$  bonds. The right corner is limited by hydrocarbon polymers, polyethylene  $(CH_2)_n$  and polyacetylene  $(CH)_n$ . For hydrogenated amorphous carbon (a-C:H), the presence of  $sp^3$  bonds is relatively low, while the content of hydrogen is relatively high, as compared with ta-C. Hydrogenated tetrahedral amorphous carbon

(ta-C:H), deposited with plasma enhanced vapor deposition, has more  $sp^3$  bonds and a lower hydrogen content, as compared with a-C:H [Robertson, 2002].

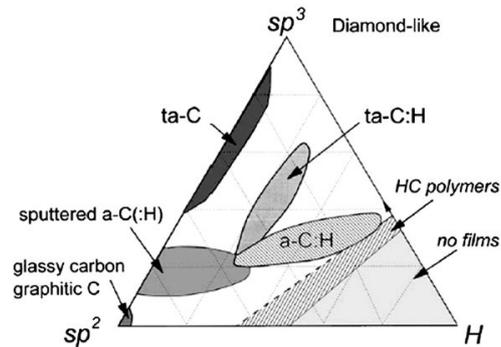


Fig. 1 – Ternary phase diagram of  $sp^2$ ,  $sp^3$ , and H contents of various forms of DLC [Robertson, 1999].

## 5-2 Deposition techniques and properties of DLC coatings

Diamond like amorphous carbon films are metastable phases formed when carbon particles are condensed on a substrate. They have been successfully deposited by a variety of vacuum deposition techniques, such as chemical vapor deposition (CVD), sputtering, laser ablation and ion implantation.

By a beam of carbon ions produced in an argon plasma, the first hard amorphous carbon coatings were deposited on room-temperature substrates [Aisenberg and Chabot, 1971]. Subsequent confirmation by Spencer et al. [1976] led to the explosive growth of this field. Several alternative techniques have been developed following the first work. The amorphous carbon coatings have been prepared by a variety of deposition techniques and precursors. These techniques include evaporation, DC, RF or ion beam sputtering, RF or DC plasma-enhanced chemical vapor deposition (PECVD), electron cyclotron resonance chemical vapor deposition (ECR-CVD), direct ion beam deposition, ion-beam assisted deposition (IBAD), pulsed laser vaporization (or deposition) and vacuum arc-discharge. The precursors involve a

variety of carbon bearing solids (e.g. graphite) or gaseous source materials [Bhushan and Gupta, 1997; Grill and Meyerson, 1994; Robertson 2002, Silva et al., 2002; Ensinger, 1992]. Coatings with both diamond-like and graphitic properties have been produced. Ion plating and evaporation techniques have been used to produce coatings with graphitic properties (low hardness, high electrical conductivity, very low friction, etc.), and all techniques have been used to produce coatings with diamond-like properties.

In general, a-C films can be prepared by carbon ion beam deposition, ion-assisted sputtering from graphite or by laser ablation of graphite, while a-C:H films containing significant contents of hydrogen are prepared by CVD. The hydrogen content in a-C:H is usually over 25 atomic %. The deposition parameters include precursor molecules, plasma ionization, (low) total pressure, and hydrogen partial pressure. The plasma activation can be radio frequency, microwave or Ar<sup>+</sup> ions. High ionization favors amorphous films while high atomic hydrogen contents favor diamond crystallite formation.

Plasma immersion ion implantation (PIII) is a rapidly developing technique for surface modification and DLC coating deposition on three dimensional workpieces for industrial applications [Miyagawa, 2002; Xu et al., 2006]. The most commonly used deposition techniques and deposition rates are compared in Table 1 [Bhushan, 2004; Bhushan and Gupta, 1997; Catherine, 1991].

Chemical structures and thus properties of DLC coatings are dependent upon the deposition technique. In particular, the hardness of DLC films is very dependant on the synthesis technique used to form it. The main mechanical properties of different DLC coatings are shown in Table 2 [Sedlaček et al., 2008].

Table 1 – The most commonly used deposition techniques and deposition rates [Bhushan, 2004]

Deposition technique	Process	Deposition rate (nm/s)
DC/RF sputtering	Sputtering of graphite target by argon ion plasma	1-10
Direct ion beam (IB)	Carbon ions produced from methane gas in an ion source and accelerated toward a substrate	0.1-1
Electron cyclotron resonance plasma chemical vapor deposition (ECR-CVD)	Hydrocarbon ions, produced by plasma decomposition of ethylene gas in the presence of a plasma in electron cyclotron resonance condition, are accelerated toward a RF-biased substrate	1-10
Filtered cathodic arc (FCA)	Energetic carbon ions produced by a vacuum arc discharge between a graphite cathode and grounded anode	0.1-1
Plasma-enhanced chemical vapor deposition (PECVD)	Hydrocarbon species, produced by plasma decomposition of hydrocarbon gases (e.g., acetylene), are accelerated toward a DC-biased substrate deposition	1-10

Table 2 – Mechanical properties of different DLC coatings [Sedlaček et al., 2008].

Types	Density (kg/m <sup>3</sup> )	E (GPa)	Micro Hardness (Hv)
Evaporation a-C	1,800-2,200	11-70	20-50
Sputtering a-C	1,800-2,400	11-70	1,000-10,000
PECVD a-C:H	1,500-2,000	5-25	1,200-3,000
Ion a-C:H	1,500-2,000	5-25	4,000-6,000

Depending on the method of preparation, DLC properties relevant to tribological application change significantly. Kvasnica et al. [2006] compared the tribological properties of DLC film obtained by PECVD with the Ti containing nanocrystalline carbon (Ti/a-C:H) film obtained by unbalanced magnetron sputter deposition (UMSD) in nN load range. It was shown that the surface roughness and the friction coefficient

of PECVD film was significantly higher than that of UMDS Ti/a-C:H film, although PECVD DLC film had higher elastic modulus and higher hardness than UMDS Ti/a-C:H film.

### 5-3 Tribological properties of DLCs

Similar to the hard ceramic coatings (e.g., TiN, CrN, TiAlN,...) which became essential in the field of cutting and forming tools, low-friction coatings (i.e. diamond, DLC, MoS<sub>2</sub>,...) are now becoming more and more important in the field of machine components, especially for automotive applications [Podgornik, 2005]. In mechanical engineering, low friction signifies a lower loss of energy, higher reliability and a better wear resistance.

Amorphous carbon films possess good tribological properties such as high hardness and low friction coefficient, which result in significant increase in wear resistance of articles with such coatings [Tsai and Body, 1987; Hiroyuki et al., 2001]. By giving excellent frictional properties and greatly improving wear resistance of contact surfaces, DLC coatings provide a great opportunity for further performance and durability improvement, and reduction of frictional losses in mechanical systems.

The mechanical and tribological properties of a carbon coating depend on (a) the sp<sup>3</sup>/sp<sup>2</sup> -bonded carbon ratio, (b) the amount of hydrogen in the coating, and (c) adhesion of the coating to the substrate.

#### (a) The sp<sup>3</sup>/sp<sup>2</sup>-bonded carbon ratio

The prevailing atomic arrangement in the DLC coatings is amorphous or quasi-amorphous with small diamond (sp<sup>3</sup>), graphite (sp<sup>2</sup>) and other unidentifiable micro- or nanocrystallites [Bhushan, 1999a]. In general, the sp<sup>3</sup>/sp<sup>2</sup> ratio of DLC coatings ranges typically from 50% to close to 100% with an increase in hardness

with  $sp^3/sp^2$  ratio, i.e., a high fraction of the  $sp^3$ -bonded carbon atoms in an amorphous network results in a higher hardness [Cuomo, 1991; Angus, 1992; Bhushan et al., 1992; Robertson, 1992].

(b) The amount of hydrogen in the coating

Hydrogenated DLC (a-C:H) coatings contain a significant amount of hydrogen. Most DLC coatings except those produced by filtered cathodic arc contain from a few to about 50 at.% hydrogen. Sometimes hydrogen and nitrogen are deliberately added to produce hydrogenated (a-C:H) and nitrogenated (a-C:N) amorphous carbon coatings, respectively, to tailor their properties.

In the physical properties, the hydrogenated carbon has a larger optical band gap, higher electrical resistivity (semiconductor), and a lower optical absorption or high optical transmission. It has a lower density probably because of reduction of cross-linking due to hydrogen incorporation.

Hydrogen is believed to play a crucial role in the bonding configuration of carbon atoms dominating the mechanical and tribological properties. Jansen et al. [1985] suggested that the incorporation of hydrogen efficiently passivates the dangling bonds and saturates the graphitic bonding to some extent. Angus and Hayman [1988] indicated that hydrogen helps to stabilize  $sp^3$  sites (most of the carbon atoms attached to hydrogen have a tetrahedral structure), the  $sp^3/sp^2$  ratio for hydrogenated carbon is higher, i.e., hydrogen causes the character of the C-C bonds to shift from  $sp^2$  to  $sp^3$ . Consequently, the presence of hydrogen appears to stabilize the formation of tetrahedra-coordination of carbon species (i.e.  $sp^3$  C-C bonds) and thus increase hardness.

Due to the high fraction of  $sp^3$ -bonds in the network of carbon matrix,

hydrogenated DLC layers possess excellent tribological properties, such as high hardness and wear resistance combined with a very low coefficient of friction under dry wear conditions [Erdemir, 2001; Erdemir, 2004]. However, it was reported that hardness decreases with an increase of the hydrogen even though the proportion of  $sp^3$  sites increases (that is, as the local bonding environment becomes more diamond-like) [Jansen et al., 1985; Kaplan et al, 1985]. Furthermore, Cho et al. [1990] and Rubin et al. [1990] observed that hardness decreased from 15 to 3 GPa with increased hydrogen content. It was also stated that a high concentration of hydrogen in the plasma in sputter deposition is undesirable [Bhushan, 1999a]. It is speculated that the high hydrogen content introduces frequent terminations in the otherwise strong three-dimensional network and hydrogen increases the soft polymeric component of the structure more than it enhances the cross-linking  $sp^3$  fraction [Bhushan, 1999a]. It was proposed [Angus and Hayman, 1988] that The optimum  $sp^3/sp^2$  in random covalent network composed of  $sp^3$  and  $sp^2$  carbon sites ( $N_{sp^2}$  and  $N_{sp^3}$ ) and hydrogen is:

$$\frac{N_{sp^2}}{N_{sp^3}} = \frac{6X_H - 1}{8 - 13X_H} \quad (1)$$

where  $X_H$  is the atom fraction of hydrogen.

Because the rising number of C-H bonds ultimately relieves stress, the hydrogenated DLC coatings have better adhesion [Bhushan, 1999a] to the substrate. However, the adhesive forces of these layers to counterparts are very low due to the formation of a softer “polymerlike” material at the interface. Such low adhesive forces,  $\pi-\pi^*$  interactions at sliding DLC-interfaces and hydration or bihydration of free or dangling  $\sigma$ -bonds of carbon atoms are responsible for excellent tribological properties [Erdemir, 2004] of hydrogenated DLC coatings. On the contrary, hydrogen-free

DLC-layers (a-C) show very low wear resistance and high frictional coefficients at dry wear conditions. This behavior can be explained with large amounts of  $sp^3$ -bonded carbon atoms in these layers, in which three  $\sigma$ -bonds are used to bond with other carbon atoms and the fourth one is free or dangled out of the surface Erdemir [2004]. Under dry wear conditions, the strong  $\sigma$ -bonds are exposed to the environment and create covalent bonds with opposing materials. However, the friction behaviors of both a-C and a-C:H change [Kim et al., 2006; Jiang et al., 2003] at wet conditions. In the case of a-C, free  $\sigma$ -bonds in hydrogen-free DLC-layers are passivated from water molecules and low coefficients of friction have been observed [Andersson, 2003]. In the case of a-C:H, gas molecules from the environment (water, oxygen, nitrogen) are weakly adsorbed to the hydrogenated DLC-layers and change the interaction to dipole-like associated with a high friction and low wear resistance. For instance, in the assessment of tribological behavior of highly hydrogenated DLC coatings ( $\sim 50$  at% hydrogen) on flat AISI 52100 steel substrates, the average friction coefficient range obtained in humid air, dry nitrogen and vacuum were, 0.22 to 0.27, 0.02 to 0.03, and 0.007 to 0.013, respectively [Vanhulsel et al., 2007].

More recently, the study of Mathis et al. [2008] further clarify the influence of hydrogen in amorphous carbon thin film of DLC type. They investigated the mechanical properties of Deuterated Diamond-like Carbon (DDLDC) in comparison with Diamond-like Carbon (DLC). The hydrogen (H) in the film was substituted by its isotope deuterium (D) through replacing  $CH_4$  by  $CD_4$  and their mixture 1:1 in the plasma. It was found that the incorporation of deuterium in the DLC layer can enhance the hardness and the apparent Young's modulus under specific  $V_{sb}$  conditions ( $-200V$  to  $-400V$ ) and allows to obtain a larger hardness range.

The tribological properties also depend on the thickness of DLC coatings. It was

reported that the wear resistance of a-C (hydrogen-free) layers is generally reduced with the increase of layer thickness, due to the increase of the surface roughness [Ronkainen et al., 1999]. It was found that the threshold thickness is 1  $\mu\text{m}$  by employing arc-PVD deposition systems. A novel combination of a thick a-C:H-layer with a thin a-C-top layer was proposed to optimize the tribological properties of DLC coatings. Thus, it is possible to combine the low coefficient of friction with high hardness. The thick a-C:H-layer (up to 2–3  $\mu\text{m}$ ) is responsible for optimized adhesion properties, homogeneity, thickness and high hardness, while a very thin homogeneous a-C-layer is responsible for low-friction coefficients in wet conditions.

(c) Adhesion of the coating to the substrate

Diamond-like carbon films generally exhibit high internal compressive stress and consequently, poor adherence to the substrate. The low adhesion strength [Takeuchi et al., 2004] results in peeling off from the substrate. In particular, the build-up of intrinsic stress in carbon thin films deposited by vapor deposition can be a major cause of delamination. This issue has been one of the main reasons why the industrial exploitation of carbon vapor deposited films has so far been of limited success. [Ha et al., 2007]

It has been found that the coating/substrate stiffness ratio influences considerably on the coating behavior in a finite element analysis and experimental observations of scratching test [Holmberg et al., 2008]. The DLC coating that had higher Young's modulus compared to the substrate material experienced high tensile stresses when loaded by the diamond sphere, while the coating that had lower stiffness compared to substrate material experienced comparatively low tensile stresses during scratching. Various approaches have been tried to reduce the internal stress including incorporating additional elements such as silicon and nitrogen [Ban et al. 2003;

Franceschini et al, 1992], metal, and ceramic [Voevodin et al., 1997; Rinon, 2001].

Although DLC coatings have been successfully deposited on variety of substrates, they mostly adhere best on silicon. Best adhesion is obtained on substrates that form carbides, e.g. Si, Fe and Ti. Based on depth profile analyses using Auger and XPS of DLC coatings deposited on silicon substrates, it has been reported that a substantial amount of silicon carbide (on the order of 5–10 nm in thickness) is present at the carbon–silicon interface for the coatings with good adhesion and high hardness (e.g. Ref. [Sander et al., 1987]). However, the major disadvantage of hard DLC film deposition is that there is often a relatively low adhesion of these films on metallic substrates caused by very high total compressive stress [Bull, 1995; Morshed et al., 2003a; Mosaner et al., 2003b; Takeuchi et al., 2004]. In addition to poor levels of adhesion and high intrinsic stresses, most commercially available DLC coatings suffer from low load-bearing capability, particularly when deposited on alloy steels. Poor adherence to non-metallic materials can be also an important negative aspect for wear resistant applications because it depends on the nature of the substrates (ceramic, polymer, etc.) and mainly on their structural and chemical surface characteristics.

To optimize adhesion properties of DLC, diverse strategies have been proposed, including different coating concepts such as: deposition of a thin metal interlayer [Takeuchi et al., 2004]; surface implantation; chemical interlayer gradients or a multilayer coating; variation of the self-bias voltage in the beginning of the deposition [Zhang, 2004]; and use of surface thermal treatments [Mosaner et al., 2003]. For good adhesion of DLC coatings to non-silicon substrates, in most cases, an interlayer of silicon is required except for cathodic-arc-deposited coatings [Bhushan, 1999a]. For growing DLC films on substrates of metallic alloy, the gradient composition interlayer is one of the most efficient strategies, although it requires a sophisticated

methodology. Other possibilities include deposition of a unique interlayer or a multilayer system between DLC and substrate, and the treatment of the substrate surface with an intense  $\text{Ar}^+$  plasma cleaning before DLC deposition [Treutler, 2005]. Some of these technologies have found wide acceptance in the market and have found applications in automotive industry (engine parts) and in biomedical devices. For instance, in Plasma Assisted Chemical Vapor Deposition (PACVD) techniques, a thin silicon interlayer is introduced between metallic substrates and a-C:H films by using different silicon precursors such as  $\text{C}_6\text{H}_{18}\text{Si}_2\text{O}$  (hexamethyldisiloxane) [Buríková et al., 2002],  $\text{Si}(\text{CH}_3)_4$  (tetramethylsilane) [Takeuchi et al., 2004], and  $\text{SiH}_4$  (silane) [Jun et al., 2000] in order to increase the coating's adherence. A continual change in the thermal expansion coefficient can be caused by the interlayers, specially the multilayers, and the stress in the DLC films is thus reduced.

Various metals have been added to reduce the internal stresses (and thus better adhesion) and to increase the toughness. These Me:C coatings are still much softer and can be used only at moderately high contact pressures. Recently, some carbon-based solid lubricant coatings have been developed that are capable of supporting high contact pressures with excellent tribological properties, whilst protecting contacting surfaces by providing a low friction transfer film [Yang et al., 2000; Jarratt et al., 2003; Field et al., 2004].

#### **5-4 Tribological mechanism of DLC**

The exact tribological mechanism responsible for the low friction characteristics of DLC films has not been unambiguously determined. Cho et al., [2005] indicated the formation of a lubricious third body layer at the friction contacts according to their results of the tribological investigations on DLC films. A hydrocarbon-rich transfer layer with low shear strength may be responsible for the low friction and wear rates of

the hydrogenated DLC films [Miyoshi, 1990; Hirvonen et al., 1990]. Based on the results of Raman scattering inside wear tracks, it has been suggested that the carbon-rich transfer layer has a graphite-like structure [Erdemir et al., 1991, 1994, 1995; Meletis and Erdemir, 1995]. It is believed that interfacial transfer layer of low shear strength, formed by a friction-induced transformation of the top layer of the DLC film controls the tribological behavior of DLC. Similar phase transformations have been known to occur at room temperature as a result of application of high normal loads for silicon [Pharr, 1992; Li et al., 2008], diamond [Gogotsi et al., 1999] and metallic glass [Kim et al., 2002] and as a result of high sliding friction for silicon [Kovalchenko, 2002]. We can thus conclude that the low friction and ultra low wear of DLC is attributed to a low shear strength graphite-like layer formed by friction-induced transformation [Erdemir et al., 1995, 1996; Voevodin et al., 1996] at the sliding interface as a result of thermal and strain effects generated during sliding. Its shear strength and its adhesion to the sliding surfaces are known to be affected by the environment and by the normal load and sliding velocity [Grill, 1997].

The studies on the phase transformation of DLC were mainly restricted to the micro- and macroscales. On the nanoscale, it was indicated that the nanowear behavior is strongly affected by variations in the normal load, number of sliding cycles, film thickness, and the deposition technique [Bhushan and Koinkar, 1995; Gupta and Bhushan, 1995b; Li and Bhushan, 1999; Sundararajan and Bhushan, 1999; Tambe and Bhushan, 2005b]. Tambe and Bhushan [2005c] presented nanoscale friction, adhesion, durability and wear data for DLC films. They provided evidence of phase transformation occurring at high normal loads, high sliding velocities and for a large number of sliding cycles on the nanoscale. They gave a contour map for friction force as a function of sliding velocity and normal load, with the contour lines representing

constant friction force. The concentric contour lines indicated that at relatively high normal loads and sliding velocities the contour map would reach a peak point, corresponding to the highest friction force. Beyond that point, any further increase in the normal load or the sliding velocity will result in a decrease in the friction force. Such a decrease implies a phase transformation whereby a low shear strength layer is formed at the sliding interface. The low friction force and high adhesive force values at high sliding velocities and the presence of wear particles are all indicative of a phase transformation by a mechanism similar to that reported on the macro- and microscales for DLC [Grill, 1997; Voevodin et al., 1996].

### **5-5 DLC for Micro/Nano-Tribological Applications**

The high hardness, good friction and wear properties, versatility in deposition and substrates and no requirements of post finishing make DLC very attractive for Micro/Nano-tribological applications. Two primary examples include overcoats for magnetic media and heads for magnetic storage devices [Bhushan, 1992, 1996a; Bhushan and Patton, 1996, 1998; Gupta and Bhushan, 1995a] and the emerging field of microelectromechanical systems (MEMS) [Bhushan, 1996b, 1998, 1999b, 1999c].

Overcoats of a-C:H [Fung et al., 2000] have long served the disk industry as the protective film for the underlying magnetic layer through the mid-1990s but have recently been replaced by amorphous nitrogenated carbon (a-C:N) [Waltman et al., 2002]. These a-C:N films are typically produced by sputtering carbon in the presence of nitrogen (N<sub>2</sub>). the physico-mechanical properties of the overcoat film are determined by the amount of N<sub>2</sub> incorporated into the CN film, along with the sp<sup>3</sup>/sp<sup>2</sup> ratio [Suzuki et al., 2004; Li et al., 2002; Neidhardt et al., 2004].

Ultra-thin film is often required for Micro/Nano-tribological applications.

However, it is noted that ultra-thin DLC coatings less than 10 nm may not uniformly coat the sample surface. In other words, coating may be discontinuous and deposited in the form of islands on the microscale. A possible reason for poor wear protection and the non-uniform failure of the coatings may be poor coverage of the thin coatings on the substrate. [Bhushan, 1999a]

## VI. Discussion

Properties of carbon allotropes, including diamond, graphite, and DLC coatings in bulk or thin film, are compared in Table 3. It is observed that the range of friction coefficient for each material is significant. This is because the dependence of friction on the crystal plane (for bulk diamond) and environment (e.g. gases and moisture). It should be noted that the tensile strength of a-C film, as shown in Table 3, is 6,100–8,500 MPa, which is based on the results of Cho et al. [2005]. They investigated the elastic and failure mechanical properties of hydrogen-free tetrahedral amorphous carbon (ta-C) MEMS structures via in situ direct and local displacement measurements of on-chip MEMS-scale specimens by conducting uniaxial tension tests that integrates atomic force microscopy (AFM) with digital image correlation (DIC). The tensile strength ( $7.3 \pm 1.2$  GPa) they measured for a-C is significantly higher than that of diamond (2.8 GPa). This seems to contradict with the general accepted concept that the tensile strength of diamond is the highest known. This issue need to be further investigated.

Table 4 illustrates the advantages and limitations of carbon allotropes from tribological point of view. It should be addressed that their tribological properties are significant influenced by the environmental factors such as humidity and gases.

Table 3 – Properties of carbon allotropes.

Property	Bulk			Thin Film	
	Diamond	Graphite	CVD Diamond	a-C	a-C:H
Hydrogen Content (H/C)	–	–	–	–	0.25-1
Growth Rate ( $\mu\text{m/hr}$ )	1000 (synthetic)	–	~1	2	5
Crystal Structure	Cubic $a_0 = 3.567\text{\AA}$	Hexagonal $a_0 = 2.47$	Cubic $a_0 = 3.561\text{\AA}$	Amorphous $sp^3/sp^2$	Amorphous $sp^3/sp^2$
Surface Topography	Faceted crystals	Trigonal pattern of atoms (STM)	Faceted crystals	Smooth or rough	Smooth
Density ( $\text{g/cm}^3$ )	3.5-3.53	2.18-2.22	2.8-3.52	1.6-3.26	1.2-2.6
Hardness ( $H_v$ )	7,000-10,000	65-79 (SSH*)	3,000-12000	20-10,000	1,200-6,000
Thermal Conductivity ( $\text{W/m K}$ )	900-2100	1800 (a, b) 8 (c)	700-1800	1.4-3.5	0.28-1.3
Refractive Index (at 591 nm)	2.418	2.15	2.38-2.41	1.5-3.1	1.6-3.1
Sound velocity [ $\text{m/s}$ ]	18,210		17,500	14,000-18,000	8,500-6,400
Friction coefficient	(100): 0.03-0.1 (111): 0.008-0.033	0.1 (in ambient air) 0.5-0.8 (in vacuum)	0.035-0.30	0.05-0.1	0.075-0.16
Poisson's ratio	0.2	0.2-0.4	0.07-0.1	0.14-0.2	0.22
Young's modulus [GPa]	1141	3.5-17	900-1140	11-780	5-590
Tensile strength [MPa]	2,800	14-83	400-1,400	6,100-8,500	
Compressive strength [MPa]	8,680	90-180	9,000		
Fracture toughness [ $\text{MPam}^{1/2}$ ]	3.40		5.5		

(\*SSH: Shore Scleroscope Hardness)

Table 4 – Advantages and limitations of carbon allotropes from tribological point of view.

	Advantages	Limitations
Fullerene	High load-bearing capacity. Low surface energy. High chemical stability. Low adhesion to the mating surface. Low friction and wear.	Poor solubility in common solvents. Wear particles are harder than as-deposited C <sub>60</sub> molecules.
Diamond	Very low wear. Low-friction in humid air or water. Relatively chemically inert. Poor adhesion with other solids. High thermal conductivity (allows dissipation of frictional heat during sliding and protects the interface). Form hydrocarbons (act as good lubrication films).	Rough surfaces (polycrystalline films with large grain size). High friction under vacuum, in dry air, dry argon and other dry and hydrogen free atmospheres. Coatings need to be deposited at high temperatures (severely limits the range of substrates). Coatings can only be deposited on selected substrates, and require surface finishing.
Graphite	An effective dry solid lubricant with relatively low friction. Friction coefficient is reduced markedly down to 0.1 level in the presence of water vapor or oxygen. Specialty items for use at very high or very low temperatures.	Lubricity depends on the adsorbed moisture. Friction coefficient is very high and fluctuated greatly under vacuum or inert atmosphere.
DLC	Can be produced at or near room temperature. Self-lubricating. Low friction coefficient. High wear resistance. Versatility in deposition and substrates. Reproduce substrate topography and do not require post-finishing. Under dry wear conditions, hydrogenated DLC (a-C:H) layers have high hardness and wear resistance combined with a very low coefficient of friction At wet conditions, hydrogen free (a-C) DLC layers show low frictional coefficients	Tribological properties vary significantly with deposition techniques. Low load-bearing capability. Decrease in hardness due to graphitization at high temperature (or power density). At dry wear conditions, a-C layers show very low wear resistance and high frictional coefficients. At wet conditions, a-C:H layers exhibit a high friction and low wear resistance. Wear resistance of a-C layers is generally reduced with the increase of layer thickness. High internal compressive stress and thus poor adherence to metallic substrates. Coatings less than 10 nm may not uniformly coat the sample surface.

## VII. Conclusions

A review of recent development in the research on the properties of carbon allotropes (fullerenes, diamond, graphite, and diamond-like carbon) is presented. It is observed that different structures and thus different properties of carbon allotropes result in significant different tribological properties. The environmental effects on the tribological behaviors are discussed.

Diamond carbon-like carbon (DLC) films show promising characteristics including high mechanical strength, high stiffness, low friction coefficient, self-lubricating properties, high wear resistance, high thermal conductivity, and high corrosion resistance. DLC protective coating is a good candidate to tribological applications. The tribological mechanism and phase transformation responsible for the low friction characteristics of DLC films is discussed in detail.

Future research on DLC coatings should be focused on seeking optimal deposition techniques with low cost and capacity to produce films at a high growth rate which have a minimum total stress, low friction coefficient, high wear resistance, and maximum adherence to substrates covering large surface areas and supporting high contact pressures.

## Reference

- Aisenberg, S. and Chabot R., 1971, "Ion beam deposition of thin films of diamond like carbon," *J. Appl. Phys.*, Vol. 49, pp. 953–2958.
- Andersson, J., Erck, R.A., and Erdemir, A., 2003, "Frictional behaviour of diamond-like carbon films in vacuum and under varying water vapor pressure," *Surf. Coat. Technol.*, Vol. 163–164, pp. 535–540.
- Andersson, J., 2004, "Microengineered CVD diamond surfaces – tribology and

- applications,” *Ph.D. Thesis* (Comprehensive summaries of Uppsala Dissertations from the Faculty of Science and Technology 977), Uppsala University.
- Angus, J.C., 1992, “Diamond and diamondlike films,” *Thin Solid Films*, Vol. 216, pp. 26–133.
- Angus, J.C. and Hayman, C.C., 1988, “Low pressure metastable growth of diamond and diamondlike phase,” *Science*, Vol. 241, pp. 913–921.
- Ban, M., Hasegawa, T., Fujii, S., and Fujioka, J., 2003, *Diamond Relat. Mater.*, Vol. 12, p. 47.
- Bhushan, B., 1992, *Mechanics and Reliability of Flexible Magnetic Media*, Springer, New York.
- Bhushan, B., 1996a, *Tribology and Mechanics of Magnetic Storage Devices*, 2nd ed., Springer, New York.
- Bhushan, B., 1996b, “Nanotribology and nanomechanics of MEMS devices,” In: *Proc. Ninth Annual Workshop on Micro Electro Mechanical Systems*, IEEE, New York, pp. 91–98.
- Bhushan, B. (Ed.), 1998, *Tribology Issues and Opportunities in MEMS*, Kluwer, Dordrecht.
- Bhushan, B., 1999a, “Chemical, mechanical and tribological characterization of ultra-thin and hard amorphous carbon coatings as thin as 3.5 nm: recent developments,” *Diamond and Related Materials*, Vol. 8, pp. 1985–2015.
- Bhushan, B. (Ed.), 1999b, *Handbook of MicroNanotribology*, 2nd ed., CRC, Boca Raton, FL.
- Bhushan, B. (Ed.), 1999c, *Springer handbook of nanotechnology*, Springer, New York..
- Bhushan, B. (Ed.), 2004, *Springer handbook of nanotechnology*, Springer, New York..
- Bhushan, B. and Gupta, B.K., 1997, *Handbook of Tribology: Materials, Coatings and Surface Treatments*, McGraw-Hill, New York, 1991. reprint ed. Krieger, Malabar, FL, 1997.
- Bhushan, B., Gupta, B.K., and Subramaniam, V.V., 1994, “Polishing of diamond films,” *Diamond Films Technol.*, Vol. 4, pp. 71–97.
- Bhushan, B., Gupta, B.K., VanCleeef, G.W., Capp, C., and Coe, J.V., 1993, “Fullerene (C<sub>60</sub>) films for solid lubrication,” *Tribol. Trans.*, Vol. 36, pp. 573–580.
- Bhushan, B., Kellock, A.J., Cho, N.H., Ager III, J.W., 1992, “Characterization of chemical bonding and physical characteristic of diamond like amorphous carbon and diamond films,” *J. Mater. Res.*, Vol. 7, pp. 404–410.
- Bhushan, B. and Koinkar, V.N., 1995, *Surf Coat Technol*, Vol. 76–77, p. 655.
- Bhushan, B. and Patton, S.T., 1996, “Pole tip recession studies of hard carbon coated thin-film tape heads,” *J. Appl. Phys.*, Vol. 79, pp. 5916–5918.
- Bhushan, B., Patton, S.T., 1998, Tribology in ultra-high-density tape drive systems: state of the art and future challenges,” *IEEE Trans. Magn.*, Vol. 34, pp. 1883–1888.
- Bijwe, J., 1997, “Composites as friction materials: recent developments in non-asbestos fiber reinforced friction materials—a review,” *Polym. Comp.* Vol. 18, No. 3, pp. 378–396.
- Blau, P.J. and Haberman, C.E., 1992, “An investigation of the microfrictional behavior of C<sub>60</sub> particle layers on aluminum,” *Thin Solid Films*, Vol. 219, p. 129.
- Bowden, F.B. and Hanwell, A.E., 1966, “The friction of clean crystal surfaces,” *Proc. Roy. Soc.*, Vol. A 295, pp. 233–243.
- Bowden, F.P. and Tabor, D., 1964, “The Friction and Lubrication of Solids. Part II,”

*Oxford University Press, Oxford.*

- Bragg W.L., 1928, *Introduction to Crystal Analysis*, Bell, p. 64.
- Broitman, E., Hellgren, N., Wänstrand, O., Johansson, M.P., Berlind, T., Sjöström, H., Sundgren, J.-E., Larsson, M., and Hultman, L., 2001, "Mechanical and tribological properties of CN<sub>x</sub> films deposited by reactive magnetron sputtering," *Wear*, Vol. 248, pp. 55–64.
- Bull, S.J., 1995, "Tribology of carbon coatings: DLC, diamond and beyond," *Diamond and Related Materials*, Vol. 4, Iss. 5-6, pp. 827-836.
- Buríková, V., Sládek, P., St'ahel, P., Zajíková, L., 2002, "Improvement of the efficiency of the silicon solar cells by silicon incorporated diamond-like carbon antireflective coatings," *Journal of Non-Crystalline Solids*, Vol. 299-302, Part 2, pp. 1147-1151.
- Casiraghi, C., Ferrari, A. C., and Robertson, 2005, *J. Phys. Rev. B*, Vol. 72, 085401.
- Catherine, Y., 1991, "Preparation techniques for diamondlike carbon" In: R.E. Clausing, L.L. Horton, J.C. Angus, and P. Koidl, Plenum (Eds.), *Diamond and Diamond-like Films and Coatings*, Plenum Press, New York, pp. 193–227.
- Cho, C.-W., Hong, B., Lee, Y.-Z., 2005, "Wear life evaluation of diamond-like carbon films deposited by microwave plasma-enhanced CVD and RF plasma-enhanced CVD method," *Wear*, Vol. 259, pp. 789–794.
- Cho, N.H., Krishnan, K.M., Veirs, D.K., Rubin, M.D., Hopper, C.B., Bhushan, B., and Bogy, D.B., 1990, "Chemical structure and physical properties of diamond-like amorphous carbon films prepared by magnetron sputtering," *J. Mater. Res.*, Vol. 5, pp. 2543–2554.
- Cuomo, J.J., Pappas, D.L., Bruley, J., Doyle, J.P., and Seagner, K.L., 1991, "Vapor deposition processes for amorphous carbon films with sp<sup>3</sup> fractions approaching diamond," *J. Appl. Phys.*, Vol. 70, pp. 1706–1711.
- Ensinger, W., 1992, *Rev. Sci. Instrum.*, Vol. 63, p. 5317.
- Erdemir, A., 2001, "The role of hydrogen in tribological properties of diamond-like carbon films," *Surface and Coatings Technology*, Vol. 146–147, pp. 292.-297
- Erdemir, A., 2004, *Tribol. Int.*, Vol. 37, p. 1005.
- Erdemir, A., Bindal, C., Fenske, G.R., Zuiker, C., and Wilbur, P., 1996, *Surf. Coat. Technol.*, Vol. 86–87, p. 692.
- Erdemir, A., Bindal, C., Pagan, J., and Wilbur, P., 1995, *Surf. Coat. Technol.*, Vol. 76–77, p. 559.
- Erdemir, A., Nichols, F.A., and Pan, X.Z., 1994, *Diamond Relat. Mater.*, Vol. 3, p. 119.
- Erdemir, A., Switala, M., Wei, R., Wilbur, P., 1991, *Surf. Coat. Technol.*, Vol. 50, p.17.
- Feng, B., 1997, "Relation between the structure of C<sub>60</sub> and its lubricity: a review," *Lubr. Sci.*, Vol. 9, pp. 181–183.
- Field J.E., 1991, In: Clausing RE, et al., editors., *Diamond and diamond-like films and coatings*, Plenum Press; New York, p. 17.
- Field, S.K., Jarratt, M., Teer, D.G., 2004, "Tribological properties of graphite-like and diamond-like carbon coatings," *Tribology International*, Vol. 37, Iss. 11-12, pp. 949-956.
- Franceschini, D.F., Achete, C.A., Freire Jr., F.L., 1992, *Appl. Phys. Lett.*, Vol. 60, p. 3229.
- Fung, M.K., Lai, K.H., Lai, H.L., Chan, C.Y., Wong, N.B., Bello, I., Lee, C.S., and Lee, S.T., 2000, *Diamond Relat. Mater.*, Vol. 9, p. 815.
- Gago, R., Abrasonic, G., Mücklich, A., Möller, W., Czigańy, Z., Radnoćzi, G., 2005a, "Fullerenelike arrangements in carbon nitride thin films grown by direct ion

- beam sputtering,” *Appl. Phys. Lett.*, Vol. 87, pp. 71901–71903.
- Gago, R., Jiménez, I., Neidhardt, J., Abendroth, B., Caertti, I., Hultman, L. et al., 2005b, “Correlation between bonding structure and microstructure in fullerene-like carbon nitride thin films,” *Phys. Rev.*, Vol. B71, pp. 125414–125416.
- Gardos, M.N., 1999, “Tribological fundamentals of polycrystalline diamond films,” *Surf. Coat. Technol.*, Vol. 113, pp. 183–200.
- Ginzburg, B.M., Shibaev, L.A., Kireenko, O.F., Sheelevskii, A.A., Baidakova, M.V., and Sitnikova, A.A., 2002, “Antiwear effect of fullerene C<sub>60</sub> additives to lubricating oils,” *Russ. J. Appl. Chem.*, Vol. 75, pp. 1330–1335.
- Gogotsi, Y.G., Kailer, A., and Nickel, K.G., 1999, *Nature*; Vol. 401, p. 663.
- Grill, A., 1997, “Tribology of diamondlike carbon and related materials: an updated review,” *Surface and Coating Technology*, Vol. 94-95, pp. 507-513
- Grill, A. Meyerson, B. S., 1994, “Development and status of diamondlike carbon,” In Spear, K. E. and Dismukes, J. P. (eds.), *Synthetic Diamond: Emerging CVD Science and Technology*, Wiley, New York, pp. 91–141.
- Gupta, B.K. and Bhushan, B., 1994, “Fullerene particles as an additive to liquid lubricants and greases for low friction and wear,” *Lubr. Eng.*, Vol. 50, pp. 524–528.
- Gupta, B.K. and Bhushan, B., 1995a, “Mechanical and tribological properties of hard carbon coatings for magnetic recording heads,” *Wear*, Vol. 190, pp. 110–122.
- Gupta, B.K. and Bhushan, B. 1995b, *Thin Solid Films*, Vol. 270, p. 391.
- Gupta, B.K., Bhushan, B., Capp, C., and Coe, J.V., 1994, “Material characterization and effect of purity and ion implantation on the friction and wear of sublimed fullerene films,” *J. Mater. Res.* Vol. 9, pp. 2823–2838.
- Ha, P.C.T., McKenzie, D.R., Bilek, M.M.M., Kwok, S.C.H., Chu, P.K., Tay, B.K., 2007, “Raman spectroscopy study of DLC films prepared by RF plasma and filtered cathodic arc,” *Surface & Coatings Technology*, Vol. 201, pp. 6734–6736.
- Ham, M. and Lou, K.A., 1989, *J. Vac. Sci. Technol. A.*, Vol. 8, p. 2143.
- Hayward, I.P. and Singer, I.L., 1989, *SDIO/IST-ONR Diamond Technology Initiative Symposium*, Crystal City, Virginia.
- Hiroyuki, H., Takayuki, Y., and Takashi, T., 2001, *IEEE Trans. Magn.*, Vol. 37, No. 4, p. 1789.
- Hirvonen, J.-P. Lappalainen, R. Koskinen, J., Anttila, A., Jervis, T.R. and Trkula, M., 1990, *J. Mater. Res.*, Vol. 5, p. 2524.
- Holmberg, K., Ronkainen, H., Laukkanen, A., Wallin, K., Erdemir, A., and Eryilmaz, O., 2008, “Tribological analysis of TiN and DLC coated contacts by 3D FEM modelling and stress simulation,” *Wear*, Vol. 264, pp. 877–884.
- Jansen, F., Machonkin, M., Kaplan, S., and Hark, S., 1985, “The effect of hydrogenation on the properties of ion beam sputter deposited amorphous carbon,” *J. Vac. Sci. Technol. A*, Vol. 3, pp. 605–609.
- Jiang, J., Zhang, S., and Arnell, R.D., 2003, “The effect of relative humidity on wear of a diamond-like carbon coating,” *Surface and Coatings Technology*, Vol. 167, p. 221-225.
- Jarratt, M., Stallard, J., Renevier, N.M., Teer, D.G. 2003, “An improved diamond-like carbon coating with exceptional wear properties,” *Diamond and Related Materials*, Vol. 12, No. 3–7, pp. 1003–7.
- Jradi, K., Schmitt, M., and Bistac, S., 2009, “Surface modifications induced by the friction of graphites against steel,” *Applied Surface Science*, Vol. 255, pp. 4219–4224.

- Jun, Y., Choi, J.-Y., Lee, K.-R., Jeong, B.-K., Kwon, S.-K., Hwang, C.-H., 2000, "Application of diamond-like carbon films to spacer tools for electron guns of cathode ray tube (CRT)" *Thin Solid Films*, Vol. 377-378, , pp. 233-238.
- Kaplan, J., Jansen, F., and Machonkin, M., 1985, "Characterization of amorphous carbon-hydrogen films by solid-state nuclear magnetic resonance," *Appl. Phys. Lett.*, Vol. 47, pp. 750-753.
- Kim, H.I., Lince, J.R., Eryilmaz, O.L., and Erdemir, A., 2006, *Tribol. Lett.*, Vol. 21, p.53.
- Kim, J.-J., Choi, Y., Suresh, S., and Argon, A.S., 2002, *Science*, Vol. 295, p. 654.
- Kolluri, D., Ghosh, A.K., and Bijwe, J., 2009, "Analysis of load-speed sensitivity of friction composites based on various synthetic graphites," *Wear*, Vol. 266, pp. 266-274.
- Kovalchenko, A., Gogotsi, Y., Domnich, V., Erdemir, A., 2002, *Tribol Trans*, Vol. 45, p. 372.
- Kratschmer, W., Lamb, L.D., and Fostiropoulos, K., 1990, "Solid C<sub>60</sub>: a new form of carbon," *Nature*, Vol. 347, p. 54.
- Kroto, H.W. and Heath, J.R., 1985, "S.C. O'Brien, C<sub>60</sub>: Buckminster fullerene," *Nature*, Vol. 318, p. 162.
- Kvasnica, S., Schalko, J.; Eisenmenger-Sittner, C.; Benardi, J.; Vorlaufer, G.; Pauschitz, A.; and Roy, M., 2006, "Nanotribological study of PECVD DLC and reactively sputtered Ti containing carbon films," *Diamond and Related Materials*, Vol. 15, No. 10, pp. 1743-1752.
- Lancaster, J. and Pritchard, J., 1980, *Journal of Physics D*, Vol. 13, p. 1551.
- Lancaster, J. and Pritchard, J., 1981, *Journal of Physics D*, Vol. 14, p. 747.
- Li, X. and Bhushan, B. J., 1999, *Mater. Res.*; Vol. 14, p. 2328.
- Li, X., Lu, J., Liu, B., and Yang, S., 2008, "Tribological behavior and phase transformation of single-crystal silicon in air," *Tribology International*, Vol. 41, pp. 189-194.
- Li, Y.W., Shue, Y.B., Chen, C.F., Yu, T.C., and Chang, J.J.K., 2002, *Diamond Relat. Mater.*, Vol. 11, p.1227.
- Litovchenko, V.G., Klyui, N.I., 2001, *Sol. Mater. Sol. Energy Cells*, Vol. 68, p. 55.
- Mathis, N., Meunier, C., Guibert, G., Mikhailov, S., and Berthout, G., 2008, "Deuterated Diamond Like Carbon films (DDLCC): Mechanical properties in relation with microstructure," *Surface & Coatings Technology*, Vol. 202, pp. 2349-2353.
- McKenzie, D.R., 1996,. "Tetrahedral bonding in amorphous carbon," *Rep. Prog. Phys.*, Vol. 59, No. 12, pp. 1611-1664.
- Meletis, E.I., Erdemir, A., and Fenske, G.R., "Tribological characteristics of DLC films and duplex plasma nitriding/DLC coating treatments," 1995, *Surface and Coatings Technology*, Vol. 73, Issues 1-2, p. 39-45.
- Meunier, C., Munnik, F., Germann, E., Schluechter, R., Pujol, M.D., Kondratiev, S.N., and Mikhailov, S., 2004, *Surf. Coat. Technol.*, Vol. 181-181, p. 234.
- Meunier, C., Stauffer, Y. Daglar, A., Chai, F., Mikhailov, S., and Hildebrand, H.F., 2006, *Surf. Coat. Technol.*, Vol. 200, p. 6346.
- Miyagawa, S., Nakao, S., Ikeyama, M., Miyagawa, Y., 2002, *Surf. Coat. Technol.*, Vol. 156, p. 322.
- Miyoshi, K., 1990, *Surf. Coat. Technol.*, Vol. 43-44, p. 799.
- Morshed, M.M., McNamara, B.P., Cameron, D.C., Hashmi, M.S.J., 2003a, "Stress and adhesion in DLC coatings on 316L stainless steel deposited by a neutral beam source," *Journal of Materials Processing Technology*, Vol. 143-144, pp.

- 922-926.
- Morshed, M.M., McNamara, B.P., Cameron, D.C., Hashmi, M.S.J., 2003b, "Stress and adhesion in DLC coatings on 316L stainless steel deposited by a neutral beam source," *Journal of Materials Processing Technology*, Vol. 141, Iss. 1, pp. 127-131.
- Mosaner, P., Bonelli, M., Miotello, A., 2003, "Pulsed laser deposition of diamond-like carbon films: reducing internal stress by thermal annealing," *Applied Surface Science*, Vol. 208-209, pp. 561-565.
- Neidhardt, J., Czigány, Z., Brunell, I.F., and Hultman, L., 2003, "Growth of fullerene-like carbon nitride thin solid films by reactive magnetron sputtering; role of low-energy ion irradiation in determining microstructure and mechanical properties," *J. Appl. Phys.*, Vol. 93, pp. 3002–3015.
- Neidhardt, J., Hultman, L., Broitman, E., Scharf, T.W., and Singer, I.L., 2004, *Diamond Relat. Mater.* Vol. 13, p. 1882.
- Pharr, G.M., 1992, In Nix, W.D., Bravman, J.C., Arzt, E., and Freund, L.B., editors. *Thin film: stresses and mechanical properties III*, Vol. 239, Materials Research Society, Pittsburgh; p. 301.
- Podgornik, B., 2005, *Surf. Coat. Technol.*, Vol. 200, p. 1982.
- Reisel, G., Wielage, B., Steinhäuser, S., and Hartwig, H., 2003, *Diamond Relat. Mater.*, Vol. 12, p. 1024.
- Rinon, C., Zambrano, G., Carvajal, A., Prieto, P., Galindo, H., Martinez, E., Lousa, A., and Esteve, J., 2001, *Surf. Coat. Technol.*, Vol. 148, p. 277.
- Robertson, J., 1992, "Properties of diamond-like carbon," *Surf. Coat. Technol.*, Vol. 50, pp. 185–203.
- Robertson, J. 1999, "Deposition and properties of diamond-like carbon," *Material Research Society Symposium Proceedings*, Vol. 555, p. 12.
- Robertson, J. 2002, "Diamond-like amorphous carbon," *Mater. Sci. Eng. R*, Vol. 37, pp. 129–281.
- Ronkainen, H., Koskinen, J., Varjus, S., and Holmberg, K., 1999, *Tribol. Lett.*, Vol. 6, p. 63.
- Rubin, M., Hooper, C.B., Cho, N.H., and Bhushan, B., 1990, "Optical and mechanical properties of dc sputtered carbon films," *J. Mater. Res.*, Vol. 5, pp. 2538–2542.
- Sander, P., Kaiser, U., Altebockwinkel, M., Wiedmann, L., Benninghoven, A., Sah, R.E., and Koidl, P., 1987, "Depth profile analysis of hydrogenated carbon layers on silicon by x-ray photoelectron spectroscopy, Auger electron spectroscopy, electron energy-loss spectroscopy and secondary ion mass spectrometry," *J. Vac. Sci. Technol. A*, Vol. 5, pp. 1470–1473.
- Seal, M. and Proc, R., 1958, *Soc. London A*, Vol. 248, p. 379.
- Sedlaček, M., Podgornik, B., and Vižintin, J., 2008, "Tribological properties of DLC coatings and comparison with test results: Development of a database," *Materials Characterization*, Vol. 59, pp. 151–161.
- Shamsa, M., Liu, W.L., Balandina, A.A., Casiraghi, C., Milne, W.I., and Ferrari, A.C., 2006, "Thermal conductivity of diamond-like carbon films," *Applied Physics Letters*, Vol. 89, p. 161921.
- Silva, S.R.P., Carey, J.D., Khan, R.U.A., Gerstner, E.G., and Anguita, J.V., 2002, In H.S. Nalwa (Ed.), *Handbook of Thin Materials*, Vol. 4, Academic Press, p. 403.
- Spencer, E.G., Schmidt, P.H., Joy, D.C., and Sansalone F.J., 1976, "Ion beam deposited polycrystalline diamondlike films," *Appl. Phys. Lett.*, Vol. 29, pp. 118–120.
- Sundararajan, S. and Bhushan, B., 1999, "Micro/Nanoscale friction and wear

- mechanisms of ultrathin hard amorphous carbon coatings using atomic force microscopy,” *Wear*, Vol. 225-229, pp. 678-689.
- Suzuki, M., Ohana, T., Tanaka, A., 2004, *Diamond Relat. Mater.*, Vol. 13, p. 2216.
- Tabor, D., 1979, In: Field, J.E. (Ed.), *The properties of diamond*, Academic Press, London, p. 325.
- Takeuchi, S., Tanji, A., Miyazawa, H., and Murakawa, M., 2004, *Thin Solid Films*, Vol. 447-448, pp. 208-211.
- Tambe, N.S. and Bhushan, B., 2005b, “Friction model for the velocity dependence of nanoscale friction,” *Nanotechnology*, Vol. 16, No. 10, pp. 2309-2324.
- Tambe, N.S. and Bhushan, B., 2005c, “Nanoscale friction-induced phase transformation of diamond-like carbon,” *Scripta Materialia*, Vol. 52, pp. 751-755.
- Treutler, C.P.O., 2005, “Industrial use of plasma-deposited coatings for components of automotive fuel injection systems,” *Surface and Coatings Technology*, Vol. 200, Issues 5-6, pp. 1969-1975.
- Tsai, H. and Body, P., 1987, *J. Vac. Sci. Technol. A*, Vol. 5, p. 3287.
- Vanhulsel, A., Velasco, F., Jacobs, R., Eersels, L., Havermans, D., and Roberts, E.W., 2007, “DLC solid lubricant coatings on ball bearings for space applications,” *Tribology International*, Vol. 40, pp. 1186-1194.
- Voevodin, A., Capno, M., Laube, S., Donley, M., Zabinski, J., 1997, *Thin Solid Films*, Vol. 298, p. 107.
- Voevodin, A.A., Phelps, A.W., Zabinski, J.S., Donley, M.S., 1996, *Diamond Relat. Mater.*, Vol. 5, p. 1264.
- Waltman, R.J. and Tyndall, G.W., 2002, *J. Magn. Soc. Japan*, Suppl., Vol. 26, p. 97.
- Wang, X., Wang, P., Yang, S., Zhang, J., 2008, “Tribological behaviors of fullerene-like hydrogenated carbon (FL-C:H) film in different atmospheres sliding against Si<sub>3</sub>N<sub>4</sub> ball,” *Wear*, Vol. 265, pp. 1708-1713.
- Wilks, E.M. and Wilks, J.J., 1972, *Phys D: Appl Phys*, Vol. 5, p. 1902.
- White, C.T., Mintmire, J.W., and Mowrey, R.C., 1993, “Buckminster fullerenes,” *VCH Press, New York*, p. 125.
- Xu, M., Li, L., Cai, X., Liu, Y., Chen, Q., and Chu, P.K., 2006, *Diamond Relat. Mater.*, Vol. 15, p. 952.
- Yan, F.Y., Jin, Z.S., Zhang, X.S., 1993, “Study on tribological behavior of C<sub>60</sub>/C<sub>70</sub> as an oil additive,” *Tribology*, Vol. 1, p. 59 (in Chinese).
- Yang, P., Huang, N., Leng, Y.X., Chen, J.Y., Fu, R.K.Y., Kwok, S.C.H., Leng, Y., and Chu, P.K., 2003, *Biomaterials*, Vol. 24, p. 2821.
- Yang, S., Camino, D., Jones, A.H.S., Teer, D.G., 2000, Deposition and tribological behaviour of sputtered carbon hard coatings,” *Surface and Coatings Technology*, Vol. 124, p. 110.
- Yen, B., 1996, *Wear*, Vol. 192, p. 208.
- Zaidi, H., Robert, F., and Paulmier, D., 1995, *Thin Solid Films*, Vol. 264, p. 46.