Plasma-deposited diamondlike carbon and related materials

by A. Grill

Diamondlike carbon (DLC) prepared by plasma-enhanced CVD is a metastable amorphous material characterized by attractive optical, electrical, chemical, and tribological properties. DLC films can be prepared at low temperatures from a large variety of precursors, and can be modified by the incorporation of different elements such as N, F, Si, or metals. The diversity of plasma conditions and precursors used for the deposition of DLC films provides flexibility to tailor their properties for specific needs and potential applications. This paper presents a review of the preparation of DLC and related materials, their properties, and their use in different applications.

Introduction

Diamondlike carbon (DLC) is an amorphous, in most cases hydrogenated, metastable material. The designation *diamondlike* has arisen because the material is characterized by properties that are to a certain extent similar to those of diamond: high hardness, high wear resistance and low friction coefficient, chemical inertness, high electrical resistance, and optical transparency in the visible and infrared. DLC films were first deposited by Aisenberg and Chabot in 1971 by quenching a beam of C^+ ions accelerated in a vacuum of 10^{-6} Torr to a negatively biased substrate [1]. The attractive properties of the material have stimulated a large amount of research on their deposition and characterization, and on the development of relevant applications.

Diamond and graphite are stable forms of carbon with well-defined crystallographic structures. Natural diamond is a crystalline material, and the diamond films fabricated by various CVD methods are composed of diamond microcrystallites up to tens of microns in size. Crystalline diamond is composed entirely of tetrahedrally coordinated sp^3-bonded carbon. Diamond and diamond films are thus constituted of a well-defined material with fixed properties. In contrast, DLC films lack any long-range order and contain a mixture of sp^3-, sp^2-, and sometimes even sp^1-coordinated carbon atoms in a disordered network. The ratio between the carbon atoms in the different coordinations depends on deposition conditions and, in hydrogenated DLC films, has been found to be a strong function of the hydrogen content of the films. While missing a long-range order, DLC may have medium-range ordering, as is discussed later. The properties of DLC therefore cover a wide range of values between those of diamond, graphite, and hydrocarbon polymers, as illustrated in **Figure 1**.

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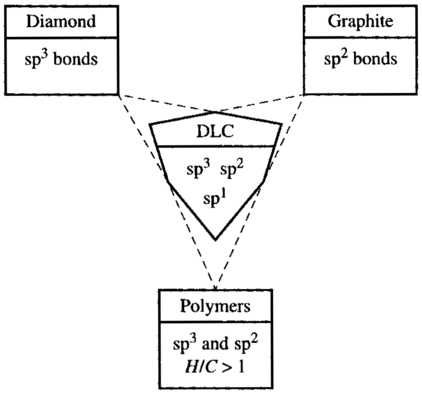

Figure 1

Delimitations of DLC properties relative to other forms of carbon materials. Adapted from [2], with permission.

"Pure" DLC composed of carbon and/or hydrogen can be classified as follows: hydrogenated amorphous carbon, a–C:H, and amorphous carbon, a–C. The first type contains from less than 10% [3] to 60% [4] hydrogen; incorporation of hydrogen in this type of DLC is important for obtaining diamondlike properties. The second type, amorphous carbon, contains less than 1% hydrogen.

In the quest to change and improve the properties of DLC films, various materials derived from carbon films have been developed. Such materials are similar in structure to DLC but, in addition to carbon and/or hydrogen, they include nitrogen (NDLC or CN_x films), silicon (SiDLC), fluorine (FDLC), and metal atoms (MeDLC). Most modifications have been made to DLC to reduce its (typically high) internal compressive stresses (N, Si, metal incorporation), or to reduce its surface energy for further lowering of its already low friction coefficients (F, Si–O incorporation) [5, 6]. In 1989 Liu and Cohen [7] made theoretical predictions of the potential existence of a crystalline material C_3N_4, similar to Si_3N_4. This has led to extensive studies of CN_x films; however, in spite of various claims, such a crystalline structure has not yet been unequivocally identified.

PECVD-deposited DLC films grow as continuous films, even at a thickness less than 50 nm; they are uniform over wide areas, and their roughness can be a fraction of an angstrom [5]. Because of their attractive properties, DLC films and their modifications have been technologically developed for a variety of applications, and new potential applications are being investigated. The following sections present a general review of the preparation techniques for DLC and related films and their structure, physical, and tribological properties, as well as an overview of the studies of such materials at the IBM Thomas J. Watson Research Center. A description of earlier studies at IBM can be found elsewhere [8].

Preparation techniques

Since diamondlike carbon is a metastable material, DLC and related films must be deposited while their surfaces are continuously bombarded with energetic ions in order to obtain diamondlike properties. The metastable structure of DLC films most likely originates from the thermal and pressure spikes produced by the impinging energetic species on the growth surface [9]. Since the deposition by Aisenberg and Chabot, a variety of techniques based on beam and plasma techniques have evolved for the preparation of DLC. Such methods include single low-energy beams of carbon ions, dual ion beams of carbon and argon, ion plating, rf sputtering or ion-beam sputtering from carbon/graphite target, vacuum-arc discharges, or laser ablation. Details of the different deposition methods and of specific references can be found elsewhere [5]. While some of the mentioned methods are being extensively used in investigations of nonhydrogenated carbon (taC = tetrahedral carbon), the main techniques for depositing diamondlike carbon films are, however, based on plasma-enhanced chemical vapor deposition (PECVD) reactors and magnetron sputtering.

PECVD deposition of DLC is generally performed in plasmas sustained by rf excitation [2, 10–13], but dc discharge systems [14–16], microwave plasmas [17], and ECR systems [18, 19] have also been used. High-density plasma (HDP) tools have been used recently for deposition of modified DLC films [20, 21]. PECVD deposition of DLC and related films is preferably performed in systems using parallel-plate reactors, as illustrated in **Figure 2**. Of the various possible geometries, parallel-plate reactors are preferred because they allow the deposition of uniform films over large areas and can be scaled up relatively easily for coating large areas. In the rf PECVD reactors, the substrates are placed on the rf-powered electrode (Figure 2), thus attaining a negative dc self bias, which is dependent on the precursor gases used, deposition parameters (e.g., power, pressure), and relative area of electrodes [22]. In dc PECVD the plasma is sustained by applying the negative dc voltage to the substrate electrode [16].

Any hydrocarbon can be used as a precursor for DLC deposition by the PECVD method, provided it has sufficient vapor pressure to be transported into the reactor. Details on the use of specific precursors can be found elsewhere [5]. Hydrogen or argon is sometimes added to the hydrocarbon precursor used in the PECVD reactors; however, the effect of such additions to the properties of DLC is not obvious [23, 24]. The growth rates of the films may decrease with dilution of the precursor with hydrogen, and in some cases the addition of hydrogen can have a detrimental effect on the film properties. In other cases it was found that under certain plasma conditions, the addition of argon to the hydrocarbon precursor can improve DLC properties [25, 26].

In addition to the large variety of precursors, DLC deposition conditions also spread over large ranges of parameters. DLC depositions have been carried out in rf PECVD systems at an rf power of 15–1000 W, a negative substrate bias of 100–1500 V dc, a pressure of 6 mTorr–7.5 Torr, and a substrate temperature between room temperature and 250°C. While power density is a more significant deposition parameter than rf power, it is not always possible to determine this value from published results, because reported depositions have been performed in reactors of different sizes and geometries. Nevertheless, it seems that power densities of the order of 0.1–0.5 W/cm^2 are generally used to obtain DLC films in PECVD systems. Deposition of DLC must be carried out at substrate temperatures below 325°C to prevent graphitization [14].

In the PECVD processes, DLC grows mainly by condensation of the radicals formed in the plasma; however, while the concentration of the ions in the plasma is several orders of magnitude smaller than that of the radicals, ion bombardment is an important factor affecting the growth and properties of the films. With use of the right conditions, the films deposited on the biased electrode of an rf reactor are hard DLC. Under the same conditions, the films deposited on the grounded electrode are soft and polymerlike. The deposition rate on the biased electrode is also much higher than on the grounded electrode. This can be explained by assuming that the ion bombardment leads to increased fragmentation of the hydrocarbon species arriving at the surface to ever more hydrogen-deficient radical species, resulting in an increased sticking coefficient on the bombarded surface [27]. The near-surface excited region is quenched by the underlying cold substrate. Angus and Jansen [28] have proposed that the composition of a DLC film, and its average nearest-neighbor coordination, adjust to a minimum possible energy state through the incorporation of hydrogen.

Deposition of DLC films by PECVD is usually performed in rf-sustained plasmas, although dc plasmas have also been used for PECVD of DLC films. It is generally believed that because of the insulating characteristic of DLC, it may not be possible to apply the dc voltage through the films in order to sustain the plasma and grow them. Therefore, dc deposition of DLC has been performed in PECVD systems with an additional screen in front of the sample electrode [14, 15] or by using a triode configuration [29]. However, it has been shown that highly insulating DLC films can be deposited on electrically conductive substrates using a dc-powered diode-type parallel-plate reactor [16]. The deposition is possible at sufficiently high bias because, as shown later, the resistivity of the DLC films is not constant and drops several orders of magnitude at high electric fields, enabling bias transfer to their surface. DLC films several micrometers thick have been grown by dc PECVD at high rates using low power densities (~0.25 W/cm^2) [16].

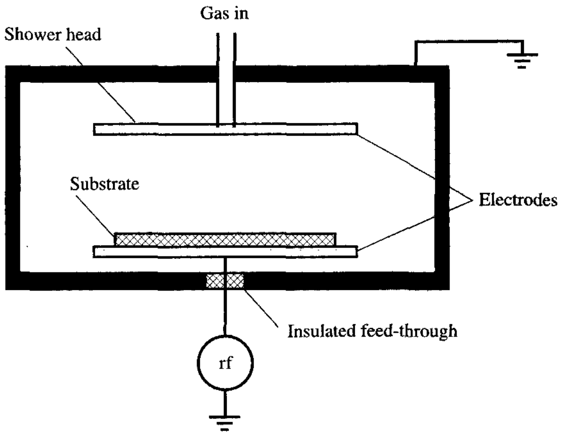

Figure 2

Schematic diagram of PECVD reactor for depositing DLC films. Note placement of the substrate on the powered electrode.

Modified DLC films can be prepared by PECVD by admixing volatile precursors of the modifying elements to the main gas feed. Thus, NDLC (or CN$_x$) films have been prepared from mixtures of hydrocarbons with nitrogen [30], SiDLC films have been prepared by adding diluted SiH$_4$ to the hydrocarbon [31], and FDLC films have been deposited from pure fluorocarbons or fluorocarbons diluted with hydrogen [32]. Metal incorporation was achieved by sputtering a metal or metal carbide target in a plasma of argon with hydrocarbon mixture [33, 34].

Bias and temperature effects

The substrate bias appears to be the dominant factor determining the properties of DLC films. Their hardness, density, and refractive index increase with increasing bias, while their hydrogen content and optical gap usually decrease with increasing bias [5, 16, 25]. It should, however, be noted that in most PECVD deposition cases the bias is not controlled directly as an independent process variable. In rf PECVD deposition systems, the substrate bias is frequently changed by changing the rf power (W) and/or the pressure in the reactor (p). According to Catherine [29], the self-bias of the substrate (V_B) in a specific reactor is related to these two parameters by the expression

$$V_B \propto \left(\frac{W}{p}\right)^{1/2}. \tag{1}$$

The substrate bias in PECVD systems can thus be varied by adjusting the bias directly, or by adjusting the rf power and/or the pressure in the reactor. Varying the substrate bias by changing the rf power affects not only the phenomena occurring at the surface of the growing film but also the fragmentation of the precursors in the plasma. Reports about the "effect of bias" on the properties of DLC films may therefore reflect the combined effects of two independent plasma parameters, W and p, and thus variations in the active source species produced in the plasma by changes in the degree of fragmentation of the precursor gas. In addition, for identical gases and identical values of pressure and rf power, the self-bias also depends on the reactor geometry, making it difficult to extrapolate results from one reactor to another.

At the relatively high pressures used in PECVD of DLC films, the ions are scattered by collisions and reach the substrate with a distribution of energies lower than the applied bias. The average impact energy (E) of ions bombarding the growing film in the rf plasma therefore depends on the dc bias and on the pressure in the reactor, according to the relation [35]

$$E \propto \frac{V_B}{p^{1/2}}. \tag{2}$$

It has been claimed [2] that a substrate bias higher than 100 V dc is required to obtain hard DLC-type films. However, this lower bias threshold can depend on the pressure during deposition, because operation at high pressure reduces the average energy of species impinging on the growth surface. At sufficiently low pressures, the threshold value is relaxed, and hard, wear-resistant films can be obtained at negative bias smaller than 100 V dc [8, 13].

The minimum bias required to obtain diamondlike characteristics can also be affected by the precursor used to deposit the films. Thus, for films deposited by dc PECVD, a higher bias is required to obtain films with DLC characteristics from cyclohexane than is required for films deposited from acetylene [25]. However, for the same deposition system, enhancement of the ion bombardment of the films by addition of argon to the precursor enables the preparation of hard DLC films from cyclohexane at the lower bias.

The substrate temperature during deposition is another parameter which can affect the properties and deposition rate of DLC films. The deposition rate of DLC increases with decreasing temperature and increasing ion bombardment. The decrease of the rate of deposition with increasing substrate temperature can be explained by assuming that growth takes place through the interaction between the surface and a physisorbed layer of hydrocarbon. This assumption is consistent with the low values of growth activation energies (0.05–0.5 eV) and with the increase of the deposition rate with increasing ion bombardment [29].

It was reported that the optical gap of DLC films decreases with increasing substrate temperature, with a rapid decrease taking place above 250°C [14, 36]. While some properties of DLC films, such as their index of refraction [37] or wear resistance, are a weak function of the deposition temperature, substrate temperature can have a significant impact on their hydrogen content and thermal stability [38]. Deposition at temperatures above 325°C has been found to result in a sharp decrease of their electrical resistivity and in significant film softening [14]. DLC deposition is therefore performed at substrate temperatures well below 300°C. Low deposition temperature may lead in certain conditions to the formation of a polymerlike film, or a polymerlike fraction embedded in a hard DLC layer [13].

Structure and composition of DLC and related materials

The properties of DLC films are determined by the bonding hybridization of the carbon atoms and the relative concentration of the different bonds, i.e., sp^3:sp^2:sp^1, as well as by the hydrogen distribution among the different types of bonds. In hydrogenated DLC films, some of the carbon bonds are terminated by hydrogen. A fraction of the hydrogen can be incorporated as single atoms, as well as molecules in voids. Voids have been assumed to explain the hardness or densities of DLC films [39, 40]. While direct evidence of such voids has not been reported, it has been shown that depending on deposition conditions, more than 50% of the hydrogen incorporated in DLC films can indeed be unbounded hydrogen [16, 41].

The structure of hydrogenated DLC films can be described as a random network of covalently bonded carbon in the different coordinations. Robertson [42] claimed that in addition to the short-range order defined by carbon hybridization and hydrogen content, a substantial degree of medium-range order on the ~1-nm scale also exists in the films. The material can accordingly be described as a network of graphitic clusters of fused sixfold rings, linked into islands by sp^3 bonds. The formation of the graphitic clusters relieves the strain in the DLC structure. According to Robertson's model, the existence of the optical gap in DLC films is the result of the correlation of hexagonal rings on a very fine scale and does not necessarily prove a preponderance of diamondlike sp^3 bonding [42]. The width of the optical gap was claimed to depend on the degree of medium-range order and was found to vary inversely with the square root of the size of the clusters, being proportional to $6N^{-1/2}$, N being the number of aromatic rings in a cluster.

Angus and Jansen have described the structure of hydrogenated DLC (a-C:H) by a random covalent fully constrained network (FCN) model [28]. The model was based on the assumption that a random covalent network is mechanically constrained when the number of constraints equals the number of mechanical degrees of freedom. The authors found that in a covalent network composed solely of sp^2 and sp^3 carbon sites, in which some clustering of aromatic rings occurs, the optimal ratio of the number of sites for each coordination, designated in [28] as sp^3/sp^2, is determined by the atomic fraction of hydrogen incorporated in the film, X_H, and is given by

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

The DLC structure can be described according to the FCN model as a three-dimensional array of rings, containing mostly six-membered rings but also five- and seven-membered rings. Such a cross-linked structure lacks long-range order, and the material appears amorphous [28]. According to Equation (3), the optimal coordinated carbon network can exist only for bound hydrogen concentrations $0.167 < X_H < 0.615$. The FCN model thus defines the range of hydrogen concentrations for which it is possible to obtain amorphous hydrogenated carbon with diamondlike properties, but does not indicate the distribution of hydrogen among the different carbon sites. The model takes into account only the concentrations of hydrogen bound to carbon atoms. Since some hydrogen can be unbound, the total hydrogen content in DLC films may extend beyond the upper limit.

- *Bonding characterization*

The structural characterization of DLC films is complicated by their amorphous nature. A variety of spectroscopic techniques, such as Fourier transform infrared absorption (FTIR), Raman, NMR, and electron energy loss spectroscopy (EELS), have been used to characterize the structure and composition of DLC films. While each of these techniques provides some qualitative information about their structure, the interpretation of the results is often indirect and sometimes even misleading.

FTIR is often used to characterize hydrogenated DLC and related films. Typical for the FTIR spectra of hydrogenated diamondlike carbon is the wide absorption band centered at about 2900 cm^{-1}. This band is a superposition of absorption peaks of stretching vibrations from different sp^m CH_n configurations, with $n, m = 1$–3 [5]. FDLC films are characterized by a large absorption band centered at about 1300 cm^{-1}, corresponding to the superposition of CF_n peaks ($n = 1$–3), and a smaller peak centered at about 1750 cm^{-1}, corresponding to superposition of $C\text{–}CF_2$ and $FC{=}CF_2$ absorption peaks [32]. The incorporation of nitrogen in DLC results in a strong increase in the IR absorption band at 1700–1100 cm^{-1}, a broad absorption band at about 3380 cm^{-1}, and a narrower peak at 2210 cm^{-1} [30]. Typical FTIR spectra are illustrated in **Figure 3**, and the interpretation of the absorption peaks can be found in the papers referenced above.

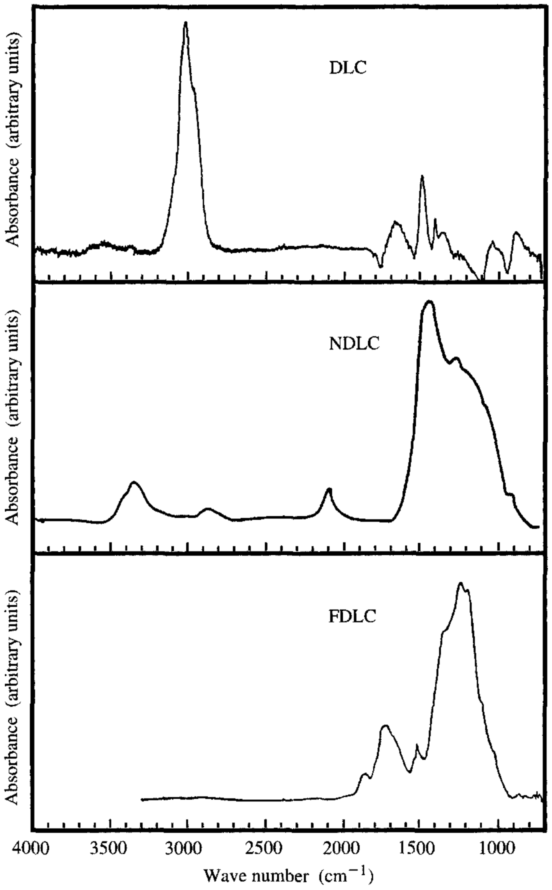

Figure 3

Typical FTIR spectra of DLC, NDLC, and FDLC films.

Because each individual sp^m CH_n configuration is characterized by a specific IR absorption peak, it is often assumed that one can use the deconvoluted FTIR peaks to analyze the relative hybridization ratio, sp^3/sp^2, of the carbon atoms and use the total intensity of the broad peak centered at 2900 cm^{-1} to quantify the hydrogen content of the DLC films [12, 43, 44]. Such analyses have been performed assuming a constant oscillator strength and no occurrence of preferential hydrogen bonding to a particular type of carbon. However, the proportionality coefficients may differ by an order of magnitude for the $-CH$ bond and the $-CH_2$ or $-CH_3$ bonds [45]. Therefore, FTIR cannot be used for determination of the carbon hybridization or hydrogen content of the films [41]. It may, however, be used for qualitative comparisons of films deposited in the same reactor, and can be used together with forward recoil elastic scattering (FRES) measurements of hydrogen content in the films to determine relative fractions of unbound hydrogen in similar films [41], or to evaluate the general types of bonding between different elements in DLC films or modified films [30, 32]. FTIR spectroscopy may also be used for qualitative identification of changes in a film undergoing postdeposition treatments, such as thermal annealing [11, 12, 26, 37].

EELS is another technique used in determining the sp^2 fraction in nonhydrogenated DLC, especially in the so-called tetrahedral amorphous carbon (taC), and then estimating the fraction of sp^3 hybridized carbon (sp^3 fraction = 1 − sp^2 fraction). The method has also been attempted on hydrogenated DLC [46], and it has been found that the films are sensitive to the electron dose exposure. By using low electron-beam doses to minimize irradiation damage, it was found that the sp^3/sp^2 ratio increases with increasing hydrogen content in the films. However, these findings are only qualitative for hydrogenated DLC films.

High-resolution ^{13}C NMR spectroscopy appears to be the most reliable method for determining the relative concentrations of sp^2- and sp^3-hybridized carbon, as well as the local atomic environment of carbon in each state in hydrogenated DLC [13, 47–49]. Taking the spectra both with and without the use of proton decoupling, one can identify the carbon atoms to which at least one hydrogen atom is bound [13]. Because the C–H spin interaction causes the carbon peak to be broadened into the baseline of the spectrum, only the signal from carbon atoms with no bound hydrogen is obtained when the proton signal is not decoupled. With the natural abundance of about 1% ^{13}C, about 100 mg of DLC is required in order to obtain a significant ^{13}C NMR signal. Such studies have shown that, within detectable limits ($\geq 2\%$), no "pure diamond" (tetrahedral carbon-to-carbon bonding) was found in the DLC films, indicating that hydrogen is required to obtain and stabilize the sp^3 coordination.

- *Hydrogen in DLC*

Incorporation of hydrogen in the carbon films deposited by PECVD or sputtering appears to be generally required in order to obtain "diamondlike" optical and electrical properties. The hydrogen content in DLC films and its depth profile with a resolution of 4 nm can be measured by the nuclear reaction $H(^{15}N\alpha, \gamma)C$:

$$^{15}N + {}^{1}H \rightarrow {}^{12}C + {}^{4}He + \gamma. \tag{4}$$

The measurement is done by bombarding the films with ^{15}N ions and counting the 4.33-MeV γ rays produced by the reaction, which is resonant at 6.4 MeV [13]. A more accessible and generally used method for measurement of the total hydrogen content of DLC films is the forward recoil elastic scattering (FRES) or elastic recoil detection (ERD) technique [38, 50]. While FRES is simpler than the nuclear reaction method, it has far inferior depth resolution (about 50 nm vs. 4 nm for nuclear reaction).

The total hydrogen content critically determines film structure at the atomic level (the ratio between sp^3- and sp^2-coordinated carbon atoms), and therefore the physical properties of the films. Hydrogen content is also key to obtaining a wide optical gap and high electrical resistivity, because it passivates the dangling bonds in the amorphous structure [51]. DLC films deposited from hydrocarbons must include hydrogen in concentrations from 17% to 61% in order to obtain diamondlike properties [28]. The loss of hydrogen through annealing at high temperatures generally causes a collapse of the structure to a graphitelike phase dominated by sp^2 bonds [37, 52]. As is discussed later, the hydrogen content of DLC films is also an important factor controlling their tribological properties [53]. It was suggested in 1981 that significant amounts of hydrogen in DLC films may not be bonded to carbon atoms, but may be trapped interstitially [40]. The existence of unbound hydrogen was proven by comparing FTIR and FRES data of different DLC films, and it was found that in some cases the fraction of unbound hydrogen in DLC can be up to about 50% of the total hydrogen incorporated in DLC films [16, 41].

- *Optical properties*

DLC films are typically transparent in the infrared, with the exception of the CH absorbing bands mentioned earlier, are weakly absorbing in the visible spectrum, and are increasingly absorbing with decreasing wave length in the UV. Their hydrogen content is critical in controlling their optical properties, and removal of hydrogen from hydrogenated DLC films causes the loss of IR transparency [54, 55].

A wide range of optical gap values (E_{opt}), spanning the range from 0.38 to 2.7 [2, 56–58], were reported for DLC films prepared under presumably similar conditions, indicating the dependence of the property on the deposition system. For otherwise similar deposition conditions, E_{opt} was found to decrease strongly for DLC films deposited above 250°C [5, 14]. This behavior reflects the role of hydrogen in stabilizing the structure of DLC layers. Films deposited at lower temperatures (in the range 25–250°C) contain significant concentrations of hydrogen; most of the sp^3-coordinated carbon atoms, as well as a substantial fraction of the sp^2-coordinated carbons, are bound to at least one hydrogen atom. When the release of hydrogen is induced in these materials, they revert to the configuration of lowest energy, i.e., graphite.

The index of refraction (both the real part n and imaginary part k) and its spectroscopic variation have been found to be dependent on the preparation conditions and hydrogen content of the films. Its value at 632.8 nm has been found to increase from 1.7 to 2.25, with an increasing rf power/pressure ratio during deposition [59]. The dependence of the index of refraction on the wavelength is strongly connected to the preparation conditions and can show opposite behaviors [60, 61]. The index of refraction at 632.8 nm of DLC films deposited from acetylene by rf PECVD at a range of substrate temperatures, a bias of -80 V, and 0.1 W/cm^2 was found to be insensitive to the deposition temperature and to have a value of $n = 1.9 \pm 0.2$ [37]. It is, however, dependent on the ion bombardment of the growing film and increases with increasing ion bombardment. Ion bombardment increases with increasing bias, decreasing pressure, and increasing Ar dilution, when Ar is added to the precursor [25], resulting in an increasing index of refraction, as illustrated in **Figure 4**.

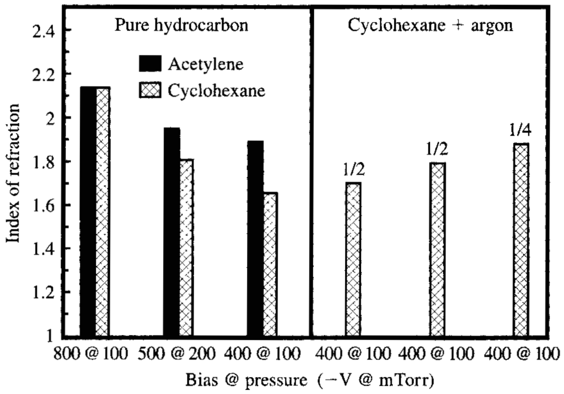

Figure 4

Index of refraction of DLC films deposited by dc PECVD as a function of deposition conditions. The numbers in the right half of the figure indicate the mass flow ratios of cyclohexane to argon. From [25], reprinted with permission.

The index of refraction is also affected by the hydrogen concentration in the DLC films, as determined by the deposition condition mentioned above. It generally increases with decreasing hydrogen content, as shown elsewhere [25, 38, 62]. It is, however, dependent on the concentration of bound hydrogen and not total hydrogen content in the film [16]. A higher index of refraction usually indicates DLC with stronger cross-linking, higher hardness, and better wear resistance [25].

- *Electrical properties*

Owing to the range of properties of the naturally occurring forms of carbon, i.e., graphite and diamond, the electrical properties of diamondlike carbon films can vary from that of a semimetal to that of a wide-bandgap insulator. Electronic transport itself is quite complex in DLC as a result of its disordered structure. Diamond is characterized by high electron mobilities and, since it is a wide-bandgap semiconductor, diamond-based devices such as diodes can continue to function properly at temperatures in excess of 500°C; a wide variety of applications for such high-temperature electronics are being considered. In contrast, DLC has neither the wide energy gap nor the thermal stability to operate in such an environment. The electronic and optical properties of hydrogenated DLC behave to a certain extent in a fashion similar to those of hydrogenated amorphous silicon.

The electrical properties of DLC films have been modeled assuming that the band structure consists of only a mobility gap and that carriers residing in gap states are localized [63]. This mobility gap produces semiconductor behavior, but the existence of a high density of such gap states significantly degrades the otherwise desirable properties of semiconducting materials. A more quantitative description of the band structure of diamondlike carbon layers can be found elsewhere [4, 63]. Hydrogenated DLC can be doped similarly to amorphous silicon; however, the doping is inefficient, since high levels of doping are required to produce significant changes in its electrical properties [63, 64].

Diamondlike carbon films are generally characterized by high electrical resistivities spanning a large range of values, from 10^2 to 10^{16} Ω-cm, depending on the deposition conditions [14, 36, 64]. Their electrical resistivity has been found to be strongly reduced by up to seven orders of magnitude by incorporation of metals [33, 65]. Nitrogen incorporation also reduces the electrical resistivity of the films.

The values of electrical resistivities of the DLC films discussed above have generally been reported at low electric fields, and in most cases no indication has been given of the dependence of the resistivity on the electric field. Electrical resistivities in fields up to several MV/cm have been measured by Grill et al. for DLC and nitrogen-

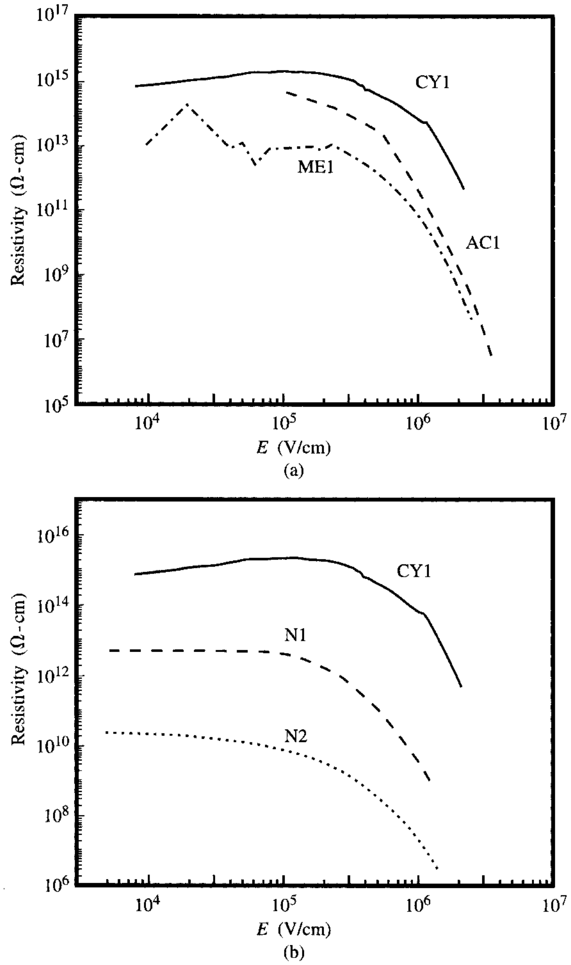

Figure 5

Electrical resistivities of DLC and NDLC films deposited at a bias of −500 V by dc PECVD as a function of the electric field: (a) DLC films deposited from AC1 – acetylene, CY1 – cyclohexane, ME1 – methane; (b) comparative resistivities of NDLC and DLC films: N1, N2 – cyclohexane + nitrogen; $N/(N + C) = 7\%$ in N1 and 11% in N2 (see details elsewhere [64]).

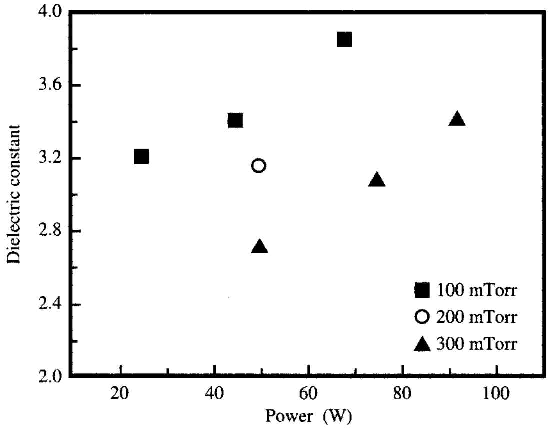

Figure 6

Dielectric constants of DLC films deposited by rf PECVD as a function of power and pressure in reactor. From [66], reprinted with permission.

doped DLC films deposited from several precursors at a variety of conditions [64]. The electrical resistivities are shown in **Figure 5** as a function of the electric field E. As can be seen, the resistivities vary strongly with E, indicating that the DLC films do not exhibit ohmic behavior. The resistivities of these DLC films change only slightly up to a field of 3×10^5 V/cm, but decrease sharply at higher fields. Furthermore, the resistivities are strongly dependent on deposition conditions, and the resistivities of dc PECVD films deposited at identical conditions are strongly dependent on the precursor used [see Figure 5(a)]. As can also be seen in Figure 5(b), the incorporation of nitrogen into the DLC films reduced their resistivity over the whole range of electric fields. Incorporation of 11% nitrogen (film N2) decreased the resistivity by about five orders of magnitude compared to the undoped film (CY1) [64].

Hydrogen, which stabilizes the sp^3 bonds and determines the carbon hybridization ratio, is therefore required for obtaining a high electrical resistivity. However, electrical resistivity differences of several orders of magnitude have been found between films having small or no differences in total hydrogen content [64]. Because the electrical properties of DLC films depend on the carbon hybridization, which in turn is affected by C–H bonding, the electrical conductivity is determined by the bound and not by the total hydrogen concentration in the films and, for films deposited under similar conditions, the conductivity decreases with increasing concentration of bound hydrogen in the films [64].

Special consideration has recently been given to the dielectric constant (k) of DLC and FDLC films [66]. Low-k materials are needed for the "back-end-of-line" (BEOL) multilevel interconnect structures of ULSI circuits to improve their performance. It was found that by adjusting deposition conditions, it is possible to change the dielectric constant of DLC films in the range 2.7–3.8, as illustrated in **Figure 6**. The integration of such films in BEOL structures, however, imposes further requirements on the low-k material, such as low stresses and thermal stability at 400°C. It has been found that for DLC films, the intrinsic stresses decrease with decreasing k values, while the thickness changes increase with decreasing k

values, as illustrated in **Figure 7**. The increased changes reflect the reduced thermal stability of films with low k values.

FDLC films with dielectric constants $k < 2.8$ (see **Figure 8**) have been prepared having intrinsic stresses below 200 MPa. The FDLC films seem to be stabilized after a first annealing at 400°C in an inert ambient. Such films are therefore potential candidates as low-k insulators in BEOL interconnect structures; however, integration issues, especially those related to potentially reactive fluorine, have yet to be effectively addressed.

- *Chemical resistance*

At room temperature, DLC films are chemically inert to practically any solvent and are not attacked by acids, alkalis, or organic solvents. The films are inert even to strong acid mixtures, such as the "acid etch" (HNO_3:HF = 7:2) and to exposure to alkali solutions at 85°C for several hours. As a result of their chemical resistance, DLC films can be used as corrosion-resistant coatings. The films and their modifications can be removed from a substrate by exposure to atomic oxygen or fluorine species generated in a plasma, which react with the carbonaceous films to produce volatile CO_x and CF_y species which are pumped out of the system. Reactive ion etching in oxygen- or fluorine-containing plasmas can be used to pattern DLC films. The rate of etching can be strongly modified by incorporating Si in the films, and SiDLC can be used as an etch stop during the etching of DLC or FDLC films [31].

- *Mechanical properties*

DLC films are characterized by high hardness, spanning the range from 10 to 30 GPa [68], associated with high intrinsic compressive stresses in the range from 0.5 to 7 GPa [9, 10, 13, 38, 39, 69]. The high internal stresses limit the thickness of films that can be used for various applications, often to less than 1 μm. Adhesive forces must overcome the high stresses in order to prevent delamination of the film from the substrate. Some of the mechanical properties of DLC have been explained by Robertson [68] using the constraint counting model of Phillips and Thorpe [69, 70], taking into consideration the elasticity of the individual bonds and the connectivity and coordination of the network.

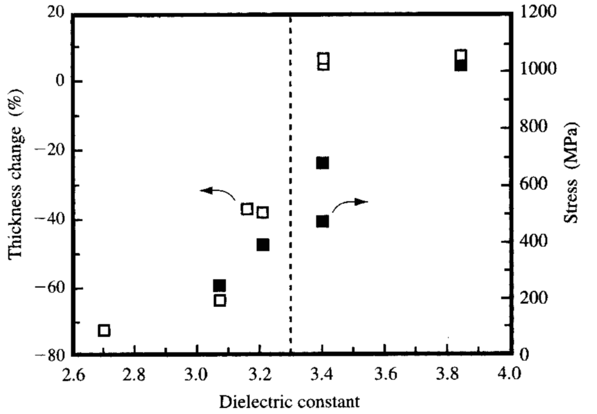

Figure 7

Thickness changes after annealing (four hours/400°C/N_2) and intrinsic stresses, each vs. dielectric constant, for the DLC films of Figure 6. From [62], reprinted with permission.

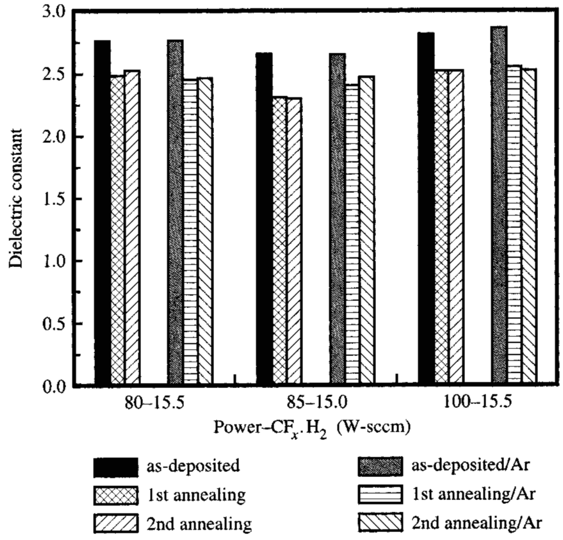

Figure 8

Dielectric constants of FDLC films deposited by rf PECVD under various conditions: as deposited and after annealing at 400°C in N_2 for four hours. The first number on the x axis indicates the value of the power; the next two numbers, separated by dots, indicate the flow rates of the precursors. From [67], reprinted with permission.

The stresses in DLC films are generally directly correlated to the fraction of sp^3 carbon [71]. For rf PECVD films, the intrinsic stresses therefore depend on the combination of deposition parameters which affect the sp^3 C hybridization. Because of the interdependence of the plasma parameters, stress dependency reported with regard to one specific parameter is valid for only a specific plasma system. Stresses were found to decrease with increasing deposition pressure [10, 39] and to have a bias relation which depends on other deposition parameters [10, 70, 71].

Of the factors affecting the sp^3 hybridization, the more important one is the average energy of the ions

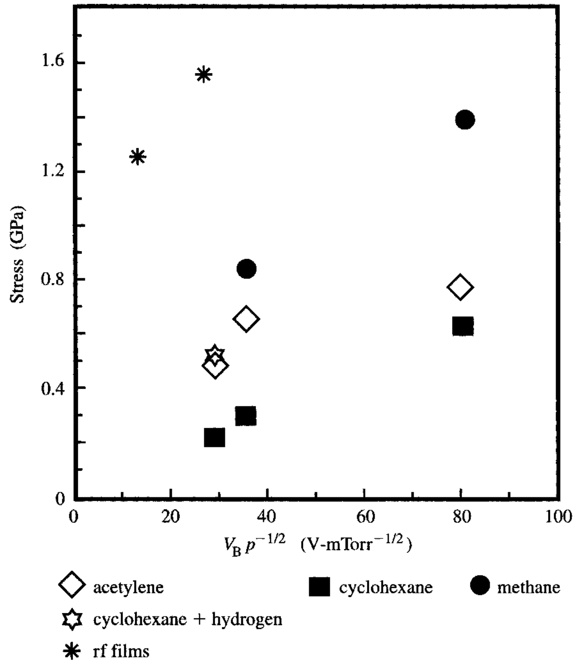

Figure 9

Stresses in DLC films deposited by dc PECVD from different precursors as a function of average ion-bombardment energy. Stresses in films deposited by rf PECVD from acetylene are also shown. From [24], reprinted with permission.

bombarding the film, which accounts for both substrate bias and pressure in the plasma and is given by Equation (2). **Figure 9**, which presents a plot of the stresses in DLC films deposited by dc PECVD from several precursors as a function of the average ion energy, shows that the stresses in the films deposited from one precursor do increase monotonically with increasing average ion energy. However, for identical average ion energies, the stresses are strongly dependent on the gases used to deposit the films. The stresses in films deposited from acetylene by rf PECVD at similar power densities [38] are also shown in Figure 9. Although the rf films were deposited at conditions corresponding to much lower ion energies (E values), the stresses are much higher in these films than in the dc films. The results shown in Figure 9 thus indicate that the factors determining the internal stresses in DLC films are much more complex than just the direct effects of bias or even of average ion energy.

The intrinsic stresses in DLC films are also correlated with changes in hydrogen content obtained by changing deposition parameters [39, 72]. Strong variations in stresses have been observed in DLC films in which the differences between the total hydrogen contents were too small to predict or explain the large differences in the stresses [16, 24]. In addition, it was observed that films containing smaller amounts of hydrogen had higher stresses than DLC films containing higher amounts of hydrogen [24]. As illustrated in **Figure 10** for dc-deposited DLC films, the stresses increase with an increasing fraction of unbound hydrogen, without reflecting a direct precursor dependence.

Stresses in DLC films have been decreased by doping the films with nitrogen [24, 30, 73] to values as low as 0.22 GPa [24]. Such NDLC films contain significant numbers of NH bonds, which increase with increasing concentrations of nitrogen [30]. The stress reduction in nitrogen-doped DLC films was explained [24, 73] by using the overconstraining model of DLC [28]. According to this model, replacement of CH with NH bonds in NDLC reduces the average coordination number and the overconstraining in the NDLC films, resulting in decreased internal stresses. However, other effects may contribute to the stress reduction in DLC as a result of nitrogen incorporation.

- *Tribological properties*

Wear protection is needed for surfaces in kinetic contact, in situations which generally also require low friction between the moving surfaces. As a result of their high hardness, DLC films are utilized as wear-resistant protective coatings for metals and for optical or electronic components. The use of DLC is especially attractive in applications where the thickness of the protective film is limited to less than 50 nm, as for example in the case of magnetic recording media, where the trend toward higher-density data storage has led to the requirement of very low flying heights between a disk and a recording head. The coating must be able to protect the magnetic media against wear and corrosion but must also be thin enough not to impede the achievement of high recording density.

Tribological (friction and wear) characterization is usually performed on a pin-on-disk apparatus [8]. The disk coated with the DLC film is rotated at a fixed speed, while a pin with a spherical tip is loaded against it with a chosen normal load. After a number of rotations, the wear of the disk is calculated from the cross section of the profile of the produced wear track. The friction force between the pin and the disk can generally also be measured in "pin-on-disk" tools, thus enabling the determination of the friction coefficient. Because detailed reviews of the tribology of DLC and related materials can be found elsewhere [6, 74], the following contains only a summary of the tribological properties of DLC films.

A variety of factors contribute to friction and wear, yet friction is controlled mainly by the formation and breaking of chemical bonds at the interface between the sliding parts, while breaking of bonds within a part controls the wear [75]. A low friction coefficient and low wear are two attractive properties of diamond. However, the friction coefficient of diamond depends strongly on the environment and is mainly controlled by surface dangling bonds. Diamond has a low friction coefficient in humid air or dry nitrogen because of the presence of a contaminant layer of low shear strength on its surface. Clean diamond surfaces can interact strongly and result in high friction coefficients. The friction coefficient of diamond against diamond in vacuum can increase to values as high as 1.0 when an increase of the temperature causes the desorption of surface hydrogen, leaving interacting dangling bonds [75]. Saturation of dangling bonds by atomic hydrogen or other adsorbates reduces the friction coefficient to $\mu = 0.02$. There is also evidence that the debris formed during sliding is contributing to the low friction in diamond [76]. Note that water [77–79] and atomic hydrogen [80] act as lubricants for graphite and improve its wear and lubricating behavior.

In spite of the high chemical inertness of DLC films, their tribological behavior is controlled to a large extent by their surface chemistry. The latter is dependent on the method used for the preparation of the films, but can also be affected by the testing environment. The tribochemical behavior of DLC films (i.e., the effect of environment on their friction and wear) is well accepted for DLC film tribology [74].

As summarized in other reviews [6, 74], DLC films deposited by PECVD have several common tribological characteristics:

1. DLC films display a behavior similar to that of diamond in UHV but not in a humid atmosphere.
2. The friction coefficient of hydrogenated DLC is low in humid nitrogen or oxygen, extremely low in dry nitrogen or ultrahigh vacuum (UHV), and very high in dry oxygen.
3. Loss of hydrogen through annealing at high temperature causes a marked increase in the friction coefficient in UHV, but not in a humid environment.
4. Both friction and wear can be affected by a transfer layer which forms in most cases during friction. The transfer layer in the wear scars was observed directly with microlaser Raman spectroscopy, which showed that the layer has a disordered graphite structure that is different from that of the original DLC film [81]. Raman spectra taken from the wear track of the DLC film also revealed evidence of graphitization.

Initial explanations of the tribological behavior of DLC materials were based on their mechanical properties and surface energy [34]. The films attain hardness values (*H*) typical of inorganic ceramics, but have Young's modulus values (*E*) significantly lower than those of ceramics. The corresponding *H*/*E* ratios are relatively high, corresponding to those of polymers. The surface energy (*S*) of DLC is also more like that of polymers than metals or ceramics. The combination of the high *H*/*E* with low *S*/*H* ratios (*S*/*H* values being smallest among the other type of materials) was used to explain the low adhesion of other materials to DLC films, their low friction coefficient, and low wear [34]. The excellent tribological performance of these materials was attributed to a combination of favorable properties which are ceramiclike on the one hand (high hardness) and polymerlike on the other (high elasticity, *H*/*E*, and low surface energy).

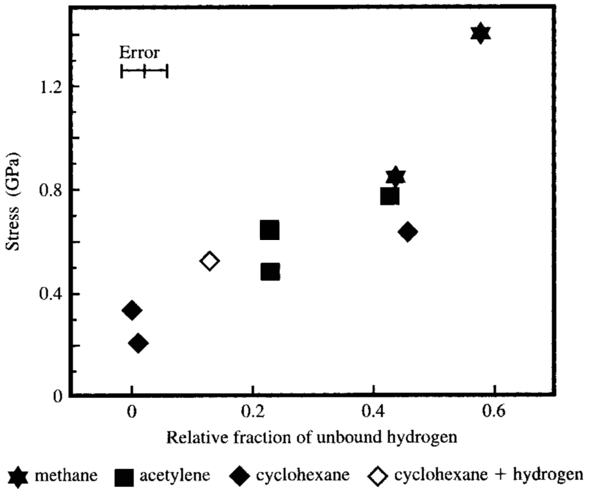

Figure 10

Stresses in DLC films deposited by dc PECVD from different precursors as a function of the relative fraction of unbound hydrogen. From [24], reprinted with permission.

However, it has become clear in recent years that in all environments the tribological behavior of DLC films is controlled by an interfacial transfer layer formed during friction. The transfer layer is formed by a friction-induced transformation of the top layer of a DLC film into a material of low shear strength. This transformation may be brought about by friction-induced annealing caused by thermal and strain effects generated during sliding [81]. The shear strength of the transfer layer and its adhesion to sliding surfaces can be affected by the environment and by contact load and sliding speed. The composition of the transfer layer can also be affected by the material of the sliding counterpart. The low friction and ultralow wear of DLC and counterparts can be explained by the low shear strength of the transfer layer [6], which can also be affected by the testing environment [82].

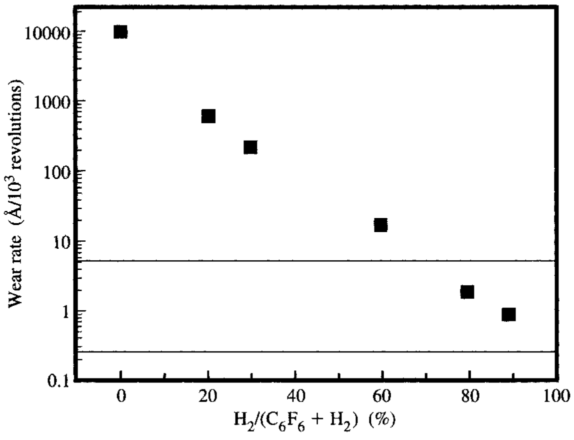

Figure 11

Wear rates of FDLC films deposited by dc PECVD as a function of precursor dilution with hydrogen. The lines delimit the range of wear rates of DLC films deposited and tribotested under similar conditions.

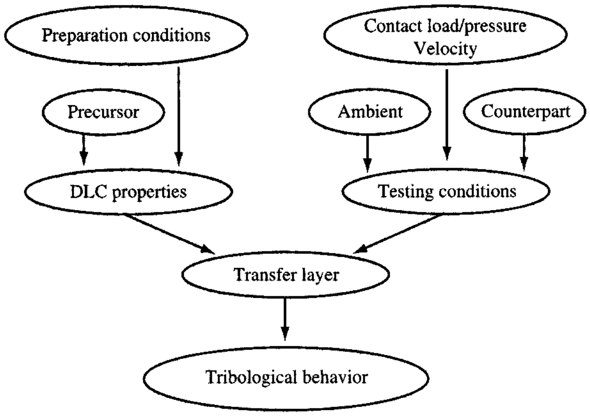

Figure 12

Schematic representation of the relationships among tribological behavior, preparation conditions, and tribotesting environment of DLC films.

A recent compilation of friction coefficients of DLC films [83] shows that their friction coefficients span a range of $\mu = 0.007–0.4$ in vacuum, below 10^{-4} Pa, while in ambient air at relative humidities of $20\% < \text{RH} < 60\%$ they span a range of $\mu = 0.05–1.00$. Most typical, however, are the ranges $\mu = 0.007–0.02$ in vacuum and $\mu = 0.1–0.4$ in ambient air. The large spread in the values of the friction coefficient are caused by variations in the structure and composition of the films. The transfer layer described above has a lubricating effect, and its formation can be enhanced by hydrogen but may be restricted in the presence of water or oxygen. The increase of the friction coefficient of hydrogenated DLC films in humid air was attributed by Gardos to the increase in the van der Waals bond strength of hydrogen bonding to adsorbed water molecules (~5 kcal/mol) compared to the bonding of hydrocarbons (~2 kcal/mol) [75].

Hydrogen passivates the dangling bonds in hydrogenated DLC films and permits only weak interactions between the DLC and the sliding partner. When hydrogen is lost from a hydrogenated DLC film by annealing, the formed dangling bonds cause strong interactions between the surfaces in contact, resulting in increased friction in UHV or dry nitrogen, similar to that reported for both diamond or graphite [80, 84]. It was shown that removal of hydrogen from DLC by annealing the films above 550°C caused an increase in the friction coefficient to $\mu = 0.68$ in UHV or dry nitrogen, indicating that the presence of hydrogen in these films is essential for obtaining very low friction coefficients [76]. It has recently also been shown that the achievement of a low friction coefficient in UHV requires a hydrogen content of more than 40% [53].

Certain applications may require modification to preserve wear resistance but change other characteristics (e.g., increase electrical conductivity or reduce surface energy). It has been shown that incorporation of F, O, N, and Si in DLC could modify water wetting angles of the modified films [85]. The incorporation of F or Si increased the contact angle of water, while the incorporation of O and N decreased the contact angle. The effect of F and Si on the surface energy of DLC films was attributed to the reduction primarily of the polar part of the surface energy, due to the loss of sp^2 C hybridization and dangling bonds [85]. Yet DLC films containing F and Si can be prepared to be as wear-resistant as the pure hydrogenated DLC [32, 86], as illustrated in **Figure 11** for FDLC films deposited by dc PECVD. Similar results have been obtained for FDLC films deposited by rf PECVD [86]. The incorporation of Si in DLC films has been reported to render their friction against steel and the wear of the steel counterpart insensitive to moisture [87]. Me–DLC films containing 15% Ta, W, Ti, or Nb, having wear resistance similar to that of DLC and friction coefficients <0.2, but higher conductivity (up to 0.005 Ω-cm), have been deposited by dc magnetron sputtering of the metals in acetylene [85]. Modified DLC films incorporating different elements such as N, Si, and metals can display tribological properties similar to those of pure DLC films, and these properties are affected more by preparation conditions and testing environments than by the incorporated element.

The dependency of the tribological behavior of DLC materials on preparation parameters and tribotesting conditions is summarized in **Figure 12**.

Applications

The unique properties of DLC films and their modifications, together with the possibility of adjusting the properties by choosing appropriate deposition parameters, make them suitable for a variety of applications. The exploited properties include high wear resistance and low friction coefficient, chemical inertness, infrared transparency, high electrical resistivity, and, potentially, low dielectric constant. Owing to their IR transparency, DLC films can be used as antireflective and scratch-resistant wear-protective coatings for IR windows or lenses made of Ge, ZnS, or ZnSe, where they also act as an antireflective coating at the used wavelength of 8–13 μm [88, 89]. Aluminum mirrors used in optical imaging deteriorate with time as a result of exposure to atmosphere. This deterioration can be prevented by coating the surface of the mirrors with DLC films [90]. Because of their absorbance in visible light, DLC coatings can be applied as scratch-resistant coatings on sunglasses. The low deposition temperatures of DLC films allow their use as a wear-protective layer on products made of plastic. Currently, DLC films are used for protection against abrasion of sunglass lenses made of polycarbonate [91].

The most widespread use of DLC films is in wear and corrosion protection of magnetic storage media. Nanosmooth DLC films are especially useful where the protective coating must be very thin (<50 nm), such as in magnetic hard drives. When the storage disk is started or stopped, sliding contact occurs between the disk and slider, and this can cause mechanical damage and wear unless a suitable protective coating is present between the surfaces in contact. The protective coating must be resistant to wear and corrosion, but also thin enough so as not to impede the achievement of high recording density; DLC coatings are ideal for such applications. DLC is used as a corrosion- and wear-protective coating for both magnetic disks and magnetic heads, and is also used for corrosion protection of metal films during the manufacturing of magnetic heads. Tapes for video recording or magnetic data storage, using ferromagnetic metal as a recording medium, as well as the metallic capstans in contact with the tapes, are also protected with DLC coatings to reduce wear and friction, thus extending the life of the tapes.

Diamondlike carbon films appear to be biocompatible, and applications are being developed for their use in biological environments. One major reason for the failure of metallic implants in the body is their corrosion by body fluids. *In vitro* tests have shown that DLC coatings allow cells to grow without inflammatory response [92]. Because of their chemical inertness and impermeability to liquids, DLC coatings could protect the implants against corrosion and serve as diffusion barriers. DLC films are being considered for use as coatings of metallic as well as polymeric (e.g., polyurethane, polycarbonate, and polyethylene) biocomponents in order to improve their compatibility with body tissues [90, 93]. Their wear resistance is another useful property for bioapplications. Diamondlike carbon films, deposited on stainless steel and titanium alloys used for components of artificial heart valves, have been found to satisfy both mechanical and biological requirements and to be capable of improving the performance of these components [94]. The same properties may make DLC films useful as protective coatings for joint implants.

As already indicated, DLC films and their modifications are currently being considered for use as low-dielectric insulators for the interconnect structures of ULSI chips. A better understanding of the means to control their thermal stability and other integration problems should improve their potential for this application.

Summary

Diamondlike carbon films can be prepared from a large variety of precursors using the PECVD technique. Film deposition is carried out at substrate temperatures between room temperature and 250°C under ion bombardment of the substrate and of the growing film. Although the term DLC was adopted to describe these films and their modifications, the films consist essentially of amorphous networks of sp^3- and sp^2-bonded carbon, containing hydrogen in amounts between 16 and 61%. The films are characterized by infrared transparency, a significant optical gap, high electrical resistivity, low dielectric constant, high hardness and internal compressive stresses, low friction coefficients, and chemical inertness.

The properties of the films are affected by preparation conditions, and, for a given preparation system, depend on the amount of hydrogen incorporated in the films. Some of that hydrogen can be incorporated as unbound hydrogen, and the relative fraction of bound or unbound hydrogen also affects the properties of the films. Although the type of hydrocarbon used as a precursor often appears to have only an insignificant effect on film properties, this is not always true. The properties of DLC can be tailored by adjusting deposition parameters such as substrate bias and temperature, power density, and precursor.

The wear resistance of DLC films appears to be strongly dependent upon their deposition conditions. It can be maintained while modifying the material through incorporation of different elements. Both the wear resistance and the friction coefficients of DLC films and their modifications are strongly affected by the testing environment and are controlled by a transfer layer formed between the surfaces in kinetic contact.

Because of their attractive properties and the ease of preparation of extremely smooth films at relatively low substrate temperatures, DLC films have found a large variety of practical applications, and it is expected that the range of applications will expand further. Although currently limited to applications at temperatures below film deposition temperatures, their applicability may eventually extend to higher temperatures.

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Alfred Grill *IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598 (grilla@us.ibm.com).* Dr. Grill is a Research Staff Member and manages the Electronic Materials and Structures group in the Telecommunication Technologies Department at the Thomas J. Watson Research Center. He received B.S., M.Sc., and Ph.D. degrees in physics from the Hebrew University in Israel in 1964, 1966, and 1973, respectively. In 1975 he joined the Materials Engineering Department at the Ben-Gurion University in Israel, where, in 1986, he became a Full Professor. In 1989, he joined IBM at the Thomas J. Watson Research Center, where he is studying the PECVD growth of diamondlike carbon and related materials as well as low- and high-dielectric-constant materials. In 1992, he received an IBM Outstanding Innovation Award for his work on carbon overcoats for magnetoresistive heads. Dr. Grill has published extensively on the plasma-assisted deposition of films and surface treatment of materials; he is an author or coauthor of 25 patents. He is a member of the Materials Research Society and the Electrochemical Society, and a member of the editorial boards of the journals *Diamond Films and Technology* and *Diamond and Related Materials*.

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