

Diamond-like carbon: state of the art

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Abstract

Diamond-like carbon films, amorphous hydrogenated or non-hydrogenated forms of carbon, are metastable amorphous materials characterized by attractive mechanical, optical, electrical, chemical and tribological properties. The films can be prepared at low temperatures by different techniques using a large variety of precursors and can be modified by incorporation of different elements such as N, F, Si or metals. The diversity of methods used for the deposition of diamond-like carbon films provides the flexibility to tailor their properties according to specific needs and potential applications. The hydrogenated form of DLC appears to reach a maturity in understanding its properties and finding old and new practical applications for it. The non-hydrogenated diamond-like carbon, or tetrahedral carbon, is at a much younger state of preparation and characterization and practical applications have yet to be proven. The paper will review the state of the art of the preparation of the different types of diamond-like carbon films, the characterization and understanding of their properties, and their practical applications. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Diamond-like carbon is a name attributed to a variety of amorphous carbon materials, some containing up to about 50 at.% hydrogen (a-C:H), other containing less than 1% hydrogen (a-C). The diamond-like carbon films contain significant fractions of sp^3 type C bonds, giving them attractive physical and mechanical properties that are, to a certain extent, similar to diamond. The a-C:H films typically contain sp^3 fractions smaller than 50%, while the a-C films can contain 85% or more sp^3 bonds. The “DLC” term is commonly used to designate the hydrogenated form of diamond-like carbon (a-C:H), while the “taC” (tetrahedral carbon) term is used to designate the non-hydrogenated carbon (a-C), containing high fractions of sp^3 hybridized carbon.

Both DLC and taC are metastable materials and have to be prepared under ion bombardment of the growing films. Studies of DLC have been performed extensively since 1971, when Aisenberg and Chabot [1] first prepared such films, and the field has reached maturity in understanding the growth mechanisms, material properties and usage in industrial applications. This is best

illustrated by the recent announcement by the Gillette corporation of their new razor blades incorporating DLC coatings. “MACH3’s patented DLC[®] comfort edges — the first major blade edge innovation in 30 years — are thinner than any other Gillette blade edges and glide through beard hairs more easily. With MACH3, the consumer experiences less drag and pull for an extraordinarily comfortable shave” [2]. taC is at a much younger stage of its development and understanding and practical applications have yet to be developed for it.

A general review of DLC can be found in Ref. [3] and a recent review of its tribological properties in Ref. [4]. The present paper will present the state of the art of hydrogenated DLC and some comparisons with the non-hydrogenated taC.

2. Deposition

2.1. DLC and taC

In order to obtain the metastable structure of DLC, such films are deposited by plasma assisted chemical vapor deposition (PECVD) or physical vapor deposition

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techniques (sputtering or ion beams) using a variety of precursors, as described in detail elsewhere [3]. In the PECVD methods, the substrates have to be at a negative bias relative to the plasma to achieve ion bombardment of the growing film. The deposition is performed in hydrogen-containing environments to obtain DLC films containing 10–50 at.% hydrogen. The hydrogen is required for obtaining “diamond-like” properties in these materials. It determines the film structure, passivates the dangling bonds in the amorphous structures, thus controlling the optical and electrical properties, and affects the internal stresses of the films. In most cases the deposition is a line-of-sight technique and the film is deposited on only one surface of the substrate. Industrial tools based on this technique have been developed and are used in manufacturing. Deposition of DLC films by a high density plasma in a helical resonator PECVD process has also been reported [5]. The growth and properties of DLC films are controlled by the substrate temperature and bias, the latter having the dominant control [3]. The hardness, density and refractive index of the films increase with increasing substrate bias. The deposition rates also usually increase with increasing bias. Even for films deposited in a helical resonator, the substrates had to be biased negatively to obtain diamond-like properties. Films deposited in this reactor on grounded substrates had polymeric characteristics [5].

A more recent technique for deposition of DLC films is the plasma source ion implantation (PSII) [6]. In this technique, the substrates are placed directly in a plasma source and then pulse-biased. This is a non-line-of-sight technique and enables the coating of complex structures. Another non-line-of-sight technique for deposition of DLC has been demonstrated in an ionitriding tool in which DLC has been deposited by bipolar-pulsed DC PECVD [7]. The films have been found to have properties similar to RF PECVD-deposited films, with the advantage of being deposited in an existing industrial reactor.

The superhard properties of taC films are achieved by the high energies of the impinging particles that form the films. It is assumed that in this case the films grow by subplantation, instead of by the conventional condensation, as in the case of DLC films [8]. The required high energies of the depositing species are achieved by different variations of vacuum or cathodic arc discharges, such as filtered arc [9], pulsed arc [10], laser controlled arc [8,10], pulsed laser depositions [8,11] or mass selected ion beams [12]. Vacuum arc discharges can cause local overheating of the cathode and microspalling, resulting in deposition of rough films. Such problems can be overcome by the mentioned modifications of the techniques to deposit smooth and very hard taC films. The PSII technique can also be used for the deposition of taC films [13]. The sp^3 fraction in the taC

films appears to reach a maximum at impinging particle energy of about 100 eV [9].

2.2. Modified DLC and taC

Various materials derived from the diamond-like carbon films have been developed to change and improve their properties. Such materials are similar in structure to DLC or taC but, in addition to carbon and/or hydrogen, include nitrogen (NDLC or CN_x films), silicon (SiDLC), silicon and oxygen, 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), to reduce its surface energy [14] for further lowering, its already low, friction coefficients (F, Si–O incorporation) [3,4,15], or to modify its electrical properties [16,17]. Nitrogen incorporation has been used to improve field emission properties of both DLC and taC [18,19]. Si incorporation in DLC has been found useful in reducing the etching rate of DLC in oxygen plasma and makes it useful as an etch stop for undoped DLC [16]. The modified diamond-like carbon films are deposited by the same techniques as the regular films by adding species containing the modifying elements to the deposition environment and details can be found in the references cited above.

3. Properties

3.1. Structure

Diamond-like carbon films are amorphous materials with carbon atoms bonded in mainly sp^3 and sp^2 hybridizations. Diamond-like carbon is a low-mobility semiconductor, with a bandgap of 1–4 eV, room temperature photoluminescence and low electron affinity [20]. The properties of the films are determined by the relative ratio of the two hybridizations. DLC films can have sp^3 fractions up to about 40% [21], while taC can reach sp^2 fractions of up to 87% when deposited at ion energies of about 100 eV [9,22]. Angus and Jahnsen [23] have described the structure of hydrogenated DLC by a random covalent, fully constrained, network model. According to this model, the DLC structure can be described as a three-dimensional array of mostly six-membered rings, which is able to contain 17–61 at.% bound hydrogen. The role of hydrogen in controlling the properties of DLC has been discussed in detail elsewhere [3,24].

Robertson [25] modeled the structure of diamond-like carbon in 1986 as a random network of covalently bonded carbon atoms in the different hybridizations, with a substantial degree of medium range order on the 1 nm scale. In a recent refinement of his model,

Roberston describes the structure of both DLC and taC as being controlled by the energy of the π bonding of the sp^2 sites [20]. According to Robertson, the π bonding of the sp^2 carbon favors clustering of sp^2 sites to maximize the π -bonding energy. The sp^2 sites can gain further energy by forming sixfold planar “aromatic” rings and fusing the rings into larger graphitic clusters. However, the energy gain resulting from increasing cluster size beyond pairing is small, therefore, the cluster size remains small. For planar graphitic clusters of sp^2 carbon, the band gap was found to be given by $E_g = 6/M^{1/2}$ eV, where M is the number of sixfold rings in the cluster [25]. According to Robertson, the small sp^2 clusters cannot explain the small bandgap of DLC and the small bandgap is caused by the fact that the distorted clusters have much smaller bandgaps [20]. The bandgap is therefore controlled by the distortion of the clusters and not their size. Robertson also found that the optical gap of all types of diamond-like carbon, hydrogenated or non-hydrogenated, depends mainly on the sp^2 fraction in the films and decreases with increasing sp^2 fraction. Non-hydrogenated taC, which has small sp^2 fractions, has a very rigid network, while hydrogenated DLC has a softer polymeric network, yet both types of films have similar bandgaps.

3.2. Characterization

The structural characterization of diamond-like carbon films is complicated by their amorphous nature. High resolution nuclear magnetic resonance (NMR) spectroscopy with its recent refinements [21] appears to be the best technique for characterization of the carbon hybridization of hydrogenated DLC. Fourier transform infrared spectroscopy (FTIR) is still being used by some authors to quantify the carbon hybridization ratios and hydrogen content in DLC films, in spite of the fact that it has been shown that the technique can give erroneous information [26]. Electron energy loss spectroscopy (EELS) has become the established method to measure the sp^2 bonding fraction in non-hydrogenated taC [20]. The technique is, however, not suitable for DLC, which is sensitive to irradiation with an electron beam [27].

FTIR can be used for qualitative characterization of different bonds in hydrogenated diamond-like carbon films or their modifications. Film compositions can be determined by Rutherford backscattering (RBS) analysis of C and heavier elements and forward recoil elastic scattering (FRES) for H concentrations. Mechanical properties are usually determined by nanoindentation measurements for hardness and Young's modulus determination and measurements of radius of curvature of coated substrates for stress determination [3,22].

3.3. Mechanical properties

Diamond-like carbon films are characterized by high hardness and a high elastic modulus, but also by high

internal stresses. These properties are directly correlated to the fraction of sp^3 C in the films. The hardness of DLC films is in the range 10–30 GPa [28], with a corresponding Young's modulus 6–10 times larger. The films are characterized by internal compressive stresses in the range 0.5–7 GPa. The stresses can be reduced by incorporating N, Si, O or metals in the films [13,24], although the reduction in stresses is often associated with a reduction in hardness and elastic modulus of the films.

The hardness of taC films can reach higher values (in the range of 40–80 GPa) [8,22], and their Young's modulus can reach values up to 900 GPa [10], but the stress can also reach high values up to 13 GPa [22]. The high internal stresses limit the thickness of films that can be used for any application, often to less than 1 μm thick. The stresses in taC have been reduced by incorporation of metals [13] or by building multilayered structures comprising soft and hard films using a filtered vacuum arc and varying the ion energy during composition [29,30]. The bias of the substrate was changed between -100 eV (to obtain the hardest layers with an sp^3 fraction of 85% and hardness of 60 GPa) and -2 kV (to deposit soft films with an sp^3 fraction of 39%) [30]. The multilayered structures had hardness (40–23 GPa) and modulus (350–245 GPa), corresponding to the fraction of the hard and soft layers, and the stresses in the films were reduced in the multilayered films from 10.5 GPa, for the hard film, to 3.8 GPa, for the film containing a 90% soft fraction.

3.4. Material stability

Both the hydrogenated and non-hydrogenated DLC are metastable materials and their structures will change towards graphite-like carbon by either thermal activation or irradiation with energetic photons or particles. Heating of hydrogenated DLC films results in the loss of hydrogen and CH_x species, starting at about 400 °C, or even lower, depending on the deposition conditions and the dopant contained in the films [3,16,17]. This causes changes in the dimensions and properties of the material and limits the use of DLC in applications involving temperatures above 400 °C. The temperature at which changes take place in the DLC films appears to be correlated to the power used for the preparation of the films [16]. The thermal instability of DLC films is generally associated with the loss of hydrogen, resulting in a collapse of the structure into a mostly sp^2 -bonded network.

It has been reported that thermal activation can also induce changes in taC films and cause the conversion of some sp^3 carbon bonds to sp^2 bonds [31]. The onset of relaxation started at temperatures as low as 100 °C and near full relaxation has been observed at 600 °C. An activation energy in the range of 1–3 eV has been

reported for this thermal relaxation [31]. The thermal relaxation reduced the internal stresses of the taC films and increased their electrical conductivity. However, it has been claimed at the present conference that taC films can be stable at least up to temperatures of 600 °C.

The diamond-like carbon films can also be changed by UV [32] or ion beam irradiation [33]. Irradiation of DLC in air with UV irradiation from a high pressure mercury lamp was found to break C–C and C–H bonds and cause oxidation of the film with formation of C–O bonds [32]. CO₂, CH₄ and H₂ evolved from the film during the irradiation, resulting in a reduction of film thickness. UV irradiation of NDLC films containing about 11 at.% nitrogen resulted in a decrease in C–H bonding and an increase in C–C, C=N and C≡N bonds. The sp² cluster size in the films became smaller, therefore, the optical gap increased. NDLC films with high N content (~37 at.%) did not show any FTIR changes after UV irradiation [32]. However, their optical gap increased, indicating a reduction of the cluster size in the absence of material loss.

Room temperature irradiation of taC films with an ion beam of 200 keV Xe⁺ transformed the material into a conducting amorphous carbon with an sp² fraction of 0.6. At higher temperatures, the same irradiation increased the sp² fraction to about 0.8 and increases the degree of ordering towards a graphitic material [33].

3.5. Field emission

In the quest for finding new applications for diamond-like carbon, a significant effort has been directed in the last few years to the investigation of the field emission properties of DLC or taC. Flat panel field emission displays (FED) use sharp Mo or Si tips for emission of electrons for the excitation of phosphor screen pixels. The sharp tips are needed to obtain the high electric field required to extract the electrons from these materials which are characterized by a high work function of about 5 eV. The hydrogenated surface of diamond has a negative electron affinity, therefore diamond or diamond-like carbon films have the potential to serve as electron emitters for FEDs, without needing the 1 μm lithography for the preparation of sharp tips [34]. It was found that the threshold field for electron emission in the taC films reaches a minimum of about 10 V μm⁻¹ when the films contain a high fraction of about 80% of sp³ bonds [18]. The addition of N to taC further reduced the threshold field, with the maximum reduction of ~5 V μm⁻¹ being obtained in taC containing 1 at.% nitrogen. A further increase in the nitrogen content reduced the sp³ fraction in the films, reduced the bandgap and increased the threshold voltage [18]. Similar behavior has been observed in N-modified hydrogenated DLC [35], however, it is assumed that

DLC may have a lower stability than taC because of the hydrogen content [18].

DLC coatings have also been found to increase the emission current from metallic FED tips [36]. Nitrogen incorporation in DLC coatings can enhance this effect. Thus, a 20 nm PECVD-deposited NDLC coating was found to enhance the emission current from Spindt type Mo tips of a FED from 160 to 1520 μA [19]. The surface roughness of the films can strongly affect the field emission effects of DLC, as was observed for DLC films deposited by laser ablation [11].

In spite of said above, it now appears that the field emission from diamond-like carbon, or other forms of carbon films, is not related to electron affinity of the materials, but is controlled instead by the nano-level roughness of the films.

3.6. Tribology

The widest use of diamond-like carbon films is mainly of the hydrogenated DLC in applications exploiting the low friction coefficients and high wear-resistance of these materials. It is therefore natural that a lot of efforts have been invested in the characterization of the tribological properties of DLC. A recent review of the tribological properties of DLC films and their modified forms [4] shows that, in all environments, the tribological behavior of DLC 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 the DLC film into a material of low shear strength. This transformation may be caused by friction-induced annealing, caused by thermal and strain effects generated during sliding [37]. 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 ultra low wear of DLC and counterparts can be explained by the low shear strength of the transfer layer [4], which can also be affected by the testing environment [38].

A compilation of friction coefficients of DLC films [39] shows that the friction coefficients of DLC span a range of $\mu = 0.007$ –0.4, in vacuum below 10⁻⁴ Pa, while in ambient air at relative humidities of 20% < RH < 60%, they span a range of $\mu = 0.05$ –1.00. 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. Water and oxygen were found to have different effects on the friction of DLC at low concentrations [40]. It was also found that the hydrogen content of DLC has

to be above a threshold of about 40 at.% to obtain very low friction coefficients in ultra high vacuums [41,42].

Metal-containing DLC films have been found to reduce friction and wear, not only in sliding, but also in vibrating contacts for a broad range of testing conditions [43]. Fluorinated DLC with high F and low H content having wear resistance similar to pure DLC has been demonstrated [15]. Because of the thermal instability of DLC films, their wear behavior is temperature sensitive and that sensitivity will be affected by the deposition conditions of the studied films. For some films, the wear behavior in ambient air has been found to change with temperature in the range 100–300 °C, with both the friction coefficient and wear resistance decreasing with increasing temperature [44].

Tribo-emission of electrons, negative and positive ions and photons were observed during tribological tests in ambient air, with diamond sliding over DLC, deposited by DC magnetron sputtering and containing 0–43 at.% hydrogen [45]. Photon emissions were observed only in films containing >15% hydrogen, while particle emissions were detected also in films containing lower concentrations of hydrogen. The tribo-emission was explained by the formation of micro-plasma by dark discharge, at low hydrogen content, and spark discharges, at higher hydrogen concentrations. Tribo-charging to local potentials up to several hundred volts were observed. The friction coefficients of these films had very high values (0.6–0.8) in air [45].

In contrast to DLC, very few results were published for the tribological properties of the non-hydrogenated taC. Friction coefficients at $RH=50\%$ of taC films deposited by a filtered cathodic vacuum arc have been reported to correlate to the sp^3 fraction in the films, reaching values down to 0.08 [22]. The wear rates of multilayered taC films described earlier were measured at $RH=30\%$ [29]. The authors found that both soft and hard monolithic films had wear rates of about

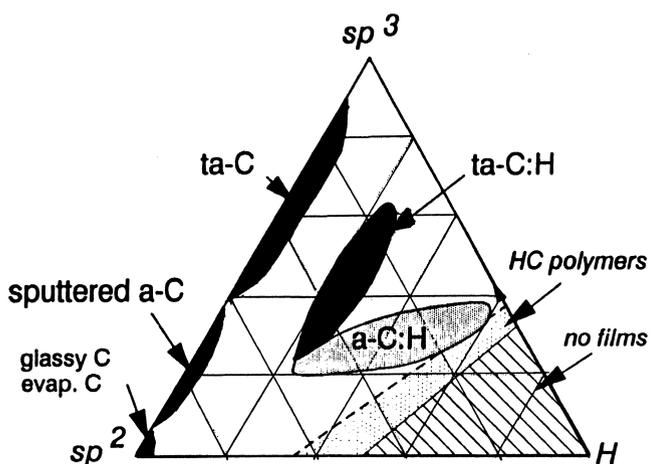


Fig. 1. Phase diagram of diamond-like carbon materials (from Ref. [20]).

$10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, however the wear rate had a minimum of about $3 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for a multilayer modulated film containing 50% soft phase [29].

3.7. DLC materials as low- k dielectrics

Special interest has recently been addressed to the dielectric constant (k) of DLC and FDLC films [17,46,47]. Low- k materials are needed for the back end of the line (BEOL) interconnect structures of ULSI (Ultra Large Scale Integrated) circuits to improve their performance. It was found that, by adjusting the deposition conditions, it is possible to obtain DLC films with the dielectric constant in the range 2.7–3.8 and FDLC films with dielectric constants $k < 2.8$ (as compared with $k = 4.0$ for the presently used SiO_2 dielectric). Integration of such films in the BEOL structures, however, imposes further requirements on the low- k material, such as low stresses and thermal stability at 400 °C. It was found that, for the as-deposited DLC films, the intrinsic stresses decrease, but so also does the thermal stability, with decreasing k values [16].

FDLC films with dielectric constants $k < 2.8$ have been prepared having intrinsic stresses below 200 MPa. Both DLC and FDLC films could be stabilized by annealing in an inert ambience [17,48] and a first metallization level in a Cu-based damascene process with DLC as the dielectric has been demonstrated [48]. Such films become attractive candidates as low- k dielectrics for the BEOL interconnect structure, however further integration issues have yet to be addressed and solved.

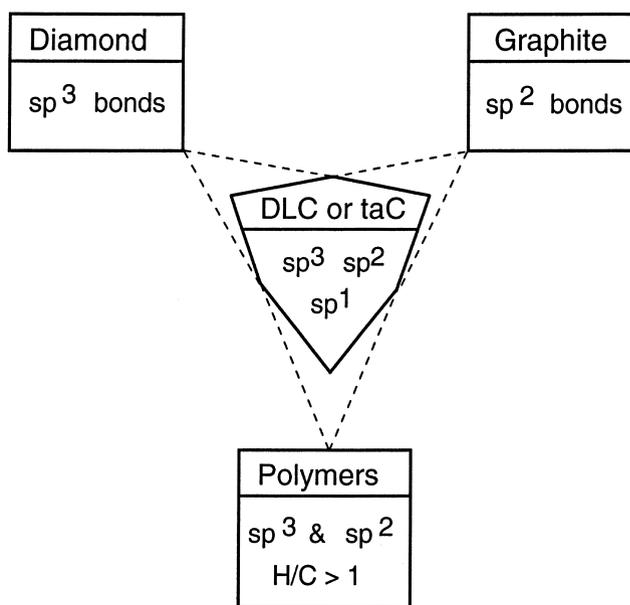


Fig. 2. Delimitation of properties of diamond-like carbon (after Ref. [60]).

Table 1

Summary of properties and applications of diamond-like carbon films. Text in parentheses indicates potential applications

Property	Type of use	Applications
Transparency in Vis and IR; optical bandgap = 1.0–4.0 eV	Optical coatings	Antireflective and wear-resistant coatings for IR optics
Chemical inertness to acids, alkalis and organic solvents	Chemically passivating coatings	Corrosion protection of magnetic media, biomedical
High hardness; $H = 5\text{--}80$ Gpa; low friction coefficient = $<0.01\text{--}0.7$	Tribological, wear-resistant coatings	Magnetic hard drives, magnetic tapes, razor blades (bearings, gears)
Nanosmooth	Very thin coatings <5 nm	Magnetic media
Wide range of electrical resistivities = $10^2\text{--}10^{16}$ $\Omega\text{ cm}^{-1}$	Insulating coatings	Insulating films
Low dielectric constants <4	Low- k dielectrics Field emission	(Interconnect dielectrics) (Field emission flat panel displays)

4. Applications

The unique properties of diamond-like carbon films and their modifications, together with the possibility to adjust the properties by choosing the right deposition parameters, make them suitable for a variety of applications. The exploited properties include the high wear resistance and low friction coefficients, chemical inertness, infrared transparency, high electrical resistivity and, potentially, the field emission properties and the low dielectric constants. While taC has properties that are similar, some of them even superior, to DLC, only DLC appears to have found practical applications so far. Due to its IR transparency, DLC can be used as an antireflective and scratch-resistant wear-protective coating for IR optics (at a wavelength of 8–13 μm) made of Ge, ZnS, ZnSe [49, 50]. The low deposition temperatures of DLC allows its use as a wear-protective layer on products made of plastic and is therefore used for protection against abrasion of sunglass lenses made of polycarbonate [51].

The most widespread use of DLC films is in wear and corrosion protection of magnetic storage media. Nanosmooth and very thin (<50 nm, even <10 nm) DLC films are used as corrosion and wear-protective coatings for both the magnetic disks and the magnetic heads. Tapes for video recording or magnetic data storage, using ferromagnetic metal as a recording media, as well as the metallic capstans in contact with the tapes, are also being protected with DLC coatings to reduce wear and friction, thus extending the life of the tapes and their reliability [52]. The announcements of the latest MACH3 razor blades by Gillette underscore the use of DLC as a coating, improving the quality and performance of the blades [2]. DLC seems to find its uses in tribological coatings for metal bearings, gears and seals [53]. Its potential use for phase shift masks for deep ultraviolet DUV lithography has been demonstrated [54].

Diamond-like carbon appears to be biocompatible and applications are being developed for its use in

biological environments. Due to their chemical inertness and being impermeable to liquids, DLC coatings could protect biological implants against corrosion and serve as diffusion barriers. DLC films are considered for use as coatings of metallic as well as polymeric, such as polyurethane, polycarbonate and polyethylene, biocomponents, to improve their compatibility with body tissues [55, 56]. Diamond-like carbon, deposited on stainless steel and titanium alloys used for components of artificial heart valves, has been found to satisfy both mechanical and biological requirements and be capable of improving the performance of these components [57]. The same properties may make DLC useful as a protective coating for joint implants. Improvement of carbon/carbon composite prosthetics by DLC coatings has also been demonstrated [58]. Presently, DLC and its modifications are being considered as low dielectric materials for the interconnecting structures of ULSI. A better understanding of the means to control their thermal stability and other integration problems will potentially expand their use in the ULSI chips.

The non-hydrogenated taC films have yet to find widespread applications. The most promising appears to be its use as cathodes in field emission-based flat panel displays or as pixel elements in large outdoor displays [59].

5. Summary

The state of the art of diamond-like carbon may be best summarized by the next two figures and one table. Fig. 1 (from Robertson [20]), describes the structure-composition of diamond-like carbon in a ternary phase diagram of sp^2 , sp^3 and H concentrations. The specific position of a diamond-like material on this diagram is determined by the deposition system, i.e. precursor, method and parameters of the method. The energy of the particles bombarding the growing film appears to be the most important parameter determining the position of the film on the ternary diagram.

Another variation of the diagram of Fig. 1 is presented in Fig. 2 (after Ref. [60]), which shows that the diamond-like carbon films, comprising sp^3 , sp^2 and even sp^1 carbon bonds, have ranges of properties delimited by the properties of diamond, graphite and polymers. These ranges of properties of hydrogenated and non-hydrogenated diamond-like carbon are summarized in Table 1, together with existing and potential applications based on the specific properties of the material.

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