



Mechanical properties of diamond and DLC thin coatings

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Abstract

This paper concentrates on recent advances in the chemical vapor deposition (CVD) and characterization of diamond and DLC films on non-diamond substrates. Arguments related to phase identification, nucleation and interfacial phenomena, morphology and defects as well as their correlation with mechanical properties are examined and discussed. Most of the information presented in this review is applicable to protective and wear resistant use of diamond coatings.

1 Introduction

Results carried out in the last twenty years in the field of thin films deposition, demonstrated that good quality diamond can be grown by Chemical Vapor Deposition (CVD) at sub-atmospheric pressures where the metastable form of carbon can exist (fig.1). In the CVD process diamond films are deposited on a substrate maintained at a temperature of about 1000K by a gas-phase chemical reaction in an activated plasma, containing the precursor molecule. Gas mixtures are usually composed of methane, diluted in hydrogen or a noble gas, which is dissociated by thermal activation (hot filament), plasma (microwave, R.F., D.C.) discharges or simply by combustion flames (oxyacetylene torches). The resulting films are polycrystalline with a morphology that is sensitive to the precise growth conditions. In general combustion methods deposit diamond at high rates (100-1000 $\mu\text{m}/\text{hour}$) but with a scarce processing control, leading to a poor film quality, which is related to the film composition (C-C versus C-H bond content) and crystallinity and to the ratio of sp^3 to sp^2 -bonded carbon atoms in the film. In

contrast, the hot filament and plasma methods have much slower growth rates (0.1-10 $\mu\text{m}/\text{hour}$), but produce high quality films.

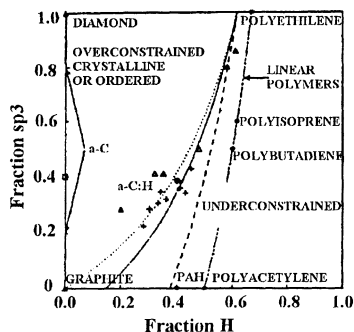


Figure 1: Fraction of C atoms with sp^3 coordination as a function of the content of H atoms¹.

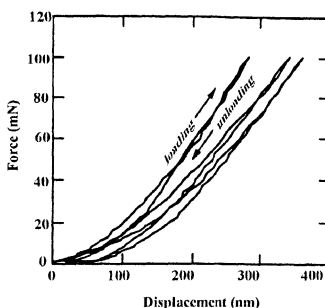


Figure 2: Loading-unloading cycles in the hardness measurements².

In addition to diamond a new class of solids, the amorphous hydrogenated carbon (a-C:H), and the amorphous carbon, known as Diamond-Like-Carbon (DLC), have been identified among the products of the CVD process of carbon based materials. The DLC has very high number density if compared to polymers and properties similar to those of diamond. The structure of DLC is still interesting matter of research. A description of these materials was attempted using the methods of fully constrained random networks, first developed by Phillips and Thorpe¹ for covalently bonded amorphous solids. According to this model DLC is a fully constrained or overconstrained network in which the completely cross-linked structure is composed of sp^2 carbon atoms forming graphite-like clusters in a network with sp^3 bonds, typical of diamond.

In the field of thin film engineering, solutions for many technological problems depend on the ability to produce coatings with good physical and mechanical properties. Among the mechanical properties of interest, hardness has been extensively adopted as a means for quality and process control in many industries. Young's modulus and internal stress are also important for the characterization of thin films, since variations in Young's modulus reflect changes in crystallinity, orientation and quality, and internal stress is responsible for the cracking of the thin films.

This paper reviews recent results of the relationship between properties and structure of diamond and DLC thin films, which show very promising characteristics for unique and different applications, such as optical systems, electronics, and mechanical coatings.

2 Elastic properties

Although diamond is the hardest natural material, diamond films prepared by CVD are general polycrystalline and their hardness depend on grain

microstructure, surface morphology, and the presence of non-crystalline material. Likewise, depending on the method of preparation and the precursor gas used, diamond and DLC films can have extremely diverse properties.

Measurements of the depth of penetration of the indenter tip as a function of the applied force are usually performed in a loading and unloading cycle to characterize the hardness of hard coatings. On CVD diamond most indents have a very small degree of hysteresis during unloading, indicating almost pure elastic behavior, consistent with the ultrahigh hardness of the diamond phase² (fig.2).

Hardness, H , can also be related to the yield stress, Y , through the following equation³:

$$H/Y = 0.07 + 0.6 \ln(E/Y) \quad (1)$$

where E is the Young's modulus standing for mechanically isotropic solids.

Ductile materials have a low value of Y/E , while brittle materials like diamond and DLC have high value of Y/E , and yield occurs by cleavage.

While the hardness of a diamond film is comparable to that of single crystal diamond, the elastic modulus is significantly lower. Savvides et al.² suggested that a reduction of the elastic modulus is due to a certain amount of hydrogen contained in the diamond films, forming sp^2 and sp^3 C-H bonds, whose "spring constant" is lower than that of the host diamond matrix. It has been shown that sp^2 sites contribute no rigidity if they form graphitic cluster. Hence graphitic bonding severely lower the hardness of amorphous carbon. A large scatter in hardness and modulus observed has been also explained in terms of surface roughness, crystallite size, variation of hardness with crystallographic direction, and microstructural defects. Moreover Savvides et al.² and Grill et al.⁴ have shown that, in the preparation of DLC films, there is a strong correlation between the ion energy per condensing carbon atom and the sp^3/sp^2 ratio. From fig.3 it is evident that hardness increases with increasing the energy of ions which bombard the substrate so providing non-equilibrium growth conditions favorable for the formation of sp^3 bonds². Often, the range of hardness is also specific of the deposition technique.

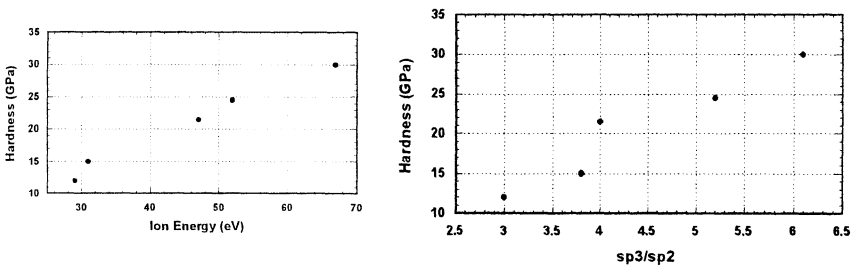


Figure 3: Properties of DLC films as a function of ion energy and sp^3/sp^2 ratio².

In certain circumstances the reduction of hardness with rising sp^3/sp^2 bonding ratio has been observed. This fact has been related to the formation of voids in the a-C:H matrix⁵, causing a reduction of density. Jiang et al.⁵ assumed that the mechanical properties also depend on the volume fraction of voids in the film and calculated a filling factor for a-C:H defined as⁵:

$$f = V_{occ} / V_{film} \quad (2)$$

where V_{film} is the total volume of a-C:H film and V_{oc} is the volume occupied by carbon and hydrogen atom in a-C:H. The f factor was calculated with a linear correlation⁶

$$f = \rho_N (X_4 V_D + X_3 V_G + X_H V_H) \quad (3)$$

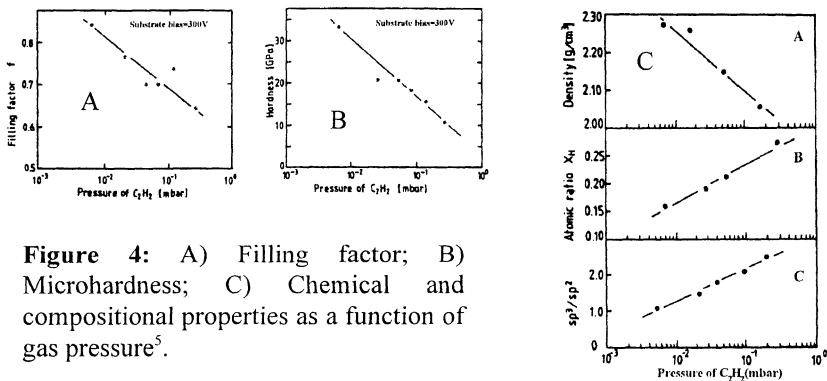


Figure 4: A) Filling factor; B) Microhardness; C) Chemical and compositional properties as a function of gas pressure⁵.

with $V_H = V_D(r_H/r_C)^3$ where ρ_N is the number density, X_H is the concentration of hydrogen, X_4 the concentration of carbon atoms with sp^3 bonds, X_3 the concentration of C with sp^2 bonds, V_D and V_G are the volume of carbon atoms in diamond and graphite and r_H and r_C are the covalent radii of hydrogen and carbon. The reduction of density with increasing pressure, as shown in fig. 4, can be well explained in terms of the filling factor. Jiang et al.⁵ also revealed that with increasing gas pressures, the film structure changes from a more compact to a very open structure, i.e., the void concentration increase raising the gas pressure.

3 Adhesion

Adhesion strength of a thin film may be thought as the energy necessary to break bonds between the film and the substrate at an interface, thus driving the extension of interfacial cracks which lead to failure of the interface and eventual delamination. According to this definition the interfacial failure of a film

deposited on a substrate comes from the combination of different quantities: the fracture resistance, the strength controlling defects and residual stresses.

The macrostructure of diamond films and DLC films, principally consists of stressed intergrown crystallites with a high defect concentration, a possible void content and the presence of other phases (graphite, carbon). The columnar growth mechanism in diamond films produces a microstructure and morphology of the growth surface which differs from that of the initial interface. As the diamond film grows the grain size increases and the morphology changes so that a difference in mechanical strength is expected⁹. Accordingly, the following mechanism of film formation¹⁰ could be considered: the growth rate of diamond is faster in diameter at early stage, and the shape of the diamond particles has the form of a cubic crystal, which results in the formation of voids between particles when these particles come into contact with each other. In the next stage, diamond only grows up in a vertical direction to the substrate. This growth mechanism may be responsible of weak adhesion, because each diamond particle composing the film is considered to be in contact with the substrate only at the vertex of a single crystal.

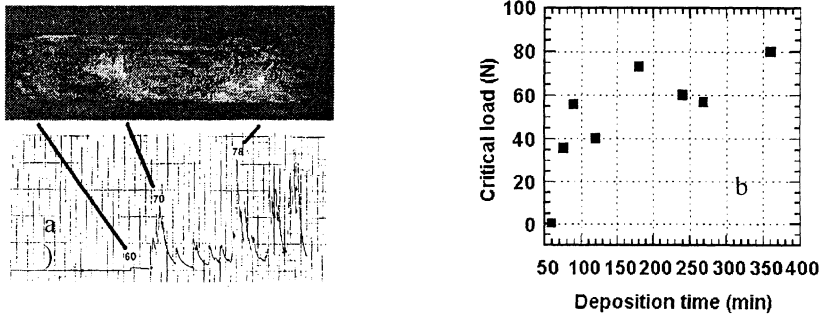


Figure 5: a) Scratch test on the film deposited at 650 °C for 4h: the top part shows the trace left by the diamond tip; The bottom part shows a diagram of the acoustic emission. The first two peaks correspond to partial detachment points before the definitive detachment (third pick); b) Critical load of films deposited on a titanium substrate for different deposition time¹⁶.

Processing time also influences the film features. The density of diamond particles becomes higher in proportion to treatment time. If the substrate is treated under appropriate conditions in order to make many nucleation sites, the diamond film would be composed of smaller particles, which would result in the formation of many contact points leading to a better adhesion¹⁰. The deposition of an intermediate layer can be a solution to this problem¹¹: a metal binder can fill the voids between the crystals, and absorb energy during the fracture process at the interface. Another interesting observation was suggested by Tabor¹² who related the low adhesion of diamond to its high modulus, which minimizes deformation around asperities on the

contacted surface, and so minimizes the area of contact.

The choice of the substrate material is also critical for the diamond-substrate adhesion. The presence of a graphitic phase at the interface reduces the film adhesion. Structural materials, Fe, Ni, Cr, Mn, Co are good catalyst for transforming sp^3 bonds to sp^2 bonds in carbon, and consequently graphitization of diamond films in contact with such metals can occur¹³. Except Cr, these metals can dissolve carbon to form solid solutions, but are generally considered weak carbide formers. A problem arising when depositing diamond on steel is the high solubility of carbon, which results in long deposition times. For steel coating, amorphous diamond seems to be the best solution, as DLC is not dissolved into steel substrates. Moreover the as-deposited DCL is often smoother than diamond films, so any post-treatment for tribological applications is not necessary. Only the thermal instability of DLC can seriously compromise its applications, as the integrity of the DLC film can not be maintained at temperatures higher than 5000°C for more than one hour¹⁴.

E. Buccioni et al.¹⁶ studied and discussed key processing parameters affecting the film structure and the film/substrate adhesion in HFCVD (hot filament chemical vapor deposition) of diamond films on titanium and Ti-6Al-4V substrates. An inversion in film texturing from the $\langle hhh \rangle$ direction to the $\langle hhh \rangle$ direction was observed as the deposition temperature raises from 650°C up to 850°C. At 650°C, TiC and TiH_2 with $\langle 110 \rangle$ crystallite orientation are formed at the interface. At higher temperatures (about 800°C) a thick and extremely hard (1050 HV) TiC layer ($\langle 111 \rangle$ and $\langle 200 \rangle$ crystallites orientation) develops without hydride formation. Its structure is irregular and porous in appearance. A cross section of the samples was obtained, in order to perform hardness measurements on interfacial layers. Increasing values were measured from the substrate towards the film: the results, correlated with the x-ray diffraction analysis, allowed a deeper understanding of the interface features and performances. A multi-step process leading to the effective film detachment was observed performing the scratch test (fig.5). Such failure mechanism is affected by the complex structure observed at the film/substrate interface. Adhesion tumbling occurs at the temperature of about 750°C, in the critical temperature range for transition in interface composition from a TiH_2 rich interlayer to a thick (about 100 μm) TiC interlayer. Although the titanium alloy showed better hardness performances (fig.5) than the pure titanium, the adhesion of the film to the substrate was similar in both materials studied.

Also Catledge et al.⁶ have made a detailed study of coating titanium components with a well adhered, thin layer of diamond. They suggest that in order to achieve a strong bond between diamond and substrate, a fundamental role is played by the intermediate layer. One of the main functions of this layer is to prevent diffusion of atoms to the diamond surface, as in substrates with high carbon diffusion the incoming carbon atoms are transported into the bulk, leading to a temporary decrease in the surface carbon concentration which delays the onset of diamond nucleation. In addition to that, this layer must also strongly adhere to the substrate and the diamond. Strong bonding with CVD

diamond is best accomplished by chemical reaction and formation of a carbide layer¹⁷, and therefore elements with great affinity with carbon are the most likely choices.

Interface delamination is caused by residual stresses given by intrinsic stresses induced during film growth and by thermal stresses. As a general rule, the comparison of the interface debonding toughness vary with the quantity¹²

$$h\sigma_R^2/E\lambda \quad (4)$$

where h is the film thickness; σ_R the residual stress; E the Young's modulus; λ the cracking number which determines whether there is enough energy stored in the film for the propagation of an interface crack.

Thermal stresses are due to the difference between the thermal expansion coefficient of diamond ($0.8 \cdot 10^{-6} \text{ K}^{-1}$ at room temperature). Pickrell²⁹ have recently determined the thermal expansion variation of CVD and that of the substrate, generated after deposition, during cooling to room temperature. For films with a substantial percentage of graphite or disordered carbon, the thermal expansion would be different from natural diamond and could be defined by a rule of mixtures of the phases present. However, the absolute concentration of sp^2 carbon in diamond films is difficult to quantify. It is also thought to be very low in well faceted, coarse-grained diamond film³⁰ while for fine grained film (grain size of about 1000\AA) the sp^2 carbon and hydrogen content can become significant. Such films may have thermal expansions which are noticeable different from single crystal diamond. Resulting thermal stresses are often compressive, except for oxides like silica or nitrides³¹. Their absolute values are very high ($>3\text{GPa}$), principally for metallurgical substrates and this is one reason that explains the important difficulties to obtain a well adherent diamond coating on these substrates.

Intrinsic growth stresses variations appear to depend on the grain boundary density. Gamlen et al.³¹ showed an unexpectedly strong correlation between the mean delamination diameter and the square root of the coating grain size. Then, the film adherence will improves as the deposition time and hence coating thickness is reduced. These observations also suggest a strong influence of the nucleation method on the film adhesion characteristics.

It has been found that the internal stress of thin diamond film normally increases compressively with rising ion dose, because interstitials are formed and voids disappear. In contrast to this general rule, for amorphous carbon an increasing dose of ion bombardment either during film growth or after growth leads to a reduction of the internal stress. This is caused by a transformation of diamond-like to graphite-like a-C:H. Jiang et al.³⁰ assumed that the internal stress is affected by a displacement of the atoms from their equilibrium position and it is possible to apply to this process the Hooke's law. In their study a decrease of elastic constant with decreasing compressive stress has be found: namely a phase transformation from diamond-like to graphite-like.

4 Fracture

The elastic constants and the fracture strength of CVD diamond are critical properties in many applications. The cleavage surface energy for the {111} plane is 5.5 J/m², the largest measured value of any material. This quantity results in high fracture toughness of natural diamond. In CVD diamond bulk cracks may be formed during the deposition process and can significantly reduce the fracture toughness²¹.

Depending on the processing conditions, the fracture mode of polycrystalline diamond can vary from nearly 100% intergranular to nearly 100% intragranular²¹. In intergranular fracture, typical of films with weak intergranular bonding, wear proceeds by cleavage of individual crystallites. Grain boundaries weakening is observed in highly oriented films and is also related to the presence of sp² bond material at grain boundaries. In materials in which intragranular mode fracture occurs, wear can be controlled by the introduction of planar defects, acting as microscopic crack deflection sites. Step formation restrains the propagation of brittle cracks by absorbing extra energy in the vicinity of the connecting riser between adjacent planes¹⁹. It is observed that planar defects and strong, randomly oriented grain boundaries in CVD films may serve as microscopic crack deflection sites that redirect cracks and absorb crack energy. As a consequence, the development of microcrystalline film structure with randomly oriented grains, as opposed to more common columnar film structure, tends to promote the highest fracture strength. In general fracture strength tends to be high for films of small grain size, in relation to the fact that in polycrystalline materials the fracture strength, σ , normally varies as the inverse square root of the grain size, d , as in the Petch number²²

$$\sigma = \alpha d^{-1/2} \quad (5)$$

where α is an interfacial constraint parameter. The fracture strength decreases increasing the sample thickness⁹: as the thickness of the growing diamond increases the grain size of the growth surface also increases.

Vickers indentation revealed a fracture toughness anisotropy on {100}

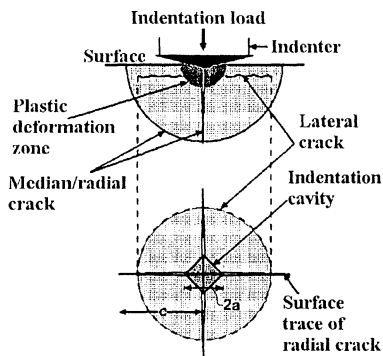


Figure 6: Schematic illustration of radial and lateral cracks generated in a brittle material due to Vickers hardness indentation²².

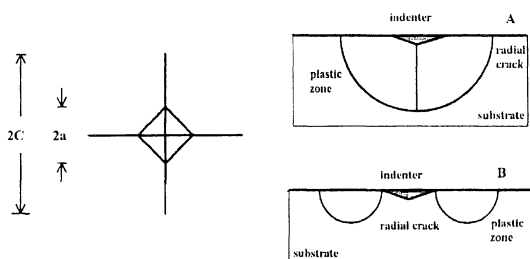


Figure 7: a) Halfpenny radial cracks;
b) Palmquist radial cracks²³

planes, as radial cracks in $\langle 110 \rangle$ direction are longer than in $\langle 100 \rangle$ at the same load²¹. Lateral cracks, typical in the indentation of brittle materials (fig.6), are absent in diamond. Shallow ring cracks are observed²² around and inside an indentation especially for indentation on $\{111\}$ planes.

At room temperature, the fracture toughness of both natural and CVD diamond is about $5 \text{ MPa m}^{1.5}$, much higher than other hard materials, such as sapphire and $\alpha\text{-SiC}$ single crystals. While halfpenny radial cracks are developed around Vickers indentation at low temperatures, radial cracks of Palmqvist type (fig.7) are formed at high temperatures²³.

The dislocation mobility and hence the plasticity of diamond sharply increase at temperatures higher than 1220°C but decreases for diamond with low nitrogen content and low dislocations densities²³.

5 Friction and wear

Wear of a surface depends on chemical and phase composition, on free-surface, and bulk properties, including strength and toughness. Several mechanism are involved: adhesive wear arises from plastic yield of a surface following adhesive contact, while abrasive wear is due to material loss from a surface by micro-cracking and local fracture. The adhesive and abrasive wear rates of a surface vary inversely with their hardness, so diamond and hard carbon can be expected to have low wear rates. Other interesting properties of diamond for the applications here considered are its high thermal conductivity and the absence of chemical wear.

The mechanical wear resistance is 10 times greater than that of polycrystalline cubic boron nitrate and 100 times that of cemented carbide. The wear resistance of diamond films is favourably affected by stresses generated during the growth process: films having compressive stress equal or higher than 1 GPa show wear resistance about three times greater than that of a stress-free diamond coating²⁴. The only application which is not possible is the machining at high temperatures of those metals in which carbon forms a solid solution, such as transition metals, because the chemical interactions with these materials accelerates the tool wear. Moreover, as diamond is a brittle material, diamond coatings are expected to fully exploit their wear resistance properties only if

deposited on tough substrates.

Another outstanding property of CVD diamond is the low coefficients of friction (on the order of 0.1) both in dry nitrogen and humid air at atmospheric pressure. One of the reasons for the low friction coefficient of diamond seems to be the surface absorption of a contaminant layer with tangential shear²⁵. A control of the film morphology, which depends on the deposition temperature and the specific carbon precursor, can substantially reduce the coefficient of friction of the as-deposited films²⁶. Better results have been obtained by growing only the {100} faces of diamond or alternatively by obtaining a micro-crystalline film morphology. Better performances in vacuum are provided by amorphous carbon coatings. DLC has both a super-hard diamond crystal structure and a solid lubricating graphite structure. This observation suggested a treatment of the diamond film by ion implantation in order to form an external layer of amorphous carbon phases, while retaining the extremely hard structure of diamond, below this layer. Also fluorination²⁸ of DLC can result in materials with low friction and microwear, incorporating fluorine in graphite structures, only partially chemically bonded to the carbon matrix.

Current applications of DLC as protective hard coating include magnetic recording media, protection of sunglasses lens and engine motor pistons²⁹.

6 Concluding remarks

Despite the current rapid rate of progresses made in the improvement of diamond CVD, there are several issues which remain to be addressed in the future, in order to provide a firm scientific base for the low pressure diamond technology. Detail on the structure of DLC and as well as the relationship between structures and mechanical properties are still uncertain. Moreover experimental and theoretical studies of defects of both bulk diamond and diamond surface will be of great utility to control and make the coatings respond to requirements of specific applications. Many interesting applications are still now envisaged in electronic and mechanic fields, and it seems likely that it will prove possible to scale CVD methods to the extent that they will provide an economically and viable alternative to the traditional high-pressure high-temperature (HPHT) synthetic diamond.

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