Relationship between hardness and optical properties of diamond-like carbon coatings

C V Suasnavas1, M O Makeev1,2, A S Osipkov1,2, N B Solano1, A E Shupenev2 and P A Mikhalev1,2

1 Peoples' Friendship University of Russia (RUDN University), Moscow, Russia
2 Bauman Moscow State Technical University, Moscow, Russia

E-mail: carlos.suasnavaslagos@gmail.com

Abstract. Correlation between hardness and optical properties of diamond-like carbon (DLC) coatings is considered. Various methods for the characterization of mechanical, chemical and optical properties of DLC coatings are used; however, some of these methods are destructive, and others are non-destructive. It was found that optical properties of DLC coatings are proportional to their hardness. The mathematical expression that allows to calculate the hardness of a DLC coating according to its refractive index is proposed. Therefore, it is possible to avoid the use of destructive methods (such as nano-indentation technique) to characterize DLC coatings.

Keywords: diamond-like carbon coating, functional properties, optical properties, non-destructive methods, hardness, refractive index, correlation.

1. Introduction

The DLC (diamond-like carbon) coatings are widely used in different fields of science, technology and industry [1-9]. The spectrum is of such magnitude that involves applications in biomedicine, goes through coatings for optical elements, and comes to contribute in the automotive industry, citing a few of the countless applications. Regardless of the application to which the DLC coating is intended, it will always be essential to measure and evaluate the properties of the obtained DLC film to ensure its benefits.

When characterizing functional properties of DLC coatings, e.g., wear resistance, adhesion force, hardness, etc., these properties and the film itself tend to be degraded because the characterization methods are often destructive. On the other hand, when it is required to characterize structural and physical-chemical properties, non-destructive methods are used. In such a way that nowadays it tends to develop mathematical models that interrelate functional, structural, and physicochemical variables of DLC coatings, which at the end will allow to determine the functional properties with high precision and using only non-destructive methods of characterization. In table 1 a summary of typical DLC characterization methods is presented, emphasizing their destructive or non-destructive character.

Table 1. Typical DLC Characterization Methods.

| Non-destructive | Destructive |
|-----------------|-------------|
| Methods         | Characteristics | Methods | Characteristics |
| Raman Spectroscopy | sp3/sp2 bonding ratio, residual stress | Nanoindentation | Young's modulus, hardness, fracture toughness, adhesion force, residual stress |
| Ellipsometry    | optical constants, thickness | Electron Energy-Loss Spectroscopy | sp3 fraction |
Scanning Electron Microscopy (SEM) | topography, composition, defectiveness | Atomic Force Microscopy (AFM) | thickness, roughness

In a second instance, establishing relationships among diverse characteristics, determining the influence of certain characteristics on others, or arriving to conclude that there is a dependence on one characteristic as a function of others, gives the opportunity of a broad understanding about the behavior of this singular amorphous carbon nanostructure, and consequently, it is transformed into valuable information, e.g., in optimization processes during deposition of DLC coatings.

A third argument, no less important, is of quantum conception. The double-slit experiment makes it clear that there is a great uncertainty when making measurements at the nanometer scale, at the quantum scale; the simple fact of making a measurement, however subtle it might be (even non-destructive), inevitably introduces a disturbance to the system, therefore, the measurement is not entirely neat. In short, the less it is measured, the less uncertainty regarding the values obtained.

2. Analysis and discussion
Finding an expression that relates a tribological property with any optical property of a DLC film, would constitute a significant advance since it is firmly aligned in the direction of the pursued objective. Regarding this approach, there is a work developed by a Japanese research team, that claims to have found a proportional relationship between hardness and the refractive index [10]. Next, details about this work are required.

Reference 10 provides a series of useful data and conclusions. The production method is a PVD: Ion beam deposition. This method generally has 2 variables, which can be adjusted or exchanged independently, to obtain a DLC film with certain characteristics. These variables or deposition parameters are the voltage applied to the substrate and the gas source. In table 2, a set of data referring to values of hardness, refractive index, extinction coefficient, hydrogen content, density, and thickness of 4 DLC films deposited on a silicon substrate is observed. The substrate voltage varies between 1 kV and 3 kV, while the gas source used is benzene for 3 of the cases, and cyclohexane for one of them.

Table 2. Characteristics of DLC films obtained by Ion beam deposition [10].

| Ion beam deposition | Deposition parameters | DLC film type | Hardness (GPa) | Refractive index (550 nm) | Extinction coefficient (550 nm) |
|---------------------|----------------------|---------------|----------------|--------------------------|-------------------------------|
| Substrate voltage   | Source gas           | Meas. Method  | Magnitude      | Meas. Method             | Magnitude                     | Meas. Method | Magnitude|
| 1 kV                | C6H6 ta-C:H          | Nanindentation| 32.3           |                          | 2.43                          |                | 0.33     |
| 2 kV                | C6H6 ta-C:H          | Ellipsometry  | 25.8           |                          | 2.25                          |                | 0.44     |
| 2 kV                | C6H12 ta-C:H         | Ellipsometry  | 21.2           |                          | 2.14                          |                | 0.41     |
| 3 kV                | C6H6 a-C:H           | Ellipsometry  | 23.6           |                          | 2.17                          |                | 0.61     |

| Ion beam deposition | Deposition parameters | DLC film type | Hydrogen content (%) | Density (g/cm³) | Thickness (nm) |
|---------------------|----------------------|---------------|----------------------|----------------|----------------|
| Substrate voltage   | Source gas           | Meas. Method  | Magnitude            | Meas. Method   | Magnitude      |
| 1 kV                | C6H6 ta-C:H          | Forward Scatter| 23.2               | X-Ray Reflectometry| 2.3           | 875          |
| 2 kV                | C6H6 ta-C:H          | Hydrogen      | 22.7                | Ellipsometry   | 2.17           | 550          |
Regarding the voltage applied, according to table 2, the following can be asserted:
- The hardness of the nanostructure decreases as the voltage applied to the substrate raises. This relationship is met only if the energy peak (100 eV), leading to the formation of sp\(^3\) bonds, has been exceeded [9]. According to reference 10, the voltage value that produces an energy of around 100 eV in the carbon cations is estimated at 1 kV.
- The extinction coefficient of the nanostructure increases as the voltage applied to the substrate is raised. Unlike the refractive index, which decreases with the growth in the applied voltage.
- By raising the voltage applied to the substrate (above 1 kV), nanostructures of a lower density are achieved.
- The hydrogen content in the nanostructure begins to decrease as the voltage applied to the substrate raises.
- When performing the analysis of the DLC film thickness, as well as the thickness of surface roughness, no clear pattern is observed, and therefore, there is no clear influence of the substrate voltage on the final achievement of a certain thickness. In other words, the substrate voltage alone does not allow to control the DLC film thickness and surface roughness. Figure 1 summarizes the found tendencies when the substrate voltage raises.

The fact that hardness decreases, while substrate voltage raises, is related to the energy acquired by the carbon cations that impact on the DLC film. Increasing the voltage in the substrate results in a greater acceleration in the cations and, therefore, the carbon cations acquire a higher energy. However, to talk about hardness means to talk about a high density of sp\(^3\) bonds in the nanostructure, and according to reference 9, C\(^+\) with energy of 100 eV generate the greatest number of sp\(^3\) links, that is, the peak of performance is reached at this value. In this way, although energy is required to achieve the task, an energy margin must not be exceeded because sp\(^3\) bonds are lost.

| Voltage | Gas Source | Ta-C:H | a-C:H | Extinction Coefficient |
|---------|------------|-------|-------|------------------------|
| 2 kV    | C\(_6\)H\(_{12}\) | 25.0  | 2.09  | 1077                   |
| 3 kV    | C\(_6\)H\(_6\) | 20.5  | 2.13  | -                      |

Analyzing now the type of gas source used in the deposition, it can be concluded that the utilization of one or another substance has a fundamental effect on the hydrogen content of the nanostructure. According to reference 10 and table 2, replacing benzene (C\(_6\)H\(_6\)) with cyclohexane (C\(_6\)H\(_{12}\)), and keeping constant the substrate voltage, produces a notorious increase in the hydrogen content of the DLC film. Also, using C\(_6\)H\(_{12}\) as gas source, it’s possible to appreciate a reduction in hardness, refractive index, and density, as compared with the case where C\(_6\)H\(_6\) is employed. The situation of extinction coefficient is different, because despite using another type of gas source, the values are practically the same. Finally,
a notable change in DLC film thickness is observed, the use of cyclohexane generates films with twice the original thickness. Figure 2 summarizes the found tendencies when C₆H₁₂ is used as gas source.

Looking closely at figures 1 and 2, there are clearly 3 properties that go hand in hand: hardness, refractive index and density. Despite the different conditions and parameters of deposition used, the mentioned characteristics always follow the same pattern or trend, in this case the 3 characteristics decrease in their respective values. This situation already becomes an existence sign of a certain relationship between this trio of characteristics.

The Japanese team of scientists decided to continue with the research on the properties of amorphous carbon nanostructures and collected a set of data from a total of 46 samples of DLC, between different laboratories and industries dedicated to the production of this nanostructure. The acquired data corresponded to the hardness and refractive index of the DLC films. It should be noted that among these 46 samples there is a broad spectrum about the method of deposition used, and of course, about the type of DLC film obtained. By joining this group of data and making a correlation between them, the result was amazing: there is a proportional relationship between hardness and refractive index. Figure 3 presents the correlation graph constructed by the research group, which in addition to the 46 samples, includes the 4 samples developed in their laboratory.

Figure 3. Correlation between the refractive index (550 nm) and hardness of several DLC films [10].

The result is quite encouraging, and since they have worked with different types of DLC films, could be hypothesized that there is a proportional relationship between hardness and refractive index regardless of the deposition method from which the DLC film comes. It would be extraordinary because would grant a degree of universality to the model that it is intended to develop.

Unfortunately, in the referenced work the raw data of the 46 samples are not published, only the data concerning the 4 samples developed in their own laboratory are known. However, as part of the present analysis and with the aim of verifying this relationship, a graph with the known data has been constructed. Linear regression has been applied to adjust a line to the set of points. Figure 4 shows the graph "Refractive Index vs Hardness" for the 4 DLC samples.

As shown in figure 4, it is a strong linear relationship, its correlation index (0.9873) corroborates this. It has been determined, in addition, the equation of the line that would allow to calculate the hardness values of the DLC film as a function of the refractive index (Equation 1).

\[ H = 36.388 \times n - 56.057 \]  

where \( H \) – hardness in units of GPa; \( n \) – refractive index.
Figure 4. Correlation between the refractive index (550 nm) and hardness of 4 DLC samples.

Using the obtained expression, the hardness values are calculated according to the measured refractive index. Table 3 shows the results of this calculation and the respective relative error. The largest error is less than 3%.

Table 3. Comparative table between measured and calculated hardness.

| Refractive index | Measured Hardness (GPa) | Calculated Hardness (GPa) | Relative error |
|-----------------|-------------------------|---------------------------|----------------|
| 2.43            | 32.3                    | 32.366                    | 0.20%          |
| 2.25            | 25.8                    | 25.816                    | 0.06%          |
| 2.17            | 23.6                    | 22.905                    | 2.95%          |
| 2.14            | 21.2                    | 21.813                    | 2.89%          |

The error margin is certainly acceptable, thus supporting the hypothesis of an apparent linear relationship between hardness and refractive index. Of course, the amount of data is insufficient; but nevertheless, it’s clear that in order to validate this hypothesis, a considerable set of data resulting from the own experimentation is required.

There are several scientific references that despite using different methods of deposition, come to determine the same close relationship between the content of sp$_2$ or sp$_3$ bonds (implicitly material hardness) and the main optical properties: refractive index and extinction coefficient. The conclusion is the following: the increase in sp$_2$ content from the graphitic structure can be considered to have a large effect on the increase in extinction coefficient, while the increase in C-C sp$_3$ content can be considered to affect the increase in refractive index [10-13]. Figure 5 summarizes this conclusion. That is, the harder the DLC film is, the higher the refractive index; likewise, as the hardness of the film decreases, it is the extinction coefficient that acquires relevance.

Figure 5. Relationship between optical constants and sp$_2$/sp$_3$ bonding ratio.
3. Experimental results

At the moment only 2 samples with DLC coating have been obtained. The technologies used were Cathodic Arc Deposition (Arc-PVD) and Pulsed Laser Deposition (PLD). Hardness and refractive index values were measured using nanoindentation and ellipsometry, respectively. The registered values are shown in Table 4.

| Hardness (GPa) | Refractive index (2µm) | sp$^3$ fraction % |
|----------------|------------------------|-------------------|
| Sample 1 (Arc-PVD) | 14.89 | 2.12 | 13 |
| Sample 2 (PLD) | 26.48 | 2.31 | 51 |

As a first approximation, given the scarcity of data, it has been decided to ubicate these results within the graph provided by reference 10. As shown in Figure 6, the obtained values are within the region that allows to assume a directly proportional relationship between hardness and refractive index.

If a line that passes through the 2 points obtained in the experiment was drawn, the equation of this line would differ in comparison to that obtained for the 4 samples of reference 10. This situation is decisive to conclude that the mathematical relationships depend strictly on the method of deposition that is used. However, there is a defined region by which the different values of hardness and refractive index are distributed. When a general line is drawn through this region, there is an evident consonance with the line obtained for the 4 samples that come from the same method of deposition. That is, both equations belong to the same family of parallel lines. This match is shown in figure 7.

The general region trend is described by the equation (2).

$$H = 36.388n - 64.771$$

where $H$ – hardness in units of GPa; $n$ – refractive index.

Figure 6. Location of the obtained values in the reference scheme.
Figure 7. General trend for a set of DLC data.

Conclusions
1. There is a directly proportional linear relationship between the hardness of DLC films and their refractive index.
2. Regardless of the deposition parameters, but if the DLC films are obtained through the same deposition method, it will be possible to determine an equation that describes the relationship between hardness and refractive index.
3. In the graph “refractive index vs. hardness” there is a certain region where all the values corresponding to different types of DLC films are distributed, and this distribution has a completely linear trend.
4. It is possible to indirectly determine variables of tribological type without incurring the use of destructive methods of characterization.

References
[1] Hauert R 2008 Tribology of diamond-like carbon films: fundamentals and applications ed C Donnet and A Erdemir (New York: Springer Science & Business Media) pp 494–500
[2] Bewilogua K and Hofmann D 2014 History of diamond-like carbon films—from first experiments to worldwide applications Surface and Coatings Technology 242 214–25
[3] Grill A 2003 Diamond-like carbon coatings as biocompatible materials—an overview Diamond and related materials 12(2) 166–70
[4] Makeev M, Zhukova E, Mikhailov P, Osipkov A and Mironov Y 2015 Physical chemical and protective properties of the diamond-like carbon coatings synthesized from separated plasma of electric arc Proc. 5th International Workshop on Computer Science and Engineering: Information Processing and Control Engineering 2015 (Chengdu, China) 255–9
[5] Piazza F, Grambole D, Schneider D, Casiraghi C, Ferrari A and Robertson J 2005 Protective diamond-like carbon coatings for future optical storage disks Diamond and related materials 14(3-7) 994–9
[6] Choi W, Kim K, Yi J and Hong B 2008 Diamond-like carbon protective anti-reflection coating for Si solar cell Materials Letters 62(4-5) 577–80
[7] Kutsay O, Gontar A, Novikov N, Dub S, Tkach V, Gorshtein B and Mozkova O 2001 Diamond-like carbon films in multilayered interference coatings for IR optical elements *Diamond and related materials* **10**(9-10) 1846–9

[8] Mironov Y, Stepanov R, Osipkov A, Mironova A, Makeev M, Mikhalev P and Sedih N 2015 Optical and mechanical properties of diamond-like carbon coatings deposited by filtered cathodic vacuum arc deposition *Proc. 5th International Workshop on Computer Science and Engineering: Information Processing and Control Engineering* (Chengdu, China) 295–300

[9] Robertson J 2002 Diamond-like amorphous carbon *Materials science and engineering: R: Reports* **37**(4-6) 129–281

[10] Hiratsuka M, Nakamori H, Kogo Y, Sakurai M, Ohtake N and Saitoh H 2013 Correlation between optical properties and hardness of diamond-like carbon films *Journal of Solid Mechanics and Materials Engineering* **7**(2) 187–98

[11] Smietana M, Szmidt J, Korwin-Pawlowski M, Miller N and Elmustafa A 2008 Influence of RF PACVD process parameters of diamond-like carbon films on optical properties and nano-hardness of the films *Diamond and related materials* **17**(7-10) 1655–9

[12] Lemoine P, Quinn J, Maguire P, Zhao J and McLaughlin J 2007 Intrinsic mechanical properties of ultra-thin amorphous carbon layers *Applied surface science* **253**(14) 6165–75

[13] Su C, Lin C, Chang C, Hung H and Lin T 2006 Mechanical and optical properties of diamond-like carbon thin films deposited by low temperature process *Thin Solid Films* **498**(1-2) 220–3