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# Diamond-Like Carbon (DLC) Coatings for Automobile Applications

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## Abstract

Diamond-like carbon (DLC) coatings are amorphous carbon material which exhibits typical properties of diamond such as hardness and low coefficient of friction, characterized based on the  $sp^3$  bonded carbon and structure. The proportion of  $sp^2$  (graphetically) and  $sp^3$  (diamond-like) determines the properties of the DLC. This coating can be applied to automobile engine component in an attempt to provide energy efficiency by reducing friction and wear. However, DLC coatings are faced with issues of thermal instability caused by increasing temperature in the combustion engine of a vehicle. Therefore, it became necessary to seek ways of improving this coating to meet up with all tribological requirements that will be able to resist transformational change of the coating as the temperature increases. This chapter discusses the need for diamond-like carbon coatings for automobile engine applications, due to their ultra-low friction coefficient ( $<0.1$ ) and excellent wear resistance (wear rate  $\sim 7 \times 10^{-17} \text{ m}^3/\text{N.m}$ ). The importance of DLC coatings deposited using PECVD technique, their mechanical and tribological properties at conditions similar to automobile engines would also be discussed. Non-metallic (hydrogen, boron, nitrogen, phosphorus, fluorine and sulfur) or metals (copper, nickel, tungsten, titanium, molybdenum, silicon, chromium and niobium) has been used to improve the thermal stability of DLC coatings. Recently, incorporation of Ag nanoparticles,  $\text{TiO}_2$  nanoparticles,  $\text{WO}_3$  nanoparticles and  $\text{MoO}_3$  nanoparticles into DLC has been used. The novel fabrication of diamond-like carbon coatings incorporated nanoparticles ( $\text{WO}_3/\text{MoO}_3$ ) using PECVD for automobile applications has shown an improvement in the adhesion properties of the DLC coatings. DLC coatings had a critical load of 25 N, while after incorporating with  $\text{WO}_3/\text{MoO}_3$  nanoparticles had critical load at 32 N and 39 N respectively.

**Keywords:** automobile, diamond-like carbon, nanoparticles, PECVD, tribological

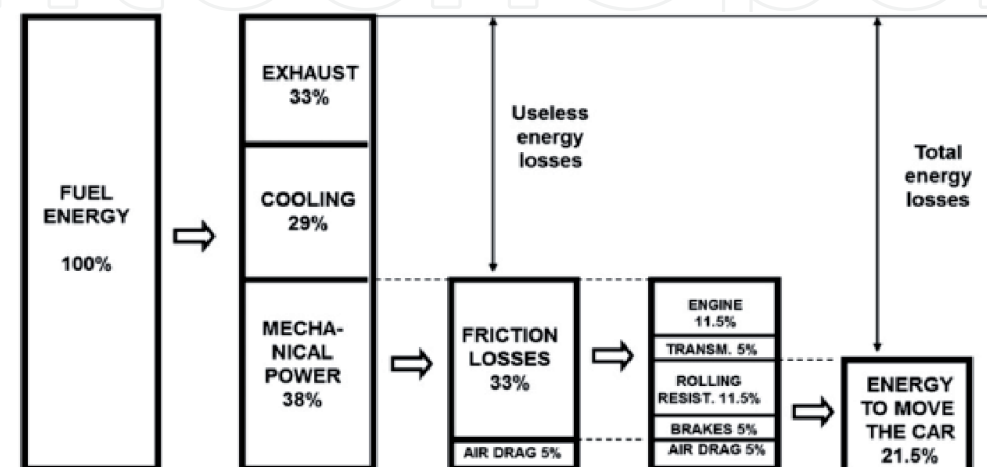
## 1. Introduction

In an attempt by the automobile industry to cut down on the consumption of fuel in the combustion engine of automobile vehicle, it is important to note that reduction in friction and wear plays an important role in reducing the energy

consumed and ensuring energy efficiency. It has been reported by Holmberg et al. [1] that approximately 11.5% energy is required to overcome friction in a combustion engine of a passenger car as seen in **Figure 1** [1]. To reduce the energy required to overcome friction in a combustion engine of a passenger car it is necessary to provide coatings that possess very low coefficient of friction and has high resistance against wear. DLC coatings have been known for their low coefficient of friction and excellent tribological properties in automobile engine parts application [1]. The hardness of DLC coatings range from 5 to 40 GPa, low friction coefficient value ( $<0.1$ ) and high wear resistance ( $\sim 3 \times 10^{-14} \text{ m}^3/\text{N.m}$ ) [2]. Although these properties may vary, depending on deposition technique such as Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) which are the two (2) main classes of deposition techniques used [3]. PECVD provides durable DLC coatings, making them important for coating automobile engine parts to withstand harsh operational conditions [4].

The major problem that may possibly arise during the application of DLC coatings on automobile engine parts at operating conditions is thermal instability. The operating temperature is usually 80 to 200°C, at this temperature the hardness reduces due to transformation of  $\text{sp}^3$  carbon to  $\text{sp}^2$  carbon, leading to a softer DLC which may easily delaminate and wear out [4, 5]. To improve the thermal stability doping (non-metal/metals) of DLC coatings has been used. Non-metals such as hydrogen, nitrogen, silicon, fluorine and sulfur, and metals such as tungsten, titanium, aluminum, chromium and molybdenum has been used to dope DLC films in an attempt to improve the DLC film [4, 5]. This has improved mechanical and tribological properties of DLC coatings by increasing the  $\text{sp}^3$  carbon bond. However, the internal residual stress in the DLC coatings becomes very high above 1 GPa, causing poor adhesion to metallic substrate. The internal residual stress is as a result of interfacial and structural mismatch between the DLC coating and doped element. In attempt to solve this problem annealing has been used to reduce the residual stress in the DLC and improve the thermal stability of DLC coatings up to 500°C [6].

Recently, the incorporation of nanoparticles into DLC has been used by first dispersing the nanoparticles into hexane or isopropanol, thereafter, introducing the dispersed nanoparticles into the reactor chamber through the nanoparticle inlet, this deposition method has been described by some authors in literature [7–13]. These nanoparticles which have been used includes Ag [7],  $\text{TiO}_2$  [8–10],  $\text{WO}_3$  [11, 12] and  $\text{MoO}_3$  [13]. In this chapter the use of diamond-like carbon coatings for automobile engine applications, due to their ultra-low friction coefficient and



**Figure 1.** Breakdown of passenger car energy consumption [1].

excellent wear resistance will be discussed. PECVD deposition technique for DLC coatings, mechanical and tribological properties at conditions similar to automobile engines would also be discussed. Discussion of the thermal stability of DLC coatings and the improvement of the DLC by non-metallic/metallic doping would be made. Lastly, the need to develop novel DLC coatings that can improve thermal stability by incorporating nanoparticles and future DLC coatings.

## 2. Diamond-like carbon coatings

Diamond-like carbon coatings are amorphous carbon material that exhibit some of the typical properties of diamond and are characterized based on the content of  $sp^3$  bonded carbon and structure [14, 15]. DLCs are usually deposited using precursors of carbon such as ethane ( $C_2H_6$ ), methane ( $CH_4$ ), acetylene ( $C_2H_2$ ), iso-butane ( $C_4H_{10}$ ), propane ( $C_3H_8$ ), benzene ( $C_6H_6$ ), and n-butane ( $C_4H_{10}$ ) [16]. DLC coatings has the potential to be used on automobile part's interface due to ultra-low friction. Yasuda et al. [17] has used DLC coatings on automobile part and their work showed reduction in friction for PECVD DLC coatings. According to Louda [18] the use of thin coatings in automotive parts brings about eco-friendly environments and economic savings.

### 2.1 Types of diamond-like carbon coatings

Diamond-like carbon (DLC) coatings varies in mechanical, physical and tribological properties depending on their type. DLC coatings are used in automotive engines due to their ultra-low friction, increase durability, and chemically inert nature. The proportion of  $sp^2$  (graphetically) and  $sp^3$  (diamond-like) determines the properties they possess. Although, such properties can usually be influenced by adding non-metals (hydrogen, nitrogen, silicon, fluorine and sulfur) or metals (tungsten, titanium, aluminum, chromium and molybdenum) as shown in Figure 2 [4, 5].

### 2.2 Deposition of DLC film with plasma enhanced chemical vapor deposition

Plasma enhanced chemical vapor deposition (PECVD) is the recently used technique to develop DLCs that are able to reach into the interior of the phase diagram [19] as represented in Figure 3. The ternary diagram majorly consists of differing ratios of  $sp^2$  and  $sp^3$  bonded carbon with differing levels of hydrogen. The ratio of these three components can be varied to provide a range of different properties.

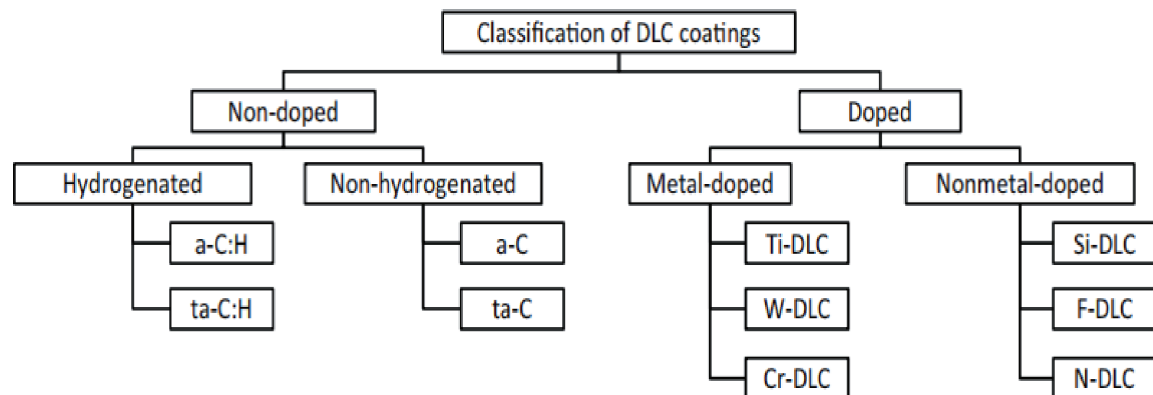
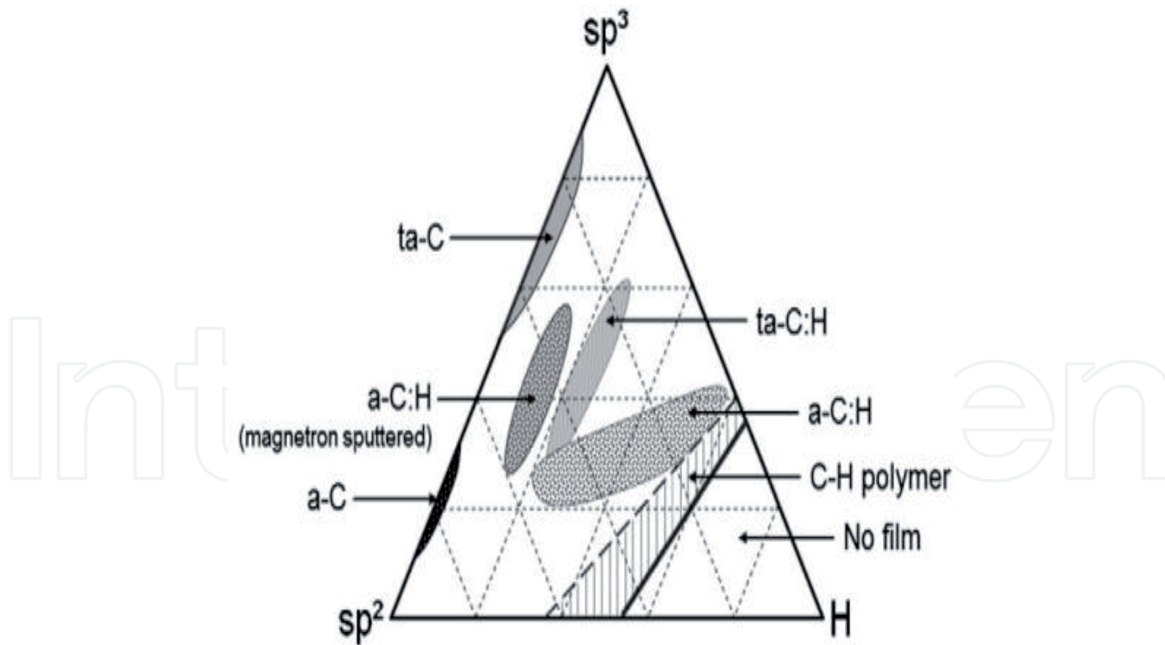


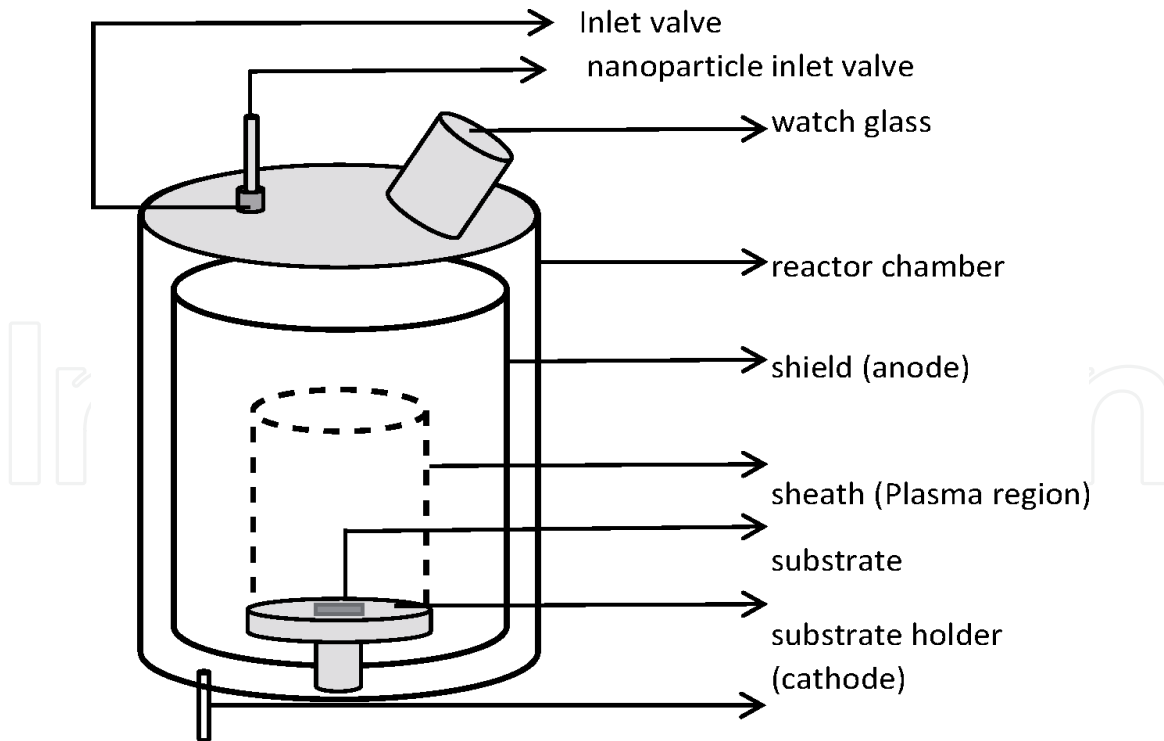
Figure 2.  
Classification of DLC coatings [5].



**Figure 3.**  
Ternary phase diagram for various forms of diamond-like carbon [5, 21].

$sp^2$  bonding is typical graphite, having a carbon molecule with one double bond to a second carbon atom or to another atom and two single bonds to another atom, leading to planar configuration. While,  $sp^3$  bonded carbon atoms have three single bonds leading to a tetrahedral configuration. Coating names are often abbreviated to ta-C (tetrahedral amorphous carbon) for coatings with very high (almost exclusively)  $sp^3$  content, a-C (amorphous carbon) for coatings with high  $sp^3$  content, between 40 and 80%, and a-C:H (amorphous carbon—hydrogenated) for samples with a greater amount of hydrogen, often coupled with an increase in  $sp^2$  [19]. PECVD technique is based on glow discharge processes supplying hydrogen gases such as acetylene ( $C_2H_2$ ), with a negatively biased substrate working at radio frequencies (13.56 MHz) or mid frequencies (10 to 100 KHZ). It is important to note that DLC coatings can be deposited at low substrate temperatures ( $<200^\circ C$ ). High power of ion acceleration (100 KHZ - 13.56 MHz), the low cost of equipment and growth of films are the advantages when using PECVD technique [20]. Radio frequency is the most common source of discharge for PECVD deposition [21]. However, some researchers found that using the PECVD technique with DC source pulsed, provides better results in terms of adherence, low friction coefficient, relatively reduced internal stress, high hardness and lower production cost when compared to RF-PECVD techniques [22].

PECVD deposition technique is based on the growth of DLC films using cold plasma, which is characterized by a lack of thermodynamic equilibrium, the ion temperature is lower than the electron temperature. Thus, the kinetic energy (as a result of the temperature) of electrons is much higher than that of ions. The plasma, has a degree ionization in which the gas consists mainly of neutral species excited. The deposition chamber in the PECVD reactor has two electrodes of different areas. The cathode (smallest area) is connected to a current source (Pulsed DC or radio frequency), and the potential difference is applied to it, or polarization voltage. The anode (biggest area) is made up of the walls of the chamber, or by a plate parallel to the cathode, and is grounded. A representation schematic can be seen in **Figure 4**. Before deposition begins, evacuation from the chamber is carried out, a gas is introduced and becomes the medium in the discharge which is initiated and sustained through the current source [22]. The electrons acquire and lose energy



**Figure 4.**  
*Schematic for pulsed-DC PECVD with nanoparticle inoculation chamber.*

quickly in a sequence of collisions, until they acquire enough energy to ionize (decouple) the gas molecules and produce secondary electrons by impact reactions. As plasma stabilization takes place, electrons are lost in the walls and in electrodes, and the flow is maintained through reactions with secondary electrons and the impact of positive ions on the electrodes. During the stable phase of the plasma, the number of electrons generated and lost is in balance and its stability is directly related to pressure, which influences the free path medium. Plasma being generated by a process of collisions between electrons free accelerated by the electric field and the atoms/molecules of the atmosphere precursor, the basic deposition mechanism involves the creation of species reactive substances such as electrons, ions, molecules, neutral and ionized radicals, causing new ionizations. These reactive species, activated by the discharge, tend to interact with the surface, chemically adsorbing and forming film [22].

The PECVD technique from a pulsed DC source consists of a discharge in low pressure plasma using a pulsed switched source for the plasma generation [23, 24]. Through this technique, different films type (a-C: H and ta-C: H) can be obtained. The structure of the films obtained is composed of the  $sp^2$  hybridization clusters inter-connected by carbons with  $sp^3$  hybridization. Several mechanisms are involved in the deposition of films a-C: H, and the strong dependence on the properties of a-C: H films deposited by PECVD with the polarization voltage (bias-voltage) and the bombardment ions, indicate that the latter have a fundamental role in the deposition of films [25], which makes it necessary to description of the physical process of ionic sub-implantation.

### 2.3 Application of DLC coatings on automobile engine components

Using DLC as coatings for automobile engine parts can assist to reduce friction and wear, which cannot be achieved by the use of lubricants alone, ensuring an improvement in engine performance and transmission components [26]. Lawes et al. [4] reported diamond-like carbon coatings to have assisted in reduction of

fuel consumption (total annual global fuel consumption reduced from 631,109 to 400,109 l/a.) in automobile engines by reducing friction loss due to its self-lubricating properties, chemical stability and weight reduction. The excellent tribological properties (low friction, wear resistance, corrosion resistance, high hardness and chemical stability) of DLC, since their discovery in 1971 has made them widely used in the automotive industry. Different types of DLC films vary in mechanical, physical and tribological properties which is usually determined by their sp<sup>3</sup> and sp<sup>2</sup> contents in the DLC coating [27, 28]. The mechanical and tribological properties have been analyzed by nano-indentation, scratch, wear and friction testing of an instrumented cam-tappet testing rig to study the tribological properties of DLC coatings for engine applications [15, 16, 29]. Success has been recorded over recent years with the application of DLC coatings to a number of automotive engine components (piston, tappet, camshaft, piston rings, gudgeon pin, valve stem and head, and rocker arm) [4, 16]. DLC coatings applied to automobile parts possess thickness ranging between 1 and 4 μm [4]. DLC coatings in engines needs careful selection of required surface finishing, mechanical properties, and tribological behavior of the coatings with engine oils [4]. The coatings hardness and stiffness are needed to determine the wear resistance of coatings, while friction is controlled by hardness, topography of the surface and tribo-chemical interactions of the dopants with the DLC coatings [4].

## **2.4 Tribological and mechanical properties of DLC films**

High hardness, wear resistance and low friction coefficient are significant for tribological-mechanical properties of the DLC, for a wide range of applications in tribo-systems [30]. Different types of industries (aerospace, automobile, bio-medical, mechanical and electronics) have used DLC films, with the intension of increasing the useful life of components and performance of mechanical systems. It can be used as a solid lubricant in environments in which liquid lubrications are not needed, such as in the space environment, food industries and clean environments, conditions of contact with high mechanical loading. Thus, the investigation of the correlation between specific tribological properties of the DLC and working conditions, such as contact pressure, sliding speed, rolling condition, lubrication condition, are very important, and can provide useful information that can aid in predicting tribological behavior of DLC coatings applied to certain machine elements [30].

### *2.4.1 Adhesion*

Adherence is work necessary to separate atoms or molecules at the interface [30]. DLC films are usually faces difficulty with adhesion, due to the high internal compressive stress, accompanies with the growth of the films. This directly interferes with the adhesion between film and metallic substrate, causing detachment of the film [31]. The total tension of the films after the formation and deposition corresponds to a sum of stress effects thermal and intrinsic tension. The thermal stress arises from the difference between the coefficient of thermal expansion of both film and substrate materials, while the intrinsic stress is attributed to the cumulative effect of failures that appear internally in the film during the formation processes [32]. Several methods have been used to decrease internal tension and increase the adhesion of the DLC film on metallic substrates. One of these methods consists of insertion of doping elements such as Ti, Cr, W, N, B and Si, to avoid diffusion of carbon into the metallic substrate, the doping elements form carbides, reducing the total tension in the doped films of DLC [33]. The deposition of DLC films

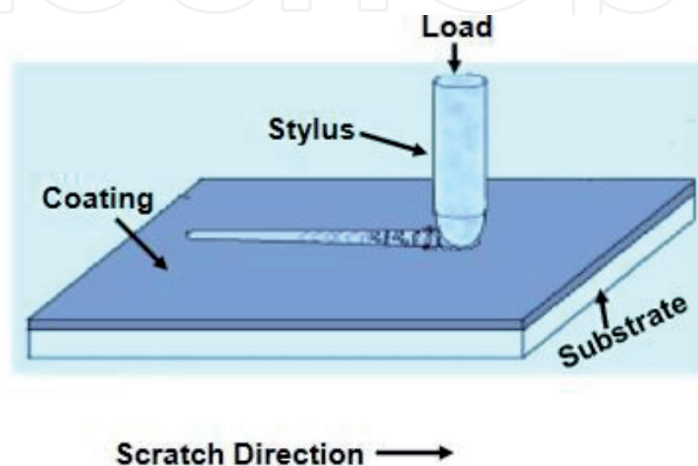
with silicon interlayers using the PECVD Pulsed DC technique has been found to improve adhesion with low coefficient of friction, and lower internal stress which is as a result of interfacial and structural mismatch between the coating and the substrate [21]. Several techniques are used in an attempt to measure film adhesion such as scratch tests or sclerometry (scratch test), scraping test, bending test, impact, cavitation and Rockwell impression [34]. **Figure 5** displays a schematic representation of the scratch test, and the tracks obtained in a test with constant load and with progressive load. The test of sclerometry is a semi-quantitative method that consists of streaking the sample using an indenter, usually diamond. This test allows the determination of properties such as hardness, roughness and specific energy [35].

#### 2.4.2 Wear resistance

Wear is the progressive loss of material from a solid body due to mechanical action (contact and movement of a solid body against a solid, liquid or gaseous body) [36, 37]. In analyzing the wear resistance of DLC films, the hardness of the film or the surface is the first correlation to be made (wear coefficient is inversely proportional to hardness) [36, 37]. The hardness of the film is dependent on the structure and will be higher, with higher concentration of the  $sp^3$  bonds. The wear on DLC coatings is due to two mechanisms namely: friction wear, (related to surface roughness); and wear through transfer of layers through the formation of a tribo-film (transfer layer) induced by contact pressure, which is responsible for decreasing the friction coefficient [20]. The hardness and roughness of the substrate are also factors that affect the wear of the DLC. On low hardness substrates, high plastic deformations occur, so that the film becomes fragile, causing it to break. Schematic of wear configuration (a) pin on disk (b) ball on disk is shown in **Figure 6**.

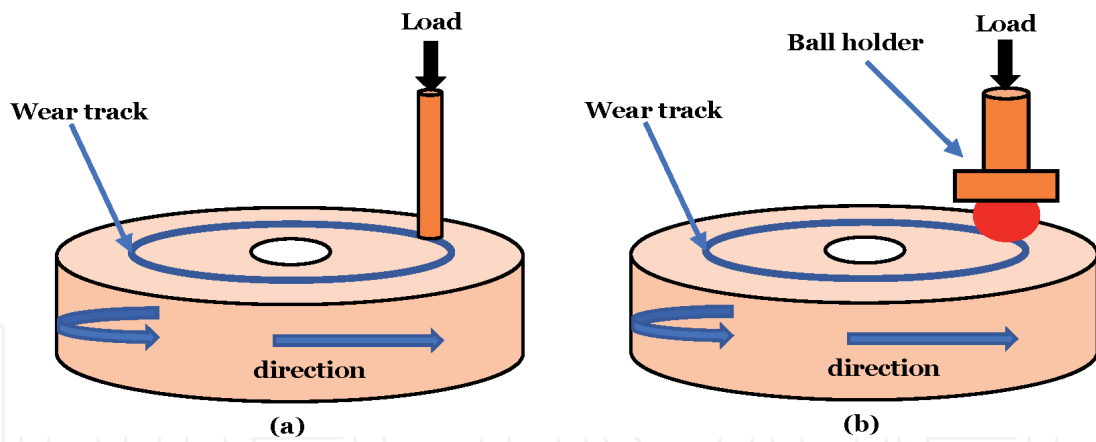
#### 2.5 Effect of annealing temperature on the thermal stability of DLC coatings

DLC coatings are commonly known for their high internal stresses, which affects their tribological properties and thermal stability. Annealing is mostly used to reduce the internal stress in DLC coatings. Annealing up to  $800^\circ\text{C}$  for ta-C is possible and reduces internal stress to an insignificant value (**Figure 7**), while annealing a-C above  $500^\circ\text{C}$  reduces the thermal stability. During annealing a cluster of  $sp^2$  bonded carbon atoms will occur, which does not affect the  $sp^3$  content [38, 39]. This may change some of the physical properties, such as optical gap, electrical resistivity, and reduce the compressive stress [38]. At higher temperatures graphitization ( $sp^3$  to

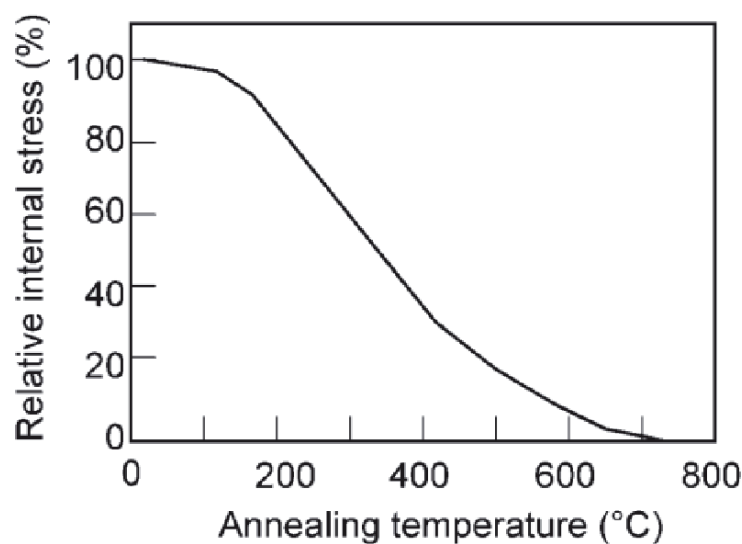


**Figure 5.**  
Schematic representation of the scratch test.





**Figure 6.** Schematic of wear configuration (a) pin on disk (b) ball on disk.



**Figure 7.** Relative internal stress against annealing temperature for ta-C coatings [6].

$sp^2$  transformation) begins, leading to a softer coating which will easily delaminate. Different amorphous DLC films deposited by different deposition methods possess different  $sp^3$  fraction at different graphitization temperature [40].

It has been reported that ta-C hardness does not reduce until about 600°C under vacuum condition [41]. The thin film thickness (nm) remain stable under vacuum condition till 400°C having little graphitization [42]. An investigation of thin films (1.5 nm) revealed changes in the Raman peak position and ID/IG of samples annealed at 300°C for 60 minutes are not due to graphitization. Ta-C film annealed at 300°C has more  $sp^2$  clustering and no reduction in  $sp^3$  content [40]. The starting temperature of oxidation for a-C and ta-C films varied based on structure and the oxidation behavior is strongly affected by the  $sp^3$  content, for a-C and ta-C films [43]. DLC has been known in the past for their poor thermal stability above 500°C, where  $sp^3$  (diamond-like) structure begins to transform to  $sp^2$  (graphitic-like) structure, thereby making the coatings softer. At about the same temperature the loss of coating thickness is above 100 nm, this implies a reduction in coating thickness as the temperature increases. Normally, breakdown and structural collapse of DLC coatings occurs at high temperature above 500°C, which may be attributed to breaking of C–H bonds. Leading to the C–C networks becoming more graphite-like to facilitate the formation of volatile C–O and metal oxide phases. Micro-wear of DLC film occurs as the annealing temperature increases above 200°C, as a result of

mechanical stress and thermal degradation of DLC as reported by Lee et al. [44]. Whenever there is a transformation to  $sp^2$  the mechanical strength degrades significantly, which consequently leads to critical failure or engine parts malfunction.

## 2.6 Modified DLC films by incorporation of additional elements

Modified or doped DLC films according to VDI 2840 standard [45] are denoted as a-C:H:X where X represents non-metallic elements, while, a-C:H:Me where Me represents metallic elements. Until recently, the incorporation of various nanoparticles into DLC has been also used to improve the adhesion properties of DLC by producing nano-clusters that are carbides. In the mid-1970s and 1980s various researchers reported silicon containing a-C:H:Si films deposited using glow discharge decomposition of silane ( $SiH_4$ ) and hydrocarbon gases (acetylene and methane) and also using d.c. magnetron sputtering [5]. Generally, both a-C:H:X and a-C:H:Me improve mechanical and tribological properties of coatings due to reduction in the residual stress. Increasing the non-metallic or metallic contents in a-C:H, increases the temperature at which structural transformation will occur for films deposited using r.f. PECVD by increasing the  $sp^3$  bonded carbon stabilizing the carbon network, leading to a reduction in graphitization. Hardness and friction coefficients remained nearly constant even after annealing at 500°C in air, whereas, a-C:H coatings failed at 400°C [5].

### 2.6.1 Metal and non-metal doped DLC coatings for automobile application

Metal-doped DLC (Me-DLC) coatings usually exhibit higher thermal stability than non-doped DLC up to 500°C, which was revealed by X-ray diffraction, transmission electron microscopy, and Raman spectroscopy. Annealing temperature above 500°C, losing high amount of hydrogen from the Me-DLC coatings, causing breakdown and structural collapse of the coatings at high temperature [46]. Non-doped DLC coating has low resistance to wear in lubricating oils containing Molybdenum Dithiocarbamates (MoDTC), this is because of the decomposition and chemical reactivity leading to the formation of oxides and nano-crystallites [47]. Si-doped DLC coating produces anti-wear film, which is usually stronger when the lubricant contains additives. Raman spectroscopy was used to analyze the tribo-chemical activity of the DLC coatings lubricants with additives. DLC coatings has been used for gear teeth with a coating thickness (1  $\mu m$ ) and deposition temperature (200°C), needing no additional surface finishing [48, 49]. The appropriate method to determine thermal stability of DLC at high temperature is the use of tribological testing equipment such as an Optimol SRV® v4 device which will determine the wear rates and coefficient of friction at high temperature range. Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and nano-scratch experiments can further be used to investigate the mechanism that affect the thermal stability of DLC during their use in internal combustion engines. It is important to note that the Optimol SRV® v4 device can operate between 25 and 900°C.

DLC doped with non-metals (hydrogen, boron, nitrogen, phosphorus, fluorine and sulfur) or metals (copper, nickel, tungsten, titanium, molybdenum, silicon, chromium and niobium) [50] has brought improvement in the thermal stability of DLC coated engine parts. The use of silicon to doped DLC comprising amorphous nano-composites can enhance the thermal stability of DLC. However, a reduction in film thickness occurs at high annealing temperature. Metal-doped DLC creates a two-dimensional array of metallic nano-crystalline clusters and metallic carbides precipitates embedded in an amorphous carbon matrix and reduces surface tension. The use of metal doped DLC helps in stabilizing DLC at high temperatures by delaying graphitization when metallic carbides precipitates are formed [51].

Tungsten and Molybdenum are most commonly used DLC dopant for coating automobile engine parts for improving thermal stability.

#### *2.6.1.1 Tungsten and molybdenum doped DLC coatings*

Tungsten and molybdenum have been reported to have been used to doped DLC films in order to reduce friction and wear rate during high temperature [52, 53]. It is important to note the both tungsten and molybdenum will form carbide precipitates when doped with diamond-like carbon coatings [51, 53]. A study of the tribological behavior of DLC-W on Aluminum alloy has been carried out under lubricated condition showed low COF (0.11) and wear rate ( $0.51 \times 10^{-5} \text{ mm}^3/\text{Nm}$ ), which was due to the presence of tungsten disulphide ( $\text{WS}_2$ ) [54]. DLC-W has been observed to possess variation of resistance against strain sensitivity which was due to deformation of metallic nano-size clusters when a strain is applied enabling its application as a smart material [55].  $\text{WC}_x$  is the general chemical composition in which tungsten carbide can exist in DLC doped with tungsten [56]. DLC-W also plays an important role in multi-layer DLC composites by reduction of residual stress and improving adhesion to metallic substrate [57]. It has been noted that DLC-W exhibit tribo-chemical interaction when in contact with lubricants which improves wear resistance and ultra-low friction [16, 51]. The tribological behavior for both room temperature and high temperature (120 and 150) °C were compared for DLC-W [57, 58]. Evaristo et al. [58] observed the presence of tribo-layer on the contact body consisting mainly of W-C, C and W-O acting against the surface of the coatings. However, when dealing with lubricants  $\text{WS}_2$  is likely to be formed which serves as tribo-film.

Mo doping of DLC increases the  $\text{sp}^2$  carbon content leading to a decrease in the hardness and elastic modulus of DLC-Mo coatings compared with DLC coatings [59]. MoC nanoparticles embedded in the cross-linked amorphous carbon matrix was responsible for the reduction of loss in hardness and elastic modulus [59]. An increase in Mo content increases the surface roughness and decreases the residual stress of the DLC coatings [60]. 3.8% at Mo was reported as the optimum amount for improved mechanical properties [49, 61]. The tribological and mechanical properties of tungsten or molybdenum containing DLC coatings have high hardness, high elasticity and low surface energy, which causes a high hardness to elasticity ratio (H/E) and a low surface energy to hardness ratio (S/H) [52]. Consequently, leading to better adhesion properties, high wear resistance, low friction coefficient and low residual stress of the DLC-W and DLC-Mo [53, 62, 63]. Tribological properties of DLC coatings sometimes maybe affected by adhesion promoter (interlayer), substrate roughness, hydrogen incorporation and coating deposition parameters such as bias voltage (750v), etching, current (1.5A), precursor gas ( $\text{C}_2\text{H}_2/\text{CH}_4/\text{SiH}_4/\text{Ar}$ ), pressure (2.3 mTorr), time (2 hours) and substrate temperature (200°C) [2]. Service condition such as temperature, sliding speed, load, relative humidity, counter surface and lubrication affects the tribology of DLC-coated parts. As the temperature in the combustion engine increases above 200°C the DLC coatings begin to undergo transformational changes from  $\text{sp}^3$  carbon bond to  $\text{sp}^2$  carbon bond, making the DLC coating softer to resist hardness and wear, therefore increasing the COF. Although there has been success in the application of DLC coatings for mass production of engine components [48].

### **3. Present and future DLC coatings**

Generally, the DLCs coatings thickness is very important to aid in resistance against wear, which further affects the coating life span. All coatings will eventually

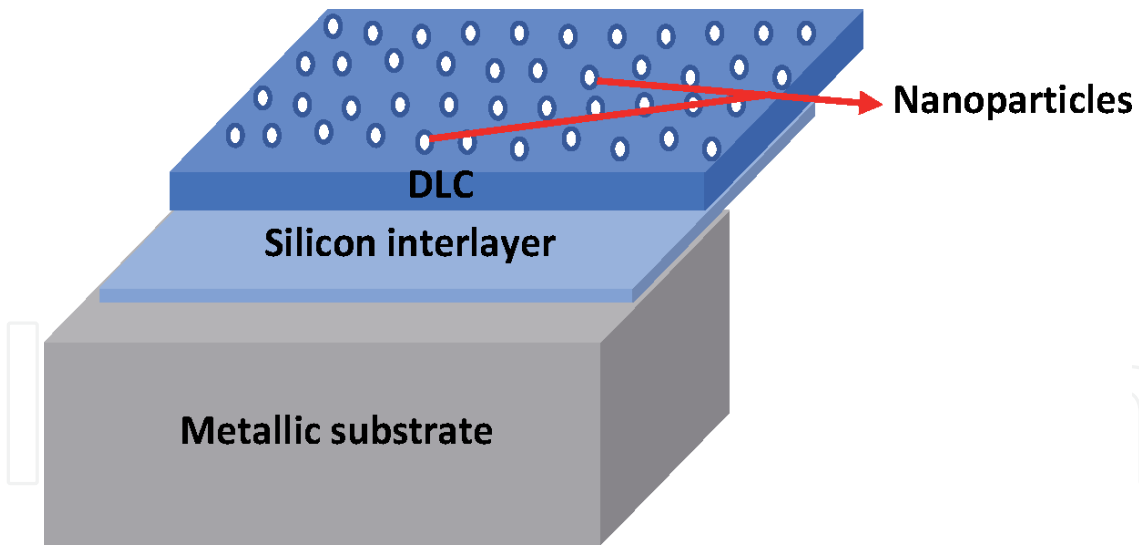
wear out due to their exposure to harsh working conditions. Erdemir [64] mentioned that the next generation of hard coatings that can generate their own tribofilms (catalytic coating) in a self-healing or continuous manner will be a big step. If engine blocks can be made from lighter materials the efficiency can be improved, coatings can play a major role in enabling such to work out. The ability to self-generate a DLC film *in situ* during engine operation is possible [64].

### 3.1 Nanoparticles incorporated DLC coatings

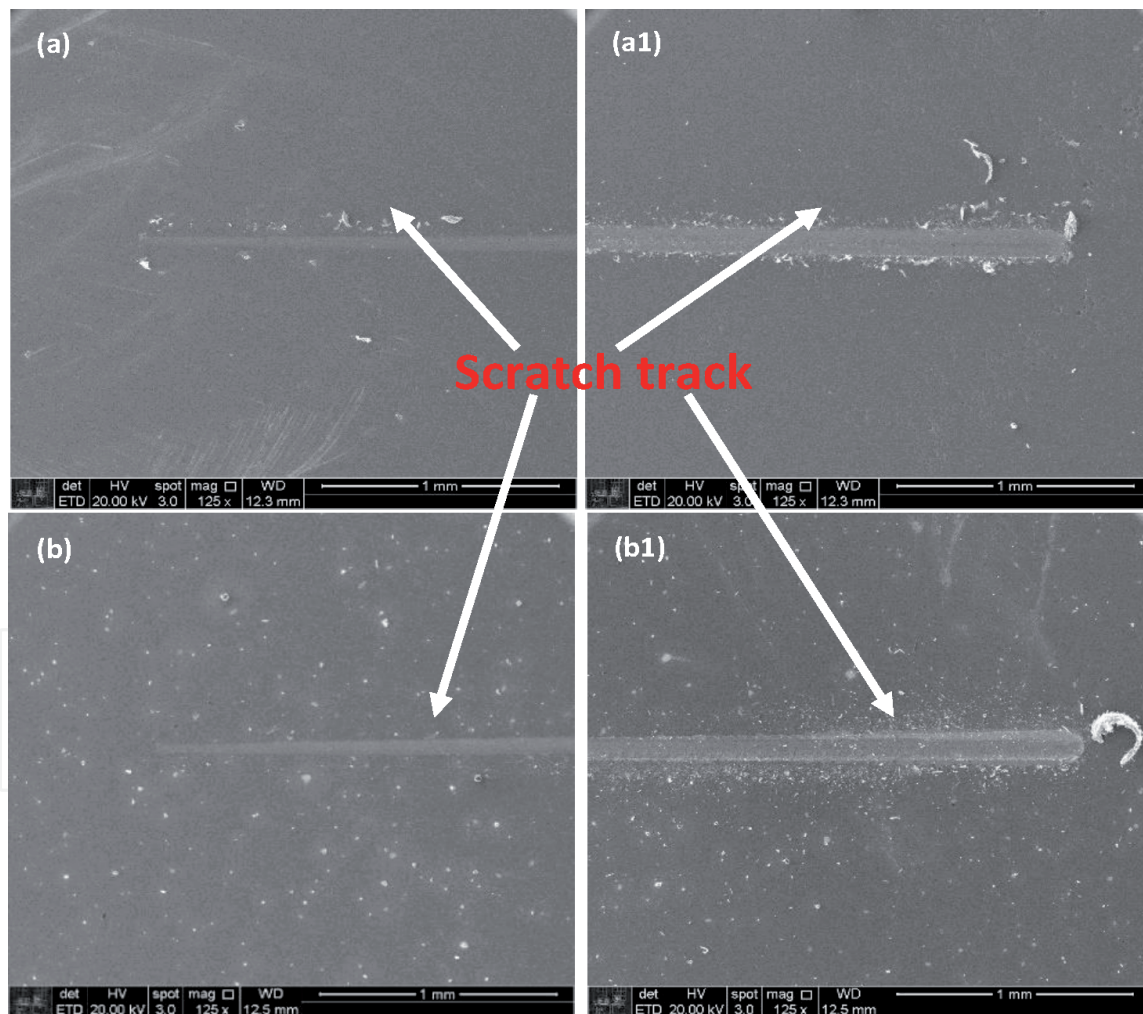
Metal ion can be incorporated into DLC coatings in a controlled manner for relevant laboratory experimental study and industrial use [65]. This also means that metallic nanoparticles can also be incorporated into DLC films, uniform dispersion of nanoparticles into the DLC film is of significant importance [7, 66]. Hexane and isopropanol solution have recently reported to be used to dissolve nanoparticles for DLC incorporation [8]. Using this technique, it is possible to achieve various types of DLCs incorporated with different nanoparticles for different applications ranging from biomedical, electronics, mechanical and automobile engine. TiO<sub>2</sub> nanoparticles incorporated DLC has been reported to increase bacteria activity interaction on DLC surfaces. While, Ag nanoparticles incorporated DLC is known for the increase in wear resistance it provides for DLC [8]. Tungsten trioxide nanocrystalline-containing DLC (WO<sub>3</sub>/DLC) has been deposited using one-step electrodeposition technique at atmospheric pressure, which was fabricated for electrical and wetting properties application. The technique makes use of an electrolytic system, a negative electrode (silicon wafer substrate) and positive electrode (platinum plate). The distance between the two electrodes was about 8 mm. Analytical pure methanol (99.5%) was used as carbon source and the concentration of tungsten carbonyl which used as an incorporated reagent was 0.2 mg/ml. The films deposition was carried out under an applied voltage of 1200 V and ambient temperature of 55 ± 2°C for 8 h [11]. Recently, tungsten trioxide (WO<sub>3</sub>) and molybdenum trioxide (MoO<sub>3</sub>) nanoparticles (DLC nanocomposite coatings) has been incorporated into DLC by first uniformly dispersing these nanoparticles into isopropanol solution and incorporated into DLC coatings deposited on a tappet valve (metallic substrate) deposition parameters for DLC-MoO<sub>3</sub> and DLC-WO<sub>3</sub> coatings is shown in **Table 1** [12, 13]. This tungsten trioxide (WO<sub>3</sub>) and molybdenum trioxide (MoO<sub>3</sub>) nanoparticles incorporated DLC coatings (DLC-WO<sub>3</sub>/DLC-MoO<sub>3</sub>) has showed improved adhesion and tribological properties having a COF of 0.075 and 0.070 for DLC-WO<sub>3</sub>/DLC-MoO<sub>3</sub> respectively [12, 13]. These coatings with its excellence adhesion and tribological properties is a novel fabricated diamond-like carbon coatings incorporated with nanoparticles using PECVD for automobile applications. The schematic is represented in **Figure 8** below.

| Precursor  | Pressure (Torr)        | Time (min) | Flow rates (sccm) | Bias (-V) |
|--|------------------------|------------|-------------------|-----------|
| Ar   | 2.3 x 10 <sup>-3</sup> | 30         | 8                 | 600       |
| Ar + SiH <sub>4</sub>  | 4.1 x 10 <sup>-3</sup> | 20         | 3.5               | 700       |
| Ar + C <sub>2</sub> H <sub>2</sub>   | 3.3 x 10 <sup>-3</sup> | 5          | 10                | 700       |
| Ar + C <sub>2</sub> H <sub>2</sub> + MoO <sub>3</sub> /WO <sub>3</sub> nanoparticles | 3.6 x 10 <sup>-3</sup> | 55         | 10                | 700       |

**Table 1.**  
 Processing parameters for deposition of DLC-MoO<sub>3</sub> and DLC-WO<sub>3</sub>.



**Figure 8.**  
Schematic of DLC incorporated nanoparticles (DLC nanocomposite coatings).



**Figure 9.**  
SEM images of scratch track (a)-(a1) DLC-MoO<sub>3</sub> (b)-(b1) DLC-WO<sub>3</sub>.

Nanoparticles (WO<sub>3</sub> or MoO<sub>3</sub>) with a higher specific surface would adsorb great amount of cation ions. Under the effect of high electric field, the migration of the cation ions toward to the cathodic substrate with the abundance of electron occurred, resulting in the growth of nc-WO<sub>3</sub> or nc-MoO<sub>3</sub> doped nanocomposite film. **Figure 9** shows the scratch track of DLC-MoO<sub>3</sub> and DLC-WO<sub>3</sub> coatings.

$m\text{CH}_3^+ + n(\text{WO}_3/\text{MoO}_3) + m\text{e}^- \rightarrow n\text{c}-(\text{WO}_3/\text{MoO}_3)$  doped DLC nanocomposite film.

### 3.2 Self-healing DLC

The coating with the ability of self-healing itself could be the solution for extending the life of engine components and subsystems. Researchers at the Argonne National Laboratory have developed a self-renewing hard and slick coating for metal parts that has the potential to revolutionize friction and wear protection [64]. The nanocomposite coating uses metal alloys including copper, nickel, palladium and platinum, which are catalytically active at the temperatures at which coatings are used in engines [64]. Structurally, the tribo-film formed during the use of the coatings is similar to diamond-like carbon, which already provides lower friction than industry-standard tribo-film. The DLC coatings interaction with oil molecules makes the DLC film to adhere to metallic substrate. However, in this new technology, when the tribo-film is worn away the catalyst is re-exposed to the lubricant, kick-starting catalysis and developing new layers of tribo-film. Ali Erdemir [64] mention that it might enable additives engine lubricants to provide not only the fluid film, but also the solid boundary film lubrication in a self-healing manner.

## 4. Conclusion

In this chapter the need for DLC coatings for automobile engine applications has been discussed, the importance of using PECVD technique to deposit DLC coatings has been discussed, together with their mechanical and tribological properties. The thermal stability of DLC coatings was also discussed and with improvement with non-metallic/metallic doping of DLC coatings. Discussion on the recent incorporation of Ag, TiO<sub>2</sub>, WO<sub>3</sub> and MoO<sub>3</sub> nanoparticles into DLC. The novel fabrication of diamond-like carbon coatings incorporated nanoparticles (WO<sub>3</sub>/MoO<sub>3</sub>) using PECVD for automobile applications has shown an improvement in the adhesion properties of the DLC coatings, which will in turn improve the wear resistance of the DLC-WO<sub>3</sub>/DLC-MoO<sub>3</sub> coatings.

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