Characterization and applications of diamond-like nanocomposites: a brief review

Kalyan Adhikary1, Sayan Das1,2, Debasish De1, Anup Mondal2,3, Utpal Gangopadhyay1,
Sukhendu Jana1,3,*

1 Center for Advanced Research in Renewable Energy and Sensor Technology, Meghnad Saha Institute of Technology, Kolkata- 700150, India.
2 Dept. of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur; India.
3 Centre of Excellence for Green Energy and Sensor System, Indian Institute of Engineering Science and Technology, Shibpur, India

ABSTRACT

Diamond-like Nanocomposites (DLN) is a newly member in amorphous carbon (a:C) family. It consists of two or more interpenetrated atomic scale network structure. The amorphous silicon oxide (α:SiO) is incorporated within diamond-like carbon (DLC) matrix i.e. a:CH and both the network is interpenetrated by Si-C bond. Hence, the internal stress of deposited DLN film decreases remarkably compare to DLC. The diamond like properties has come due to deform tetrahedral carbon with sp3 configuration and high ratio of sp3 to sp2 bond. The DLN has excellent mechanical, electrical, optical and tribological properties. Those the properties of DLN could be varied over a wide range by changing deposition parameters, precursor and even post deposition treatment also. The range of properties are: Resistivity 10-4 to 1014 Ωcm, hardness 10-22 GPa, coefficient of friction 0.03-0.2, wear factor 0.2-0.4 10-7mm^3/Nm, transmission Vis-far IR, modulus of elasticity 150-200 GPa, residual stress 200-300 Mpa, Dielectric constant 3-9 and maximum operating temperature 600ºC in oxygen environment and 1200ºC in O2 free air. Generally, the PECVD method is used to synthesis the DLN film. The most common procedures used for investigation of structure and composition of DLN films are Raman spectroscopy, Fourier transformed infrared spectroscopy (FTIR), HRTEM, FESEM and X-ray photo electron spectroscopy (XPS). Interest in the coating technology has been expressed by nearly every industrial segment including automotive, aerospace, chemical processing, marine, energy, personal care, office equipment, electronics, biomedical and tool and die or in a single line from data to beer in all segment of life. In this review paper, characterization of Diamond-like Nanocomposites is discussed and subsequently different application areas are also elaborated.

Keywords: Amorphous carbon; DLC; DLN; PECVD.

1. Introduction

Carbon is a fascinating element in nature. It has so many allotropes with versatile properties. Diamond, graphite, graphene, carbon nanotube, fullerene, etc. are made by carbon atoms but different structures and bonding hence unique their properties. Diamond is a crystalline allotrope of carbon with unique properties. Diamond has highest hardness and thermal conductivity compared to any bulk material. These properties result from the strong covalent bonding within its atoms and crystal structure. However, diamond cannot be synthesized in room temperature and atmospheric pressure. To synthesize it in lab, same environment to be created as at the depth of 140 to 190 km in the Earth’s mantle. To overcome this problem, diamond like materials are developed which can be synthesized in lab environment and at the same time exhibits some properties closely resemblance with natural diamond. Diamond-like material’s chemical bonding i.e. mostly sp3 states complies with natural diamond. Due to this closeness in chemical bonding dia-
Diamond-like material shows close resemblance in case of chemical inertness, hardness, thermal stability, thermal conductivity etc. in comparison with natural diamond.

Diamond-like or graphite-like are the umbrella terms which refer to different forms of amorphous carbon that exhibit some of the unique properties of natural diamonds or graphite and that can be synthesized in the lab environment. Diamond-like carbon or DLC is an amorphous hydrogenated carbon which is a blend of sp^3 bonded carbon atoms into sp^2 bonded carbon clusters. In DLC atomic structure, hydrogen can be present with an atomic concentration ranges from 0% - 50%. DLC acronym was first used by Aisenberg and Chabo[1] who for the first time synthesized amorphous carbon films exhibiting some of the unique characteristics of natural diamond. Beauty of the DLC film is that, its properties can be tailored based on the concentration of sp^2 – sp^3 bonded carbon atoms and hydrogen concentration. Due to the room temperature deposition possibility, almost all materials those are compatible with vacuum environment can be coated with DLC films. Unique and tunable properties of DLC are: material hardness, low friction and high wear resistance, chemical inertness, optical transparency (visible light - infrared light), thermal conductivity, electrical resistivity, radiation resistance etc. Most of the present industrial applications of DLC films are protective coating but this application can be extended up to “data to beer storage”[2,3]. However, the major limitation of application of DLC is high internal stress leads to peel off from substrate. Moreover, its thermal stability is also very poor. Sp^3 bonds transform to sp^2 bond at around 300°C. Those the difficulties of DLC films could be controlled further by doping them with different chemical elements or compounds like silicon, oxygen, etc. Thus a new class of amorphous hydrogenated carbon is formed whose chemical bonding complies with crystalline diamond and wisely termed as Diamond-like nanocomposite or DLN.

DLN consists of two interpenetrating networks, one is atomic scale diamond like (carbon network), a-C:H, another is quartz like (silicon network), a-Si:O. In carbon network, mainly consist of sp^3 hybridization, i.e. diamond like bonds and chemically stabilized by “H” atoms. In silicon network, Si atoms are chemically stabilized by “O” atoms[4]. Due to the presence of Quartz like Oxygenated Silicon network (a-Si:O), it is found that DLN has good adhesion property compare to its predecessor DLC and hence it is suitable to coat almost any type of materials[5]. Due to the interpenetrating network of hydrogenated carbon and oxygenated silicon, the internal stress is reduced and thus DLN composite shows good tribological performance over its predecessor DLC.

DLN coating have been in existence since early 1990s. V.F. Dorfman first reported and synthesized this unique class of material[6]. Later on Bekaert Advanced Coating Technologies (formerly known as Advanced Refractories Technologies) and Russian and American scientists patented DLN coatings for various protective coatings applications[6-15]. Bekaert Advanced Coating Technologies, Belgium used plasma enhanced chemical vapor deposition (PECVD) method for growing such composite films. Chinese researchers have successfully used ion beam technology for growing DLN films[16]. South Korean researchers have reported thermally activated CVD process for growth of DLN films[17]. DLN coatings also have been used in micro-electromechanical systems (MEMS) applications like LIGA (German acronym for Lithographie, Galvaniformung und Abformung) structures[18]. Moreover Diamond-like carbon/nanosilica composite films have been deposited on silicon substrates, making use of the electrolysis of methanol–dimethylethoxydisilane (DDS) solution at low temperature[19]. DLN coating also have been used in many application[20]. DLN was deposited with same type of reactor, used by Bekaert Advanced Coating Technologies, Belgium by a research group to deposit the thin film over Co-Cr alloy based knee implant of complex shape[5].

Various researchers have recorded various unique characteristic of DLN thin film since its inception. Yang Won Jae et al[21], reported the relationship of I_D/I_G ratio with structural and mechanical properties of DLN thin film by varying bias voltage from -100V to -400V dc. The thermal stability of Diamond-like nano composite coating over a wide temperature range was investigated by Yang Won Jae et al[22]. The performance of DLN film from a tribological perspective was investigated by Venkatraman C et al[23]. The performance was satisfactory up to 400° C. Later, D. Neernick et al in one of their paper stated low-friction, low-wear combined with low internal stress and good adhesion of DLN coating make it suitable for tribological application[24]. Again D. Neernick et al reported low-friction and
low-wear behavior of Diamond-Like Nanocomposite coatings even in humid environments. They also reported that DLN film is suitable for industrial applications as hard, self-lubricating coatings on sliding parts in the automotive, chemical, pharmaceutical or biomedical industry[25]. Later, Bozhko A et al. showed non-ohmic effects in the electronic transport in tungsten and silicon containing diamond-like films[26] Sliding wire behavior of DLN was studied by Kester D J et al[27]. The dependence of Diamond-like atomic scale composite (DLASC) parameter on deposition conditions thermal and radiation treatment was studied and reported by Polyakov V I et al[28]. Scharf T W et al investigated the fundamental mechanisms of friction and interfacial shear strength in DLN coatings and the roles of contact stress and environment on their tribological behavior[29]. Roger J. Narayan reported Hydroxyapatite which is a bioactive ceramic that mimics the mineral composition of natural bones. Hydroxyapatite-diamond like carbon bilayer film is developed to improve adhesion and mechanical integrity. Thus Hydroxyapatite diamond-like carbon bilayer film serves as a good biomaterial for various orthopedic implants[30]. Bursikova Vilma et al recorded Laser ablation of Nitrogen-doped DLN thin layer using commercially available MALDI-TOF MS instrumentation and performed identification of ablated species from DLN materials[31]. Mechanical properties of diamond-like nanocomposite thin films on a non-conducting ceramic substrate, here silicon nitride were investigated by A. Pandit et al 2003 and hardness and modulus were measured by nanoindentation and subsequently interfacial toughness of this hard film brittle substrate system were determined by vicker indentation[32], C. Venkatraman et al deposited DLN films comprising of C, H, Si, O and metal atoms on metallized silicon substrates via an accelerated plasma approach. They concluded the tailorability of electrical and Diamond-like properties of DLN thina film make them suitable for application requiring both wear resistance and electrical tailorability[33]. T.W.Scharf et al 2003 reported the frictional behavior of amorphous diamond-like nanocomposite coatings in low speed, dry sliding contact using a home-built in-situ Raman tribometer[34]. Hauert R et al investigated on tailored tribological and biological behaviour of DLC[35]. Later, Mallouf R et al reported biocompatibility of DLC and DLN material and showed the application area of DLC and DLN as biosensors[36], Pollak F H et al showed unique surface and bulk properties of diamond-like atomic scale composite materials deposited on Si (001) substrate through atomic force microscopy investigation[37]. The superiority of DLC coating over different materials used in hip joint prostheses was investigated by Platon F et al[38]. D. Sheeja et al reported the tribological characteristic of surface modified UHMWPE against DLC coated Co-Cr-Mo. Coating both the sliding surfaces of UHMWPE and Co-Cr-Mo with DLC coating reduces the wear rates of the sliding surfaces to a noticable extent[39]. Kobayashi S et al showed the wear properties of DLC coated UHMWPE and PMMA and the result was satisfactory[40]. Later, Logothetidis S 2007 compared the Haemocompatibility property between amorphous carbon (a-C) and amorphous hydrogenated carbon (a-C:H). Amorphous hydrogenated carbon showed better result as Haemocompatible material and may be used as biocompatible coatings on biomedical implants[41].

DLN coating have excellent bulk and surface property as well as thermal stability. This can be used as tribological coatings, chemical protective coatings[23, 25,27,34] and abrasion resistant coatings. It has optical transparency over a wide bandwidth which includes visible light and infrared. Due to this reason, DLN coating is used as antireflection coating over the solar cell to enhance the overall efficiency of the system. Due to low residual stress DLN coating has excellent adhesion to variety of substrate materials[30,32]. Researchers at Department of Cardiology, University Hospitals Leuven, Belgium[42] reported the biocompatibility of DLN film resulting in decreased thrombogenicity and decreased neointimal hyperplasia. Awadesh Kr Mallik et al reported that deposition of DLN coating by PECVD method over different substrate used as load bearing orthopedic implant and the result was satisfactory[5].

Since its inception, DLN films are being received huge attention due to its attractive electrical mechanical optical and tribological properties such as reduced stress level, increased thermal stability, high hardness, low friction visible and infrared transparency etc. Dielectric permittivity and refractive index of DLN is lower than the DLC, whereas optical transparency is higher than the DLC films. In this paper depositions, structure, chemical composition as well as mechanical, optical, electrical, properties of DLN composite films are elaborated and industrial and prospective applications of DLN films are discussed.
2. Deposition method

Two types of thin film deposition methods are generally used, CVD and PVD. In CVD reactive gases interact with substrate. Generally it is used to deposit Si and dielectrics. Quality of the deposited film is good and this method has good step coverage. On the other hand PVD is used to deposit metals, purity of the deposited metal is high. But one disadvantage is that it requires line of sight operation. Various types of CVD are APCVD, LPCVD, PECVD and HDPCVD. Steps in CVD are:

- Transport reactants via forced convection to reaction region
- Transport reactants via diffusion to wafer surface
- Adsorb reactants on surface
- Surface processes: chemical decomposition, surface migration, site incorporation, etc.
- Desorption from surface
- Transport byproducts through boundary layer
- Transport byproducts away from deposition region

PVD is versatile deposition method, deposits almost any material. Substrate damage is less and very few chemical reactions are required. PVD undergoes some limitation like line of sight operation, shadowing, thickness uniformity and difficult to evaporates materials with low vapour pressure. It has two types, evaporation and sputtering.

3. DLN deposition method

PECVD is mostly used for deposition of DLN film over a substrate surface. PECVD reactor has five rotating substrate holder whose rotating speed can be controlled by a speed controller. Rotation of the substrate holder can be made in two mode, manual and automatic\(^5\). During substrate attachment on the substrate holder, manual rotation is provided to adjust the position between holder and the operator. Automatic rotation is generally provided during the deposition process. In our PECVD reactor, liquid precursor is feeded at the bottom of the vacuum chamber and due to the difference of pressure level between the reactor chamber and the ambience, precursor evaporates into vapour form. An inverted U-shaped tungsten filament is placed over the precursor outlet. Filament is kept at negative potential and it emits electrons which ionize the precursor vapour inside the reactor chamber. Precursor ions are pulled by negatively charged substrate holder where substrates are fixed. Thus precursor ions are finally deposited on the substrate surface and hence substrates are DLN coated. Prior to the coating process, inert gas Ar is introduced into the vacuum chamber to produce the plasma. These argon ions strike the substrate surface and clean the surface by ion etching process.

So, coating process includes the following mandatory steps:

- Ion etching of the substrate to reduce the chance of contamination and better adhesion of coated material over the substrate surface.
- Vapourization of material to be deposited
- Formation of radical of the material to be deposited
- Transportation of radicals towards the substrate surface
- Deposition/condensation of material onto the substrate surface

4. Precursors

DLN films can be synthesized using composite material of silicon and oxygen\(^43\). These precursors might be gaseous (Silane – (SiH\(_4\)) and oxygen (O\(_2\)) mix\(^44\), tetra methyle silane- TMS ((CH\(_3\))\(_3\)SiH and oxygen mix\(^45\) or liquids Hexamethyldisiloxane HMDSO (C\(_6\)H\(_{18}\)OSi\(_2\))\(^46-51\), or tetraethoxysilane (TEOS, (C\(_2\)H\(_5\)O)\(_4\)Si\(^52\), or tetraethylohsilicate-TEOS (Si\(_2\)H\(_4\)O\(_4\))\(^53,54,21\), hexa methyle disilane-HMDS (C\(_6\)H\(_{18}\)Si\(_2\))\(^55\) and mixed siloxane and silazane precursors. Liquid precursors are mostly used for their easy handling and various choices\(^17\). These carbon, silicon, oxygen or nitrogen containing precursors are mixed with hydrocarbon gas (CH\(_4\), C\(_2\)H\(_4\) etc) or inert gas Argon (Ar). This mixture are used to coat the substrate under vacuum condition. Silane gas is rarely used as DLN film due to its highly flammable nature and toxicity. So, instead SiH\(_4\), HMDSN, HMDSO are commonly used as precursor liquid now a days due to its less toxicity and flammability.
5. Structure and composition of DLN composite films:

Raman spectroscopy, Fourier Transformed Infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) are frequently used techniques to study the structure and chemical composition of synthesized DLN films. Combination of these techniques gives a overall information about the structure and composition of DLN thin films. XPS is a surface sensitive quantitative spectroscopic technique that measures the chemical composition, electronic states etc of the elements present on the surface of a film. It was found that DLN film consists of carbon, silicon, hydrogen and oxygen, yet it is not possible to determine the amount of hydrogen using XPS technique. Analyzing the position and shape of the peak obtained due to C, Si and O atom, one can draw the quantitative and comprehensive picture of chemical bonding (C-C, Si-C, O-C-O, Si-O) present in the DLN films[53].

Raman spectroscopy is a fast and non-destructive way to study amorphous carbon as it can reveal the information of clustering of sp² phase and orientation of sp² phase as well as the hydrogen content[56]. In Raman spectra, all carbons show common features in the (800-2000) cm⁻¹ region, G and D peaks lie at ~1560 cm⁻¹ and ~1360 cm⁻¹ respectively in visible excitation and T peak at ~1060 cm⁻¹ and visible only for UV excitation[56]. G peak is due to bond stretching of all pairs of sp² atoms in both rings and chains. D peak is due to the breathing modes of sp² atoms in the rings. T peak is due to the C-C sp³ vibration[53].

6. Properties:

6.1 Mechanical Properties

In DLN film, hydrogenated carbon and oxygenated silicon are penetrating to each other in the microstructure of the film. Thus internal stress substantially is lower in the DLN material[55]. Stress of DLN film deposited using HMDSO precursor vapour by ICP PECVD was ~1.5 GPa compared to 11 GPa stress of DLC films diposited using CH₃ gas. Stress can be further decreased by increasing the Si atomic concentration[55]. Hardness and Young modulus are decreased in DLN film in comparison with DLC film[22][45][46][53][54][58][99].

6.2 Coefficient of friction and wear resistance

Study reveals that Coefficient of friction of DLN films was lower than DLC films. Coefficient of friction of DLN films does not depend monotonically with chemical composition[24]. Lowest and highest reported coefficient of friction ranges were reported as 0.04-0.08 and 0.1-0.2 respectively. Friction coefficient depends upon substrate bias[53]. Friction of coefficient <0.05 was reported when substrate bias was in between -100V to -200V and coefficient of friction increased >2 times with increase of substrate bias up to -500V.

It is already reported that, wear resistance of DLN with impurity like SiO₂ is 15-20 times lower than the wear resistance of DLC film[58]. It has been also reported[5] that wear resistance of DLN film is in the range of 0.2 -0.4 compared to wear factor of DLC film 0.5-1. Wear resistance is further decreased with increased concentration of Si and O[24]. In general DLN film has lower residual stress, lower coefficient of friction in dry as well as humid atmospheres. Deposition parameter must be chosen carefully to fabricate DLN films with desired level of hardness, Young’s modulus and wear resistance.

6.3 Optical Properties:

In amorphous hydrogenated carbon (a-C:H), there is a coexistence of sp² and sp³ carbon atoms. So, it has both π and σ electrons. Optical properties of amorphous carbon is determined by π-π* and σ-σ* electronic transitions, along with π-σ* and σ-π* transitions[60]. Optical properties are characterized by optical band gap E_g (Tauc gap), energy E_0 and Urbach energy E_U. Incorporation Si, O atoms in amorphous carbon (a-C:H) causes change in optical properties like optical band gap and refractive index in the DLN films (a-C:H; a-Si:H), it is reported that increase in optical band gap causes increase in optical transparency,[66,62,63].

d. Electrical Properties:

Dielectric constat depends upon different substrates used for deposition of DLN films (Ti, Si, Al, Cr). Such dependence is due to different structure of the films as well as different roughness of the used substrates[64]. Experiment reveals that DLN film has good dielectric properties. DLN films are used as an insulating material in a MIM (Metal-insulator-metal) capacitor and shows good results[65].

Result based on the experiments made by Awadesh Kr Mallik et al[5] are tabulated below:
<table>
<thead>
<tr>
<th>Property</th>
<th>Range of obtainable values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-efficient of friction</td>
<td>0.03-0.2</td>
</tr>
<tr>
<td>Adhesion</td>
<td>107-109 N/m², Adhere to a wide range of substrates including metals, plastics and ceramics; no interlayers required</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Stable to 400-600 °C in air; capable of 1000-1200 °C in absence of oxygen</td>
</tr>
<tr>
<td>Physical flexibility</td>
<td>Very flexible; does not crack when bent</td>
</tr>
<tr>
<td>Corrosion and erosion</td>
<td>Resistant to acids, alkalis and particulates due to pore free structure</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>Undoped: $10^{12}$-$10^{14}$ Ohm cm, Metal doped: up to $10^4$ Ohm cm</td>
</tr>
<tr>
<td>Hardness</td>
<td>10-22 Gpa</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>150-200 Gpa</td>
</tr>
<tr>
<td>Residual stress</td>
<td>200-300 Mpa</td>
</tr>
<tr>
<td>Transmission</td>
<td>70-80% at 05-20 microns</td>
</tr>
</tbody>
</table>

7. Applications

In DLN, two microstructures (hydrogenated carbon and oxygenated Silicon) are interpenetrating two each other and thus internal stress is decreased and adhesion property is increased and hence this composite has improved adhesion to almost all kind of substrate. It has huge application in the field of biomedical implants. This can be used as biomedical sensors as well. DLC coatings can be used as protective wear resistant coating in joint prostheses. Awadesh Kr et al already deposited DLC coatings by PECVD method over various substrate like SS 316 L, glass, Si(100), ceramic(Al₂O₃) ultra-high molecular weight polyethylene (UHMWPE), Co–Cr alloy, Ti6Al4V alloy, etc. Most of these materials have been in use as load-bearing orthopedic implants, like hip joint, knee joint, etc. As its coefficient of friction is very less, DLN films can be used as wear resistant coating. As it is anticorrosive, this composite can be used as anti-corrosive coating on wrist watches, brass made show pieces etc to enhance their longevity. Mechanical properties of DLN material along with the low refractive index and higher transparency compared with other thin film material makes DLN an attractive option for choosing DLN as a protective coating. T.S. Santra et al reported DLN films have their unique number of structural, mechanical and tribological properties which are quite similar with MEMS material. Due to these unique properties of DLN films, these are suitable for MEMS/NEMS devices manufacturing. The high mechanical properties of DLN films make it applicable for design of high frequency resonator and comb derivar for sensing and actuating applications. DLN film is a biocompatible material. So, we can use DLN films for detection of bio-molecules in biological research and disease diagnosis. Due to its infrared transparency, this can be used as anti-reflective coating on solar cell, glass etc. Sukhendu Jana et al reported diamond-like nanocomposite film behaves as a dielectric medium. DLN thin film based MIM capacitor is applicable for high capacitance and high frequency operation. Thus DLN thin film MIM capacitor has great potential for use in electrical/ electronic circuit. It has already been reported that DLC are used for optical wave guiding sensing systems, transistors and high temperature sensing up to 600 °C. As DLN is a improved version of DLC, there is a possibility to use DLN for the same purpose. Diamond film grown on p-Si substrates using MWPECVD technique may be used as antenna for harsh environment in aviation application. So, in DLN, the highest physical limits of mechanical, electronic and “sensor” properties can be combined and thus smart future material can be constructed. The DLN film has been applied on silicon solar cell as antireflection and passivation coating with significant enhancement of solar cell efficiency.

8. Conclusion

Diamond-like Nanocomposite has become an interesting material due to its tunable unique properties. This material could be deposited on various types of materials by PECVD method at low temperature. The different
properties of the film could be varied over wide range by changing deposition parameters, precursor, doping and even post deposition treatment also like annealing. Low residual stress, high hardness, high young modulus and low wear make them a suitable material as wear protecting coating, MEMS, etc. In addition, biocompatibility of the film expands its application to medical area also. C-Si/ a:DLN heterojunction is used to sensing different toxic gasses. Recently this film has been used as an antireflection coating on crystalline silicon solar cell due to its excellent optical property.

Acknowledgement
The authors most sincerely acknowledge the DST, Govt. of India for financial support and Meghnad Saha Institute of Technology for infrastructural support.

References


