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Review Article

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

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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 structures. The amorphous silicon oxide (a: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 have come due to deform tetrahedral carbon with sp^3 configuration and high ratio of sp^3 to sp^2 bond. The DLN has excellent mechanical, electrical, optical and tribological properties. Those 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 10^{14} Ωcm, hardness 10–22 GPa, coefficient of friction 0.03-0.2, wear factor 0.2-0.4 $10^{-7}mm^3/Nm$, transmission Vis-far IR, modulus of elasticity 150-200 GPa, residual stress 200-300 Mpa, dielectric constant 3-9 and maximum operating temperature 600°C in oxygen environment and 1200°C in O_2 free air. Generally, the PECVD method is used to synthesize 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 etc.

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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 materials' chemical bonding i.e. mostly sp^3 states complies with natural diamond. Due to this closeness in chemical bonding, 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^2 bonded carbon atoms into sp^3 bonded carbon clusters. In DLC atomic structure, hydrogen can be present with an atomic concentration ranges from 0% to 50%. DLC acronym was first used by Aisenberg and Chabot[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 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, and another is quartz-like (silicon network), a-Si:O. Carbon network mainly consists of sp^3 hybridization, i.e. diamond-like bonds are 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 comparing 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 coatings have been in existence since early 1990s. V.F. Dorfman first reported and synthesized this unique class of material[4]. 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, Galvano-formung 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 coatings also have been used in many applications[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 *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, Neernick *et al.* in one of their papers stated low-friction, low-wear combined with low internal stress and good adhesion of DLN coating, making it suitable for tribological applications[24]. Again 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 VI *et al*[28]. Scharf TW *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 implant-s[30]. Bursikova Vilma *et al.* recorded laser ablation of nitrogen-doped DLN thin layer, used 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.* and hardness and modulus measured by nanoin-dentation and subsequently interfacial toughness of this hard film brittle substrate system were determined by vicker indentation[32]. 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 thin film make them suitable for application requiring both wear resistance and electrical tailorability[33]. Scharf *et al.* reported the frictional behavior of amorphous diamond-like nanocomposite coatings in low speed, dry sliding contact using a home-built in-situe 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 FH *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]. 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 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 may be used as biocompatible coatings on biomedical implants[41].

DLN coatings 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. On the one hand, 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, and 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:

1) Transport reactants via forced convection to reaction region.

2) Transport reactants via diffusion to wafer surface.

3) Adsorb reactants on surface.

4) Surface processes: chemical decomposition, surface migration, site incorporation, etc.

5) Desorption from surface.

6) Transport byproducts through boundary layer.

7) Transport byproducts away from deposition region.

PVD is a versatile deposition method. It can deposit almost any material. Substrate damage is less and very few chemical reactions are required. PVD undergoes some limitations 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 holders whose rotating speed can be controlled by a speed controller. Rotation of the substrate holders can be made in two modes, 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 fed 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:

1) Ion etching of the substrate was used to reduce the chance of contamination and better adhesion of coated material over the substrate surface.

2) Vapourization of material to be deposited.

3) Formation of radical of the material to be deposited.

4) Transportation of radicals towards the substrate surface.

5) Deposition/condensation of material onto the substrate surface.

4. Precursors

DLN films can be synthesized using composite materials of silicon and oxygen[43]. These precursors might be gaseous (Silane – (SiH_4) and oxygen (O_2) mix)[44], tetra methyle silane-TMS ($(CH_3)_3SiH$ and oxygen mix)[45] or liquids hexamethyle disiloxane HMDSO ($C_6H_{18}OSi_2$)[46-51], or tetraethoxysilane (TEOS, $(C_2H_5O)_4Si$[52], or tetraethylorthosilicate-TEOS (SiC_{8}- $H_{20}O_4$)[21,53,54], hexa methyle disilane-HMDS (C_6H_{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_2H_2 etc) or innert gas Argon (Ar). This mixture is used to coat the substarte under vacuum condition. Silane gas is rarely used as DLN film due to it 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 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 presented 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) presented 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 sp^2 phase and orientation of sp^2 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 ~1560cm^{-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 sp^2 atoms in both rings and chains. D peak is due to the breathing modes of sp^2 atoms in the rings. T peak is due to the C-C sp^3 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[57]. Stress of DLN film deposited using HMDSO precursor vapour by ICP PE-CVD was ~ 15 GPa compared to 11 GPa stress of DLC films diposited using CH_4 gas. Stress can be further decreased by increasing the Si atomic concentartion[52]. Hardness and young modulus are decreased in DLN film in comparison with DLC film[22,45,46,53,54,58,59].

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 and -200V and coefficient of friction increase-d >2 times with increase of substrate bias up to -500V.

It is already reported that, wear resistance of DLN with impurity like SiO_x 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 sp^2 and sp^3 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_{04} and Urbach energy E_U. Incorporating 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[46,62,63].

6.4 Electrical properties

Dielectric constant 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 1. Results of property and range of obtainable values

Property	Range of obtainable values
Coefficient of friction	0.03-0.2
Adhesion	107-109 N/m^2 Adhere to a wide range of substrates including metals, plastics and ceramics; no interlayers required
Thermal stability	Stable to 400-600 °C in air; capable of 1000-1200 °C in absence of oxygen
Physical flexibility	Very flexible; dows not crack when bent
Corrosion and erosion	Resistant to acids, alkalis and particulates due to pore free structure
Electrical resistivity	Undoped:10^{12}-10^{14} Ohm cm; Metal doped: upto 10^{-4} Ohm cm
Hardness	10-22 Gpa
Modulus of elasticity	150-200 Gpa
Residual stress	200-300 Mpa
Transmission	70-80% at 05-20 microns

7. Applications

In DLN, two microstructures (hydrogenated carbon and oxygenated silicon) are interpenetrating each other and thus internal stress is decreased and adhesion property is increased and hence this composite has improved adhesion to almost all kinds of substrates. 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 DLN coatings by PECVD method over various substrates like SS 316 L, glass, Si (100), ceramic (Al_2O_3), ultra-high molecular weight polyethylene (UHMWPE), Co-Cr alloy, Ti_6Al_4V alloy, etc[5]. Most of these materials have been in use as load-bearing orthopedic implants, like hip joint, knee joint, etc[66]. 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 materials, makes DLN an attractive option for choosing DLN as a protective coating[44]. Santra TS *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 deriver 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[67]. Due to its infrared transparency, this can be used as anti-reflective coating on solar cell, glass etc. Sukhendu Jana *et al.*[65] 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 or electronic circuit. It has already been reported that DLC are used for optical wave guiding sensing systems[68], transistors[69] and high temperature sensing up to 600°C[70]. As DLN is an 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[71-73] 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[74-75].

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 sense different toxic gasses. Recently, this film has been used as an antireflection coating on crystalline silicon solar cell due to its excellent optical property.

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