

Deposition and characterization of diamond-like nanocomposite coatings grown by plasma enhanced chemical vapour deposition over different substrate materials

AWADESH KR MALLIK^{a,*}, NANADADULAL DANDAPAT^a, PRAJIT GHOSH^b,
UTPAL GANGULY^b, SUKHENDU JANA^b, SAYAN DAS^b, KAUSTAV GUHA^c,
GARFIELD REBELLO^d, SAMIR KUMAR LAHIRI^b and SOMESWAR DATTA^a

^aCentral Glass & Ceramic Research Institute, CSIR, 196, Raja S. C. Mullick Road, Kolkata 700 032, India

^bMeghnad Saha Institute of Technology, Techno India Group, Kolkata 700 107, India

^cDepartment of Chemistry, Durham University, Durham DH1 3LE, UK

^dPerkin Elmer Technology Innovation Centre, Mumbai 400 059, India

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Abstract. Diamond-like nanocomposite (DLN) coatings have been deposited over different substrates used for biomedical applications by plasma-enhanced chemical vapour deposition (PECVD). DLN has an interconnecting network of amorphous hydrogenated carbon and quartz-like oxygenated silicon. Raman spectroscopy, Fourier transform–infra red (FT–IR) spectroscopy, transmission electron microscopy (TEM) and X-ray diffraction (XRD) have been used for structural characterization. Typical DLN growth rate is about 1 $\mu\text{m}/\text{h}$, measured by stylus profilometer. Due to the presence of quartz-like Si:O in the structure, it is found to have very good adhesive property with all the substrates. The adhesion strength found to be as high as 0.6 N on SS 316 L steel substrates by scratch testing method. The Young's modulus and hardness have found to be 132 GPa and 14.4 GPa, respectively. DLN coatings have wear factor in the order of $1 \times 10^{-7} \text{ mm}^3/\text{N}\cdot\text{m}$. This coating has found to be compatible with all important biomedical substrate materials and has successfully been deposited over Co–Cr alloy based knee implant of complex shape.

Keywords. Diamond-like carbon; plasma CVD; coatings; tribology.

1. Introduction

Protective coatings over steel and other metals, ceramics, glasses and polymers are deposited to increase the lifetime of different components for engineering applications. TiN, CrN, AlTiN and different multilayer coatings are commercially available under different trade names. Apart from these nitride coatings, another method of enhancing the surface properties is to treat the engineering component under nitrogen plasma. Generally nitridation under definite surface bias potential penetrate the surface upto a certain depth (depending on the applied voltage and plasma treatment time) and thereby increase the surface hardness and corrosion resistance property of the metal component under engineering applications (Mukherjee *et al* 2004; Rao *et al* 2005). Carburisation is also a standard method of surface hardening. It is a heat treatment process in which iron or steel is heated in the presence of another material (in the range of 900–950 °C) which liberates carbon as it decomposes. Depending on the amount of time and temperature, varying amount of carbon diffuses into the part and the outer surface becomes

hard via the transformation from austenite to martensite during quenching, while the core remains soft and tough as a ferritic and/or pearlite microstructure. Now other than these conventional methods of surface engineering (by nitridation or carburization), another class is carbon based coating material popularly termed as diamond-like carbon (DLC) coatings which have been in use for decades. But the main drawback of this type of coating is incompatibility with steel and other metals which has carbon solubility in the structure. There is a need of interlayer of chromium or titanium nitride before depositing DLC layer to prevent carbon diffusion into the substrate structure. Moreover the tribological performance of DLC reduces due to inherent stress inside the structure in the order of GPa. An unique class of material has been found which can be deposited over any substrate material with good tribological performance. This material is an interpenetrating network of amorphous hydrogenated carbon and quartz-like oxygenated silicon and is called diamond-like nanocomposite (DLN). Due to the presence of silicon in the structure, the adhesion to different substrates increases and internal stress reduction occurs.

DLN coatings have been in use since early 1990s. Dorfman (1992) first reported the synthesis of such unique class of material. Later on Bekaert advanced coating

* Author for correspondence (amallik@cgcricri.res.in)

technologies (formerly known as advanced refractories technologies) and Russian and American scientists patented DLN coatings for various protective coating applications (Dorfman and Pypkin 1994, 1995; Emerson and Gu 1996; Dorfman and Goel 1998; Bosley and Miller 1998; Hooshang 2000; Neerincx and Goel 2001; Neerincx and Persoone 2001; Jacquet and Wietig 2006; Cooper et al 2007). DLN coatings are also used in micro-electromechanical systems (MEMS) applications like LIGA (German acronym for lithographie, galvanofornung und abformung) structures (Prasad et al 2003). Bekaert advanced coating technologies, Belgium have used plasma-enhanced chemical vapour deposition (PECVD) method for growing such composite films. Chinese researchers have successfully used ion beam technology for growing DLN films (Ding et al 1999). South Korean researchers have reported thermally activated CVD process for the growth of DLN films (Yang et al 2000). 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 (Yan et al 2004). In the present work, we have used PECVD with similar reactor used by Bekaert advanced coatings technology, Belgium. The reactor was available with one of our research collaborator, Meghnad Saha Institute of technology, Techno India group.

DLN have been characterized by various researchers (Pollak and Dorfman 1997; Polyakov et al 1997; Venkatraman et al 1997, 1999; Bozhko et al 1998; Dorfman 1998; Neerincx et al 1998a, b; Kester et al 1999; Platon et al 2001; Hauert and Muller 2003; Pandit and Padture 2003; Scharf and Singer 2003; Yang et al 2003a, b; Narayan 2005; Sheeja et al 2005; Kobayashi et al 2006; Maalouf et al 2006; Bursikova et al 2007; Logothetidis 2007; Scharf et al 2007). They have unique bulk and surface properties including an excellent thermal stability (Yang et al 2003a, b). The applications of DLN films include tribological coatings, chemical protective coatings (Neerincx et al 1998a, b; Kester et al 1999; Venkatraman et al 1999; Scharf and Singer 2003; Scharf et al 2007) and abrasion-resistant coatings for IR windows. They have unique control over optical properties and electrical properties (Polyakov et al

1997; Bozhko et al 1998; Dorfman 1998). Moreover it finds indirect application in the field of biomedical implants. Hydroxyapatite is widely used as plasma-sprayed coating for osteointegration of implants. DLN films have been reported to improve the adhesion of these coatings to the substrates (Narayan 2005). It has an excellent adhesion (Pandit and Padture 2003) to a variety of substrate materials due to a low residual stress, Moreover these films have found application as biosensors (Maalouf et al 2006). DLC coatings have been tried as protective wear resistant coating in joint prostheses (Platon et al 2001; Sheeja et al 2005). Diamond-like carbon (DLC) films were deposited onto UHMWPE and PMMA substrates using plasma CVD process (Kobayashi et al 2006). To improve adhesion of DLC films, substrates were plasma treated before DLC deposition. Carbon-based films have found to be haemobiocompatible as well (Logothetidis 2007). But so far there are not many literatures about DLN films in biomedical applications. Researchers at Department of Cardiology, University Hospitals Leuven, Belgium (De Scheerder et al 2000) have used either DLN (or Dylun, Bekaert, Kortrijk, Belgium) coated or non-coated stents, randomly implanted in two coronary arteries of 20 pigs. The results indicate that the diamond-like nanocomposite stent coatings are compatible, resulting in decreased thrombogenicity and decreased neo-intimal hyperplasia. DLN coatings may have been in use commercially worldwide with different trade names, but there is no reported data available about its use in orthopedic applications. DLN films represent a significant advance over conventional diamond-like films in both stability and ability to tailor specific properties over a wide range. The properties are summarized in table 1 and compared with diamond and DLC coatings.

In the present study we have deposited DLN coatings by PECVD method over different substrates like, SS 316 L, glass, Si (100), ceramic (Al_2O_3), 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 (Rahaman et al 2007). Generation of UHMWPE wear particles is prime concern for failure of such implants. Many protective coatings like TiN, CrN (Ionbond® coatings) or oxidized

Table 1. Comparison of properties among diamond, diamond-like carbon (DLC) and diamond-like nanocomposite (DLN) coatings.

Properties	Diamond	DLC	DLN
Resistivity (Ω cm)	$> 10^{16}$	10^{10} – 10^{13}	10^{-4} – 10^{14}
Hardness (GPa)	90	10–32	10–22
Coefficient of friction (against steel)	–	0.1–0.2	0.03–0.2
Wear factor (10^{-7} mm ³ /Nm)	–	0.5–1	0.2–0.4
Transmission	UV–Vis–IR	Vis–IR	Vis–far IR
Modulus of elasticity (GPa)	1145	100–340	150–200
Residual stress	Almost nil	8–10 GPa	200–300 MPa
Dielectric constant	–	–	3–9
Maximum operating temperature (°C)	–	300	600 (O ₂ atm) 1200 (O ₂ free)

zirconium (oxinium, Smith & Nephew®) have so far been used to reduce polyethylene wear of implants. But deposition of these coating materials involves high temperature processing of implant materials, which enhances the chances of losing its mechanical property at high processing temperatures. DLN coating has been deposited at as low as 100 °C, thereby enabling to coat even polymeric materials. So far DLN may not have been used as protective coating for biomedical applications. Although there are reports of DLC being used as protective coating in orthopedic implants (McNamara *et al* 2001; Platon *et al* 2001; Grill 2003; Hauert 2003; Hauert and Muller 2003; Sheeja *et al* 2005; Kobayashi *et al* 2006; Logothetidis 2007). Hauert (2003) in his review article, after describing contradicting results from various literatures has commented that the superior tribological properties of DLC in various environments can not probably be easily applied for hip joints and other load bearing implants as the build up of a transfer layer does not take place, and the UHMWPE counterpart still shows wear. According to Hauert (2003), DLC coated load bearing implants sliding against DLC coated counterparts or against ceramics may show good 'ceramic like' tribological properties, but he questioned of any real improvement in wear performance against the existing ceramic/ceramic or metal/ceramic bearings. Therefore, an attempt has been made to find an alternative DLN based protective coating, which does not have intrinsic stress and do not require interlayer to prevent carbon dissolution. Diamond-like nanocomposite coating is expected to enhance the tribological performance of orthopedic implants. Moreover DLN has been proven to be non-toxic. We hope that

DLN coating would be suitable material for biomedical tribology. The coating has been characterized by Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), X-ray diffraction (XRD) for structural evaluation and mechanical properties like hardness and young's modulus have been tested. Thicknesses of the coatings have been calculated by stylus profilometer and growth rates were calculated from thickness measurements. Moreover tribological behaviour has been evaluated by ball-on-disc tribometer.

2. Materials and methods

2.1 PECVD reactor

One plasma-enhanced chemical vapour deposition (PECVD) reactor was used for deposition of DLN coatings as depicted in figure 1. This reactor had been in use for commercial production of Dylyn® protective coatings. It had a rotating substrate holder at the top, which rotates at 2–3 rpm speed. There was a liquid precursor feeder at the bottom, through which liquid siloxane entered into the vacuum and due to the difference in pressure, evaporated into vapour form. There was one tungsten filament forming an arc above the liquid precursor feeder. This filament was negatively biased and there was an electron emission from the filament, which ionized the precursor vapour. These ionized precursor species were attracted by the substrate holder, which was again negatively biased at higher voltage. Before starting the precursor flow, argon

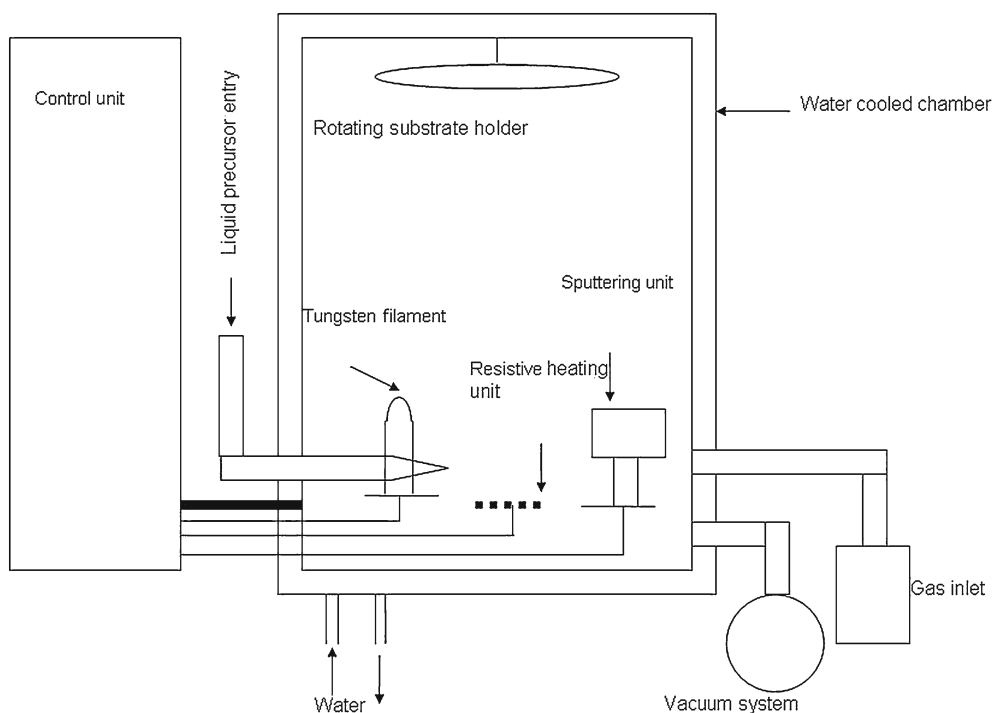


Figure 1. Schematic of PECVD reactor.

gas was introduced into the reactor chamber to form plasma. Heavy argon ions bombarded the substrates and etched it to clean the substrates prior to deposition. There were provisions for resistive heating evaporation and sputtering of metal atoms for co-deposition inside this reactor. But during these set of experiments metal co-deposition was not done. The whole chamber was water cooled. There was a provision for substrate holder cooling as well. This is specially required for polymer substrates.

Deposition can be described in four steps: (a) plasma etching of the substrate by bombardment of the substrate by ions of an inert gas such as Ar (b) introducing a liquid organic precursor containing the elements C, H, Si, O to be deposited in suitable proportions (remains substantially constant during the deposition process), in the vacuum chamber, at a working pressure between 5×10^{-3} and 5×10^{-2} mbar (c) forming a plasma from the introduced precursor by an electron-assisted d.c.-discharge using a filament with a filament current of 50–150 Å, a negative filament bias d.c. voltage of 50–300 V and with a plasma current between 0.1 and 20 Å and (d) depositing the composition on the substrate, to which a negative d.c.-bias of 200 to 1200 V was applied, in order to attract ions formed in the plasma. Table 2 describes the substrates used during experiments and corresponding processing parameters.

2.2 Physical characterizations

Fourier-transform infrared spectroscopy (FT-IR) of the deposited films were done using Perkin Elmer Spectrum 100. Scan range was from 4000–650 cm^{-1} . Source was MIR and detector was MIR TGS. Beamsplitter used was OptKBr and the instrument resolution was 4.00 cm^{-1} . IR accessory type was Universal ATR and UATR. Crystal combination was diamond/ZnSe.

Raman spectroscopy was by far the best non-destructive way to study the bonding structure and quality of DLN films. The Raman microprobe studies were carried out in Durham University, UK. The Raman spectrometer was based on a commercial Raman microscope (Ramascope 1000, Renishaw) equipped with a 50 \times ULWD, 0.55 NA objective (Olympus). The DLN films were probed by a diode-pumped

solid-state laser (Opus 532, Laser Quantum), which emitted light at the green region of spectrum at 532 nm. The laser (5 mW intensity at source) beam was focussed to about $< 2 \mu\text{m}$ diameter spot and spectra were obtained with 5 min acquisition time.

Transmission electron microscopy (TEM) was done using model Tecnai G² 30 ST of FEI Company, Europe. X-ray diffraction patterns of the samples were recorded in X'pert Pro MPD diffractometer (PANalytical) operating at 45 kV and 35 mA using Ni-filtered $\text{CuK}\alpha$ radiation. XRD data were recorded in X'celerator from 10° to 100° with glancing angle thin film attachment. DLN coatings were seen under scanning electron microscope (LEO 430i STEROSCAN, UK) for microstructural evaluation of wear track along with EDAX analysis. Roughness was measured by surface profilometer (Surtronic 3p, Form Talysurf Plus, Rank Taylor Hobson Ltd, UK). Double-sided tape was used as masking material to form an uncoated portion on the substrate. Scanning of the coating, starting from coated portion to uncoated portion, produced a step in the roughness profile of the substrate. The height of the step was the thickness of the coating. If this thickness was divided by the deposition time of the coating, we get the growth rate of the plasma-enhanced chemical vapour deposition (PECVD).

2.3 Mechanical characterization

The microhardness on DLN coated steel and glass substrates was measured according to standard ASTM E2546 using Nanovea microhardness tester (MHT) at Micro Photonics Inc. The test conditions were as follows: Vickers diamond indenter, maximum force applied was 0.10 N, loading rate was 0.20 N/min and unloading rate was also 0.20 N/min. The values were computed using Oliver & Pharr method.

Scratch resistance was measured by using sphero-conical stylus (Nanovea micro scratch tester of Micro Photonics Inc.) of 10 μm radius with an initial load of 0.045 N and a final load of 2.0 N at loading rate of 2.0 N/min. Scratch length was 3 mm and scratching speed was 3.07 mm/min.

Wear and friction experiments were done on DLN-coated substrates with a ball on disc arrangement. Radius of the steel ball was 6.35 mm and a constant load of 1 N was applied while rotating in a 4 mm diameter circle at constant speed.

Table 2. PECVD deposition conditions.

Substrates	Precursor flow rate (ml/10 min)	Time of deposition (min)	Total precursor used (ml)	Bias voltage (V)	Plasma current (Å)	Base pressure (mbar)
SS 316L	1.7522	100	19.09	550	0.8	1×10^{-4}
Ti6Al4V alloy and Co-Cr alloy	1.3831	127	17.57	600	0.8	9.5×10^{-5}
UHMWPE and glass	1.0199	29	2.96	600	0.8	9.6×10^{-5}
Acetabular cup	0.8863	65	5.761	700	0.8	1×10^{-4}
Co-Cr alloy based knee implant	1.6526	93	15.371	700	0.8	5×10^{-5}

3. Results and discussion

3.1 Physical properties

Diamond-like nanocomposite is composite in nature at the molecular level. The chemical formulae of the siloxane precursor used for DLN synthesis composed of units of the form R_2SiO , where R is a hydrogen atom or a hydrocarbon group. A siloxane has a branched or unbranched backbone of alternating silicon and oxygen atoms $-Si-O-Si-O-$ with side chains R attached to the silicon atoms. Here we have used triphenyl nona methyle penta siloxane precursor. Liquid precursor is bubbled into the vacuum inside the reactor, where it evaporates into the vapour form. These neutral molecules get ionized by electrons emitted thermionically from tungsten filament and form charged hydrocarbon and SiO species, which are being attracted towards the negatively biased substrate holder. DLN coating thus deposited is amorphous in nature and can be described as networks of amorphous hydrogenated carbon and oxygenated silicon entangled with each other.

Raman spectra of DLN films deposited on different substrates are shown in figure 2. The broad asymmetric bands

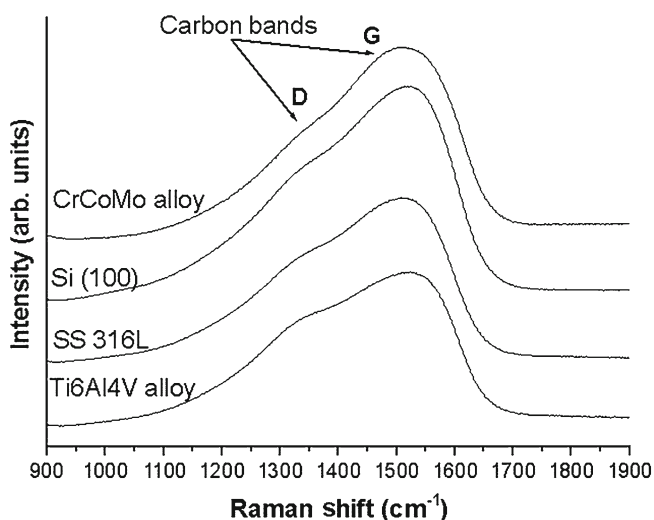


Figure 2. Raman spectra from DLN films coated on four different substrates: CrCoMo alloy, Si(100) wafer, SS 316 L, Ti6Al4V alloy (532 nm laser, 5 mW power, 5 min acquisition).

in the 1000–1700 cm^{-1} are typical characteristics of amorphous carbon or diamond-like films (Yang *et al* 2003a, b). The Raman spectra were curve fitted to obtain a Gaussian deconvolution into D and G peaks as shown in table 3. The G peak is a characteristic of single crystalline graphite, which results due to E_{2g} C–C stretching vibrations in the graphite layer and the D peak is a characteristic of disordered graphite, which results due to the A_{1g} vibrational modes (Robertson 2002). Hence D stands for ‘disorder’ and G stands for ‘graphite’. In amorphous carbon films, the electronic properties are controlled by the sp^2 sites with π bonds, and the mechanical properties are controlled by the sp^3 sites with σ bonds (Robertson 1994).

Therefore, physical properties of DLN films can be explained by the sp^3/sp^2 ratio, which is correlated to the position and intensity ratio (I_D/I_G) of the D and G peaks. The positional shift of the Raman D and G peaks can reflect the difference in actual film structures (Yang *et al* 2003a, b); however, the peaks can also be a little shifted due to the difference in light source of the Raman spectrometer, curve fitting parameters applied and so on. In table 3, the comparison shows that the I_D/I_G ratio in the Raman spectra of DLN films coated on different substrates have gradually increased from 1.53 for CrCoMo alloy to 2.71 for Ti6Al4V alloy. This increase in I_D/I_G ratio is associated with a relative increase in the sp^3 site content (or a relative decrease in the sp^2 site content) in the respective DLN films. It is regarded that a higher graphite (or sp^2) content in the amorphous carbon films reduces the hardness of the films. Therefore we can predict to observe an increasing order of hardness in the DLN films with an increasing value of I_D/I_G ratio.

Figure 3 shows FT-IR spectra of DLN films on stainless steel and glass substrates. Major absorption band of the Si–O stretching in the 1100–1000 cm^{-1} range is observed in both the FT-IR spectra of DLN films. Second prominent absorption band we could find in the 3100–2800 cm^{-1} range, was of the C–H stretching. The C–H absorption band in the 3100–2800 cm^{-1} range is typical for sp^3 - and sp^2 -bonded carbon. These C–H and Si–O stretching peaks prove that DLN films mainly consist of hydrogenated carbon (C:H) and oxygenated silicon (Si:O) networks. Apart from the interpenetrating networks of Si:O and C:H, there were also the presence of non-graphitic carbon and Si–C like bondings. There is a small hump of Si–C stretching in the 800 cm^{-1} region. Presence of non-graphitic bonding of carbon is confirmed by

Table 3. Gaussian analyses of Raman spectra deconvoluted into D and G peaks in DLN films coated in different substrates (ν : position, Γ : full width at half maxima and I : integrated intensity).

Substrates	ν_D (cm^{-1})	Γ_D (cm^{-1})	ν_G (cm^{-1})	Γ_G (cm^{-1})	I_D/I_G
CrCoMo alloy	1396.4	272.733	1536.91	156.493	1.53
Si(100)	1385.5	305.251	1533.94	146.974	2.05
SS 316 L	1382.9	300.112	1529.08	145.306	2.19
Ti6Al4V alloy	1390.78	304.394	1541.07	138.599	2.71

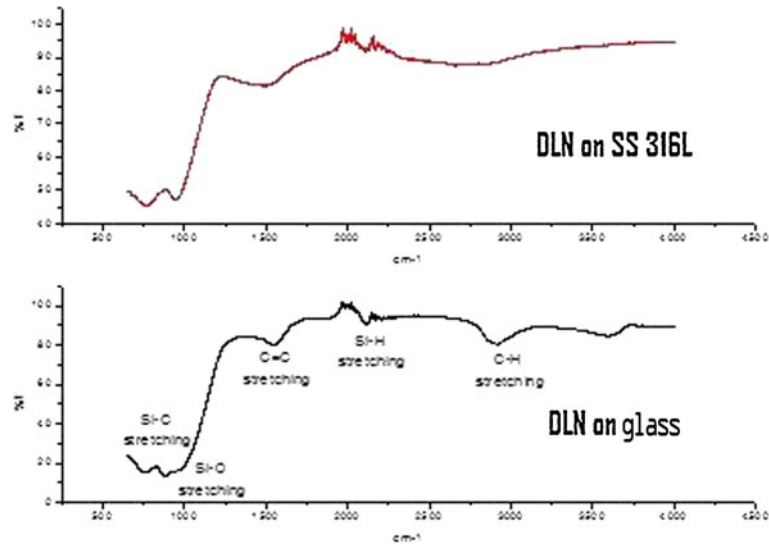


Figure 3. FT-IR spectra of DLN films deposited on SS 316 L and glass substrates.

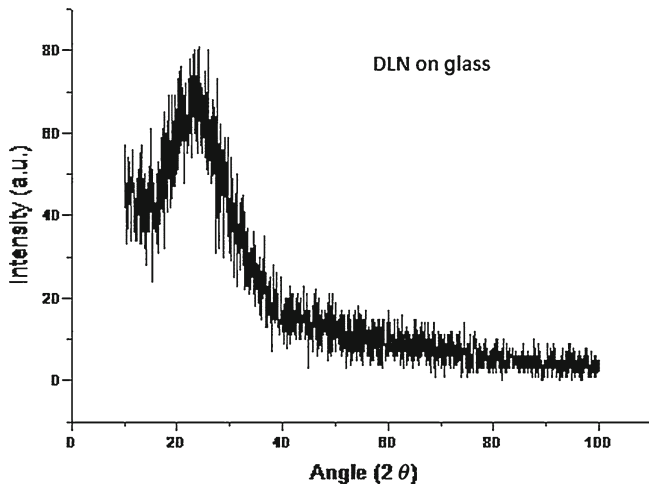


Figure 4. XRD micrograph of DLN deposited on glass showing amorphous nature of deposited film.

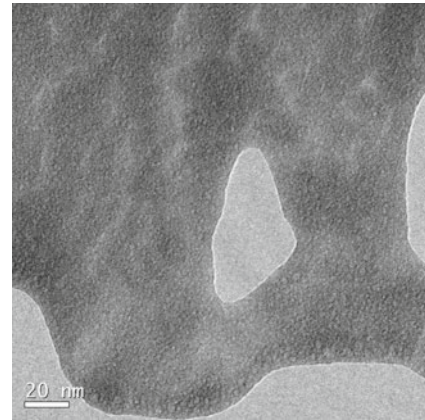


Figure 5. TEM micrograph around plasma-etched hole.

C=C stretching peaks appearing in the 1580 cm^{-1} region. Also we could see Si-H stretching appearing in 2100 cm^{-1} region. Our results exactly match with reported literature values (Yang *et al* 2003a, b). Chemical composition was also studied using an EDAX of the worn films.

Figure 4 indicates that XRD could not detect any crystallinity within its resolution. XRD patterns were taken from DLN coatings on glass substrates. The hump around $2\theta = 26.5^\circ$ in the scan is typical for amorphous films grown on quartz microscope slides, due to the presence of SiO_2 in the bottom glassy substrate. To further prove the amorphous nature of the film, transmission electron microscopy was done on DLN coatings. DLN deposited onto $50\text{ }\mu\text{m}$ thick aluminum foil has been plasma-etched from the opposite uncoated side of the foil, so as not to damage the DLN coating. Once one hole has been created in the foil, DLN film was

seen in and around the created hole under transmission electron microscope. Figure 5 shows typical TEM micrographs, which are characteristics of amorphous structure (Yang *et al* 2003a, b).

The average R_a , roughness of the bare steel substrates before deposition was found to be $0.1\text{ }\mu\text{m}$. DLN coatings follow the contours of the underlying substrate. The R_a , roughness does not vary much after deposition. It is found to be $0.15\text{ }\mu\text{m}$. Roughness of DLN films deposited on laboratory glass slide substrates was beyond instrument range as it followed the very smooth surface of glass slides. The advantage of this is that there is no need of post-deposition polishing of DLN coating on well polished substrates. Any other wear resistance protective coating has to be polished to reduce the surface roughness prior to application. Upper scan profile of figure 6 shows a $1.75\text{ }\mu\text{m}$ step in the profilometer scan of the substrate for DLN on SS 316 L combination. The coating had been grown for 100 min, thus the growth rate was calculated to be $1.04\text{ }\mu\text{m/h}$. Bottom scan profile of figure 6 shows one

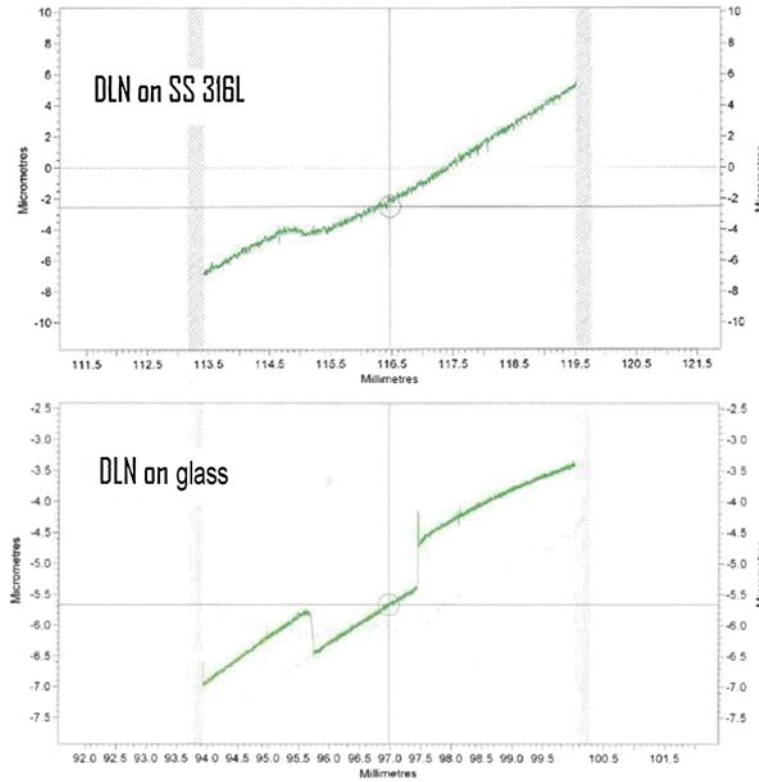


Figure 6. Typical profilometer scan of DLN coating for thickness measurement: (a) SS 316 L substrate and (b) glass substrate.

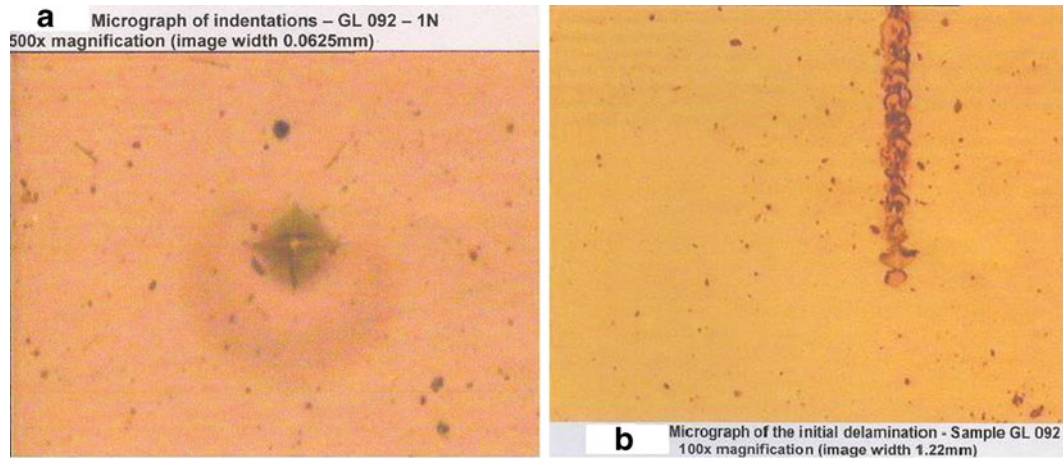


Figure 7. Optical micrographs of (a) microindentation mark on DLN-coated glass substrate and (b) scratch resistance test mark on DLN-coated glass sample.

Table 4. Mechanical properties of DLN coatings.

Sample	Roughness, R_a (μm)	Thickness (μm)	Hardness (GPa)	Young's modulus (GPa)	Critical load L_C (N) with standard deviation
DLN on SS 316 L substrates	0.1003 (bare) 0.1466 (coated)	1.75	17	132	0.618 ± 0.004
DLN on glass substrates	Very smooth before and after coating	0.66	14	73	0.196 ± 0.023

Table 5. Wear and friction data of steel ball sliding against DLN-coated silicon substrate.

Temperature (°C)	No. of revolutions	Wear (mm ³ /N-m)	Coefficient of friction
28.8	90 000	1.26 E-7	0.043
30.4	110 000	1.33 E-7	0.092
28.4	150 000	1.79 E-7	0.143

trough in the scan profile of DLN on glass slide, as the stylus moves from coated portion through uncoated portion to other side of the coated portion of the substrate. The thickness was found to be 660 nm. Deposition time was 29 min (table 2). So the growth rate was calculated to be 1.365 $\mu\text{m}/\text{h}$. It has been found that typical growth rate varies between 1 and 3 $\mu\text{m}/\text{h}$.

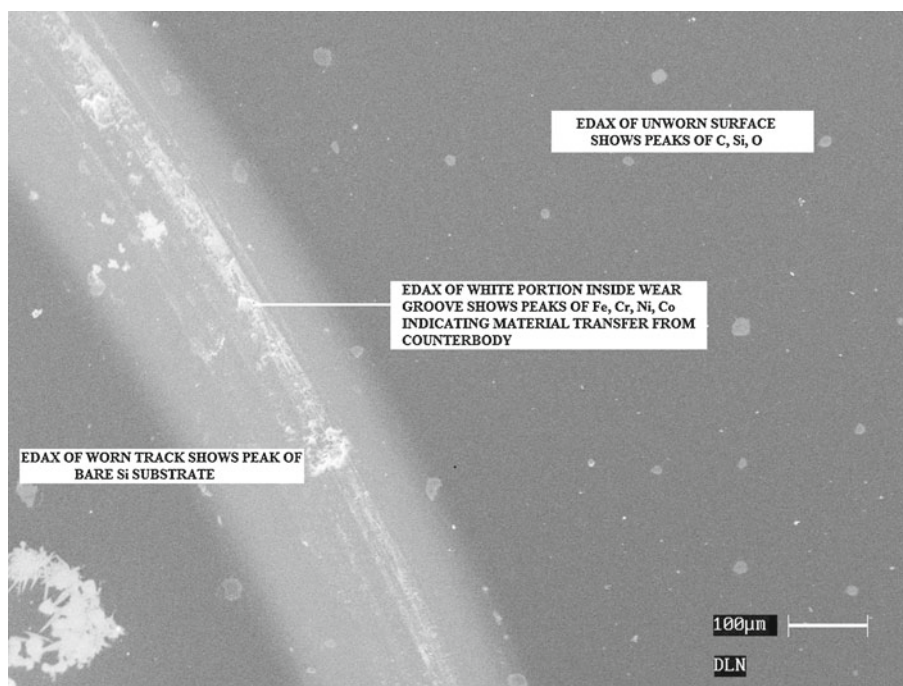
3.2 Mechanical properties and tribology

Mechanical properties along with roughness values of DLN coatings on steel and glass substrates have been tabulated in table 4. Indentation with 0.1 N load was not clearly visible, so tests were performed with 1 N and 3 N loads. Figure 7(a) shows micro-indentation mark on DLN coating. It is found that DLN deposited on stainless steel has higher hardness value of 17 GPa in comparison to hardness value of 14 GPa of DLN coatings deposited on glass substrates. Not only the hardness values are higher for steel substrates but also Young's modulus for steel substrates is 132 GPa when

compared to 73 GPa for glass substrates. The literature values of hardness for this class of materials vary between 12 and 17 GPa (Bozhko *et al* 1998), which is in complete agreement with present findings. Now, whereas plasma immersion ion implantation (PIII) techniques could give only 8–9 GPa of surface hardness of AISI 304 L stainless steel (Rao *et al* 2005).

Scratch resistance has been reported by critical force, L_C , at which damage of the coating occurs. The critical load is optically defined by the point where the substrate is completely uncovered in the scratch track for a length equal or greater than the scratch width. The optical micrograph in figure 7(b) shows typical scratch track. At least five measurements were done on each sample to calculate the average L_C . The critical load L_C for DLN coatings on steel substrates was found to be 0.618 N and the L_C for DLN coatings on glass substrates was found to be 0.196 N. With such good adhesive strength and hardness values, DLN could find wide application as wear-resistant coating.

Sliding wear behaviour of steel ball sliding against DLN coating under dry conditions is shown in table 5. The experiments were conducted under room temperature conditions. Steel ball was made to revolve in 4 mm diameter circle on DLN-coated substrates. The steady state coefficient of friction (COF) changes from 0.043 to 0.092 when revolution changes from 90 000 to 110 000. The corresponding calculated wear factors are $1.26 \times 10^{-7} \text{ mm}^3/\text{N-m}$ and $1.33 \times 10^{-7} \text{ mm}^3/\text{N-m}$, respectively. Obviously, the wear volume will increase if the ball is made to revolve for higher number of revolutions of 150 000, but in that case the average COF strikingly increases to 0.143, much higher than 90 000 and

**Figure 8.** Portion of wear track of DLN film with EDAX analysis from wear groove and unworn surface.

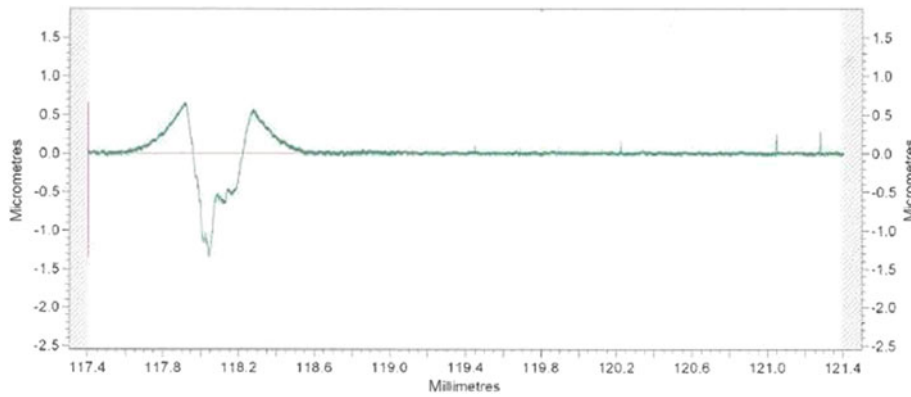


Figure 9. Profilometer scan across wear track.

110 000 revolutions. Whereas the reported literature COF values for such wear experiments have always been below 0.1 (Neerinc *et al* 1998a, b). This anomaly in COF values between reported and available literature may be due to the fact that, as the ball is made to slide for longer duration, the underneath substrate comes out due to wearing of DLN coating and thus the resultant values of friction correspond to the values between steel ball sliding against bare Si substrate. This is evident from the SEM images of figure 8, where bare silicon substrate is visible due to wearing out of DLN coating. Moreover the EDAX from whitish portion of the wear groove indicates presence of Fe, Co, Ni and O which is typical of the steel ball composition. Thus there is a clear evidence of material transfer between ball and coated substrate. Figure 9 shows profilometer scan of the wear groove. The depth of the groove shows 1.5 μm whereas the coating thickness was $< 1 \mu\text{m}$. This difference between coating thickness and wear track depth further confirms exposure of the underneath silicon substrate.

4. Conclusions

4.1 PECVD

- (I) DLN has been successfully deposited on many types of substrates, including polymers, glass, ceramics and metals (including aluminum, stainless steel and silicon) by PECVD.
- (II) There was no need for interlayer prior to DLN deposition on all substrates.
- (III) Large area deposition ($\sim 3000 \text{ cm}^2$) has been achieved in PECVD reactor.

4.2 DLN coating

- (I) DLN films mainly consist of hydrogenated carbon (C:H) and oxygenated silicon (Si:O) networks, as evident from FT-IR spectra.
- (II) Presence of sp^3 carbon and sp^2 graphite inside the structure is evident from Raman spectroscopy.



Figure 10. Femoral components of knee implant: (a) uncoated Co-Cr based alloy and (b) DLN-coated.

- (III) Films are not only X-ray amorphous but also it is nanocomposite in nature under TEM micrograph.

4.3 Mechanical properties

- (I) DLN coatings follow the contours of the underlying substrate with the advantage of non-requirement of post-deposition polishing of well-polished parts.
- (II) Substantial enhancement of the surface hardness is achieved with DLN coating.
- (III) Adhesion strength is better with metallic substrates than glass substrates which is essential for adhesive wear applications like hip joints and knee joints.
- (IV) After depositing over different materials of biomedical importance, we have successfully deposited DLN coating on femoral components of Co-Cr alloy-based knee implants of complex shape as shown in figure 10. With such good mechanical performance DLN is a potential coating for biomedical tribology.

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