Deposition and Characterization of Diamond-like-Nanocomposite Coatings Grown by Plasma Enhanced Chemical Vapor 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]; Someswar Datta[a]

[a]Central Glass & Ceramic Research Institute, CSIR , 196, Raja S. C. Mullick Road, Kolkata – 700032, India

[b]Meghnad Saha Institute of Technology, Techno India Group, Kolkata – 700107, India

[c]Department of Chemistry, Durham University, DH1 3LE, United Kingdom

[d]PerkinElmer Technology Innovation Centre, Mumbai – 400059, India

*Corresponding Author. Tel: +91 33 24733477. Fax: +91 33 24730957, E-mail address: amallik@cgcri.res.in (A. K. Mallik)

Abstract: Diamond like Nano-composite (DLN) coatings have been deposited over different substrates used for biomedical applications by plasma enhanced chemical vapor 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 µm/hr, 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 0.6N 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 1×10^{-7} mm^3/N-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.

Key words: Diamond like-carbon; plasma CVD; coatings; tribology

1. Introduction:

Protective coatings over steel and other metals, ceramics, glasses, polymers are deposited to increase the lifetime of the 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 to 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 carburisation) 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. V. F. Dorfman first reported synthesis of such unique class of material (Dorfman 1992). 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 (Dorfman et al 1994, Dorfman et al 1995, Cooper et al 2007, Emerson et al 1996, Dorfman et al 1998, Bosley et al 1998, Hooshang 2000, Neernick et al 2001, Neernick et al 2001, Jacquet et al 2006. DLN coatings also have been used in micro-electromechanical systems (MEMS) applications like LIGA (German acronym for Lithographie, Galvanoformung und Abformung) structures (Prasad et al 2003). Bekaert Advanced Coating Technologies, Belgium have 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 (Ding et al 1999). South Korean researchers have reported thermally activated CVD process for 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 (Yang et al 2003, Yang et al 2003, Venkatraman et al 1999, Neernick et al 1998, Bozhko et al 1998, Kester et al 1999, Dorfman 1998, Polyakov et al 1997, Scharf et al 2007, Narayan 2005, Bursikova et al 2007, Pandit et al 2003, Venkatraman et al 1997, Neernick et al 1998, Scharf et al 2003, Hauert et al 2003, Maalouf et al 2006, Pollak et al 1997, Platon et al 2001, Sheeja et al 2005, Kobayashi et al 2006, Logothetidis 2007). They have unique bulk and surface properties including excellent thermal stability (Yang et al 2003). The applications of DLN films include tribological coatings, chemical protective coatings (Venkatraman et al 1999, Neernick et al 1998, Kester et al 1999, Scharf et al 2007, Neernick et al 1998, Scharf et al 2003) and abrasion-resistant coatings for IR windows. They have unique control over optical properties and electrical properties (Bozhko et al 1998, Dorfman 1998, Polyakov et al 1997). Moreover it finds indirect application in the field of biomedical implants. Hydroxyapetite is widely used plasma sprayed coating for oseointegration of implants. DLN films have been reported to improve the adhesion of these coatings to the substrates (Narayan 2005). It has excellent adhesion (Pandit et al 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 (Scheerder et al 2000) have used either DLN (or Dylyn, 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 neointimal hyperplasia. DLN coating 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 the 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 316L, Glass, Si (100), ceramic (Al_2O_3), Ultra High Molecular Weight Polyethylene (UHMWPE), CoCr 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 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 chance of losing its mechanical property at high processing temperatures. DLN coating has been deposited at as low as 100^{o}C, thereby enabling to coat even polymeric materials. So far DLN may have not been used as protective coating for biomedical applications. Although there are reports of DLC being used as protective coating in orthopedic implants (Hauert et al 2003, Platon et al 2001, Sheeja et al 2005, Kobayashi et al 2006, Logothetidis

2007, McNamara et al 2001, A. Grill 2003, R. Hauert 2003). R. Hauert in his review article (2003) after describing contradicting results from various literatures has commented that the superior tribological properties of DLC in various environments can probably not 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 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 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 behavior has been evaluated by ball-on-disc tribometer.

2. Materials & Methods:

2.1 PECVD Reactor

One plasma enhanced chemical vapor deposition (PECVD) reactor has been 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 has a rotating substrate holder at the top, which rotates at 2-3 rpm speed. There is a liquid precursor feeder at the bottom, through which liquid siloxane enters into the vacuum and due to difference in pressure evaporates into vapor form. There is one tungsten filament forming an arc above the liquid precursor feeder. This filament is negatively biased and there is electron emission from the filament, which ionizes the precursor vapor. These ionized precursor species is attracted by the substrate holder, which is again negatively biased at higher voltage. Before starting the precursor flow, argon gas is introduced into the reactor chamber to form plasma. Heavy argon ions bombard the substrates and etch it to clean the substrates prior to deposition. There are 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 has not been done. The whole chamber is water cooled. There is 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 (remain substantially constant during the deposition process), in the vacuum chamber, at a working pressure of between 5×10^{-3} and 5×10^{-2} mbar, c) forming a plasma from the introduced precursor by an electron assisted DC-discharge using a filament with a filament current of 50-150 A, a negative filament bias DC voltage of 50-300 V and with a plasma current between 0.1 and 20 A, d) depositing the composition on the substrate, to which a negative DC-bias of 200 to 1200 V is 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 (FTIR) 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 is by far the best non-destructive way to study the bonding structure and quality of the 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 50x 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 μm diameter spot and spectra were obtained with 5 minute acquisition time.

Transmission electron microscopy (TEM) was done using model Tecnai G^2 30 ST of FEI Company, Europe. The X-ray diffraction patterns of the samples were recorded in X'pert Pro MPD diffractometer (PANanalytical) operating at 45 kV and 35 mA using Ni-filtered CuKα radiation. The XRD data were recorded in X'celerator from 10^o to 100^o with glancing angle thin film attachment. DLN coatings were seen under scanning electron microscope (LEO 430i STEROSCAN, U.K.) 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. U.K.). Double sided tape had been used as masking material to form an uncoated portion on the substrate. Scanning of the coating, starting from coated portion to uncoated portion, produces a step in the roughness profile of the substrate. The height of the step

is the thickness of the coating. If this thickness is divided by the deposition time of the coating, we get the growth rate of the plasma enhanced chemical vapor deposition (PECVD).

2.3 Mechanical Characterizations

The micro-hardness on DLN coated steel and glass substrates was measured according to standard ASTM E2546 using Nanovea Micro Hardness Tester (MHT) carried out 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 micron radius with initial load of 0.045 N and final load of 2.0 N at loading rate of 2.0N/min. Scratch length was 3 mm and scratching speed was 3.07mm/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.

3. Results & Discussions

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 triphenyle nona methyle penta siloxane precursor. Liquid precursor is bubbled into the vacuum inside the reactor, where it evaporates into vapor form. These neutral molecules get ionised by electrons emitted thermoionically from tungsten filament and form charged hydrocarbon and SiO species, which are being attracted towards the negatively biased substrate holder. The DLN coating thus deposited is amorphous in nature and can be described as networks of amourphous hydrogeneted carbon and oxygeneted silicon entangled with each other.

Raman spectra of DLN films deposited on different substrates are shown in figure 2. The broad asymmetric bands in the 1000-1700 cm^{-1} are typical characteristics of amorphous carbon or diamond-like films (Yang et al 2003). The Raman spectra were curve fitted to obtain a Gaussian deconvolution into D and G peaks as shown in the 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 (J. 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 and controlled by the sp^3 sites with σ bonds (J. Robertson 1994).

Therefore the physical properties of the 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 2003)**Error! Bookmark not defined.**; 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 the 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 & 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 sp3- and sp2-bonded carbon. These C-H and Si-O stretching peaks prove that the 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 are 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 C=C stretching peaks appearing in the 1580cm^{-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 2003). Chemical composition was also studied using 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 $2\theta = 26.5^o$ 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 of DLN coatings. DLN deposited onto 50 micron thick aluminium

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 2003).

The average Ra roughness of the bare steel substrates before deposition was found to be 0.1 micron. DLN coatings follow the contours of the underlying substrate. The Ra roughness does not vary much after deposition. It is found to be 0.15 micron. 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 micron step in the profilometer scan of the substrate for DLN on SS 316 L combination. The coating had been grown for 100 minutes, thus the growth rate can be calculated to be 1.04 µm/hr. Bottom scan profile of figure 6 shows one 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 minutes (table 2). So the growth rate can be calculated to be 1.365 µm/hr. It has been found that typical growth rate varies between 1 – 3 µm/hr.

3.2 Mechanical Properties & Tribology

Mechanical properties alongwith roughness values of DLN coatings on steel and glass substrates have been tabulated in table 4. Indentation with 0.1N load was not clearly visible, so tests were performed with 1N & 3N loads. Figure 7a 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 in compare to 73 GPa for glass substrates. The literature values of hardness for this class of materials vary between 12-17 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 304L 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 7b 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 behavior of steel ball sliding against DLN coating under dry condition 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 90000 to 110000. The corresponding calculated wear factors are 1.26×10^{-7} mm^3/N-m and 1.33×10^{-7} mm^3/N-m respectively. Obviously the wear volume will increase if the ball is made to revolve for higher number of revolutions of 150000, but in that case the average COF strikingly increases to 0.143, much higher than 90000 and 110000 revolutions. Whereas the reported literature COF values for

such wear experiments have always been below 0.1 (Neernick et al 1998, Neernick et al 1998). 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 clear evidence of material transfer between ball and coated substrate. Figure 9 shows the profilometer scan of the wear groove. The depth of the groove shows 1.5 micron and whereas the coating thickness was less than one micron. This difference between coating thickness and wear track depth further confirms exposure of the underneath silicon substrate.

4. Conclusions

4.1 PECVD

1. DLN has been successfully deposited on many types of substrates, including polymers, glass, ceramics & metals (including aluminum, stainless steel, silicon) by PECVD.

2. There was no need for interlayer prior to DLN deposition on all the substrates.

3. Large area deposition (~ 3000 cm^2) has been achieved in the PECVD reactor.

4.2 DLN Coating

1. DLN films mainly consist of hydrogenated carbon (C:H) and oxygenated silicon (Si:O) networks, as evident from FT-IR spectra.

2. Presence of sp^3 carbon and sp^2 graphite inside the structure is evident from Raman Spectroscopy.

3. Films are not only x-ray amorphous but also it is nanocomposite in nature under TEM micrograph.

4.3 Mechanical Properties

1. DLN coatings follow the contours of the underlying substrate with the advantage of non-requirement of post-deposition polishing of well polished parts.

2. Substantial enhancement of the surface hardness is achieved with DLN coating.

3. Adhesion strength is better with metallic substrates than glass substrate which is essential for adhesive wear applications like hip joints and knee joints.

4. After depositing over different materials of biomedical importance, we have successfully deposited DLN coating on femoral components of CoCr 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.

Acknowledgements

We express our sincere gratitude to Dr. K. H. Sancheti for allowing us to coat indigenously developed “Indus Knee” orthopedic implant. Authors thank Dr. D. Dasu, Head, Bioceramics and Coatings Division to allow us to conduct the above research. Dr. Raghu Bhattacharyya helped in solving many technical problems through discussions. Soumya Sarkar has done the profilometer measurements. Dr. Sandip Bysakh kindly did the TEM measurements. Authors also thank Dr. (Mrs) S. Sen and Mrs S. Roy for their help in taking SEM micrographs. We are thankful to Dr. S.

Majumdar for allowing us to do XRD measurements. Mr. Guillaume Begin of Micro Photonics Inc. and Mr. Rajkishore Sahani of Material Testing & Metallurgy Group, Aimil Ltd. Kolkata have done hardness and scratch resistence testing of DLN coatings. We are grateful to Prof. Colin Bain for allowing us to use Raman facility.

References:

Bosley Robert W, Miller Ronald F 1998 October United States Patent 5827040

Bozhko A, Chudinov S M, Evangelisti M, Stizza S, Dorfman V F 1998 Materials Science and Engineering **C5** 265

Bursikova Vilma, Rehulkab Pavel, Chmelikb Josef, Albertia Milan, Spaltc Zbynek, Jancaa Jan, Havel Jose 2007 Journal of Physics and Chemistry of Solids **68** 701

Cooper Clark V, Tredway William K, Guile Roy N, Rhemer Chris C, Minick Alan B, Chapman Leonard W 2007 November Cryogenic bearings, United States Patent 7296965

D J Kester A, Brodbeck C L, I L Singer, Kyriakopoulos A 1999 Surface and Coatings Technology **113** 268

De Scheerder I, Szilard M, Yanming H, Ping X B, Verbeken E, Neerinck D, Demeyere E, Coppens W, Van de Werf F 2000 J Invasive Cardiol **12** 389

Ding Xing-zhao, Zhang Fu-min, Liu Xiang-Huai, Wang P W, Durrer W G, Cheung W Y, Wang S P, Wilson I H; 1999 Thin Solid Films **346** 82

Dorfman B F 1998 Thin Solid Films **330** 76

Dorfman V F 1992 Thin Solid Films **212:1/2** 267

Dorfman Veniamin F, Goel A 1998, March United States Patent 5728465

Dorfman Veniamin F, Pypkin Boris 1994 October United States Patent 5352493

Dorfman Veniamin F, Pypkin Boris 1995 November United States Patent 5466431

Emerson Terence P, Gu Alston L 1996 June United States Patent 5529464

F Platon, P Fournier, S Rouxel 2001 Wear **250** 227

Fred H Pollak, Benjamin Dorfman 1997 Thin Solid Films **292** 173

Grill A 2003 Diamond and Related Materials **12** 166

Hauert R, Muller U 2003 Diamond and Related Materials **12** 171

Hauert R 2003 Diamond and Related Materials **12** 583

Heshmat Hooshang 2000 December United States Patent 6158893

Jacquet J M, Wietig F G, 2006 30 November Patent number: WO 2006/125683

Kobayashi S, Ozeki K, Hirakuri K K, and Aoki H, 2006 Key Engineering Materials **309-311** 1289

Logothetidis 2007 Diamond & Related Materials **16** 1847

Maalouf R, Jaffrezic-Renault N, Vittori O, Sigaud M, Saikali Y, Chebib H, Loir A S, Garrelie F, Donnet C, Takeno T, Takagi T 2006 Journal of Advanced Science **18** 31

McNamara B P, Murphy H, and Morshed M M 2001 Diamond and Related Materials **10** 1098

Mukherjee S, Raole P M, Kumar A, Chattoraj I, Rao K R M, Manna I 2004 Surface & Coatings Technology **186** 282

Neerinck D, Persoone P, Sercu M, Goel A, Kester D, Bray D 1998 Diamond and Related Materials **7** 468

Neerinck D, Persoone P, Sercu M, Goel A, Venkatraman C, Kester D, Halter C, Swab P, Bray D 1998 Thin Solid Films **317** 402

Neerinck Dominique, Goel Arvind 2001 March United States Patent 6200675

Neerinck Dominique. Persoone Peter 2001 May United States Patent 6228471

Pandit A, Padture N P 2003 J Mat Sc Lett. **22** 1261

Polyakov V I Rukovishnikov A I, Perov P I, Khomich A V, Sukhanov A A, Dorfman B F, Pypkin B N, Abraizov M G, Druz B 1997 Thin Solid Films **292** 91

Prasad S V, Christenson T R, Dugger M T, Michael J R, and Vanecek C W 2003 American Society for Precision Engineering, Winter Topical Meeting - Volume 28

Rahaman M N, Yao A, Bal B S, Garino J P, Ries M D 2007 J. Am. Ceram. Soc., **90** 1965

Rao K. Ram Mohan, Mukherjee S, Raole P M, Manna I, 2005 Surface & Coatings Technology **200** 2049

Robertson J 1994 Pure Appl. Chem. **66** 1789

Robertson J 2002 Materials Science and Engineering R, **37** 129

Roger J Narayan 2005 Materials Science and Engineering: C **25** 398

Scharf T W and Singer I L 2003 Tribology Letters, **14** 3

Scharf T W, Ohlhausen J A, Tallant D R and Prasad S V 2007 J. Appl. Phys. **101** 0635211

Sheeja D, Tay B K, Nung L N 2005 Surface & Coatings Technology **190** 231

Venkatraman C, Brodbeck C, Lei R 1999 Surface and Coatings Technology **115** 215

Venkatraman C, Goel A, Lei R, Kester D, Outten C 1997 Thin Solid Films **308–309** 173

Yan Xing-bin, Xu Tao, Chen Gang , Xue Qun-ji, Yang Sheng-rong 2004 Electrochemistry Communications **6** 1159

Yang Won Jae, Auh Keun Ho, Li C, Niihara K 2000 J Mat. Sc. Lett. **19** 1649

Yang Won Jae, Choab Yong-Ho, Sekinoc Tohru, Shima Kwang Bo, Niiharac Koichi, Auha Keun Ho 2003 Materials Letters **57** 3305

Yang Won Jae, Choab Yong-Ho, Sekinoc Tohru, Shima Kwang Bo, Niiharac Koichi, Auha Keun Ho 2003 Thin Solid Films **434** 49

LIST OF FIGURE CAPTIONS

LIST OF TABLE CAPTIONS

Figure 1

Click here to download high resolution image

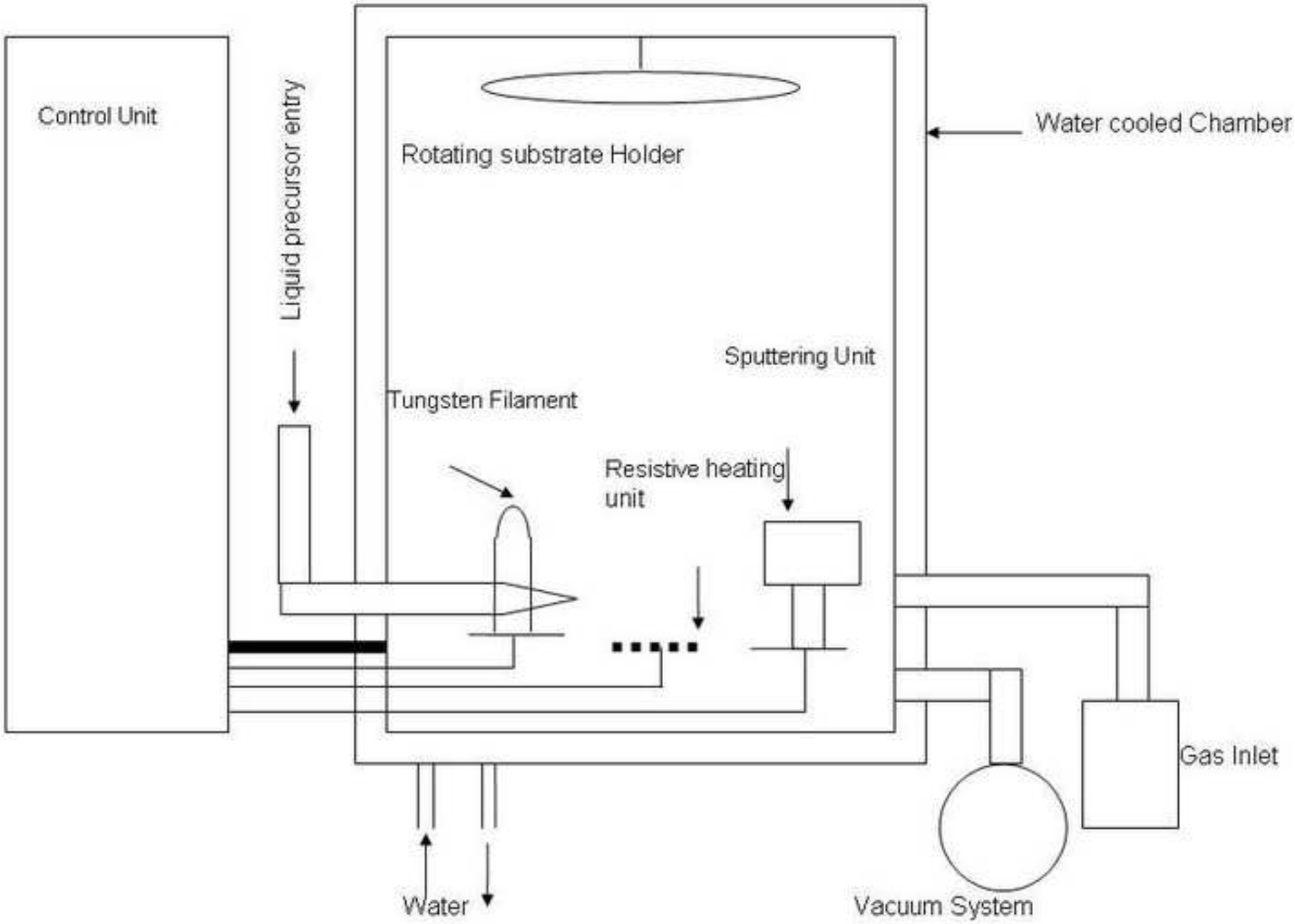

Figure 2

Click here to download high resolution image

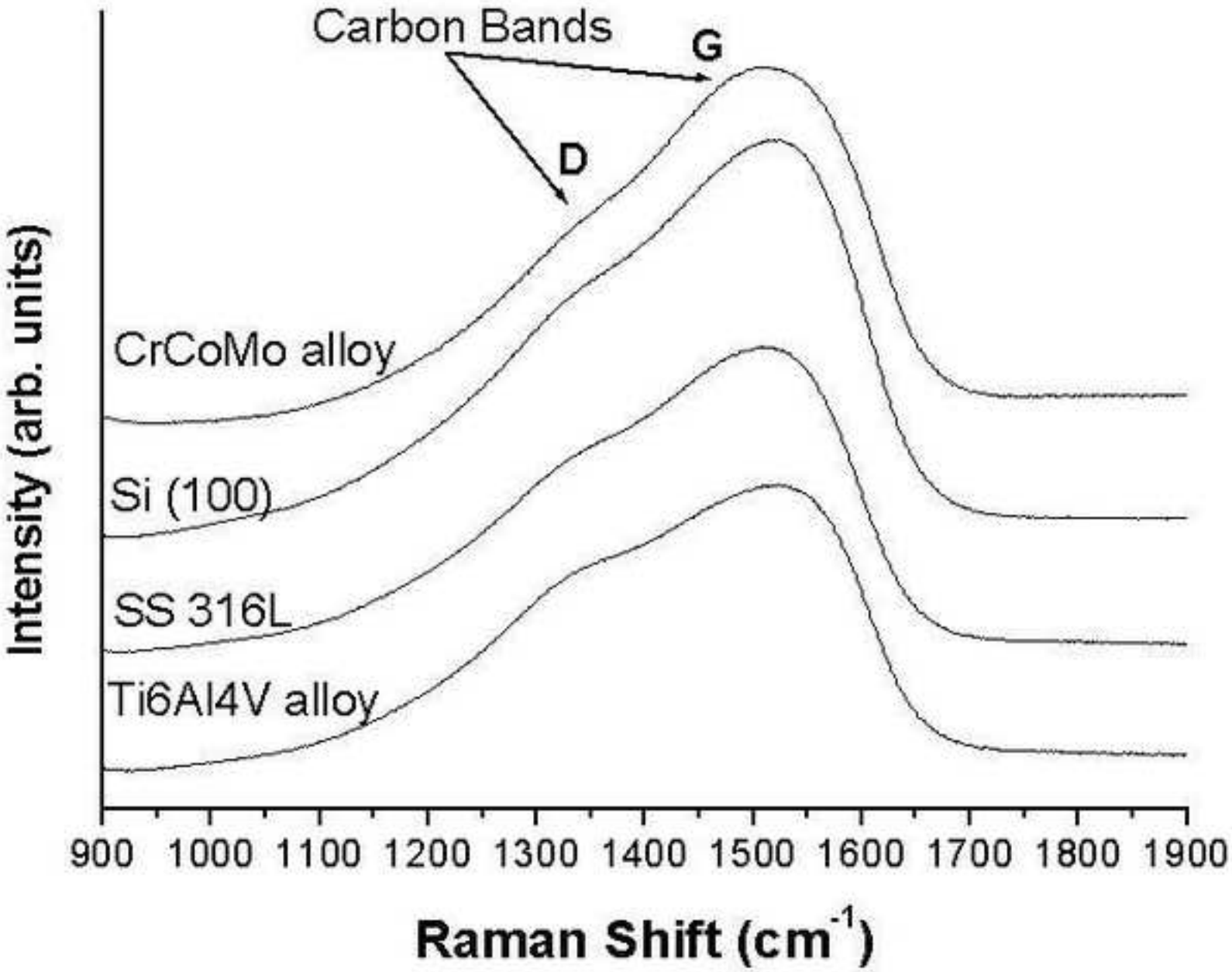

Figure 3

Click here to download high resolution image

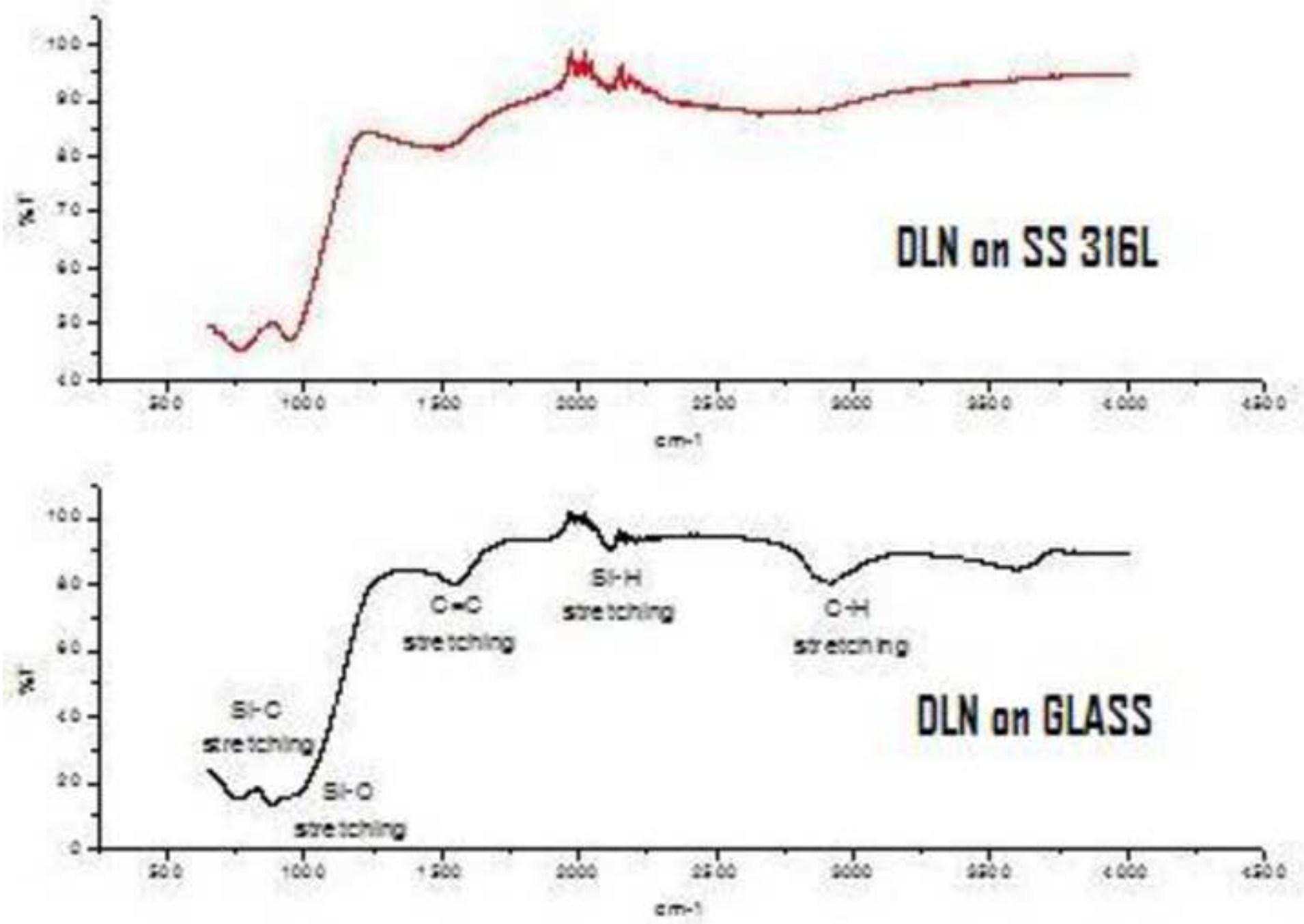

Figure 4

Click here to download high resolution image

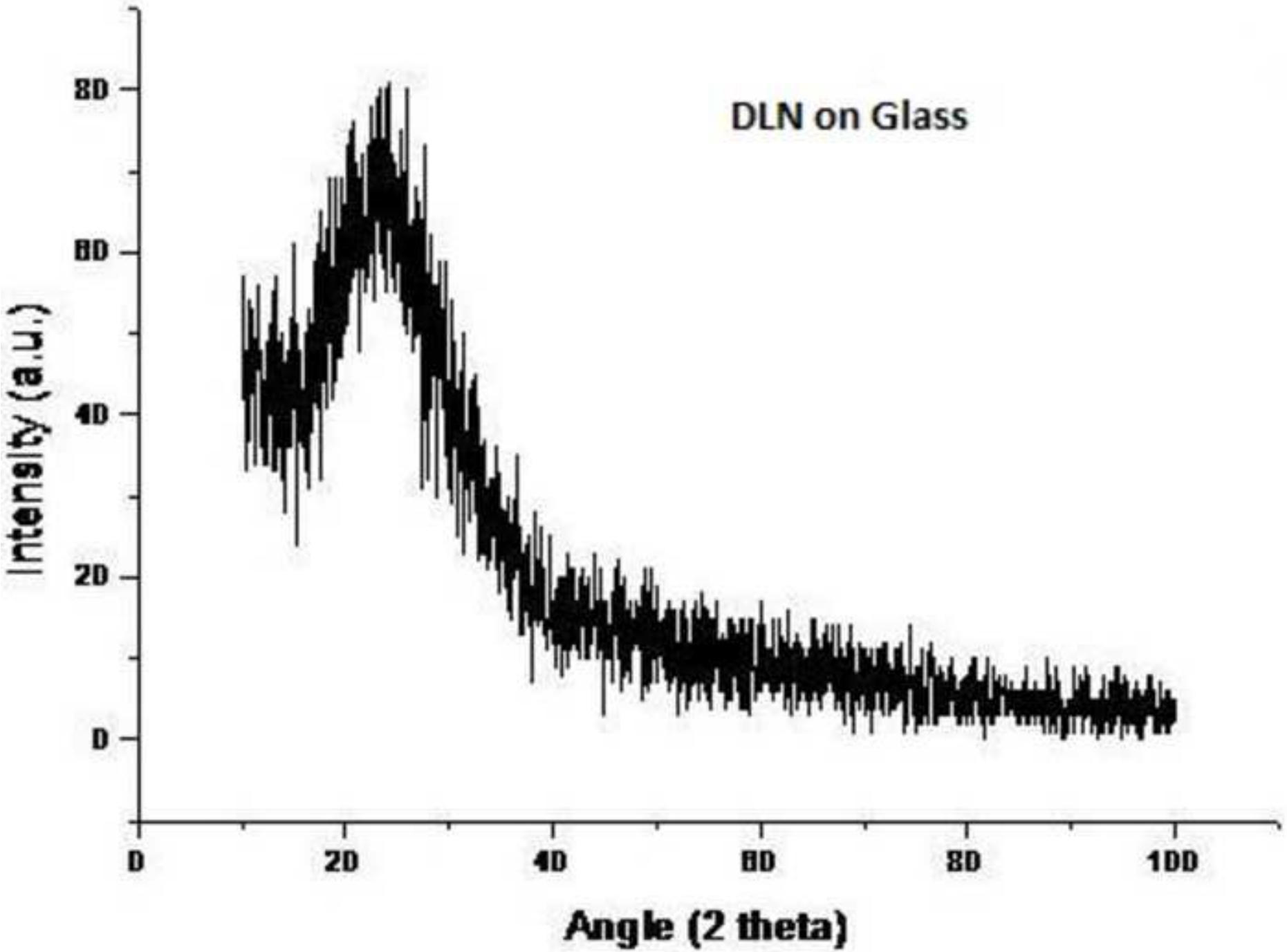

Figure 5
Click here to download high resolution image

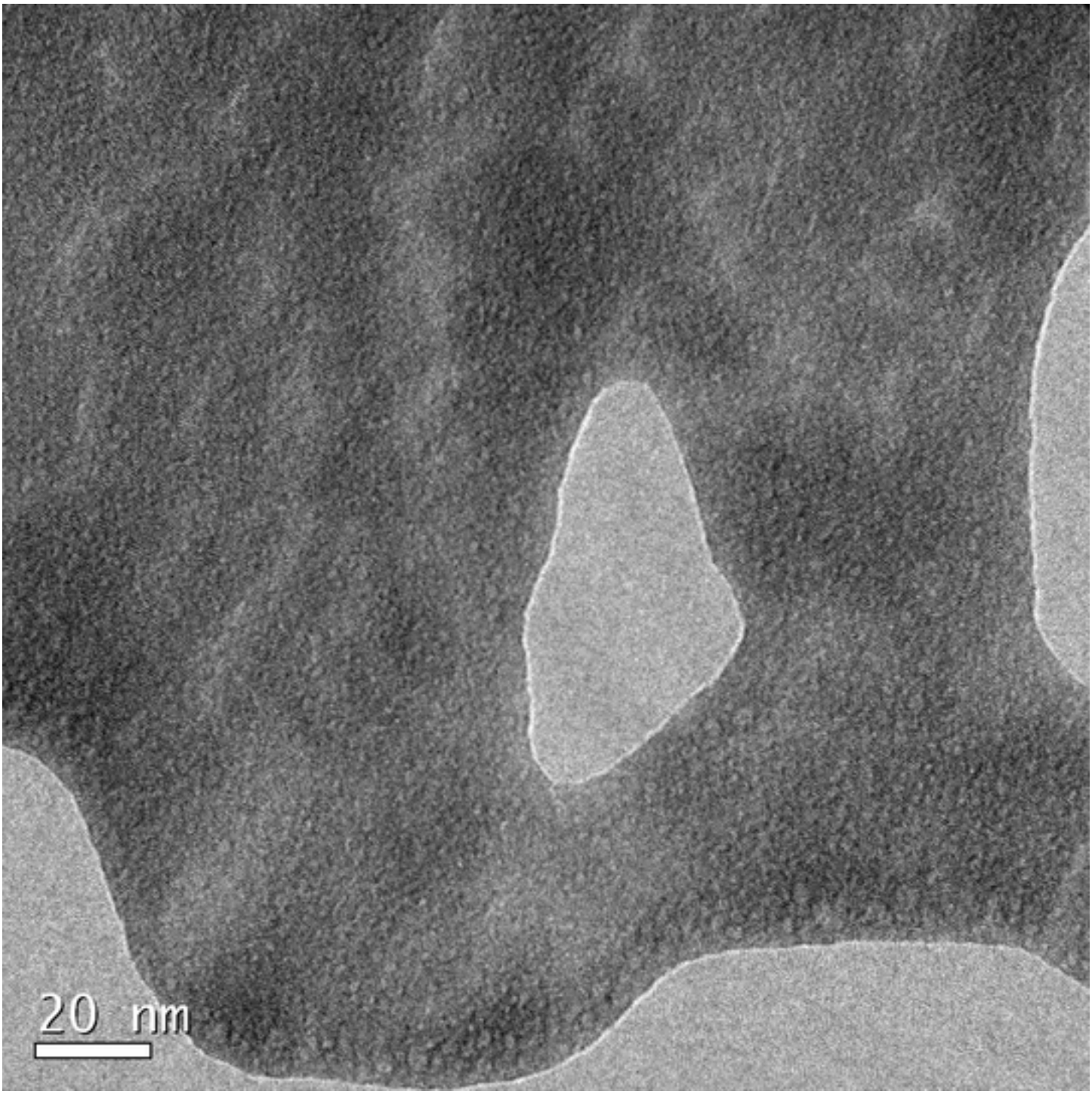

Figure 6

Click here to download high resolution image

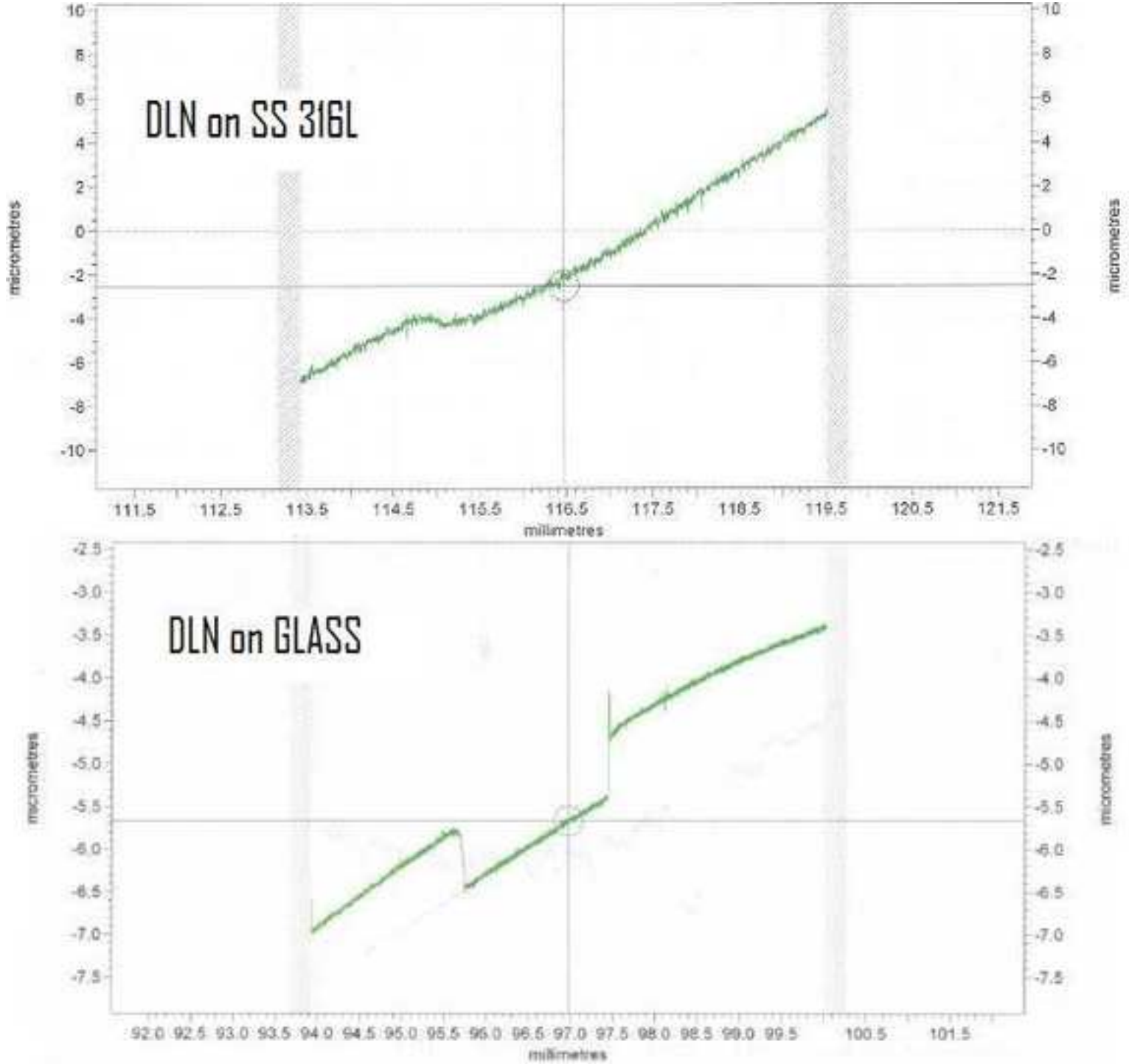

Figure 7
Click here to download high resolution image

FIGURE A Micrograph of indentations – GL 092 – 1N
500x magnification (image width 0.0625mm)

FIGURE B Micrograph of the initial delamination - Sample GL 092
100x magnification (image width 1.22mm)

Figure 8

Click here to download high resolution image

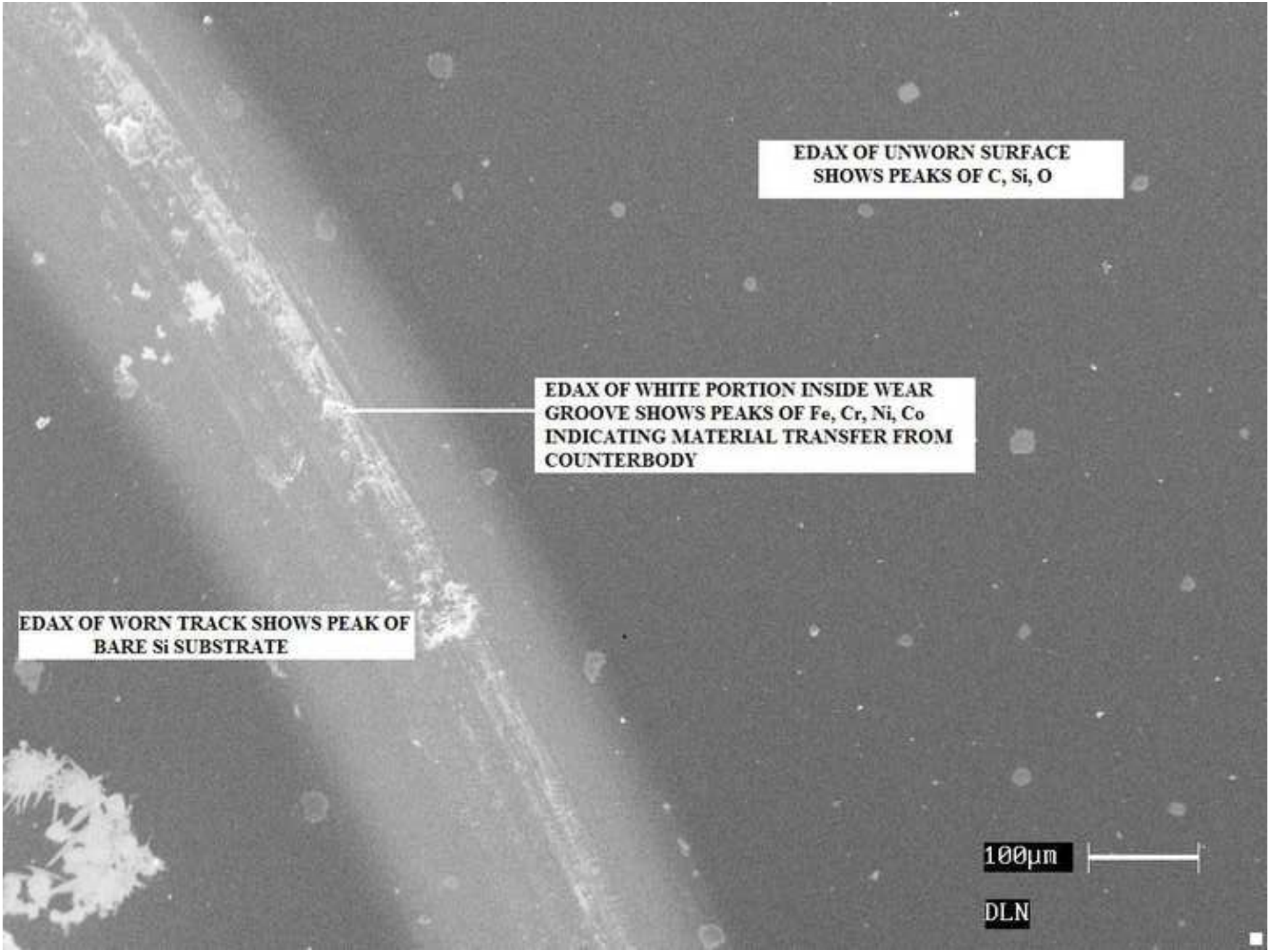

Figure 9

Click here to download high resolution image

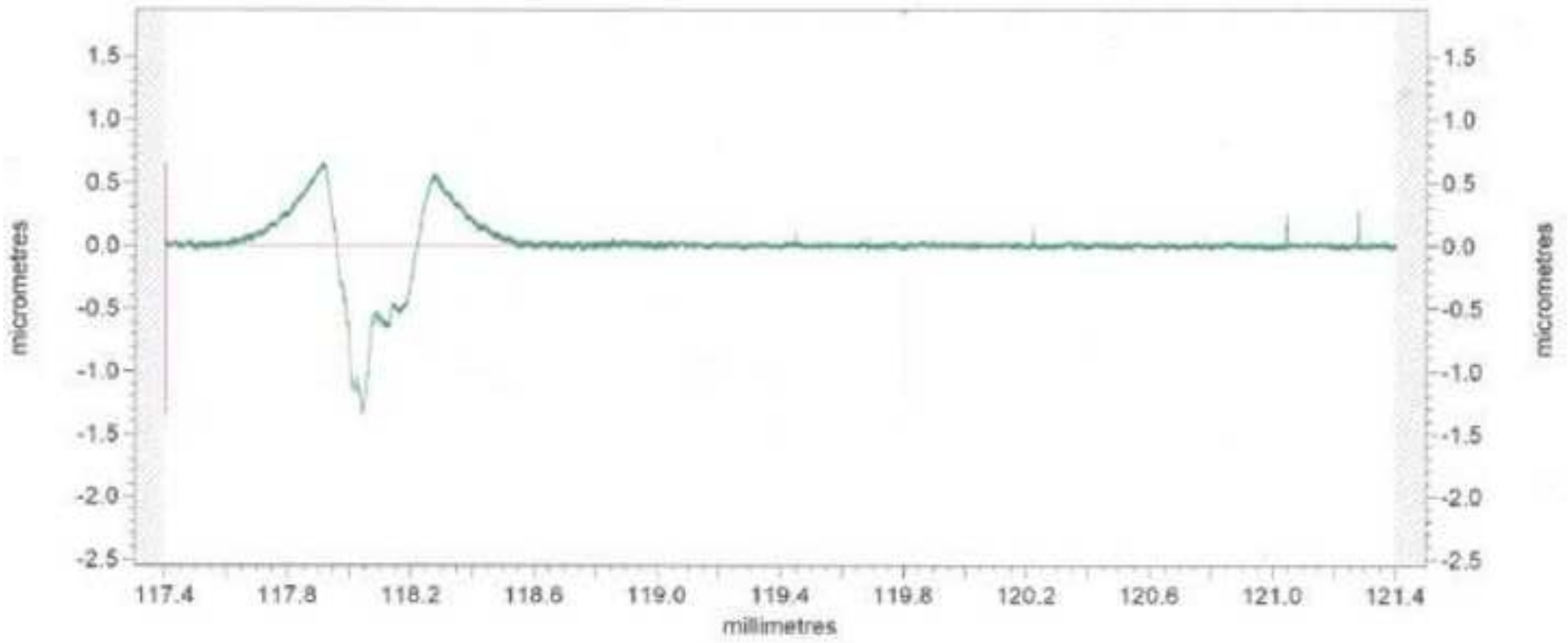

Figure 10

Click here to download high resolution image

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	8-10GPa	200-300 MPa
Dielectric Constant	-	-	3-9
Maximum Operating Temperature (^oC)	-	300	600 (O_2 atm) 1200 (O_2 free)

Table 2. PECVD Deposition conditions

Substrates	Precursor Flow rate (ml/10min)	Time of Deposition (min)	Total Precursor Used (ml.)	Bias Voltage (V)	Plasma Current (A)	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	5.76l	700	0.8	1×10^{-4}
Co-Cr alloy based Knee implant	1.6526	93	15.37l	700	0.8	5×10^{-5}

Table 3: Gaussian analyses of Raman spectra deconvoluted into D and G peaks in DLN films coated in different substrates (*v*: position, *Γ*: Full Width at Half Maxima, *I*: Integrated intensity)

Substrate	v_D **(cm^{-1})**	Γ_D **(cm^{-1})**	v_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 316L	1382.9	300.112	1529.08	145.306	2.19
Ti6Al4V alloy	1390.78	304.394	1541.07	138.599	2.71

Table 4. Mechanical Properties of DLN coatings

Sample	**Roughness Ra (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 ^{o}C	No. of revolutions	Wear (mm^3/N.m)	Co-efficient of friction
28.8	90000	1.26 E-7	0.043
30.4	110000	1.33 E-7	0.092
28.4	150000	1.79 E-7	0.143