DEPOSITION OF NANO DIAMOND LIKE CARBON FILMS USING DENSE PLASMA FOCUS DEVICE.

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ABSTRACT

Nano-Diamond like Carbon (Nano- DLC) thin films have been deposited for the first time using highly energetic, high fluence argon ions generated in Dense Plasma Focus (DPF) device in the absence of hydrogen atmosphere, which is reported in this paper. The films were characterized for their tribological, electrical, structural and optical properties. The films have smooth surface topography with a roughness average of 70Å – 100Å .The films have high deposition rate of 450 Å per shot of 100 ns duration. The films are free from compressive stress or pinholes. They have resistivity of the order of few mega ohms. The films having transmittance ~80% in the Ultra Violet region. Raman spectra of the films indicate presence of sp^3, sp^2 and even sp^1 coordinated carbon atoms in a disordered network. The SEM micrographs indicate presence of nanocrystallites in the films.

I. INTRODUCTION

Carbon exists in nature in different allotropic forms. It can be trigonally bonded graphite or tetragonal bonded diamond. Nano- Diamond like Carbon (Nano-DLC) is formed by controlled combination of diamond and graphite in an intimately mixed amorphous structure. The term DLC was first used by Aisenberg and Chabot[15] in reference to the films deposited by carbon ion beam. In contrast to amorphous carbons, this new form of carbon was hard, electrically insulating and wear resistant. Though it exhibited Diamond like properties, but the crystalline diamond order was missing. Due to its unique structural, mechanical, optical and electronic properties, DLC films have wide range of potential applications[7,9]. They are used for antireflection and protective coatings in IR and UV optics and tribological applications such as a mechanically hard, scratch resistant layer to coat cutting tools so as to protect them against wear and corrosion. DLC films also have potential application for electronic packaging, passivation and thermal heat sinks for high power devices because of their high thermal conductivity and electrical resistivity. Being biocompatible, wear resistant, and chemically inert, DLC films are also used to coat heart valves, rods inserted inside human limbs and contact lenses.

The potential applications of DLC films have stimulated a great deal of interest in present decade. Aisenberg and Chabot[15] were the first ones to make DLC films using ion beam deposition technique. Since then a variety of methods like dc sputtering, rf sputtering, magnetron sputtering, ion beam sputtering plasma assisted physical vapour deposition, plasma assisted chemical vapour deposition, ion beam deposition, fast atomic beam bombardment (FAB) technique, carbon arc evaporation, laser evaporation, VHF PECVD technique, etc. have been used to deposit DLC films.

In this paper we have presented the results of first ever deposition of DLC films by Dense Plasma Focus (DPF) device.

II. EXPERIMENTAL DETAILS

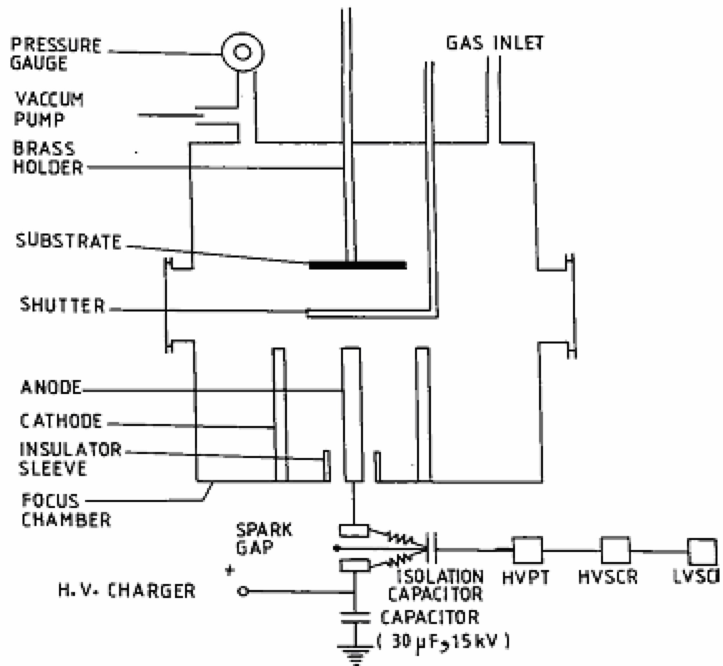

Figure 1: Schematic of Dense Plasma Focus device for deposition of nano DLC films

The Dense Plasma Focus Device (DPF) produces high temperature (1-2 keV) high-density plasma (10^{26} m^{-3}) for duration of about hundred nanoseconds having cylindrical shape[10]. The DPF is a coaxial gun accelerator consisting of two coaxial electrodes separated by an insulator sleeve. In Plasma research laboratory of Delhi University, we have a DPF device of Mather type. The schematic of DPF Device showing various subsystems is shown in Fig.1. The various subsystems of DPF are (i) focus chamber made of chromed mild steel. It is a cylindrical chamber consisting of coaxial assembly of electrodes with one anode surrounded by six symmetrically placed cathode around it (ii) the anode is made up of copper and graphite. (iii) High voltage power supply to charge the capacitors, (iv) the spark gap as fast switching device to transmit the high voltage from capacitor to the electrodes inside the focus chamber, (v) the triggering electronics to activate the spark gap switches and, (vi) focus diagnostic data acquisition system. The DPF Device is having energy of 3.3 kJ that is obtained by discharging a 30μf capacitor charged to15 kV. This device was used for depositing thin carbon films and fullerene films[1, 2] as well as for processing of materials [11 ,12,14].

The highly energetic, high fluence ions of DPF Device have been used for depositing thin films of Diamond like Carbon. The substrate is placed inside the vacuum chamber from top of the chamber with the help of a brass rod which can move up or down along the axial direction of central electrode. The substrate is connected to a heater and a thermocouple system. The focus chamber is evacuated and filled with Argon gas. The pressure inside the chamber is maintained in the range of 80-120 Pa. The focus is formed on the top of anode during radial pinch phase. We have deposited NANO DLC films on various substrates like silicon,glass and quartz at different substrate temperatures from 0 ^{o}C - 300^{o}C. However in the present paper we are presenting the results for the film deposited on quartz substrate at 300^{o}C

III. RESULTS AND DISCUSSION

TRIBOLOGICAL PROPERTIES

A. COLOUR AND PIN SCRATCH TEST

It was observed that films deposited were transparent ,scratch resistant and chemically inert to conc. HCl and conc. HNO_3. The films have shown no sign of peeling off even after months of deposition. This clearly indicates that films have low compressive stress.

B. SURFACE PROFILE AND THICKNESS MEASUREMENTS

The surface profiles and thickness measurements of the films have been investigated using Dektak profilometer. The average thickness of the films was 1800Å with four focused shots of carbon ions from Dense Plasma Focus device. Thus average deposition rate in the present case is 450 Å per shot. One DPF shot is of 100ns duration. The rate of deposition is much higher than most of the reported values in the literature[3,5,6]. The surface profiles of the films deposited by DPF device exhibit a smooth topography with a low roughness average ~70 Å -100 Å. Figure 2 shows a roughness average of 78 Å over a cross-section of 2 mm^2. We have measured the Knoop hardness of NANO DLC films using Volpert VTD-12 Knoop hardness indenter under a load of 50 grams. Thehardness of the films was found to be around 1800 kg/mm^2. The tabulated values for DLC films have been reported[3,5,6,8]to lie in the range of (900-3000) kg/mm^2 and our measured values are also found to lie in this range. DLC films with high hardness indicate the presence of major fraction of sp^3 bonded carbon atoms in the films.

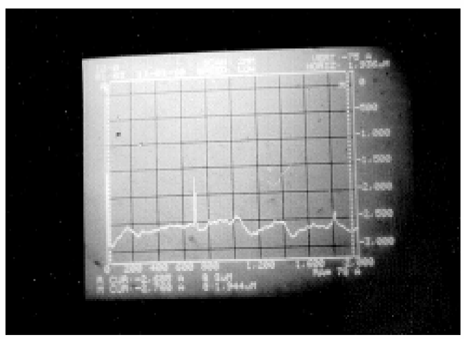

Figure 2: Surface profile of DLC film deposited by DPF device

ELECTRICAL MEASUREMENTS

Resistivity measurements on NANO DLC films were carried out by making two contacts on the film in a planar configuration. A dc voltage was applied between the two contacts using an Aplab 7336, medium voltage (0-300V) dc power supply. The current was measured by electrometer. The order of resistivity for films at moderate substrate temperatures is ~ 10^6-10^7 Ω cm. This indicates a large increase in sp^3 fraction in the films. Thus, the NANO DLC films deposited by DPF device are insulating in nature and can be used for electronic packaging.

1. STRUCTURAL PROPERTIES

A. X-RAY DIFFRACTION PATTERN

X-Ray diffraction spectra of the films were carried out using Phillips PW-1840 X- ray diffractometer. The diffraction pattern of the film is depicted in figure 3 and it indicates that the films do not possess a long-range order.

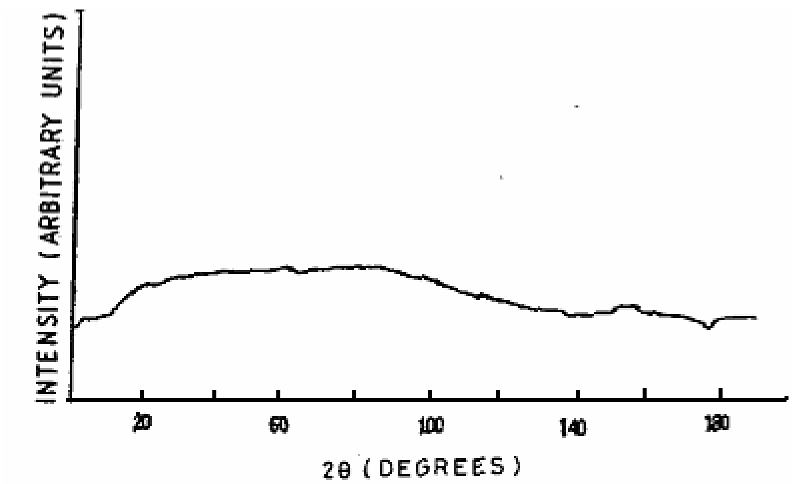

Figure 3: XRD Spectrum of DLC film deposited by DPF device

B. SCANNING ELECTRON MICROSCOPY

We analyzed the micrographs of our films using JEOL, JSM-1840 Scanning Electron Microscope. Fig. 4 depicts SEM micrographs of the NANO DLC film grown at 300^{o}C substrate temperature. The micrographs indicate the films are devoid of any holes or pits. The films are smooth. There is presence of nanocrystallite structures in the films.

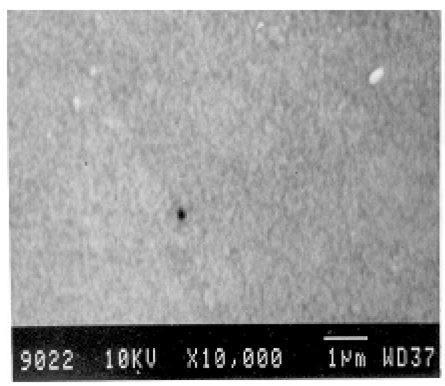

Figure 4: SEM Micrograph of DLC film deposted by DPF device

C. RAMAN SPECTROSCOPY

The Raman spectra has been recorded at room temperature with 514.5nm line of a spectra Physics 2030 Ar^+ laser in the backscattering geometry with a laser power of 5mW on the sample and 1200 lines/mm grating dispersed the scattered light. The spectra were recoded with a Spex Triplemate recorder equipped with a liquid Nitrogen cooled charge coupled device. A natural diamond was used for calibration of the spectra. Fig. 5 depicts the Raman spectra of the DLC film deposited by DPF device at 300 ^{o}C substrate temperature. The spectrum is asymmetric and broad. It was analyzed by deconvulating the spectra using Lorentzian fits and has been resolved into three peaks at 1350 cm^{-1}, 1500 cm^{-1} and 1580 cm^{-1}. The peak at 1580cm^{-1} corresponds to G band whereas that at 1350cm^{-1} corresponds to the D band. D band is activated by disorder induced in graphitic carbon due to sp^3 bonded carbon. The origin of the broad band around 1500 cm^{-1} is not clear although it has been reported in earlier works also[5,16]. This band cannot be associated with diamond phase whose structure does not allow any first order Raman modes higher than 1332 cm^{-1} even in the presence of disorder[16]. The Carbon films grown by pulsed laser evaporation of graphite[16] has this broad band and it is assigned to the five member carbon rings as observed through scanning tunnel microscopy. The broad bands as seen in the Raman Spectrum indicate an amorphous network of sp^2 and sp^3 bonded carbon atoms in our films. We have also estimated the percentage of sp^2 and sp^3 fractions in our films using Raman spectra. The sp^3 fraction n the DLC films deposited by DPF device has been found to be in the range of 40-60%.

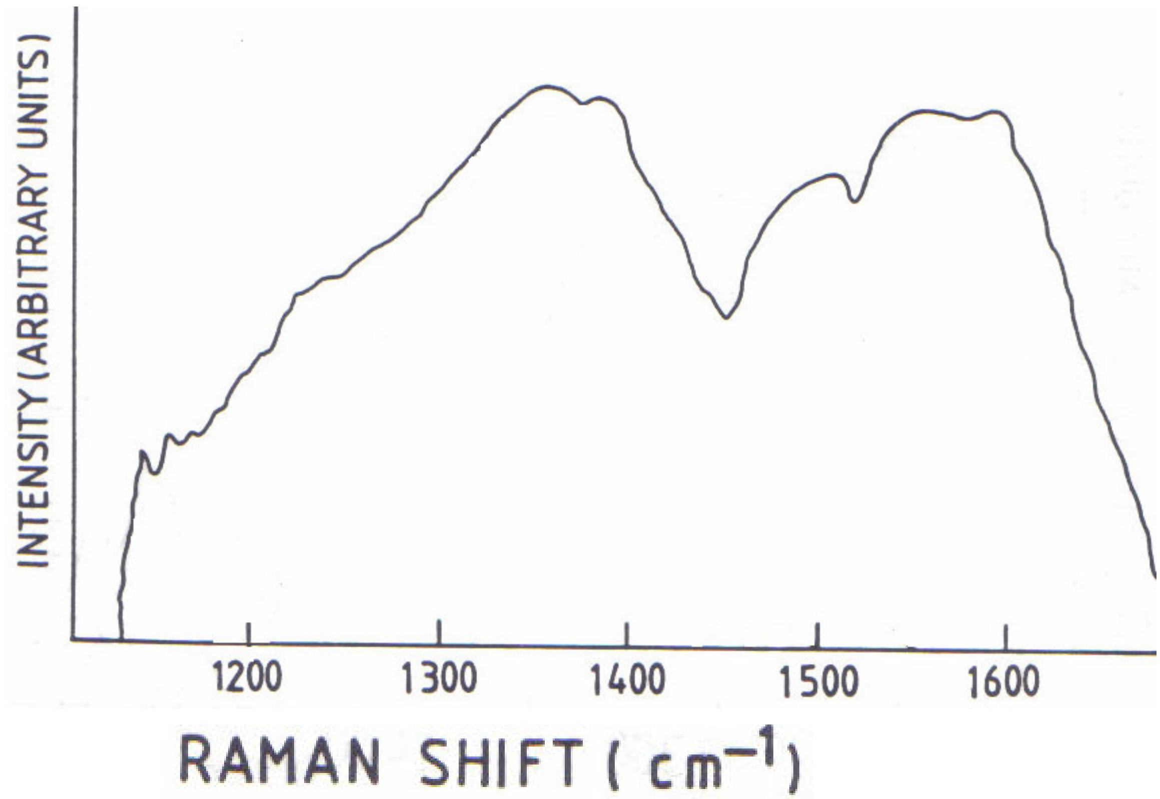

Figure 5: Raman spectrum of DLC film deposited by DPF device

2. OPTICAL CHARACTERIZATION

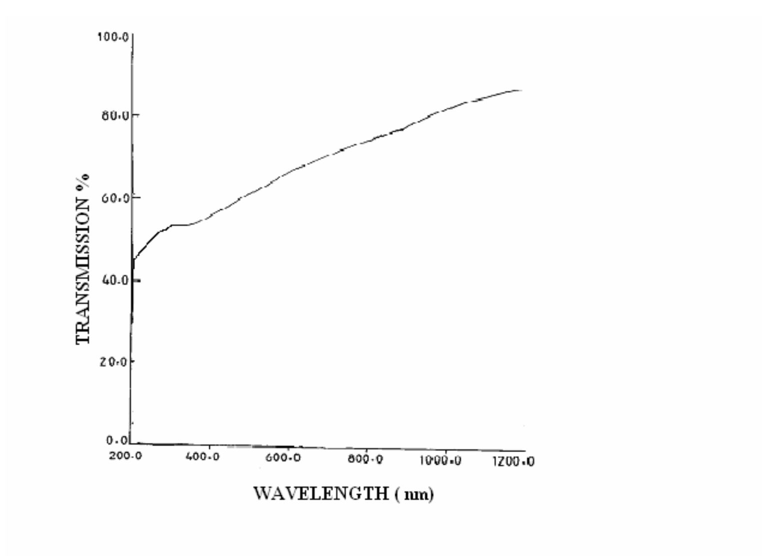

Figure 6: UV spectrum of DLC film deposited by DPF device

A. UV SPECTROSCOPY

The NANO DLC films were characterized for their optical properties in UV- visible range (200-1200nm) by using UV-260 spectrophotometer. Fig.6 shows the UV spectrum of the DLC film deposited by DPF device. The transmittance of the films was found to vary from 50% to above 80%in the wavelength range of 200-1200nm.

B. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The FTIR studies of the film was carried out using 510P Fourier transform infrared (FTIR) spectrometer. Fig. 7 depicts the transmission spectra of the films in the range 2200 cm^{-1} - 4000 cm^{-1} showing a transmittance of around 10%.

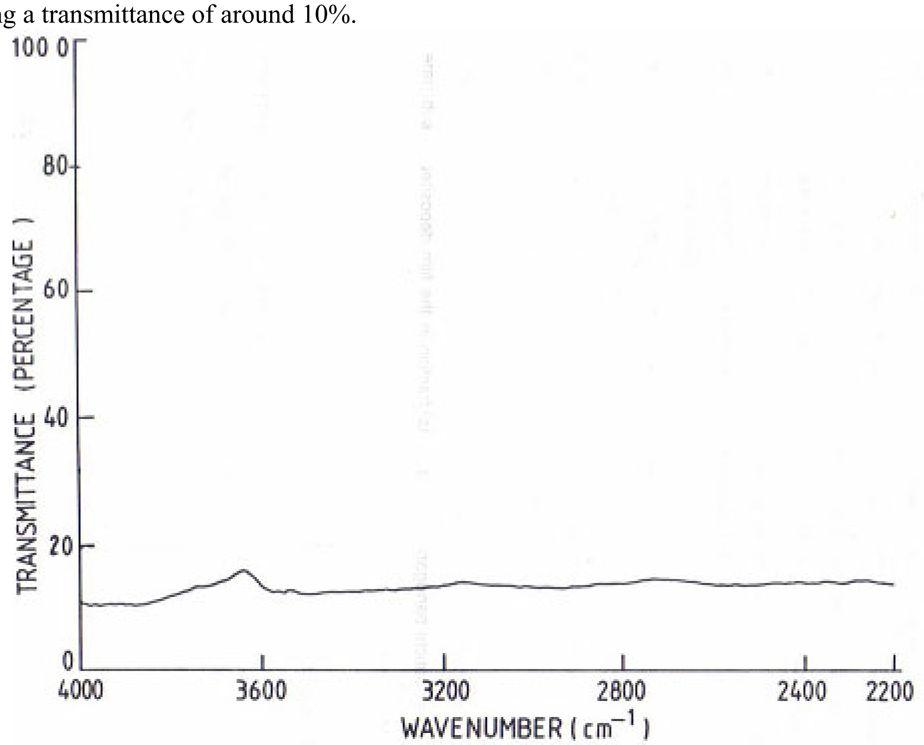

Figure 7: FTIR spectrum of the DLC film deposited by DPF device

IV. CONCLUSION

To conclude, we have deposited Nano-Diamond like Carbon films using Dense Plasma Focus Device on quartz substrate at moderate temperatures. This technique results in the growth of good quality Nano-DLC films in the absence of hydrogen atmosphere. Though the detailed dynamics of deposition of Nano-DLC thin films using DPF device is still under investigation by our group, we believe that most likely such DLC films originate from the thermal and pressure spikes produced by the impinging energetic species on the substrates. The formation of focus in DPF device occurs on the top of anode in radial pinch phase. In this phase, the plasma is compressed to very high densities due to radially inward $\mathbf{J_Z \times B_\theta}$ force leading to an anomalously high plasma resistance. Further due to the onset of certain micro instabilities, strong plasma heating occurs leading to the formation of a plasma plume with temperature of the order of 1-2 keV. This enormous high temperature of the plasma plume causes ablation of graphite. The ablated material moves towards the substrate and gets deposited in the form of thin film of Diamond like Carbon.

Nowadays most of the efforts are directed towards growing DLC films that have low compressive stress and good adhesion to substrates. Our films have shown no sign of compressive stress and no peeling off of the films have been observed even after months of deposition. Thus quality and properties of our films is good making the technique suitable for commercial applications.

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VI. REFERENCES

1. Chhaya R.Kant, M.P.Srivastava and R.S.Rawat 1997, Carbon film deposton using energetic ons of DPF device. Phys. Lett.A 226, 212.
2. Chhaya R.Kant, M.P.Srivastava and R.S.Rawat,1998, Fullerene films using energetic ions of DPF device, Phys. Lett A239, 109 .
3. C.V.Deshpandey and R.F.Bunshah,1989, Diamond and diamondlike films: Deposition processes and properties J.Vac.Sci.Technol.A7, 2294
4. D.Beeman, J.Silverman, R.Lynds and M.R.Anderson,1984, Surface characterization of various graphites by x-ray photoelectron, secondary ion mass, and Raman spectroscopies Phys. Rev. B 30, 870
5. D.Tither, A. Matthews, A.G.Fitzgerald, B.E.Storey, A.E.Henderson, P.A.Moir *et.al.*1990 Characterisation of carbon films containing boron and nitrogen, Carbon 27, 899.
6. D.Tither, A.Dehbi, P.Holiday, A. Matthews, A.G.Fitzgerald, A.E.Henderson, B.E.Storey, T.J.Dines, P.John and J.I.B.Wilson, 1990, The characterization of ultra-hard carbon films produced from pre-processed carbon powder in a hybrid physical vapor deposition system Carbon 28, 641.
7. H.Dimigen, H.Hubsch and R.Memming, 1987, Tribological and electrical properties of metal-containing hydrogenated carbon films, Appl. Phys. Lett. 50, 1056 .
8. J.C.Angus, P.Koidl and S.Domitz, 1986 "Plasma deposited thin films", ed.J.Mort and F. Jensen, CRC Press, Baca Raton: FL.
9. J.Robertson,2002, Diamond Like amorphous carbon, Mat.Science Eng R 271, 1-153
10. J.W.Mather, 1964, DPF Device, Phys. Fluids 7.
11. M.P.Srivastava, S.R.Mohanty, S.Annapoorni and R.S.Rawat,1996, Diode Like behaviour of ion irradiated polyaniline film, Phys. Lett. A215, 63.
12. P.Agarwala, S.Annapoorni, M.P.Srivastava, R.S.Rawat and Pratima Chauhan,1997, change of phase in hametite using DPF device, Phys. Lett. A231, 434.
13. R.J.Nemanich and S.A.Solin, 1979 First- and second-order Raman scattering from finite-size crystals of graphite, Phys. Rev. B20, 392.
14. R.Sagar and M.P.Srivastava,1993, Amorphization of CdS films, Phys. Lett.A183, 209 .
15. S.Aisenberg and R.Chabot, 1971, Ion-Beam Deposition of Thin Films of Diamondlike Carbon J.Appl.Phys. 42, 2953.
16. S.K.Solin and A.K. Ramdas, 1970, Raman Spectrum of Diamond Phys. Rev. B1,1687.
17. S.Scaglione and G.Emiliani,1989, Mechanical properties (hardness and adhesion) of *a*-C:H thin films produced by dual ion beam sputtering , J.Vac.Sci.Technol. A7, 2303.