Structure of hydrogenated diamond like carbon by Micro-Raman spectroscopy

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Abstract

The first-, second- and higher order Raman spectra of hydrogenated diamond like carbon (HDLC) are analyzed considering the effect of partial hydrogenation of hexagonal sp2 carbons on the characteristic G and D bands of graphitic materials. That coherency of sp3 C–H and sp2 C=C carbons in HDLC can produce a continuous, non-porous thin film having atomically smooth surface is reported as a new result.

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1. Introduction

The reactive chemical groups (C=C, C–H) present in the hydrogenated diamond like carbon (HDLC) film, provide a model substrate for protein immobilization onto it and its biosensing properties [1]. These unique characteristics of HDLC have been characterized by Micro Raman spectroscopy in the present work.

2. Experimental

The synthesis of HDLC film is described elsewhere [1]. The cross sectional view and also the morphology of the surface of the HDLC film have been analyzed by transmission electron microscopy (TEM), and atomic force microscopy (AFM), scanning electron microscopy (SEM) respectively. Raman spectra were obtained using a confocal Micro Raman spectrometer (LabRAM HR Vis, Horiba Jobin Yvon SAS France). For the excitation wavelength 488 nm, grating 1800 g/mm, 100× objective having numerical aperture (NA) 0.9 giving the best confocality i.e. the depth of focus ~2 μm, there is no loss of Raman signal with the confocal hole size 100 ± 5 μm. Since the maximum diameter of the illuminated spot (~1.22 × λ/NA) on the HDLC sample is less than 1 μm, there is hardly any loss of Raman signal from the sample under the above mentioned operating conditions of the spectrometer. Also the depth of focus (~2 μm) being much larger than the thickness (~168 nm) of the sample as shown in the TEM cross-sectional view (Fig. 1), the Raman spectrum measures bulk of the sample. The observed Raman spectrum (Fig. 2A), recorded at exposure 10 s and repetitions 10, extends over a range of frequencies with a non-zero line width. In addition, it's center shifted from its well defined central frequency (~1580 cm−1). A Gaussian profile describes broadening effect due to randomly distributed Raman signals from the sample, with no associated shift, while a Lorentzian profile describes both effects — broadening and shift, due to the structure of the sample interacting coherently. Raman spectra are deconvoluted in expectation of multiple chemical environments within the HDLC film, a graphite-based system [2]. Lorentzian peak shapes are used for all Raman modes, resulting in best fits of the broad spectral envelope.

3. Results and discussion

Typical Raman spectrum of HDLC film over the 1000–4000 cm−1 range (Fig. 2A) exhibits an increasing photoluminescence background which is typical of disordered sp2 carbon structure [3,4]. In the case of a disordered hydrogenated carbon sample we can expect various effects on the position and broadening of G and D bands etc. [2,4]. Thus as per our expectation, the broad peak envelops corresponding to first-, second- and higher-order Raman features after subtraction of the photoluminescence background are shown in Fig. 2B–D respectively.

The first-order Raman spectrum (Fig. 2B) is comprised of six overlapping Lorentzian peaks; the red-shifted G band (~1540 ± 1 cm−1) to lower frequencies follows a 1/n dependence on the number of sp2 carbon layers n [5] and is a signature of strained carbon–carbon bonds [6]; the D band (~1366 ± 1 cm−1) is a signature of lattice motion away from the center of the Brillouin zone lying between 1270 and 1450 cm−1 depending upon the excitation wavelength and indicating symmetry breaking i.e. disorder induced in the hexagonal sp2 carbons due to hydrogenation [7]; presence of nanocrystalline diamond (NCD) line (~1255 cm−1) having significant downshift (Δν~77 cm−1) w.r.t
pure diamond (sp³ C–C) line (~1332 cm⁻¹) signifies conversion of sp² C–C into sp³ C–H due to hydrogenation and large broadening (full width at half maximum, FWHM ~173±16 cm⁻¹) of the Raman line is interpreted as phonon confinement in NCD (sp³ C–H) domains of less than 1 nm in size [8]; the estimated ratio of G and D band intensities (I_G/I_D) being less than 1 can be interpreted as size of defects should be less than 1 nm in size [4] i.e. if we assume sp³ C–H domains as defects in the sp³ C=C carbon matrix, then our above interpretations from broadening of Raman line and ratio of G and D band intensities seem to be plausible. The sum and difference in combinations of C–C chain stretching and C–H wagging modes [ν₁ and ν₂ modes of trans-polyacetylene (trans-PA)] appear at ~1145±4 cm⁻¹ and ~1485±3 cm⁻¹ respectively [9]. The dumbbell defect in NCD, called D′, appears at ~1593±1 cm⁻¹ [8]. Thus the first-order Raman spectrum (Fig. 2B) signifies effects of (i) strain in carbon–carbon bonds, (ii) multilayer of sp³ C–H carbons embedded in sp³ C=C carbon matrix and (iii) disorder induced in the sp³ C=C carbon matrix by its hydrogenation.

The second-order Raman spectrum (Fig. 2C) comprising of 4 overlapping Lorentzian peaks is a signature of four possible double resonance (DR) Raman scattering processes in the hexagonal sp² C=C carbon matrix [7]. The four bands 2701±4 cm⁻¹, 2644±3 cm⁻¹, 2677±2 cm⁻¹ and 2733±4 cm⁻¹ correspond to that for pristine monolayer of graphite (PMG), red-shifted 2D band due to high and low strain on PMG, and blue shifted 2D band of multilayer of sp³ C–H carbons embedded in sp³ C=C carbon matrix respectively [4,6]. This result on second-order Raman spectrum (Fig. 2C) indicates double resonance Raman scattering process in the thin HDLC film as predicted for all kinds of sp³ carbon materials [7].

The higher-order Raman spectrum (Fig. 2D) comprising of five peaks (2858±0.3 cm⁻¹, 2993±0.6 cm⁻¹, 3076±2 cm⁻¹, 3130±3 cm⁻¹, 3247±2 cm⁻¹) is a signature of stretch modes of sp³ C–H, sp²=C=C=H bands [10], G+D′ band, due to defects introduced by the hydrogenation of sp³ C=C carbon matrix [4].

Thus Raman spectroscopy suggests that HDLC carbon film is made of multilayer of coherent domains of sp³ C–H and sp² C=C carbons.

From the position of G band in the Raman spectrum of HDLC film we can estimate, using an empirical relation sp³ content = 0.24–48.9 (ω–0.1580), approximately 45% sp³ and 55% sp² carbons in the film [11]. Our result is similar to the 40:60 ratio observed in amorphous hydrogenated carbon films having hexagonal graphite and diamond as coherent domains [12].

Hydrogenation of hexagonal sp² carbon matrix deposited onto Si (1 0 0) substrate should produce stress in the film, which can be studied from the shape and width of Raman lines [13]. Accordingly, stress

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**Fig. 1.** Typical TEM cross sectional view of the HDLC film measured with a Philips CM 200 kV TEM machine operated at 200 kV with LaB₆ filament; the cross sectional sample was prepared by the TEM sample preparation equipments of Gatan, USA.

**Fig. 2.** A. Typical Raman spectrum of HDLC film over the range 1000–4000 cm⁻¹. B. First-order Raman spectrum of HDLC film over the range 1030–1800 cm⁻¹. C. Second-order Raman spectrum of HDLC film over the range 2600–2750 cm⁻¹. D. Higher-order Raman spectrum of HDLC film over the range 2800–3300 cm⁻¹.
α (GPa) within the HDLC film is estimated from the Raman shift Δν (cm⁻¹) of the NCD line using the relationship \( Δν = ν - ν_0 = -ασ \), where α is pressure coefficient and \( ν_0 \) is taken to be the Raman peak position (-1332 cm⁻¹) of natural diamond when no pressure is applied. The NCD line near \( ν = 1255 \) cm⁻¹ is less than \( ν_0 \), indicating a positive tensile film stress. Net stress within a deposited film \( σ_{net} \) has been construed to arise from three potential contributions following the simple additivity relationship \( σ_{net} = σ_{TH} + σ_{IN} + σ_{lum} \), where \( σ_{TH} \) is thermal stress, \( σ_{IN} \) is the sum of all internal stresses, and \( σ_{lum} \) is stress due to lattice mismatch. HDLC Raman spectra are consistent with tensile stress, suggesting that \( σ_{TH} \) does not dominate \( σ_{net} \) and we have consequently assumed that \( σ_{TH} \) can be neglected as a first-order approximation. Furthermore, we observe that the Raman shift associated with lattice stress is only ~77 cm⁻¹, to be compared to 200 cm⁻¹ anticipated for large lattice mismatches. Thus, it is apparent that \( σ_{IN} \) is small compared to \( σ_{net} \) and that \( σ_{IN} \) could be ignored as a first-order approximation. Collectively, these considerations led to the conclusion that total tensile stress in HDLC film is due primarily to \( σ_{IN} \).

Bagilo et al. [14] states that \( σ_{TH} \) is due to attractive forces across grain-boundaries and that \( σ_{IN} \) can rise to GPa proportions for nanometer-sized crystallites, sufficient to cause grain coalescence. In our case, sp³ and sp² carbons exist coherently in the film as concluded from Raman analysis above and thus the internal stress in the film should develop as a result of a partial conversion of sp² → C into sp³ C – H. Indeed, using \( α ≈ 1.9 \) cm⁻¹/GPa and \( Δν = 77 \) cm⁻¹, we estimate the \( σ_{net} \) associated with the NCD line in HDLC to be tens of GPa, implying that sp³ C – H domains within HDLC must be nanometer in dimension, consistent with Raman analysis above [13]. Furthermore, FWHM of the 1255 cm⁻¹ NCD line (~173 ± 16 cm⁻¹) is consistent with phonon confinement in nanometer-sized regions [13]. All evidence taken together led us to conclude that internal tensile stress within HDLC film is caused due to partial hydrogenation of sp² → C=–C carbon matrix, resulting in sp³ C – H carbons.

Fig. 3A is typical featureless secondary electron (SE) image of the HDLC surface and Fig. 3B is typical AFM topography image of the HDLC surface, giving its roughness value (~0.01 nm). These results (Fig. 3A and B) are consistent with an atomically smooth, non-porous continuous film. It may be referred [15] that ultrananocrystalline diamond of uniform grain size (3–5 nm) can produce continuous film having surface roughness ~7–15 nm only after achieving its thickness greater than 300 nm. Therefore our results show that instead of discrete grains, coherent domains of sp³ → C – H and sp² → C – C carbons can produce continuous, non-porous thin film having atomically smooth surface.

4. Conclusions

In conclusion, that coherency of sp³ C – H and sp² C=–C carbons in the HDLC can produce a continuous, non-porous thin film having atomically smooth surface, instead of discrete uniform grains as in the case of ultrananocrystalline diamond film, is a new result.

Acknowledgments

NRR thanks the Department of Atomic Energy, Govt. of India, for funding XI plan project Diamond Nanotechnology for BioApplications. We thank Prof. T. K. Chini and Mr. S. Banerjee for recording SEM images, Dr. A K Srivastava for recording cross-sectional TEM view and Mr. S. S. Sil and U. S. Sil for technical help.

References

Study of depth profile of hydrogen in hydrogenated diamond like carbon thin film using ion beam analysis techniques

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Abstract

The Hydrogenated Diamond Like Carbon (HDLC) thin films are deposited on Silicon substrate at room temperature using asymmetric capacitively coupled RF plasma with varying flow rates of methane. These films are undergone annealing at high vacuum (\~{}10^{-7} \text{torr}) and high temperature (750 and 1050 \text{C}) furnace. The as-prepared and annealed HDLC films have been depth profiled for hydrogen using the resonance at 6.44 MeV in $_{1}^{1}\text{H}(^{19}\text{F},2\gamma)^{16}\text{O}$ nuclear reaction. The as prepared films exhibit non-uniform depth distribution of hydrogen: it decreases with depth. Annealing in vacuum brings about is a significant desorption of hydrogen from the films. Loss of hydrogen, albeit in much lower proportions, is also induced by the bombarding beam. The films also experience a mild loss of carbon, as shown by proton backscattering spectrometry, during high vacuum annealing. The depth profiles of hydrogen in the annealed films are indicative of the prevalence of graphitic carbon near film–substrate interface.

1. Introduction

In recent years, diamond like carbon (DLC) films has attracted a great deal of research interest as they have enormous possibility for technological applications [1,2]. Depending upon atomic structure of DLC films, the behavior of the film is diamond like. For example, opaque samples with hardness one-fifth of that of diamond and the transparent ones nearly as dense and hard as diamond [3] have considered as DLC films. The films with 20–40% of hydrogen content are commonly known as hydrogenated DLC (HDLC) films. In general, the physical and chemical properties of carbon materials, having sp3 (diamond like) and sp2 (graphite like) bonds in different ratio in the carbon matrix, may be different compared to pure graphite or diamond. We have demonstrated earlier [4,5] that HDLC films, deposited onto Si (100) substrate by reactive gas-plasma process, are composed of an ordered hexagonal structure of carbon atoms with lattice parameters $a = 2.62 \text{Å}$ and $c = 6.752 \text{Å}$ different to those present in a hexagonal graphite structure. Further structural investigation by confocal micro Raman spectroscopy [5,6] shows that coherency of sp3 C–H and sp2 C=C carbons in the HDLC can produce a continuous nonporous thin film (thickness $\approx 168 \text{ nm}$) having atomically smooth surface. Recently, the signature of interlayer disorder region in the HDLC film has been observed when Raman spectra of as-prepared HDLC and annealed HDLC samples are compared [5,6]. Due to existence of layer disorder, the 3D crystallinity of the HDLC should be lost, while only the 2D crystallinity should be preserved [7]. The Raman spectra do not tell us about why and how the interlayer disorder region is created in the HDLC film. The main effect of hydrogen in HDLC films is to modify its C–C network at different depth of the film. How these modifications occur at various depth of the HDLC film during its synthesis onto Si(100) substrate cannot be studied by Raman spectroscopy or X-ray photoelectron (XP) spectroscopy method, because (i) the skin depth of the 488 nm excitation source, which we have used in Raman measurements, is $\approx 6 \mu \text{m}$ and using this technique we get information for the whole material rather than at different depth of the thin film having thickness $\approx 168 \text{ nm}$ (ii) XP spectroscopy [8,9] is a surface sensitive probe in our case, because here the skin depth for X-rays is $\approx 5 \text{ nm}$. These earlier works [5–7] motivate us to explore the distribution of hydrogen in the film along its depth by ion beam analysis (IBA) techniques, viz., nuclear reaction analysis (NRA), Rutherford backscattering (RBS) techniques, in order to know how hydrogen modify C–C network in the HDLC film onto Si(100) substrate.

Keywords:
Hydrogen
Depth profile
Diamond like carbon
Thin film
Ion beam analysis

Article info

Article history:
Received 28 November 2013
Received in revised form 24 February 2014
Accepted 24 February 2014

http://dx.doi.org/10.1016/j.nimb.2014.02.127
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2. Experimental

The HDLC thin films are deposited on mirror-polished Si (100) substrate at room temperature using asymmetric capacitively coupled RF 13.56 MHz plasma system. The depositions are made systematically as follows: a pretreatment of the bare mirror-polished Si (100) substrate has been done for 15 min using pure hydrogen plasma at pressure of 0.2 mbar and dc self-bias of −200 V. The deposition has been made for 30 min at pressure of 0.7 mbar keeping the flow rate of helium (He) at 1500 SCCM (SCCM denotes cubic centimeter per minute at STP), hydrogen (H2) at 500 SCCM, and varying the flow rate of methane (CH4).

Four samples for which the CH4 flow rates are 20, 30, 40 and 70 SCCM, thus grown with varying H2 to CH4 ratio during deposition at room temperature (RT), will be represented as samples A, B, C and D, respectively, in the rest of the article. The samples A–D, annealed at high temperatures 750 °C and 1050 °C in high vacuum (~1 × 10−7 torr) furnace, in order to study removal of hydrogen from the samples, will be represented as annealed (750 °C/1050 °C) samples A–D in the rest of the article.

Nuclear reaction analysis (NRA) [10,11], a non-destructive nuclear method for depth profiling, has been applied for the quantitative determination of hydrogen at different depths of the nuclear method for depth profiling, has been applied for the quantitative determination of hydrogen at different depths of the as-prepared and annealed samples A–D, using the resonant at 6.44 MeV for the reaction 1H(19F,3+) beam in the scattering chamber under vacuum 10−6 mbar. The Rutherford backscattering (RBS) [12–14] on the as-prepared and annealed samples A–D, with 1.0 MeV proton beam is carried out to measure the thickness of HDLC films. Both NRA and RBS measurements are carried out by a 3 MV Tandetron accelerator at the surface and profile measurement laboratory of the National Center for Compositional Characterization of Materials (NCCCM), Hyderabad, India.

2.1. NRA measurements

Depth profiling of hydrogen in the samples A–D are accomplished by bombarding the sample at normal incidence with a well-collimated (dia. 2 mm, current 3 nA) trisupersized fluorine ion (19F3+) beam in the scattering chamber under vacuum 10−6 mbar. The characteristic gamma rays for the reaction 1H(19F,2γ)16O are monitored using a bismuth germanate (BGO) semi-conductor detector having efficiency ~10% and placed at a distance of 2 cm behind the sample along the direction of the incident beam. The characteristic gamma rays from the produced isotope 16O are 6.1, 6.9 and 7.1 MeV. A guard ring, with a bias of −900 V is positioned in front of the sample to suppress secondary electrons. The beam current incident on the sample is measured by Faraday cup arrangement [15]. The γ-ray yield of the reaction was obtained from the integrated counts between 4.8 and 7.1 MeV energy window of the PC-based multichannel analyzer, and this is found to give significant counts in the present experimental set.

The measurements for depth profiling in the sample and standard (viz., mylar) [16–18] are performed in the following steps: (i) γ-yield is measured at off-resonance region (beam energy below 6.44 MeV) to have the contribution of the background for each sample (ii) energy of the incident ion beam is increased in steps of 20 keV/40 keV above the resonance energy 6.44 MeV till the integrated counts in the region of interest are equal or less than that of the off-resonance counts. In the above two steps, the typical beam currents for both sample and standard are of the order of 3 and 2 nA for a ~2 mm diameter spot. Two sets of measurement (in steps of 20 and 40 keV) are carried out for each sample in the different regions to get the reproducibility of the results. The desorption phenomenon is studied for our specimen and standard which are treated at the same conditions of the beam and the integrated counts in the multichannel analyzer are recorded in every 250 nC, until total charge in the Faraday cup is 5000 nC.

2.2. RBS measurements

RBS measurements on HDLC thin films (as prepared and annealed) are carried out in the scattering chamber under vacuum ~5 × 10−6 mbar by with 1.0 MeV proton beam from the same Tandetron accelerator. The backscattered particles are detected by a silicon surface barrier (SSB) detector at an angle of 170°.

2.3. Methodology and technical details

2.3.1. Expression for hydrogen content determination using NRA technique

The atomic fraction of hydrogen in the HDLC film (considering as a binary film, C1xH2−x) is estimated by the following equation [19]

\[ f_{\text{HDLC}}^H = \frac{f_{\text{std}}^H}{Y_{\text{std}} + f_{\text{std}}^H (\varepsilon_{\text{HDLC}} - \varepsilon_{\text{HDLC}}^H)} \]

where \( Y \) is the ratio of gamma yields for standard and sample, \( f \) is the atomic fraction of hydrogen in the film material given in subscript, \( \varepsilon \) and \( \varepsilon' \) are the stopping power for the standard and the ith element having in the superscript. The ratio of yields, \( Y \), is obtained from the γ-ray yields in the NRA measurements. The stopping power and atomic fraction of hydrogen for the standard Mylar is 1.841 × 102 eV/(1015 at./cm²) and \( f_{\text{std}} \) 0.3636, respectively, are known. The stopping power data in this work is calculated using SRIM-2008.04 [20].

The depth \( x_n \) is related to the incident beam energy \( E_i \) by the equation

\[ x_n = \frac{E_i - E_R}{\varepsilon} \]

where \( E_R \) is the resonance energy and \( \varepsilon \) is the stopping power. The depth in at./cm² is converted into linear dimension using density (3.0 gm/cc [4]) of the film of known film thickness determined by other methods.

The stopping power of a multi-elemental film using Bragg’s law of linear additively can be written as

\[ \varepsilon = \sum_{i=1}^{N} f_i \varepsilon_i \]

where \( f_i \) and \( \varepsilon_i \) are the atomic fraction and the atomic stopping power of the ith constituent, respectively and \( N \) is the total no. of constituents in the film.

2.3.2. Expression for thickness determination using RBS technique

The energy loss of a 1.0 MeV proton beam in a thin film of thickness \( t \), related to the stopping power of the material is given below [13–14]

\[ t = \frac{\Delta E}{\varepsilon_{\text{FWHM}}} \]

\[ \varepsilon_i = \frac{K_i}{\cos \theta_1} \left[ \frac{dE}{dX} \right]_{\text{in}} + \frac{1}{\cos \theta_2} \left[ \frac{dE}{dX} \right]_{\text{out}} \]

where \( t \) is the thickness, \( \Delta E \) is the FWHM of the peak, \( \varepsilon_i \) is the stopping power of the ith element and the subscripts “in” and “out” refer to the (constant) values of stopping power \( \left( \frac{dE}{dX} \right) \) along the inward and outward paths, \( \theta_1 \) and \( \theta_2 \) are the angles between the sample normal and the direction of the incident beam and of the scattered particle respectively.
3. Results and discussions

3.1. NRA measurements

Fig. 1 shows typical γ-ray yield (due to nuclear reaction $^1\text{H}(^{19}\text{F},\gamma)^{19}\text{O}$), as a function of (i) energy difference between energy of incident $^{19}\text{F}$ ion beam ($E_{in}$) and the resonance energy ($E_R$) as recorded in a PC-based multichannel analyzer, (ii) hydrogen concentration at different depth of the film, estimated using stopping power value of HDLC. For $E_{in} < E_R$, the γ-ray yield corresponds to ‘background yield’ and for $E_{in} = E_R$ the γ-ray yield corresponds to the presence of hydrogen atoms onto the surface of HDLC sample. With the increase of energy of the beam penetrating into the sample, the γ-ray yield starts decreasing from the surface of the target, as evident in Fig. 1. The typical behavior of declining of γ-ray yield at different depth of as prepared and annealed HDLC sample are observed to be similar.

The as-prepared samples (A–D) when annealed at different temperatures 750 °C and 1050 °C in high vacuum, show that the yields, and hence the hydrogen content of the annealed films, in all the cases, are lower than that of the as-prepared samples. A typical result for the as-prepared sample B is shown in Fig. 2. As expected, the hydrogen content should decrease with the increase of the annealing temperature. Therefore, the results in Fig. 2 clearly indicate significant loss of bonded hydrogen atoms from the HDLC sample due to annealing effect. Since the decades, it has been well known that the heating of amorphous hydrogenated carbon above 300 °C will produce the exo-diffusion of hydrogen molecules through the recombination of small sized hydrogen atoms within the bulk of the materials. Such formation of $\text{H}_2$ molecules is favorable due to the higher bond energy of H–H than that of the C–H bond. Therefore, annealing leads to the transformation of sp$^3$C–H (diamond like) to sp$^2$C=C (graphite like) structure in the HDLC sample.

The variation of hydrogen content with the depth of the as-prepared samples (A–D) is shown in Fig. 3. The hydrogen concentration is maximum just inside the surface which is approximately within 10 nm from the surface in most of the samples. This result may indicate that the unsaturated bonds of carbon are being terminated by hydrogen, thus leaving almost no unsaturated bonds in the samples at the end of their deposition. Since the decades, it has been well known that the heating of amorphous hydrogenated carbon above 300 °C will produce the exo-diffusion of hydrogen molecules through the recombination of small sized hydrogen atoms within the bulk of the materials. Such formation of $\text{H}_2$ molecules is favorable due to the higher bond energy of H–H than that of the C–H bond. Therefore, annealing leads to the transformation of sp$^3$C–H (diamond like) to sp$^2$C=C (graphite like) structure in the HDLC sample.
The maximum depth of hydrogen content in the HDLC film depends upon flow rate of methane (Fig. 3) and for a given as-prepared HDLC film the maximum depth of hydrogen content decreases with increasing annealing temperature (Fig. 2). Therefore, the direction of flow out of hydrogen during annealing of HDLC sample is from the interface towards the surface. Vainonen et al. [27,28] and Thomas et al. [29] have studied the migration of hydrogen in DLC films by NRA, RBS, and SIMS techniques and found migration of hydrogen towards the interface between the film and substrate and also release of hydrogen from the surface region. On contrary to this observation, the migration of hydrogen towards surface from the interface in our HDLC sample seems to be plausible due to the fact that during the annealing process, the heat is transferred from the sample holder to the backing silicon material and then into the sample; hence, the interface of the sample and the Si is at higher temperature than the surface of the HDLC samples. Therefore, there might be a possible chance of little rearrangement of hydrogen bonds through the process of dehydrogenation and hydrogenation [30] within the sample. In some hydrogenous carbon materials loss of hydrogen under ion irradiation is reported earlier [31,32]. Due care, therefore, is to be taken while carried out the hydrogen determination. In such cases, the concentration of hydrogen should be measured as a function of ion dose and the initial hydrogen content can be obtained by extrapolation to the zero dose condition. This result is shown in Fig. 4. The yields at zero dose condition are also shown along the dotted line for the as-prepared and annealed samples. These values were obtained from the polynomial fitting of the γ-ray yields vs. charge density. The stability of the standard samples under ion beam irradiation has already been studied [16]. This can be minimized by using the lower mass of the projectiles, which don’t transfer large electronic energy as excitation energy in the sample. Nearly constant integrated counts (as shown in Fig. 4) for every 250 nC charge, were observed for the standards (Si$_3$N$_4$) for total 20 number of times exposure at primary beam energy of ~6.5 MeV. In contrary, the counts were slowly decreased for annealed samples and rapidly for the as-prepared samples as shown in Fig. 4. This could be explained if we assume that the hydrogen is present in the film as bonded by chemical forces and also as non-bonded due to physical forces or weak Vander Wall forces. Therefore, the weakly bonded hydrogen readily desorbs from the thin films on heating. This desorption is maximum for the as-prepared films compared to annealed films.

### 3.2 RBS measurements

The backscattered spectra for as prepared and annealed samples are recorded using 1.0 MeV proton beam and are shown in Fig. 5. The higher channel number (i.e., higher energy) side of the RBS spectrum is due to the backing silicon materials (thickness ~2000 nm). The Si-edge of sample A was different compared to sample B. There are two factors responsible, one is channeling and other is cross section which is even more non-Rutherford in this energy range. Again the cross section varies sharply at the Si-edge. The sharp peak is observed over the broad plateau of silicon is due to the carbon. It is clear from the inset picture where there is no peak for the virgin silicon sample but sharp peaks for carbon onto silicon. The sharp peaks of carbon in the inset of Fig. 5, show increase of peak area from 417 ± 24 to 774 ± 34 to 1936 ± 65 counts/µC, and FWHM from 10.7 ± 0.5 to 11.2 ± 0.7 to 14.71 ± 0.8 keV with the increase of flow rates of methane in the as-prepared samples viz., A, B, D, respectively. Therefore, the thickness of the film increases with flow rates of methane.

The RBS spectra for the as prepared and annealed HDLC samples are measured. The FWHM for samples B (30 SCCM) both as prepared and annealed at 750 and 1050 °C were 11.2 ± 0.7, 11.1 ± 0.5, 10.4 ± 0.5 keV at 722 ± 3 keV and the integrated area under the peaks are 813 ± 46, 774 ± 34, 670 ± 27 counts/µC respectively. These values were obtained using Lorentzian fittings. It is observed that the as prepared films have higher peak yields and higher FWHM compared to that of annealed one as shown in Fig. 6. This result indicates thickness of as-prepared samples is larger than that for annealed one.

Kazunori et al. [33] and Wang et al. [34] have studied the erosion behavior of deuterated soft amorphous carbon thin film by heat treatment in air and vacuum, using elastic recoil detection (ERD) and proton enhanced scattering (PES) techniques. When the films are heated in air above 550 K for 1 h, the film thickness, and the areal densities of carbon and deuterium both decrease. Moreover oxygen is incorporated into the films. But when annealed in vacuum, erosion starts at above 600 K and decrease in thickness along with the decrease of all other components. Thermal desorption spectroscopy of the soft films reveals the evolution of hydrocarbon. They have also studied the thermal erosion behavior of hard a-C:H thin films under vacuum. This showed predominantly the release of hydrogen molecule to give semi-hard a-C:H films with very low hydrogen content. This implies that the soft films sublime and hard film desorbs in vacuum during annealing. We have also observed the similar desorption and decrease in at.% of...
hydrogen and that in thickness for HDLC thin film, when treated under vacuum at high temperature. The diagnosis by NRA measures the content of hydrogen whereas RBS techniques measures content of carbon. Therefore, the decrease of HDLC film thickness due to annealing (Fig. 6) should be caused by removal of carbon and hydrogen both.

3.3. Estimation of hydrogen content and thickness of HDLC sample

The atomic fraction of hydrogen in the as prepared HDLC film is estimated using Eq. (1) based upon NRA measurements. The results are given in Table 1.

The thickness of the as prepared HDLC film along with their uncertainties is measured by NRA using Eq. (2) and by RBS using Eq. (3). These results are given in Table 2. The experimental detection limit of the sample has been estimated on the basis of three times standard deviation value (3σ) of background counts in the region of a peak of the γ-ray spectrum of samples as per our experimental parameters and the value is ~3.0 at. %.

The overall error in the NRA and RBS measurement have been estimated by error propagation formula from the errors in counting statistics of the gamma ray yields, stopping power, resonance width and fitting errors and it lies within 10–20%. Thickness of HDLC film by NRA is based upon maximum depth of hydrogen availability whereas that by RBS is based upon maximum depth of carbon availability in the film. Since toward interface between substrate and HDLC film, graphitic (sp² C=C) character is predominant than diamond (sp³ C–H) character, it is obvious that the observed thickness by NRA smaller than that by RBS (Table 2) is reasonable.

The structure of the modified films due to the annealing effect making a denser networking structure remained almost same even after further annealing at elevated temperatures. The minute change in the thickness is due to removal of hydrogen (Table 3). Hence there are not significant different of thickness of the films when annealed at 750 and 1050 °C.

4. Conclusions

We conclude that HDLC is composed of coherently coupled sp³C–H and sp²C=C carbons producing a continuous non-porous atomically smooth surface [5,6]. As prepared and annealed HDLC films, have been investigated by IBA techniques as described above by determining the depth profiling of hydrogen of the films and its thickness. This study reveals the nature of attachment of hydrogen atom to the carbon network of the film and also shows that the hydrogen content is maximum at the surface of the films. This hydrogen terminates the unsaturated bonds of carbon in the film surface at the end of their deposition. The hydrogen content increases with the increase of flow rate of methane at a constant flow rate of hydrogen and helium. The predominant character of graphitic layer towards the interface between the substrate and HDLC film have been substantiated from the thickness measurements by IBA techniques having high depth resolution of ~10 nm. The hydrogen content decreases with the depth of the films. This result matches with the Robertson model [25] of diamond/graphite/Si(100) interface which minimizes the lattice mismatch and interfacial energy. Therefore our HDLC film may be considered a graphene/graphitic structure, sandwich between the top diamond like structure (hydrogenated graphene: sp³C–H) and silicon substrate. Hydrogenated graphenes (also called graphane) are expected to have a tunable band gap via the extent of hydrogeneration [35]. This material has been predicted to be a semiconductor in contrast to metallic graphene, thus finding applications in electronic devices such as transistors [36]. The studies described above, satisfactorily corroborate the expected variation in thicknesses of the film, both as prepared and annealed. These studies also exhibit the chemical phenomena like desorption of hydrogen from the film during both annealing process and bombardment with ion beams. Thus IBA techniques are very useful tools for the characterization of HDLC thin film. The denser networking structure, composed of carbon and hydrogen, remained almost the same even after the irradiation. This property should be useful for their application as protective coatings in the construction of radiation detectors.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flow rate of CH₄ (SCCM)</th>
<th>Hydrogen content (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>30.1 ± 3.2</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>30.5 ± 3.4</td>
</tr>
<tr>
<td>C</td>
<td>40</td>
<td>32.9 ± 3.5</td>
</tr>
<tr>
<td>D</td>
<td>70</td>
<td>34.1 ± 3.9</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flow rate of CH₄ (SCCM)</th>
<th>Depth of hydrogen in the film by NRA (nm)</th>
<th>Thickness of the film by RBS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>52 ± 10</td>
<td>124 ± 15</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>83 ± 10</td>
<td>130 ± 16</td>
</tr>
<tr>
<td>C</td>
<td>40</td>
<td>98 ± 12</td>
<td>134 ± 17</td>
</tr>
<tr>
<td>D</td>
<td>70</td>
<td>158 ± 17</td>
<td>144 ± 20</td>
</tr>
</tbody>
</table>

![Fig. 6. RBS measurements on HDLC thin films B onto Si backing materials (30 SCCM, both as prepared and annealed at 750 and 1050 °C) were carried out with 1.0 MeV proton beam from Tandetron accelerator. The backscattered particles were detected by a silicon surface barrier (SSB) detector at an angle of 170°. For each of the above measurements fresh samples were annealed.](image-url)
Acknowledgement

NRR thanks the Department of Atomic Energy, Govt. of India, for financial assistance. We thank Mr. S.S. Sil and Mr. U.S. Sil, SINP for their technical help in this work.

References

Signature of Misoriented Bilayer Graphenelike and Graphanelike Structure in the Hydrogenated Diamond-Like Carbon Film

Nihar R. Ray, Jagannath Datta, Hari S. Biswas, and Someswar Datta

Abstract—In the present experimental work, we have described the signature of misoriented bilayer graphenelike and graphanelike structure in the hydrogenated diamond-like carbon film having interlayer disorder region and high specific surface area. Our new results have implications for bilayer graphene/graphanelike electronic devices.

Index Terms—Graphane, graphite, high-field-effect mobility, hydrogenated diamond-like carbon (HDLC), interlayer disorder, misoriented bilayer graphene, Raman spectroscopy.

I. INTRODUCTION

GRAPHENE IS a promising material for future electronic applications, due to its high-field-effect mobility and optical transparency [1]. The highest performing graphene samples produced by mechanical exfoliation of graphite [2] seem to be not very good for device applications, because of very low specific surface area on the order of few tens of square nanometers per gram. We have demonstrated earlier [3] that hydrogenated diamond-like carbon (HDLC) films, having large specific surface area ~10^{12} nm^2/g deposited onto a Si (100) substrate and produced by reactive gas–plasma process, are composed of an ordered hexagonal structure of carbon atoms with lattice parameters \( a = 2.62 \, \text{Å} \) and \( c = 6.752 \, \text{Å} \) different to those present in a hexagonal graphite structure. These lattice parameters are similar under different orientations of the sample. These results seem to correspond to hydrogenation of the hexagonal structure of carbon atoms, called graphane [4]. Further structural investigation by micro Raman spectroscopy [5] shows that coherency of sp^3 C–H and sp^2 C = C carbons in the HDLC can produce a continuous nonporous thin film (thickness ~168 nm) having atomically smooth surface. These earlier works [3], [5] motivate us to explore the structure of HDLC films, in order to address the issues related to graphene-based materials. In this paper, we report the experimental signatures of misoriented bilayer graphenelike and graphanelike structure in the as-deposited HDLC film, having some interesting electronic properties.

II. EXPERIMENT

The HDLC film [3], [5] was heated at a fixed temperature of 1050 °C for 30 min in high vacuum ~1 \times 10^{-6} \text{torr} and cooled to room temperature after heating. Raman spectra were obtained using a confocal micro Raman spectrometer (LabRAM HR Vis., Horiba Jobin Yvon S.A.S., France). Under the operating conditions of the spectrometer as described elsewhere [5], the Raman spectrum measures bulk of the sample. The current–voltage (I–V) characteristics in ambient air, of the as-prepared HDLC and annealed HDLC films, were measured in the form of series current (I)-versus-voltage (V) measurement with a simple bias current using a Keithley 2635 single-channel current source meter. Using scanning tunneling microscopy (STM) under the constant-tunneling-current mode, a topographic image of the sample was obtained by a multimode scanning probe microscope (Agilent AFM 5500 series system, USA) having a multipurpose small scanner with a scan range \( Z \) of 0–2 mm and a noise level \( Z \) of < 0.02 nm rms. In this instrument, a feedback loop maintains a constant tunneling current during scanning by vertically moving the scanner at each \((X–Y)\) data point until reaching a given set-point value (0.5 nA). The computer stores the vertical position of the scanner at each \((X–Y)\) data point to form the topographic
image of the sample surface which is to be conductive or semiconductive.

III. RESULTS AND DISCUSSION

A typical Raman spectrum of the as-prepared HDLC film [Fig. 1(a)] and that of the annealed sample at 1050 °C [Fig. 1(b)] clearly show the presence of photoluminescence (PL) background and the disappearance of PL background, respectively, superimposed upon the Raman scattering spectrum. These results clearly indicate significant loss of bonded hydrogen atoms from the HDLC sample due to annealing effect, since it is thought that PL is due to recombination of electron–hole pairs within $sp^2$-bonded clusters in an $sp^3$-bonded hydrogenated carbon matrix [6].

The first-order Raman spectrum [Fig. 2(a)] of the as-prepared HDLC film shows typical Raman modes of amorphous carbon having a broad asymmetric peak at $\sim 1546 \pm 0.66$ cm$^{-1}$ (G-band [5], [7]) along with other peaks at $1366 \pm 0.54$ cm$^{-1}$ (D-band [8]), $1245 \pm 0.9$ cm$^{-1}$ (nanocrystalline diamond (NCD) line [5], [9] due to hydrogenation of $sp^2$ C = C into $sp^3$ C–H), $1121 \pm 1$ cm$^{-1}$ and $1495 \pm 2.4$ cm$^{-1}$ (trans-PA modes [5], [10] due to C–H wagging modes), and $1598 \pm 1.3$ cm$^{-1}$ (dumbbell defect in the NCD line [5], [11]). The first-order Raman spectrum [Fig. 2(c)] of the annealed HDLC film shows typical Raman modes at $1357 \pm 0.57$ cm$^{-1}$ and $1601 \pm 0.57$ cm$^{-1}$ which correspond to interlayer “disorder mode” and characteristic G-band, respectively, in the turbostatic structure of graphitic material [12]–[14]. These results in Fig. 2(a) and (c) signify that the HDLC film, having been found to be a hydrogenated hexagonal crystal structure of carbon atoms [3], [4], is composed of layers of graphitelike crystalline structures which have parallel c-axes and which are connected to one another by disordered regions. In fact, the measured value of interlayer separation $3.376$ Å for HDLC is larger than that for crystalline graphite which is $3.354$ Å, signifying the existence of interlayer disorder regions in the HDLC sample. The interlayer disorder mode (D-band) and the G-band are active for crystallites of finite size in the nanometer range, and the ratio $I_D/I_G$ inversely varies with their diameter; the D-band and G-band do not depend upon the mutual arrangement of graphite planes [12]–[14].

A comparison between the results in Fig. 2(a) and (c) shows the following: 1) The ratio $I_D/I_G$ increases from 0.8 to 2.0
(approximately), indicating a reduction of size of the domain of crystallinity [12]; 2) the intensities of the peaks at 1245 ± 0.9 cm⁻¹, 1121 ± 1.2 cm⁻¹, 1495 ± 2.4 cm⁻¹, and 1598 ± 1.3 cm⁻¹ in Fig. 2(a) significantly disappeared in Fig. 2(c), indicating loss of sp³ C–H in the HDLC [9]–[11]; and 3) the frequency shift ∼54 cm⁻¹ toward higher wavenumber is found for the G-band in Fig. 2(c), indicating a reduction of size of the domain of crystallinity [12]. In our earlier studies [5], it is seen that sp² C = C and sp³ C–H carbons exist coherently, and due to the annealing effect, in the present work, the size of the sp³ C–H domains in the HDLC is reduced by the loss of bonded hydrogen atoms in the hydrogenated hexagonal crystal structure of carbon atoms. Hence, the aforementioned results 1)–3) seem to be plausible for the annealed HDLC.

The second-order Raman spectrum of the as-prepared HDLC film [Fig. 2(b)] and that of the annealed sample at 1050 °C [Fig. 2(d)] show the presence of G′-band and the second order of the D-band, respectively [15]. The D- and G′-bands originate from a double-resonance Raman process [16] in 2-D graphite. Therefore, the present results, as shown in Fig. 2(b) and (d), signify the HDLC sample, having turbostatic behavior as found from the first-order Raman spectra, to behave as 2-D graphite due to interlayer disorder regions between the layers having been separated by 3.376 Å. Since the G′-band is very sensitive to the stacking order of the graphene layers along the c-axis [13]–[15] and identification of the number of layers in the turbostatic graphite is done by the number of peaks in the G′-band [17], we have deconvoluted the G′-band with best fits by Lorentzian peaks. Both Fig. 2(b) and Fig. 2(d) show the following: 1) Four Raman modes aside from the peak at ∼2700 cm⁻¹ correspond to single-layer graphene; 2) full-width at half-maximum for all the five modes lies in the range of 15–40 cm⁻¹; and 3) I_G'/I_G ≪ 1. These results correspond to turbostatic multilayer graphene in general [17]. According to the calculation of Latil et al. [19], a Bernal bilayer (AB) and a rotationally disordered graphene (A′) should simply exhibit the sum of the spectra from a bilayer (i.e., a broadband with four components) plus the unique peak of graphene. Our experimental results, as shown in Fig. 2(b) and (d), correspond to that theoretically predicted and experimentally confirmed for misoriented bilayer graphene [18], [19].

Thus, from all evidences taken together from the first- and second-order Raman spectra [Fig. 2(a)–(d)], we can say that
the layers of the hexagonal structure of carbon atoms in the HDLC sample [3]–[5] stay perfectly parallel but their mutual orientation along the c-axis is random (turbostatic) due to the existence of interlayer disorder; as a result, the 3-D crystallinity of the HDLC should be lost, while only the 2-D crystallinity should be preserved [12]. Therefore, the as-prepared HDLC film can be assumed to have misoriented bilayer graphenelike structure, and the annealed HDLC film can be assumed to have misoriented bilayer graphenelike and graphanelike structure within the coherent structure of the film. The Raman spectra [Fig. 2(a)–(d)] do not tell us about why and how the interlayer disorder region is created in the HDLC film.

The typical $I-V$ characteristic of the as-prepared HDLC film, as shown in Fig. 3(a), shows the following: 1) Ambipolar conductance with wide bandgap ($\sim 4.5$ eV) indicates a typical wide-bandgap semiconductor property, and 2) the ratio of negative current (due to $sp^3$ C–H as electron acceptor) to positive current (due to $sp^2$ C–H as electron donor) is $\sim 0.13$. Comparing these results 1) and 2) to the $I-V$ characteristic of a p-doped Si (100) substrate having a bandgap less than 1 eV, as shown in the inset of Fig. 3(a), it may be said that majority carriers of current in the as-prepared HDLC film are electrons and those in the p-doped Si (100) substrate are holes. The typical $I-V$ characteristic of the annealed HDLC film, as shown in Fig. 3(b), shows correspondence to an ohmic curve of a conductor having zero bandgap. From the observed results on the $I-V$ characteristics of the as-prepared HDLC film and annealed HDLC film, it is plausible that the former one should behave as an n-type wide-bandgap semiconductor and the latter one should behave as a metallic conductor.

The constant-current STM image of the as-prepared sample cannot be measured, but that of the annealed one is possible, as shown in Fig. 4. These results support that the as-prepared HDLC film is resistive but the annealed one is conductive. A structure to understand schematically the resistive nature of the as-prepared HDLC film is shown in Fig. 5(a), where, primarily, the presence of $\sigma$-bonded electrons is shown, and similarly, that to understand the conductive nature of the annealed HDLC film is shown in Fig. 5(b), where, primarily, the presence of $\pi$-bonded electrons is shown. The observed bright spots in Fig. 4 seem to correspond to the simulated constant-current STM image of the unoccupied states in the honeycomb lattice of the $A'$ face of the ABA system [19]. Occupied states in the honeycomb lattice in the form of dark spots are also seen in Fig. 4. Bright spots are interconnected by dark spots indicating the HDLC film [5] comprising coherent domains of $sp^2$ and $sp^3$ carbons.

A typical tunneling-current-versus-distance characteristic and a semilogarithmic plot of this characteristic for the annealed HDLC film are shown in Fig. 6(a) and (b), respectively. This result corresponds to a typical current-versus-height relation, in the absence of a condensate on the surface of electrodes in STM measurements, indicating approximately an exponential decay with a characteristic length of a few angstroms [20]. The estimated work function of the film from the slope of the curve [Fig. 6(b)] $\sim 0.013$ eV is about 350 times less than the work function of a free-standing graphene film which is $\sim 4.5$ eV [21]. Reduction of the work function of free-standing graphene by several orders of magnitude is predicted to be due to the presence of adsorbate in the electrodes [20]. Recently, it has been found that interaction of graphene with a metallic or insulating substrate may shift the Fermi energy level, causing significant change of work function [21], [22]. The work function of the annealed HDLC film seems to be less than 4.5 eV. The estimated value of tunnel-current density in air $\sim 100 \mu A/cm^2$, using constant-current value $\sim 0.5$ nA and STM probe diameter $\sim 0.25$ mm, and the observed value of work function of the annealed HDLC film tell us that the annealed HDLC can be expected to be a good high-field-effect electron current emitter in high vacuum.

IV. CONCLUSION

That the HDLC thin film grown onto large substrate area $\sim 25$ mm $\times$ 25 mm behaves as a 2-D graphitic film has been demonstrated in the present experimental work. The new experimental signatures of misoriented bilayer graphenelike and graphanelike structures in the HDLC film having thickness
\(\sim 168\) nm and their properties as mentioned previously create scientific interest for their electronic applications. Knowledge of electronic properties like temperature-dependent Hall effect, carrier mobilities, and change of work function due to different kinds of substrates will tell us the possible unique applications of our 2-D graphitic film in electronic devices. We have planned to measure these electronic properties in the future.

**ACKNOWLEDGMENT**

The authors would like to thank S. S. Sil and U. S. Sil for their technical help in the present work.

**REFERENCES**


