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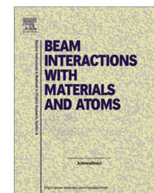

Study of depth profile of hydrogen in hydrogenated diamond like carbon thin film using ion beam analysis techniques

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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 ($\sim 10^{-7}$ torr) and high temperature (750 and 1050 °C) furnace. The as-prepared and annealed HDLC films have been depth profiled for hydrogen using the resonance at 6.44 MeV in ^{1}H(^{19}F,$\alpha\gamma$)^{16}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.

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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 sp^3 (diamond like) and sp^2 (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 $a = 2.62$ Å and $c = 6.752$ Å different to those present in a hexagonal graphite structure. Further structural investigation by confocal micro Raman spectroscopy [5,6] 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. 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 interlayer 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 ∼6 μm and using this technique we get information for the whole material rather than at different depth of the thin film having thickness ∼168 nm (ii) XP spectroscopy [8,9] is a surface sensitive probe in our case, because here the skin depth for X-rays is ∼5 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.

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2. Experimental

The HDLC thin films are deposited on mirror-polished Si (1 0 0) 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(1 0 0) 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 (H_2) at 500 SCCM, and varying the flow rate of methane (CH_4).

Four samples for which the CH_4 flow rates are 20, 30, 40 and 70 SCCM, thus grown with varying H_2 to CH_4 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 ($\sim 1 \times 10^{-7}$ 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 as-prepared and annealed samples A–D, using the resonance at 6.44 MeV for the reaction $^{1}H(^{19}F,\alpha\gamma)^{16}O$ in the present experiment. 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) tripositive fluorine ion ($^{19}F^{3+}$) beam in the scattering chamber under vacuum 10^{-6} mbar. The characteristic gamma rays for the reaction $^{1}H(^{19}F,\alpha\gamma)^{16}O$ 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 ^{16}O 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 over 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 phenomenomenon 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 $\sim 5 \times 10^{-6}$ 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, C_xH_y) is estimated by the following equation [19]

$$f^{H}_{HDLC} = \frac{f^{H}_{Std} \cdot \varepsilon^{C}_{HDLC}}{Y\varepsilon_{Std} + f^{H}_{Std} \cdot (\varepsilon^{C}_{HDLC} - \varepsilon^{H}_{HDLC})} \quad (1)$$

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, ε_{Std} and ε^{i} 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 ε_{std} 1.841×10^{2} eV/(10^{15} at./cm^{2}) and f^{H}_{Std} 0.3636, respectively, are known. The stopping power data in this work is calculated using SRIM-2008.04 [20].

The depth χ_R is related to the incident beam energy E_i by the equation

$$\chi_R = \frac{E_i - E_R}{\varepsilon} \quad (2)$$

where E_R is the resonance energy and ε is the stopping power. The depth in at./cm^2 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

$$\varepsilon = \sum_{i=1}^{N} f_i.\varepsilon_i \quad (3)$$

where f_i and ε_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]

$$t = \frac{\Delta E}{[\varepsilon_i]} \quad (4)$$

$$[\varepsilon_i] = \frac{K_i}{\cos\theta_1}\left[\frac{dE}{dX}\right]_{in} + \frac{1}{\cos\theta_2}\left[\frac{dE}{dX}\right]_{out} \quad (5)$$

where t is the thickness, ΔE is the FWHM of the peak, ε_i is the stopping power of the ith element and the subscripts "in" and "out" refer to the (constant) values of stopping power (dE/dX) along the inward and outward paths, θ_1 and θ_2 are the angles between the sample normal and the direction of the incident beam and of the scattered particle respectively.

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