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Structural modifications of diamond like carbon films induced by MeV nitrogen ion irradiation

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ABSTRACT

Diamond-like carbon (DLC) films were deposited on Si(1 0 0) substrates using plasma deposition technique. The deposited films were irradiated using 2 MeV N^+ ions at fluences of 1×10^{14}, 1×10^{15} and 5×10^{15} ions/cm^2. Samples have been characterized by using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM). Analysis of Raman spectra shows a gradual shift of both D and G band peaks towards higher frequencies along with an increase of the intensity ratio, $I(D)/I(G)$, with increasing ion fluence in irradiation. These results are consistent with an increase of sp^2 bonding. XPS results also show a monotonic increase of sp^2/sp^3 hybridization ratio with increasing ion fluence. Plan view TEM images show the formation of clusters in the irradiated DLC films. HRTEM micrographs from the samples irradiated at a fluence of 5×10^{15} ions/cm^2 show the lattice image with an average interplanar spacing of 0.34 nm, revealing that the clusters are graphite clusters. The crystallographic planes in these clusters are somewhat distorted compared to the perfect graphite structure.

1. Introduction

Diamond-like carbon (DLC) films are well known for their excellent properties, such as, low frictional coefficient, high hardness, chemical inertness, biocompatibility, optical transparency, etc. [1]. The unique combination of the above properties provides substantial potential for applications of DLC films in electromechanical systems, biomedical field, flat-panel displays, particle detectors, etc. [2–4]. DLC films are extensively used as protective coatings in both magnetic and optical data storage devices [4,5]. Ion beams have been used to modify the optical, electrical and structural properties of DLC films [6–8]. Baptista et al. reported the formation of sp^2-bonded hard amorphous carbon network in 400 keV N^+-irradiated amorphous carbon and fullerene films [9]. Ion irradiation using various ions of tens of keV energy has been found to reduce the intrinsic stress present in DLC films [10]. The growth of microcrystalline graphite in DLC films following 85 MeV Ni ion irradiation has been reported [11]. Since DLC films find applications in electronic and electro-mechanical systems the behavior of these films under extreme conditions of heat, radiation, etc. is important for the reactor based and space applications of these devices. The existence of carbon in sp, sp^2 and sp^3 hybridization with the possibility to obtain systems having different percentages of carbon bonding, makes ion irradiation of various carbon allotropes interesting for both basic as well as applied fields of research [12].

Ion irradiation introduces a wide range of defects in a controlled manner and is used to tailor the structural and even the magnetic properties of materials. Recent reports of magnetism in ion-irradiated carbon systems have stimulated renewed interest in ion irradiation of various carbon allotropes [14–16].

Changes in the structure and hybridization cause changes in physical, electrical and other properties of DLC films. In order to investigate the ion beam induced changes in the structure and hybridization in DLC films, we have performed ion irradiation experiments as a function of the fluence of 2 MeV N^+ ions. The

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projected range of 2 MeV nitrogen ions is more than the thickness of the DLC film and the modifications of structure and hybridization are mainly due to the defects produced during the passage of ions through the film. The ions are eventually buried in the underlying substrate. Using high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy we have investigated the structural changes in our DLC films. X-ray photoelectron spectroscopy (XPS) has been employed for understanding the nature and strength of the carbon bonding.

2. Experiment

Diamond-like carbon thin films were deposited on mirror polished Si(1 0 0) substrates at room temperature using asymmetric capacitively coupled rf (13.56 MHz) plasma system utilizing pure hydrogen (H_2), helium (He) and methane (CH_4) gases. The thickness of the films were estimated to be $\sim$100 nm.

Ion irradiations were carried out using the 3 MV 9SDH2 tandem Pelletron accelerator facility in our institute. The samples were irradiated uniformly by rastering the ion beam on the sample. The ion fluence used for irradiation were 1×10^{14}, 1×10^{15} and 5×10^{15} ions/cm^2. The beam current during irradiation was kept at $\sim$20 nA. The pressure in the irradiation chamber was 1×10^{-6} mbar. Raman spectra were recorded at room temperature in the back-scattering geometry using photons of 514.5 nm wavelength as exciting radiation, U1000 monochromator and a CCD detector. XPS measurements were made using Omicron Multiprobe spectrometer fitted with an EA 125 hemispherical analyzer. A monochromatized Al Kα X-ray source operating at a base pressure of 2×10^{-10} mbar was used for the measurements. Plan view TEM measurements were carried out using 200 kV (JEOL 2010) HRTEM using GATAN TV camera for data acquisition with point to point resolution of 0.19 nm and lattice resolution of 0.14 nm. The sample preparation for TEM was carried out by using an ultrasonic disc cutter, a laping and polishing system, a dimple grinder and a precision ion polishing system for the final thinning of the sample.

3. Results and discussions

Table 1
The D, G peak positions and $I(D)/I(G)$ ratios for the pristine and 2 MeV N$^+$-irradiated samples

Irradiation fluence (ions cm^{-2})	D (cm^{-1})	G (cm^{-1})	$I(D)/I(G)$
0 (pristine)	1320	1539	0.44
1×10^{14}	1364	1538	0.66
1×10^{15}	1404	1553	1.40
5×10^{15}	1415	1564	2.0

The Raman spectrum of DLC films consists of a broad skewed peak centered at about 1500–1550 cm^{-1}[1]. The Raman spectra from the pristine DLC film and the films irradiated at fluences of 1×10^{14}, 1×10^{15} and 5×10^{15} ions/cm^2(hereafter samples A, B, C and D, respectively) are shown in Fig. 1(a)–(d). The spectra are fitted using two Lorentzians and a linear background as shown in Fig. 1. The component in the low wave number region is identified as the D mode and the one at higher wave number region is the G mode. The G peak is due to bond stretching of all pairs of sp^2 atoms in both carbon rings and chains. The D peak is caused by the breathing modes of sp^2 atoms in the aromatic sixfold carbon rings.

In the pristine sample the D and the G peaks are found to be at 1320 and 1539 cm^{-1}, respectively. In the case of purely sp^2 hybridized systems, such as graphite, the G peak is expected to be at 1580 cm^{-1}. But in the case of DLC films the position of the G peak is found to shift to a lower wave number depending on the amount of tetrahedral bonding [13]. It can be seen that the D and G peaks are shifted to higher wave numbers in the irradiated samples [Fig. 1(a)–(d)]. The position of D and G peaks and the ratio of the intensities of D peak to G peak ($I(D)/I(G)$) are given in Table 1. The large width of the peaks can be associated to distortions of sp^2 bond angle [9]. The $I(D)/I(G)$ ratio in the pristine film (sample A) is 0.44 and it increases to 2.0 in the case of sample D. The Raman frequencies of idealized five-, six- and seven-membered π-bonded carbon rings have been calculated theoretically by Doyle and Jamson and the D mode is estimated to be at 1444 cm^{-1} in the case of fivefold rings [17]. Since five- and seven-membered ring structures lack inversion symmetry, the vibrational modes with *A* symmetry dominate, i.e., an increase in the intensity of D mode is expected [17,18]. The shifting of the G peak to higher wave number with increasing ion fluence indicates an increase of sp^2 hybridization in the irradiated samples. The D mode is at 1320 cm^{-1} in the pristine sample. It has shifted to 1415 cm^{-1} in the sample irradiated at a fluence of 5×10^{15} ions/cm^2. This shifting of D mode is an indication of the presence of non-six-membered ring structures in the sample [18]. All the features in the Raman spectra, namely the shifting of the D and G peaks along with the increase of $I(D)/I(G)$ ratio point towards an increase of sp^2 bonding and

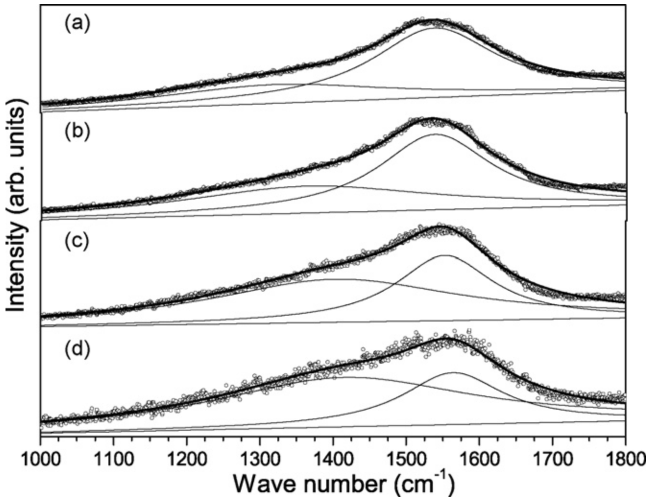

Fig. 1. Raman spectrum of (a) pristine DLC/Si(1 0 0) sample, and samples irradiated at a fluence of (b) 1×10^{14} ions/cm^2, (c) 1×10^{15} ions/cm^2 and (d) 5×10^{15} ions/cm^2.

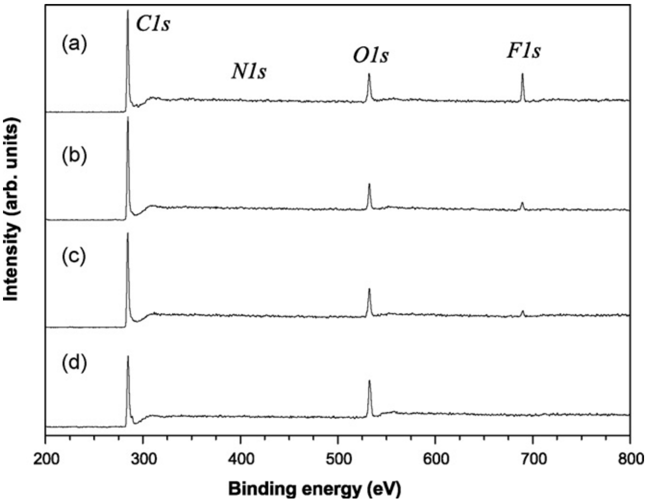

Fig. 2. XPS spectra from (a) a pristine DLC/Si(1 0 0) sample, and samples irradiated at a fluence of (b) 1×10^{14} ions/cm^2, (c) 1×10^{15}ions/cm^2 and (d) 5×10^{15} ions/cm^2.