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Nanostructuring of tetrahedral carbon films by carbon ion implantation

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Abstract

The formation of nanostructures in the matrix of tetrahedral amorphous carbon (ta-C) films induced by ion beam implantation at high doses has been studied by high-resolution transmission electron microscopy, transmission electron diffraction and Raman spectroscopy. The ta-C films were deposited by a filtered cathodic vacuum arc and subsequently implanted by carbon ion beams extracted from a metal vapor vacuum arc ion source. The carbon ions were implanted to doses ranging from 3×10^{13} to 3×10^{17} ions/cm^2. In accord with the thickness of ta-C films and ion ranges (39–75 nm) required the ion energy was determined to be within a range of 25–50 keV. The analysis of Raman spectra indicates that originally abundant sp^3 carbon atomic bonding of ta-C is gradually converted to a graphitic phase during the course of ion bombardment. The local order, growth and clustering the sp^2 bonded carbon atoms in the ta-C films by ion implantation is also indicated by Raman spectroscopy. However, the analysis of implanted amorphous carbon films on an atomic scale shows the formation of structure with the higher degree of order. The graphitic basal planes are formed preferably along the ion tracks. The results are discussed in the context of previously reported studies of implanted ta-C films and glassy carbon. This article shows a critical damage level of 0.24 displacements per atom when the onset of the transformation occurs and demonstrates that the initially amorphous phase with short ordered sp^3 bonding configuration can be nanostructured to the higher degree of an ordered structure using proper ion energies and doses.
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1. Introduction

It has been shown previously that the deposition of amorphous carbon films by the filtered cathodic vacuum arc (FCVA) plasma beams [1,2] can produce the film structures with a high portion of the tetrahedral carbon bonds ($>80\%$) and a density of approximately 3.3 g/cm^3 [3]. This allotropic carbon form, therefore called tetrahedral amorphous carbon (ta-C), can exhibit high hardness (~ 70 GPa) and wide band gap (~ 3.5 eV) being less than a half of that reported for intrinsic diamond (5.51 eV) [3]. The ta-C films confine less than 30% of sp^2 hybridized atoms within a tetrahedral carbon matrix [4].

The studies on the ion implantation of ta-Cs [5] performed previously indicate consequential ion damage and relation to the structure and properties of ta-C films formed. Unlike such studies this article reports the structural changes induced by both ion implantations and annealing carried out in sequence and with reference to non-implanted, however, annealed ta-C films. The motivation for this investigation is further inside and understanding of the ion implantation effects on the ta-C films and likely novel structure induced. In terms of possible applications, ta-C films can be structured by precision ion implantation at proper ion energies and doses to novel nanostructures possessing the properties of interest, such as high electron field emission or electrochemical properties.

2. Experimental

The 100 nm thick ta-C films were deposited onto silicon (1 0 0) substrates using a FCVA deposition system. Prior to the film deposition the substrates were ultrasonically cleaned in acetone and ethanol baths for 15 min. Native oxide was stripped off in a 5% hydrofluoric acid solution. The FCVA system was operated in a pulse mode with a pulse width of 2.5 ms and a repetition frequency of 7–25 Hz. All the ta-C films were deposited at negative direct current (d.c.) bias $V_b = -90$ V applied to the substrates. The base and operation pressures were 2×10^{-4} and 4×10^{-4} Pa, respectively.

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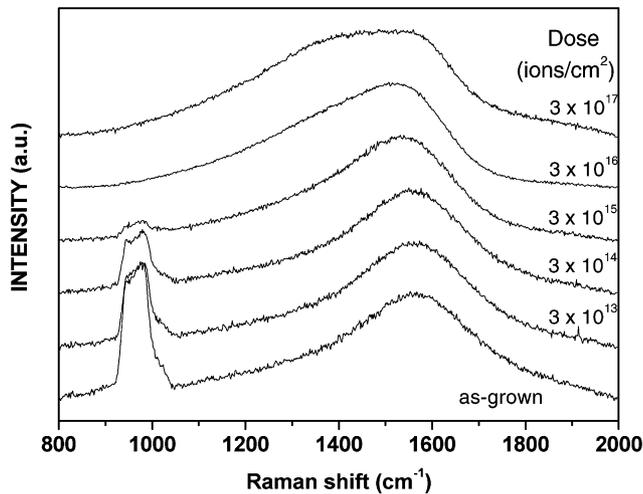E-mail address:* apibello@cityu.edu.hk (I. Bello).

Fig. 1. Raman spectra taken from the 100 nm thick ta-C films implanted at the $E_i = 25$ keV to different doses.

Fig. 2. The coupling coefficient (Q) of BWF lineshape as a function of the implanted ion dose.

The ta-C films then were implanted in situ by carbon ion beams to doses ranging from 3×10^{13} to 3×10^{17} ions/cm^2. The carbon ion beams were extracted from a metal vapor vacuum arc (MEVVA) ion source and accelerated by 25–50 kV. The MEVVA ion source was operated at 5×10^{-4} Pa in a pulse regime. The pulse width and repetition rate were 1 ms and 3–7 Hz, respectively. The implantation was carried out at an ion current density of 2.5 μA/cm^2 over an area of 200 cm^2. The chosen ion energy provided the carbon stopping range corresponding to the central zone of the film thickness in order to avoid the implantation of carbon into the silicon substrate. Assuming target ta-C with a mass density of 3.3 g/cm^3 [3] and single charged ions with energies (E_i) from 25 to 50 keV the calculated stopping ranges are 39 and 75 nm. The projected range (R_p), longitudinal straggling of the implanted carbon ions and other collision parameters were calculated using a Monte Carlo TRIM code [6]. Non-polarized Raman spectra were recorded in backscattering geometry employing a Renishaw micro-Raman spectrometers which uses argon laser with the 514.5 nm excitation line. Laser beam transmitted via a microscope objective with $50 \times$ magnification was restricted to maximum 10 mW in order to minimize a possible beam heating effect and consequential atomic reconstruction. The structural changes induced in carbon structures were observed by cross-sectional high-resolution transmission electron microscopy (HRTEM). The samples for the HRTEM analysis were prepared by slicing, sandwich-gluing, mechanical polishing and low angle argon ion milling. The HRTEM and transmission electron diffraction (TED) analyses were preformed using a Philips CM 200 microscope operating at 200 kV with a point resolution of 1.9 Å.
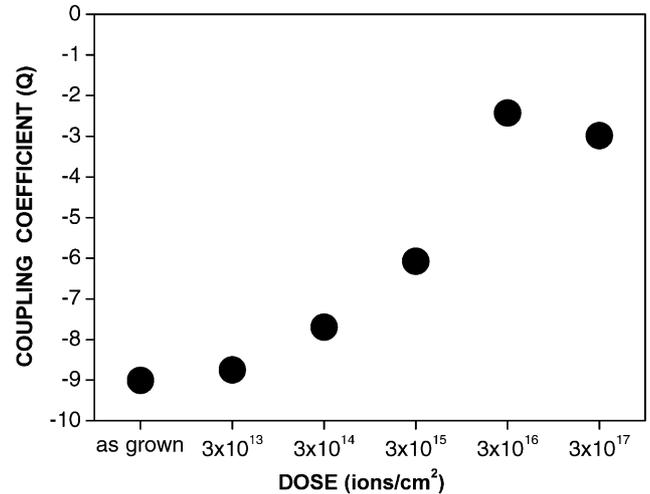
3. Results and discussion

Raman spectra of both the implanted to different carbon ion doses and as-grown ta-C films are shown in Fig. 1. The samples implanted to the doses lower than 3×10^{15} ions/cm^2 show similar spectral features with two distinguished components. The first one is a nearly symmetrical G peak at ~ 1580 cm^{-1} being identified to originate in the lattice vibrations within the basal plane of graphite-like rings [7–10]. The second one is the second order Si peak at ~ 970 cm^{-1}, which is the indicative of optical transmittance of 100 nm ta-C films. The G peaks in Figs. 2 and 3 fitted by Breit–Wigner–Fano (BWF) lineshapes [11–15] (Fig. 4) do not show apparent differences when the ion doses are lower than 3×10^{15} ions/cm^2. It means that the sp^3 matrix of ta-C films was not affected considerably at low carbon ion doses. However, with growing the ion dose above
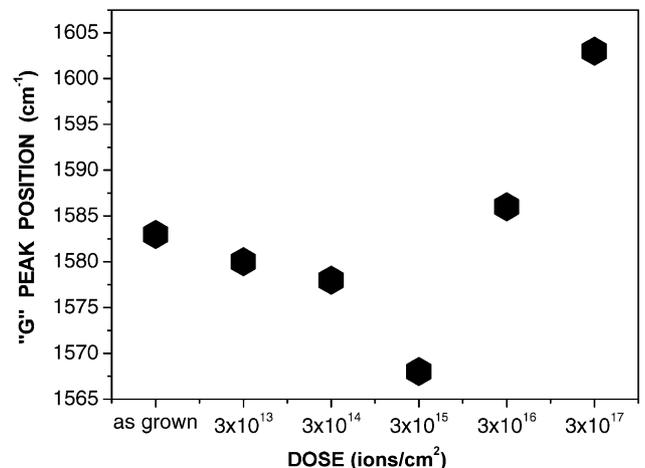

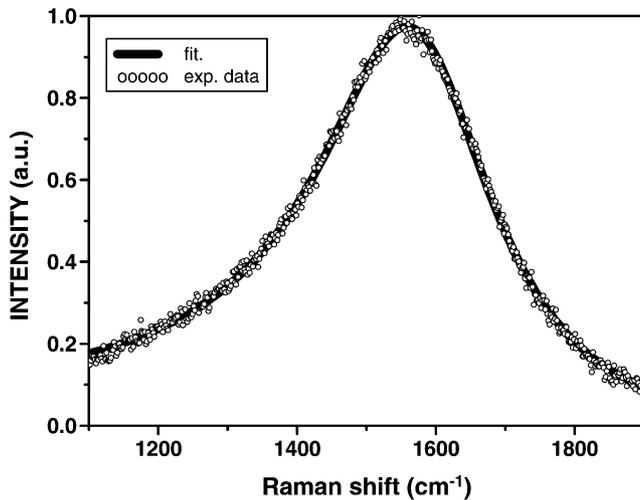Fig. 3. The G peak position as a function of the implanted ion dose.

Fig. 4. The comparison of the experimental Raman spectral data with those arising from the BWF lineship fitting for the film implanted to a dose of 3×10^{14} ions/cm^2.

3×10^{15} ions/cm^2 the G peak became increasingly broader and asymmetric, which indicates a graphitization process. The further implantation to higher doses ranging from 3×10^{16} and 3×10^{17} ions/cm^2 induced sizeable changes in ta-C target materials yielding very different Raman spectra. The precise fitting of these spectra (corresponding to doses of 3×10^{16} and 3×10^{17} ions/cm^2) were obtained using a combination of BWF lineshape for the broader asymmetric G peak and additional Lorentzian D peak which confirms nano-sized graphitic domains and a linear background [15]. The maximum of the BWF lineshape is used to define the G peak position. The fitting shows the variation, upon the dose used, of the G peak position (Fig. 3) and the ratio of the Raman scattering intensities of the D and G peaks (I_D/I_G). The I_D/I_G ratios are 0.54 and 2.1 for the ion doses of 3×10^{16} and 3×10^{17} ions/cm^2, respectively. The shift of G peak towards the higher wavenumbers suggests the increase in amount of sp^2 bonding and the enhancement in structural ordering within the sp^2 fraction. The increase in intensity ratio I_D/I_G implies the enlargement in cluster size and number of disordered graphitic-like rings within the films concerned.

The effect of ion energy deposited per a single carbon atoms on the structural changes in ta-C films was investigated by analyzing the skewness of characteristic Raman peaks (Fig. 5). The Raman spectra were collected from the samples exposed to carbon ion beams with two different energies, i.e. $E_i = 25$ and 50 keV, however, implanted to the same ion doses of 3×10^{15} ions/cm^2. The number of vacancies per a single ion are 57 and 85 for the 25 and 50 keV carbon ions, respectively. Taking into account the projected ranges 392 and 741 Å of ions, the corresponding densities of vacancies are 4×10^{22} and 3.1×10^{22} vacancies/cm^3 for the 25

and 50 keV carbon ions in that order. Thus, within the investigated range of carbon ion energies and exposed carbon structure, the higher density of vacancy is for the lower ion energies (25 keV) because the implanted volume and energy increase are in non-linear relationships.

Raman spectra in Fig. 1 were collected from carbon films of equal thickness, however, exposed to the 25 keV carbon ion beam with different ion doses. Vanishing the intensity of the second order silicon peak at ~970 cm^{-1} with the increase in ion dose indicates that the carbon films become less optically transparent at higher ion doses. Changing the optical properties with the increase in ion energy reflects the structural variation from the rich sp^3 structure to the structure enriched in sp^2 inclusions. Similarly, the 50 keV carbon ion exposures with variable doses cause structural changes, however, the films implanted at this energy and equal doses, in overall, contain more extensive sp^2 inclusions embedded in the sp^3 matrix than those of the film implanted at the lower ion energy (25 keV).

Although the transformation from ta-C structure (abundant sp^3 carbon bonding arrangements) to the sp^2 enriched structure is induced by ion bombardment from the lowest doses, the detectable changes are observed only above a certain ion dose. At lower doses only small clusters (<2 nm) are formed. The formation of the larger sp^2 bonding carbon arrangements can be induced above certain defect densities, which are profound only at higher ion doses. The analysis can be conceivable because of the absence of the D peak in Raman spectra. On the other hand, the analysis of G peak in Raman spectra [7] can further elucidate the structure formed. The G peak position and coupling coefficient (Q) of fitting BWF lineshape of the G peak change little at lower ion doses though the optical
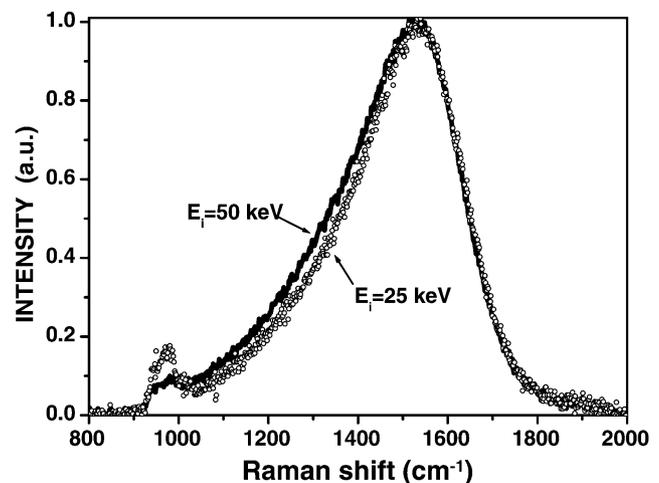

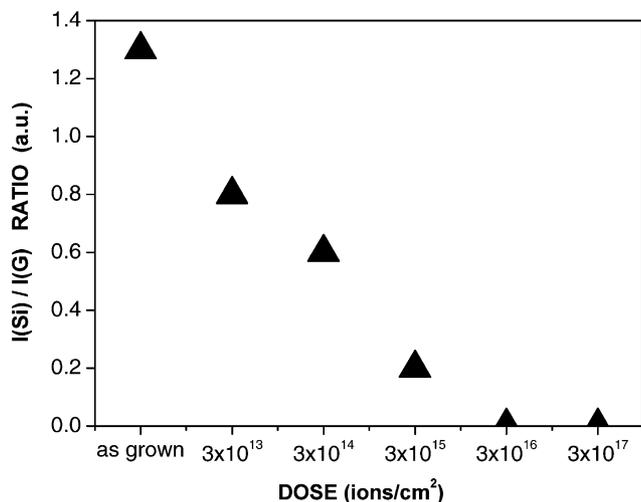Fig. 5. Raman spectra acquired from ta-C films implanted to an ion dose of 3×10^{15} ions/cm^2.

Fig. 6. The ratio of the intensities of the second order Si line (I_{Si}) and G peak (I_G) as a function of the implanted ion dose.

Fig. 7. HRTEM image collected from the film implanted to 3×10^{16} ions/cm^2 at $E_i = 25$ keV. The arrow in figure shows the ion beam direction.

transmittance of the implanted films decreases dramatically. The intensity ratio I_{Si}/I_G (second order silicon to G peak) drops from 1.28 to 0.17 for the film as grown and the film implanted to a dose of 3×10^{15} ions/cm^2, respectively (Fig. 6). The structures formed upon ion beam bombardment were also evaluated by coupling coefficient being the measure of asymmetry of G peak. The coupling coefficient changes from a reference value of -9 for the as-grown film to a value of -2.5 for the film implanted to a dose of 3×10^{16} ions/cm^2, respectively. Such variation in coupling coefficient, the increase in the intensity ratio I_D/I_G and the shift of the G peak position towards the higher frequency region with the increase in ion dose is the indicative of growing the graphitic sp^2 fraction embedded in sp^3 carbon matrix.

Similar and complementary conclusions can be drawn from HRTEM and TED analysis of the ion implanted ta-C films. While the referenced original ta-C film indicates typical amorphous phase, the films implanted to higher doses than 3×10^{15} ions/cm^2 shows evolution of graphitic nano-sized carbon domains (>2.5 nm). The further increase in dose to 3×10^{16} ions/cm^2 the films is structured with preferential orientation of graphitic basal planes along the ion track as illustrated by a HRTEM image in Fig. 7. Correspondingly electron diffraction (TED) patterns vary upon the ion dose used. For example, Fig. 8 represents a cross-sectional TED pattern collected from the film implanted by carbon ions at 25 keV to a dose of 3×10^{16} ions/cm^2. The diffraction patterns taken from the films implanted to lower doses showed only diffuse rings indicating an amorphous structure. In contrast the patterns acquired from the films implanted to higher doses than 3×10^{16} ions/cm^2 shows a significant degree of preferential orientation. In addition to sharp diff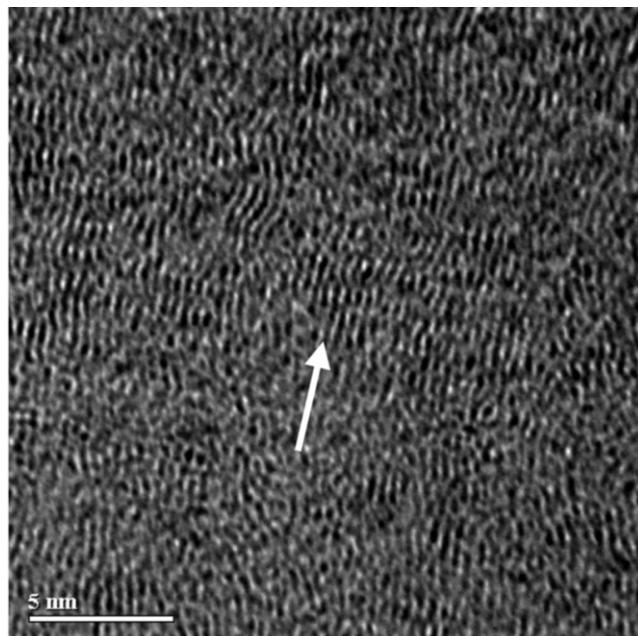raction spots arising from silicon substrate, the two symmetrical elongated bright spots near the central ring of the TED pattern, in Fig. 8, correspond to a *d* spacing of ~ 3.5 Å, referring to the {0 0 2} planes like found in monocrystallite graphite with a *d* spacing of 3.354 Å.
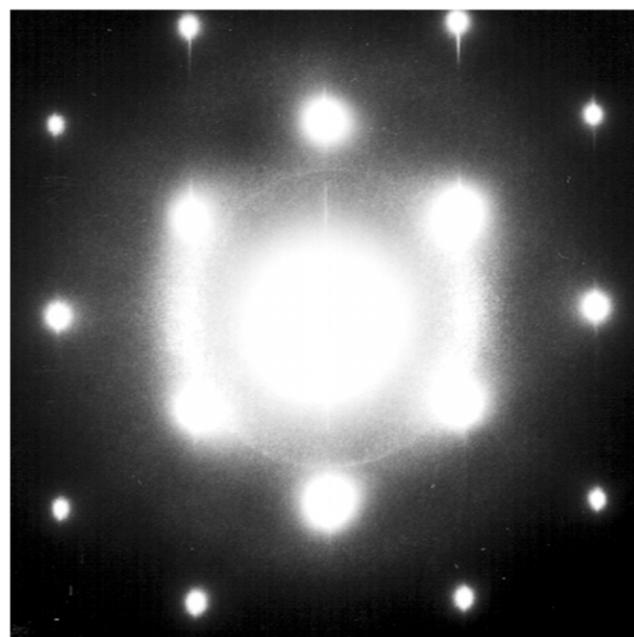

Fig. 8. TED pattern of film implanted to 3×10^{16} ions/cm^2 at $E_i = 25$ keV. The arrowed elongated diffraction spots arise from microcrystalline graphite.
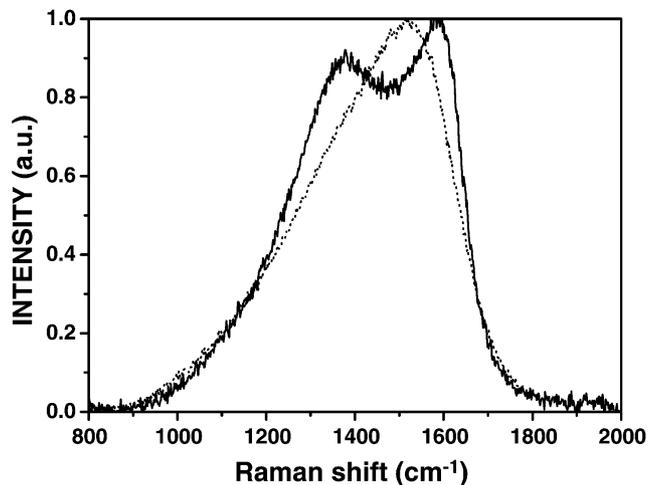
Fig. 9. Raman spectra acquired from both the implanted and annealed film (solid line) with reference to the implanted sample (doted line). The used ion dose was 3×10^{16} ions/cm^2.

McCulloch et al. [5] reported their studies on the exposure of very thin (20 nm) ta-C films deposited on silica substrates to high energy carbon (50 keV) and xenon (200 keV) ion beams. Unlike our study, the projected ion range of carbon was higher than the film thickness so only a part of carbon ions of the tail of energy distribution could be implanted into ta-C structure, while majority of ions were introduced into the substrates. In addition this study is based on the analysis of Raman spectra acquired from xenon ion implanted films only. Comparing the features of Raman spectra of cited work above and presented herein, they are very similar though in the later work practically all carbon ions were implanted. However, the overall localized increase in atomic density of the original ta-C structure could not be crucial because of the ion energies and doses used. All the analysis carried out here were in systematic increase of ion dose referenced to the films as grown in order to study the character of phase transformation. Further Raman spectra with narrower and resolved D peak were received by annealing of both implanted and reference as-grown ta-C films. Examples of representative films annealed at 973 K are given in Fig. 9. They show relaxation processes in ta-C films [16] and indicate smaller levels of sp^2 fraction disordering when compared to the cited work [5]. The difference is in annealing. In the referred work the annealing had to take place during, for example, xenon ion implantation because the energy deposited per a unit area and second (200 W/cm^2) is extremely large and therefore the heat developed upon ion impact hardly can dissipate efficiently. Consequently the substrate temperature has to increase to a considerable value. In order to prevent the heating effects induced and estimate the structural changes induced by ion beam the energy deposited per

a unit area and second was 0.2 W/cm^2 only in this work. Such an approach enables to correlate the atomic displacement quantitatively obtained by Monte Carlo simulation with the data of structural modification acquired using Raman spectroscopy, HRTEM and TED analyses for estimating the threshold values of implantation treatment when the onset of the structural transformation occurs. Since, the atom density of ta-C films is approximately 1.65×10^{23} atoms/cm^3 and the calculated average defect density is 4×10^{22} vacancies/cm^3 the onset damage density corresponds to approximately 0.24 displacements per atom (dpa). The determined 0.24 dpa is a critical value correlating to a critical dose of 3×10^{15} carbon ions/cm^2 (at 25 keV) which is consistent with that of 0.21 dpa reported for ion-beam-induced modification of glassy carbon [14,17].

4. Conclusions

This article presents studies on nanostructuring of ta-C films by the impact of energetic carbon ions. Using high carbon ion energies and considerable ion doses the initial ta-C structure with high content of sp^3 bonding ($>70\%$) can be restructured in a nanoscale range giving rise to expansion of existing sp^2 bonding sites and even the formation of new sp^2 bonding sites on the detriment of the sp^3 matrix bonding sites. The selection of proper ion energies and doses for ion implantation may induce the films with properties of interest. As demonstrated herein, ta-C films with typically high sp^3 fraction converted to a graphitic layer with the basal plane perpendicular to the surface. Detail examining the change in fitting parameters of G peak as a function of ion dose showed that the transformation from sp^3 to sp^2 fraction begins to occur at a damage level of ~0.24 dpa in ta-C films.

Due to the facts above the ion implantation is a nearly ideal method to introduce controlled amounts of damage inside ta-C films. At high doses the initially amorphous ta-C structure can even be turned to a nanocrystalline structure in the controlled zone of the film. Fine controlling the size and the structure of the sp^2 carbon nanostructures as well as the sp^3 carbon matrices, in which sp^2 inclusions or more extensive nanostructure may be embedded, is expected to yield systematic guidelines for the tailoring of desired optical, electrical and mechanical properties.

Acknowledgments

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