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Effect of swift heavy ion irradiation on single- and multiwalled carbon nanotubes

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ABSTRACT

The effect of irradiation with swift heavy ions on the structure and properties of carbon nanotubes was investigated by Raman spectroscopy. It was found that disordering of the system occurred mainly at the surface. No ordering phenomena have been observed over a whole range of both fluences and electronic stopping powers studied. The disorder parameter (i.e., the ratio of the D and G band intensities (I_D/I_G)) increases non-linearly with the irradiation dose, showing a tendency to saturate at high fluences. The increase in the disorder parameter upon irradiation was proportional to the square root of the ion fluence. The radiation stability of the few-walled nanotubes was ca. 1.6 higher than that of the single-walled ones. The irradiation with both the Xe and Kr ions leads to essentially the same increase in the I_D/I_G ratio with respect to the deposited electronic energy density. In the case of the Ar ion irradiation, the observed increase in the I_D/I_G ratio is much lower, suggesting that the electronic stopping power threshold for defects creation in carbon nanotubes is lower than that for graphite.

1. Introduction

Irradiation of carbon nanotubes (CNTs) with energetic ions and electrons was proved to be a useful tool for tailoring their mechanical, electronic, and optical properties [1]. The electron and high energy ion beam irradiation was demonstrated to induce a variety of interesting phenomena, such as the cutting of nanotubes [2], coalescence [3], welding [4,5], formation of bonds between the respective nanotubes (cross-linking) [6] as well as between the nanotubes and the substrate (binding) [7]. Locally enhanced reactivity, resulting from the presence of structural defects, could successfully be applied for selective chemical functionalization, as evidenced both theoretically and experimentally [8–10]. Possible applicability of the CNT-based nanosensors and nanodevices under extreme environmental and operational conditions in many areas, including aerospace, nuclear reactors, and fuel storage devices, is an additional driving force for the investigation of these issues [11].

In recent years, the irradiation of carbon nanostructures with swift heavy ions (SHIs) has been drawing increasing attention. As opposed to the low-energy ions, SHIs transfer their energy predominantly to the electronic subsystem of the material being irradiated. Under typical experimental conditions, the nuclear energy losses are usually negligible, thus providing the possibility of investigating the effects caused by dense electronic excitation. Despite the increasing number of the relevant studies, the effects of SHI irradiation on CNTs are not yet fully understood since both the experimental results reported by different scientific groups and their interpretation are often inconsistent. For example, the disorder parameter, derived from the Raman spectroscopy measurements and usually used as a measure of the excess of radiation damage, is frequently being reported to undergo various changes as the irradiation proceeds. Some authors reported the ordering phenomena to occur at low irradiation doses [11,12], whereas the others noticed even more complex changes in the disorder parameter [13,14]. To explain the observed phenomena, different mechanisms have been proposed, like the occurrence of two competing processes, namely production and healing of defects [11], three-stage mechanism including formation of amorphous carbon at a final step [13], and damage accumulation mechanism assuming the necessity of some level of damage to accumulate for further irradiation to cause ordering of the CNT system [14]. This lack of universal explanation, frequently accompanied by discrepancy between the results of analogous experiments carried out by different groups, gives rise to the question whether the observed complex behavior of the disorder parameter originates in some cases more likely from experimental errors and wrong choice of commercially available samples than from the irradiation.

Based on the above considerations, the aim of the present study was to undertake systematic investigation with regard to explain

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the possible effects of SHI irradiation on the structure and properties of CNTs. In order to resolve this issue as well as possible, high-quality CNT samples were chosen and many spectra were recorded and averaged for each specimen at a designated spatial distance. In particular, we focused on differences in the radiation stability of single- and thin multi-walled nanotubes.

2. Experimental

2.1. Materials and sample preparation

Commercially available single-walled nanotubes, denoted as SWNTs (purity > 95 vol%, SWNT content > 90 vol%, length 5–30 μm) were obtained from Nanostructured & Amorphous Materials, Inc. Analysis of the Raman radial breathing modes (RBMs) has shown that the sample is characterized by a broad distribution of tube diameters ranging from at least 0.85–1.7 nm, which is in agreement with 1–2 nm range given by the manufacturer. The samples labeled as FWNT-3B and FWNT-3N (purity > 90%, amorphous carbon < 5%, length 0.5–40 μm) were obtained from Helix Material Solutions, Inc. These samples are being distributed by the producer as the single-walled and double-walled nanotubes, respectively. Earlier studies proved that both samples are multi-walled nanotubes (MWNTs). The FWNT-3B and FWNT-3N specimens contained mainly tubes with three or more graphene layers [15], with a maximum of the size distribution centered at ca. 3–4 nm in both cases. According to Furmaniak et al. [15], the FWNT-3B sample exhibits a broader size distribution than FWNT-3N does.

Nanotube thin films (so-called buckypapers) with a thickness of ca. 5 μm were prepared using a vacuum filtration method. A portion of the nanotube powder placed in an aqueous solution of the Triton X-100 surfactant, after being sonicated at a low-power pulsed mode to form a stable suspension, was passed through a membrane filter. The resulting CNT films were then extensively washed with deionized water to remove any residual surfactant and dried.

2.2. Irradiation

Buckypapers were irradiated at room temperature with the ^{40}Ar (50 MeV), ^{86}Kr (107 MeV), and ^{132}Xe (167 MeV) ions at the IC-100 cyclotron at FLNR JINR, Dubna. The incident electronic (S_e) and nuclear (S_n) stopping powers, calculated using the SRIM-2010 code [16] while assuming the density of carbon nanotubes to be equal to that of graphite (2.26 g/cm^3), are collected in Table 1.

2.3. Raman spectroscopy measurements

Raman spectra were recorded with a RamanMicro 300 spectrometer (PerkinElmer), using a 785 nm near-infrared laser source and a 50× objective lens. The applied spectral parameters were as follows: laser power 10 mW, resolution 2 cm^{-1}, CCD temperature −50 °C, and total integration time 600 s. In all the experiments, the laser spot was maximally defocused to avoid the specimens from being overheated locally. With each sample, a point-by-point mapping was performed with the 1-mm spacing on an area of 4 mm × 4 mm, which resulted in at least 8 and 12 spectra per sample for SWNTs and FWNTs, respectively. In some selected cases, the Raman spectra were acquired on the exit surface and in the bulk (after mechanically removing the surface layer). The resulting spectra were de-spiked, background-corrected, using an algorithm for minimizing a non-quadratic cost function implemented in MATLAB [17], and then normalized to the G-mode intensity of 1.

Table 1
Ion irradiation parameters

Ion type	Energy (MeV)	S_e (keV/nm)	S_n (eV/nm)
Xe	167	17.3	80
Kr	107	11.4	36
Ar	46	5.65	14

3. Results and discussion

The Raman spectra of virgin and irradiated SWNT specimens are presented in Fig. 1. The spectra of the non-irradiated specimens consist of several spectral features with the high-energy G-mode (at ca. 1584 cm^{-1}), corresponding to planar vibrations of carbon atoms in a perfect graphene lattice, disorder-induced D-mode (max. 1307 cm^{-1}), and its second-order overtone G′ (with a maximum at 2590 cm^{-1}), being the most prominent ones. In both types of the specimens, the G-band is split into a low-frequency G$^-$ component originating from vibrations along the circumferential direction and a high-frequency G$^+$ component associated with vibrations along the nanotube axis. RBM modes (100–300 cm^{-1}), resulting from a coherent motion of carbon atoms in the radial direction of the nanotube (i.e., contraction and expansion), are clearly visible in the spectra of the non-irradiated SWNTs. It is known from the literature that, with an increasing number of walls due to superposition of contributions originating from individual inner tubes of different diameters, the G-band splitting diminishes and blurs, finally leading to a slightly asymmetric line for typical MWNTs [18]. Also, MWNTs usually exhibit RBM modes of low intensity only. Few-walled nanotubes, as those used in this study, can be considered in terms of the transition form between single- and typical multi-walled nanotubes. They preserve some characteristic features of single-walled nanotubes. Thus, some splitting of the G-band as well as quite intensive RBM modes are visible in the respective Raman spectra (not shown).

The D bands are present in the spectra of all non-irradiated CNTs specimens, giving the corresponding disorder parameter values of 0.06, 0.215, and 0.46 for SWNT, FWNT-3N, and FWNT-3B, respectively. Pure MWNTs, due to significant contribution of nanotube ends to the D-band intensity, are usually characterized by higher values of the initial disorder. However, such a high I_D/I_G as determined for the FWNT-3B specimen, if one assumes that the tubes are of a regular length, should be considered as indicative of the presence of structural defects and/or impurities.

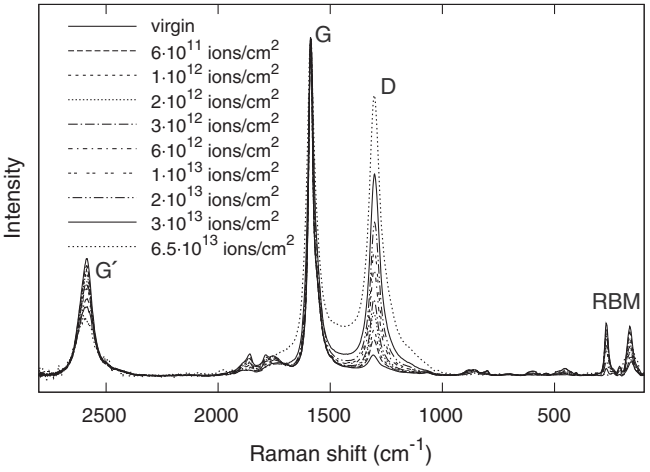

Fig. 1. Raman spectra of virgin and Xe ion-irradiated SWNT specimens.