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1 Introduction

The extraordinary electrical, thermal and mechanical properties of SWNTs are tied to their perfect defect free structure. However, in the case of more bulky ensembles of SWNTs, like buckypapers and yarns, the presence of defects can to some extent lead to improvements. This behaviour was reported in studies where bulk SWNT samples were irradiated by a highly energetic electron beam [1] or by gamma-rays [2, 3]. Obviously, defects strongly influence all the properties of SWNTs (individual tubes, bulk ensembles). In the case of gamma-irradiation, the dynamics of defects creation due to highly energetic photons was studied by Raman spectroscopy [4]. A focused electron beam leads to defect formation and reconstruction or to cross-links between nanotubes [5].

In this paper, we compare how Ar$^+$-irradiation affects electrical conductivity in various configurations: an individual semiconducting SWNT (s-SWNT), a thin network of SWNTs and a SWNT buckypaper.

2 Experimental

Purified HiPCO SWNTs were purchased from Carbon Nanotechnologies, Inc. (Texas).

These SWNTs were suspended in a 1% aqueous solution of sodium dodecyl sulfate (SDS) followed by ultra-sonication and a centrifugation, and then dispersed onto palladium electrodes pre-patterned using electron beam lithography on a highly doped Si substrate with a silicon oxide layer of 200 nm in thickness. The distance between the source and the drain electrode was approximately 0.8 μm.

To make thin networks, SWNTs suspended in water with SDS were air-brushed on the surface of Si/SiO$_2$ wafers.

A free-standing thick SWNT film was prepared from a suspension of SWNTs in water with SDS by vacuum filtration. The thickness of the thick film was 50 μm.

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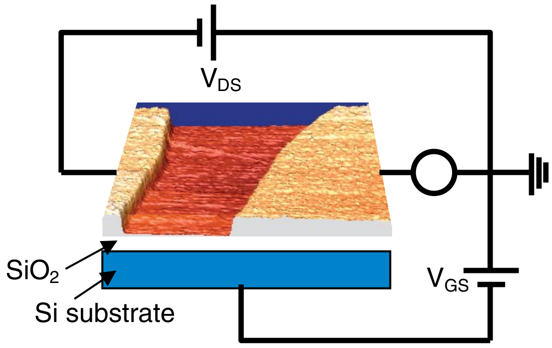

Fig. 1 Schematic diagram for two-terminal method used for electrical measurements of the individual SWNT.

An individual SWNT on Si substrate, nanotube networks and thick SWNT film were introduced into an ion implanter and irradiated with Ar^+ ions of 30 keV, using a low dose of $D = 5 \times 10^{11}$ ions/cm^2 for individual SWNT, and higher doses for thin networks (up to 10^{13} ions/cm^2) and for a thick film made of SWNTs (up to 4×10^{12} ions/cm^2). The ion current was $I = 0.9$ µA, and the irradiation was done at normal incidence.

For the individual SWNT, the current–voltage characteristics between source and drain electrode ($I_D - V_{DS}$) were measured at various temperatures down to liquid helium temperature, applying the two-terminal measuring method (Fig. 1) before as well as after Ar^+-irradiation.

The electrical conductance of the SWNT buckypaper and of the thin SWNT network was measured by the four probe method, from liquid He to room temperature.

Raman spectra were measured using microscope laser Raman spectroscopy with a Jobin Yvon–LabRam spectrometer. The laser excitation wavelength was 632 nm with a spectral resolution of 4 cm^{-1}.

Stress–strain characteristics were measured using a tensile-testing machine (Zwick & Roell).

3 Results and discussion

3.1 Raman spectra

Figure 2A shows Raman spectra of pristine and Ar^+-irradiated SWNT thick film (buckypaper) obtained at incident photon wavelength 633 nm. The data are normalized to the D*-mode intensity at about 2600 cm^{-1}. The D-mode at about 1302 cm^{-1}, as a result of 1st-order double-resonant scattering, is induced by defects in the planar graphene structure [6]; therefore, it reflects the damage caused by Ar^+-irradiation as an increase of the intensity of the D-mode (see inset of Fig. 2A). The dependence of the

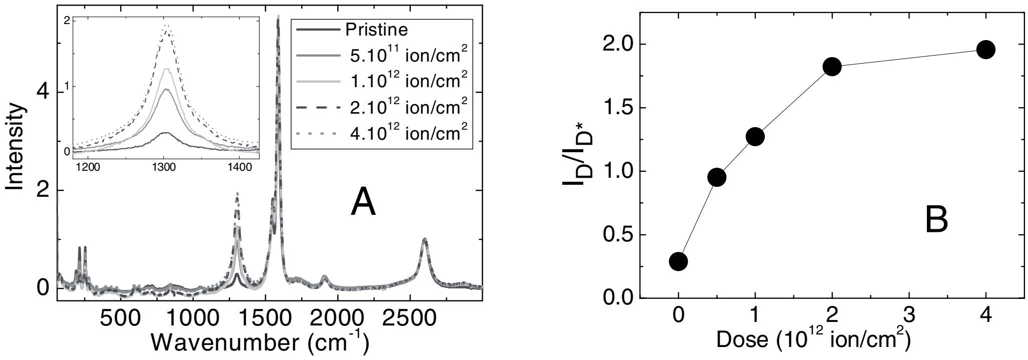

Fig. 2 (A) Raman spectra of pristine and Ar^+-irradiated SWNT buckypaper, (B) normalized intensity (I_D/I_{D*}) of the Raman D-mode to D*-mode vs. dose of Ar^+ ions.

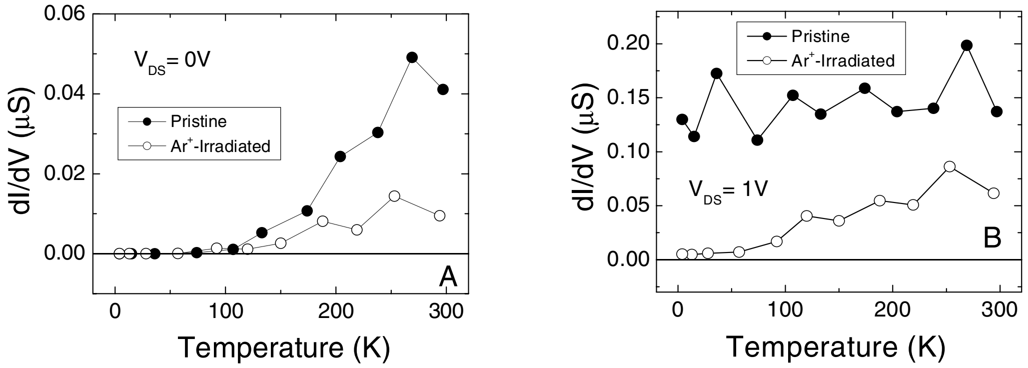

Fig. 3 Temperature dependence of differential conductance (dI_D/dV_{DS}) of an individual s-SWNT before and after Ar$^+$-irradiation at drain–source voltage (A) $V_{DS} = 0$ and (B) 1 V.

normalized intensity I_D/I_{D*} on the dose of Ar$^+$-irradiation is plotted in Fig. 2B. With the increasing dose, the early steep growth of the intensity I_D/I_{D*} saturates at about 2×10^{12} ions/cm^2, doubling its starting value. In our previous paper [4], a similar effect due to gamma-irradiation of thick SWNT film is interpreted as the result of equilibrium in the dynamics of creation and recombination of the defects when the critical number of defects is reached.

3.2 Electrical conductance of individual SWNT

The semiconductive nature of the tube was determined from the gate dependence of current I_D (not shown here) in FET configuration. The temperature dependence of the differential conductance dI_D/dV_{DS} of the s-SWNT at drain-source voltage $V_{DS} = 0$ (Fig. 3A) and 1 V (Fig. 3B) significantly changes after Ar$^+$-irradiation with a dose of 5×10^{11} ions/cm^2. The ions create predominantly single- and multi-atom vacancies in the nanotube walls and penetrate into the substrate [7]. At this relatively small dose, considering a nanotube with a diameter of 1 nm and 1 µm long, five Ar$^+$-ions would collide with the nanotube, creating from five to ten vacancies in the body of the tube. This damage significantly affects the conductance, reducing it to 1/3 of its value before irradiation. At low bias voltages ($V_{DS} = 0$ V), the temperature dependences of dI_D/dV_{DS}, both before and after irradiation, are thermally activated and changed by several orders of magnitude. For $V_{DS} = 1$ V, electronic transport in the pristine tube is fully activated in the whole temperature range, unlike in the after-irradiation tube. Defects form localized energy states in the energy gap, thus diluting the density of states in the valence and conductance bands, calculated in a recent theoretical study [8].

3.3 Electrical conductance of thin SWNT networks

Figure 4A shows that the room temperature conductance of the thin SWNT networks decreases with the dose of Ar$^+$-irradiation by several orders of magnitude. The temperature dependence of the normalized conductance $G(T)/G(300\ \mathrm{K})$ before and after irradiation at a dose of 10^{13} ions/cm^2 is shown in Fig. 4B. Before irradiation, the shape of $G(T)$ has a convex character. This is typical of conductive networks, where the resistance of contacts between the tubes in the network is much larger than the intrinsic resistance of the tubes themselves, thus limiting the charge transport [9]. After irradiation, a concave shape of the $G(T)$ demonstrates a significant change in the transport mechanism, due to a structural disorder induced by irradiation. The intrinsic resistance of the defective nanotubes predominantly limits the current passing through the network.

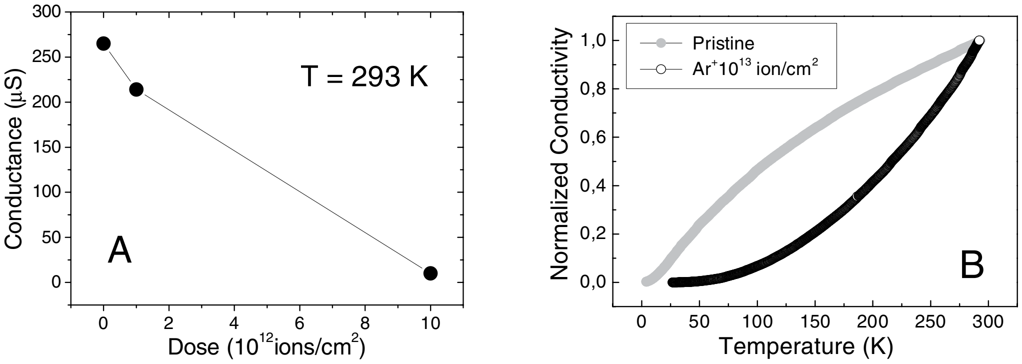

Fig. 4 (A) Room temperature conductance of the thin SWNT networks vs. dose of Ar^+ irradiation, (B) temperature dependence of the normalized conductance $G(T)/G(300\text{ K})$ before and after irradiation at a dose of 10^{13} ions/cm^2.

3.4 Electrical conductance of thick self-standing SWNT film

Figure 5A presents the dose dependence of the conductivity of a thick SWNT film. Unlike both the individual SWNT and the thin SWNT network, we see a clear increase of the conductivity value after irradiation, with a maximum at about $(0.5-1)\times 10^{12}$ ions/cm^2. The penetration depth of the 30 keV Ar^+ ions into graphite substrates is estimated to be 30–40 nm by calculations done with the TRIM code. The D-mode of Raman spectra indicates that Ar^+ ions do not penetrate through the thick SWNT film either. As the energy of the colliding ions decreases, the type of defects created in SWNTs might vary. At specific energy conditions, cross-links might form between neighbouring tubes. A delicate balance between the destruction of the graphene order and the number of cross-links could result in an increase of electronic transport through the network. Since the structure of the irradiated SWNT film varies in different

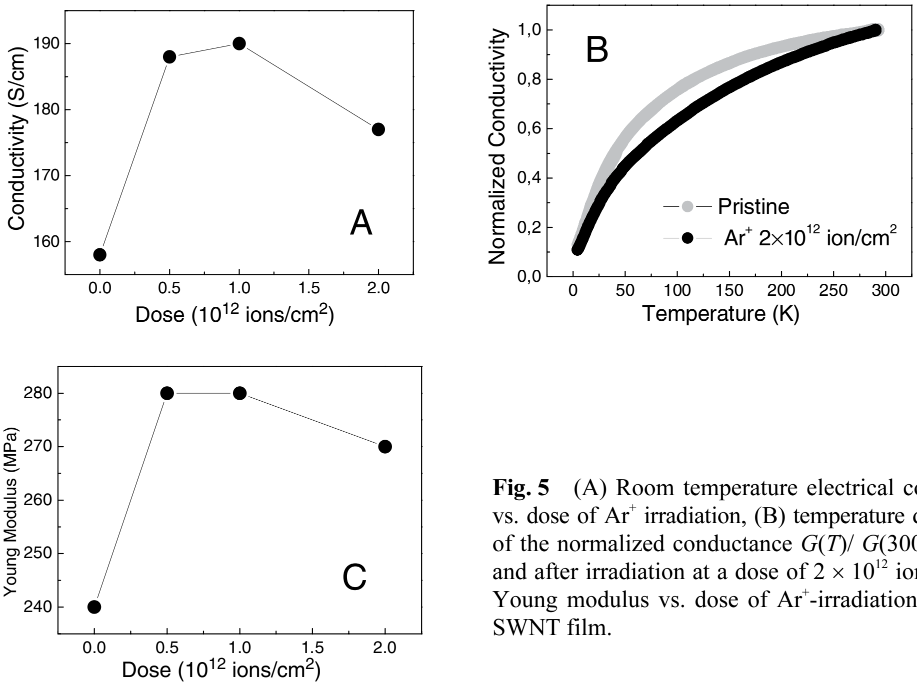

Fig. 5 (A) Room temperature electrical conductivity vs. dose of Ar^+ irradiation, (B) temperature dependence of the normalized conductance $G(T)/G(300\text{ K})$ before and after irradiation at a dose of 2×10^{12} ions/cm^2, (C) Young modulus vs. dose of Ar^+-irradiation of a thick SWNT film.

layers, transport realizes through the path of lowest resistivity. The change in the transport mechanism after irradiation is reflected by a flattening of the shape of the temperature dependence $G(T)$, as in Fig. 5B. The change in the Young modulus of the thick SWNT film with the dose of Ar$^+$-irradiation (Fig. 5C) copies the behaviour of its electrical conductivity. This is similar to observations on gamma-irradiated SWNTs reported in [2, 3].

4 Conclusion

1. The electrical conductance in both individual SWNTs and thin SWNT networks is strongly reduced by highly energetic Ar$^+$ ions.
2. On contrary, thick SWNT films exhibit an increase of electrical conductivity and Young modulus after Ar$^+$-irradiation.

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