

Electrical properties of C⁴⁺ irradiated single-walled carbon nanotube paper

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ity of the samples is changed progressively by the irradiation: whereas the pristine sample exhibits mixed metallic-nonmetallic character consistent with the usual model of metallic conduction interrupted by thin barriers through which fluctuation-assisted tunnelling occurs, the temperature dependence loses its metallic character and follows three-dimensional variable-range hopping for the most irradiated sample.

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1 Introduction Nano-engineering to tailor the properties of carbon nanotubes by irradiation [1, 2] with high-energy ions or electrons has been demonstrated experimentally and by theoretical simulations. Ion irradiation modifies conduction in individual single-wall carbon nanotubes (SWNTs) [3] and in SWNT networks [4], with remarkable correlations between changes in Young's modulus, Raman line frequencies and conductivity [5].

In this paper we report the effects of bombardment by ions of high energy (23 MeV) chosen so that the majority of ions will pass right through the SWNT paper. We find that there is a qualitatively different effect on the conductivity compared to our earlier measurements using irradiation by 30 keV Ar⁺ and N⁺ ions, which came to rest and deposited essentially all their kinetic energy in the SWNT paper [4, 6]. We use carbon ions for the irradiation, which means that no impurities of different elements are introduced when some ions are stopped in the sample.

2 Experimental

2.1 Sample preparation Single-walled carbon nanotube paper of 40 μm thickness was prepared by vacuum filtration of HiPCO material suspended in 1 % SDS and subsequent washing with deionized water to remove surfactant. By use of the microgram scale balance the volume density of CNT paper was estimated to 0.7 g/cm³.

Taking into account the volume density of the paper, it was calculated using the SRIM (Stopping and Ranges of Ions in Matter) code [7] that ¹²C⁴⁺ ions of energy 23 MeV would have a penetration depth of 57 μm, sufficient to pass through the 40 μm paper. During irradiation, the sample was held by aluminium foil which also served as a mask (Fig. 1).

Four samples have been exposed to the 23 MeV ¹²C⁴⁺ beam. The accelerator used for this study was a 5 MV tandem accelerator of the Accelerator Laboratory, University of Helsinki. The irradiation conditions concerning doses, time and current are summarized in Table 1.

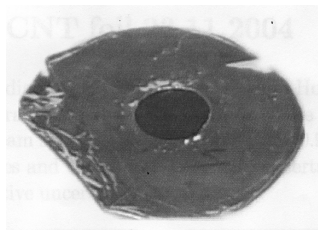


Figure 1 Aluminium sample holder with the sample inside. The diameter of the opening is 1 cm.

Table 1 Irradiation parameters.

Dose, ions/cm ²	Time, s	Current, nA
1×10^{13}	132	48.5
3×10^{13}	365	52.6
1×10^{14}	1113	57.5
3×10^{14}	4668	41

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

The electrical conductivity of the SWNT paper fixed on the surface of Si/SiO₂ wafers was measured using the four-probe method by evaporating four chromium (20 nm)/gold (200 nm) strips of the same geometry for all the samples, i.e. 0.3 mm distance between the strips. A constant current was applied during the temperature dependence measurements from liquid helium temperature up to room temperature.

3 Results and discussion Raman spectra were measured on both surfaces of the samples: the front side (directly irradiated) as well as the back side. It is well known [8] that increasing defect concentration in carbon structures with sp² electron orbital configuration causes an increase of the Raman D line, in our case with the peak maximum at about 1313 cm^{-1} (excitation light wavelength of 633 nm) and, therefore, we use this as an indication of the structural damage caused by ion irradiation. To compare the spectra of the samples with different doses of ion irradiation, the spectra were normalized to the intensity of the second order mode related to the D line, the D* mode at 2614 cm^{-1} . Although the intensity of this mode depends on the helicity of the tubes [9], it shows only little dependence on the defect concentration [10]. In our case if normalized to G mode, both D and D* intensities increase upon irradiation but while the D* mode rises by only 30%, the D mode increases more than 10 times compared to that of the pristine sample. The relative changes of the intensity of the D line normalized to that of the D* line are plotted versus dose of ion irradiation for the front and the back sides of the samples in Fig. 2A. Since the increase of the D

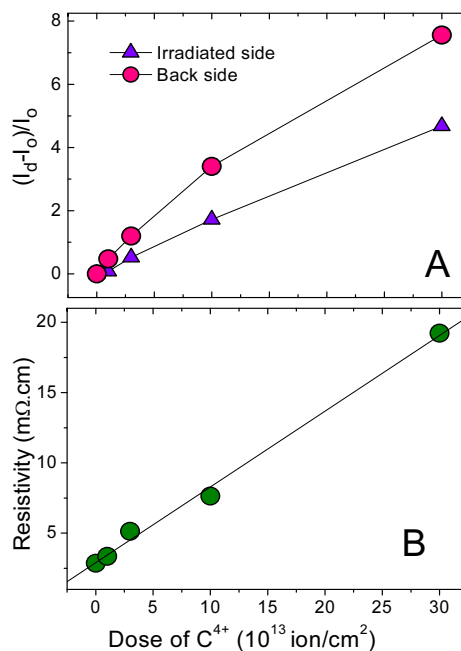


Figure 2 (A) Relative increase of intensity of the D line measured on the front (violet triangles) and the back (pink circles) surfaces of the samples and (B) electrical resistivity at room temperature versus dose of C⁴⁺ ion irradiation.

line is so large, normalizing by the G+ line intensity instead of the D* line yields almost identical plots in Fig. 2A.

Figure 3 shows the displacement per atom (DPA) as a function of sample depth for two irradiation doses, as calculated with the code SRIM [7]. The threshold energy for displacing carbon atom was equal to 15 eV [2]. Based on our SRIM calculations, one can expect that the amount of damage caused by C⁴⁺ ions with the energy of 23 MeV should be higher at the back side. This is confirmed by the measured data, which show a greater increase in D line intensity at the back side of the sample (Fig. 2A).

Figure 2B shows how the resistivity of the samples increases approximately linearly with the irradiation dose following the relation:

$$\rho = 0.00286 + 5.4 \times 10^{-17} d \text{ } \Omega\text{cm}, \quad (1)$$

where d is the dose of 23 MeV C⁴⁺ ions per cm². It is clear that the defects introduced by irradiation drastically increase the resistance so that the resistance at higher doses is strongly dominated by these irradiation defects.

We now turn to an analysis of the temperature dependence of the conductivity $\sigma(T)$ of the samples (plotted in Fig. 4) to give an indication of the conduction mechanisms occurring, following our earlier modelling of conduction in SWNT paper irradiated with 30 keV Ar⁺ and N⁺ ions [4, 6]. For the pristine sample (before irradiation), there is no significant difference (Fig. 4) for decreasing temperature and increasing temperature at double the current (0.5 mA and

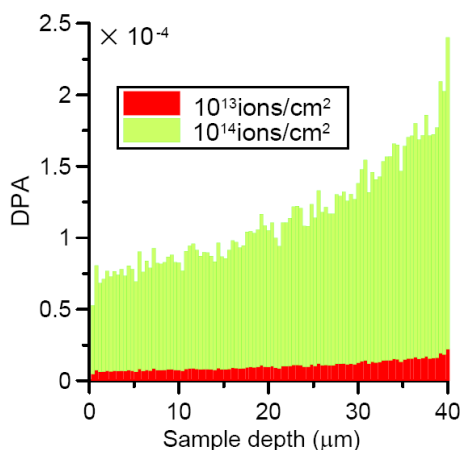


Figure 3 SRIM calculations of the damage created by C⁴⁺ ions with the energy of 23 MeV in the SWNT paper with a density of 0.7 g/cm³ and thickness of 40 μm.

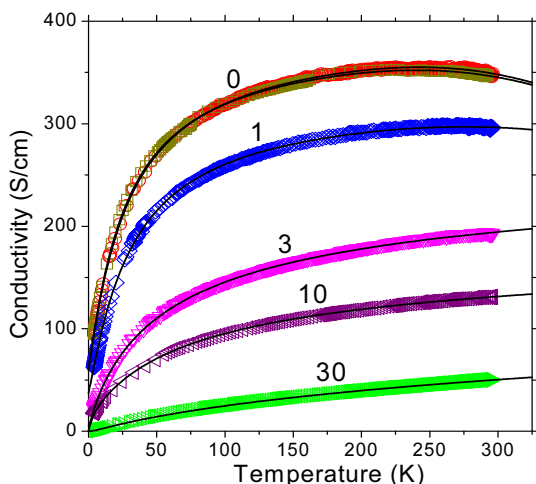


Figure 4 Temperature dependence of the conductivity of the SWNT paper samples, with the dose of C⁴⁺ ions given beside the data sets in units of 10¹³ ions/cm²; two data sets are shown for the sample prior to irradiation, one with a current of 0.5 mA for decreasing temperature (red circles), and the other at 1 mA for increasing temperature (dark yellow squares). The lines through the data points are fits to Eq. (2) for data sets 0 and 1, and to Eq. (3) for the others, as explained in the text.

1 mA respectively), illustrating the absence of hysteresis effects and dependence on current level.

The pristine data show the characteristic features of highly conducting SWNT networks [6] where conduction is dominated by the metallic nanotubes, with a finite conductivity still present in the zero-temperature limit, and a turnover to metallic sign for the conductivity temperature dependence as temperature increases above approximately 240 K. However, the increase of conductivity with temperature up to 240 K indicates the presence of thermally-assisted conduction, ascribed to tunnelling through thin barriers that allow conduction even at zero temperature. An

excellent fit to the data for the pristine data sets, and for the lowest-dose irradiated sample which shows similar behaviour, is given by our model [6] of quasi-one-dimensional (quasi-1D) metallic conduction [11] with fluctuation-assisted tunnelling [12] through defect barriers between and along nanotubes:

$$\frac{1}{\sigma(T)} = B \exp\left(\frac{T_b}{T_s + T}\right) + A \exp\left(-\frac{T_m}{T}\right). \quad (2)$$

Here A and B are coefficients depending on geometrical factors that can often be taken as independent of temperature [6]. The order of magnitude of typical barrier energies is indicated by the value of $k_B T_b$ and the extent of the remaining tunnelling conductivity at low temperatures is indicated by the ratio T_s/T_b . The energy $k_B T_m$ is that of the phonons that dominate scattering of the carriers [12]. The values of the fit parameters (listed in Table 2) are comparable to those of earlier samples, corresponding to small tunnelling barriers $k_B T_b$ of approximately 2 meV, and zone-boundary phonon energies $k_B T_m$ as expected [6].

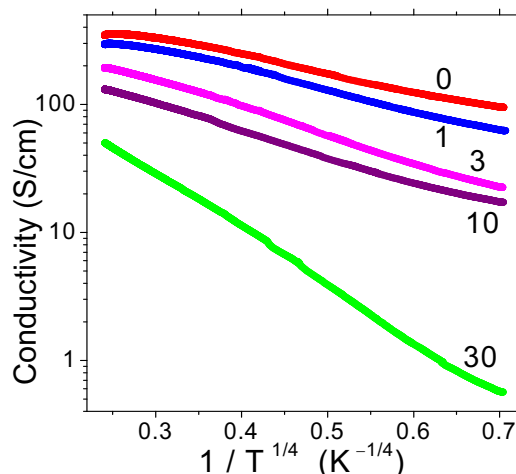


Figure 5 Demonstration of 3D-VRH behaviour of conductivity as a function of temperature at the highest dose of 30×10^{13} ions/cm² (except at the lowest temperatures); the other data sets show significant lessening of slope at high and low temperatures.

We focus here on the effect of irradiation by 23 MeV C⁴⁺ ions. As we have seen, for the lowest dose of 10¹³ ions/cm², the irradiation reduces the magnitude of conductivity while the qualitative behaviour of Eq. (2), including the changeover to metallic temperature dependence near room temperature, is retained. However, for higher doses, Eq. (2) can no longer account for the data which is then well explained by a three-dimensional variable-range hopping (3D-VRH) term in parallel with the fluctuation-assisted tunnelling term (the quasi-1D metallic contribution now making no significant contribution). This is the behaviour we found for SWNT paper thicker than the ion penetration depths [4, 6]. For parallel conduction, we add the conductances:

$$\sigma(T) = C \exp\left(-\frac{T_b}{T_s + T}\right) + H \exp\left(-\left(\frac{T_0}{T}\right)^{1/4}\right), \quad (3)$$

where C and H are approximately temperature-independent parameters indicating the contributions of each term, and T_0 is the Mott hopping parameter that depends on the localization length and density of states for the carriers involved in the hopping [13, 14]. This model accounts very well for the conductivity for the three most highly-irradiated samples, as shown by the fits in Fig. 4, with values of the fit parameters listed in Table 3. The fluctuation-assisted tunnelling term becomes smaller until for the most highly irradiated sample the conductivity is well accounted for by the 3D-VRH term alone (with a large value of T_0 , i.e. highly localized carriers), as shown directly by the linearity of the corresponding plot of $\log(\sigma)$ versus $1/T^{1/4}$ in Fig. 5 (except possibly at very low temperatures). The value of the barrier energy $k_B T_b$ increases with irradiation as expected, while the value of T_s shows no significant change.

Table 2 Fit parameters for fits of Eq. (2) to the highest conductivity samples.

Dose (ions/cm ²)	A^{-1} (S/cm)	T_m (K)	B^{-1} (S/cm)	T_b (K)	T_s (K)
0	23	1770	390	23	12
1×10^{13}	18	1800	330	27	12

Table 3 Fit parameters for fits of Eq. (3) to the lowest conductivity samples.

Dose (ions/cm ²)	H (S/cm)	T_0 (K)	C (S/cm)	T_b (K)	T_s (K)
3×10^{13}	330	330	88	42	11
1×10^{14}	235	210	47	70	11
3×10^{14}	475	7600	0		

4 Conclusion We have shown that the room-temperature resistivity of SWNT networks of thickness 40 μm irradiated by 23 MeV C^{4+} ions increases approximately linearly with dose, mirroring the increase of the defect density determined from Raman D-line intensity measurements. The increase of D-line intensity at the back side confirms that a large fraction of C^{4+} ions penetrate across the sample leaving damage distributed throughout the whole sample. Due to the very high energy of the ions, a larger defect rate is observed at the samples' back surfaces, where the kinetic energy of the penetrating ions is reduced significantly so that the cross section for defect production is larger.

The temperature dependence of conductivity is well described by quasi-1D metallic conduction interrupted by fluctuation-assisted tunnelling through small barriers for the pristine and lightly-irradiated samples. At higher C^{4+} ion doses, 3D variable-range hopping makes a significant contribution to conduction, and dominates the total conductivity at the highest dose. This dominance of 3D VRH

conduction was also what we observed in thin transparent SWNT networks irradiated with 30 keV Ar^+ and N^+ ions that also penetrated through these very thin samples [14].

In contrast to the case of 23 MeV C^{4+} ions, lower energy 30 keV Ar^+ and N^+ ions incident on SWNT paper of thickness approximately 50 μm penetrate at most a few μm and Raman D-line measurements confirm that none reach the back side of the SWNT paper [4]. In that case, we concluded that annealing by heat propagating along SWNTs from the impact region affected a region of the sample much larger than the surface impact layer itself, leading (at low doses) to an increase in conductivity in this region due to annealing of small barriers along SWNTs, consequent delocalization of charge carriers, and removal of impurity dopants that increased the carrier density. This scenario accounted for the peaks in conductivity observed as a function of ion irradiation dose [4, 5].

For the case of 23 MeV C^{4+} ions in this paper, however, the whole of the sample is affected so there are no highly-conducting layers left undamaged and VRH makes the dominant contribution to resistance across the whole sample at the highest doses.

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