

Effects of ion beam heating on Raman spectra of single-walled carbon nanotubes

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(Received 5 December 2008; accepted 12 January 2009; published online 18 February 2009)

Free standing films of single-wall carbon nanotubes were irradiated with energetic N^+ and C^{4+} ions. The observed changes in the Raman line shape of the radial breathing mode and the G band of the C^{4+} irradiated samples were similar to those found for a thermally annealed sample. We ascribe these changes to thermal desorption of volatile dopants from the initially doped nanotubes. A simple geometry of the experiment allows us to estimate the temperature rise by one-dimensional heat conduction equation. The calculation indicates that irradiation-mediated increase in temperature may account for the observed Raman spectra changes. © 2009 American Institute of Physics. [DOI: 10.1063/1.3077311]

When an energetic ion penetrates a solid target, it loses its energy by two mechanisms.¹ At low energies (normally in the keV range, the crossover energy depends on the ion mass¹ and material properties²), the ion mostly knocks target atoms out from their positions due to ballistic collisions and creates vacancies, interstitials, and other defects in the sample. At higher energies, the ion dissipates its energy inelastically through electronic excitation of the target atoms, which may or may not result in the formation of defects.³ In either case, the energy of the ions is absorbed during their slowing down in the sample, and it is assumed that the considerable amount of the absorbed energy converts finally into heat.⁴

The *in situ* annihilation of irradiation-induced defects has been observed in carbon nanotubes heated up to mild temperatures (>200 °C) under the electron irradiation.^{5,6} Moreover, ordering of fullerene and carbon nanotube films was recently reported at low dose ion irradiation with 200 MeV Au and 60 MeV ions,⁷ as manifested by the changes in the Raman spectra of the irradiated samples. This counterintuitive result was explained in terms of the trade-off between damage production and its *in situ* annealing due to the local heating of the sample by high-energy ions. The competing processes of defect creation and annihilation in nanocarbon materials can result in very interesting effects such as pressure accumulation in carbon onions,⁸ increase in electrical conductivity⁹ of nanotube films, and even self-organization phenomena.¹⁰ Thus the precise knowledge on the role of ion-beam-induced heating is required for the complete understanding of irradiation effects in carbon nanomaterials.

Here, by combining ion-irradiation experiments with Raman spectroscopy and calculations based on the solution of heat equation with an account for radiation losses from the sample surface, we study the effects of beam heating on single-wall carbon nanotube (SWNT) samples. The shape of the Raman G band is sensitive to the doping state of a sample¹¹ which, in turn, can be controlled by heat treatment.

For that, we correlate the results of calculations with the changes observed in the Raman spectra of the samples irradiated with 30 keV N^+ and 23 MeV C^{4+} ions and a sample subjected to high-temperature treatment without irradiation.

Free-standing strips with the thickness of 40 μm made of HiPCO SWNTs were prepared for the experiments. The details of the experiments were described elsewhere.¹² One set of the samples were then exposed to the 30 keV N^+ beams and another one to the 23 MeV C^{4+} beams at normal incidence evenly irradiating the whole sample surface. The experimental conditions are summarized in Table I. Raman spectra were collected by a Labram system equipped with a microscope and a 632.8 nm laser excitation line at room temperature. They are shown in Figs. 1 and 2 for the samples irradiated with N^+ and C^{4+} ions, respectively. For easier comparison of the development of the G band upon irradiation, the spectra were normalized with respect to its intensity.

The D -mode intensity increases in all the irradiated samples reflecting the accumulation of defects, as reported previously.¹² In the spectrum of the N^+ irradiated sample, RBMs decrease continuously with the increasing irradiation dose. On the other hand, the shape of the G band is not substantially changed by irradiation. On the contrary, in the case of the C^{4+} irradiated samples, RBMs of metallic nanotubes (below ≈ 250 cm^{-1}) increase in intensity while those of semiconducting ones (above 250 cm^{-1}) do the opposite. The lower-energy component of the G band at about 1560 cm^{-1} gets broader and asymmetric with a characteristic Fano line shape.

The theoretical analysis of our experimental results was based on TRIM (Ref. 13) calculations of ion stopping in carbon nanotube samples. It shows that 23 MeV C^{4+} ions create less defects per ion in the nanotube sample skin region probed by Raman scattering (about 300 nm in depth¹⁴) than 30 keV N^+ ions by a factor of about 300–400. Even though the highest dose of C^{4+} was more than 20 times higher than that of N^+ , we estimate that the number of defects produced by ballistic collisions of C^{4+} ions is still 15–20 times smaller than the number of defects produced by N^+ ions at the high-

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TABLE I. Experimental conditions for the irradiation with the N^+ and C^{4+} ions: dose J , irradiation time t_i , incident power density Q/S .

	J (ion/cm ²)	t_i (s)	Q/S (W/m ²)
N^+	0.5×10^{12}	30	0.8
N^+	13×10^{12}	120	5.2
C^{4+}	3×10^{13}	365	2760
C^{4+}	30×10^{13}	4668	2160

est dose. This is consistent with the Raman results for the D line to G band intensity ratio. It is larger for the N^+ irradiated sample than that for the C^{4+} one.

In order to explain the radiation-induced evolution of the G band in the C^{4+} irradiated sample, we have first to specify the state of the unirradiated one. In Fig. 3 we compare the spectra of the unirradiated samples with those of samples chemically p -doped in H_2SO_3 .¹⁵ The spectrum of the unirradiated nonheated sample is very similar to that of the H_2SO_3 -treated sample. Therefore, the former is also doped most likely through the purification process. There is also a spectrum of a H_2SO_3 -treated sample after thermal annealing in vacuum at 500 °C in Fig. 3. RBMs gain intensity and the low-energy component of the G band is significantly broadened. Here, the sample becomes charge neutral when H_2SO_3 desorbs at elevated temperatures. Almost the same changes were observed for RBMs and the G band in the unirradiated sample heated up to 500 °C (Fig. 3) and the irradiated ones shown in Fig. 2. We conclude that the changes observed in the irradiated samples are also due to the dopant desorption evoked by the ion beam heating in this case.

In the following, we analyze this assumption by a simple model based on heat conduction equation and TRIM calculations. According to the latter, the C^{4+} ions lose their energy leaving the rear surface of the sample with an average kinetic energy of 2 MeV. In contrast, all the N^+ ions are captured within the nanotube sample. The maximal stopping range is ~ 200 nm being just a fraction of the total sample thickness. In this case the heat is completely released on the sample's surface at the rate Q (in watt) and propagates from the front surface at $x=L$ toward the rear surface at $x=0$. The temperature distribution within the sample follows the heat equation in one dimension: $T_x(x,t) - aT_{tt}(x,t) = 0$. The boundary con-

ditions are $T_x(0,t) = 0$ and $T_x(L,t) = Q/(\lambda S)$ and the initial condition is $T(x,0) = 0$. $a = \lambda/(c_v \rho)$ is thermal diffusivity, λ is thermal conductivity, c_v is specific heat, $\rho = 0.9$ g cm⁻³ is the sample's density and S is the surface area. The solution of the heat equation reads

$$T(x,t) = T_m \left[\frac{t}{\tau} + 3 \frac{x}{L} - \frac{1}{6} + \frac{2}{\pi} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k^2} e^{-k^2 \pi^2 t / \tau} \cos\left(\frac{k \pi x}{L}\right) \right], \quad (1)$$

where $T_m = QL/(\lambda S)$ and $\tau = L^2/a$ is the thermal diffusion time. For $\lambda = 75$ W/m K,¹⁶ $c_v = 600$ J kg⁻¹ K⁻¹,¹⁷ and $L = 40$ μ m we get $a = 1.39 \times 10^{-4}$ m² s⁻¹ and $\tau = 1.15 \times 10^{-5}$ s. The power density Q/S can be calculated from the radiation dose J , the energy loss of the ions ΔE , and the irradiation time t_i as $Q/S = J \cdot \Delta E / t_i$ and is also shown in Table I.

The very short diffusion time means that heat propagates quickly through the sample. The ratio t/τ greatly exceeds 1 for typical irradiation times thus reducing Eq. (1) to the simple relation $T(x,t) = (T_m/\tau)t$. The temperature increases linearly with time and is the same everywhere in the sample. We can think of that as having the heat released homogeneously throughout the volume of the sample no matter where the ions actually stop. Importantly, this allows us to analyze the heat effects for both the N^+ and C^{4+} irradiated samples on an equal footing from now on.

However, a steady increase in the temperature is not a realistic assumption. Rather, thermal radiation from the sample's surface will eventually balance the heat uptake from ion irradiation and a stationary temperature T_s is acquired. This process can be modeled by the equation

$$\frac{\partial T(t)}{\partial t} = T_m/\tau - 2 \frac{\epsilon \sigma}{\rho c_v L} (T(t)^4 - T_0^4) \quad (2)$$

with an initial condition $T(0) = T_0$. $\sigma = 5.67 \times 10^{-8}$ W/m² K⁴ and emissivity $\epsilon = 1$ for blackbody radiation and $\epsilon < 1$ otherwise. The factor of 2 in Eq. (2) accounts for the two radiating surfaces of the sample.

In the stationary state $\partial T(t)/\partial t = 0$ and for the temperature T_s , we get $T_s = T_0 [1 + (Q/S)/(2\epsilon\sigma T_0^4)]^{1/4}$. The stationary temperature does not depend on the physical properties of

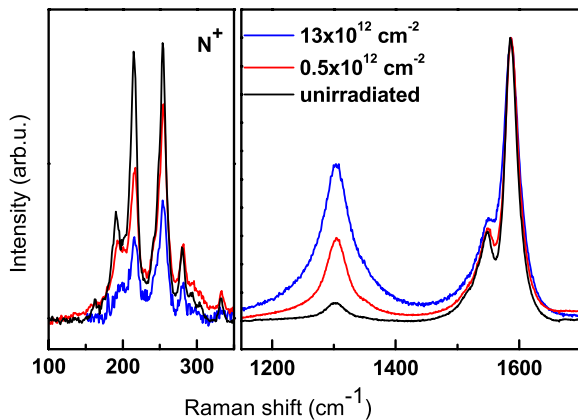


FIG. 1. (Color online) Raman spectra of an unirradiated SWNTs sample and of samples irradiated by 30 keV N^+ ions with different irradiation doses. RBMs (left panel) and the D (~ 1300 cm⁻¹) and the G bands (right panel).

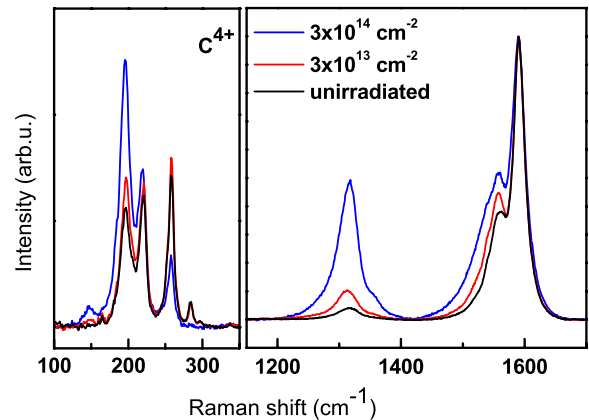


FIG. 2. (Color online) Raman spectra of an unirradiated SWNTs sample and of samples irradiated by 23 MeV C^{4+} ions with different irradiation doses. RBMs (left panel) and the D and the G bands (right panel).

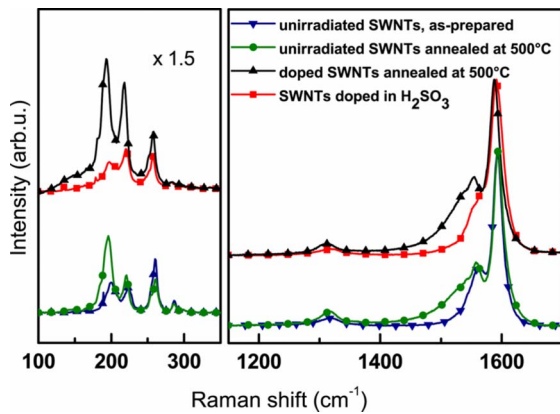


FIG. 3. (Color online) Comparison of Raman spectra of a SWNTs sample *p*-doped by chemical treatment in H_2SO_3 before and after heating at $500\text{ }^\circ\text{C}$ and of an as-prepared unirradiated SWNTs sample before and after heating at $500\text{ }^\circ\text{C}$. RBMs (left panel) and the *D* and the *G* bands (right panel).

the sample. It is simply determined by the ratio of the incident power density and the sample emissivity, the latter being the only sample-specific quantity. For $\epsilon=1$ and $T_0=300\text{ K}$, we have $T_s\sim 424$ and 406 K , for C^{4+} irradiation doses of 3×10^{13} and 3×10^{14} ions/ cm^2 , respectively. The higher temperature for the smaller dose is because a higher ion current density J/t_i was used for irradiation. For the N^+ irradiated samples $T_s\sim T_0$ and the samples are not heated up by the incident ion beam at all.

Besides the temperature, there must be a long enough period of time for desorption of dopants to influence the Raman spectra. In other words, the warming-up phase must be much shorter than the total irradiation time. A fairly good [when compared to the numerical solution of Eq. (2)] estimate can be obtained by linearizing Eq. (2). The assumption that $T(t)=T_0+\Delta T(t)$ and the replacement of the brackets in the last term of Eq. (2) by $4T_0^3\Delta T(t)$ convert the latter into a linear equation for $\Delta T(t)$. For its solution, $\Delta T(t)\sim[1-\exp(-t/t^*)]$ holds with $t^*=\rho c_p L/8\epsilon\sigma T_0^3$ characterizing the duration of the warming-up phase. For $T_0=300\text{ K}$, $t^*\sim 1.8\text{ s}$ indicating that this phase is complete within a few seconds after the irradiation started.

The results above depend critically on the actual values of the incident power density and emissivity. Simulations of TRIM agree well with those from more accurate molecular dynamics simulations for carbon nanotubes.¹⁸ Blackbody radiation was observed for nanotubes heated up to high temperatures.¹⁹ On the other hand, the temperature is still not high enough to anneal sufficiently the defects.²⁰ Therefore, we believe that our approach is reasonable and that the calculated values of the stationary temperature are a good estimate.

A natural question arises, whether the temperature is high enough to undope the nanotubes and change the Raman spectra as observed in Fig. 2. It was shown in Ref. 21 that a portion of covalently bonded fluorine was released from nanotubes even at temperatures below $200\text{ }^\circ\text{C}$. Therefore, the changes observed in Fig. 2 can be explained by thermal desorption of the dopants. The latter depends on the temperature and time the temperature acts on the sample. The level of undoping is thus the highest for the longest irradiation

time, as seen from the Raman measurements.

Keeping in mind the importance of beam-induced heating for the response of a nanosystem to irradiation, we estimated the current density required for the heating of our system to $500\text{--}600\text{ K}$ under these same irradiation conditions, when *in situ* annealing of defects under irradiation occurs.^{5,6,10} According to our model, a current density of $0.1\text{--}0.3\text{ }\mu\text{A}/\text{cm}^2$ should substantially slow down the amorphization of the SWNT target. Our future experiments will check this conjecture.

In conclusion, we showed that a simple approach based on the solution of a one-dimensional heat conductance equation can describe the heating of a thin nanotube film by an ion beam. Our results indicate that irradiation-mediated increase in temperature may indeed be high enough for desorption of volatile dopants during irradiation. We support this statement by results from Raman measurements. The changes observed in Raman spectra of irradiated samples correlate with those seen in a thermally annealed sample.

M.H. and V.S. acknowledge the Center of Excellence CENAMOST (Slovak Research and Development Agency Contract No. VVCE-0049-07) with support of project 06-628. V.S. and S.R. acknowledge support from the EC project SANES.

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