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Abstract

The authors investigate the effect of electron irradiation on the resonant frequency of single-walled carbon nanotube bundles. Electron beam irradiation was employed to induce the formation of intertube cross-linking. An increase in the resonant frequency was observed at low electron doses as the bending modulus was enhanced by cross-link formation. Higher doses induced amorphization and knock-on damage in the bundle, resulting in an overall reduction of the bending modulus. The effect of stiffness enhancement is more pronounced in larger diameter bundles due to the more compliant initial condition. At 45 nm diameter, an increase in bending modulus of 115% is observed.

Keywords

carbon nanotubes, nanotube devices, oscillators, electron beam effects, bending, elastic constants, amorphisation, micromechanical devices

Comments

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Tuning the resonant frequency of single-walled carbon nanotube bundle oscillators through electron-beam-induced cross-link formations

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The authors investigate the effect of electron irradiation on the resonant frequency of single-walled carbon nanotube bundles. Electron beam irradiation was employed to induce the formation of intertube cross-linking. An increase in the resonant frequency was observed at low electron doses as the bending modulus was enhanced by cross-link formation. Higher doses induced amorphization and knock-on damage in the bundle, resulting in an overall reduction of the bending modulus. The effect of stiffness enhancement is more pronounced in larger diameter bundles due to the more compliant initial condition. At 45 nm diameter, an increase in bending modulus of 115% is observed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2472535]

Nanoelectromechanical systems (NEMSs) have shown increasing promise for applications in ultrasensitive force detection,^{1,2} biological sensing,³ scanning probes,⁴ and wireless communications.⁵ The mechanical resonant mode operation enables the frequency modulation of the output, greatly improving the stability/noise immunity of the reading. The sensitivity of NEMS devices depends critically on the size and stiffness of the resonating materials. The unique structure and properties of carbon nanotubes make them an attractive candidate for such NEMS structures. Their high strength, high aspect ratio, and low density make them suitable for the development of high frequency resonators that would allow the analysis of extremely small displacements and forces at the molecular scale.

Resonators with tunable stiffness might be used in applications where selectivity of the resonant frequency can be implemented.⁶ In this letter, we report the irreversible tuning of the resonant frequency of single-walled carbon nanotube (SWNT) bundle resonators via cross-link formations upon electron beam irradiation. We employ *in situ* analysis of vibrations in the transmission electron microscope (TEM) to study the effect of electron irradiation on the mechanical resonance properties of SWNT bundles. The ability to controllably modify the structure of the carbon nanotube in order to achieve specific properties could enable the development of high performance nanoscale resonators that can provide both high quality resonance and sensing specificity. This tuning process is compatible with solid-state device fabrication process and facilities.

Carbon nanotube bundles consist of loosely interacting packs of parallel and individual SWNTs held together by van der Waals (vdw) interactions. Using a technique similar to the one employed by Poncharal *et al.*,⁷ we have recently investigated the mechanical resonances of such bundles and observed that the weak interaction between tubes results in an effective bundle bending moduli in the $E_b=71\text{--}446$ GPa

range,⁸ rather than the theoretical $E=1.2$ TPa for SWNTs.⁹ This reduced modulus is directly related to the weak vdw forces that bind the tubes together, resulting in relatively low shear moduli in the thick bundles. In fact, the overall mechanical properties of SWNT bundles are increasingly compromised as the bundle diameter increases due to the increasing importance of shear between the tubes.

The opportunity to control the stiffness of SWNT bundles exists due to the sensitivity of carbon nanotubes to electron and ion irradiations.^{10,11} An inelastic interaction between electrons or ions of the irradiating beam and the valence electrons of the carbon atoms can induce a change from the sp^2 hybridized state to the sp^3 hybridized state. The occurrence of two sp^2 to sp^3 events on neighboring tubes could result in the formation of a cross-link between the constituent tubes of a bundle. It is not known whether the existence of a nearby sp^3 hybridization affects the cross section for this beam-induced sp^2 to sp^3 reaction. Also unknown is the capture volume for the cross-link formation. It is also possible that cross-linking occurs via direct nanotube-nanotube bonding or through a bridging mechanism utilizing a residual impurity molecule leftover from the synthesis or processing. An atomic force microscopy study reported by Kis *et al.*¹² has shown that such irradiation-induced cross-linking increases the static mechanical stiffness of suspended nanotube bundles. In this letter, we investigate the effect of irradiation on the resonant properties of bundles.

The SWNT materials were prepared similarly to our previous experiments.^{8,13} The SWNT bundles studied in this experiment possessed diameters varying from $D=11$ to 45 nm, lengths varying from $L=2.58$ to 5.00 μm , and aspect ratios ranging from 80 to 250. The mechanical resonances of nanotube bundles were characterized in a JEOL 2010 TEM operating at 80 keV. The same energy is also used to irradiate the bundles, which is below the theoretical threshold energy for knock-on damage of 86 keV.¹⁰ This is critical to preserve the tubular structure of nanotubes during property modification and was explored in depth in prior work.¹⁰

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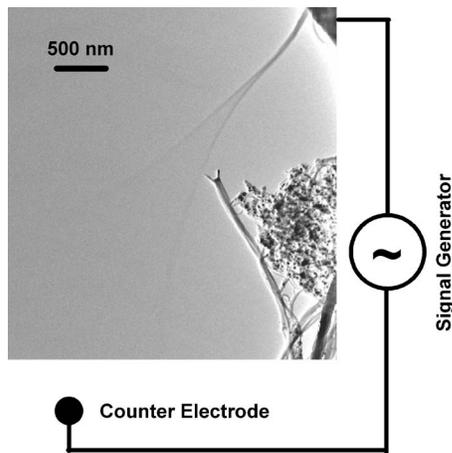


FIG. 1. Experimental setup. A SWNT bundle is actuated with an ac signal to induce vibration at its resonant frequency.

An actuating ac signal was applied between the sample and a tungsten counterelectrode using a Wavetek stabilized sweep function generator. The actuation signal was manually tuned until mechanical resonance was visually observed (Fig. 1), and the observed resonant frequencies f_o were recorded as a function of bundle diameter, length, and irradiation dose. The nature of the connection between the nanotube bundle and the substrate can influence the observed mechanical properties. In this letter, only tightly anchored bundles in which the observed pivot points of the oscillations were located at the substrate edge were included in the data. The initial resonance frequency of each bundle was first assessed at low magnification and low beam current density in order to minimize the effects of irradiation during this initial assessment. We then converged the beam to increase the dose rate. The magnification was adjusted to have the total length of the bundle spanned approximately 2/3 of the beam size. Since the electron beam has a Gaussian distribution profile, the irradiation dose varied somewhat along the length. Approximating the bundles cross section as being circular, the relationship between resonant frequency and size is derived from the elementary beam theory of a cantilevered beam,¹⁴

$$f_i = \frac{B_i^2 D}{8\pi L^2} \sqrt{\frac{E_b}{\rho}}, \quad (1)$$

where f_i is the resonant frequency, L is the length of the bundle, D is its diameter, E_b is the effective bending modulus, ρ is the density, and B_i is a constant for the i th harmonic oscillation; $B_0 = 1.875$.¹⁴

Figure 2 shows the dose-dependent resonant frequency of a SWNT bundle with $D = 11$ nm and $L = 2.58$ μm . The resonant vibration initially moves toward higher frequency before undergoing a substantial decrease upon further irradiation. The change in the resonant frequency relates to the structural evolution of SWNT bundles under the electron beam. According to Eq. (1), the resonant frequency of a beam with specific D and L is proportional to $\sqrt{E_b/\rho}$. At low dose, the increase of f_o is a result of the enhanced E_b due to the formation of cross-links induced by inelastic interactions between the beam electrons and the valence electron of the nanotube or through bridging molecules. This interaction produces covalent attachment of neighboring tubes and impedes the shear flows that affect the bending modulus in the bundle. Species such as oxygen and nitrogen molecules ad-

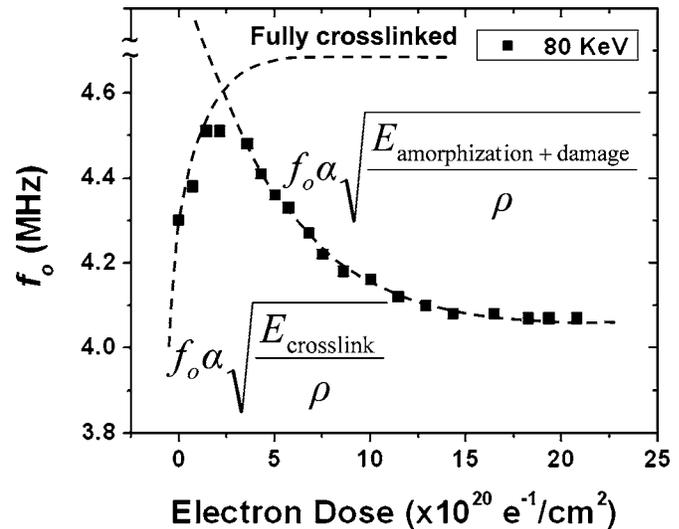


FIG. 2. Change in resonant frequency of a SWNT bundle as a function of electron irradiation dose taken from a SWNT bundle of $D = 11$ nm and $L = 2.58$ μm . The rate of change in f_o is a result of two competing mechanisms, cross-link formation and damage or amorphization in the structure. The effect of these mechanisms will be to increase and decrease the effective modulus, respectively (dashed curves). The plateau in the cross-linking case is based on the intuitive concept that, in the absence of damage, cross-linking will saturate and the SWNT bundle will behave as a monolithic beam.

sorbed from air or hydroxyl and carboxyl groups resulting from the acid purification treatment could particularly participate in such cross-linking.¹² The nanotubes inside the bundle are separated by a vdw gap of 3.4 \AA . This distance is much larger than the C-C bond distance, and thus the formation of fourfold coordinated carbon atoms is indeed unlikely. Yet, we do not entirely disregard this possibility. According to Smith and Luzzi,¹⁰ a carbon atom that is a part of the curved wall of a nanotube has asymmetry in the p orbital and can form the delocalized π complex due to the repulsion of valence shell electrons. Therefore, a strong overlap in p orbital may occur between adjacent nanotubes whose curvatures are directly opposing each other.

Figure 2 also shows a dramatic reduction of f_o at higher irradiation doses, which is likely due to amorphization or the accumulation of damage on the tube walls, resulting in a lower E_b . It is known that electrons with energy of 80 keV do not damage isolated SWNTs, but do cause extensive structural changes in SWNT bundles.¹⁰ The structural changes in bundles are manifested as loss of crystal signature in high-resolution TEM followed by extensive loss of material at high doses. While the detailed damage mechanisms are not known, these processes could involve interstitial atoms or molecules trapped in the bundle or direct electronic interaction between neighboring nanotubes. Irradiation-induced heating can also occur,¹¹ which could result in the loss of mass from the surface of the bundle although the very high thermal conductivity of nanotubes should minimize this effect.¹⁵ Since damage may occur continuously throughout the irradiation process, the overall change in bending modulus is therefore the net result of a competition between the rate of cross-link formation and the rate of damage accumulation.

Since initial bending modulus of a bundle depends on its diameter,⁸ cross-linking can produce different levels of stiffness enhancement in SWNT bundles of different sizes. We

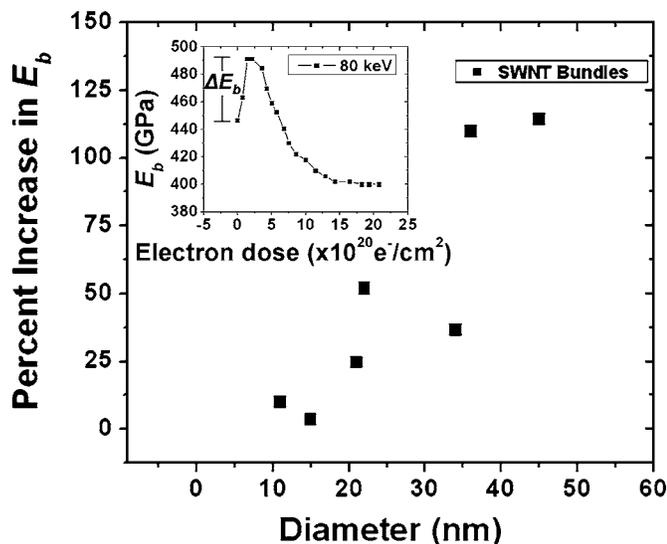


FIG. 3. Dependence of percent increase in E_b on SWNT bundle diameter. The bending modulus of a thin bundle was initially quite high, and E_b did not change much after the bundle was irradiated with an electron beam. For a larger diameter bundle, the initial E_b was low as a result of increasing shear flow in its structure. After irradiation, thicker bundles have shown higher percent increases in E_b , as the final E_b of the fully cross-linked bundles should be independent of diameter. The inset shows the evolution of E_b as a function of electron dose.

further investigated this by calculating the rate of stiffness enhancement and plotting as a function of bundle diameter. Knowing that the cross-sectional structure of a SWNT bundle is a two-dimensional triangular lattice¹⁶ with a vdW gap between tubes of 3.4 Å,¹⁷ and knowing that SWNTs produced by the pulsed-laser-vaporization method have a nominally uniform diameter of 1.36 nm, the density of a bundle is calculated to be $\rho = 1.3 \times 10^3 \text{ kg/m}^3$. Using this value, the bending modulus was calculated for each bundle according to Eq. (1). Figure 3 shows the percent increase of E_b , as computed at the highest value of the modulus achieved by irradiation, as a function of bundle diameter. The inset shows the evolution of E_b of a single bundle during irradiation. A higher enhancement is obtained in bundles of larger diameter since the initial value of E_b is lower due to the domination of the elastic properties by shear. An increase of as much as 115% was observed in a 45 nm diameter bundle.

In summary, we have employed inelastic interactions through electron beam irradiation to induce cross-links in SWNT bundles. At 80 keV, low to moderate doses of electrons can conceivably provide sufficient energy to generate

chemical bridges between tubes or induce changes from sp^2 to sp^3 hybridization on adjacent tubes. Due to the increase in stiffness caused by this cross-linking, the resonant frequency of nanotube bundles rises with irradiation dose with increases as large as 115% observed. Damage to the bundles also occurs with irradiation dose even at 80 keV beam energy and eventually dominates the properties. This study presents the possibility to controllably alter the resonant frequency of nanotube bundles which could be utilized for the development of functional SWNT-bundle-based oscillators. In these devices, specific resonant frequencies could be achieved by locally subjecting the structure to electron irradiation.

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