Mechanical Properties of Beams from Self-Assembled Closely Packed and Aligned Single-Walled Carbon Nanotubes

Yuhei Hayamizu,[1] Robert C. Davis,[3] Takeo Yamada,[1] Don N. Futaba,[1] Satoshi Yasuda,[1]
Motoo Yumura,[1] and Kenji Hata[1,2,*]

[1] *Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan*
[2] *Japan Science and Technology Agency (JST), Kawaguchi, 332-0012, Japan*
[3] *Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602, USA*

(Received 8 January 2009; published 28 April 2009)

To demonstrate the potential for microelectromechanical systems, nanotube beams composed from self-assembled closely packed and aligned single-walled carbon nanotubes were fabricated and their mechanical properties were measured. We found that the nanotube beams behave as a cohesive, rigid, and elastic body with a sound velocity of 10 100 m/s.

DOI: 10.1103/PhysRevLett.102.175505 PACS numbers: 62.30.+d, 61.46.Fg, 62.25.Jk

The large Young's modulus of 1 TPa [1,2], flexibility, and lightness of carbon nanotubes (CNTs) makes this material an ideal building block for mechanical devices spanning from composites to probe microscopy [3–6]. For example, a suspended nanotube with tension was used as a tunable electromechanical oscillator [7]. Also, a nanotube mechanical resonator served as an inertial balance to detect mass with atomic resolution [8,9]. These devices were composed from single or bundled nanotubes. This limits the ability to control the structure and mechanical properties because placing individual nanotubes with predetermined structures at prescribed locations with controlled orientations is difficult.

One approach to circumvent this limitation is to fabricate devices with predetermined configurations from a three-dimensional continuous nanotube medium composed from a massive number of nanotubes. Recent development of a bottom-up and top-down hybrid methodology has enabled fabrication and processing of such nanotube media. Specifically, vertically aligned yet sparse nanotube films were grown by chemical vapor deposition (CVD). Then these films were transformed into a continuous media, denoted as "CNT wafers," composed from closely packed and laterally aligned nanotubes [10]. Mechanical components, such as beams and membranes, could be created from the CNT wafers by standard lithography analogous to how Si-mechanical structures are etched from Si wafers. If these nanotube mechanical components possess promising mechanical properties, they could serve as basic components for new nanotube microelectromechanical systems (MEMS).

In this Letter, we have investigated the mechanical properties of nanotube beams composed from self-assembled closely packed and aligned single-walled carbon nanotubes (SWNTs) to assess their potential as micromechanical materials. SWNT beams with prescribed configurations were fabricated and optically actuated to probe the fundamental frequency and quality factors (Q factors). The nanotube beams elastically acted as a single cohesive unit, the mechanical properties followed the classical theory of elasticity, and the sound velocity was calculated as 10 100 m/s.

Our approach starts from growing vertically aligned SWNT forest films with 1 mm height by water-assisted CVD ("supergrowth") [11]. In brief, growth was carried out at 750 °C with C_2H_4 and water on pseudo-1D catalyst Al_2O_3/Fe (10 nm/1 nm) islands (width: 4 μm) patterned by lithography. With the assist of water, SWNTs grew and self-assembled into vertically aligned and homogeneous forest films. The forest was a very sparse material where SWNTs occupy only 3%–4% of the total volume [12]. A $\sim 1 \times 1$ mm forest film was placed on a 500×500 μm SiO_2 thin layer window made by etching the back side of a Si wafer with CsOH [Fig. 1(a)]. When forest films were immersed in an isopropyl alcohol liquid layer and dried, the SWNTs were zipped together into a closely packed and aligned nanotube medium (CNT wafer) [10,13]. Standard lithography with hydrogen silsesquioxane electron-beam resist and O_2 reactive ion etch was used to fabricate an array of nanotube beams from the nanotube media with varying predetermined lengths. Beams with nanotubes perpendicularly aligned could not survive the fabrication process, stressing the importance of the alignment direction. Finally, the SiO_2 thin layer window was removed by hydrofluoric acid vapor to suspend the nanotube beams [Figs. 1(b) and 1(c)].

The fundamental resonant frequencies of nanotube beams were investigated by dynamically measuring the photothermally excited oscillation in an air ambient [Fig. 2(a)] [14]. Specifically, the nanotube beam was photothermally oscillated near the clamped end by a modulated 405 nm drive laser (PicoQuant, LDH-P-C-405B). A Si photodiode (New Focus, 1 GHz low-noise photoreceiver) was used to detect the reflected intensity of a 632.8 nm He-Ne probe laser focused near the free end of the beam. A spectrum analyzer (Agilent, E4402E) was

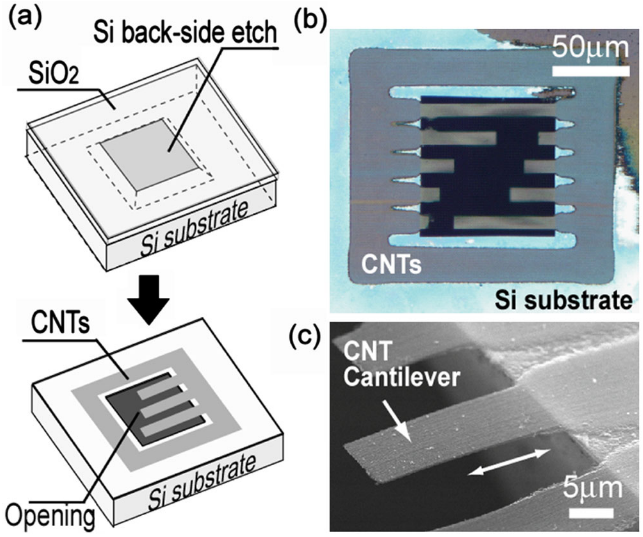

FIG. 1 (color online). (a) Schematic of the fabrication processes. (b) Optical image and (c) SEM image of nanotube beams. The dimension of the beams (250 nm thickness, 10 μm width, and length from 10 to 70 μm) was lithographically controlled. An arrow indicates the direction of the alignment of carbon nanotubes.

used to deliver the modulation signal to the drive laser and analyze the signal from the photoreceiver. As demonstrated in Fig. 2(b), the beams showed a clearly resolved single peak at a specific resonance frequency and a flat signal elsewhere within the measured range. As expected for a rigid body, the resonance frequency increased with decreased length and remained unvarying after an hour of continuous operation. These data highlight that the nanotube beam acts as a cohesive rigid body at these oscillation amplitudes, albeit being an agglomeration of self-assembled nanotubes zipped together only by van der Waals interaction.

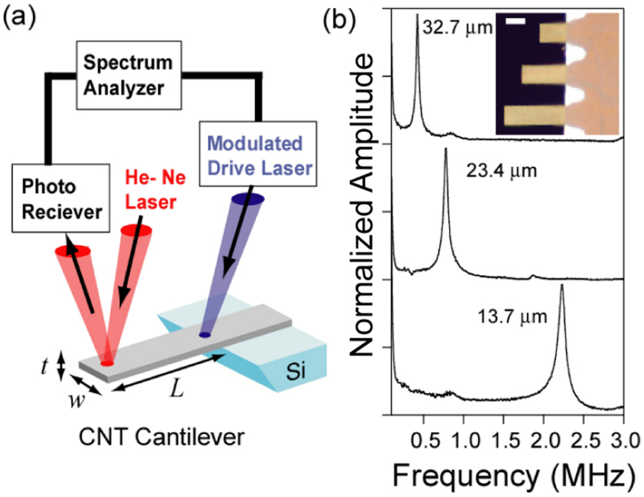

FIG. 2 (color online). (a) Schematics of measurement system for photothermally excited oscillation of nanotube beams. (b) Oscillation amplitude spectra of a series of nanotube beams with different lengths (13.7, 23.4, and 32.7 μm) in ambient air. All measured beams have 250 nm thickness and 10 μm width. The inset shows an optical image of nanotube beams from the top view.

We compared the experimental fundamental resonance frequencies of the nanotube beams and the theory of standard continuum mechanics. Continuum mechanics describe the fundamental frequencies of a beam harmonic oscillator on its geometry as

$$f = \beta \frac{t}{L^2}\sqrt{\frac{E_{\text{bend}}}{\rho}}, \tag{1}$$

with f the fundamental frequency, E_{bend} the flexural modulus of bending, ρ the density, t the thickness, and L the length. β is a geometrical coefficient that is 0.162 and 1.03 for a singly and doubly clamped beam, respectively. Accordingly, the fundamental frequencies increased linearly with a slope of $\beta\sqrt{E_{\text{bend}}/\rho}$ with respect to the effective geometer (t/L^2) factor. The fundamental frequencies of singly and doubly clamped nanotube beams with varying lengths (10–70 μm) were plotted (dots) versus the effective geometry (t/L^2) factor (Fig. 3). Several important points were drawn from the comparison between the experiments and theory. First, the data of singly clamped nanotube beams ($\beta = 0.162$) excellently fitted with a single line passing the origin as predicted. From the slope of the fitting line, the sound velocity ($\sqrt{E_{\text{bend}}/\rho}$), an inherent material property, was calculated as 10 100 m/s. Second, an additional line with a calculated slope from the geometrical coefficient of a doubly clamped beam ($\beta = 1.03$) and the obtained sound velocity were shown to match well with the experimental data. This meant that the mechanical response was elastic and thus provided evidence that the nanotube beams behaved as a continuous elastic media.

A continuum concept assumes that the substance of the body is distributed throughout—and completely fills—the space it occupies; however, nanotubes within the beams do not. Structural characterizations revealed that the nanotube beams (density 460 kg/m^3) were composed from defective and wavy SWNTs (2.8 nm mean diameter) [10] as indicated by the low G-band to D-band ratio ($G/D \sim 5$) in the Raman spectra. These SWNTs were imperfectly aligned as evidenced by a scanning electron microscope (SEM) [13]. The mean distance between SWNTs was 4.1 nm, meaning that the SWNTs occupied only 48% of the total volume. Even with this nonideal packing, the self-assembly nanotubes behaved as a continuous elastic medium, and we believe that the imperfect alignment provided the essential lateral interconnection between SWNTs to attain mechanical cohesiveness.

Comparison of the sound velocity ($\sqrt{E_{\text{bend}}/\rho}$) of the nanotube media with other materials revealed the potential

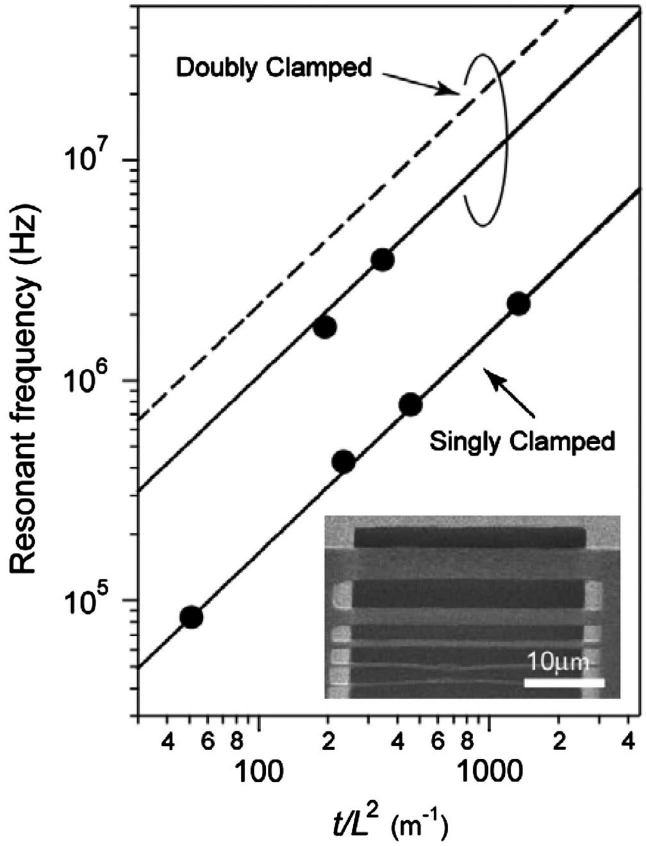

FIG. 3. Fundamental resonant frequencies of singly and doubly clamped nanotube beams with varying lengths (10–70 μm) were plotted (dots) versus the effective geometry (t/L^2) factor. The thickness and width of the beams was 250 nm and 10 μm, respectively. The black line shows a fitting line with the sound velocity of 10 100 m/s. The dashed line shows an expected line of an ideal carbon nanotube ($E = 1$ TPa and $\rho = 2270$ kg/m^3). The inset shows a SEM image of doubly clamped nanotube beams with different width.

of self-assembled nanotubes as a substance for high speed operation. Sound velocity is an important mechanical property that describes the speed of transmission of a small disturbance through a medium. Hence, the sound velocity expresses how fast the media can deform, oscillate, and resonate, providing an indicator of the ability of high speed operation. The estimated sound velocity for the nanotube beams as 10 100 m/s represents one of the highest ever obtained, being superior to Si crystal (8500 m/s), and approaches the level of high sound velocity materials such as SiC (13 000 m/s) and diamond (12 000 m/s). In sharp contrast, the sound velocity of a nonaligned random nanotube assembly (buckypaper: density 540 kg/m^3, Young's modulus 2.3 GPa [15]) was calculated as only 2100 m/s, and this was the same level as paraffin, emphasizing the importance of alignment.

In addition to elastic bending, shear deformation can contribute to the flexural deflection of the nanotube beam. According to the superposition principle, for a singly clamped beam, the generalized Hook's law describes the relationship among the flexural modulus E_{bend}, Young's modulus E, and shear modulus G as

$$\frac{1}{E_{\mathrm{bend}}} = \frac{1}{E} + \frac{3}{10}\frac{1}{G}\left(\frac{t}{L}\right)^2. \tag{2}$$

As shown in Eq. (2), the flexural modulus greatly depends on the anisotropicity of the beam: For long and thin beams driven at low amplitudes, shear between nanotubes is negligible, and the flexural modulus corresponds closely to the Young's modulus. Conversely, for short and thick beams, the shear governs the mechanical properties. According to Eq. (2), when shear contributes, the flexural modulus increases with increased length. However, a constant flexural modulus was obtained for nanotube beams with different lengths from the fit of the experimental fundamental frequencies to Eq. (1) (Fig. 3). This meant that the shear deformation was negligible for our nanotubes beams and that the flexural modulus corresponded closely to the Young's modulus.

Since the shear deformation was negligible, the Young's modulus of the nanotube media (beams) was calculated from Eq. (1) as 47 GPa from the measured sound velocity (10 100 m/s) and density (460 kg/m^3). From the Young's modulus of the nanotube media, the effective Young's modulus (E_f) of individual SWNTs was estimated by a simple model [16]. An ideal 2D close-packed regular array of SWNTs with a lattice constant $a = 4.1$ nm (mean distance) was assumed, with the cross-section area occupied by each tube as $A_t = a^2 \cos(\pi/6)$. The SWNTs were represented by a graphene sheet with a width equal to the circumference ($C_t = 2\pi R$, $R = 2.8$ nm) and thickness equal to the interplanar spacing of graphite ($c = 0.3354$ nm). With these assumptions, the effective Young's modulus (E_f) of individual nanotubes was estimated as $E_f = (cC_t/A_t)E = 230$ GPa. This value was lower than the 1 TPa strength [5] of the in-plane graphite or perfect SWNTs and similar to that reported for multiwalled carbon nanotubes (300 GPa) [17]. We believe that defects caused this deterioration. For comparison, a beam composed from ideal nanotubes with an effective Young's modulus (E_f) of 1 TPa would possess a sound velocity of 21 000 m/s (dashed line in Fig. 3).

Another important mechanical property of the nanotube beam is the quality factor Q, the ratio of the energy stored in the oscillator to the energy lost per cycle owing to damping. The Q factors were estimated from the full width at maximum of the oscillation amplitude of the resonance peak (Fig. 4) as 36 in air and 131 in vacuum (<0.01 Pa), respectively. To investigate the cause of the energy loss, the theoretically estimated Q factor for beams limited by air drag was calculated by the kinetic theory of gases as 15 in air and 1×10^7 in vacuum [18]. Consequently, the Q factor in air was determined mainly by air damping, while the Q factor in vacuum reflected the intrinsic property. The Q

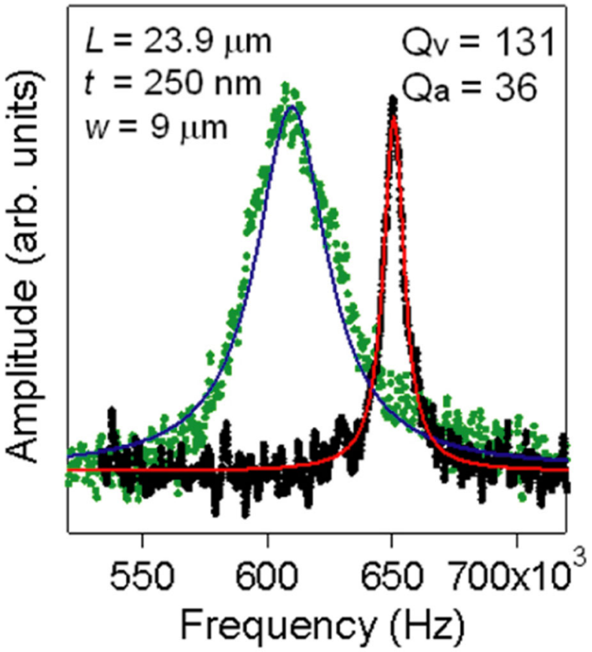

FIG. 4 (color online). Oscillation amplitude spectra of a nanotube beam in ambient air (green dots) and vacuum condition (black dots). Red and blue curves shows fitting curves with a Lorentzian function. The obtained quality factors were $Q_a = 36$ (air) and $Q_v = 131$ (vacuum).

factor of 131 was in good agreement with the range of 40–200 reported for CVD nanotubes [7,19] but lower than the range of 500–1000 reported for arc discharge nanotubes [6,9]. The energy loss in nanotube beams is thought to be due to sliding between loosely linked nanotubes. From a positive standpoint, such low Q nanotube beams might be useful for high frequency mechanical microswitching devices because of quick dumping of vibration. Another interesting direction would be sensors in liquids, as in such an environment the Q factor is limited by the liquid while the high surface area of the nanotube beams would be important for high sensitivity. In addition, we believe the Q factor could be improved by approaches to suppress the sliding among nanotubes via cross-linking between nanotubes [20] and filling the intertube spacing among nanotubes by other materials, such as polymers.

In conclusion, the mechanical properties of nanotube beams composed from self-assembled, closely packed, and aligned SWNTs were studied. The nanotube beams behaved as a cohesive, rigid, and elastic body with a sound velocity of 10 100 m/s. We believe that the promising mechanical properties of the nanotube media revealed by this work and other properties such as the flexibility and high surface area of nanotubes would develop into unique MEMS devices in the future.

---

*Corresponding author.
kenji-hata@aist.go.jp

[1] M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, Nature (London) **381**, 678 (1996).
[2] P. Poncharal *et al.*, Science **283**, 1513 (1999).
[3] J. N. Coleman *et al.*, Carbon **44**, 1624 (2006).
[4] P. Kim and C. M. Lieber, Science **286**, 2148 (1999).
[5] S. W. Lee *et al.*, Nano Lett. **4**, 2027 (2004).
[6] H. Dai *et al.*, Nature (London) **384**, 147 (1996).
[7] V. Sazonova *et al.*, Nature (London) **431**, 284 (2004).
[8] H. B. Peng *et al.*, Phys. Rev. Lett. **97**, 087203 (2006).
[9] K. Jensen, Kwanpyo Kim, and A. Zettl, Nature Nanotech. **3**, 533 (2008).
[10] Y. Hayamizu *et al.*, Nature Nanotech. **3**, 289 (2008).
[11] K. Hata *et al.*, Science **306**, 1362 (2004).
[12] D. N. Futaba *et al.*, J. Phys. Chem. B **110**, 8035 (2006).
[13] D. N. Futaba *et al.*, Nature Mater. **5**, 987 (2006).
[14] B. Ilic *et al.*, Appl. Phys. Lett. **86**, 193114 (2005).
[15] J. N. Coleman *et al.*, Appl. Phys. Lett. **82**, 1682 (2003).
[16] J. P. Salvetat *et al.*, Phys. Rev. Lett. **82**, 944 (1999).
[17] D. Garcia-Sanchez *et al.*, Phys. Rev. Lett. **99**, 085501 (2007).
[18] F. R. Blom *et al.*, J. Vac. Sci. Technol. B **10**, 19 (1992).
[19] R. P. Gao *et al.*, Phys. Rev. Lett. **85**, 622 (2000).
[20] A. Kis *et al.*, Nature Mater. **3**, 153 (2004).