

NANOSCALE STRAINING OF INDIVIDUAL CARBON NANOTUBES BY MICROMACHINED TRANSDUCERS

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Abstract: We report on the (opto-)mechanical properties of integrated single-walled carbon nanotubes. Individual nanotubes were integrated into micro-actuators by a simple location-controlled integration process. These structures allowed for reproducible strain-dependent Raman analysis of individual nanotubes under various levels of tensile strain. The nanotubes were suspended in air, reducing the support interaction and enabling characterization based on transmission beams.

Keywords: NEMS, carbon nanotubes, process integration

1. INTRODUCTION

Single-walled carbon nanotubes are predicted to exhibit significant changes in the electronic band structure and in the Raman shift of certain phonons under uniaxial strain [1, 2]. Experimental evidence for these changes was provided by measuring the Raman shift of nanotube composite materials. However, these measurements were averaged over many nanotubes with different chiralities and different orientations. As a result various strains were applied and strain-induced effects from individual tube were averaged and eventually canceled out [3]. The effect of strain is further complicated from the assembly process (epoxy curing) which causes a hydrostatic pressure-induced shift in the Raman modes and also by fracture of the epoxy which leads to inhomogeneity of the applied strain [4, 5]. More recently Cronin *et al.* [6] succeeded in probing individual single-walled carbon nanotubes by resonant Raman spectroscopy. Effects of ensemble averaging were thus eliminated, however, only two strain states could be recorded. AFM tip was used to remove the tube slack and apply a longitudinal strain by pulling the tube in the transversal direction.

In order to exclude support interaction and kinking effects, together with the quest for more than a single data-point from the same nanotube we present a new design of experiment. Freestanding individual SWNTs were integrated

into micro-actuators which applies pure uniaxial strains of different magnitudes to the tubes. This experimental setup allows for the investigation of the mechanical properties and, in particular, the strain-induced Raman shift of individual SWNTs without additional spectral perturbations.

2. RESULTS & DISCUSSION

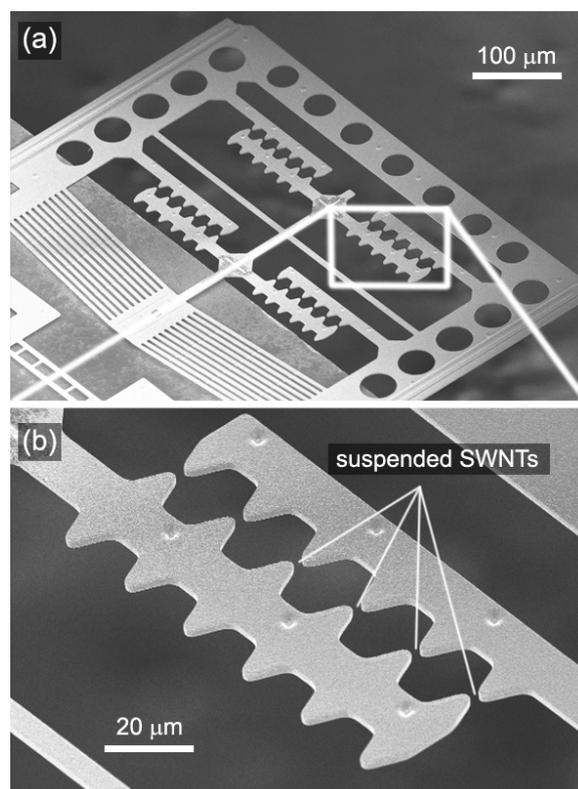


Figure 1. (a) SEM of a thermal actuator comprised of 24 tip-pairs. (b) Close-up of array of 6 tip-pairs defining gaps for the SWNT integration

Micro-actuators were fabricated and released from a standard surface micromachining process as shown in Fig. 1 [7]. They incorporate up to three structural layers of polycrystalline silicon sandwiching silicon oxides of various thicknesses. Catalyst was deposited onto the topmost layer by sputtering a 10 nm Al + 1 nm Ni bimetal. Chips were then heated under Ar to a temperature of 850°C. Hydrogen pretreatment was performed for 10 min at a pressure of 200 mbar. Then, thermal CVD under a 150 mbar/50 mbar mixture of CH₄/H₂ at 850°C during 15 min was carried out for the growth of SWNTs. Cooling was done in vacuum and nitrogen venting after cooling to at least 250°C. Support shaping as shown in Fig. 2 was found to control the location and orientation of the SWNTs. That is, successful tube bridging occurred only at specific locations defined by shaping the catalyst support (the micro-actuator tips) to force the SWNTs to span only over two neighboring tips which face each other directly.

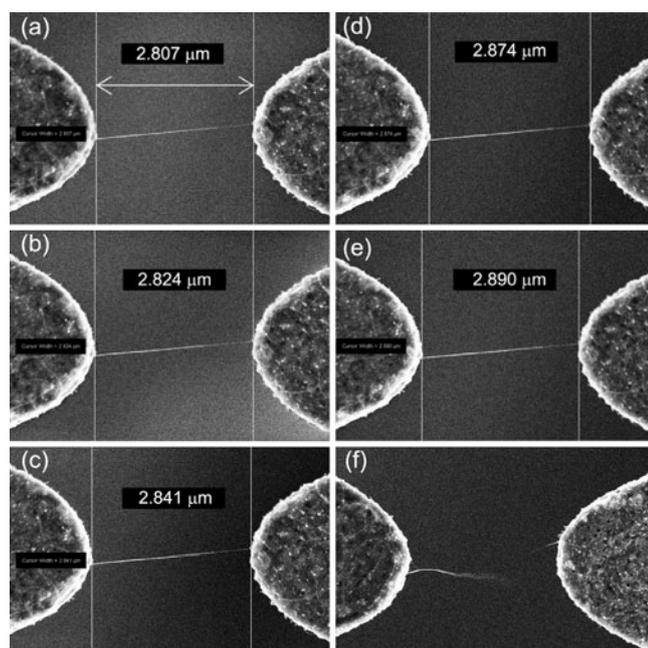


Figure 2. SEM snapshots of a SWNT suspended between to poly-Si tips subjected to increasing axial load from (a) to (f). The maximum elongation was about 100 nm. (f) shows a ruptured SWNT with both ends remaining attached to the supporting tip-pair. (Measured fracture strain: 4%)

Fig. 2 shows snapshots of the same nanotube subjected to different elongations. Failure occurred at a strain of about 4%. The fact that the tube ruptured not at the contact points is an indicator for good mechanical contacting of the tube end with the micro-actuator tips (Fig. 2f).

In the following, in-situ Raman spectroscopy of a bridged single-walled carbon nanotube is described. Although strain-dependent phonons of a single-walled carbon nanotube cannot be readily measured in a simple sensing scheme as a device, their strong coupling to the electronic structure might yield some particular insights. Samples were measured at room temperature using a confocal Raman setup (WITec CRM200). Raman spectra were recorded using a 532 nm green laser delivered through a single mode optical fiber.

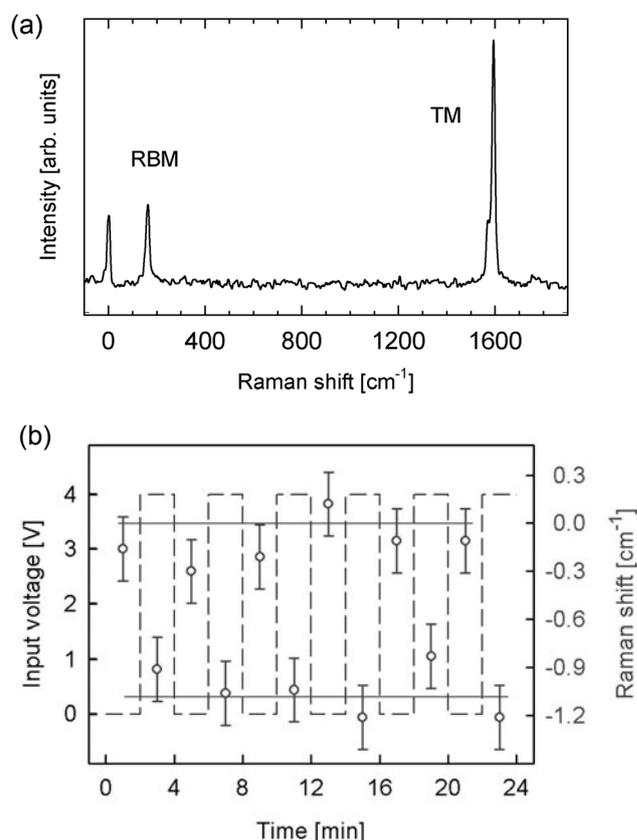


Figure 3. (a) Typical Raman spectrum of a suspended SWNT showing RBM (145 cm^{-1}) and a TM (1590 cm^{-1}) feature. (The feature at 0 cm^{-1} comes from elastically scattered light and does not involve a phonon.) (b) Raman shift of the TM mode provoked by repetitive actuator voltage steps.

This type of fiber supports only a single transversal mode which can be focused to a diffraction-limited spot of about 400 nm (100× objective of NA = 0.8). The backscattered light was cut by a super-notch filter and focused into a 50 μm pinhole. The spectrometer was equipped with a Peltier-cooled CCD-camera. The spectral resolution was 1 cm⁻¹. Precise positioning of the sample under the laser was enabled by a scan table with a capacitive feedback.

In a first experiment the sample was powered repeatedly to the same 'ON' and 'OFF' steady-states. Actuation occurred by flowing electrical current through the bent-beam thermal actuator. Raman spectra of the complete suspended tube structure were recorded. Individual spectral analysis showed that both the radial breathing mode (RBM) and the tangential mode (TM) were preserved along the entire freestanding tube segment. Thus all spectra from the same Raman image were averaged for the peak position fitting. Repeatability of the Raman shift is demonstrated in Fig. 3b. The TM phonon is shown to return to the un-strained frequency upon cycling and can thus be considered as a powerful tool to investigate the strain-dependent electronic properties of tubes quantitatively.

The same nanotube was then subjected to increasing loads and simultaneous Raman recording. Both the RBM and the TM were found to red-shift under the application of tensile strain as shown in Fig. 4. The error bars were evaluated by the following procedure. Raman images of the same tube but for different strain levels were recorded. From each Raman image, the nanotube spectra were selected and the positions of the RBM and the TM modes were fitted. Error bars were then computed by evaluating the standard deviation from the fitted data. The phonon softening of both modes was fitted to a linear characteristic. The TM mode was found to be more sensitive to strain than the RBM mode as seen in the slopes $a_{TM} = 2.06 \text{ cm}^{-1}/\text{W}$ compared to $a_{RBM} = 1.02 \text{ cm}^{-1}/\text{W}$. This can be explained by the fact that the TM develops along the tube axis, i. e. the direction of the applied strain, whereas the RBM is a circumferential mode and thus less affected by tensile loading. Independently, strain-dependent Raman scattering from AFM-based

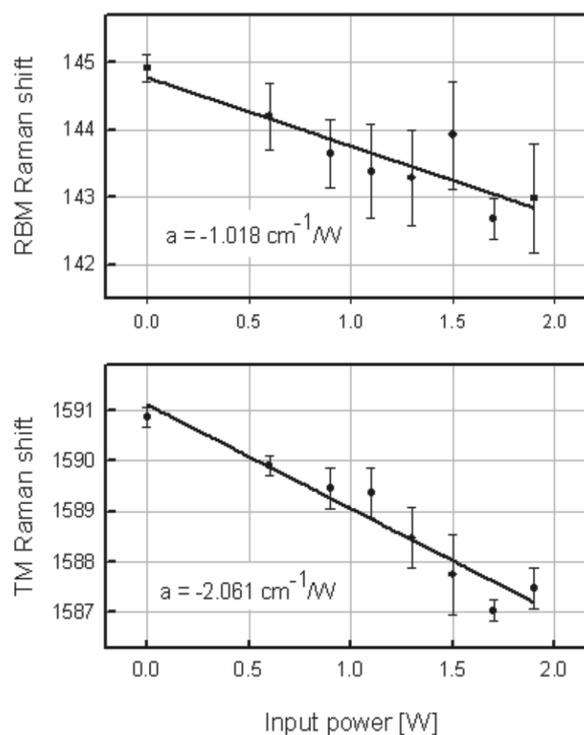


Figure 4. RBM and TM Raman shifts as a function of the applied actuator power. (Tube diameter estimate from the RBM frequency: $d=1.7 \text{ nm}$)

loading also showed TM softening which confirmed the measurements [8].

Considering the unstrained phonon frequency of the RBM, tentative index assignment can be attempted. As the RBM appears relatively intense one can assume the tube to be resonantly enhanced. Thus the laser energy $E_L = 2.33 \text{ eV}$ matched a specific separation energy of a specific nanotube. One can match the recorded RBM Raman shift of $\omega_{RBM} = 145 \text{ cm}^{-1}$ to a (20,3)-tube. This tube belongs to family (43) and the fourth transition was resonantly excited (E_{44}^S). Actually the resonance E_{44}^S is precisely 2.22 eV but it lies within the resonance window. We thus imaged a semiconducting chiral tube of 1.7 nm diameter. As $n \gg m$ the chiral angle of $\Theta = 6.89^\circ$ is close to that of a zig-zag tube.

Because of the resonance enhancement the Raman intensity should be very sensitive to any change in the position of the van Hove singularities which may arise due to strain. However, we measure no significant change in the Raman intensity as a function of strain. Cronin *et*

al. [8] reported no significant change in the Raman intensity for semiconducting tubes but measured changes for metallic ones [6]. It is surprising that the semiconducting SWNTs remain strongly resonant with the laser energy during perturbations in their lattice. This indicates that the positions of the van Hove singularities in the electronic band structure of the nanotube do not change significantly with strain. It can be shown from calculations that the strain-dependent shift of the band gap can be as much as 100 meV/%. The range of laser energies over which the Raman signal of a nanotube can be observed is known as the resonance window which is expected to be 100 meV for the RBM [9]. The (20,3)-tube is of the (43) family and should thus have a positive gauge factor meaning that their energy gaps are enlarged upon straining. As the unstrained energy separation is smaller than the excitation energy ($E_{ii} = 2.22$ eV, $E_L = 2.33$ eV), the 100 meV resonance window is enlarged as the energy separation is scanned through the laser excitation.

3. CONCLUSION

Individual single-walled carbon nanotubes were strained uniaxially from MEMS actuators. From in-situ experiments in a scanning electron microscope the MEMS actuators were proven to strain the tubes to their failure. This enabled the study of tube failure under pure axial loads from a batch-fabricated sample. In-situ Raman experiments of individual SWNTs under strain revealed reproducible phonon frequency downshifts. Interestingly, the strain did not affect their Raman intensity which was initially guessed from strain-induced separation energy calculations.

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REFERENCES:

- [1] R. Heyd, A. Charlier, and E. McRae, "Uniaxial-stress effects on the electronic properties of carbon nanotubes," *Phys. Rev. B*, vol. 55, pp. 6820–6824, 1997.
- [2] L. Yang and J. Han, "Electronic structure of deformed carbon nanotubes," *Phys. Rev. Lett.*, vol. 85, pp. 154-157, 2000.
- [3] S. Ogata and Y. Shibutani, "Ideal tensile strength and band gap of single-walled carbon nanotubes," *Phys. Rev. B*, vol. 68, p. 165409, 2003.
- [4] R. B. Capaz, C. D. Spataru, P. Tangney, M. L. Cohen, and S. G. Louie, "Hydrostatic pressure effects on the structural and electronic properties of carbon nanotubes," *Phys. Status Solidi B*, vol. 241, pp. 3352–3359, 2004.
- [5] H. Jiang, G. Wu, X. P. Yang, and J. M. Dong, "Linear optical properties of deformed carbon nanotubes," *Phys. Rev. B*, vol. 70, p. 125404, 2004.
- [6] S. B. Cronin, A. K. Swan, M. S. Unlu, B. B. Goldberg, M. S. Dresselhaus, and M. Tinkham, "Resonant Raman spectroscopy of individual metallic and semiconducting single-walled carbon nanotubes under axial strain," *Phys. Rev. B*, vol. 72, p. 035425, 2005.
- [7] A. Jungen, S. Hofmann, J.C. Meyer, S. Roth, J. Robertson, and C. Hierold, "Synthesis of single-walled carbon nanotube bridges controlled by surface micromachining", *J. Micromech. Microeng.*, vol. 17, pp. 603-608, 2007.
- [8] S. B. Cronin, A. K. Swan, M. S. Unlu, B. B. Goldberg, M. S. Dresselhaus, and M. Tinkham, "Measuring the uniaxial strain of individual single-wall carbon nanotubes: Resonance raman spectra of atomic-force-microscope modified single-wall nanotubes," *Phys. Rev. Lett.*, vol. 93, p. 167401, 2004.
- [9] A. Jorio, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus, "Structural (n,m) determination of isolated single-wall carbon nanotubes by resonant raman scattering," *Phys. Rev. Lett.*, vol. 86, pp. 1118–1121, 2001.