Spectroscopic Imaging of Single-Walled Carbon Nanotubes by Resonant Raman Scattering

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Abstract:

Resonant Raman Scattering from single-walled carbon nanotubes (SWNTs) provides an effective and nondestructive means to characterize electronic and vibrational properties on a single nanotube level. In this work, SWNTs are grown by chemical vapor deposition over lithographically patterned trenches etched in quartz. A tunable Ti:Sapphire laser is employed to locate individual nanotubes in resonance with the laser energy. The Raman radial breathing mode (RBM) from these resonant nanotubes is spectroscopically mapped versus spatial coordinates with submicron precision.

Introduction:

A SWNT can be envisioned as a honeycombed graphite sheet rolled into a tube of nanometer scale diameter. Among the many characteristics that carbon nanotubes possess, their strong absorption and emission of light render them potential candidates for use in future optical devices [1]. As with any nanoscale device, a substrate support is necessary, therefore, understanding effects of nanotube / substrate interaction is of crucial importance.

The presented research project focuses on utilizing resonant Raman scattering to study the optical effect of this interaction on two particular nanotubes.

Fabrication Process:

To isolate an individual nanotube for analysis, a multi-step fabrication process was developed, yielding SWNTs suspended over trenches. To mask the quartz substrate from subsequent reactive ion trench etching, ~ 40 nm of chromium are thermally evaporated on its surface (Figure 1A). Electron beam resist is spun on top of the Cr (1B), and subsequent electron beam lithography (1C) yields the desired CAD patterned trenches in the resist. Cr etchant is used to etch the exposed Cr down to the quartz level (1D). The resist is removed with acetone (1E) and the sample is subjected to a CF_4 reactive ion etch (1F). The exposed quartz is etched downward, while the Cr masks the rest of the substrate. After the etch, the mask is removed with Cr etchant, leaving a substrate with trenches 700 nm deep and widths ranging from 20 nm-2 μm (1G). To catalyze the formation of SWNTs by chemical vapor deposition, ~ 1 nm of iron particles are evaporated on the substrate prior to nanotube synthesis (1H). Growth of nanotubes occurs within minutes in a furnace supplied with methane and hydrogen gas at 900°C (1I).

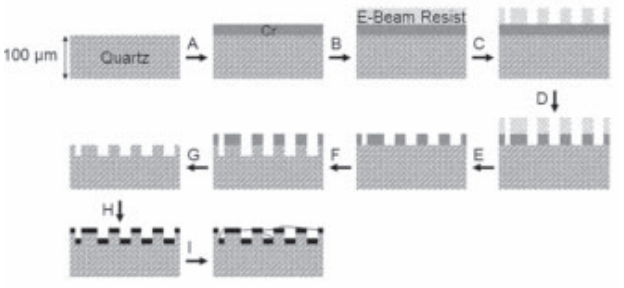

Figure 1: Fabrication process schematic.

Experimental Procedures:

Unlike bulk sample measurements, optical

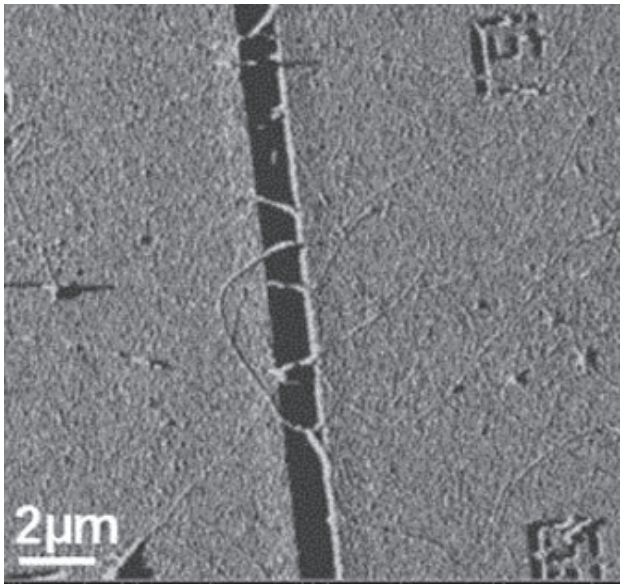

Figure 2: AFM of nanotubes grown over a trench.

absorption and emission in a single nanotube is strongly resonance enhanced [1]. The laser energy that matches a nanotube's electronic band transition is determined by tuning the laser through a maximum in RBM intensity. In our experiments, a 100x objective is used to focus a 2 mW laser beam onto a ~ 1 μm spot on the sample. The emitted light is collected and a single grating spectrometer diffracts the light into a CCD camera. The determined resonant wavelength is used to perform an area scan of the nanotube and its surroundings. Submicron control of the microscope stage allows for precise spatial mapping of RBM intensity.

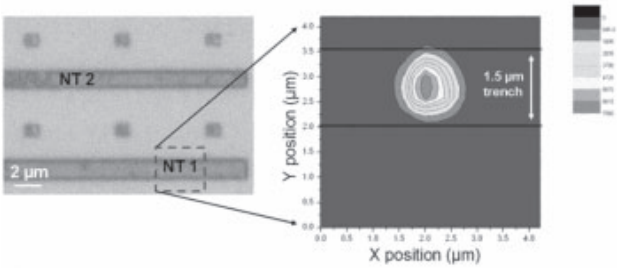

Figure 3: Spectroscopic map of NT1. (4 x 4 μm scan, 0.2 μm steps, 30 seconds at each step, E_{laser} = 770 nm.)

Results and Discussion:

As is evidenced by atomic force microscopy in Figure 2, we have successfully fabricated nano-structures with SWNTs suspended over trenches. Individual nanotubes are selected for analysis based on the above described resonance requirements. Two distinct nanotubes (NT1 and NT2) are analyzed in this report. Figure 3 plots the intensity of NT1's RBM (206 cm^{-1}) in a 4 x 4 μm area confined to the dashed square outlined on the optical image. The resonant wavelength of NT1 was determined to be 770 nm. A clear maximum in the RBM intensity is observed directly in the center of the trench, suggesting a strong optical enhancement from the suspended portion of the nanotube.

The trench position on the spectroscopic map (marked by solid lines), was determined by analyzing before and after scan optical images. The RBM signal from the substrate area was below noise level, indicating that a longer collection time is needed to observe the signal, or perhaps the nanotube is confined in the trench, thereby not in the vicinity of the laser spot away from the trench. NT2 (RBM = 256 cm^{-1}), imaged in Figure 4 was resonant at E_{laser} = 786 nm. Two maxima in intensity are evident, both on and off the trench. This suggests that the strong signal from the substrate area arises from nanotube suspension over a local micro trench introduced during the highly reactive ion etching process. These micro trenches, however, are too small to observe with light microscopy.

Clearly, two data sets are not enough evidence to claim suspension enhanced signals. However, this possibility is supported by line scans performed independently on multiple trenches and on the substrate, with the latter exhibiting no RBM features between 100 and 300 cm^{-1}, while the former displays tens of resonant nanotubes per trench. Since all the nanotube atoms are on its surface, we hypothesize that the fading of the RBM intensity on the substrate possibly arises from the nanotube's shift in resonant frequency as an effect of nanotube / substrate interactions occurring at the atomic level. This can be tested by spectroscopically mapping the same area at different laser energies.

Conclusions:

We have developed a technique of spectroscopically imaging individual resonant nanotubes using Raman scattering. The RBM intensities of two distinct nanotubes were mapped versus their spatial positions over trenches etched in quartz. This method probes locally sensitive electronic and vibrational features of nanotubes, and can be a powerful tool in characterization of nanotube / substrate phenomena.

Acknowledgments:

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References:

[1] M.S. Dresselhaus, G. Dresselhaus, Ph. Avouris, Carbon Nanotubes: Synthesis, Structure, Properties, and Applications (Springer, Berlin, 2000).

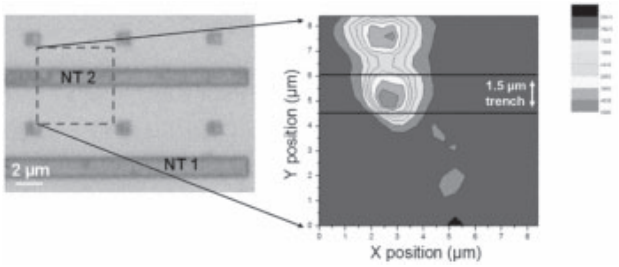

Figure 4: Spectroscopic map of NT2. (8 x 8 μm scan, 0.4 μm steps, 120 seconds at each step, E_{laser} = 786 nm.)