

ACCVD Synthesis and Raman Characterization of Vertically Aligned Single Wall Carbon Nanotubes



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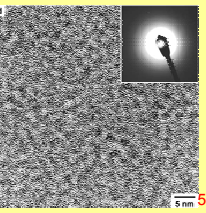
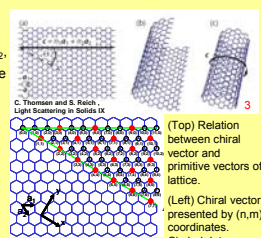
Abstract

Single wall carbon nanotubes (SWNTs) were discovered in 1993 by Iijima. Synthesis methods used for SWNTs are the laser arc, laser furnace, high pressure carbon monoxide (HiPco), chemical vapor deposition (CVD), and other techniques. Alcohol catalyst CVD was used with a cobalt molybdenum catalyst deposited on quartz substrate and ethanol feedstock. The catalyst size and dispersion produced allowed for SWNT growth of relatively high lateral density, leading to uniform, vertical nanotube alignment.

The VA-SWNTs were characterized with Raman spectroscopy to test anisotropic scattering relative to the angle between the nanotube axis and polarization of light. This was done to test the polarization dependence of the SWNT RBM peaks and compare with the results of a similar study by Murakami¹. The Raman signals were also obtained from samples produced by the HiPco process⁹. Different wavelengths of Raman laser were used to observe nanotubes of varying chirality.

Carbon Nanotubes²:

- Defined by the chiral vector, $C_n = n\mathbf{a}_1 + m\mathbf{a}_2$.
- C_n defines the direction in which a nanotube is rolled
- C_n is the circumference of the nanotube, while C_n/π is its diameter.
- Can also be defined by diameter, d_n , and chiral angle θ from nearest primitive vector
- SWNTs metallic if $n-m = 0$, semimetallic if $n-m = 3j$ ($j = \text{integer}$), otherwise semiconducting.

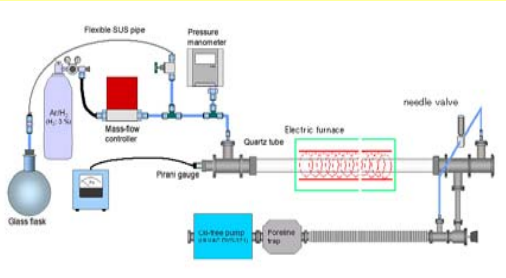


ACCVD

Substrate Dip-Coat⁵:

- Quartz substrate dipped in Mo-Acetate and Co-Acetate, then oxidized.
- Catalyst mono-dispersion
- Co-molybdate stabilize Co particles, Mo-carbides provide carbon source.

HR-TEM image of dip coated quartz substrate, after reduction in CVD chamber.

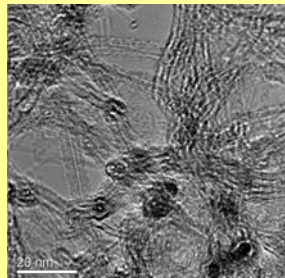
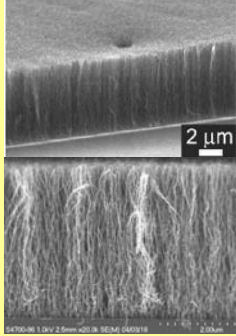


CVD apparatus used in ACCVD procedure.

CVD Procedure¹⁰:

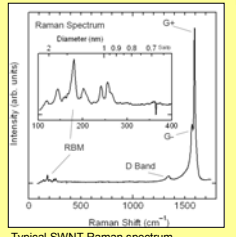
- Substrate inserted into the CVD chamber; Ar/H₂(3%) flown for 30 minutes at 35scm.
- Ar/H₂ flown at 300 sccm as chamber temperature increases to 750°C.
- Ar/H₂ flow stopped, ethanol flown into the chamber at 1.3kPa (~10 torr), 750°C, for 15 minutes.

SEM side images of ACCVD SWNTs

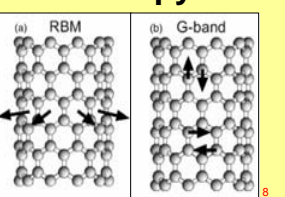


Top view TEM images of VA-SWNT: •SWNT bundles are smaller (<10 nm diameter) than depicted by side view.

Raman Spectroscopy



Typical SWNT Raman spectrum.



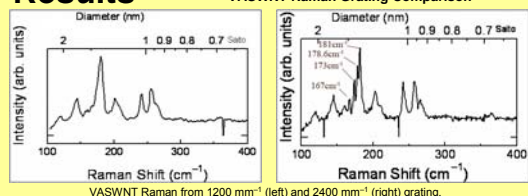
A. Jorio, M.A. Pimenta et al., New J. Phys. 5 (2003) 139

Experiment Procedure

- Raman measurements taken of VA-SWNT (ACCVD) sample and HiPco⁹ sample.
- Measurements of VA-SWNT made at different substrate angles relative to laser (flat, ~30°, 45°, and ~75°).
- 2400 mm⁻¹ gratings used for higher resolution of RBM and G band ranges.
- Measurements taken with laser $\lambda = 488, 632.8$ nm.

Results

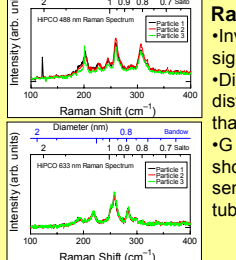
VASWNT Raman Grating Comparison



VASWNT Raman from 1200 mm⁻¹ (left) and 2400 mm⁻¹ (right) grating.

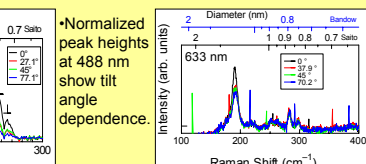
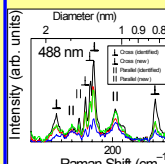
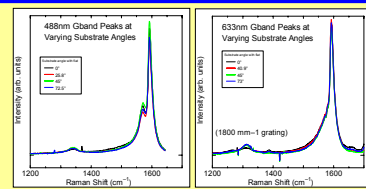
HiPco Sample Raman Spectra

- Invariance in RBM signals
- Diameters distributed smaller than VASWNTs
- G band splitting shows metallic and semiconducting tubes

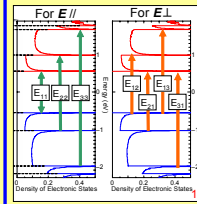
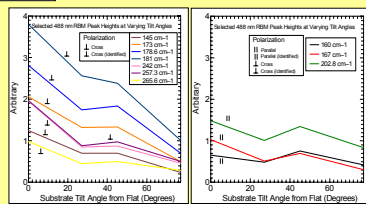


Optical Anisotropy of VASWNTs:

- No significant change in G band intensity.
- Mix of metallic and semiconducting tubes shown.

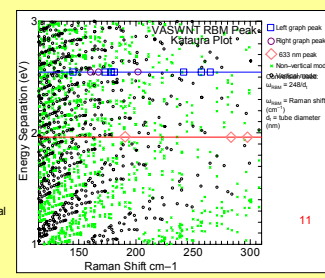


- Peak intensity trends suggest similar optical anisotropies.
- Peaks indicated attributed to cross polarized (left) and parallel polarized (right graph) light¹.



SWNT band gap energy for RBM vertical (left) and nonvertical (right) scattering

- Cross-polarized peaks attributed to nonvertical scattering modes¹.



VASWNT RBM Peak Kataoka Plot

Conclusions

- HiPco sample showed uniform, randomly oriented SWNTs, with thinner diameters than ACCVD sample.
- G bands show mix of semiconducting and metallic tubes, with no significant tilt angle dependence.
- High resolution grating at 488 nm revealed that 180 cm⁻¹ is composed of three peaks (173, 178.6, 181 cm⁻¹).
- Peaks at 145, 180, 242, 257 cm⁻¹, attributed to cross polarized nonvertical scattering by Murakami¹, showed similar relation to loss of cross polarized light as 173, 178.6, and 265.6 cm⁻¹ peaks.
- Peaks at 160 and 202.8 cm⁻¹, attributed to parallel polarized vertical scattering by Murakami¹, and peak at 167 cm⁻¹, did not show a consistent trend with loss of cross polarized light.

References

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12. Courtesy of Y. Murakami

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