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

Dvir Kafri, Erik Einarsson, Zhengyi Zhang, Shigeo Maruyama

Single wall carbon nanotubes (SWNTs) were discovered in 1993 by Iijima. They can be described as graphene sheets folded into cylinders and capped by a fullerene hemisphere. Typical SWNT diameters range from .5 to 3 nm. The angle along the graphene lattice in which the SWNTs are folded determines their chirality, on which electrical and optical properties are dependent. The primary synthesis methods used for SWNTs are the laser arc, laser ablation, high pressure carbon monoxide (HiPCO), and chemical vapor deposition (CVD) techniques. Alcohol catalytic chemical vapor deposition (ACCVD) is a variation of CVD in which ethanol is used as the carbon feedstock for growth on a substrate coated with catalyst metal. It is useful in exclusively producing pure, defect-free SWNTs. This method was used with a cobalt molybdenum catalyst deposited on quartz substrate through a dip-coating process. The catalyst size and dispersion produced allowed for SWNT growth of high lateral density, leading to uniform, vertical nanotube alignment.

Raman spectroscopy has been used to characterize SWNTs through analysis of radial breathing (RBM) , D and G band phonon modes. When laser light is aimed at the nanotubes, π bond electrons can be excited into higher energy virtual states; Raman scattering is achieved when the electrons emit or absorb phonons (lattice vibrations), leading to inelastic scattering of photons as the electrons return to energy states that differ from their initial states. This scattering process is greatly enhanced if the band gap energy, which is dependent of nanotube chirality and diameter, matches this energy difference between these states.

The VA-SWNTs were characterized with Raman spectroscopy to determine if they showed anisotropic scattering relative to the angle between the nanotube axis and polarization of light. The spectrometer laser was aimed at VA-SWNTs standing on a quartz substrate. The substrate orientation was then altered relative to the direction of the laser. This was done to test the polarization dependence of the SWNT RBM peaks, and compare with the results of a similar procedure by Murakami. The Raman signals were also compared to samples produced by the HiPCO process. Different wavelengths of Raman laser were used to observe nanotubes of varying chirality.

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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 Murakami[1]. The Raman signals were also obtained from samples produced by the HiPco process[9]. Different wavelengths of Raman laser were used to observe nanotubes of varying chirality.

Carbon Nanotubes[2]:

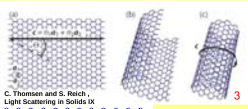
•Defined by the chiral vector, $C_h = na_1 + ma_2$,

•C_h defines the direction in which a nanotube is rolled

•$|C_h|$ is the circumference of the nanotube, while $|C_h|/\pi$ is its diameter.

•Can also be defined by diameter, d_t, and chiral angle θ from nearest primitive vector

•SWNTs metallic if n-m = 0, semimetallic if n-m = 3j (j = integer), otherwise semiconducting.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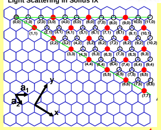
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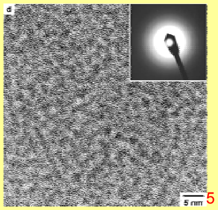
(Top) Relation between chiral vector and primitive vectors of lattice.

(Left) Chiral vector presented by (n,m) coordinates. Circled dots represent metallic nanotubes.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HR-TEM image of dip coated quartz substrate, after reduction in CVD chamber.

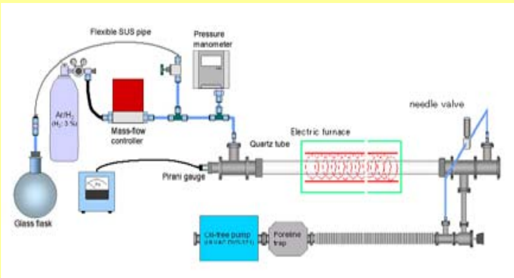
ACCVD

Substrate Dip-Coat[5]:

•Quartz substrate dipped in Mo-Acetate and Co-Acetate, then oxidized.

•Catalyst mono-dispersion

•Co-molybdate stabilize Co particles, Mo-carbides provide carbon source.



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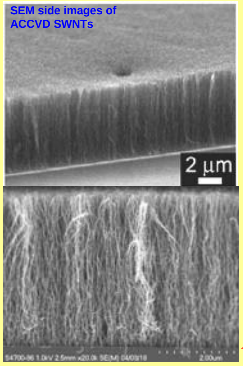
CVD apparatus used in ACCVD procedure.

CVD Procedure[10]:

•Substrate inserted into the CVD chamber; Ar/H_2(3%) flown for 30 minutes at 35sccm.

•Ar/H_2 flown at 300 sccm as chamber temperature increases to 750°C.

•Ar/H_2 flow stopped, ethanol flown into the chamber at 1.3kPa (~10 torr), 750°C, for 15 minutes.



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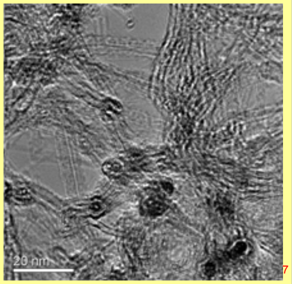

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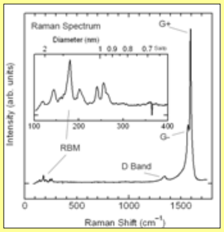
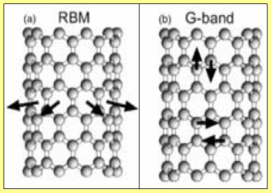
Top view TEM images of VA-SWNT:
•SWNT bundles are smaller (<10 nm diameter) than depicted by side view.

Raman Spectroscopy



Typical SWNT Raman spectrum.



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RBM and G band phonon/vibrational modes.

Experiment Procedure

•Raman measurements taken of VA-SWNT (ACCVD) sample and HiPCO[9] sample.

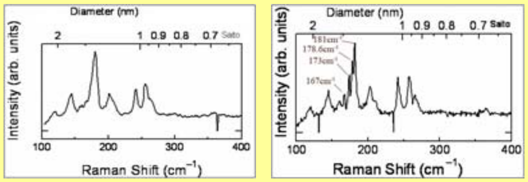
•Measurements of VA-SWNT made at different substrate angles relative to laser (flat, ~30°, 45°, and ~75°).

•2400 mm^{-1} gratings used for higher resolution of RBM and G band ranges.

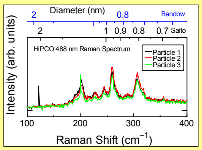
•Measurements taken with laser λ= 488, 632.8 nm.

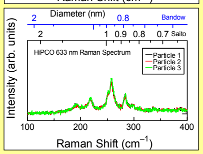
Results

VASWNT Raman Grating Comparison



VASWNT Raman from 1200 mm^{-1} (left) and 2400 mm^{-1} (right) grating.



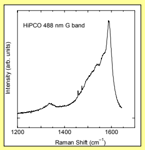


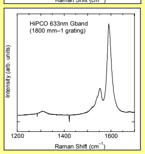
HiPco Sample Raman Spectra

•Invariance in RBM signals

•Diameters distributed smaller than VASWNTs

•G band splitting shows metallic and semiconducting tubes

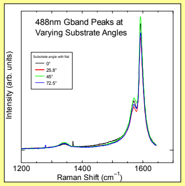


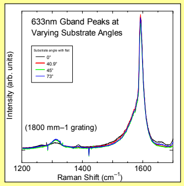


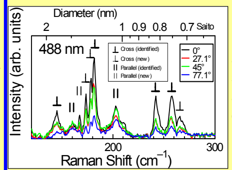
Optical Anisotropy of VASWNTs:

•No significant change in G band intensity.

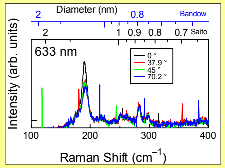
•Mix of metallic and semiconducting tubes shown.





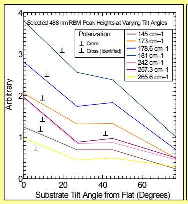


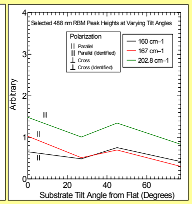
•Normalized peak heights at 488 nm show tilt angle dependence.

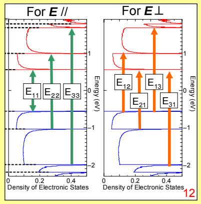


•Peak intensity trends suggest similar optical anisotropies.

•Peaks indicated attributed to cross polarized (left) and parallel polarized (right graph) light[1].







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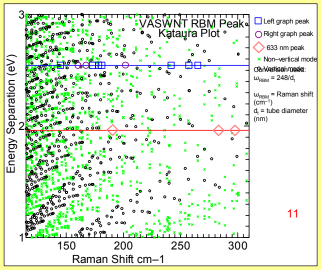
SWNT band gap energy for RBM vertical (left) and nonvertical (right) scattering

•Cross-polarized peaks attributed to nonvertical scattering modes[1].



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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 Murakami[1], 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 Murakami[1], and peak at 167 cm^{-1}, did not show a consistent trend with loss of cross polarized light.

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