Direct Growth of Sub-nm-Diameter SWNT Films on Si/SiO_2 Substrates by Alcohol Catalytic Chemical Vapor Deposition

Benjamin K. Wang,[1,2] Hua An,[1] Kehang Cui,[1] & Shigeo Maruyama[1]

[1]*Department of Mechanical Engineering, The University of Tokyo, Tokyo 113-8656, Japan*

[2]*Department of Chemical and Biomolecular Engineering and NanoJapan: International Research Experience for Undergraduates Program, Rice University, Houston, TX 77005, United States*

Due to their unique and tunable properties, single-walled carbon nanotubes (SWNTs) possess excellent potential for applications in the fields of nanotechnology, electronics, and optics. Perhaps the most sought after objective of SWNT research is their chirality-specific growth. SWNTs possess unique structure-function relationships that are determined by their chiral properties—nanotube diameter and wrapping angle—which allow them to exhibit either metallic or semiconducting properties. In this study, we demonstrate the diameter modulation of SWNTs grown by alcohol catalytic chemical vapor deposition (ACCVD) on Si/SiO_2 substrates. Importantly, compared to bulk gas-phase synthesized nanotubes, the direct growth of SWNTs on flat substrates is advantageous because it allows for the immediate use of grown SWNTs in nanodevice applications. We show temperature-dependence studies of SWNTs grown from Co/Mo and Co/Cu bimetallic catalysts, and then shift our focus to Co/Cu-grown nanotubes, which revealed efficient growth of sub-nanometer SWNTs. Radial breathing mode (RBM) frequencies of resonant Raman scattering and scanning electron microscopy (SEM) indicated the synthesis of thin film networks characterized by sub-nanometer SWNTs. Our results suggest that lower temperatures favor smaller diameter SWNTs. Moreover, we observed decreasing SWNT diameters as a function of reducing the total feedstock pressure. This trend suggests that higher partial pressures of ethanol (high feedstock supply rate) poison smaller-diameter catalyst nanoparticles, thus reducing the population of small diameter nanotubes. We anticipate that these results will have wide-ranging implications for the highly desired diameter-specific growth of SWNTs. Furthermore, our sub-nanometer SWNTs have promising potential for use in CNT-Si and CNT-Perovskite solar cells.

Direct Growth of Sub-nm-Diameter SWNT Films on Si/SiO_2 Substrates by Alcohol Catalytic Chemical Vapor Deposition

東京大学 THE UNIVERSITY OF TOKYO

Benjamin Wang,[†,‡] Hua An,[†] Kehang Cui,[†] & Shigeo Maruyama[†]

[†]Department of Mechanical Engineering, The University of Tokyo, Tokyo 113-8656, Japan

[‡]Department of Chemical and Biomolecular Engineering & NanoJapan: International Research Experience for Undergraduates Program, Rice University, Houston, TX 77005, United States

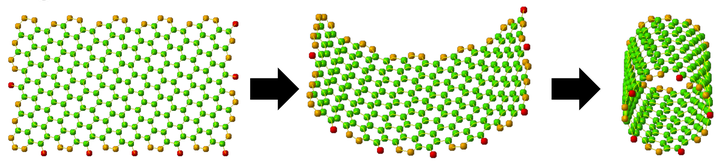
Contact: Benjamin Wang ~ bkw2@rice.edu

RICE

NanoJapan International Research Experience for Undergraduates

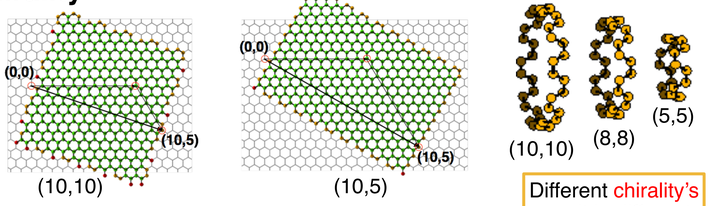
Introduction

Single-walled Carbon Nanotubes



Rolled up graphene sheet (planar honeycomb sp^2 hybridized C); high aspect-ratio[1]

Chirality



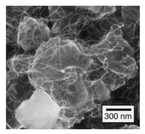
Geometry of the nanotube can be defined by the chiral vector *(n,m)* of the hexagonal lattice[1]

Different chirality's result in different SWNT diameters[1]

Nanodevice Applications

Unique properties:
- Mechanical strength
- Semiconducting or metallic
- Optical absorption

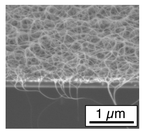
Direct synthesis on Si/SiO_2 substrate allows for immediate use in nanodevices; however, less control over catalyst size and distribution—difficult to produce high quality sub-nm SWNTs



Growth on support[2]

Goal: determine conditions for pure, high-quality direct growth of sub-nm diameter SWNTs on flat Si/SiO_2 substrates.

[1]S. Maruyama Website; www.photon.t.u-tokyo.ac.jp

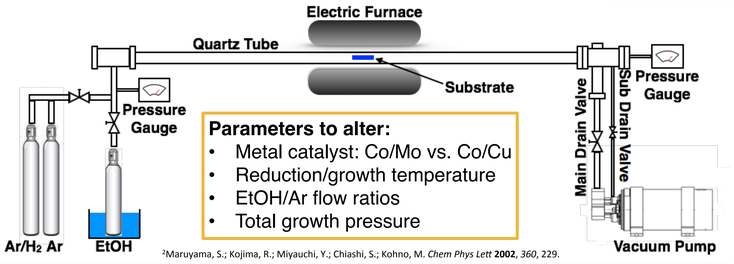


Growth on substrate

Methods

Alcohol Catalytic Chemical Vapor Deposition[2]

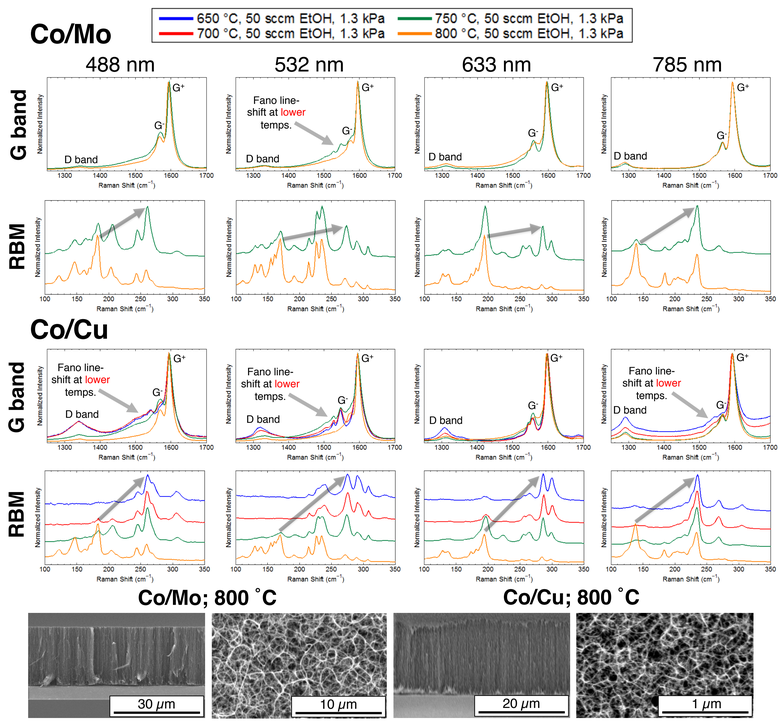
Dip-coat clean Si/SiO_2 substrate with metal catalyst → Reduce and anneal metal oxide catalyst at high temperature with Ar/H_2 for 40 min → Flow mixture of EtOH (feedstock) and Ar gas over Si/SiO_2 substrate for 5 min → Characterize samples with SEM, Raman Spectroscopy



Parameters to alter:
- Metal catalyst: Co/Mo vs. Co/Cu
- Reduction/growth temperature
- EtOH/Ar flow ratios
- Total growth pressure

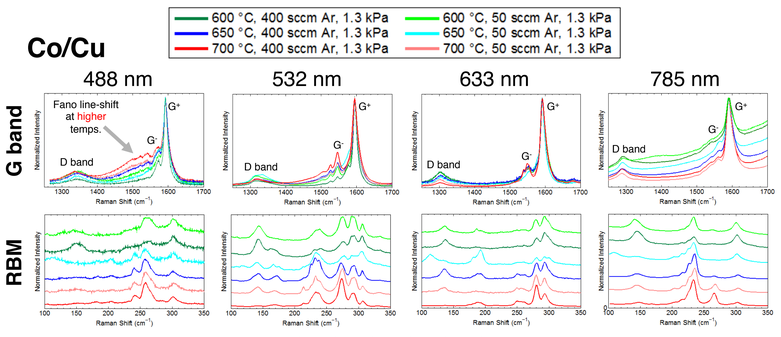
[2]Maruyama, S.; Kojima, R.; Miyauchi, Y.; Chiashi, S.; Kohno, M. *Chem Phys Lett* **2002**, *360*, 229.

Temperature

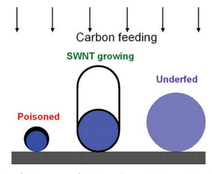


Lower temperatures favor smaller diameter SWNT growth

Partial Pressure



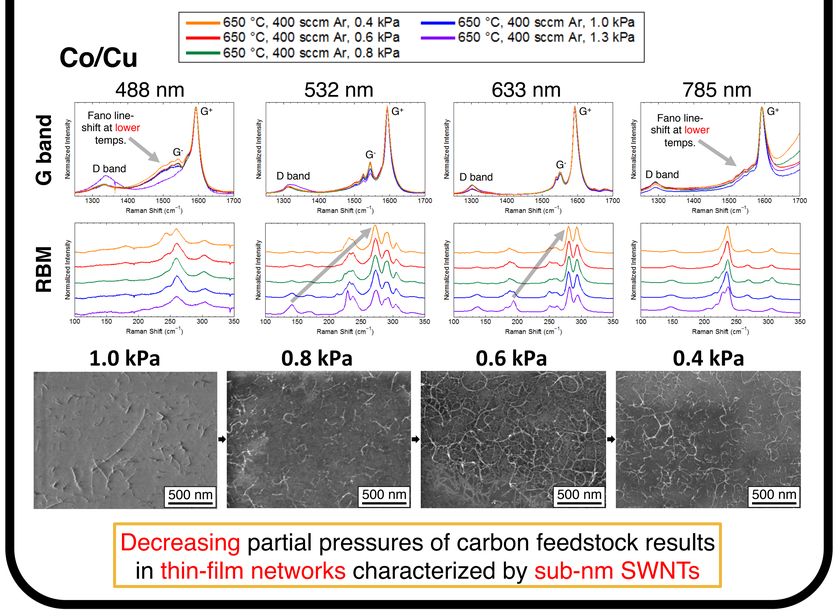
Trends not consistent with temperature-dependence studies; suggests additional growth factor



Small-diameter catalyst nanoparticles are poisoned at high partial pressures of carbon feedstock[3]

[3]Li, Y.; Cui, R. L.; Ding, L.; Liu, Y.; Zhou, W. W.; Zhang, Y.; Jin, Z.; Peng, F.; Liu, J. *Adv Mater* **2010**, *22*, 1508.

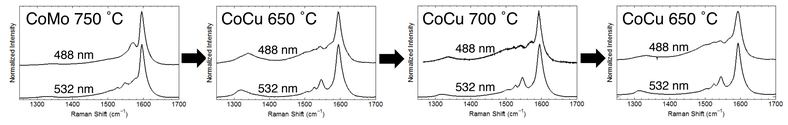
Total Pressure



Decreasing partial pressures of carbon feedstock results in thin-film networks characterized by sub-nm SWNTs

Conclusion & Future

General temperature studies with Co/Mo → Temperature studies with Co/Cu; similar trends → Partial pressure experiments to further decrease SWNT diameters; results do not follow expected trends → Decreasing partial pressure of feedstock results in smaller SWNTs; suggests catalyst poisoning



- ~0.8-0.9 nm diameter SWNTs synthesized from Co/Cu
  - Semiconducting: (10,0), (9,2), (6,5), (7,5), (8,3)
  - Metallic: (7,7), (8,5), (12,1), (10,5)
- SWNT diameter further decreases as feedstock partial pressure decreases

- Decrease EtOH total pressure by several orders of magnitude while holding partial pressure constant
  - 1.0 kPa; 1.0 kPa; 0.1 kPa, 0.01 kPa
- Use sub-nm SWNTs for various nanodevice applications
  - CNT-Si and CNT-Perovskite solar cells

Acknowledgements

This research project was conducted as part of the 2014 NanoJapan: International Research Experience for Undergraduates Program with support from a National Science Foundation Partnerships for International Research & Education grant (NSF-PIRE OISE-0968405). For more information on NanoJapan see http://nanojapan.rice.edu.