Direct Growth of Sub-nm-Diameter SWNT Films on Si/SiO₂ Substrates by Alcohol Catalytic Chemical Vapor Deposition

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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/SiO₂ 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-Peroxikite solar cells.
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**Introduction**

Single-walled Carbon Nanotubes

![Image](image1.png)

- Rolled up graphene sheet (planar honeycomb sp² hybridized C); high aspect-ratio
- Geometry of the nanotube can be defined by the chiral vector (n,m) of the hexagonal lattice

**Nanodevice Applications**

- Unique properties: Mechanical strength, Semiconducting or metallic, Optical absorption
- Direct synthesis on Si/SiO₂ substrate allows for immediate use in nanodevices; however, less control over catalyst size and distribution—difficult to produce high quality sub-nm SWNTs

**Methods**

**Alcohol Catalytic Chemical Vapor Deposition**

- Dip-coat clean Si/SiO₂ substrate with metal catalyst
- Reduce and anneal metal oxide catalyst at high temperature with Ar/H₂ for 40 min
- Flow mixture of EtOH (feedstock) and Ar over Si/SiO₂ substrate for 5 min
- Characterize samples with SEM, Raman Spectroscopy

**Temperature**

- 488 nm
- 532 nm
- 633 nm
- 785 nm

**Total Pressure**

- 1.0 kPa
- 0.8 kPa
- 0.6 kPa
- 0.4 kPa

**Partial Pressure**

**Conclusion & Future**

- General temperature studies with Co/Mo vs Co/Cu: similar trends
- Temperature studies with Co/Cu to further decrease SWNT diameters; results do not follow expected trends
- Decreasing partial pressures of carbon feedstock results in thin-film networks characterized by sub-nm SWNTs

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