In situ Measurements of Nanotube Growth Kinetics – *The Race to Nanotube-Based Composites*

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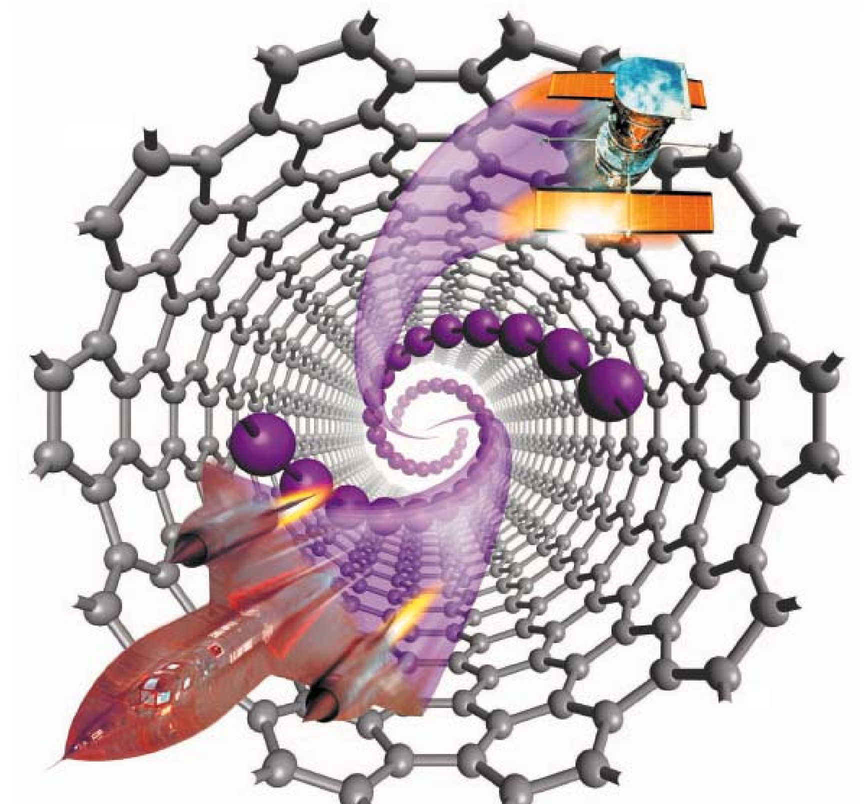


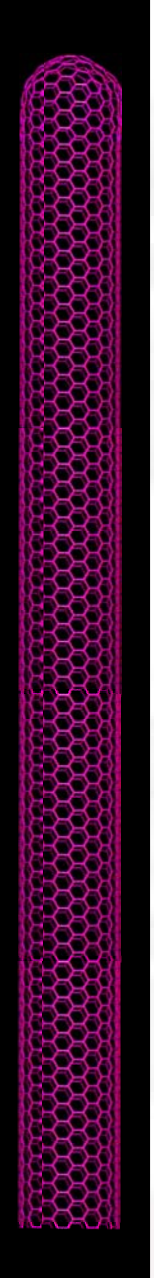
OAK RIDGE NATIONAL LABORATORY
Laboratory Directed Research and Development

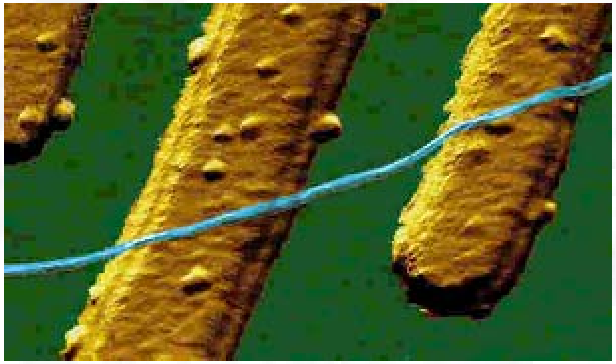
Outline
Carbon Nanotube Growth for Composites

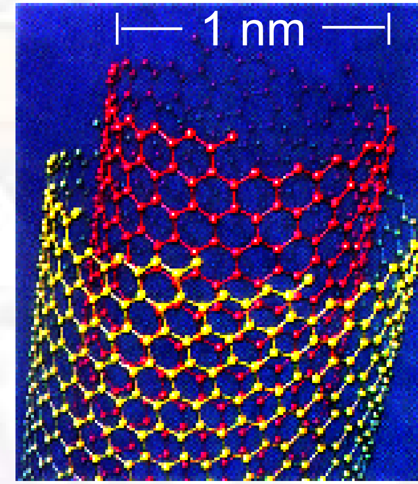
- **Nanotube-based composites - *A brief introduction***

- **In situ diagnostics of growth -**
  - **Loose nanotubes - *grown by laser vaporization***
  - **Aligned nanotube arrays on substrates - *grown by chemical vapor deposition***
  - ***growth rates measured, lengths controlled, growth mechanisms elucidated***

Carbon Nanotubes - Properties







Electronic Properties - Devices

- The best field emitters known
- Already developed for field emission displays, lighting.
- Molecular wires
- Semiconducting or metallic
- Single-electron transistors demonstrated
- Ballistic transport (10^9 A/cm^2) - up to 1 mA per tube!
- Sharp optical transitions - fluorescence/electroluminescence demonstrated

Needs: Small quantities, controlled structure, for predictable properties

Structural Properties - Composites

- Strongest material known to man
- > 1 TPa axial Young's modulus
- 130 GPa predicted bundled strength
- 100 times stronger than steel, only one-sixth the weight.
- Stiffness-to-weight ratio 40X higher than that of aluminum
- Electrical conductivity better than copper
- Thermal conductivity greater than diamond
- Hollow - Gas Storage, Drug delivery
- Actuation demonstrated

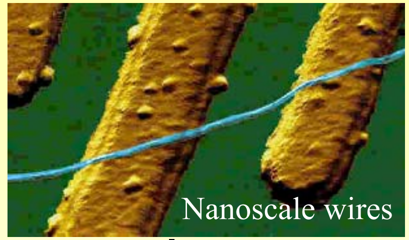
Needs: Large quantities, efficient fabrication into tough composite

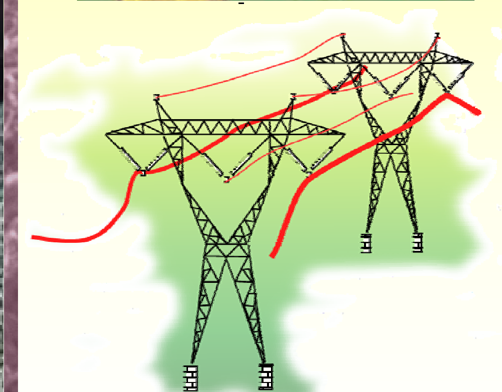
Aligned SWNT - Multifunctional Supermaterials

Mechanical

1 TPa Young's Modulus

Electrical Wires



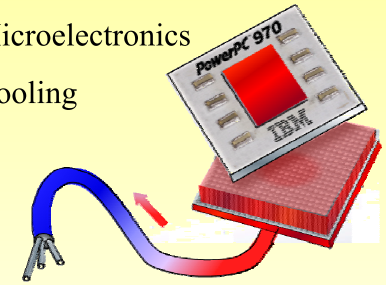


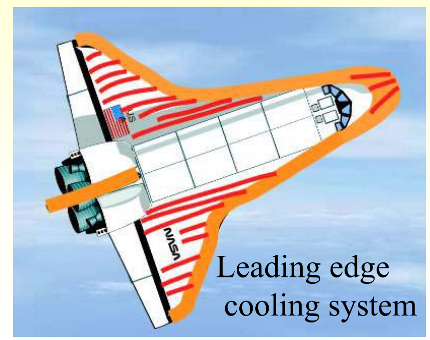
Power transmission cables

Ballistic Transport

Heat Pipes

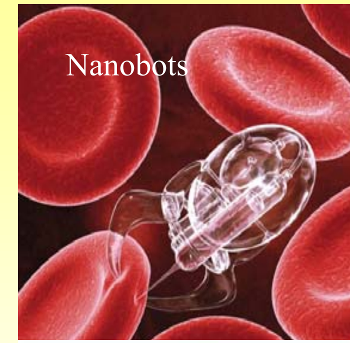
Microelectronics cooling





3000 W/mK

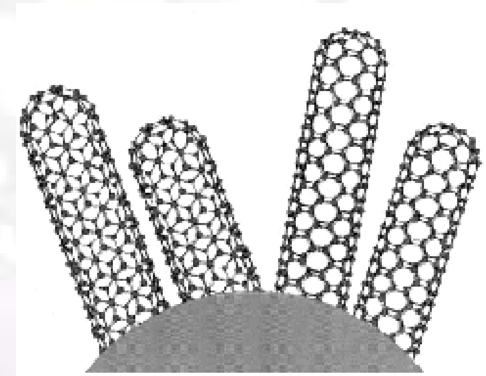
Actuators



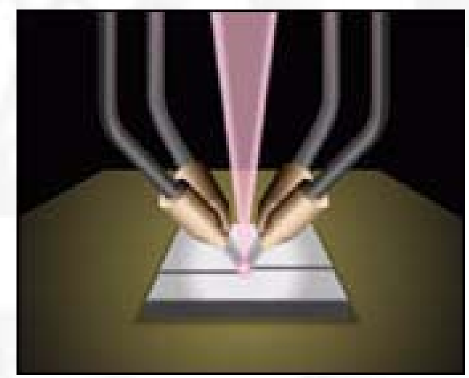
Low voltage

Alignment - The key to directional transport properties

Grand Challenges in SWNT Synthesis

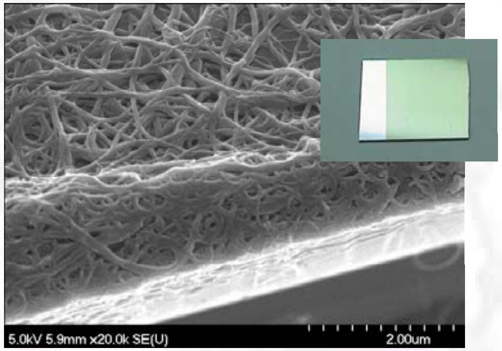


- **Atomic scale control over synthesis**
  - ***Must understand <u>nucleation</u> step***
    - *Control over chirality*
    - *For <u>predesigned</u> electronic properties*
    - *And **controllable <u>lengths</u>***
- **Economic, large-scale production**
  - **Optimize *<u>growth</u>* process**
  - ***high rate** growth*
  - *to **long lengths** for fibers, composites*
    - *Ultimately, the growth of a perfect SWNT crystal*

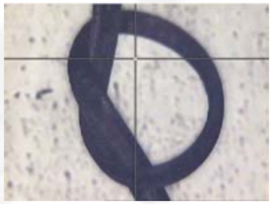


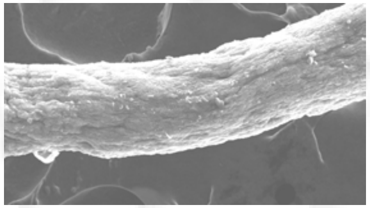
Two Approaches for Nanotube Composites

- **Loose Nanotubes**
  - **Spun, cast, blended into fibers, sheets, monoliths**
    - **Synthesis Methods: Arc, laser, floating catalyst CVD**



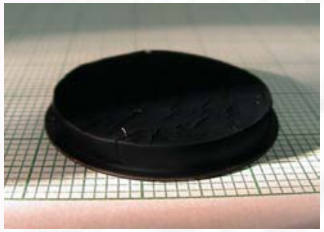
Films, sheets, coatings

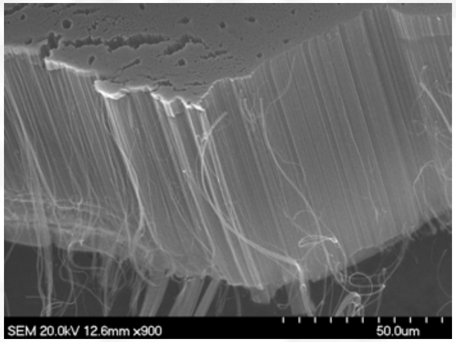


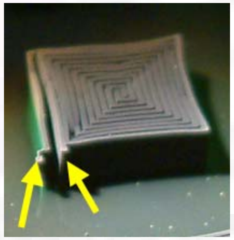


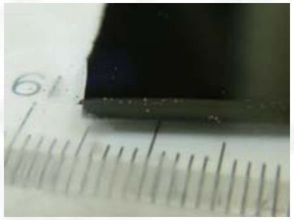
Fibers

- **As-Grown Nanotubes**
  - **Directly aligned on substrates**
    - **Synthesis Methods:** ***Chemical Vapor Deposition of Aligned Arrays***







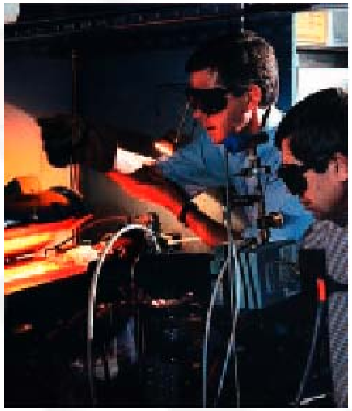


As-grown, vertical arrays

Loose SWNT Grown by Laser Vaporization

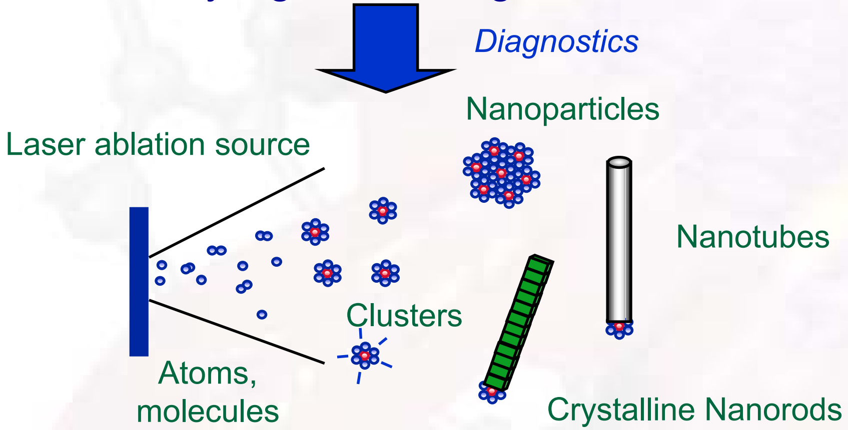
GOAL

Understand SWNT Synthesis Mechanism in order to Control and Scale Growth



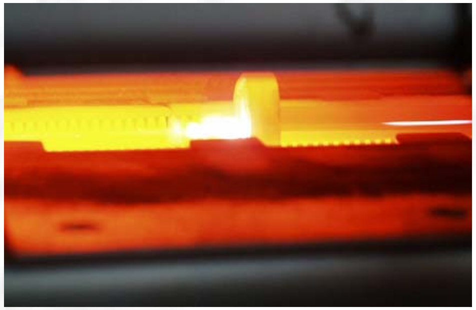
APPROACH

- **Time-Resolved, In Situ Measurements**
  - Laser-Induced Luminescence
  - Gated ICCD Imaging
  - Optical Emission/Absorption Spectroscopy
  - Laser-induced incandescence
  - Rayleigh scattering

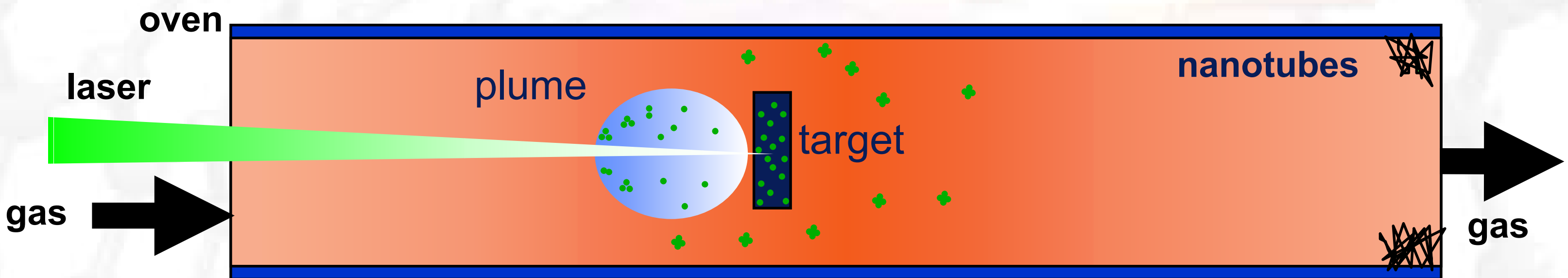


ADVANTAGES

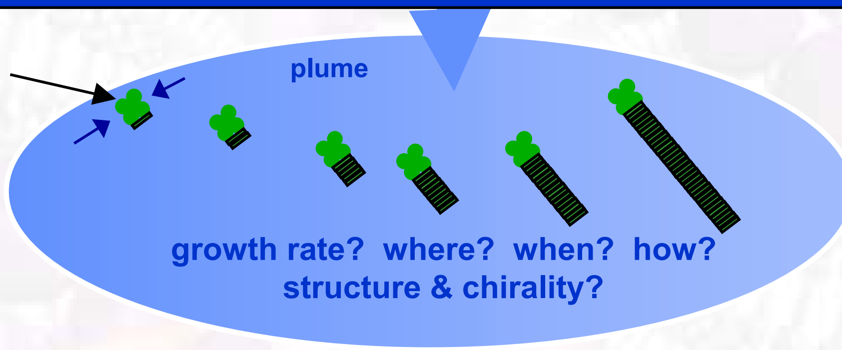
- Pulsed LV especially suitable for time-resolved measurements
- Vaporizing pulse lasts only ~ 10 ns
- SWNTs then grow undisturbed
- Measurements can extend to many seconds, and single laser shots

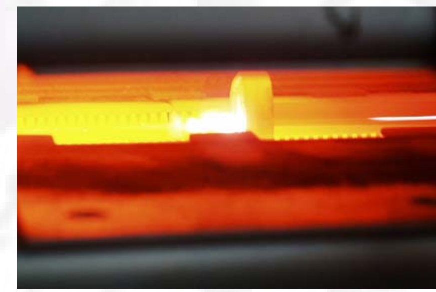


Synthesis of Single-Walled Carbon Nanotubes (SWNT) by Laser Vaporization

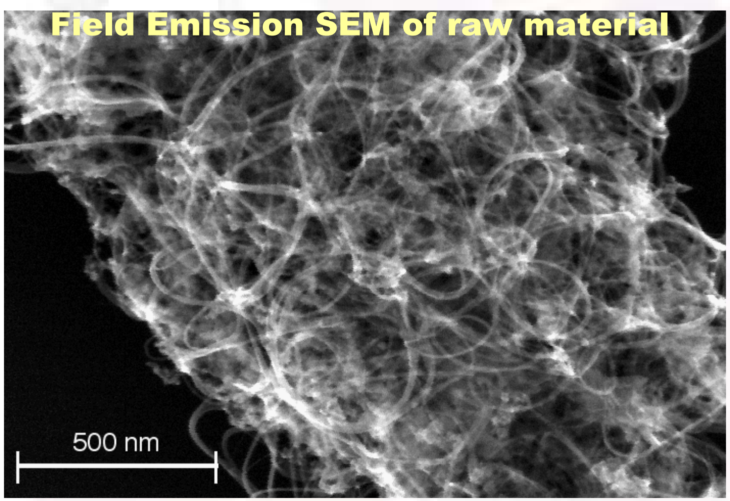


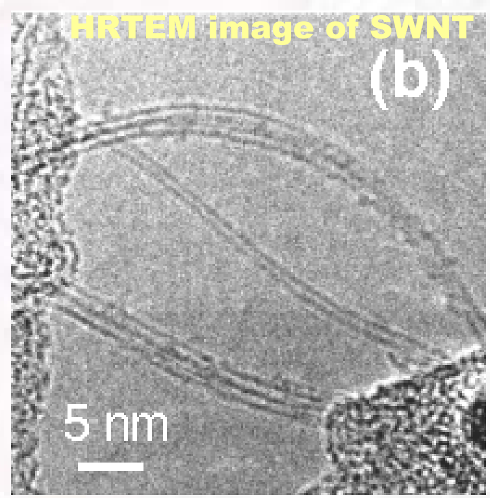
metal catalyst cluster
M = Ni, Co, Fe...





- High purity
- Exclusively SWNT





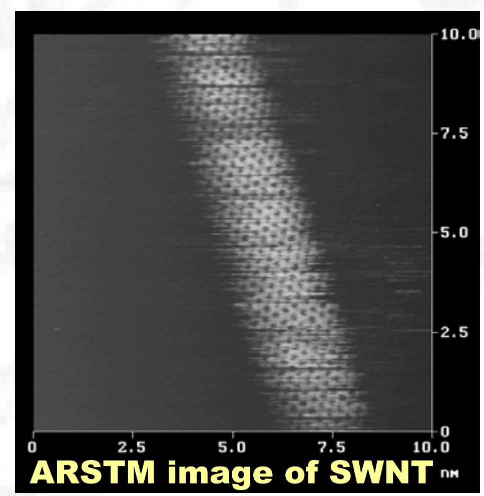
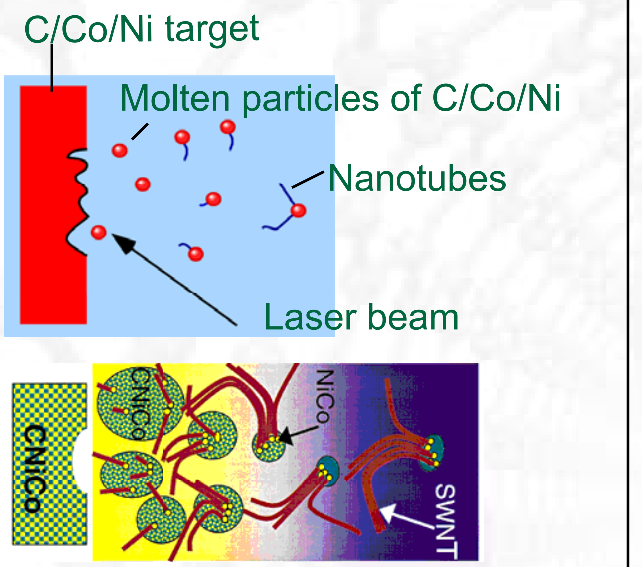


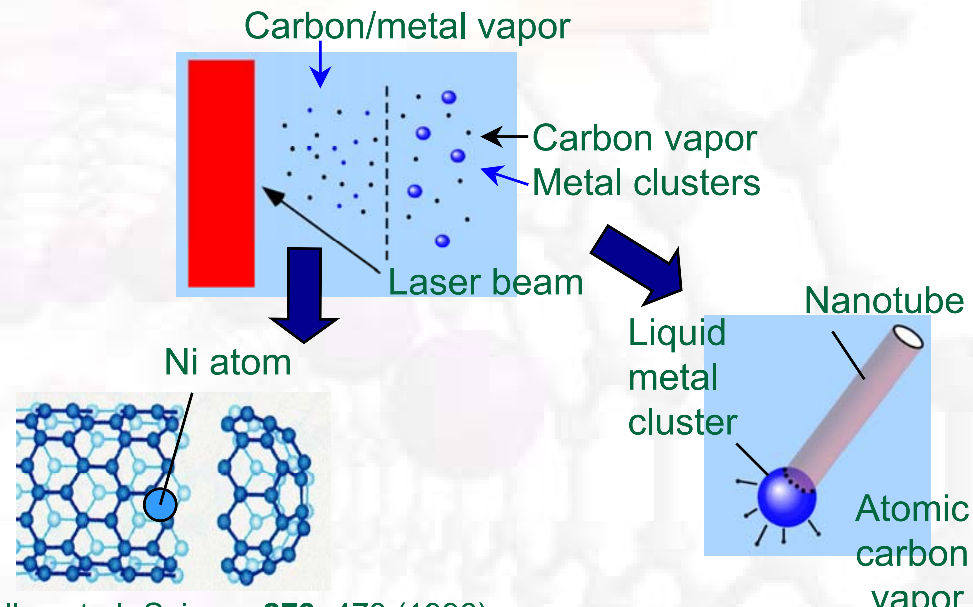
image by M. Guillorn

Mechanisms and general picture of SWNT growth



Iijima et al, *J. Phys. Chem*. **103**, 6224 (1999)

Growth from ejected molten particles

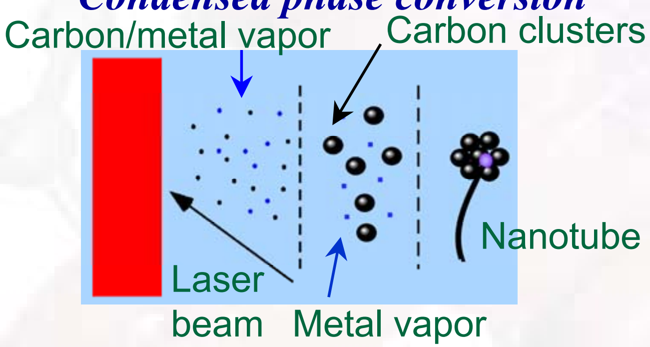


Smalley et al, *Science* **273**, 473 (1996)

Scooter mechanism

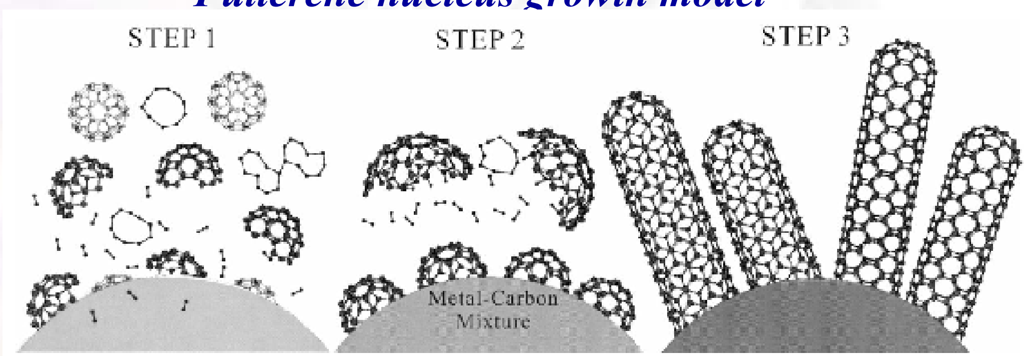
Vapor Liquid Solid mechanism

Condensed phase conversion



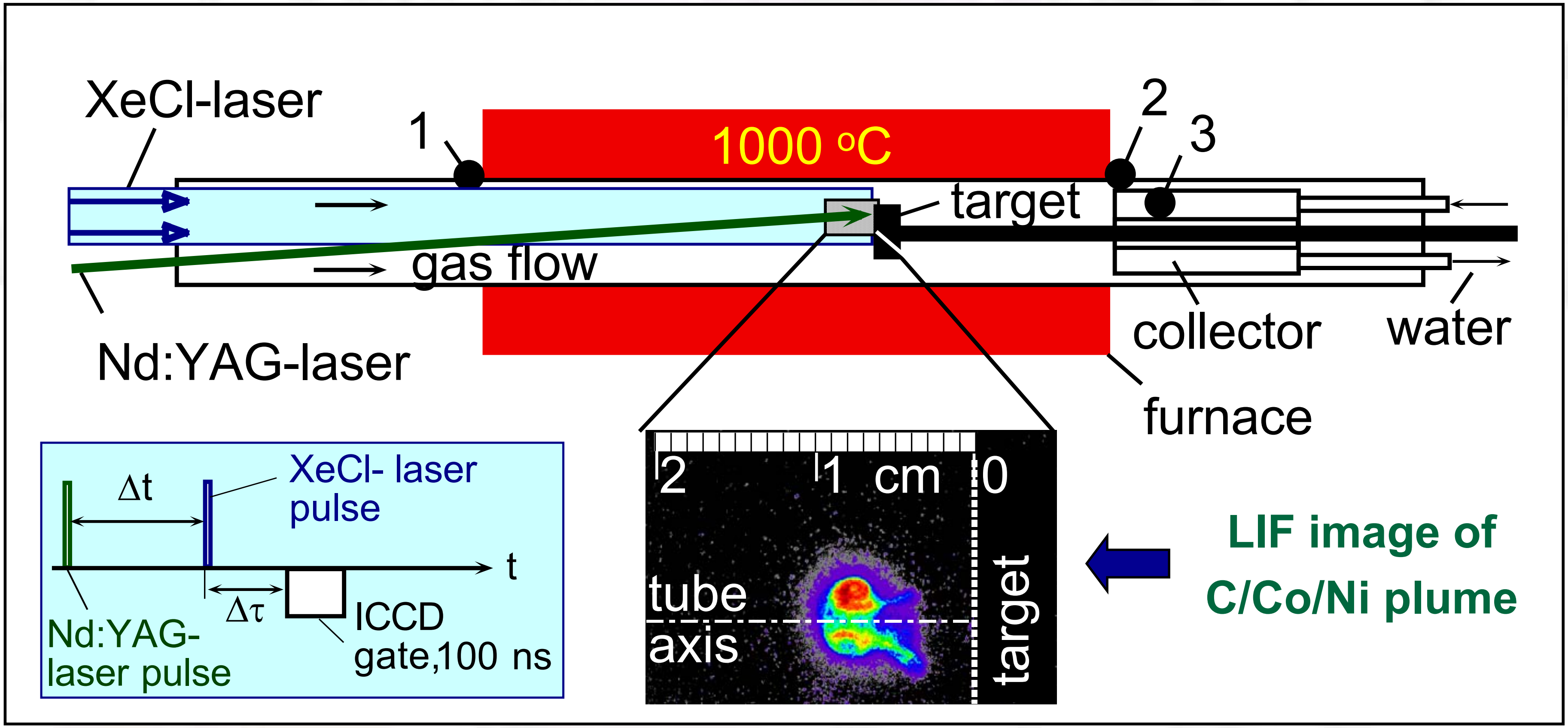
Geohegan et al, Fall MRS'99. APL **76**, 182 (2000)

Fullerene nucleus growth model

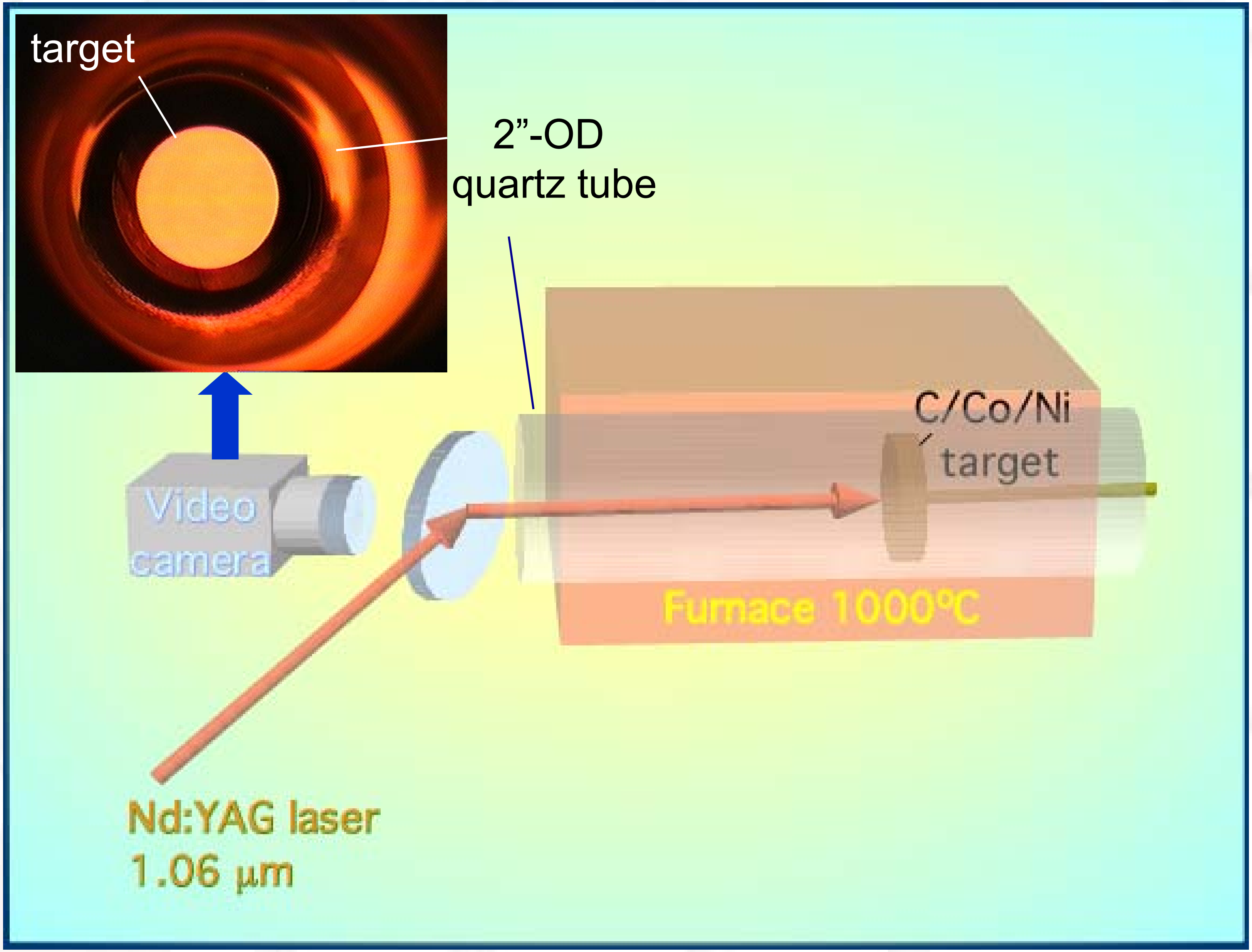


Kataura et al, *Carbon*. **38**, 1691 (2000)

Laser Induced Fluorescence Imaging of Nanotube Growth Environment



Video camera imaging of C/Co/Ni plume during SWNTs growth

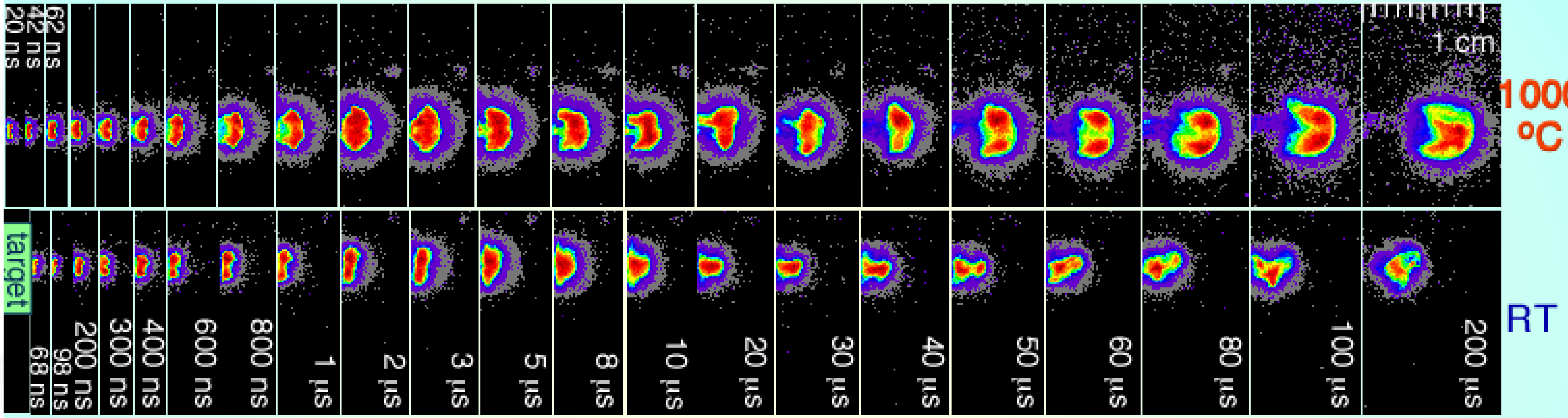


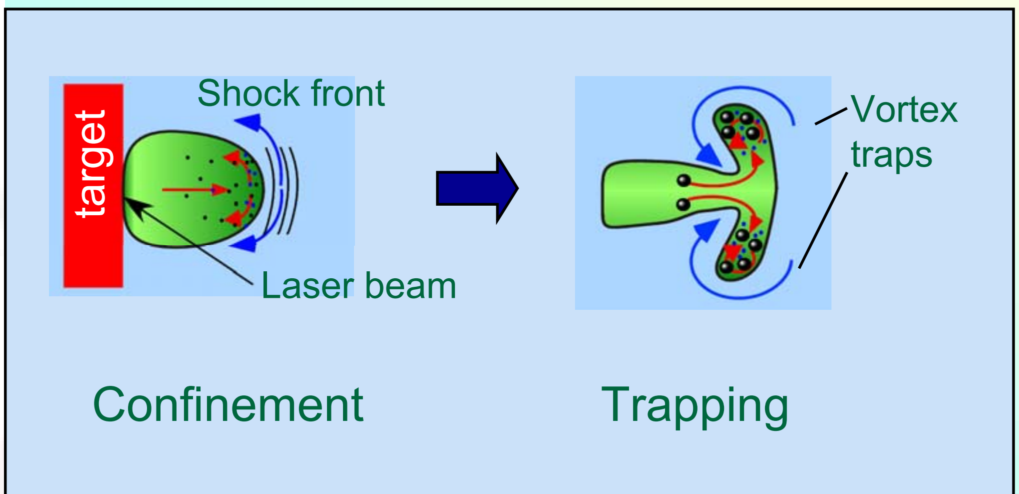
Video camera imaging of C/Co/Ni plume during SWNTs growth

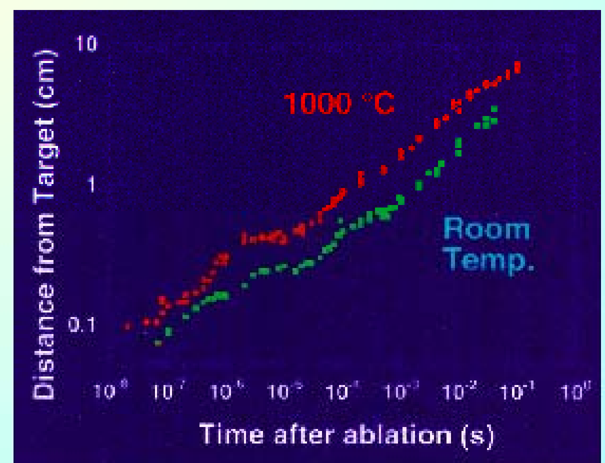
Early C/Ni/Co Plume Dynamics (0<Δt< 200 μs)

ICCD Imaging of plasma emission

- 500 Torr Argon
- Expansion in stages
- Self-focusing
- Internal shocks

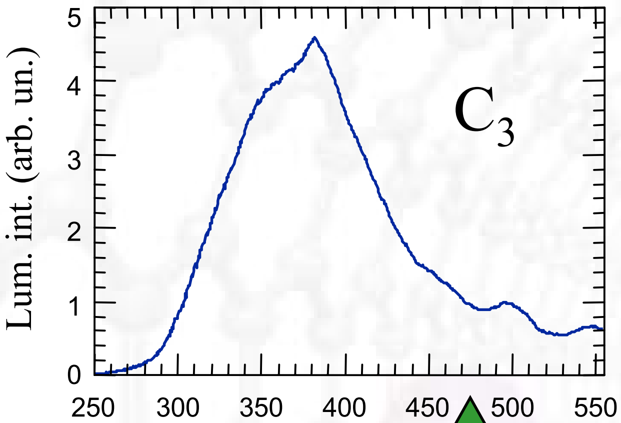


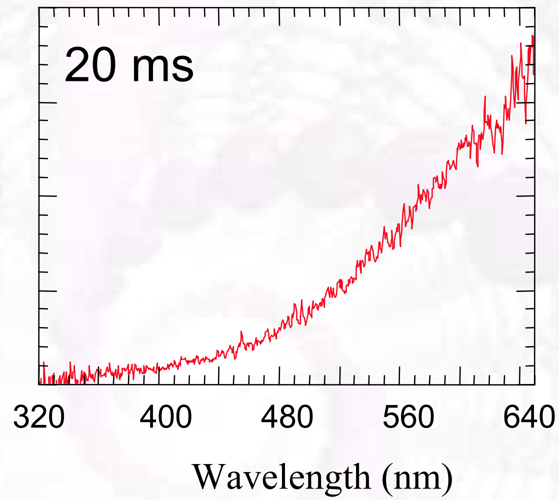


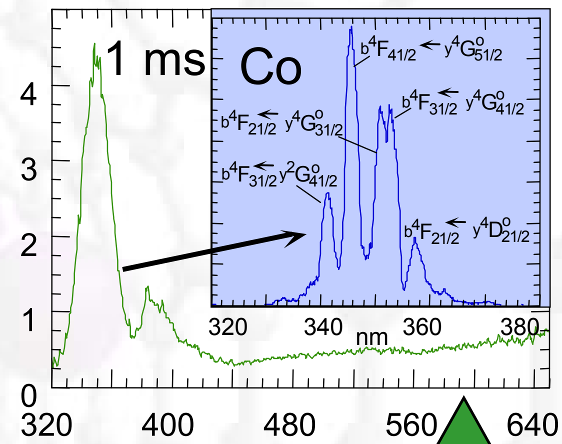


Shock wave and vortices confine and trap the ejected material in a small volume

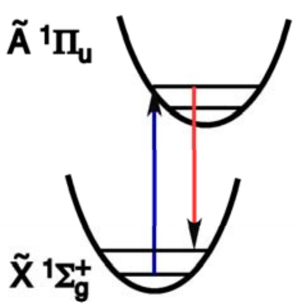
Laser-Induced Emission Spectra of C/Co/Ni Plume at 1000° C During Nanotube Growth







LIF of molecular C_3

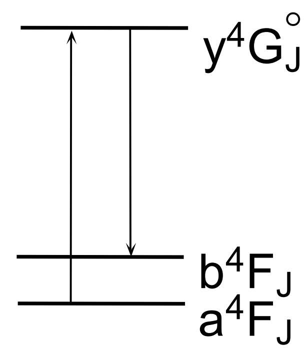


LII of nanoparticles

$$I = \sigma (T + \Delta T)^5$$

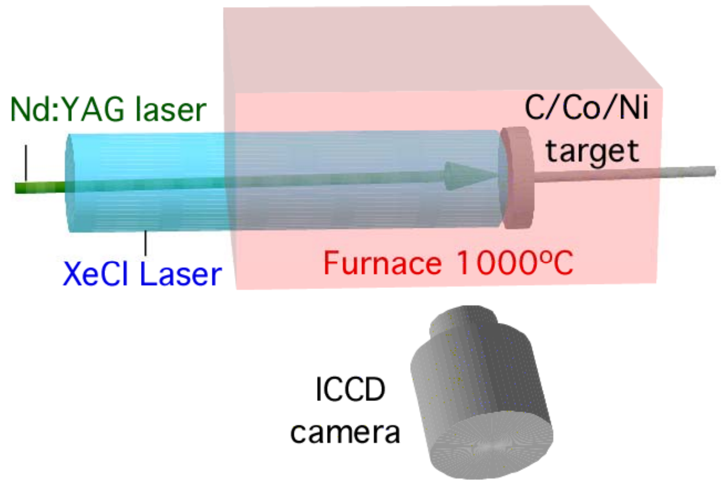
T is the oven temperature.
ΔT is the temperature increase due to the 308 nm-laser heating

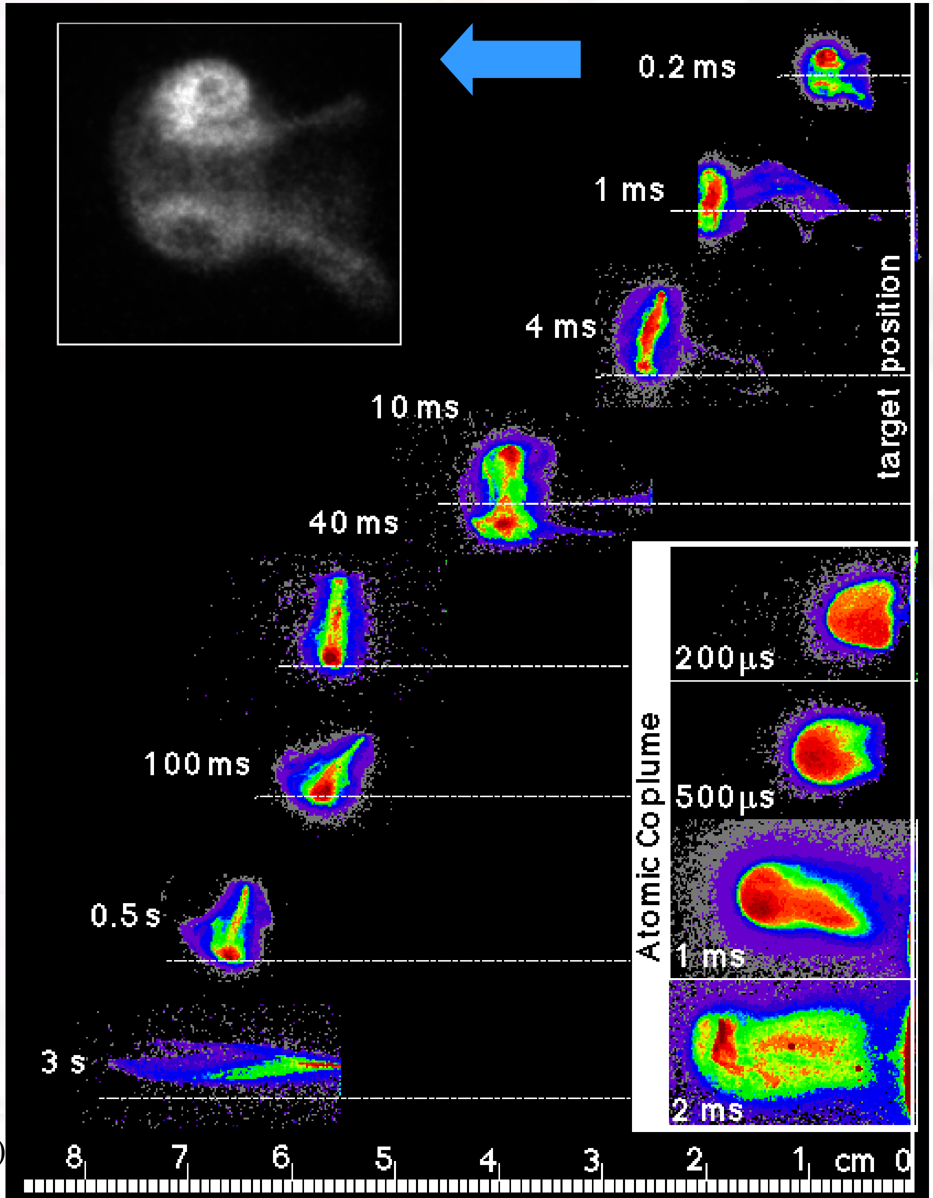
LIF of atomic Co



Using 308 nm-laser-induced emission we can monitor ground state species of C_3 and Co and probe carbon nanoparticles in the C/Co/Ni plume.

Imaging and Spectroscopy Diagnostics of SWNT Growth



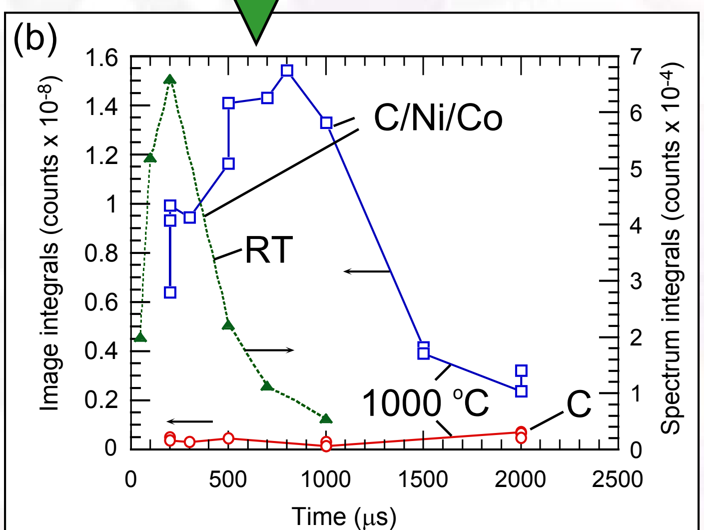


- ❒ First imaging of plume dynamics during SWNT growth by laser vaporization
  - ✥ Utilizes LIF-excitation
  - ✥ Permits first estimates of growth rates. (with ex situ TEM).
- ❒ Spectroscopy gives plume composition, nucleation times.
  - ✥ Reveals when/where nanotubes grow
  - ✥ Spectroscopic imaging spatially locates different plume species

Appl. Phys. Lett. **76**, 182 (2000). *Appl. Phys. A* **70**, 153 (2000).
Appl. Phys. Lett. **78**, 3307-3309 (2001). *Phys. Rev. B* **65**, 245525 (2002)

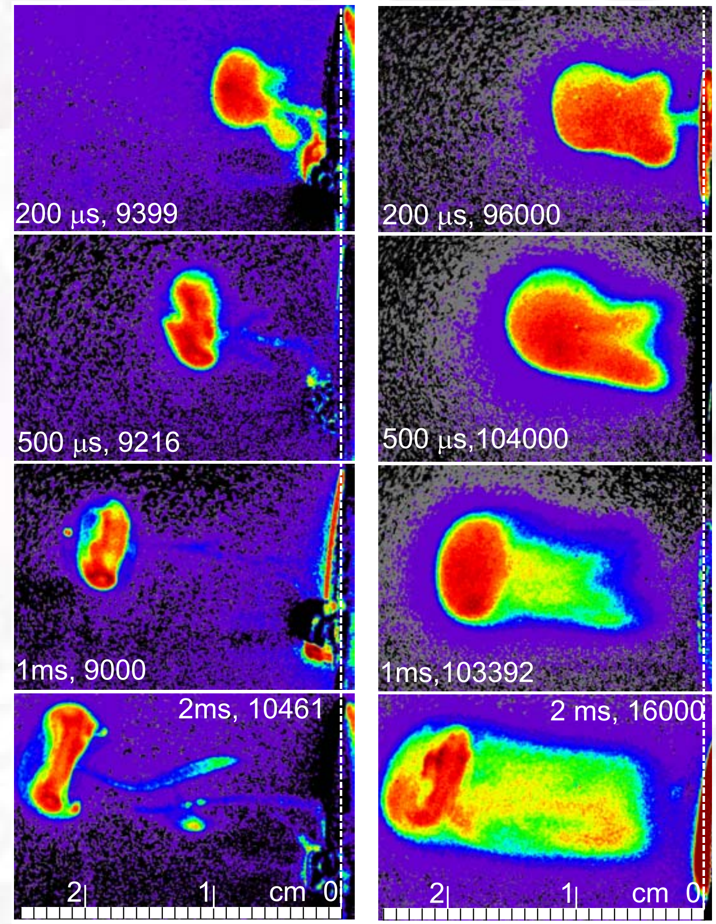
Spatially Locating Carbon Clusters and Cobalt Atoms in the Ablation Plume with Spectroscopic Imaging

- Integrated images give kinetic lifetimes
- Carbon converts to clusters very early (~0.2 ms at 1000 C)
- Cobalt converts to clusters *much later* (~1.5 ms at 1000 C)



Carbon clusters *(blackbody continuum)*

Cobalt Atoms *(350 nm)*



After Δt ~ 2 ms, nearly all species are condensed into clusters/nanoparticles

Condensed phase growth at extended times

Plasma and Laser Induced Luminescence Spectra of Different Species During SWNT Growth by Laser Ablation

- *Carbon converts to clusters very early (~ 0.2 ms)*
- *Co converts to clusters much later (2 ms)*

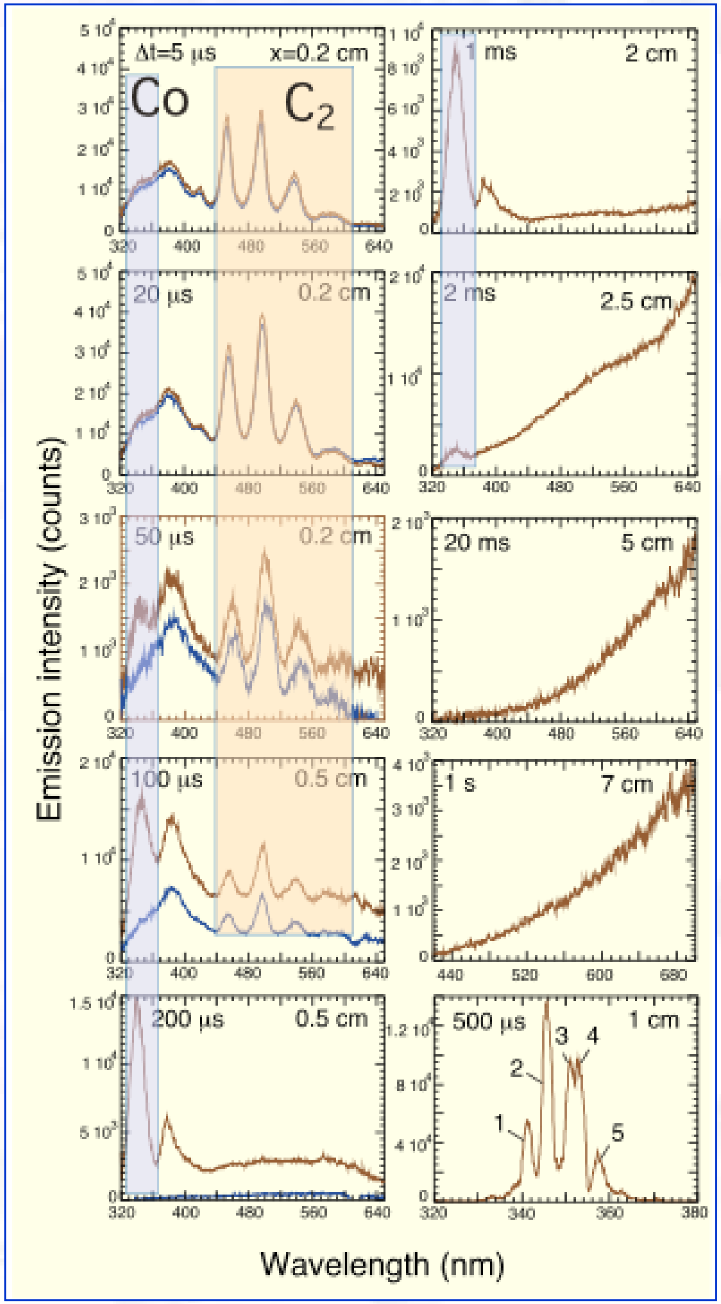
5 µs
C_2^*, C_3^*

20 µs
C_2^*, C_3^*

50 µs
C_2^*, C_3^*, clusters

100 µs
C_2^*, C_3^*, Co, clusters

200 µs
Co, clusters



1 ms
Co, clusters

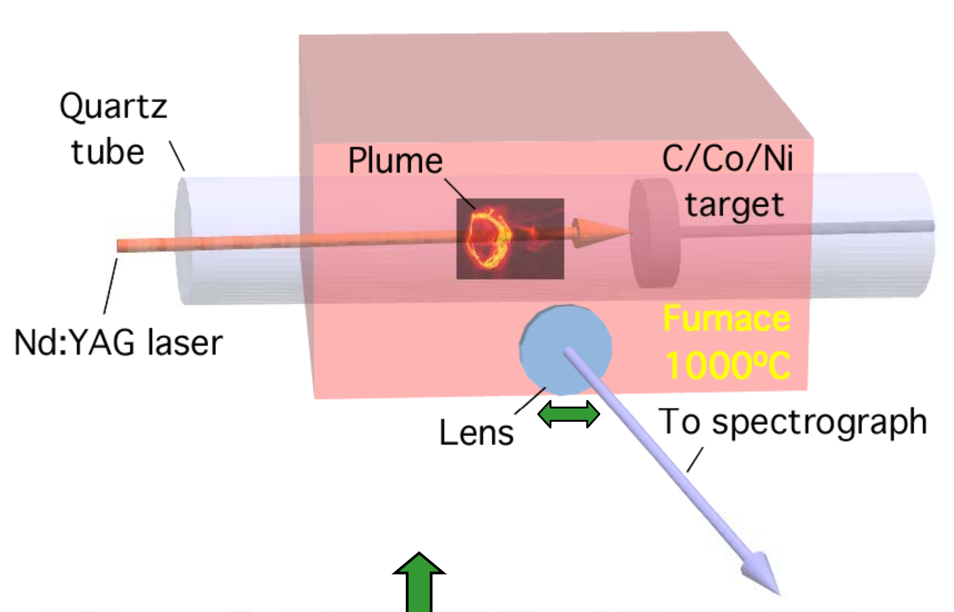
2 ms
clusters nanotubes

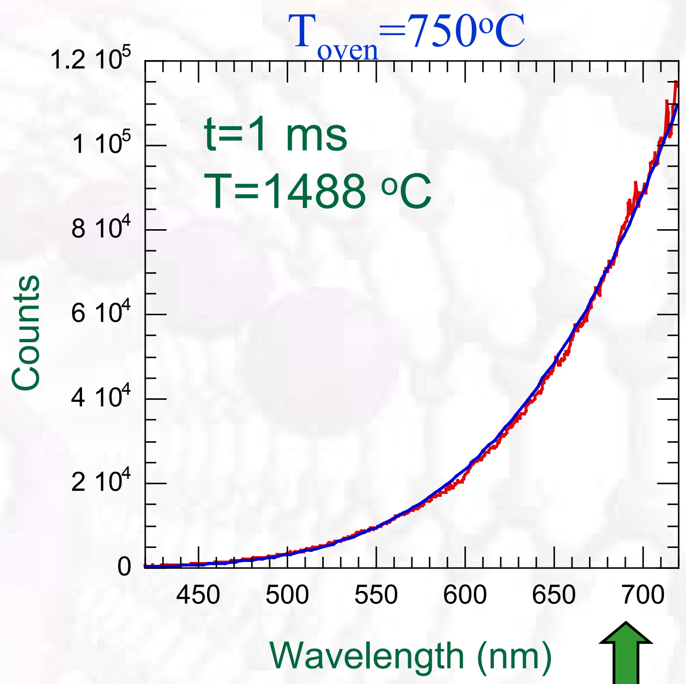
20 ms
clusters nanotubes

1 s
clusters nanotubes

Co

Plume Temperature Measurements Inside the Propagating Microreactor



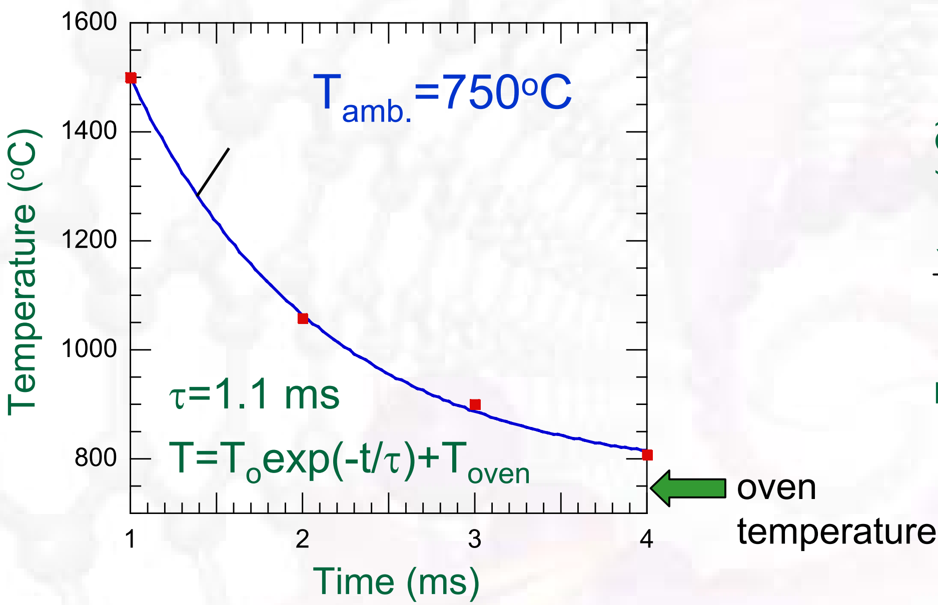


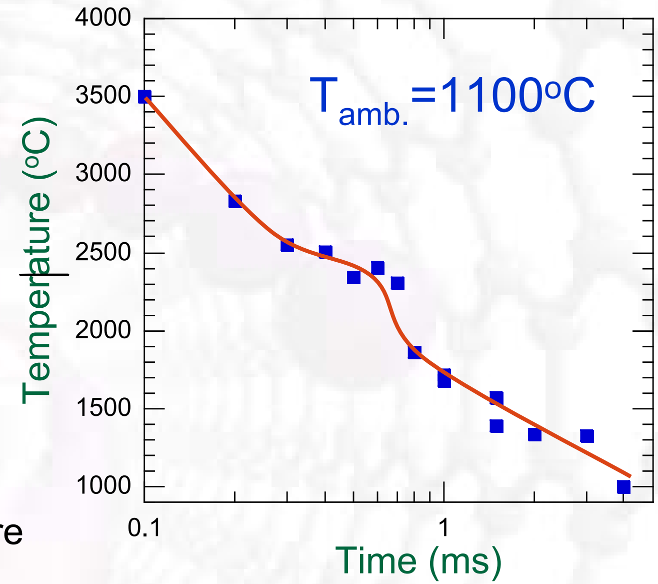
- Temperature vs. time
  - From blackbody emission spectra
  - At different positions and times

- The plume emission spectra were fitted with the Planck blackbody function
  - Small particles: emissivity, $\varepsilon \sim 1/\lambda$
  - Large particles: $\varepsilon \sim$ const.

Measured blackbody emission spectra give particle temperatures

How does the plume cool?





- The temperature of the plume approaches the ambient temperature ~ 4 ms after ablation

- For $T_{amb.}$=1100ºC a plateau is observed at T~2500ºC in the time interval 0.3-0.7 ms

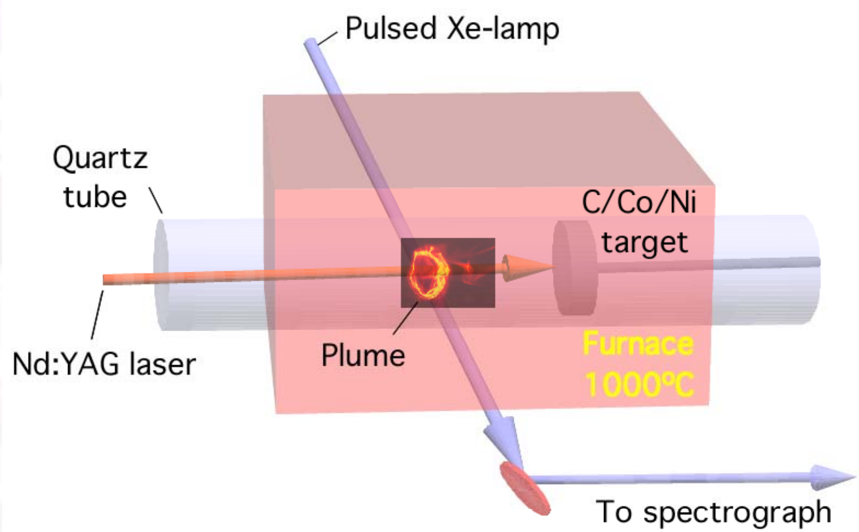
An exothermic process, probably formation of fullerene-like structures, keeps the plume temperature constant from 0.3 to 0.7 ms.

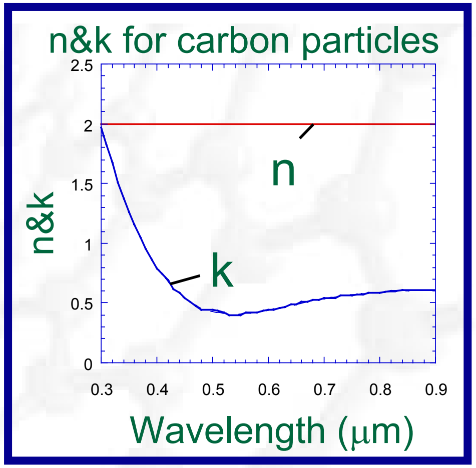
Similar plateau (in plume emission intensity) was observed by Y. Achiba et al.

In situ absorption spectroscopy of carbon nanoparticles

Estimating Particle Size

- Measuring extinction spectra, $Q_{abs}(\lambda,t)$
  - scattering
  - absorption
- Estimate particle size from shape of extinction spectrum
  - small particles: $2\pi a<0.3\lambda$ (λ=300 nm)
    - ☐ for a<14 nm, $Q_{abs}(\lambda) \sim 1/\lambda$
    - ☐ no size information
  - larger particles
    - ☐ for a>14 nm, Mie theory for spherical particles
    - ☐ $Q_{abs}(\lambda)$ sensitive to particle size

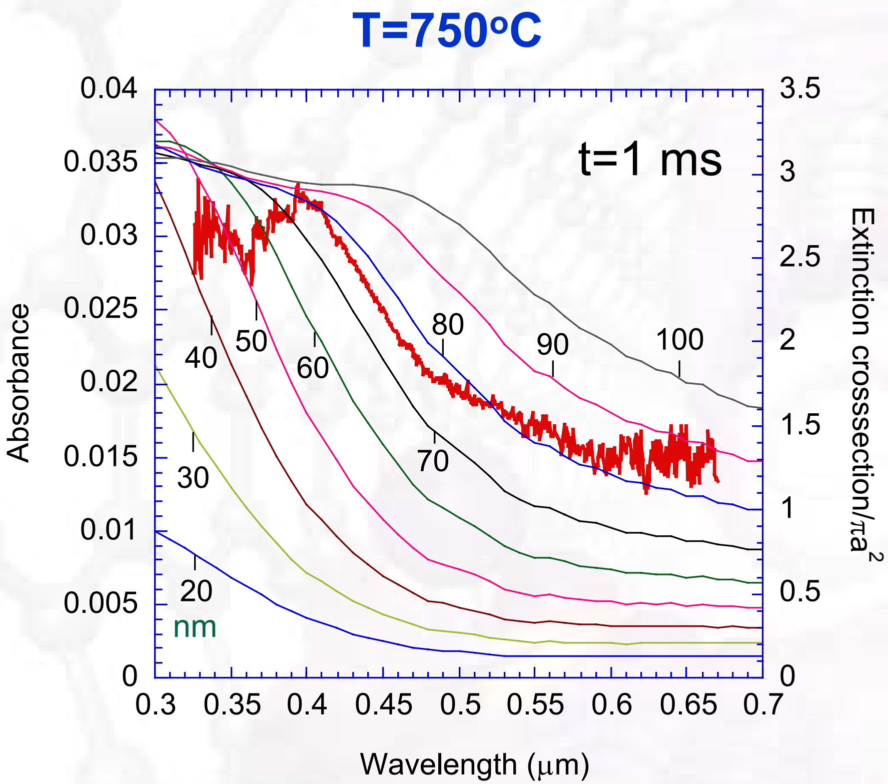


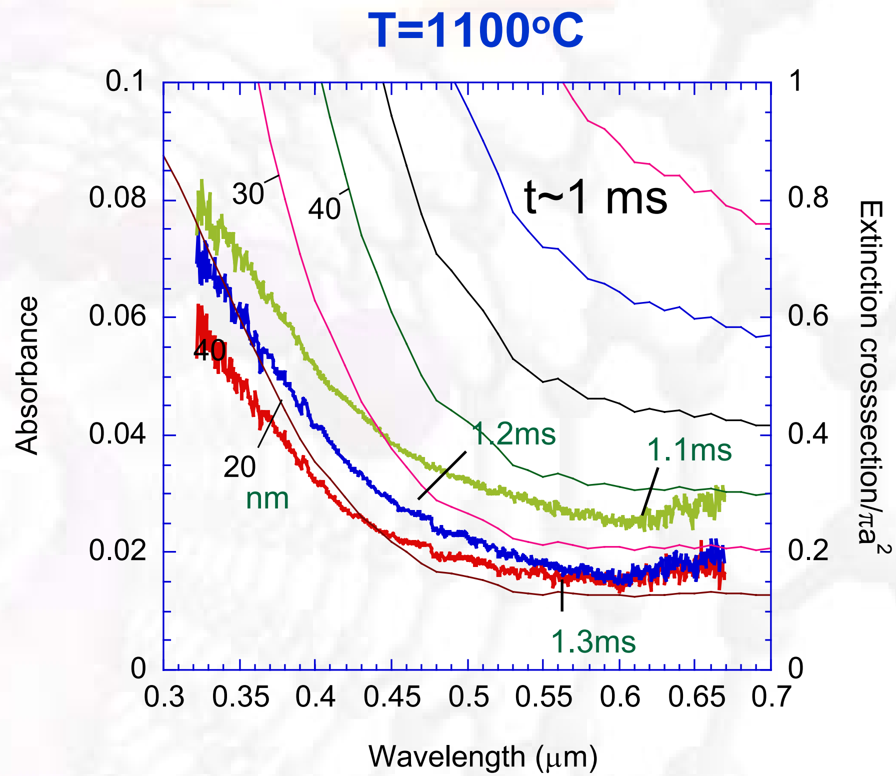


E.A. Rohlfing, *J.Chem.Phys.* **89**, 6103 (1988)

The shape of the extinction spectrum gives an estimate of the particle size

Extinction Spectra at Two Oven Temperatures

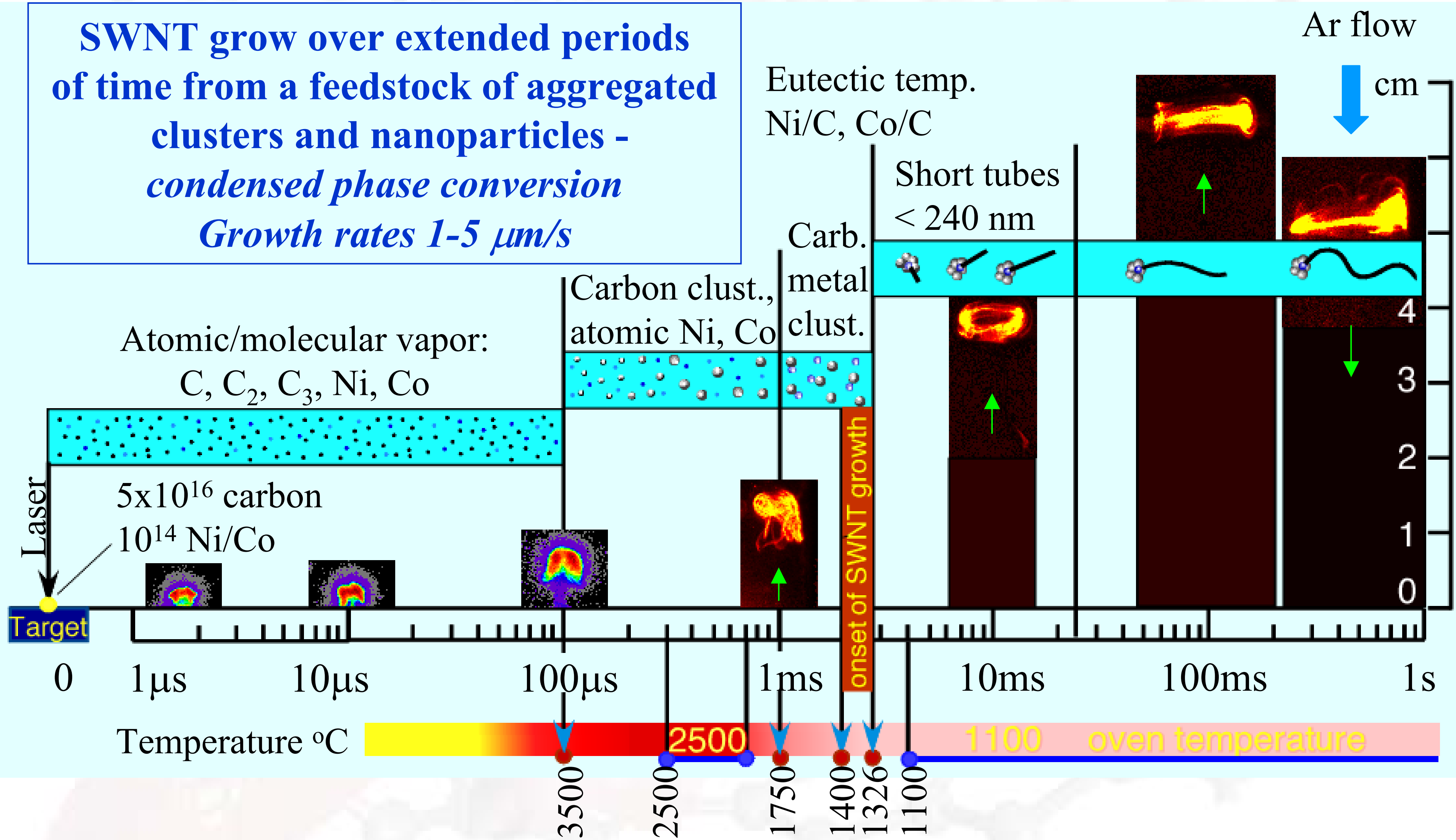




- At 750°C oven temperature aggregates have already reached 80 nm in size by t=1 ms
- In the 1100°C oven aggregates remain < 20 nm in size up to 4 ms after ablation

Carbon nanoparticles aggregate much slower at higher temperatures

General picture of SWNT growth by laser vaporization based on spectroscopic diagnostics of ejected material



A. A. Puretzky et al, *Phys. Rev. B* **65**, 245525 (2002).

UT-BATTELLE

in situ Diagnostics of Carbon Nanotube Growth by Chemical Vapor Deposition

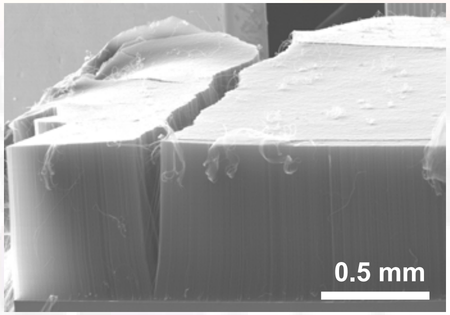
- Growth of vertically-oriented nanotube arrays

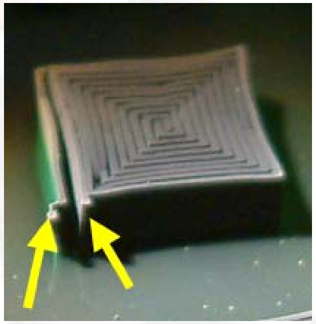
Vertically-Aligned Carbon Nanotube Polymer Composites

- Vertically-aligned multiwall carbon nanotubes (VA-MWNT) grown by CVD over large areas
  – or *selectively* grown on lithographically-patterned catalyst films
  - Rapid growth to millimeters lengths
  - Or controlled growth to precise lengths with *in situ* diagnostics (in the nanometers to microns regime)
  - Alignment achieved for large diameter multiwalled nanotubes (MWNT) down to double-walled nanotubes (DWNT)

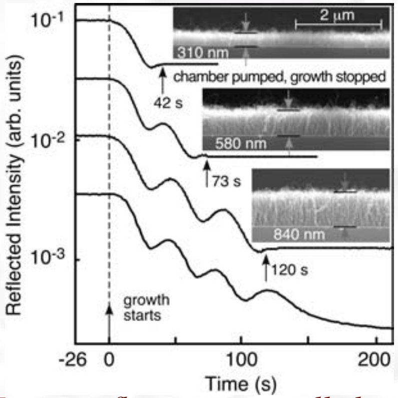
- Infiltration of VA-MWNT with polymers for composites
  - Methods developed to preserve alignment
  - Young's modulus significantly enhanced
  - Increased oxidative thermal stability
  - Electrical conductivity in 3D, dissipates static charge
  - Enhanced thermal conductivity
  - Embedded sensor structures
  - Optically reflective coatings, optical filters

I. N. Ivanov, A. A. Puretzky, D. B. Geohegan, G. Eres, M. A. Guillorn and J. Y. Howe

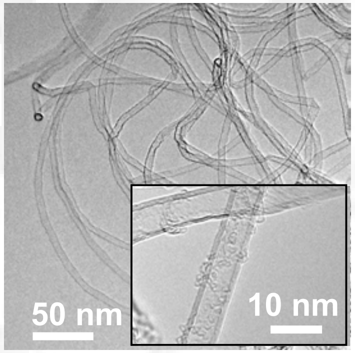




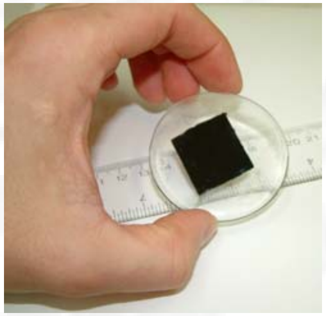
Macroscopic growth over large areas, or selective patterns

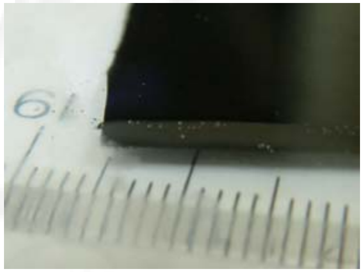


In situ reflectivity controlled-growth



HRTEM of DWNT

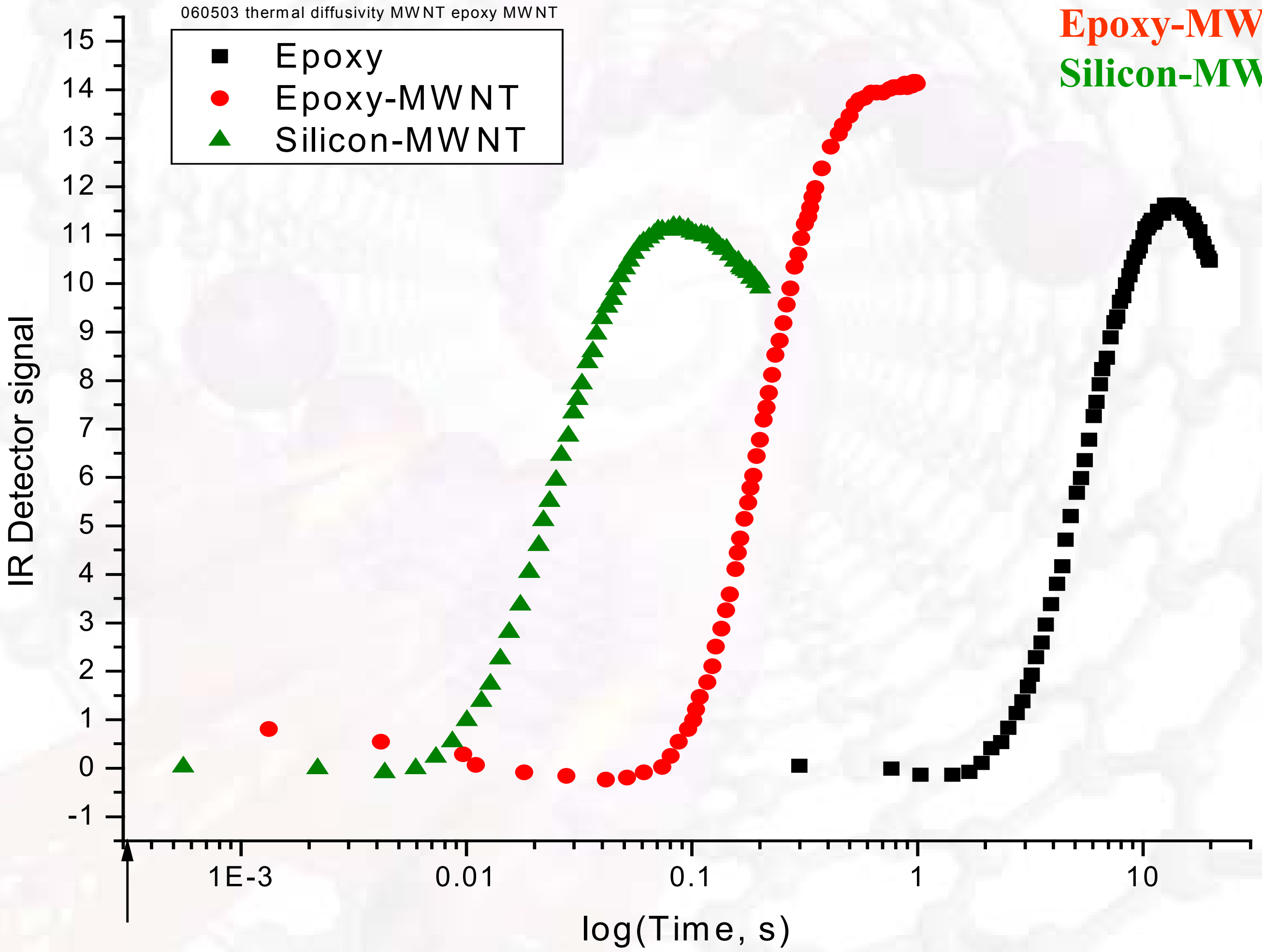




2 mm VA-MWNT in epoxy

Work funded by NASA, DARPA, ORNL-LDRD

Thermal Diffusivity of Epoxy-Infiltrated VA-MWNT



Thermal diffusivity, cm^2/s

Epoxy- 0.0013

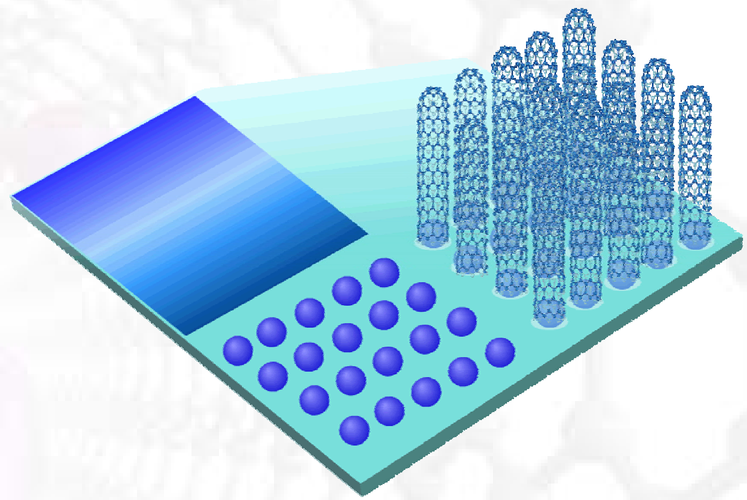
Epoxy-MWNT- 0.028

Silicon-MWNT- 0.48

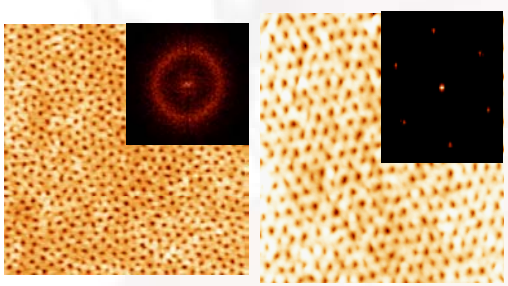
I. N. Ivanov, D. B. Geohegan, A. A. Puretzky, S. Jesse, G. Eres, and J. Y. Howe, (in preparation).

Growth of Aligned Nanotube Arrays – *from self-assembled templates*

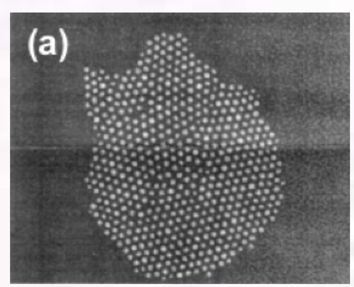
- Utilize self-alignment of nanotubes due to crowding and bundling to produce highly aligned fibers and monoliths
- Must produce high-densities of well-aligned catalyst nanoparticles AND induce high nucleation fractions
    - Thin metal catalyst film roughening
    - Self-assembled ensembles pre-synthesized nanoparticles
    - Use of block copolymer templates to order pre-synthesized nanoparticles



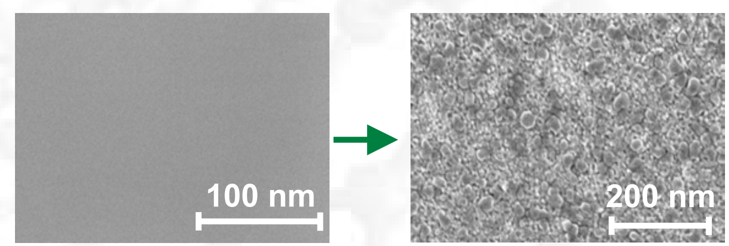
Catalyst self-assembly and nanotube growth



Random and ordered block copolymer domains (M. Dadmun, S. Fontana)

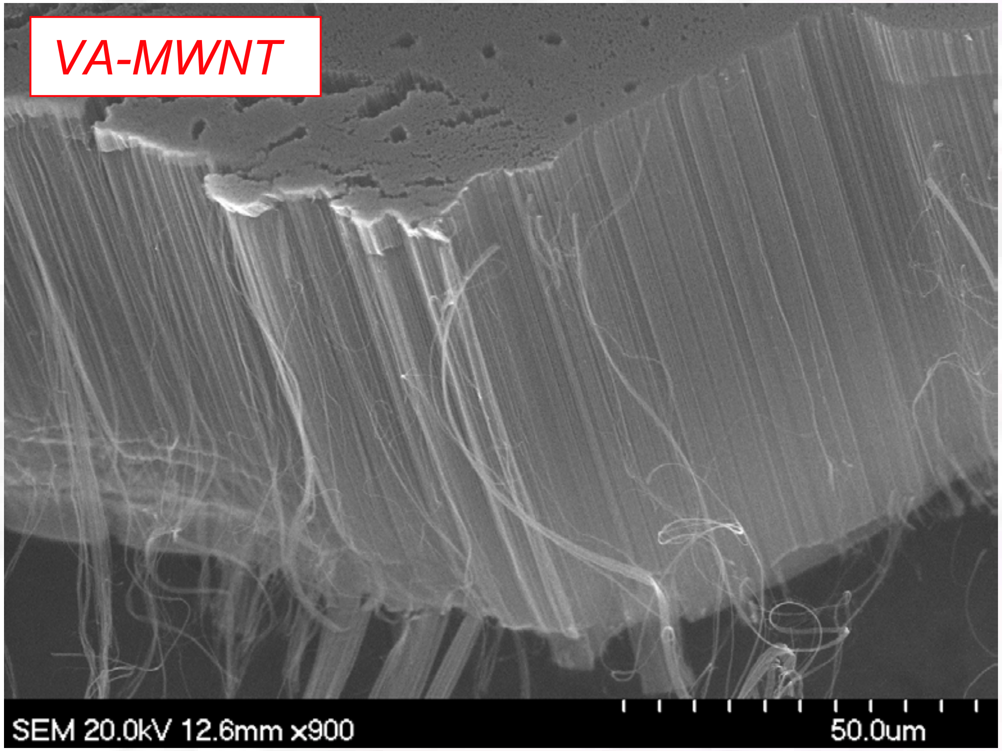


Self-assembled, chemically-synthesized nanoparticles - (Jie Liu)



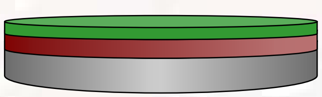
Roughening of thin metal catalyst film (our work)

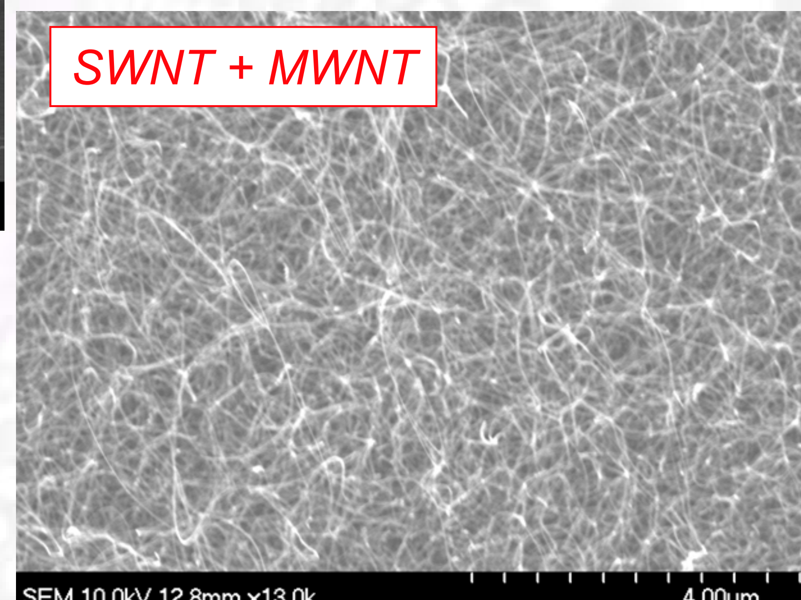
Vertically-Aligned MWNT by CVD *(+ SWNT)*



- **Grown to 4 mm lengths**
- **Wide temp. range for vertical alignment**
- **Multiwalled, 5 to 20 nm diameter**
- **Mixed with SWNT for T > 700 C**

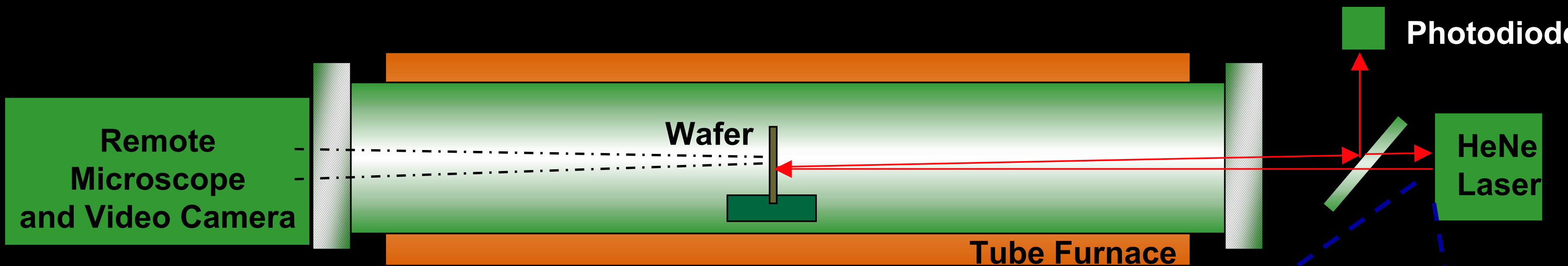
- **Grown using evaporated metal catalyst multilayer films - applicable to large areas Al(10nm)/Fe(1nm)/Mo(0.2nm)**
- **Ar/H_2/C_2H_2 ~700C**

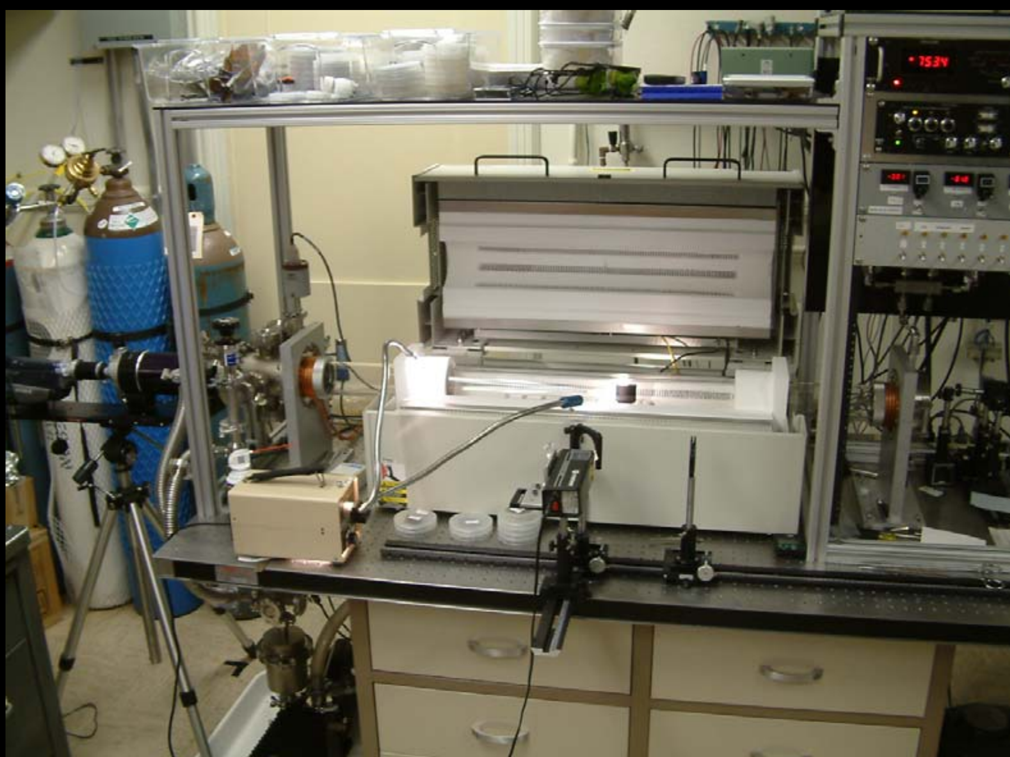


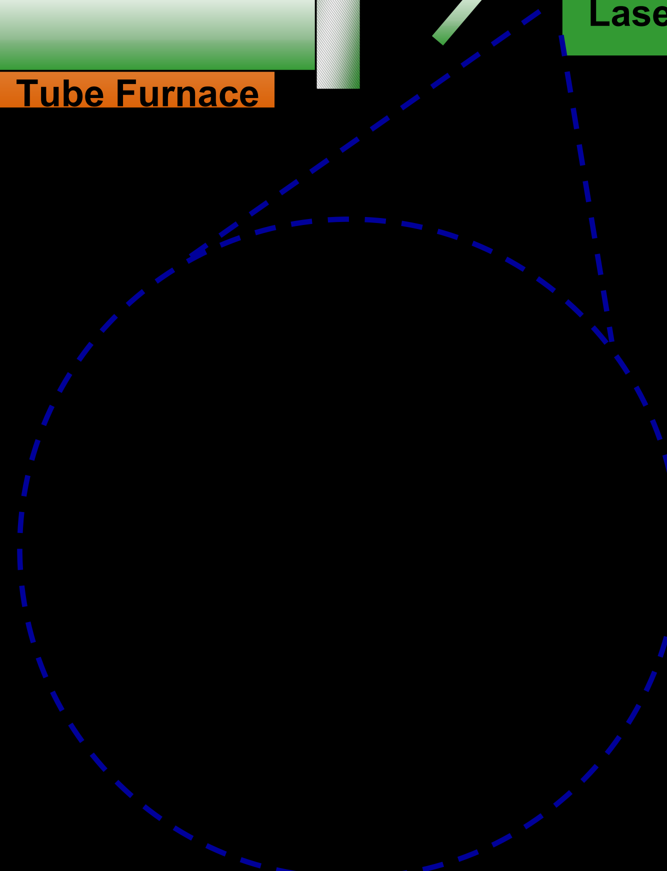


D. B. Geohegan, A. A. Puretzky, I. N. Ivanov, S. Jesse, G. Eres, J. Howe Appl. Phys. Lett. **83***, 1851 (2003)*

In situ laser-interferometry, irradiation, and imaging during CVD



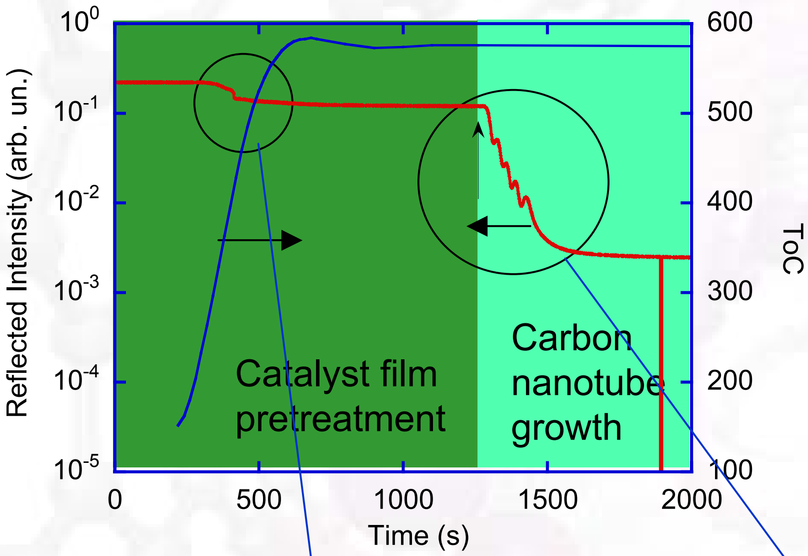


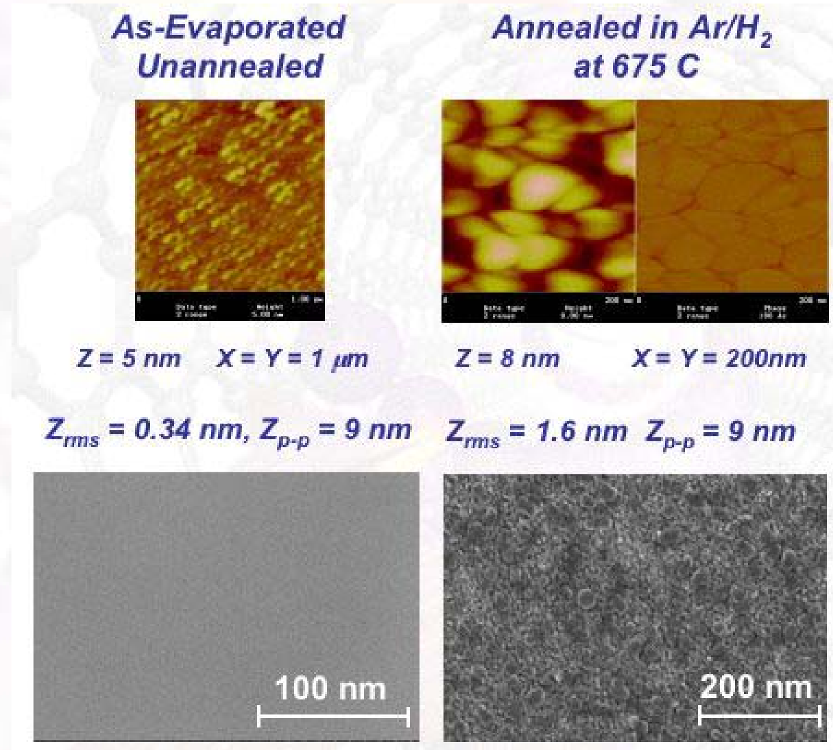


Reflected Spot

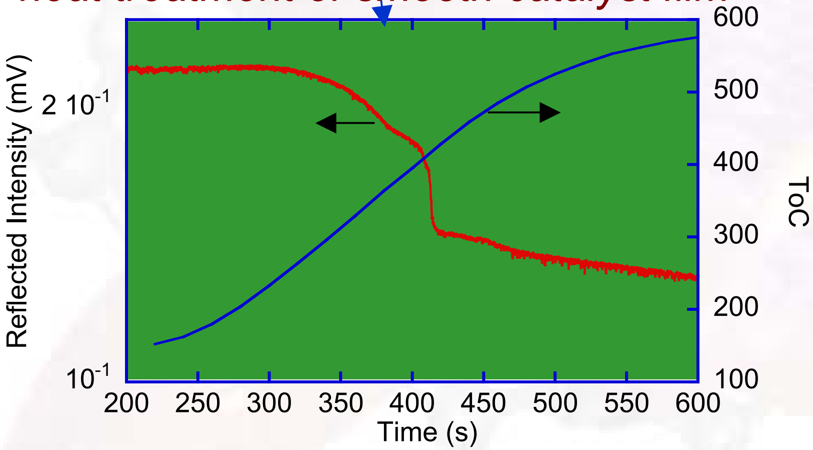
D. B. Geohegan, A. A. Puretzky, I. N. Ivanov, S. Jesse, G. Eres, and J. Y. Howe, Appl. Phys. Lett. **83**, 1851 (2003)

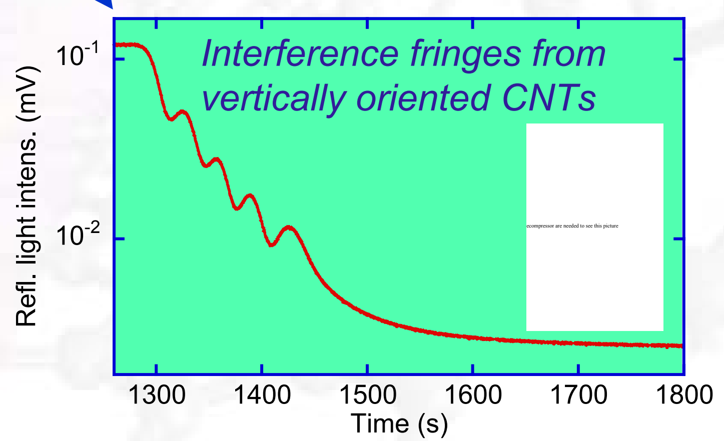
Reflectivity During Catalyst Pretreatment and Nanotube Growth





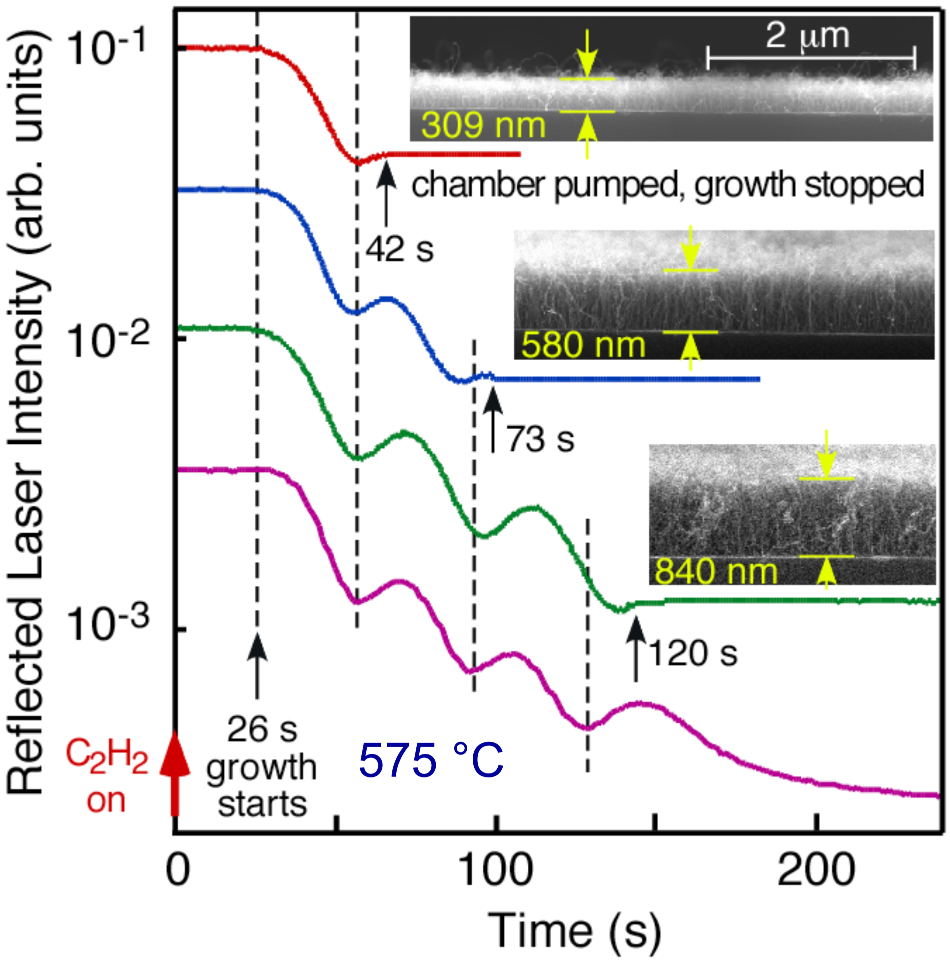
The sharp transition in reflectivity during heat treatment of smooth catalyst film





D. B. Geohegan, A. A. Puretzky, I. N. Ivanov, S. Jesse, G. Eres, and J. Y. Howe, Appl. Phys. Lett. **83**, 1851 (2003)

Controlling the length of VAA-MWNT

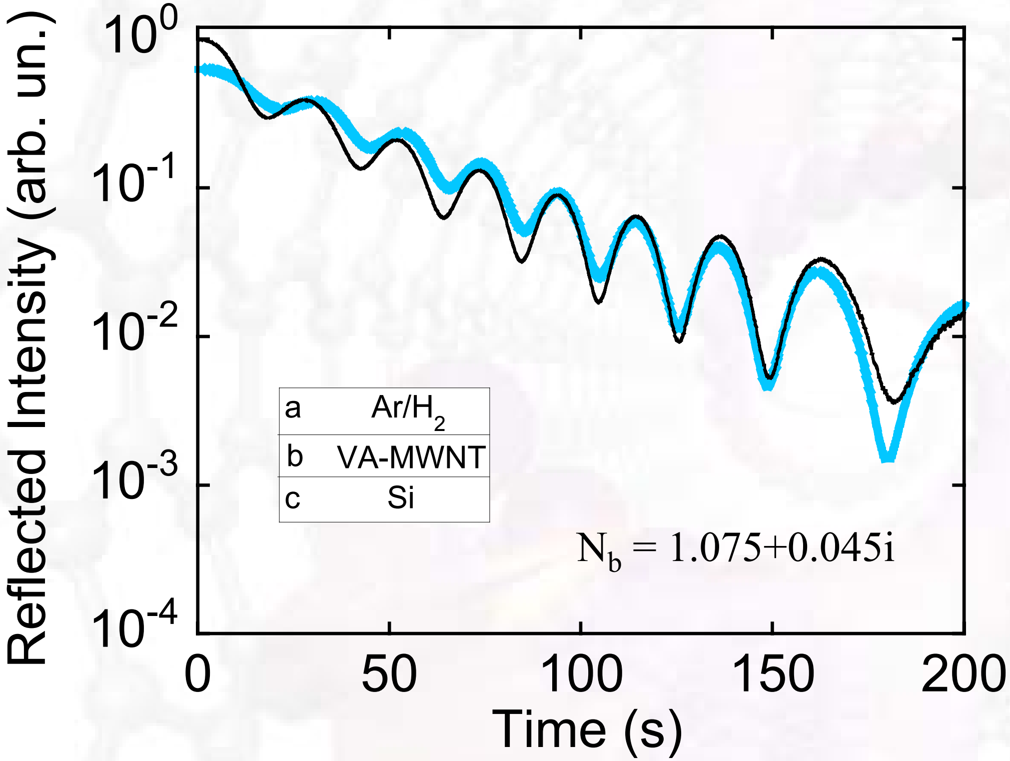


- Reflectivity can be used to monitor *and control* the length of vertically-aligned nanotube arrays
- Rapid evacuation of growth gas at predetermined lengths
- Can see growth stop.
- Can stop and restart growth of CVD grown "seeds", as in LV.
- $n_{eff}d = m\lambda/2$ (λ=633 nm)

  d ≈ 300±20 nm
  n_{eff} ≈ 1.075, k=0.047
  absorption coefficient, $\alpha \approx 0.9 \cdot 10^4$ cm^{-1}

D. B. Geohegan, et al. Appl. Phys. Lett. ***83****, 1851 (2003)*

Modeling of experimental interference fringes



Porosity of VAA-MWNTs

Looyenga formula:

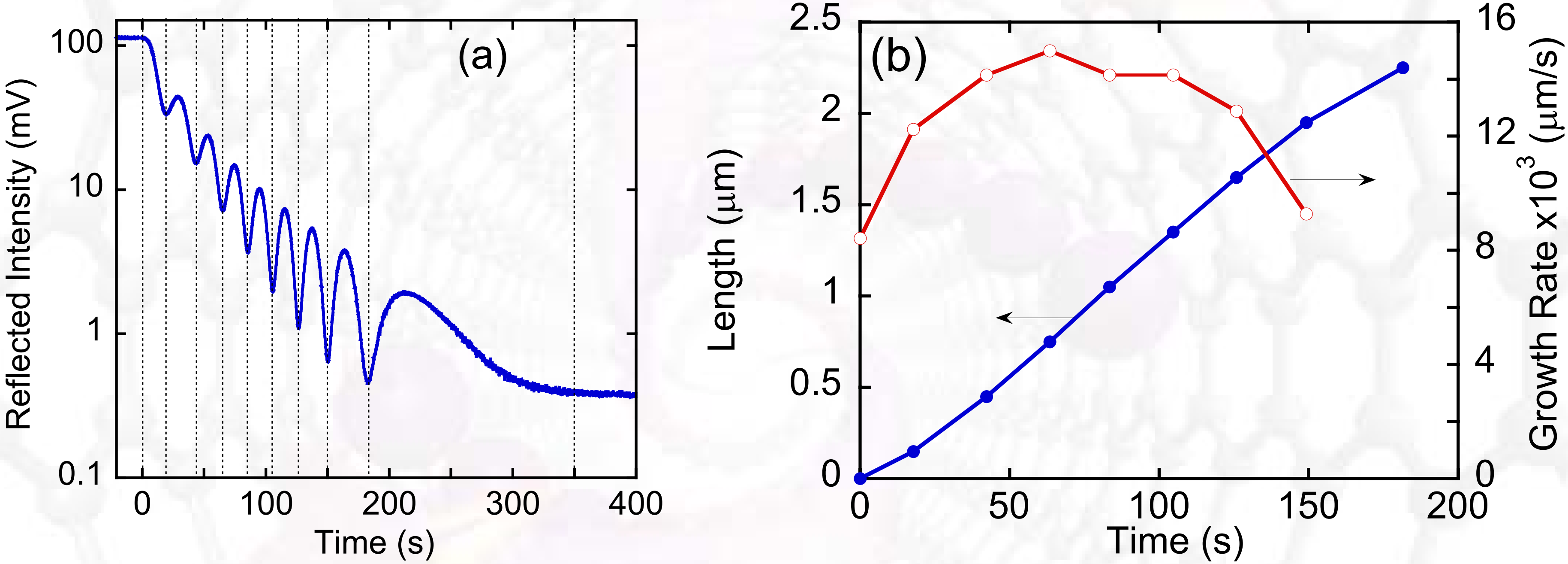
$$\varepsilon_{eff}^{1/3} = (1-p)\varepsilon^{1/3} + p\varepsilon_m^{1/3},$$

where ε, ε_m are the dielectric functions of carbon nanotubes ($\varepsilon \sim 4$), and the host material (ε_m~1), p is the porosity (p~0.92)

- Theoretical modeling of the measured interference fringes gives the effective complex refractive index of VAA-MWNTs.
- The effective media refractive index permits estimate of VAA-MWNT porosity.

A. A. Puretzky, D. B. Geohegan, I. N. Ivanov, S. Jesse, G. Eres, and J.Y. Howe (in preparation)

Measuring VAA-MWNT growth rates

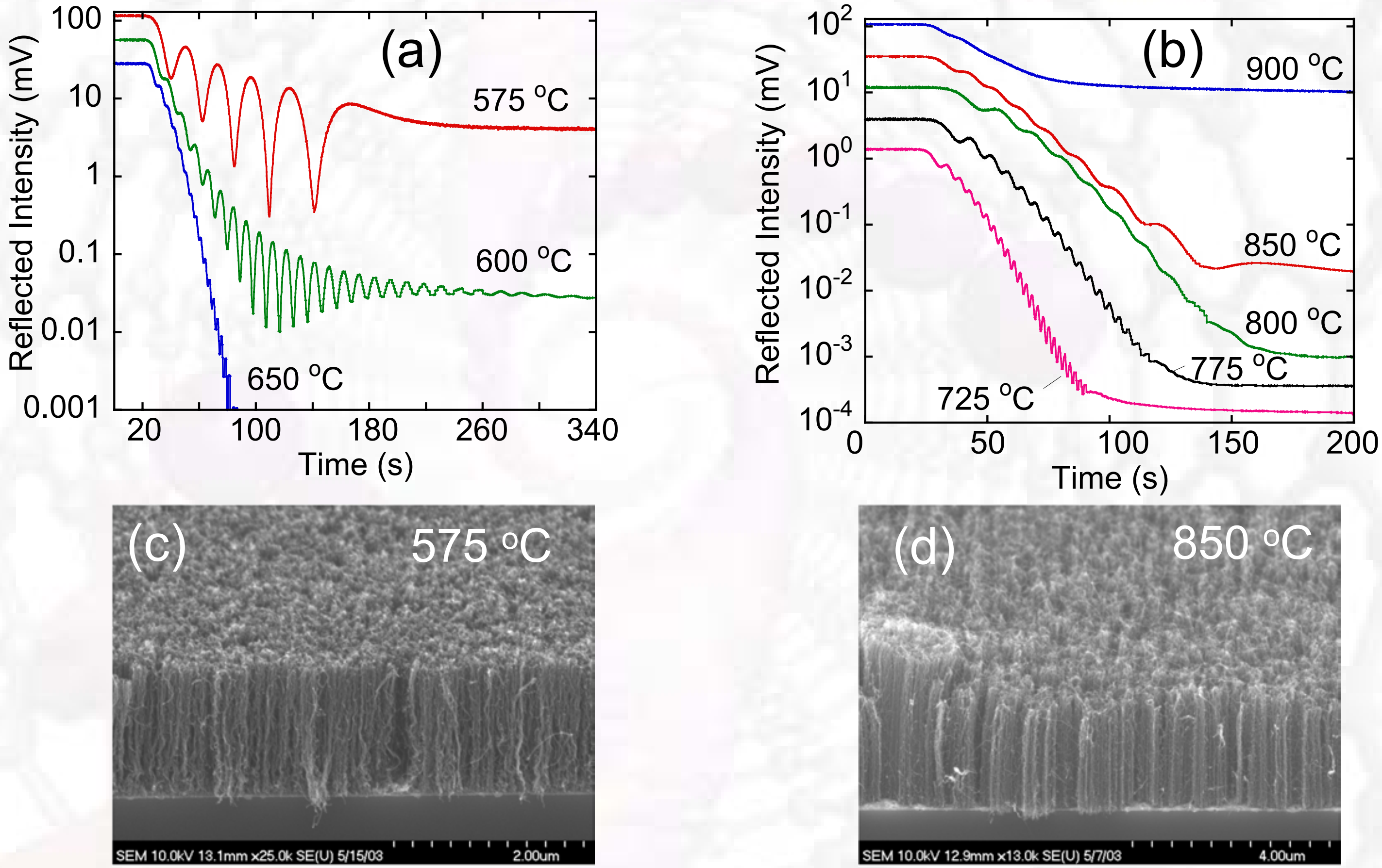


Interference fringes in reflected light intensity permit array growth to be measured ***throughout the run***

First direct kinetics information of nanotube growth during CVD

A. A. Puretzky, D. B. Geohegan, I. N. Ivanov, S. Jesse, G. Eres, and J.Y. Howe (in preparation)

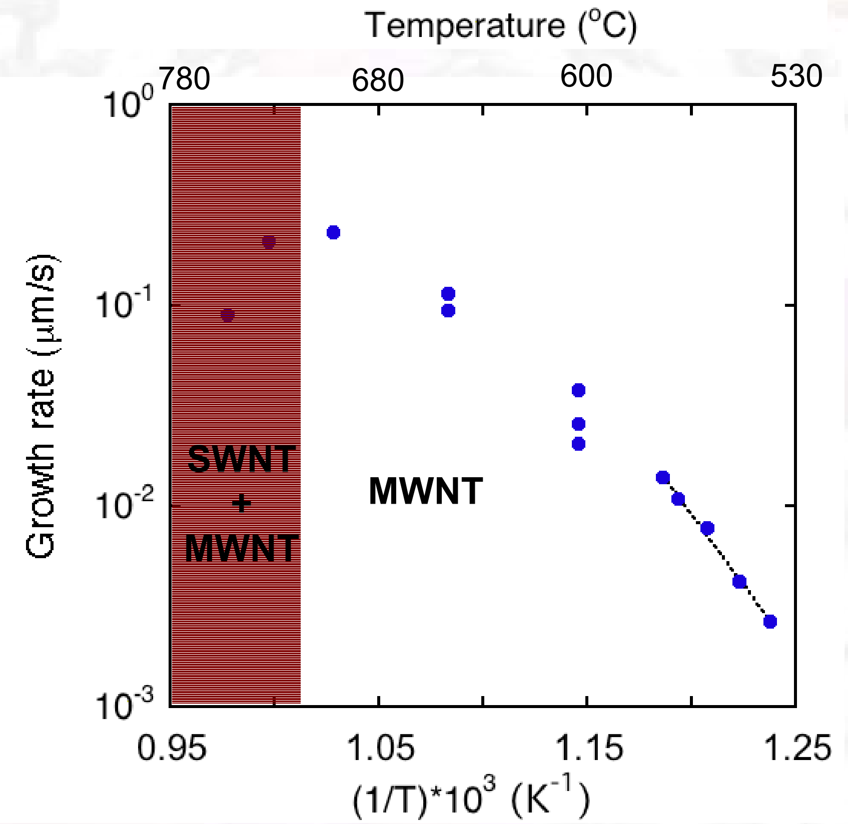
Time resolved reflectivity at different growth temperatures



Interference fringes in the TRR signal provide the method for fast *in situ* measurements of growth kinetics at different temperatures

A. A. Puretzky, D. B. Geohegan, I. N. Ivanov, S. Jesse, G. Eres, and J.Y. Howe (in preparation)

Temperature Dependence of VAA-MWNT Growth Rate



- Growth conditions: atmospheric pressure, 10 sccm C_2H_2, 400 sccm H_2, 2000 sccm Ar.
- SWNT/DWNTs grow together with MWNT at T> 700 °C.
- The temperature range 750-800 °C corresponds to highly unstable growth conditions as growth modes transition to prefer DWNT/SWNT formation over MWNT.

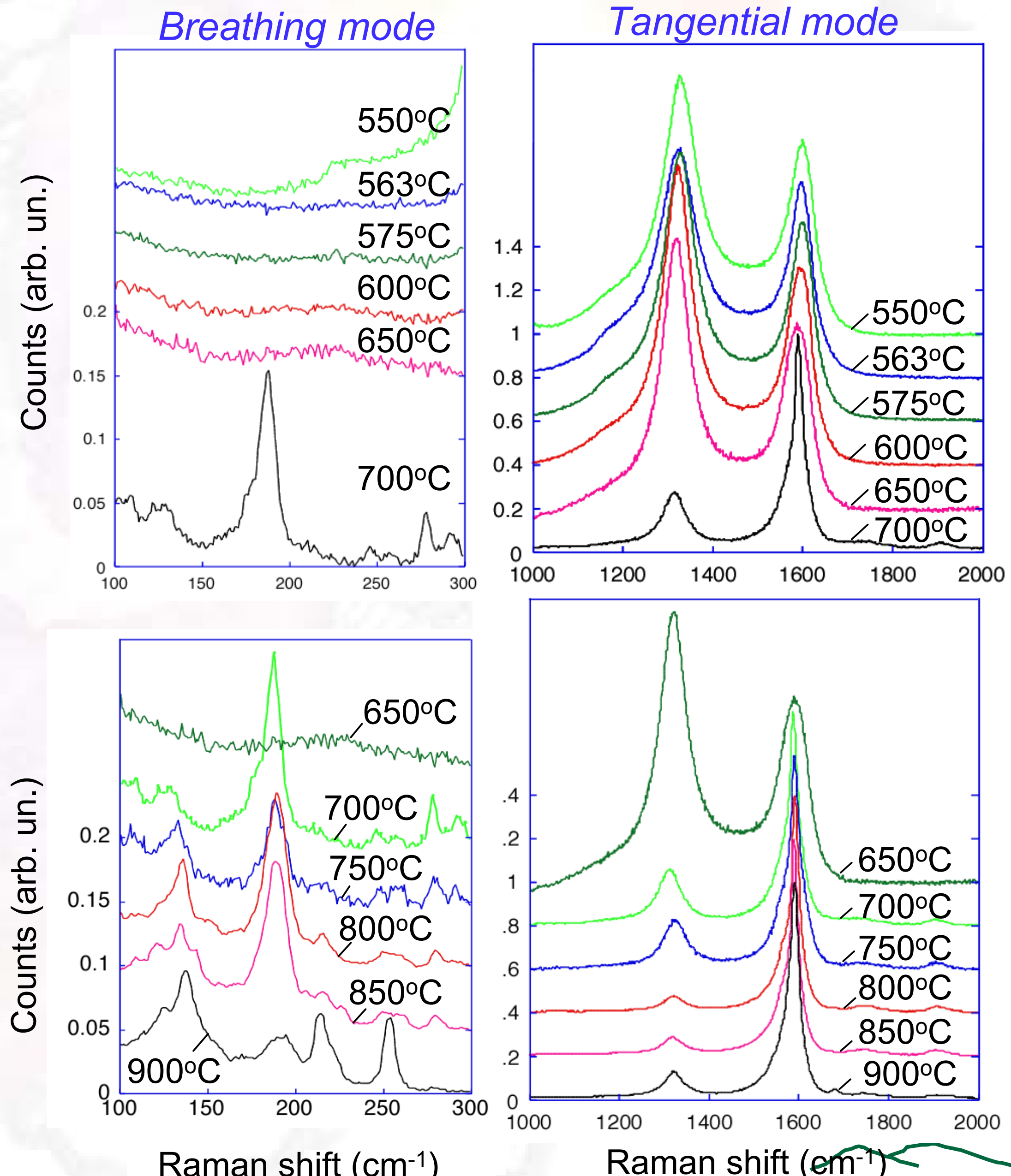
A. A. Puretzky, D. B. Geohegan, I. N. Ivanov, S. Jesse, G. Eres, and J.Y. Howe (in preparation)

Raman Spectra of Nanotubes vs. Growth Temperature

The breathing and tangential modes in the Raman spectra show clear onset of SWNT/DWNT growth at T> 700 °C

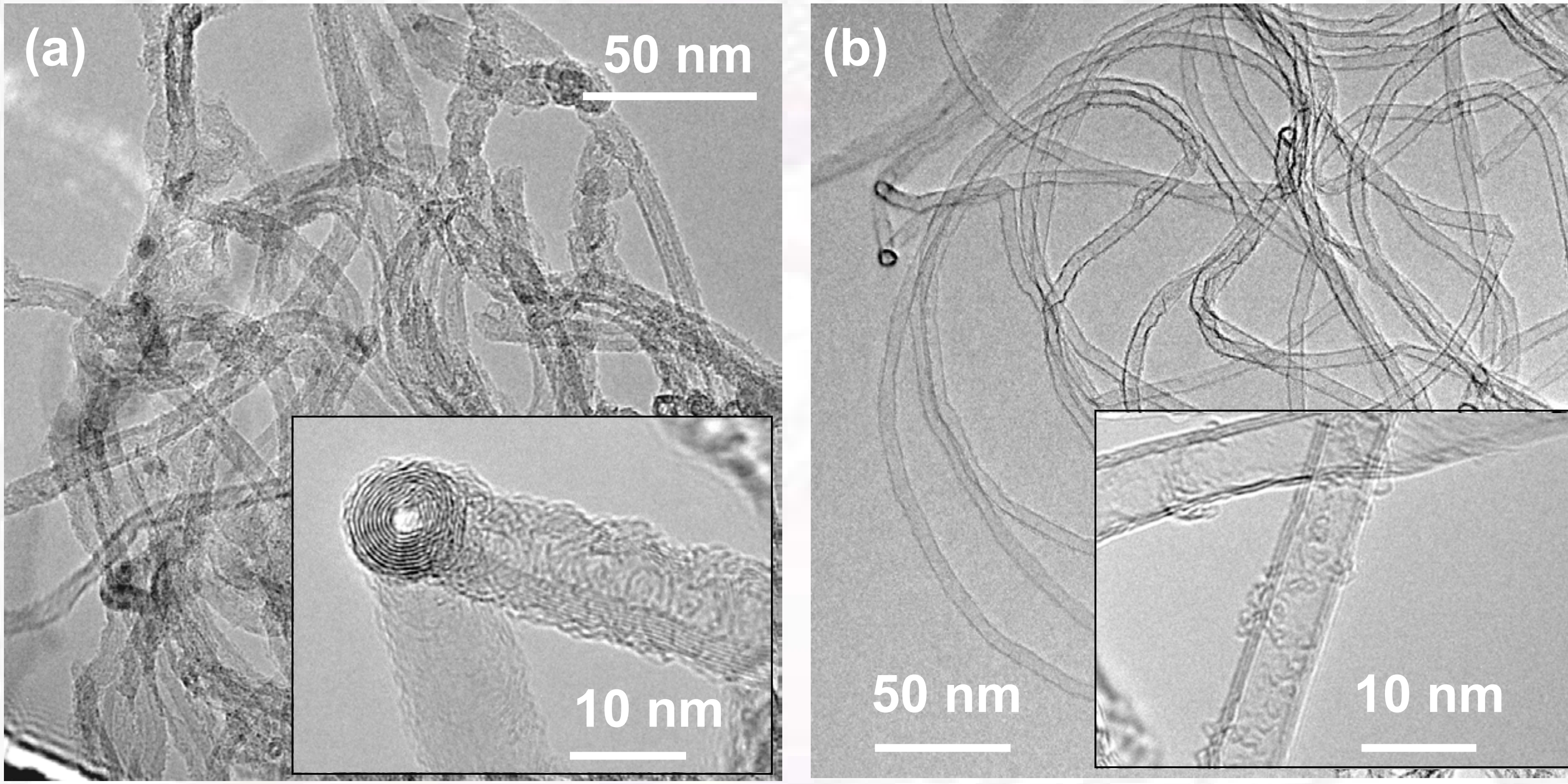
QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

Nanotubes grown at 775 °C



A. A. Puretzky, D. B. Geohegan, I. N. Ivanov, S. Jesse, G. Eres, and J.Y. Howe in preparation.

TEM images of carbon nanotubes grown at different temperatures



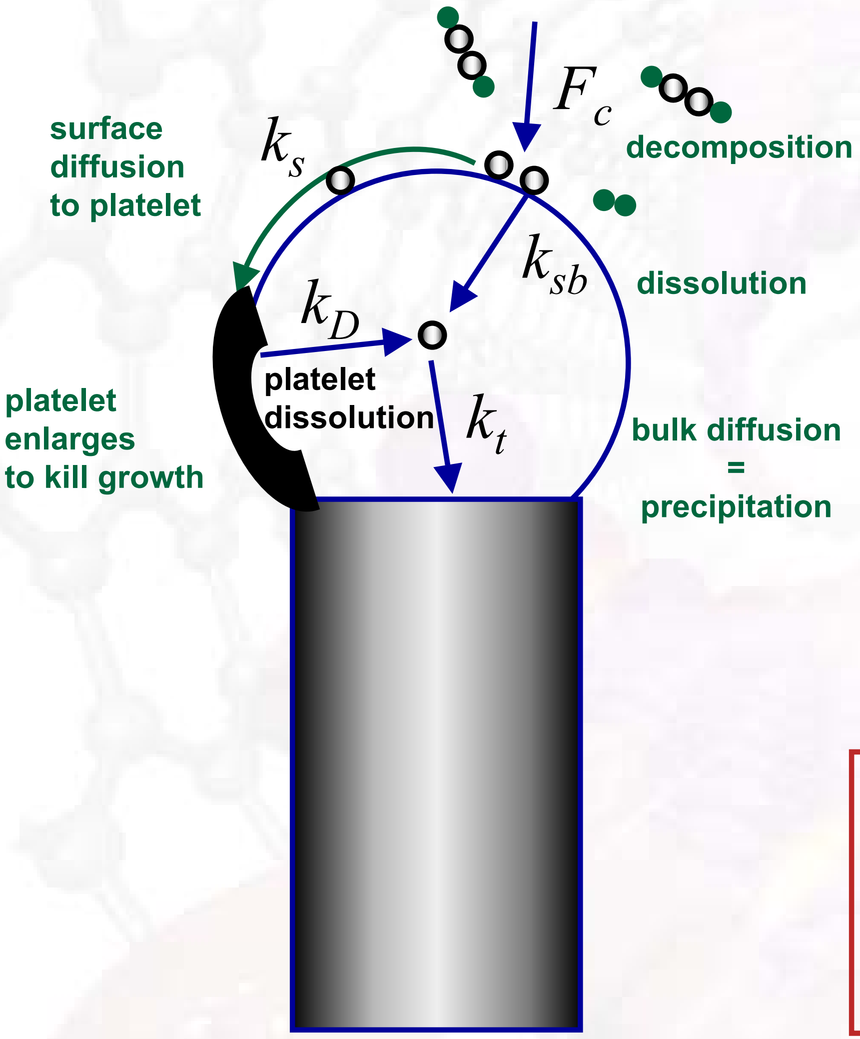
575 °C

725 °C

- The number of walls in MWNTs decreases at higher temperatures
- Optimizing the growth temperature yields VAA-MWNTs with a large fraction of DWNTs

 D. B. Geohegan, A. A. Puretzky, I. N. Ivanov, S. Jesse, G. Eres, and J. Y. Howe, Appl. Phys. Lett. **83**, *1851 (2003)*

Carbon Nanotube Growth Model



Feedstock Decomp.

$$\frac{dN_0}{dt} = F_c\left(1 - \frac{N_c}{S_0 \alpha N_m}\right) - (k_{sb} + k_s)N_0,$$

Surface Carbon

$$\frac{dN_c}{dt} = k_s N_0 - k_D N_c,$$

Dissolved Carbon

$$\frac{dN_b}{dt} = k_{sb} N_0 - k_t N_b + k_D N_c,$$

Precip. Carbon

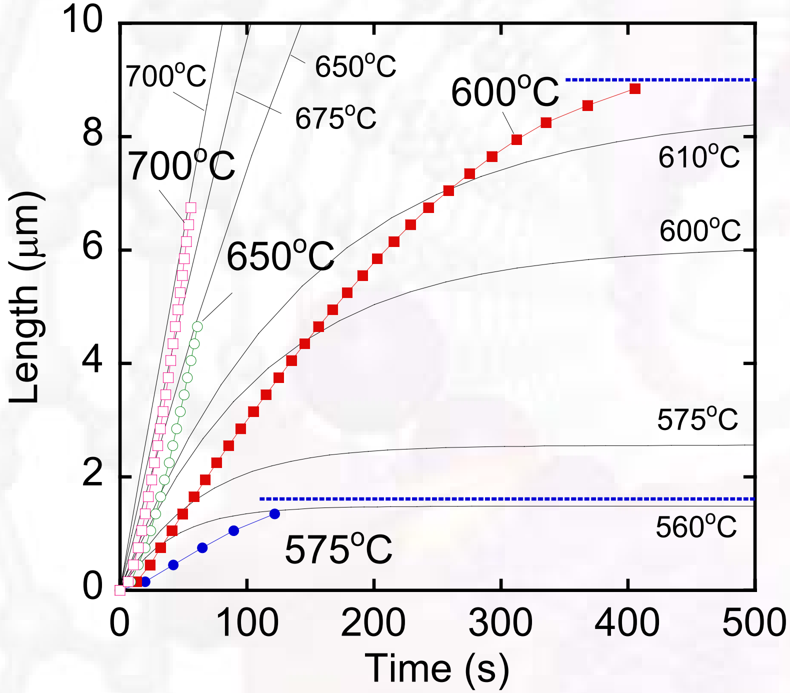
$$\frac{dN_t}{dt} = k_t N_b,$$

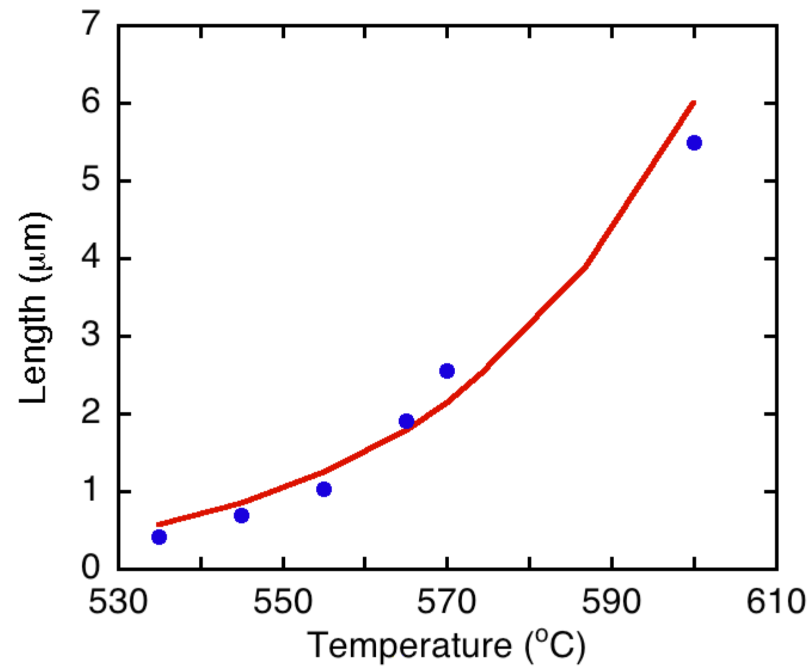
- Simplified rate equation model - 5 rates
- Explains termination of growth
  - when surface of catalyst becomes covered with undissolved carbon
- Predicts ultimate lengths of nanotubes

A. A. Puretzky, D. B. Geohegan, I. N. Ivanov, S. Jesse, G. Eres, and J.Y. Howe (in preparation).

Terminal Nanotube Length

Experiment vs. Model

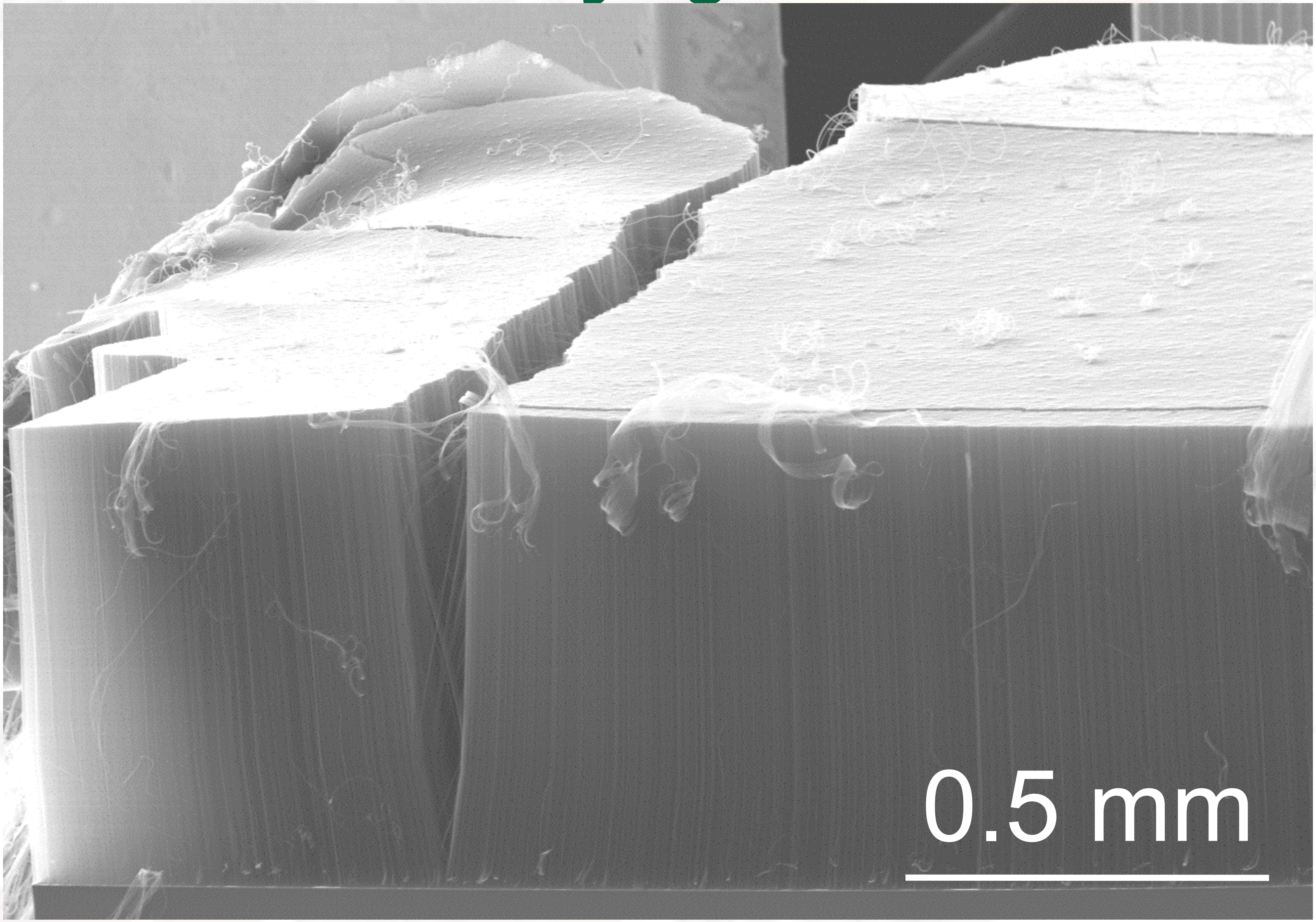




Good agreement between *both* model and experimentally-measured **growth rate** and **terminal length** over a range of temperatures

A. A. Puretzky, D. B. Geohegan, I. N. Ivanov, S. Jesse, G. Eres, and J.Y. Howe (in preparation).

VAA-MWNT Arrays grown at 730°C



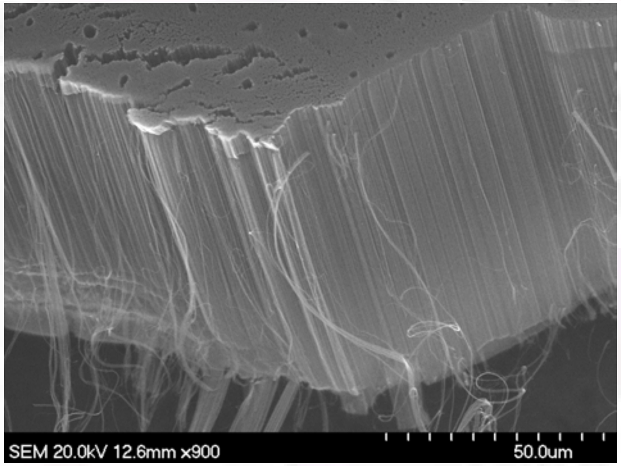
D. B. Geohegan, A. A. Puretzky, I. N. Ivanov, S. Jesse, G. Eres, and J. Y. Howe, Appl. Phys. Lett. **83**, *1851 (2003)*

Determining CVD Growth Mode using Laser Ablation

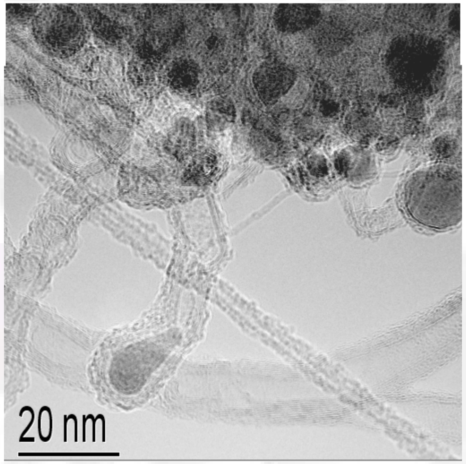
Mechanisms of VAA-MWNT Growth

- Growth Mechanism?
  - Tip or base?
  - Uniform lengths
  - Coordinated tip growth?

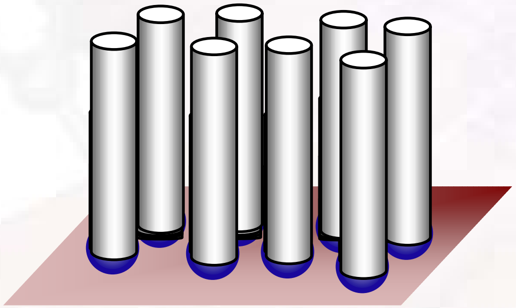
- Laser ablation answers the question...
  - with *in situ* photography of nanotube growth



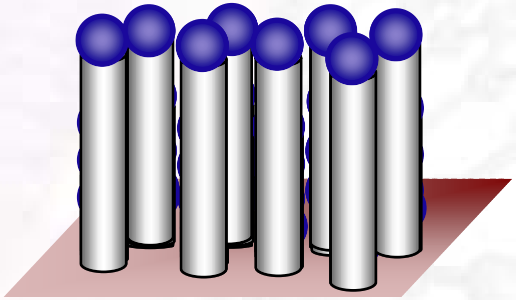
SEM - uniform lengths



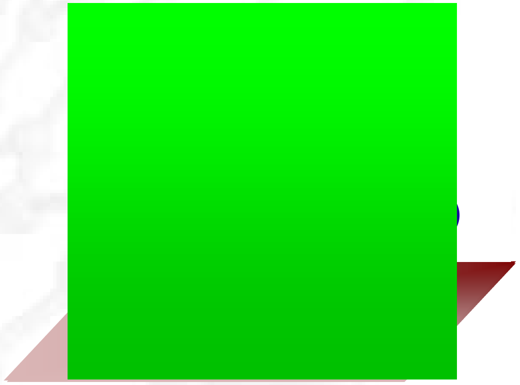
HRTEM - particles at tips and bases



Base Growth



Tip Growth



Experiment

D. B. Geohegan, A. A. Puretzky, (in preparation)

Time-Lapse Photography of Nanotube Growth - *with laser ablation*

Carbon Nanotube "Monolith"

Si wafer thickness is 380 μm

Summary

- Laser Synthesis of SWNT
  - Growth rates measured – 1-5 μm/s ... for 0.2 g/hour production rates
  - Factor of 1000 improvement in both growth rate and production rate possible at high laser powers
- Chemical vapor deposition of VAA-MWNT
  - First direct *in situ* measurements - up to 1 μm/s measured
  - Sustained at rates of 0.3 μm/s to 4 mm lengths over large areas
  - Length monitored and controlled (to 20 nm accuracy) using laser interferometry
  - Time-resolved imaging and laser ablation used to understand growth mechanism, kinetics, and termination
  - Growth to long lengths sensitive to catalyst composition