Aligned SWCNT Growth in SNF using FirstNano CNT Furnace

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Outline

- **Motivation and Goals**
- **Introduction to CNT Growth**
- **Previous work and Initial Conditions**
- **Ethanol Growth Development**
- **Demonstrations of consistency and usefulness**
- **Summary**

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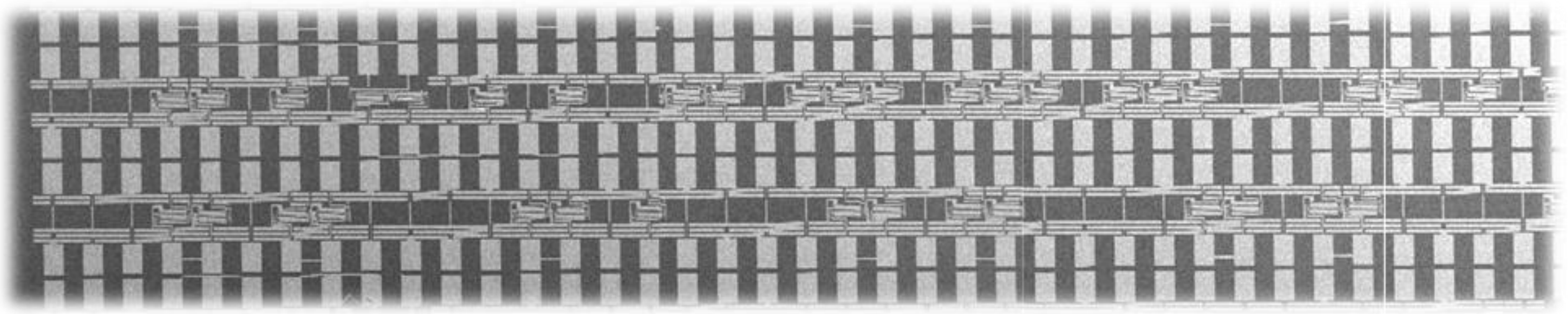
Applications for aligned single-walled CNTs:

- **Platform for Transistors and Systems with CNT** [1]
- **CNT VLSI has 10x EDP benefit at sub-7nm tech. nodes** [2]
- **Enables Monolithic 3D & heterogeneous integration**[3,4]
- **Bio-Sensors and biological interfaces** [5]



Aligned CNTs the materials foundation for these applications

1) M. Shulaker, et. al. Nature 2013
2) G. Tulevski, et. al. ACS Nano 2014
3) H. Wei, et. al. IEDM 2013
4) M. Shulaker, et. al. IEDM 2014
5) J. Geng, et. al., Nature 2014

Project Goals

1. **Startup the FirstNano CNT Growth tool in SNF**
   – Installed in February 2015
2. **Create recipes for aligned CNT Growth > 5 CNT/μm**
   – Methane Carbon Source
   – Ethanol Carbon Source
3. **Explore process window for CNT Growth**
4. **Demonstrate consistency & wafer scale uniformity**
5. **Characterize the CNTs to confirm properties**

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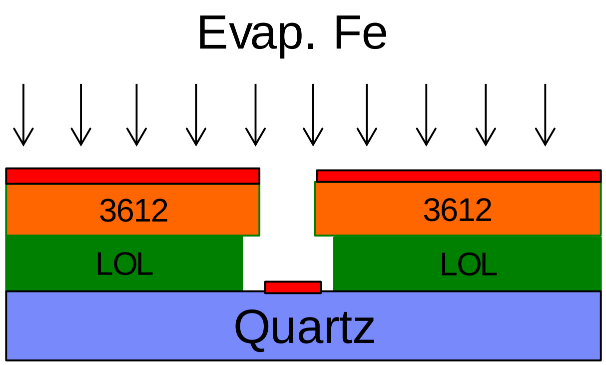
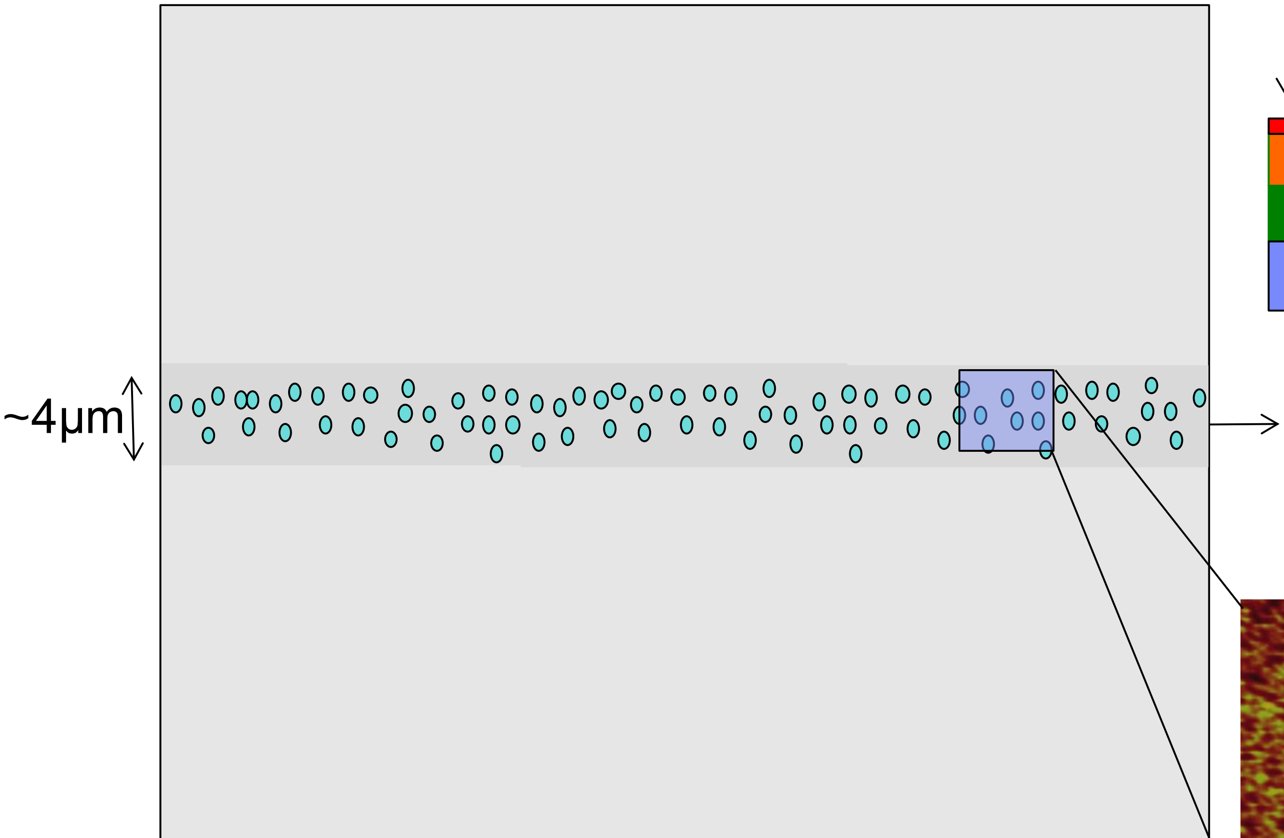
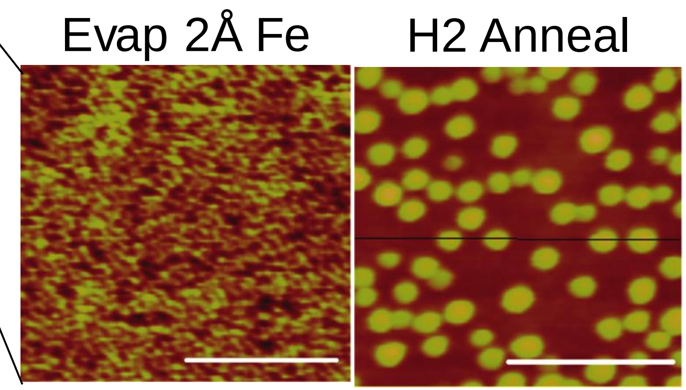
Carbon Nanotube Aligned CVD Growth – Cartoon #1

- Deposit a thin film of metal or nanoparticles
  - 2-4Å of Fe, Ni, Cu, Mo, W, etc...







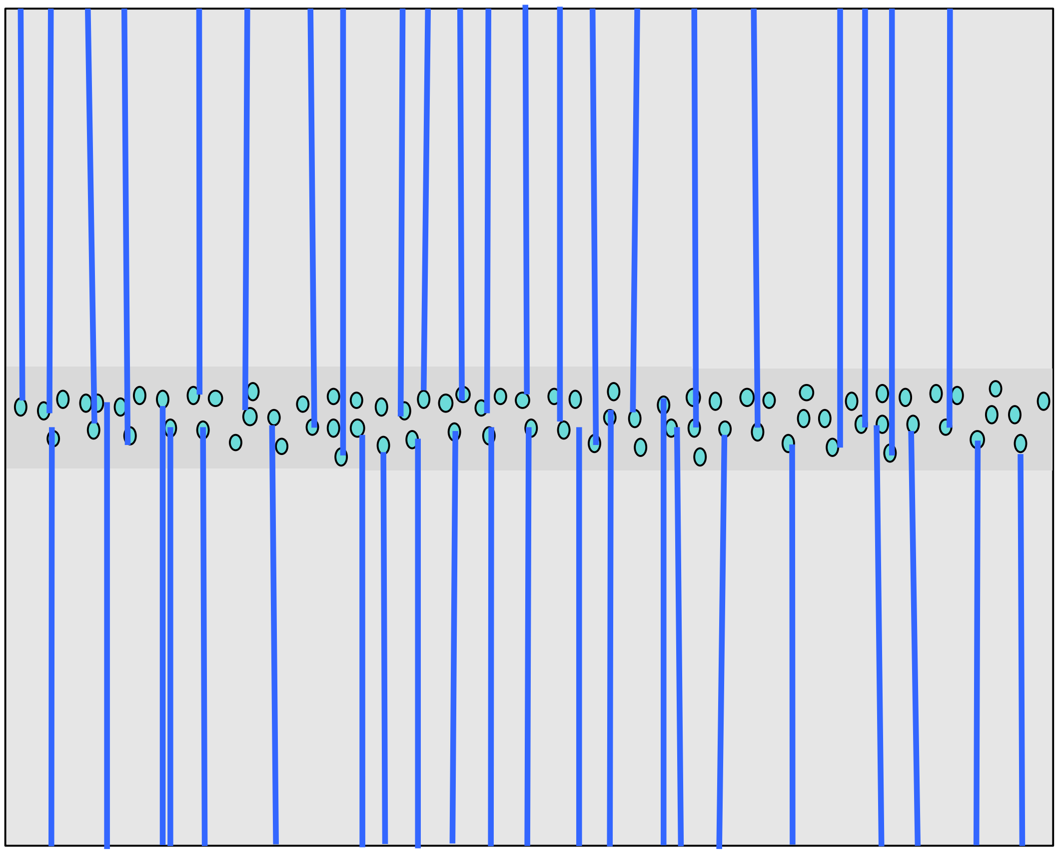
Scale Bar = 100nm

- Quartz or Sapphire Substrate

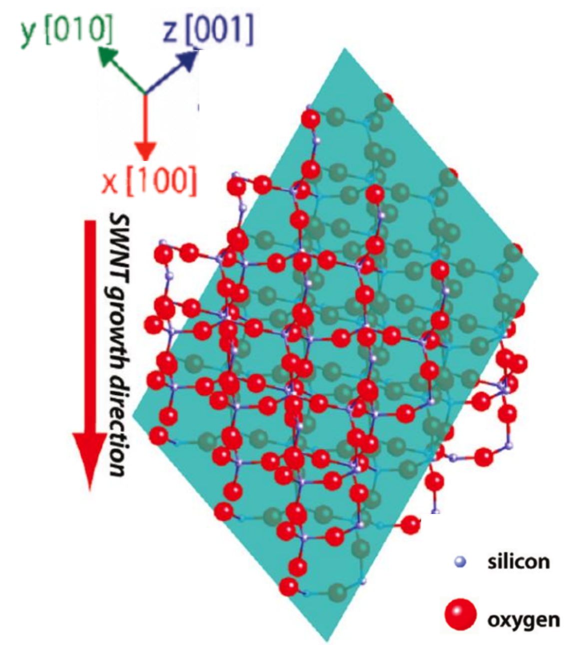
Carbon Nanotube Aligned CVD Growth – Cartoon #2

- Decompose Carbon precursor at 800-1000°C
  - CH_4, C_2H_6O, C_3H_8O, etc... limitless # of Carbon sources

~4μm



Aligned Carbon Nanotubes

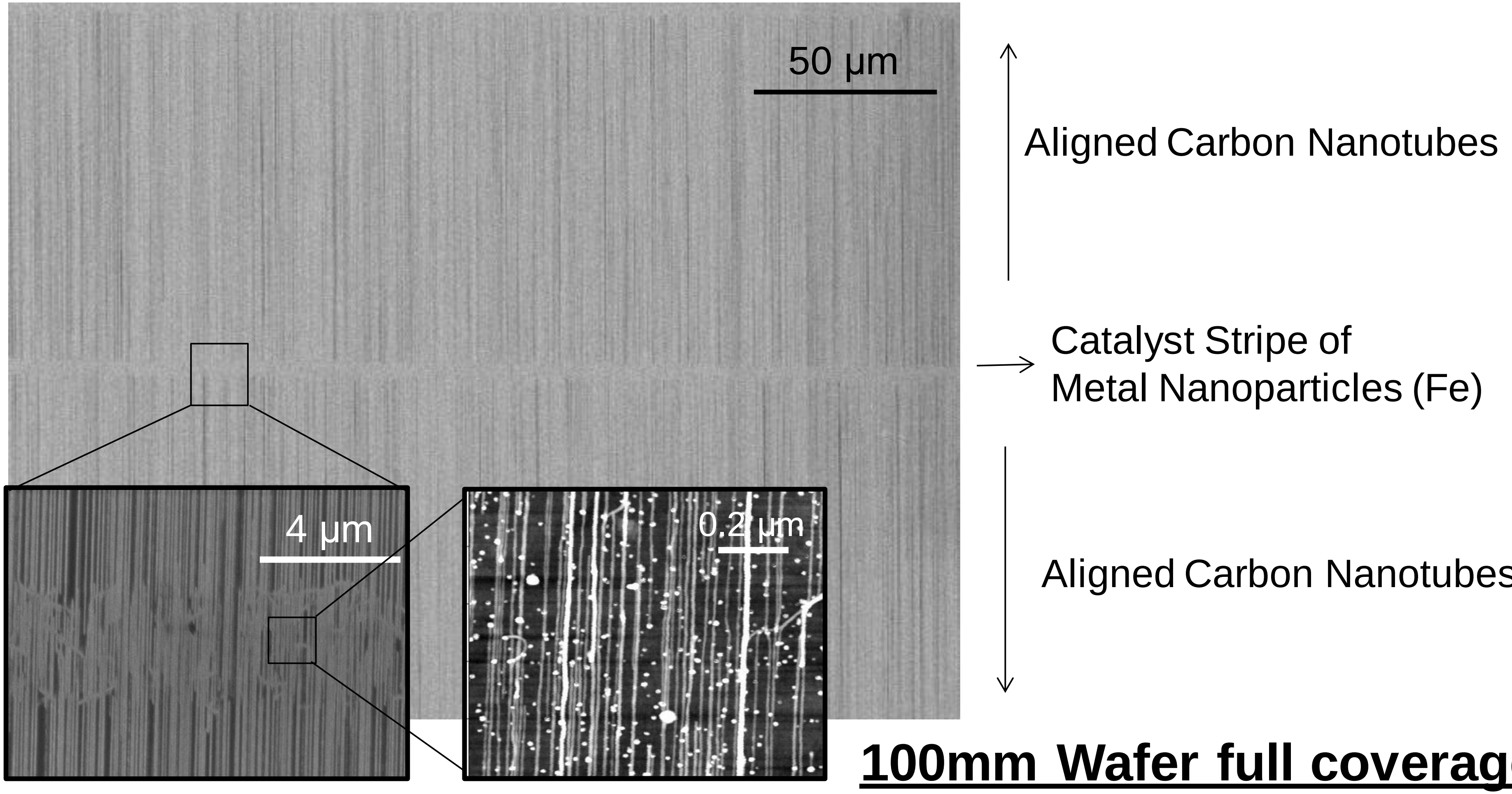


β-phase Quartz (01$\bar{1}$1)

- Alignment along crystal plane by Van der waals Force
  - ST Quartz: [100] direction on (01$\bar{1}$1) surface or Sapphire

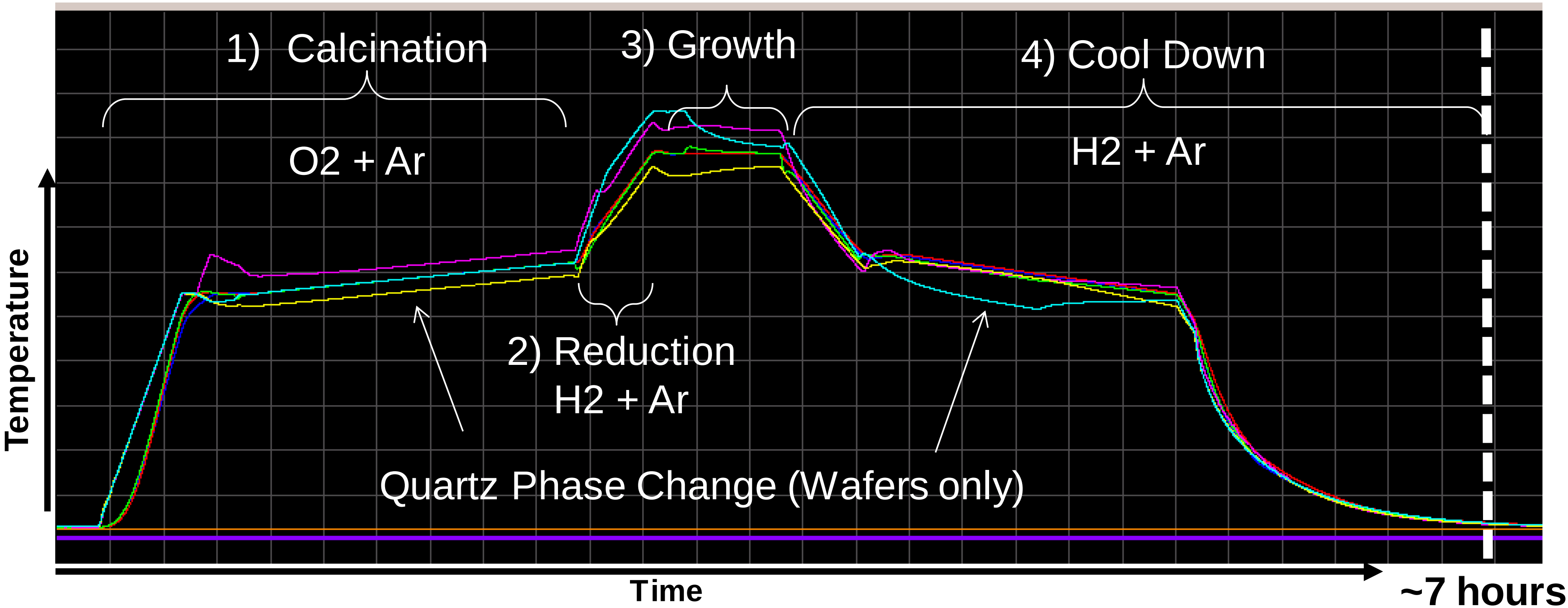
CNT Aligned CVD Growth Mechanism – Exp. Results

- Decompose Carbon precursor at 800-1000°C
  - CH_4, C_2H_6O, C_3H_8O, etc... limitless # of Carbon sources



100mm Wafer full coverage

CNT CVD Growth Cycle



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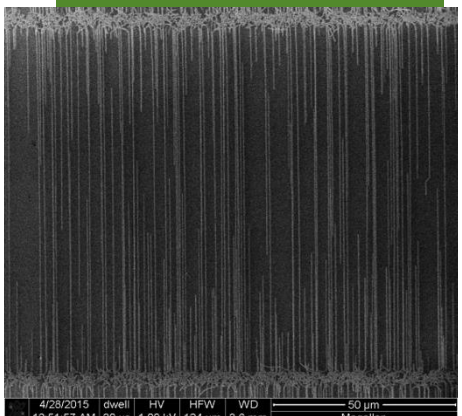
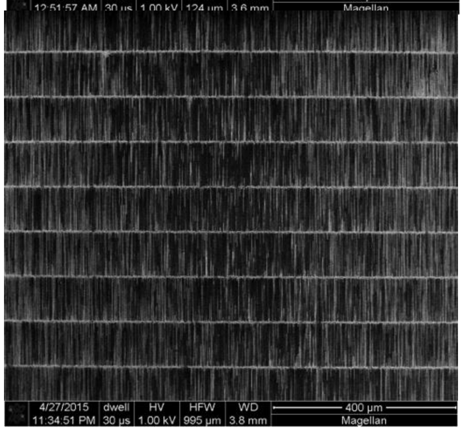
FirstNano Methane Growth – Failed to achieve goals

Growth Series: Each growth had reference piece with 3Å Fe

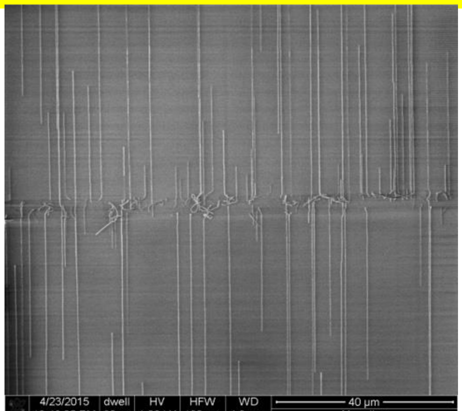
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24

Better Growths

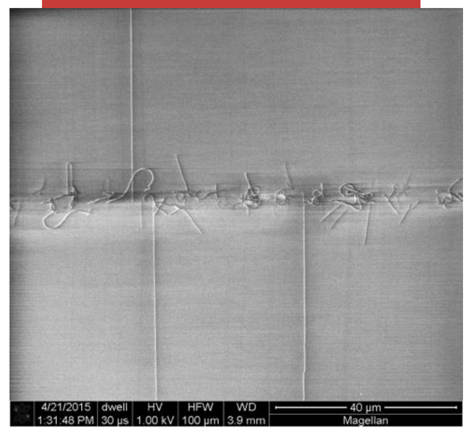




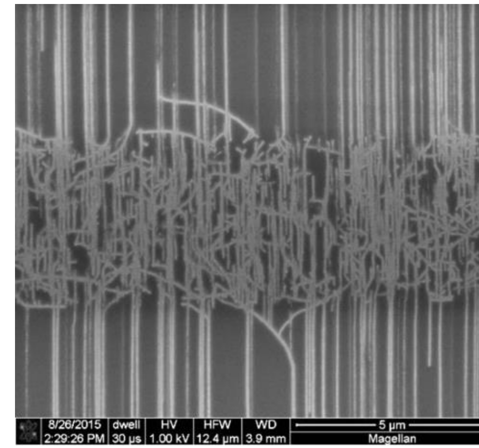
Moderate Growths



Wrong Recipe!



Best Methane Result



1) Achieved ~1 CNT/um often
2) Demonstrated consistency
3) Explored Sample Preparation

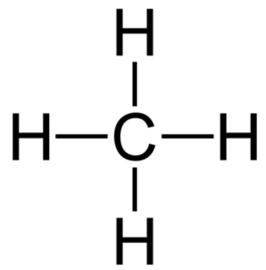
Failed to achieve density goals

Min. Goal: 5 CNT/um for usefulness
Real Goal: 15 CNTs/um or higher

Difference between Methane and Ethanol

Methane – The simplest saturated chain carbon molecule

CH_4 =



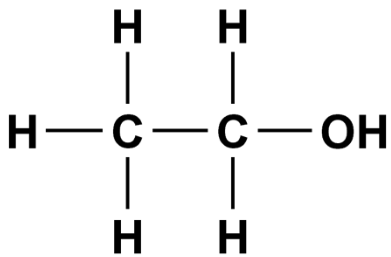
Thermal Decomposition Pathway

1)
$$CH_4 \rightarrow CH_3 + H$$
$$H + CH_4 \rightarrow CH_3 + H_2$$
$$2CH_3 \rightarrow C_2H_6$$
$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$
$$C_2H_5 \rightarrow C_2H_4 + H$$

C.-J. Chen, M. H. Back, R. A. Back, Canadian Journal of Chemistry, 1975, 53(23): 3580-3590

Ethanol – The 2nd simplest alcohol, after methanol.

C_2H_5OH =



Thermal Decomposition Pathway

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

→ weak etchant for carbon

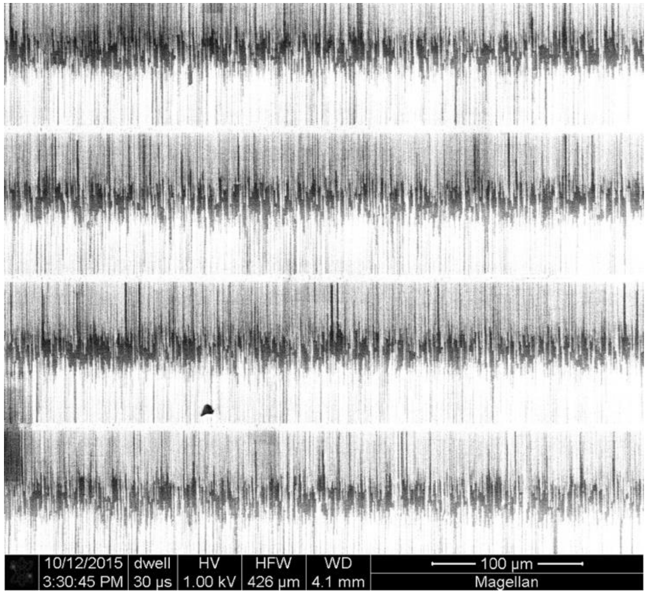
J. Li, A. Kazakov, F. Dryer, Journal of Physical Chemistry A, 2004, 108 (38), pp 7671 - 7680

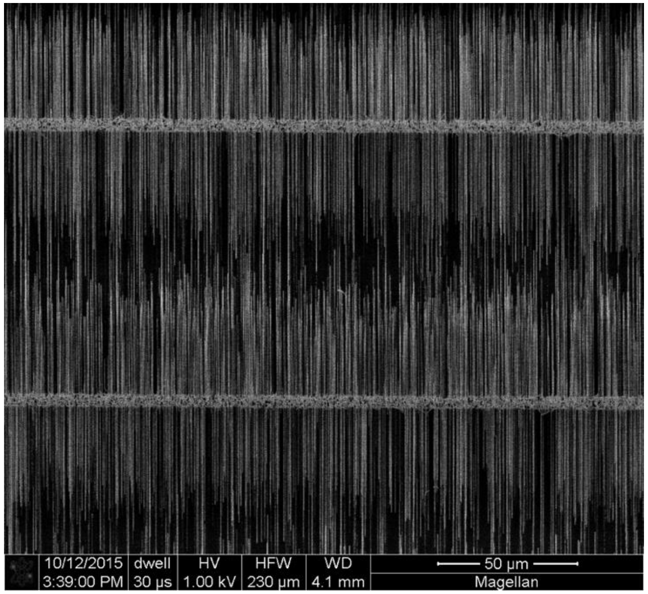
Acetylene – **C_2 is the closest precursor to a building block for CNT Assembly**

$$C_2H_2 = H-C\equiv C-H$$

G. Zhong, et. al., J. Phys. Chem. C, 113, 17321-17325
G. Eres, et. al., J. Phys. Chem. C, 2009, 113, 15484-15481
H. Kimura, et. al., Scientific Reports, 2013, Vol.3 p.3334

Initial guess at recipe: 864°C, 760 Torr, 7.8 sccm EtOH





Approach: Since tubes are short – try to grow longer!

**All lengths in µm

Tube Length vs. Growth Time	5 Min	15 Min	30 Min	60 Min
Sample 1: 3.2Å Fe	26.2	32.92	19	55
Sample 2: 3.2Å Fe	8.4	24.3	6.47	35.7
Sample 3: 3.2Å Fe	20	14.7	7.05	26.3
Sample 4: 3.2Å Fe	13.9	23	11.1	35.7

Observation: No trend of tube length with time, therefore growth stops early.

Challenge: Understand why growth stops early.

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Modeling EtOH vapor flow

$$\log_{10} p = A - \frac{B}{C+T}$$

- **Antoine Coefficients for Ethanol**

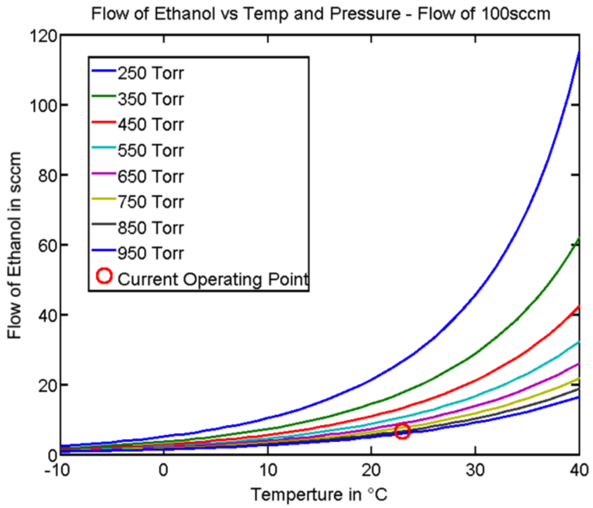
$A_{Ethanol}$ = 8.2
$B_{Ethanol}$ = 1642.89
$C_{Ethanol}$ = 230.3
T_{Range}: -20°C → +80°C

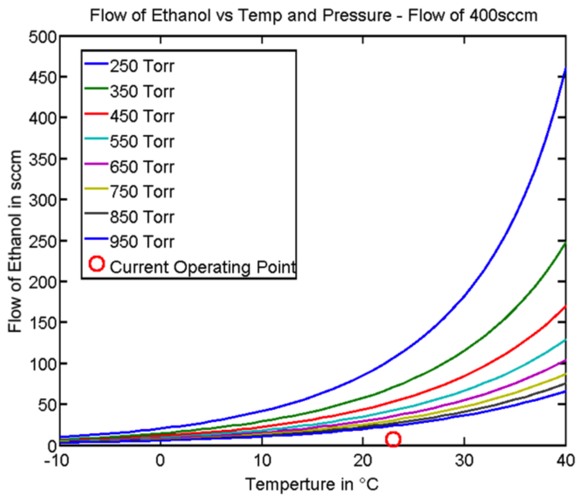
Source: http://ddbonline.ddbst.de/AntoineCalculation/AntoineCalculationCGI.exe

- **Flow Equation**

$$F_{Out} = F_{in} * \frac{P_{EtOH}}{P_{Bubbler} - P_{EtOH}}$$

- **Range of Variables**
  - F_{in} → Argon: 0 – 400 sccm
  - P_{EtOH} → Ethanol Partial Pressure: 5.5 – 133 Torr at 40°C.
  - $P_{Bubbler}$ → Bubbler Pressure: Chamber Pressure – 1000 Torr





Can translate from process controls to process conditions inside the furnace.

DOE – Ethanol Flow vs. Temperature

Sample B11 W2: 3.2Å Fe Liftoff

< 1 CNT/um | 1-5 CNT/um | >5 CNT/um

Growth Temp / Ethanol Flow:	7.4 sccm	14.8 sccm	22.2 sccm	29.7 sccm	61.0 sccm
800C			0.6	0	
850C	Short	Short	1.5	6.6	
900C	3.5	8.8	8.8	6.4	6.8
Bubbler Temp	23 C	23 C	23 C	23 C	**40 C**
Ar Flow Through Bubbler	**100 sccm**	**200 sccm**	**300 sccm**	**400 sccm**	300 sccm
Bubbler Pressure	850 Torr	850 Torr	850 Torr	850 Torr	850 Torr

*All density values from SEM averaged over at least 12 um

- Too-low ethanol flow or temperature will starve growth
  - Mechanism 1: Not enough carbon to sustain CNT growth
    - Both mass flow and source thermal decomposition play a role
  - Mechanism 2: Temperature affects reactions at the catalyst.
  - Which is rate limiting: EtOH mass flow or catalyst reaction?

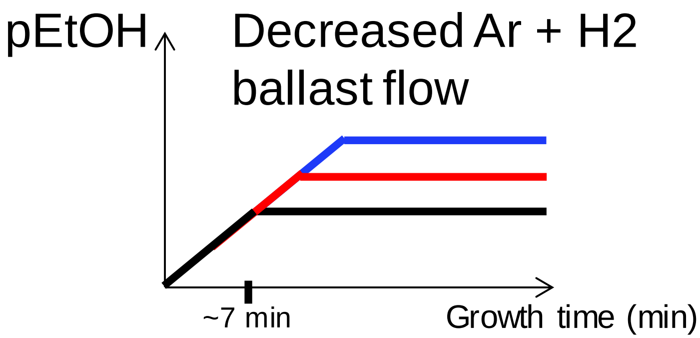
Bottom line: A growth window exists, starting density >5 CNT/um

= Initial process condition 865°C, 7.4sccm EtOH.
Explains short tubes, and occasional low-density results in early runs.

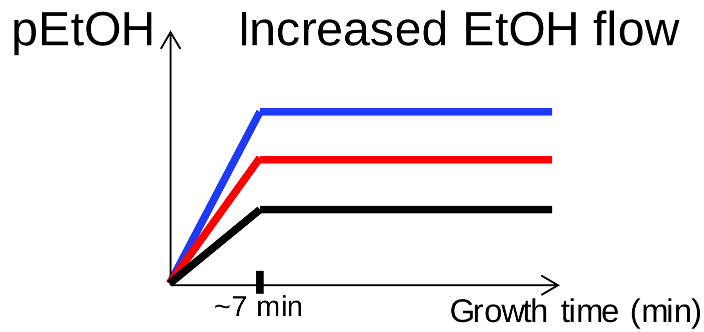
Further efforts to improve CNT Single-growth Density

- **Further increase EtOH partial pressure:**

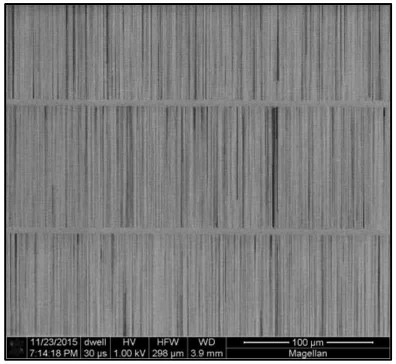
Option 1



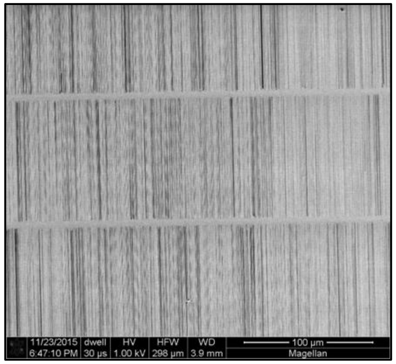
Option 2



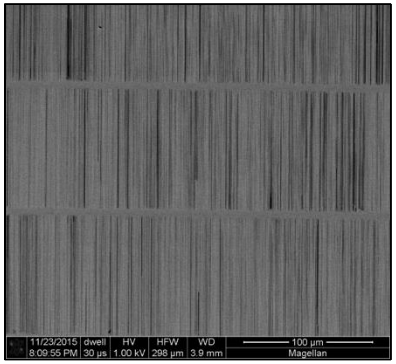
10 minutes



30 minutes



60 minutes



	CNTs per micron			
Growth Time	Sample 1	Sample 2	Sample 3	Sample 4
10 Minutes	10.5	8.3	8.1	8.4
30 Minutes	9.4	6.1	6.3	6.2
60 Minutes	10.7	10.9	8.4	8.3

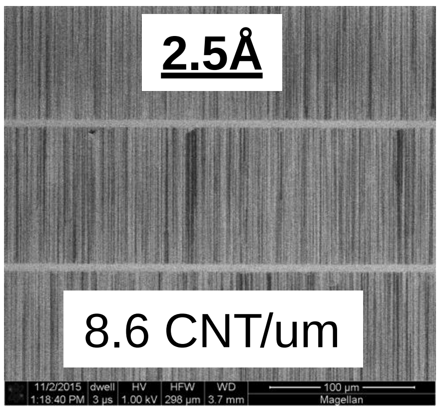
- **10 minutes is just as dense as 60 minutes**
- **Must increase EtOH flow**
- **Tried 22, 33, and 61 sccm EtOH, w/ no trend**

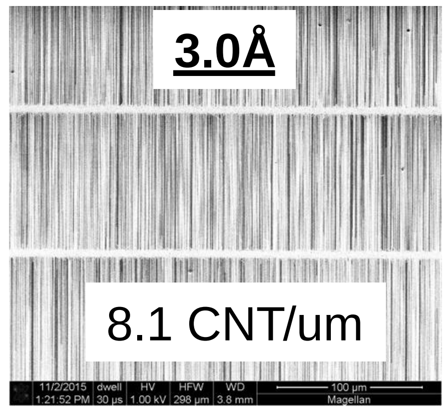
Best results so far: >10 CNT/um, seen 6 times.

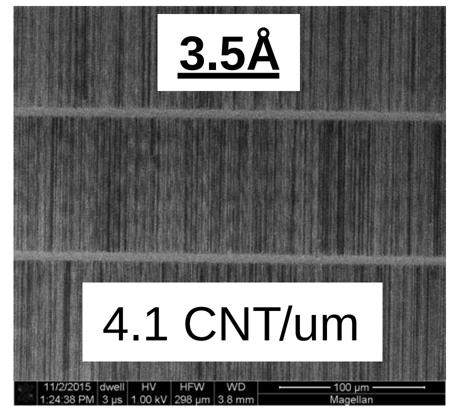
Further efforts to improve CNT growth density

- **Catalyst Thickness and Deposition**
  - We looked at this some, but did not include a large enough range to draw a trend.
  - Past experience says this is very key sample parameter.
  - Systematic treatment necessary, can yield >15 CNT/um.

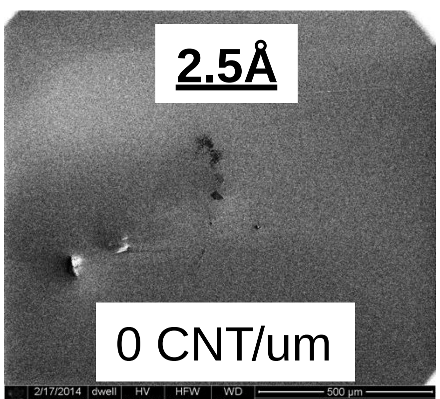
Recent example:

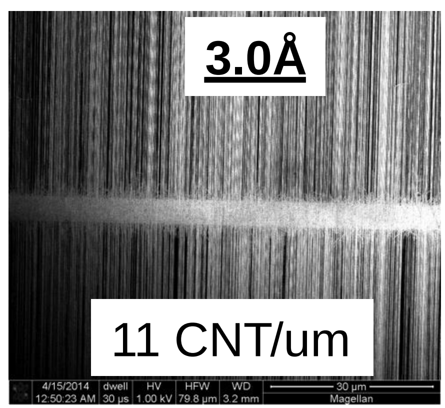


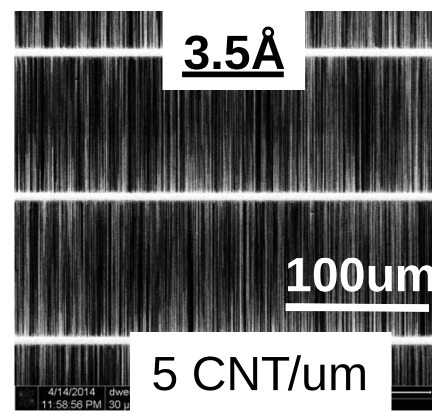




Older Example 2014:







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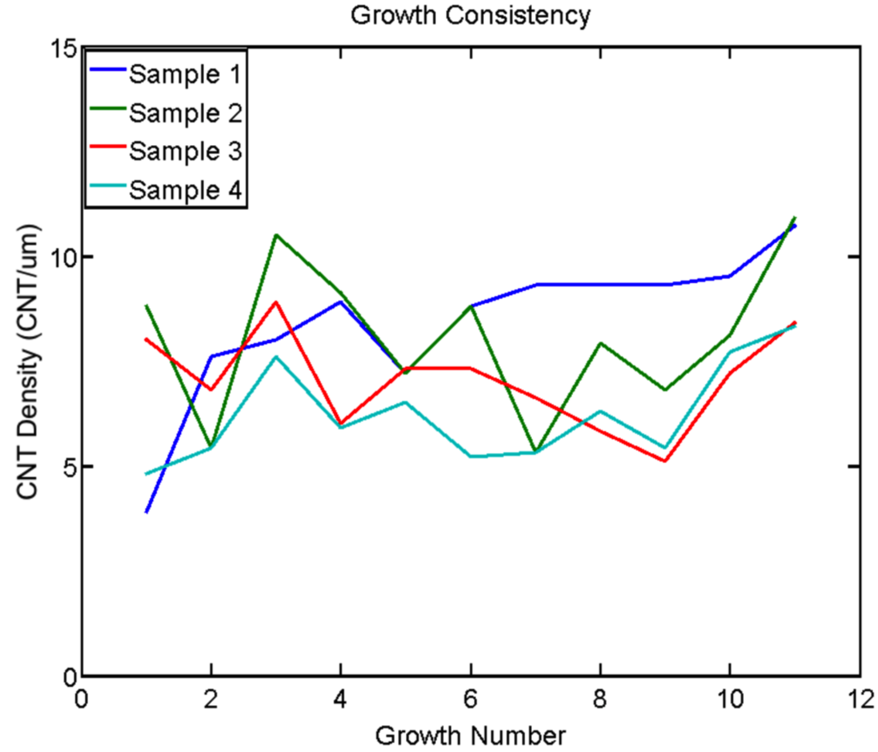
Consistency Demonstration – very important!

- **Samples: 4 wafers, 3.2Å Fe prepared by liftoff**
- **Growth Condition: 900°C, 22.2 sccm EtOH, 760 Torr**

22.2 sccm EtOH, 900°C growth, 760 Torr

	CNTs per micron			
	Sample 1	Sample 2	Sample 3	Sample 4
Run 1:	3.9	8.8	8.0	4.8
Run 2:	7.6	5.4	6.8	5.4
Run 3:	8.0	10.5	8.9	7.6
Run 4:	8.9	9.1	6.0	5.9
Run 5:	7.2	7.2	7.3	6.5
Run 6:	8.8	8.8	7.3	5.2
Run 7:	9.3	5.3	6.6	5.3
Run 8:	9.3	7.9	5.8	6.3
Run 9:	9.3	6.8	5.1	5.4
Run 10:	9.5	8.1	7.2	7.7
1 week later:	10.7	10.9	8.4	8.3

	Sample 1	Sample 2	Sample 3	Sample 4
Mean	8.4	8.1	7.0	6.2



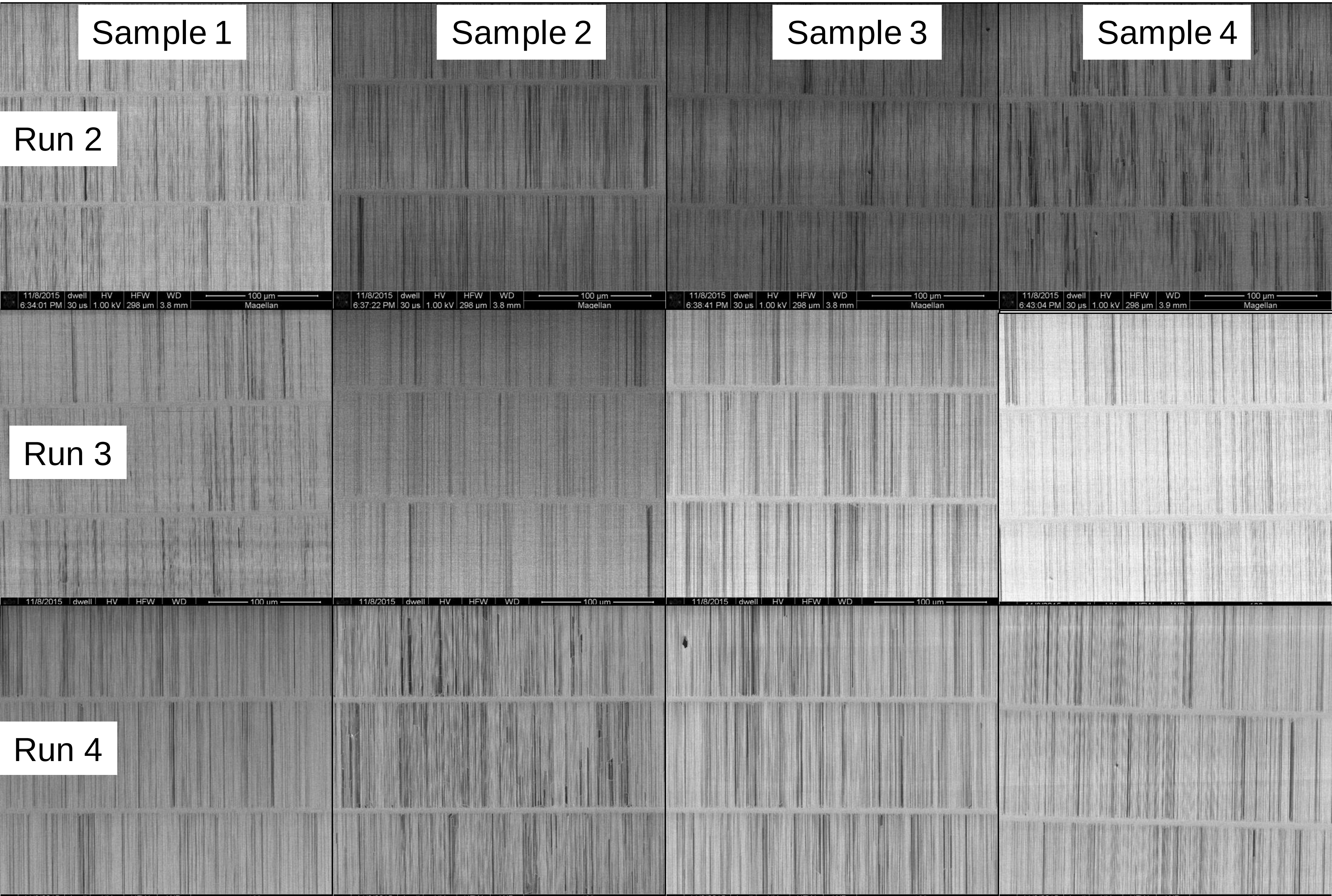
Bottom line: We observe consistent 5-10 CNT/µm. EE412 Goal Met!

Run 1 → 10 did not clean tube between runs. Run 10 was the 22nd growth on tube.
Run 11: 1 week later with re-filled source, O2 cleaned tube, was ≈30th growth on tube.

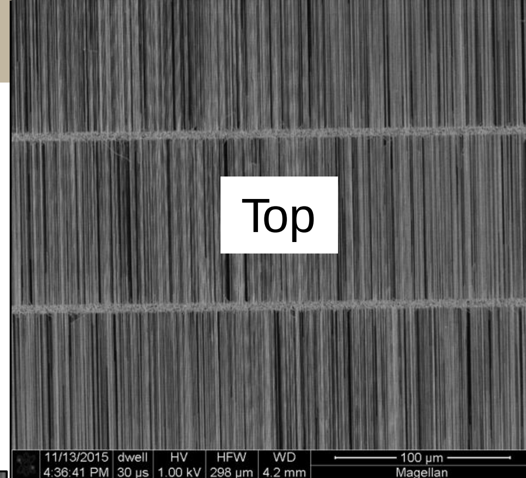
900°C, 22.2 sccm EtOH

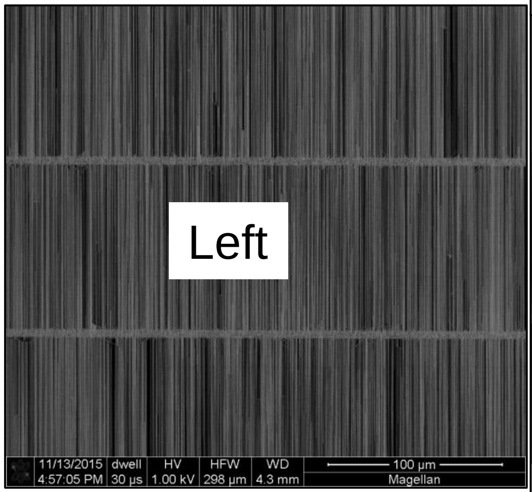
3.2Å Fe, Liftoff

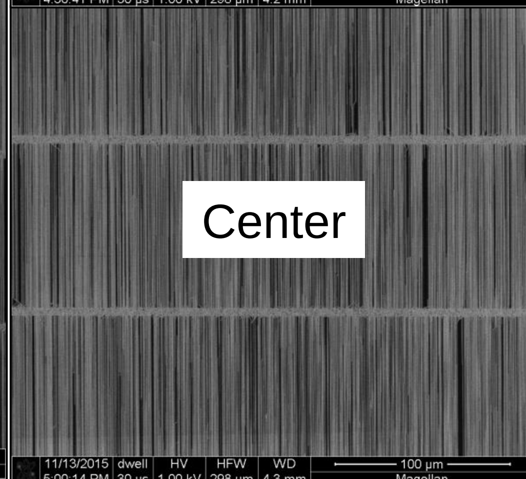
*All images 300 um wide

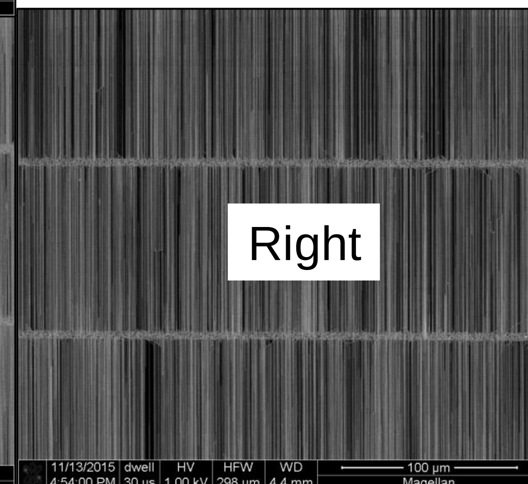


100 mm Wafer CNT Growth Uniformity:

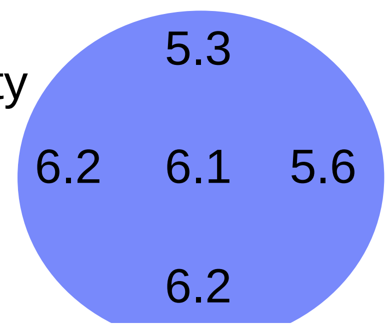




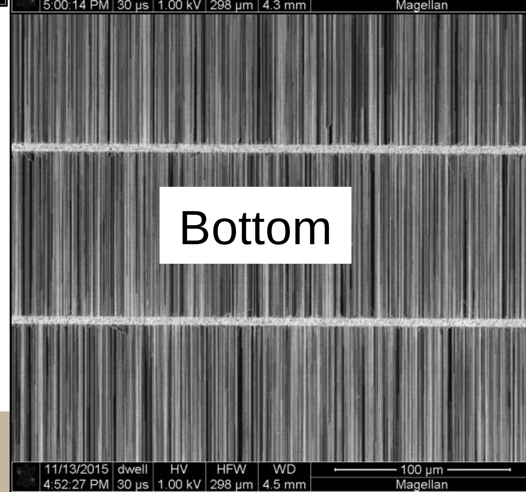




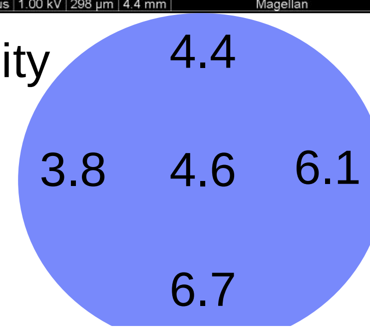
Density Map:



Wafer 1



Density Map:

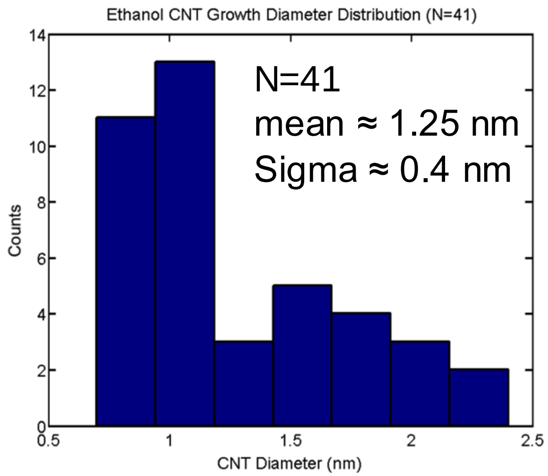


Wafer 2*

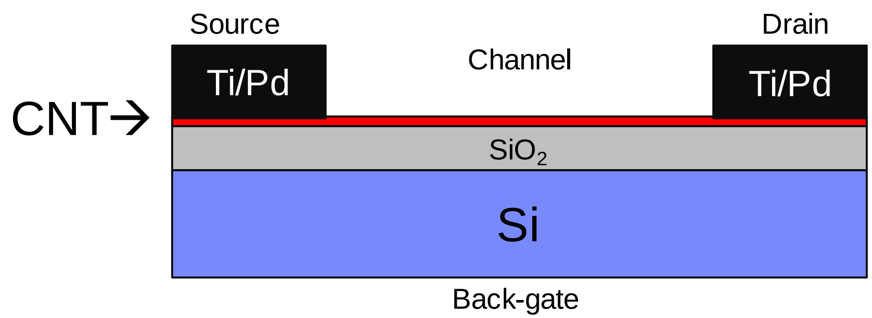
*Wafer 2 looked damaged, causing lower density

CNT Characterization

Diameter Distribution

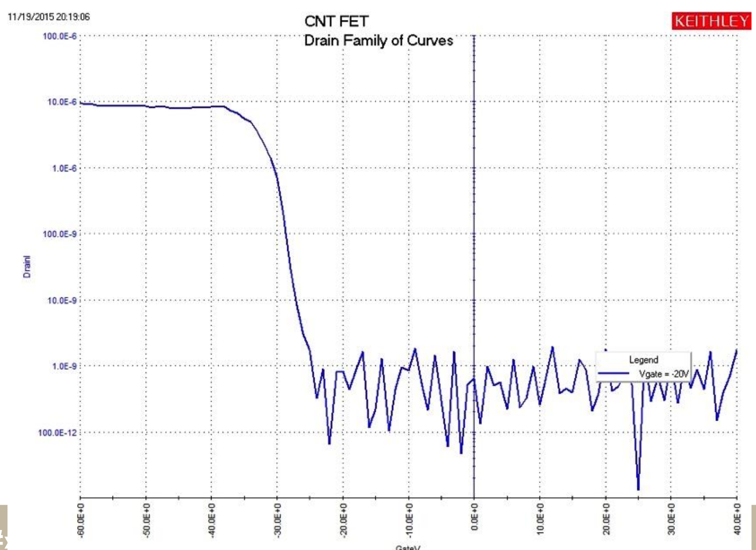


Back-gate FET Structure

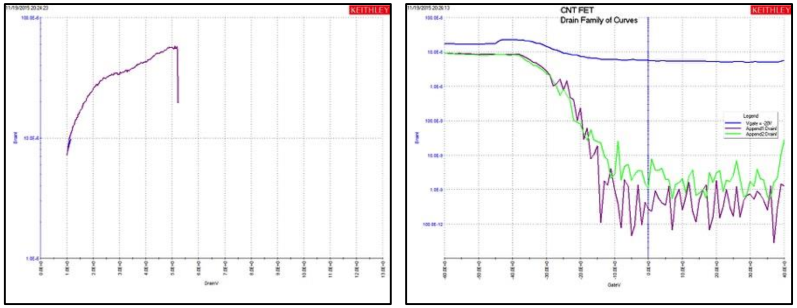


Electrical Characterization

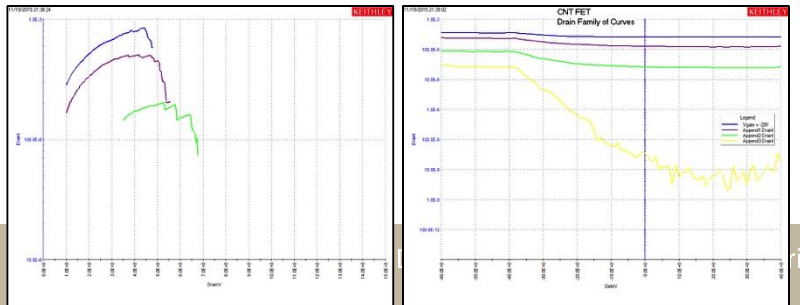
1um Wide s-CNTs Only



1um Wide Device



5um Wide Device



Summary of Project Goals

☑ **1. Startup the FirstNano CNT Growth tool in SNF**

– Installed in February 2015

☑ **2. Create recipes for aligned CNT Growth > 5 CNT/µm**

☒ – Methane Carbon Source – ≈1 CNT/um.

☑ – Ethanol Carbon Source – 6-10 CNT/um

☑ **3. Explore process window for CNT Growth**

☑ **4. Demonstrate consistency & wafer scale uniformity**

☑ **5. Characterize the CNTs to confirm properties**

Recipes & training manual are available to SNF users *Today*!