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Graphene Innovations Drive Nanomaterial Manufacturing Technologies

Karlheinz Strobl, V.P. of Business Development

Mathieu Monville, Riju Singhal, and Samuel Wright

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Operations & Manufacturing

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Operations

- ✓ In business > 33 Years
- ✓ Headquarters in Central Islip, NY
- ✓ Additional facility in Saugerties, NY
- ✓ ~ 190 employees
- ✓ Recently moved into a 130,000 square foot company owned facility increasing Company owned facilities to a total of 152,000 square feet

Sales – Worldwide

- ✓ Direct sales
- ✓ Sales representatives
- ✓ Application Laboratory
- ✓ CVD Materials Corporation

Manufacturing Model

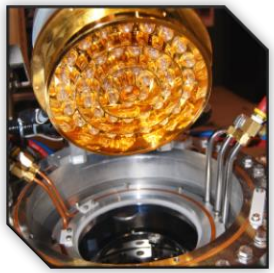
- Vertically integrated for rapid system development and control of project timing (low cost manufacturing)
- Outsource significant portions as needed for higher volume systems

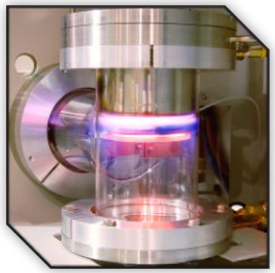
CVD = Chemical Vapor Deposition

= Chemistry + Temperature + Pressure Control

Chemical Vapor Deposition is the Controlled Decomposition ("cracking") of Gases/Liquids used to Deposit or Grow a Film of Material onto a Surface

It requires MULTIDISPLINARY KNOW-HOW
to Design and Manufacture Safe Processing Systems having isolated Process Chambers with Precise and Safe Process Control over Gas/Liquid Dispensing, Flow Delivery, Temperatures and Pressures to obtain Controlled Deposition of the Growth Environment to achieve the desired Material Growth and Safely process the Exhaust Gases





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We sell CVD Systems for Research and Production

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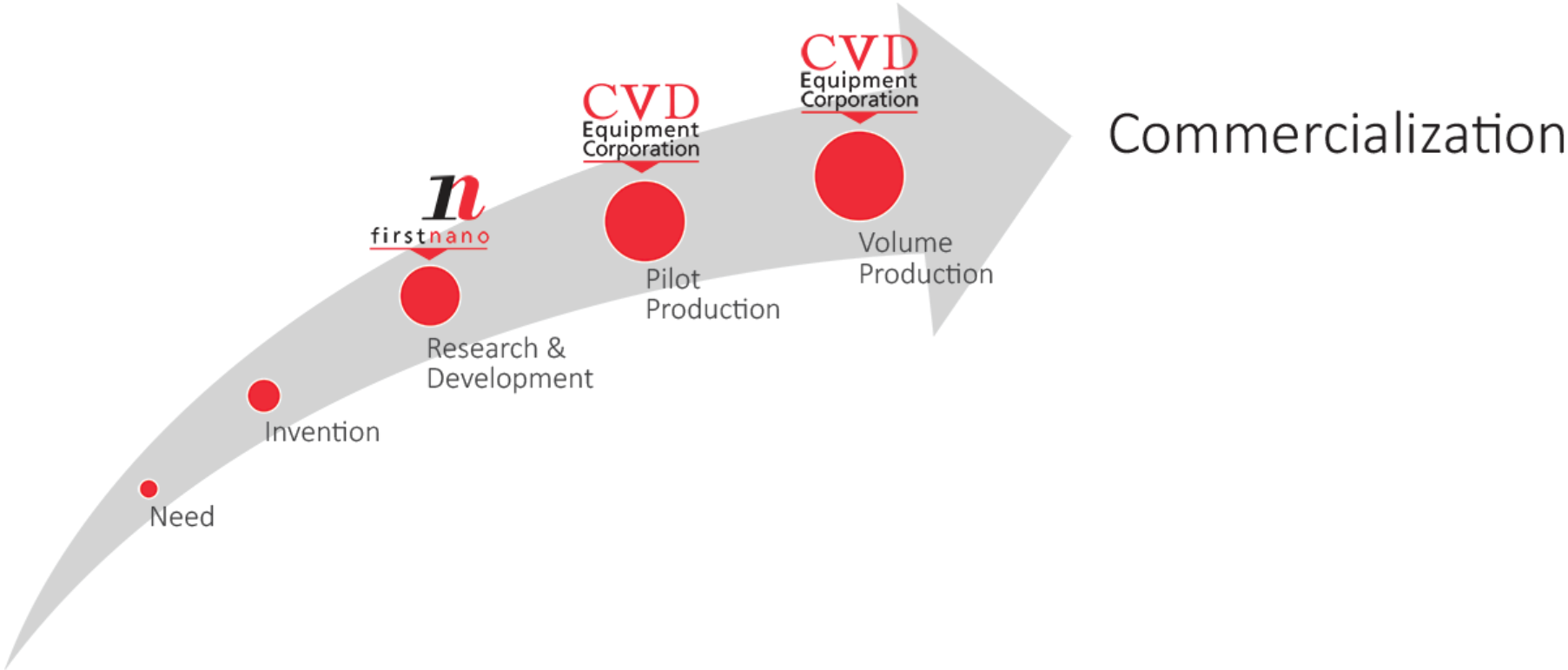
FirstNano™ Systems for Research

- ✓ EasyTube®
- ✓ EasyGas™
- ✓ EasyExhaust™

CVD Systems for Production

- ✓ Photovoltaic
- ✓ Transparent Conductive Oxide (TCO)
- ✓ Reel-to-Reel CVD deposition
- ✓ Liquid Phase Epitaxial Deposition
- ✓ Medical Components
- ✓ Aerospace Composites
- ✓ SiQC system for Polysilicon QC
- ✓ Gas Handling and Exhaust Systems

Commercialization of Nanomaterials



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Designs and manufactures both Standard and Configurable R&D, Pilot & Production chemical vapor deposition systems

Operates an Application Laboratory

- ✓ Performs Contract Process Development
- ✓ Develops Process and Equipment for Research Materials
- ✓ Works with Researchers to help Accelerate the Commercialization of Nanomaterials

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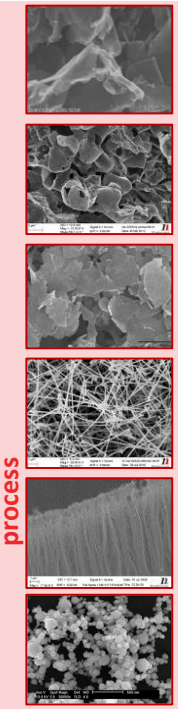
Novel NanotoMacro™ Manufacturing Platform

Raw nanomaterial manufacturing process



3D graphene, carbon-derived-carbons, hollow carbon structures, etc. — 3D

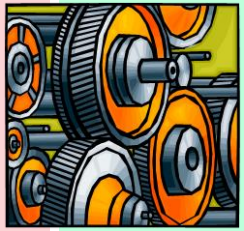
Nano platelets: graphene vermiculite, clay BN, MoS2… — 2D

Nanowires: Si, GaN, BN, TiO2… — 2D

Nanotubes: VACNT, BN NT — 1D

Nanoparticles: LiFePO4… — 0D

NanotoMacro™ Manufacturing Platform



Sheet manufacturing process

- ✓ Larger range of nano-enabled macroscopic material formulations
- ✓ Economical manufacturing process no high-temperature step
- ✓ Universal process for a wide range of nano materials

OPTIMIZED FOR:

- ✓ Thickness
- ✓ Surface density
- ✓ Density
- ✓ Electrical conductivity
- ✓ Thermal conductivity
- ✓ Surface area
- ✓ Capacitance
- ✓ Fire retardant
- ✓ High temperature durability
- ✓ UV-FIR absorption
- ✓ Mechanical interlocking
- ✓ Shock absorption
- ✓ Compression resistance
- ✓ Strength, etc.

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300 mm Graphene System

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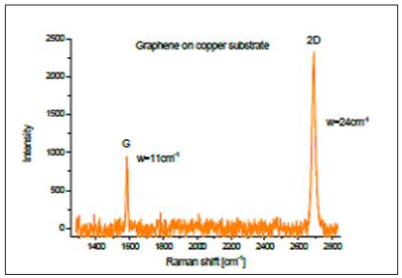
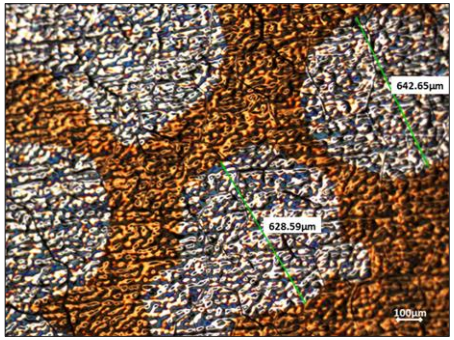
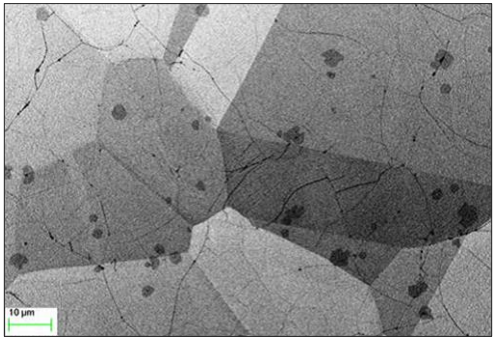
Some of the Innovations reported later in the presentation have been **inspired by a custom configured 300 mm Graphene System order from Nano Carbon (Booth 519)**

Graphene Samples are available from www.grapheneshop.pl

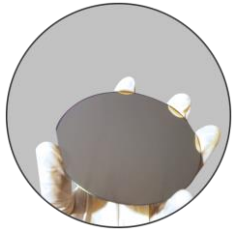
- ✓ Developed in cooperation with ITME and Nano Carbon to produce low-cost high quality graphene
- ✓ The system is a very advanced chemical vapor deposition process tool configured for graphene deposition
- ✓ The measurements of graphene layers grown using the 300mm Graphene system show the high quality of the structure – reflected in large grains (size at least 640 µm)
- ✓ Raman spectra with extremely low 2D band FWHM (24 cm -1) and a small number of islands indicating nucleation of 2nd graphene layer



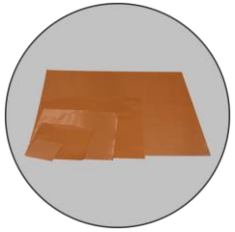




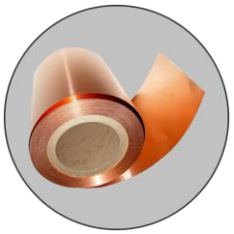
How to get to a UNIVERSAL Low cost, High Volume, High or higher Quality CVD Graphene Manufacturing Solution



WAFER



FOIL



ROLL

FOAM

Wide range of CVD growth Substrates in use today

- ✓ **Materials** (Cu, Ni, Pt, Cu-Ni, Cu-Ag alloys, etc.)
- ✓ **Forms** (solid, porous, etc.)
- ✓ **Shapes** (thin film, thin sheet, roll of thin sheet, bulk 3D shapes, etc.)

Future: Fibrous, powders, what's next?

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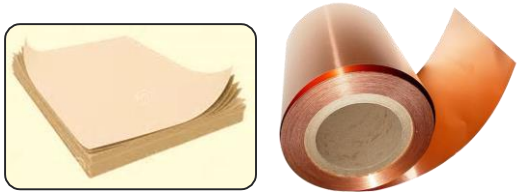
R&D
Sheet Process Demo
2-5 cm

PILOT
Sheet Application Demo
20-30-60 cm



PRODUCTION
Multiple Sheets or Roll
10-100 sheets, or
20-60 cm x 10-100m roll

Wide range of CVD growth Substrates Size

How to port a process developed and demonstrated in R&D in a traditional tube furnace first to Pilot and then Production without major technological changes

How to minimize economical and business risks and obtain maximum flexibility for future changes in application needs and process innovations

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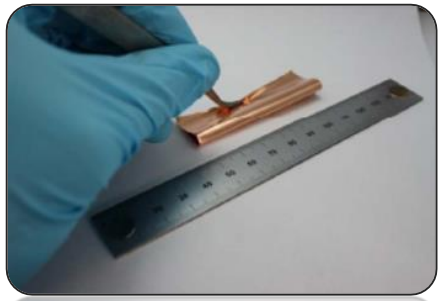
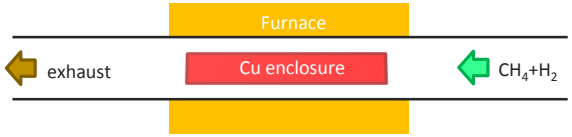
'Copper enclosure'

A copper pocket Is made by folding a piece of copper foil (99.8% Alfa Aesar) and crimping the three edges.



The copper enclosure is placed in the tube furnace for graphene growth via CVD



f_{H2}=2 sccm (p=3.0 E-2 mbar). f_{CH4}=0.5 SCCM (p=4.0 E-2 mbar. T=1035 ^{o}C. T=90 mins.

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Li, X S.; Magnuson, C, W.; Venugopal, A; Tromp, R. M.; Hannon, J. B.; Vogel, E; Colombo, L; Ruoff, R. S., Large Area Graphene Single Crystals Grown by Low Pressure Chemical Vapor Deposition of Methane on Copper. JACS, Accepted for publication.

The University of Texas at Austin Rod Ruoff Nanotechnology

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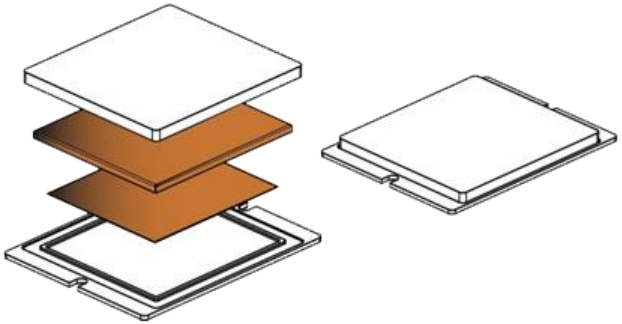
The rest of our Inspiration is our 33 years of know-how in custom CVD system design, solutions, and manufacturing!



"Cu-foil-pocket"

Enclosure Box

Proposed Single Cu Sheet Solution:
Replace "Cu-foil-pocket" with a Process Compatible Enclosure Box (Patent Pending)

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Our Patent Pending, Single Sheet Solutions are compatible with CVD tube furnaces

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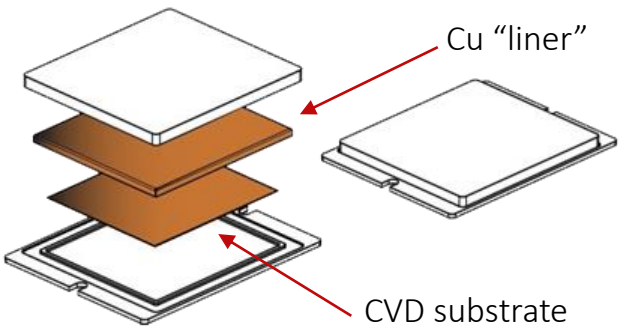
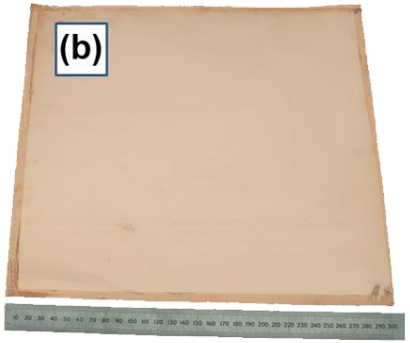
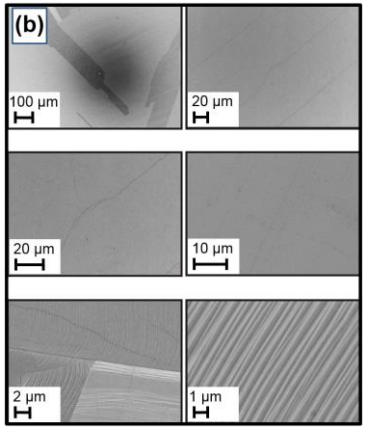
Benefits: (optimization still ongoing)

- ✓ **Enclosure Box** acts as thermal integrating sphere providing large area thermal uniformity
- ✓ Diffusion of process gas into box through **diffusion seal** keeps "impurities" out and provides more uniform processing conditions (no precursor depletion >300 mm)
- ✓ Works from **100 mTorr -> 760 Torr** (minimal Cu vapor escape coating process tube (LP and AP demonstrated)
- ✓ Enables **process operation up to a few °C of substrate melting** without normal maintenance penalties widening the process window



Higher Purity, Higher Quality





Our Patent Pending, Single Sheet Solutions are compatible with CVD tube furnaces

Benefits: (optimization still ongoing)

- ✓ Enables > 10 cm Cu grains
- ✓ Enables > mm size single crystal graphene grains
- ✓ Enables a mixture of high and low pressure processes without usual maintenance and reproducibility penalties
- ✓ Allows strait forward scaling of a process developed on small system to larger size substrate
- ✓ Can shorten annealing and growth times (mm size grains in 30 min possible (still in development)
- ✓ Compatible with B and N doping (under development)
- ✓ FORWARDS COMPATIBLE WITH YOUR FUTURE PROCESS INNOVATIONS

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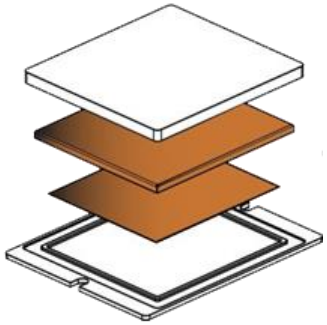
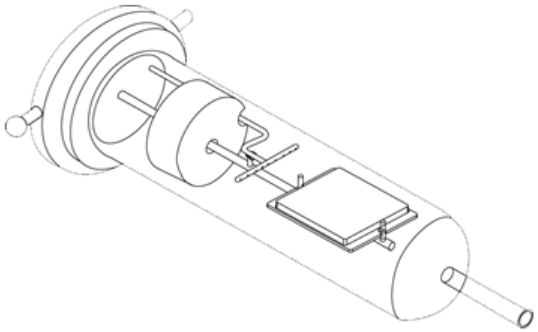
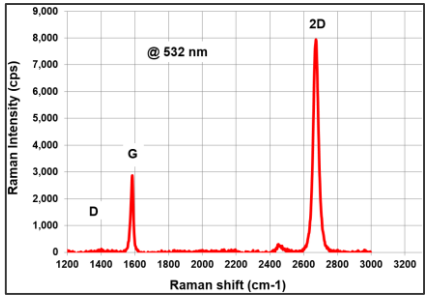
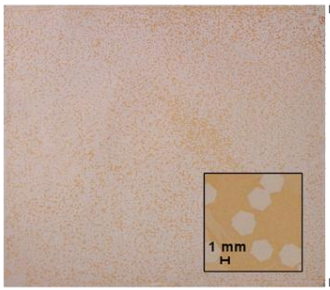




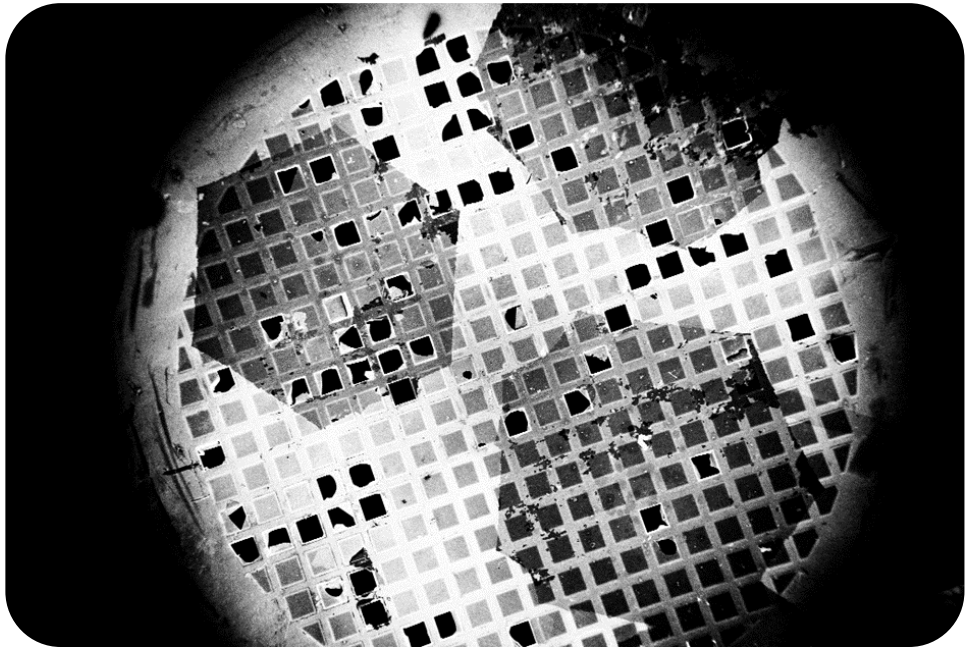
300 mm





300 mm

What is the crystal structure of individual graphene islands?



Method of investigation:

Selected Area Electron Diffraction on CVD graphene islands transferred on a 3 mm diameter TEM grid

Research carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

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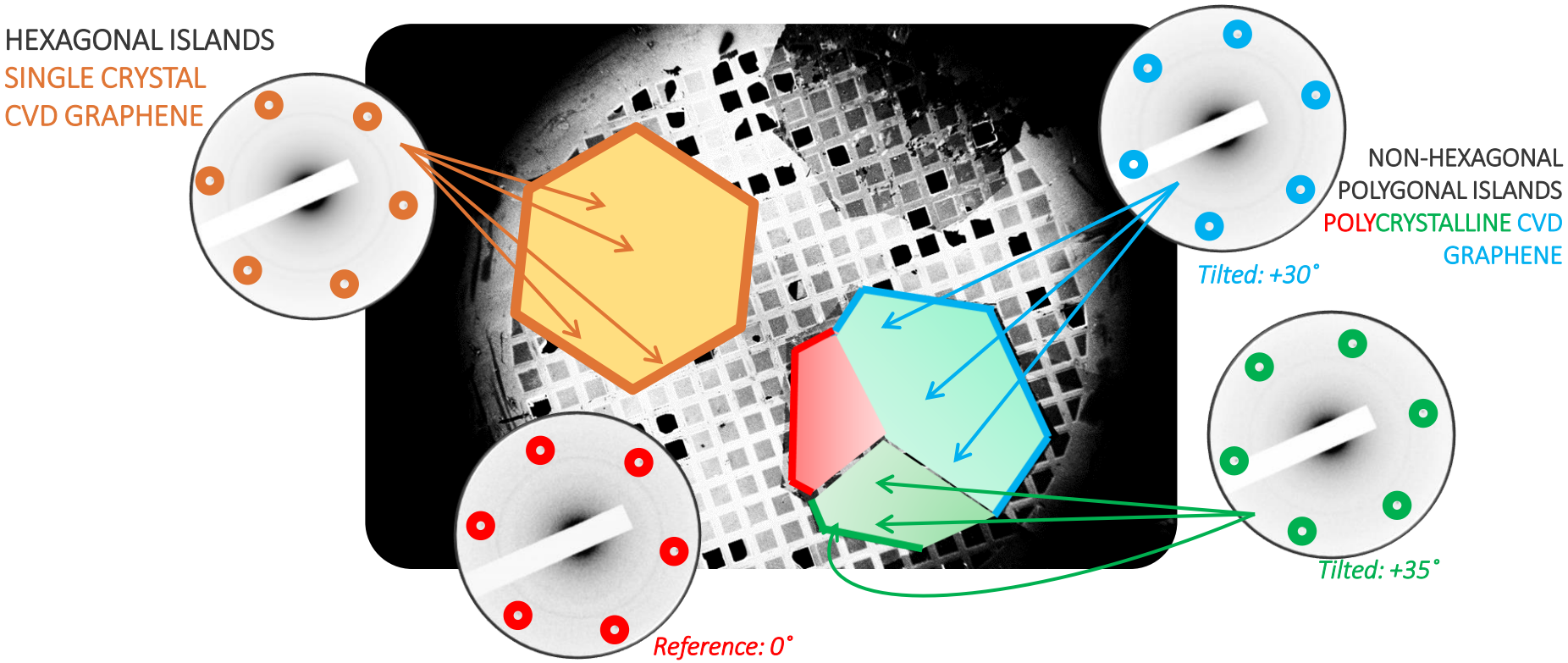

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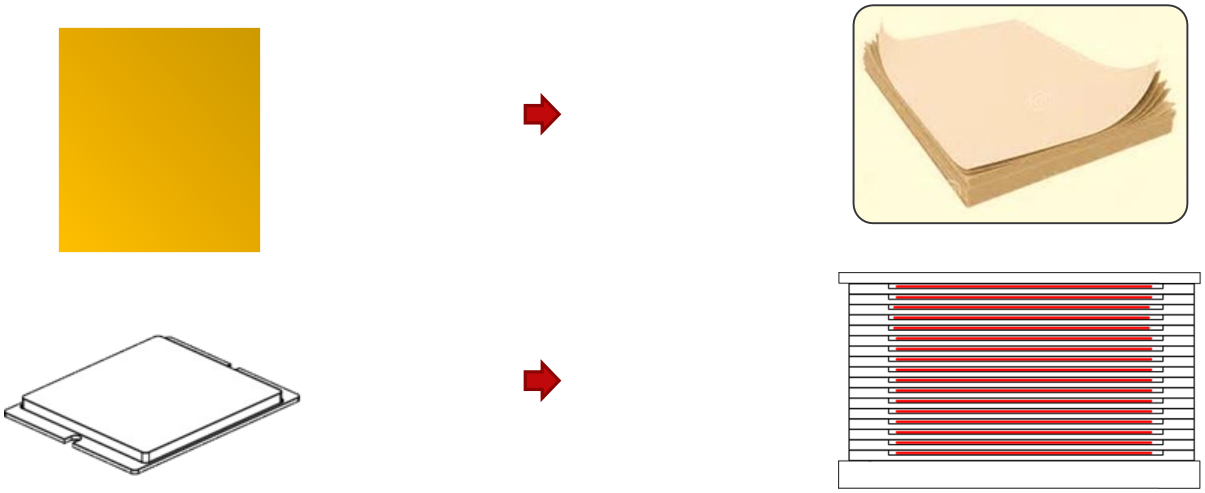
How to get to a UNIVERSAL Low cost, High Volume, High or higher Quality CVD Graphene Manufacturing Solution!



Proposed Multiple Cu Sheets Solution:
Parallel Processing: Vertically Stack thin Enclosure Boxes (Patent Pending)

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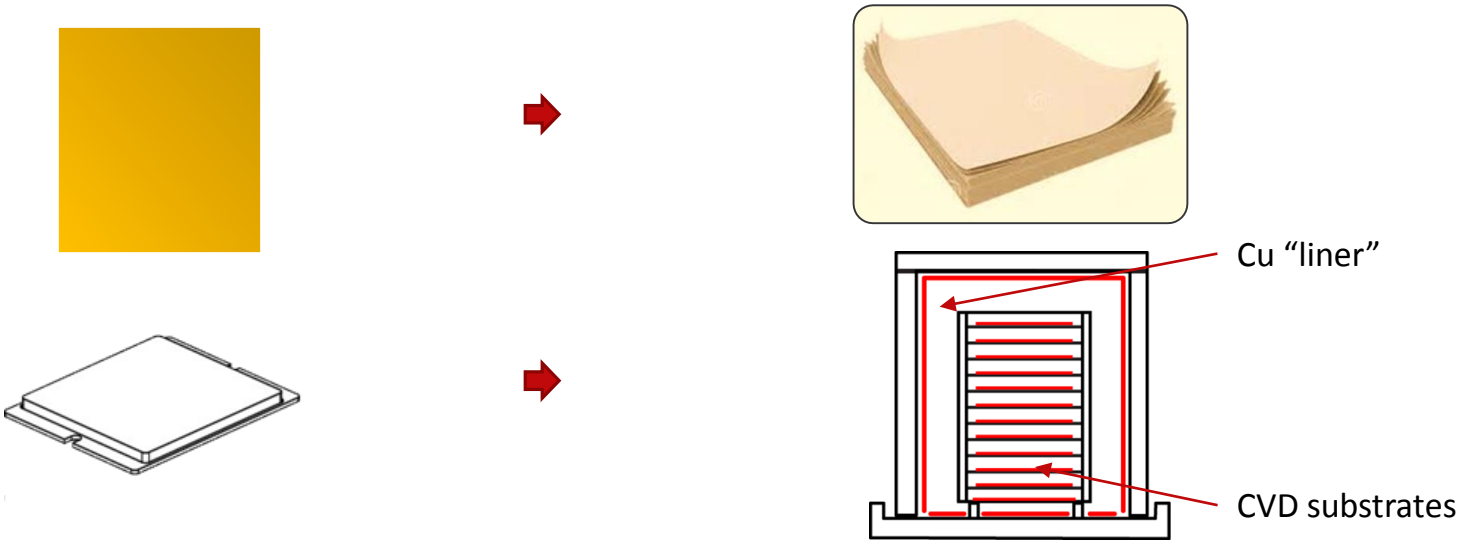

Proposed Multiple Cu Sheets Solution:
Vertically stacked substrates sheets inside tall Enclosure Box (Patent Pending)

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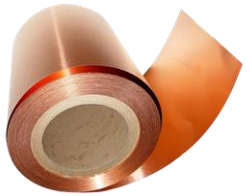
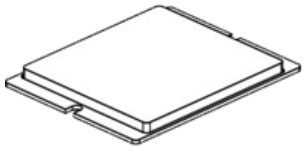
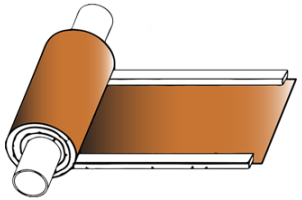
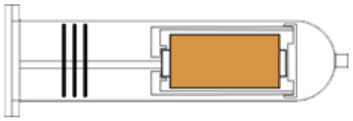






Archimedes Spiral wound
CVD Substrate Roll



Archimedes Roll
in Enclosure Box

Proposed Roll of flexible Substrate Processing in Batch CVD Tube Furnace
with novel tooling resulting in Arichmedes spiral wound
CVD Substrate Roll inside an Enclosure Box (Patent Pending)

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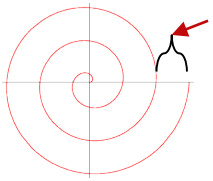
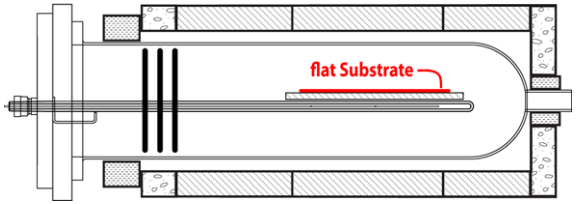
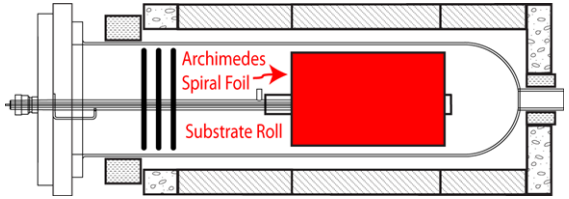
How to Increase the Batch Size for a given CVD Tube Furnace for a Flexible Foil Substrate



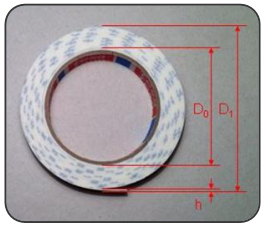
Roll Substrate Foil into an Archimedes Spiral



Prior Art



New Solution



(Patent pending)

For online calculator see: http://www.giangrandi.ch/soft/spiral/spiral.shtml

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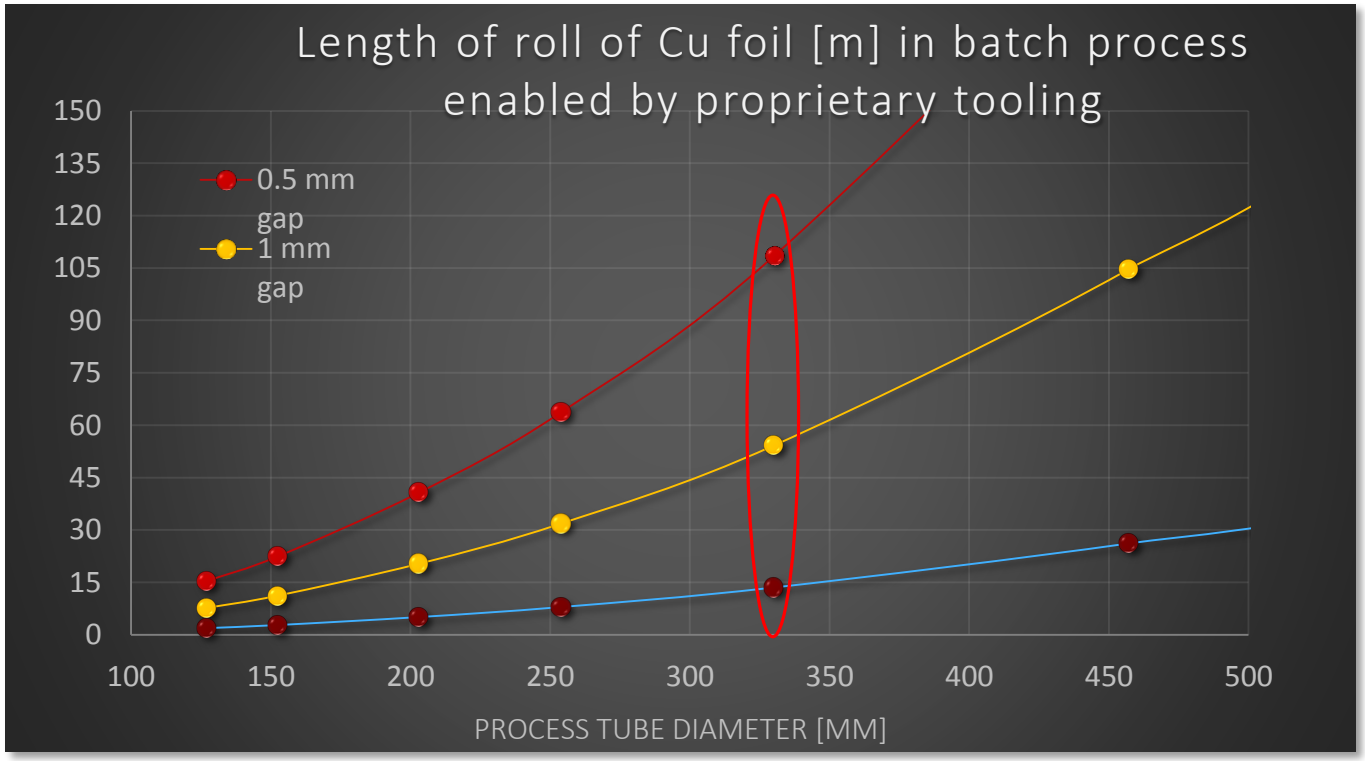
Maximum Substrate Length for Archimedes Spiral Foil Substrate for 80% inner process tube diameter utilization



Capacity ~ $\varnothing^2$, Economy of Scale: Area Gain ~ $\varnothing$

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Maximum Substrate AREA Gain for 80% process tube inner diameter utilization

Process tube ϕ	Process tube ϕ	typical flat substrate width	D0 = inner ϕ	D1 = outer ϕ	Length of roll	Max area gain	Length of roll	Max area gain	Length of roll	Max area gain
					0.5 mm gap		1 mm gap		4 mm gap	
[inch]	[mm]	[m]	[mm]	[mm]	[m]		[m]		[m]	
5	127	0.1	25	102	15	151	7.7	76	1.9	19
6	152	0.12	25	122	22	184	11	92	2.8	23
8	203	0.16	25	163	41	251	20	125	5.1	31
10	254	0.2	25	203	64	314	32	157	8.0	39
13	330	0.26	25	264	108	411	54	205	14	51
18	457	0.37	25	366	209	573	105	286	26	72
22	560	0.45	25	448	314	702	157	351	39	88
40	1016	0.81	25	813	1037	1,276	519	638	130	160

Depending on gap between the layers an AREA GAIN > 5 – 400 X is theoretically possible with a new, patent pending, Batch CVD Process Solutions.

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Maximum Substrate AREA Gain for 80% process tube inner diameter utilization

Roll to Roll ⟷ Batch

Reel size = ?
Line speed = ?

Equipment development Cost	+++
Process development Cost	+++
Chemical delivery system	++
Exhaust treatment system	++
Capital cost	$$$
Variable cost	$$
Operational time	?
Maintenance time	++
Floor space/facility	+++
$/m^2	depends

Substrate size = ?
Cycle time = ?

Equipment development Cost	+
Process development Cost	+
Chemical delivery system	+
Exhaust treatment system	+
Capital cost	$
Variable cost	$
Operational time	+
Maintenance time	+
Floor space/facility	+
$/m2	depends

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EasyTube® CVD Processing Systems

- ✓ Scales CVD graphene processes in size and production volume with low execution risk
- ✓ Operates with a wider process window to manufacture CVD graphene at lower cost and/or time
- ✓ Enables the development of new process windows
- ✓ Enables Volume Production Scale-Up Process Simulation

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50 mm Substrate

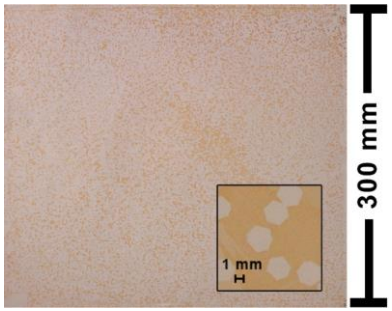
100 mm Substrate

200 mm Substrate (can be modified for 300 mm)

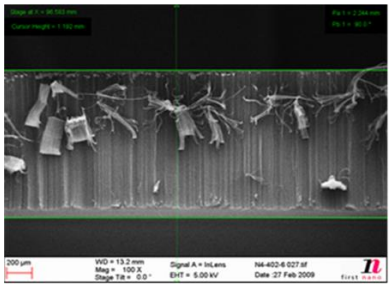
Many CVD Processes Need a Substrate to Grow High Quality Nano-Structured Materials

2D Graphene ⇒ 1D Nano Materials

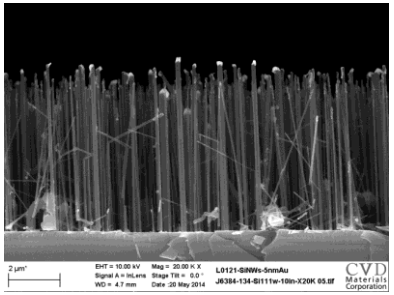
CVD Graphene on Cu foil



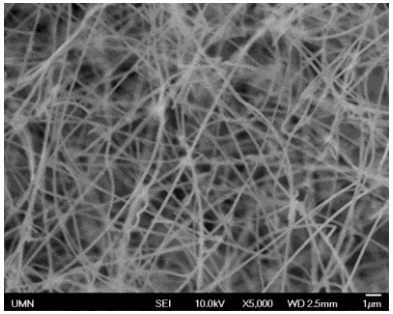
VACNT on SS foil



VASiNW on Si (111)



RASiNW on SS foil



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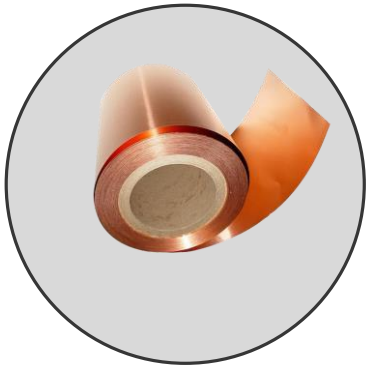
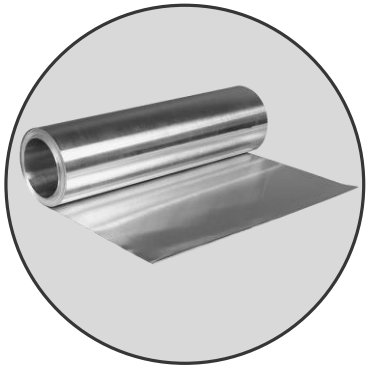
Many CVD Processes Need a Substrate to Grow High Quality Nano-Structured Materials



Copper Foil



Aluminum Foil

Stainless Steel Foil

CVD processing of a Flexible Foil Substrate Roll makes subsequent nano-structured material harvesting/processing much more cost efficient (automatable)than many small size substrates

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Case Study: CVD Graphene Volume Production for 300 mm wide Cu Foil

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Roll to Roll CVD system:

2 m long hot zone

- Line speed = 4 or 2 m/h
- Max production = 29 or 14 m2/24h

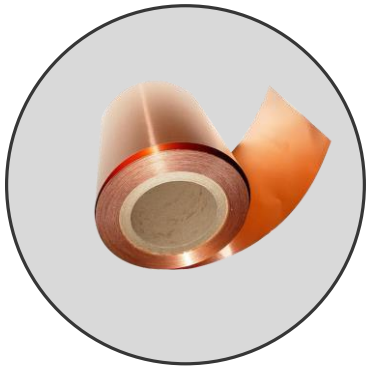
New Archimedes Spiral Batch Process System:

- < 90 min heat up, < 45 min cool down
- Cycle time < 165 or 195 min

For layer gap: 2 mm

- Max length = 27 m/batch
- Max production (double foil) = 16.2 m2/batch
- Max production (double foil) = 142-120 m2/24h
- = 18K-15K 6cm X 13 cm thatch screen/24h

15 or 30 min annealing + 15 or 30 min growth @ 1040 C, AP or LP



Improvement Potential

- ✓ 5-9X productivity gain
- ✓ Capital cost: ≈ 30%-50%
- ✓ Gas consumption cost: < 50 %
- ✓ AP or LP capable

Possible Applications

- ✓ Cell phone thatch screen
- ✓ LED
- ✓ Sensors
- ✓ RF electronic, etc.

Case Study: 1 mm tall VAMWCNT Volume Production with 300 mm wide SS Foil

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Roll to Roll CVD system:

2 m long hot zone

- Line speed = 1.4 m/h
- Max production = 10 m2/24h
  = 0.32 kg/24h

New Archimedes Spiral Batch Process System:

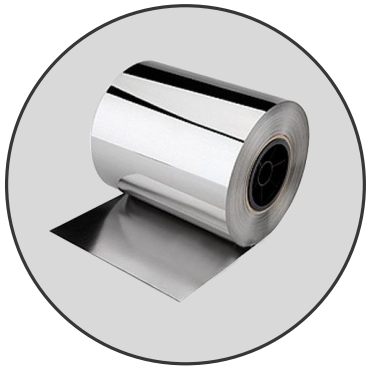
- < 60 min heat up, < 60 min cool down
- Cycle time < 195 min

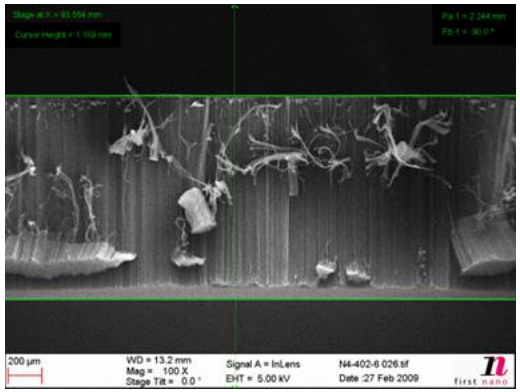
For layer gap: 5 mm

- Max length = 11 m/batch
- Max production (double sided) = 6.6 m2/batch
- Max production (double sided) = 49 m2/24h

  = 1.6 kg/24h

15 min Soak @ 600 oC + 60 min Growth @ 750 oC AP





Improvement Potential

- ✓ 5X productivity gain
- ✓ Capital cost: ≈ 50%
- ✓ Gas consumption cost: < 50 %
- ✓ 760 Torr Operation

Possible Applications

- ✓ Nano-to-Macro™ sheets
- ✓ Composites
- ✓ EMI shielding
- ✓ Sensors, etc

Case Study ≈ 50 µm RA Si NW Volume Production with 300 mm wide SS Foil

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Roll to Roll CVD system:

2 m long hot zone

- Line speed = 3 m/h
- 100 Torr Operation
- Max production = 22 m2/24h

New Archimedes Spiral Batch Process System:

- < 50 min heat up, < 50 min cool down
- Cycle time < 140 min

For layer gap: 3 mm

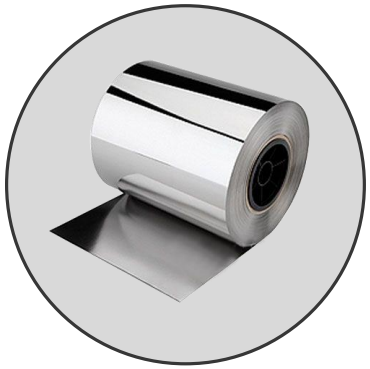
- Max length = 18 m/batch
- Max production (double sided)

  = 11 m2/batch
- Max production (double sided)

  = 111 m2/24h

  = 1.6 kg/24h

10 min Soak @ 550 oC + 30 min Growth @ 550C 100 Torr

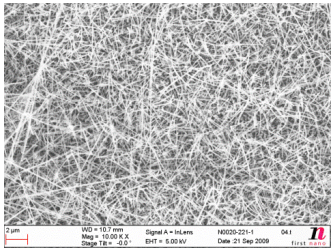


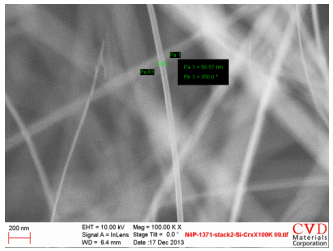
Improvement Potential

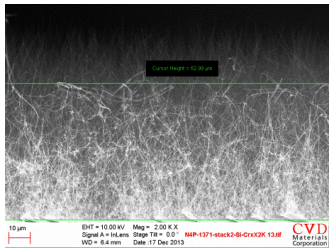
- ✓ 5X productivity gain
- ✓ Capital cost: ≈ 35%
- ✓ Gas consumption cost: < 50 %
- ✓ 100 Torr Operation

Possible Applications

- ✓ Wound dressing
- ✓ Bio-diagnostic
- ✓ Other Sensors etc.







Ever widening CVD graphene manufacturing options lead to more process equipment challenges

Case Study: Investigation of bi-layer CVD graphene growth on Cu foil with Ethanol bubbler, inspired by work of Prof. Shigeo Maruyama (Tokyo University) and driven by request of Prof. Rodney Rudolf Ulsan National Institute of Science and Technology (UNIST),
to find an industrial relevant, stable and scalable process for Bi-layer graphene production

➢ lead us to our next family of innovation steps for our CVD Window Process Control Software: CVDWinPrC™ which can be optionally applied to future EasyTube® System (graphene and non graphene based) as long as the appropriate hardware is installed:

✓ Automated Bubbler Fill Level check Utility
✓ Automated Bubbler pickup efficiency check Utility
✓ Automated Oven check Utility
✓ Automated Oven control PID check Utility
✓ Automated Pumping capacity check Utility for different precursors gases
✓ Automated MFC check Utility
✓ Automated Pressure control check Utility

Some of these enhancements are needed to obtain higher process stability over time.

Others are beneficial for preventive maintenance planning, recipe fine tuning and for accelerating processes into production.

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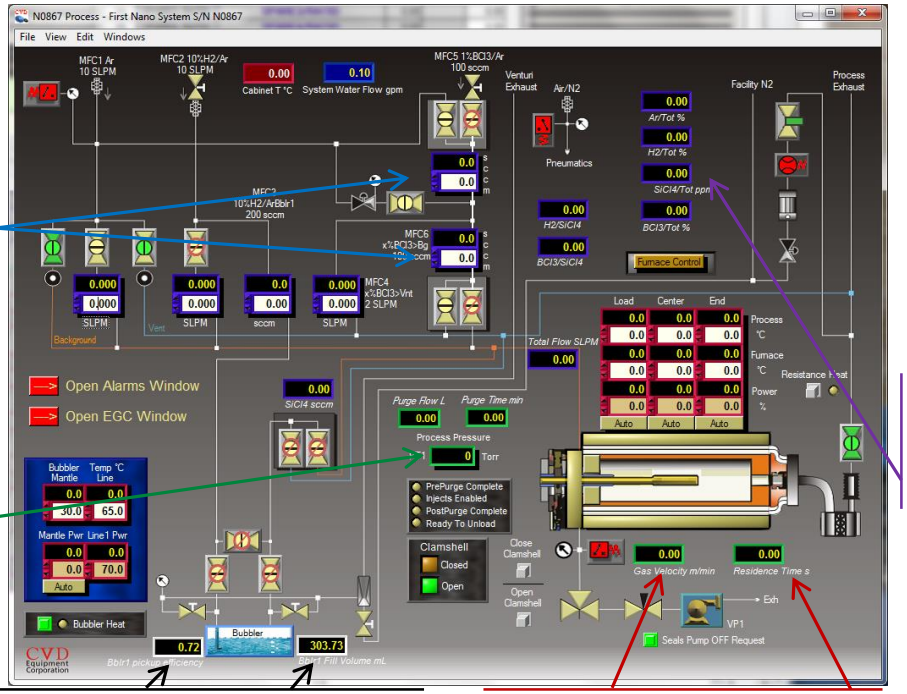
Additional Process feedback can be provided on the EasyTube® system platform

WYSIWYG: Auto ranging MFC's display and control is independent on which type of gas is flowing through MFC

Auto ranging Pressure display and control independent of actual pressure range



Bubbler pick up efficiency and fill level feedback

Gas velocity and residence time feedback

CONCEPT GUI ENHANCEMENT OPTIONS
final details are still under development

Color coding for different parameter groups:

- ✓ Precursors
- ✓ Pressure/Purge
- ✓ Heating
- ✓ Bubbler Info
- ✓ Cooling

OPTIONAL Online calculator for
- Total Flow
- Concentration
- Gas Ratios as appropriate for different processes

These novel CVD*WinPrC*™ software capability extensions also enable a future set of self compensating recipes writing options.

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Summary

- ✓ CVD Equipment Corporation continues to expand capabilities in:
  - ✓ Equipment design and process control
  - ✓ Process development
  - ✓ Material applications
- ✓ CVD Application Laboratory supports custom process and material development opportunities to advance the state of the art and pilot production scale-up demonstrations and to support startup businesses.
- ✓ Our EasyTube® and EasyGraphene™ platforms are designed to enable both R&D and pilot production scale-up development efforts.
- ✓ Patent pending hardware and process solutions with EasyTube® or EasyGraphene™ systems enable straightforward scaling to Volume production of nano-structured materials: 4 Start Small and Scale-Up when needed!
- ✓ With our patent pending Nano-structured Material CVD Manufacturing Solutions:
  - ✓ 5-100X production gain over traditional tube furnace system are possible
  - ✓ 5-10X gains over roll to roll systems are possible at 2-3 X lower capital costs and risks
  - ✓ Batch CVD processing can win over roll to roll for many applications
- ✓ New low cost system diagnostic and feedback utilities options will be available soon
- ✓ => These options can speed up process development by helping minimize process setup inaccuracies and process transfers errors from one system to another for scale-up and help with preventive maintenance and recipe fine tuning.
- ✓ We collaborate with Startups and Universities to accelerate the Commercialization of CVD graphene and other Nano-structured Materials for a wide range of Applications.

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For more info: www.cvdequipment.com | www.firstnano.com | www.easygraphene.com

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