

CVD

Equipment Corporation

Large-scale Production of AB-Stacked Bilayer Graphene Using Ethanol as Precursor

Karlheinz Strobl, V.P. of Business Development

Mathieu Monville, Riju Singhal, and Samuel Wright

Facilities



Headquarters – Central Islip, NY
130,000 ft² facility



Application Lab – Central Islip, NY
6,000 ft² facility

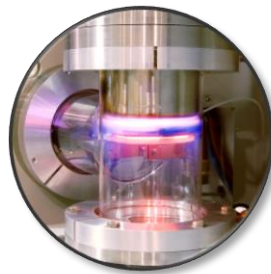


SDC Division – Saugerties, NY
22,000 ft² facility with 4,000 ft² cleanrooms

CVD = Chemical Vapor Deposition

= Chemistry + Temperature + Pressure Control

- ✓ Chemical Vapor Deposition is the controlled decomposition of gases used to deposit a material onto a surface
- ✓ Requires multidisciplinary engineering: process chamber design, temperature control, gas and vapor flow, pressure control, and automation to achieve the desired deposit
- ✓ The Chemical Vapor Deposition process has proven itself to be robust, economical and scalable over many years in semiconductor manufacturing. For 33 years we have been successfully applying this technology to other industries



CVD Systems for Research and Production

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✓ FirstNano™ R&D Systems

- ✓ EasyTube® processing
- ✓ EasyGas™ gas delivery
- ✓ EasyExhaust™ abatement

✓ CVD Equipment Production Systems

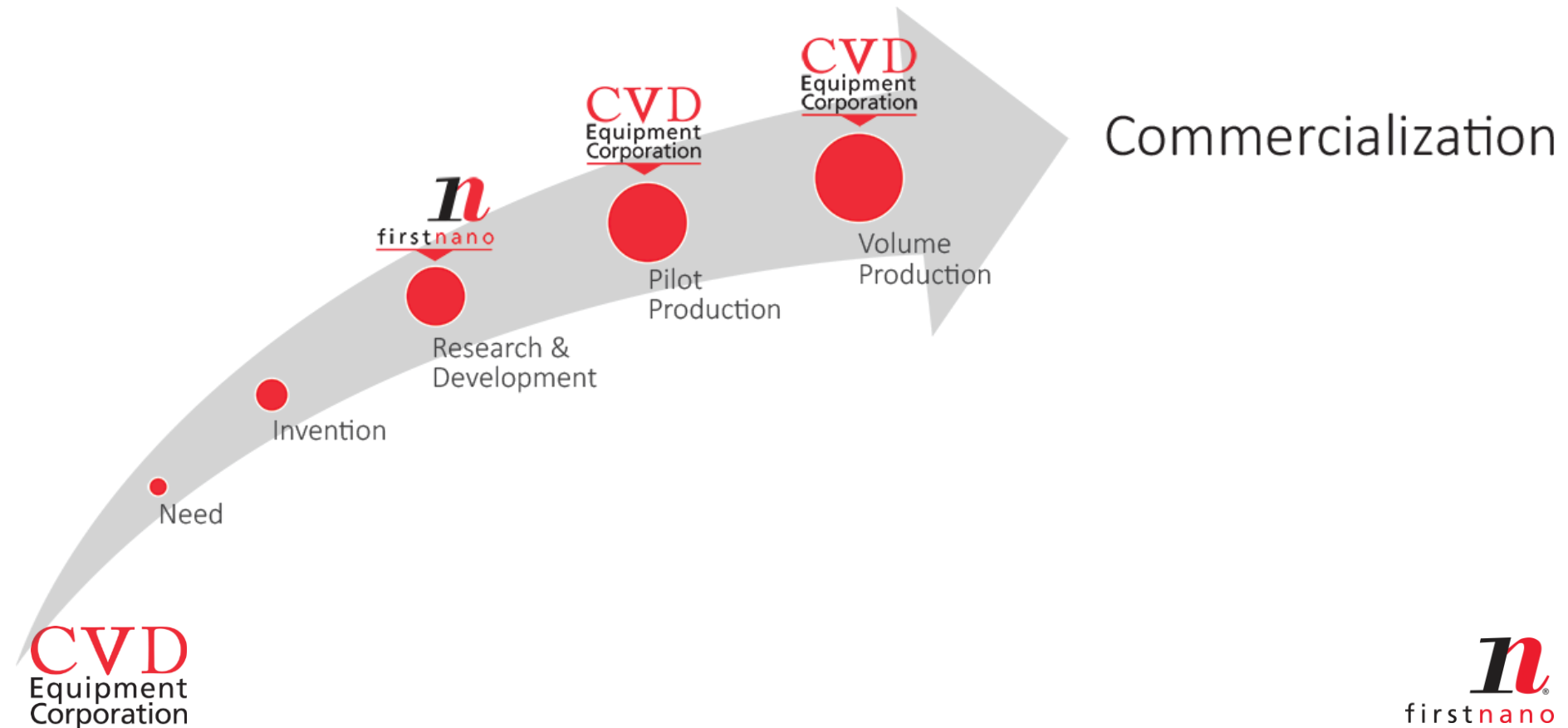
- ✓ Chemical vapor infiltration
- ✓ Transparent conductive oxides (TCOs)
- ✓ Liquid phase epitaxial deposition
- ✓ Medical implant coatings
- ✓ Aerospace composites
- ✓ Reel-to-Reel CVD

✓ SDC® Ultra High Purity Gas and Chemical Delivery Systems

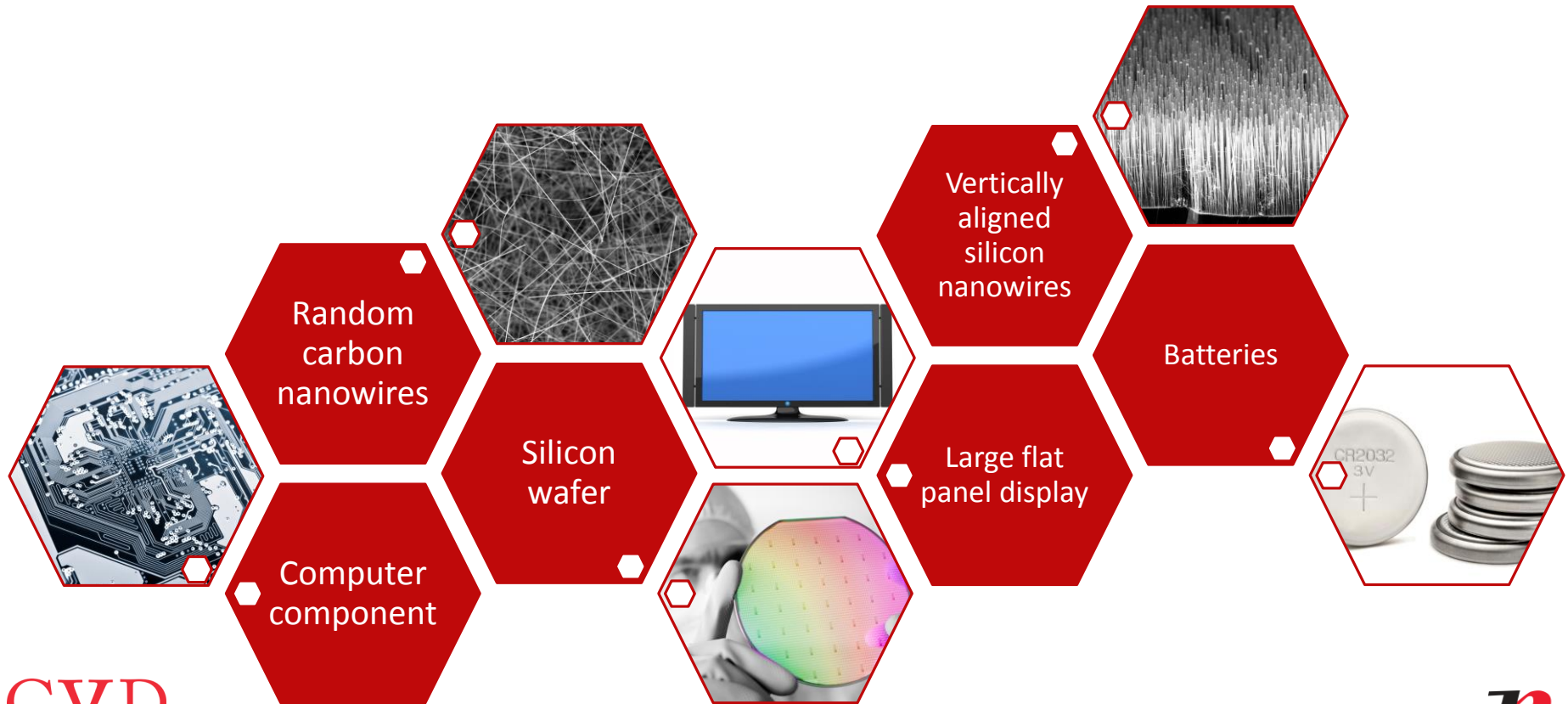
- ✓ Ciphercon™ Cabinets
- ✓ FlexGas™ Cabinets
- ✓ MicroLine™ Panels
- ✓ SymplicityY™ Panels



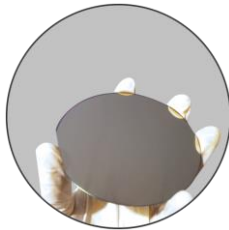
Commercialization of Nano-Structured Materials



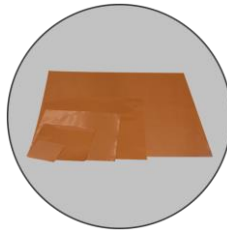
Nanomaterials & Applications



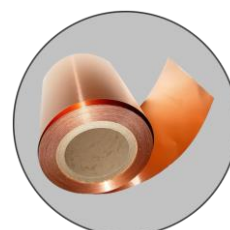
How to get to a UNIVERSAL Low cost, High Volume, High or higher Quality CVD Graphene Manufacturing Solution



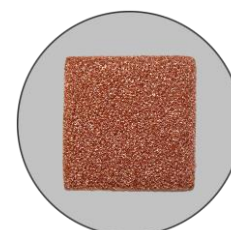
WAFER



FOIL



ROLL



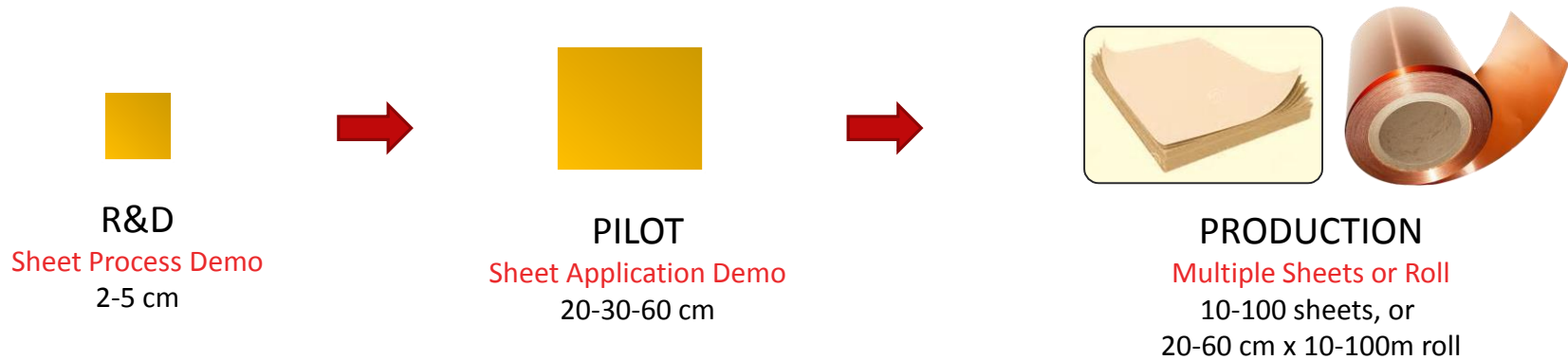
FOAM

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?

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



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**

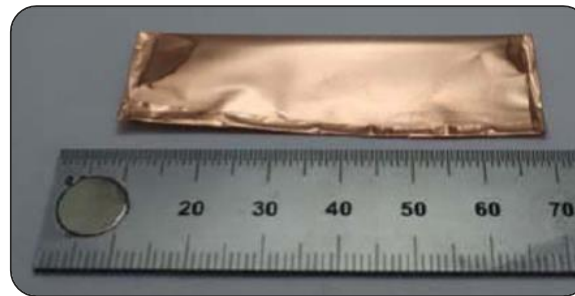
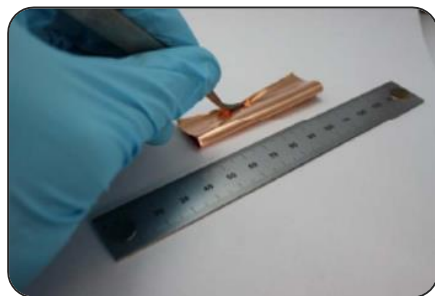
How to minimize economical and business risks and obtain maximum flexibility for future changes in application needs and process innovations

Take Research Innovations and RE-engineer them to be Practical

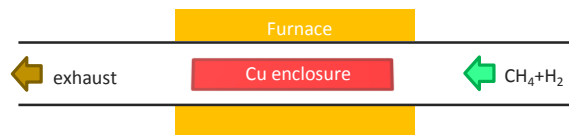
1st Step: Inspiration from YOUR Research

'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

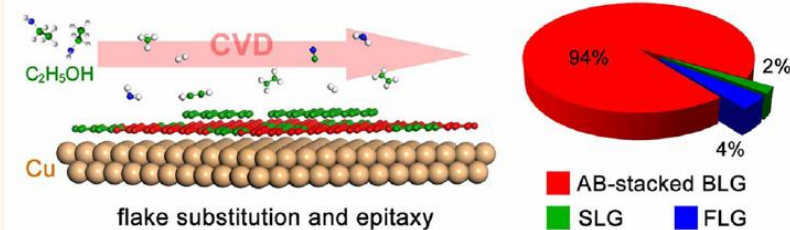


$f_{H_2}=2$ sccm ($p=3.0 \text{ E-}2$ mbar). $f_{CH_4}=0.5$ SCCM
($p=4.0 \text{ E-}2$ mbar. $T=1035$ °C. $T=90$ mins.

Take Research Innovations and RE-engineer them to be Practical

2nd Step: More Inspirations from YOUR Research!
Which one is more important than others?

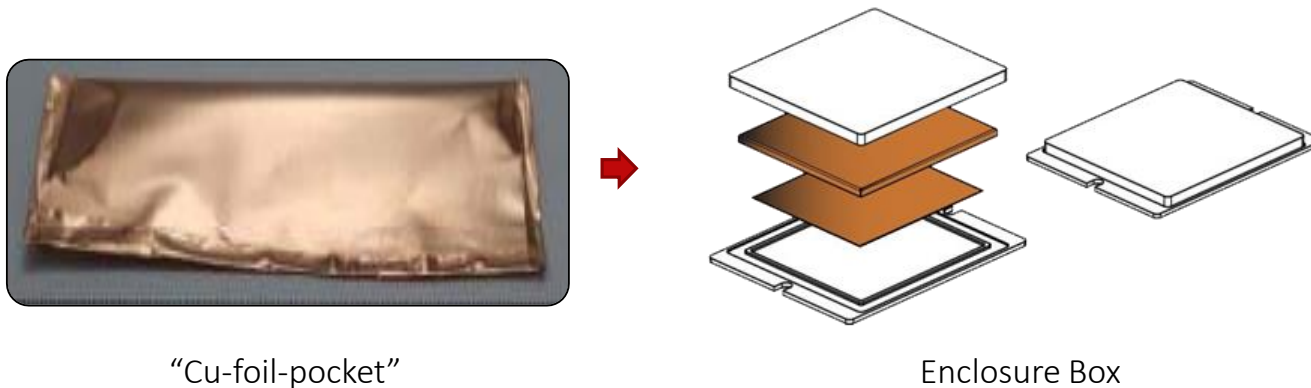
ABSTRACT Using ethanol as the carbon source, self-limiting growth of AB-stacked bilayer graphene (BLG) has been achieved on Cu via an equilibrium chemical vapor deposition (CVD) process. We found that during this alcohol catalytic CVD (ACCVD) a source-gas pressure range exists to break the self-limitation of monolayer graphene on Cu, and at a certain equilibrium state it prefers to form uniform BLG with a high surface coverage of $\sim 94\%$ and AB-stacking ratio of nearly 100%. More importantly, once the BLG is completed, this growth shows a self-limiting manner, and an extended ethanol flow time does not result in additional layers. We investigate the mechanism of this equilibrium BLG growth using isotopically labeled ^{13}C -ethanol and selective surface aryl



Can such different process be done on same platform?

How to develop a UNIVERSAL, Multipurpose Low cost, High Volume, High Quality Graphene Manufacturing Solution?

3rd Step: Apply our 33 years of know-how in custom CVD system design, solutions, and manufacturing to develop practical solutions



“Cu-foil-pocket”

Enclosure Box

Proposed universal graphene production solution for single Cu sheet:
Replace “Cu-foil-pocket” with a Process Compatible Enclosure Box (Patent Pending)

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

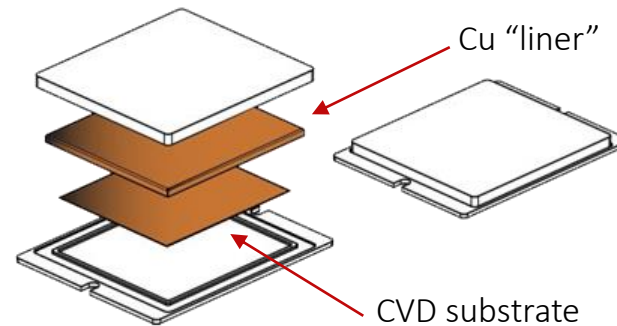
Benefits: (optimization still ongoing)

- ✓ **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

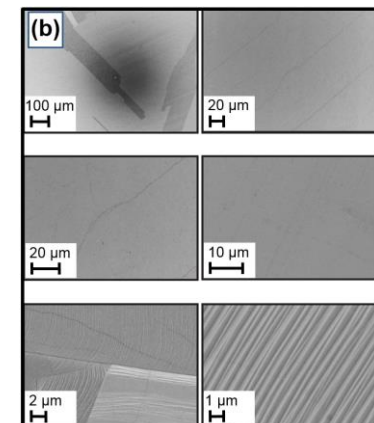
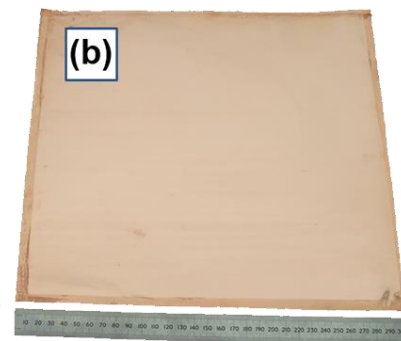
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Higher Purity, Higher Quality



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

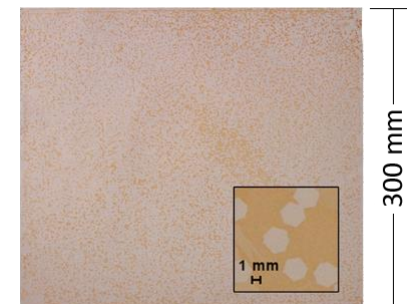
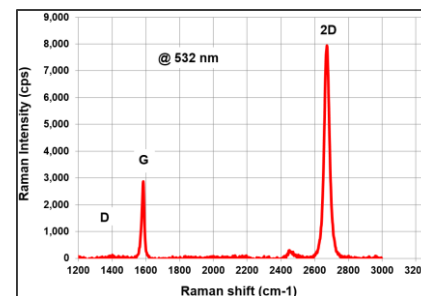
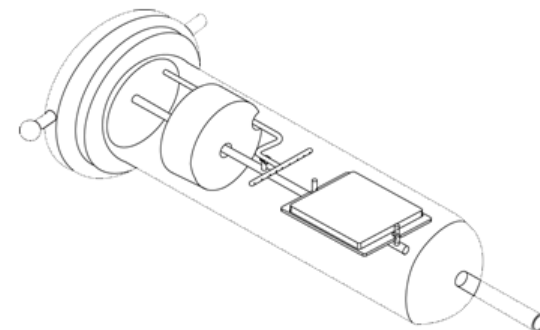
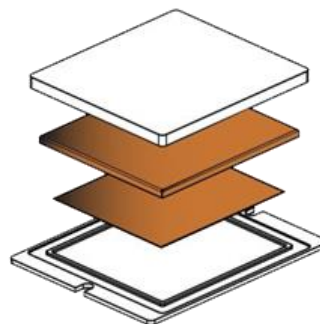
Benefits: (optimization still ongoing)

- ✓ 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

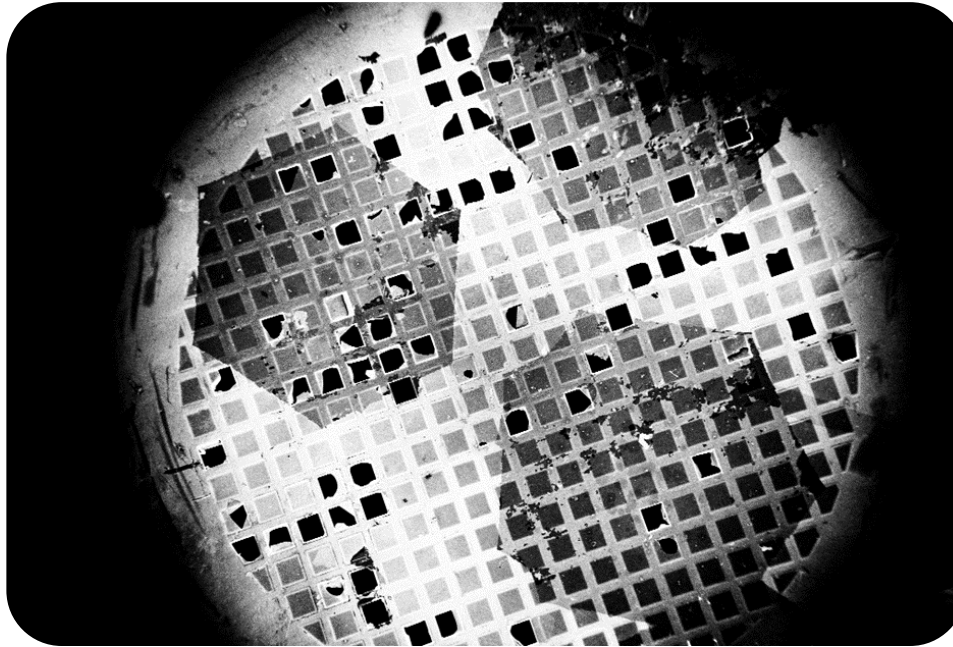
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What is the crystal structure of individual graphene islands?

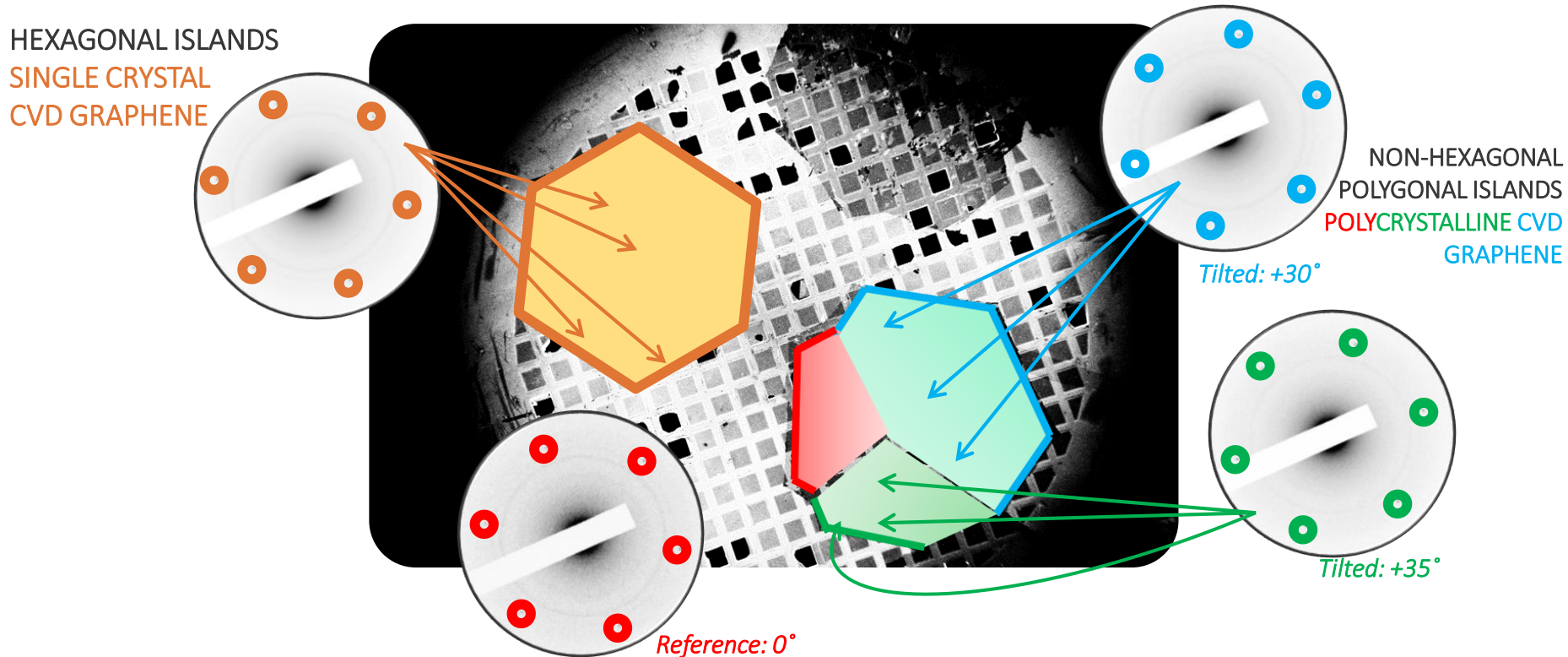


Method of investigation:

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

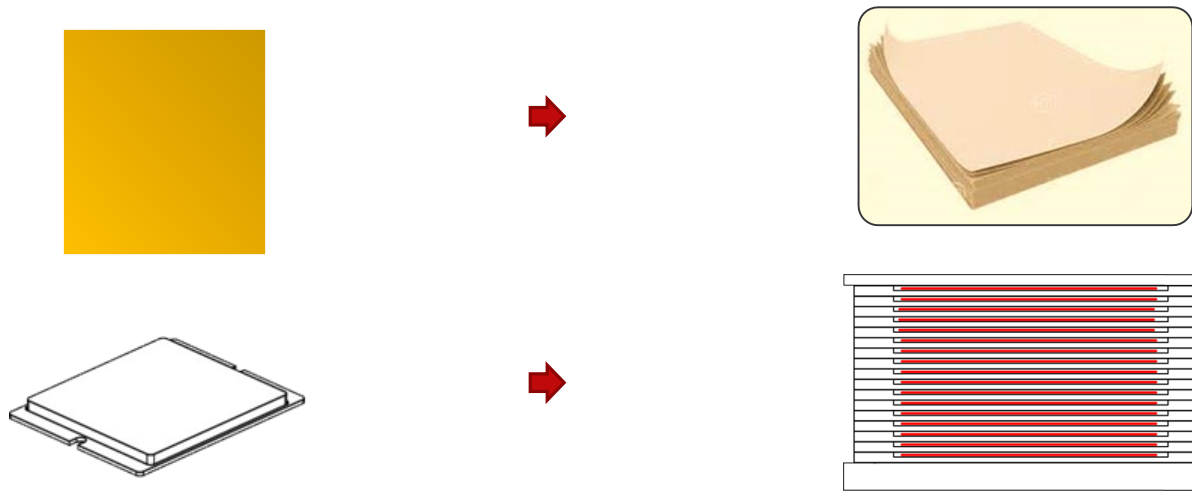
Research carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

What is the crystal structure of individual graphene islands?



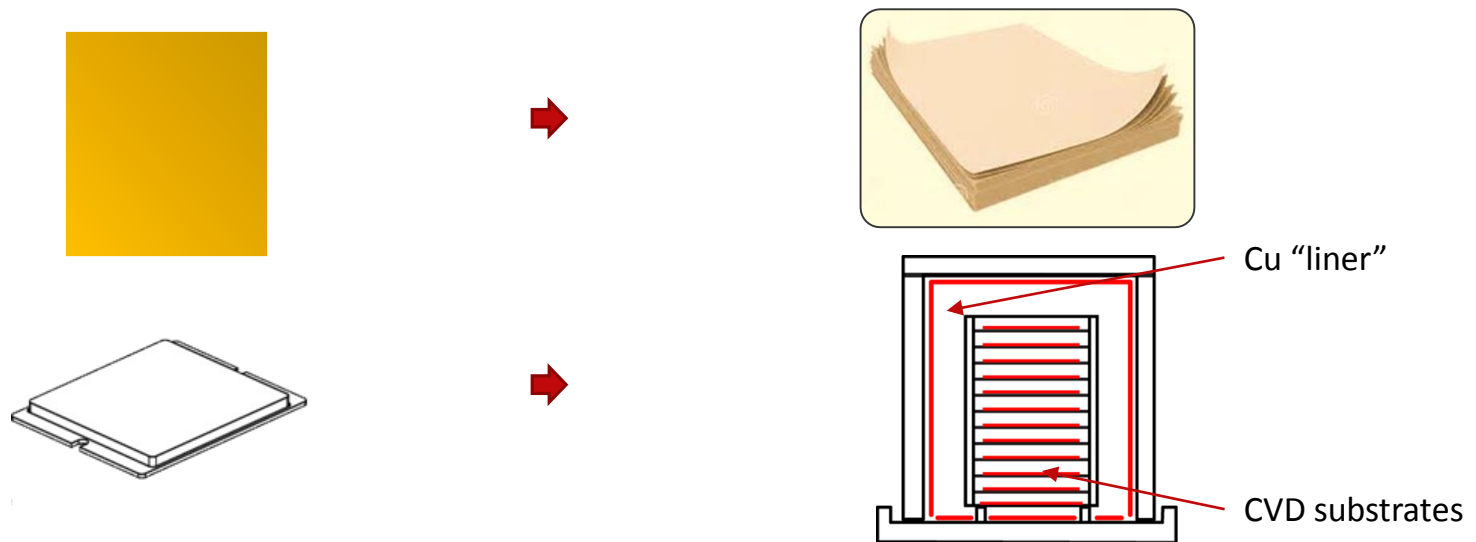
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How to get to a UNIVERSAL Low cost, High Volume, High or higher Quality CVD Graphene Manufacturing Solution!



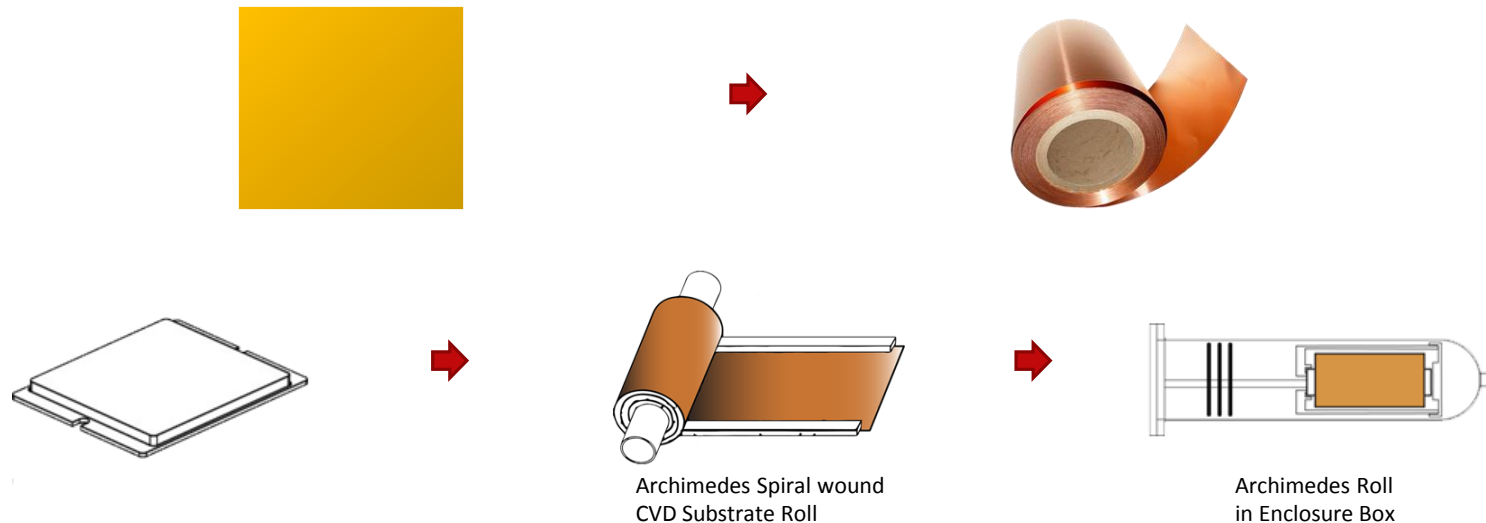
Proposed Multiple Cu Sheets Solution:
Parallel Processing: Vertically Stack thin Enclosure Boxes (Patent Pending)

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



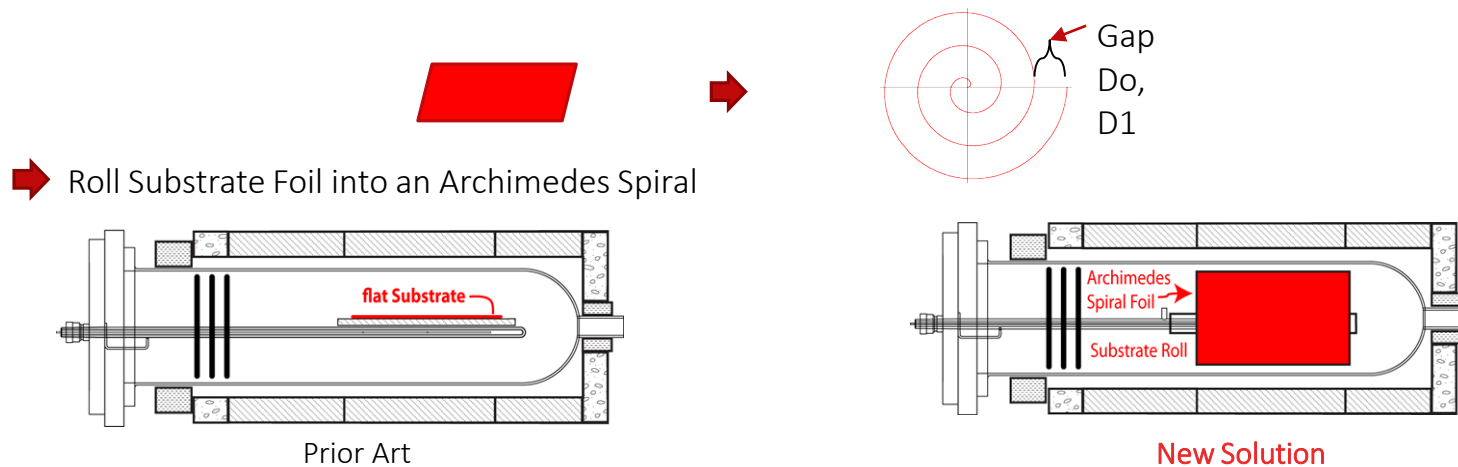
Proposed Multiple Cu Sheets Solution:
Vertically stacked substrates sheets inside tall Enclosure Box (Patent Pending)

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



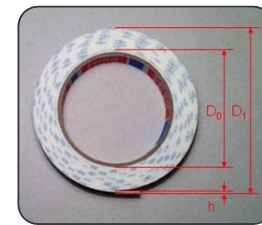
Proposed Roll of flexible Substrate Processing in Batch CVD Tube Furnace
with novel tooling resulting in Archimedes spiral wound
CVD Substrate Roll inside an Enclosure Box (Patent Pending)

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

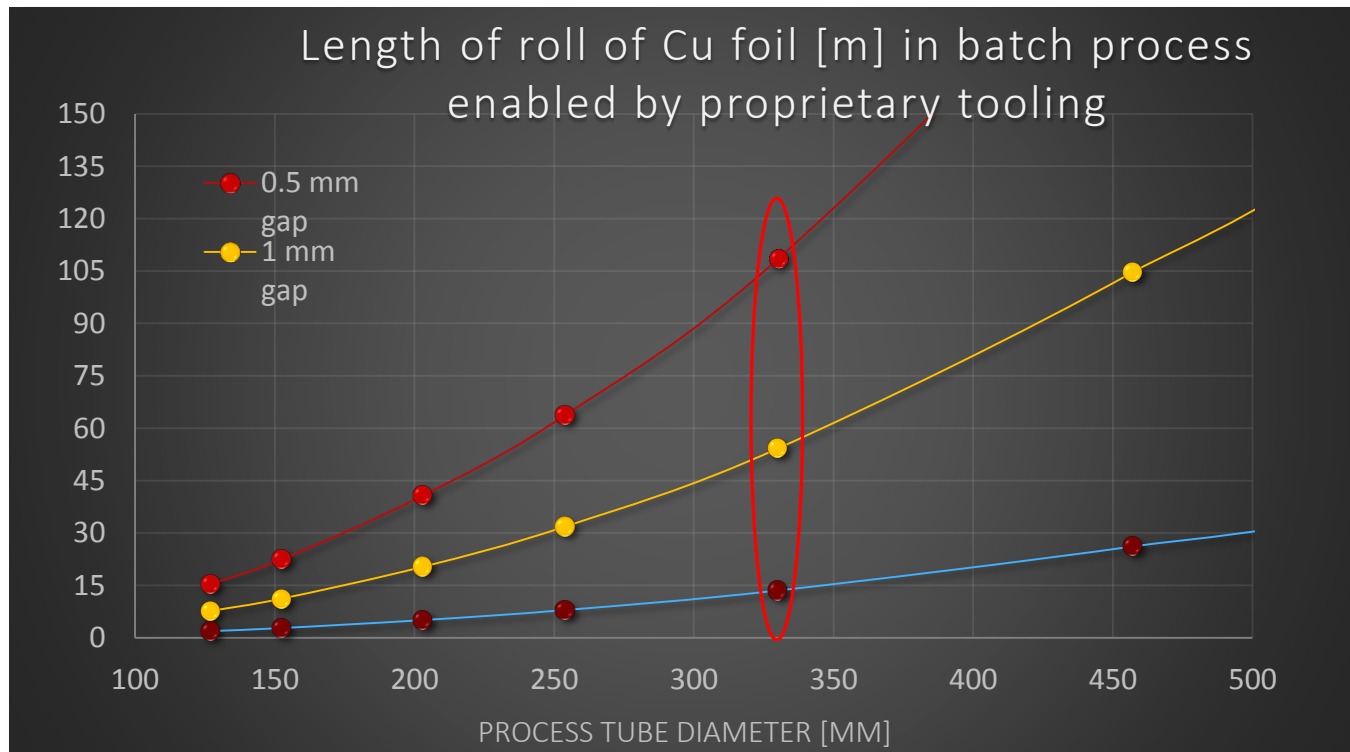


(Patent pending)

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



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



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

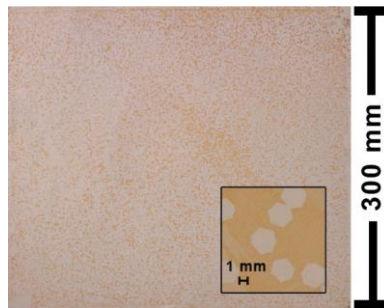


200 mm Substrate (can be modified for 300 mm)

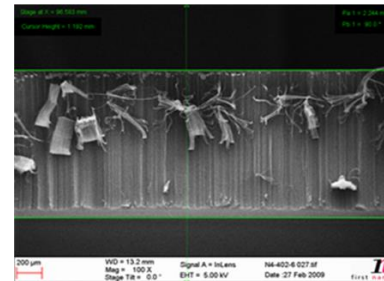
Many CVD Processes Need a Substrate to Grow High Quality Nano-Structured Materials

2D Graphene \Rightarrow 1D Nano Materials

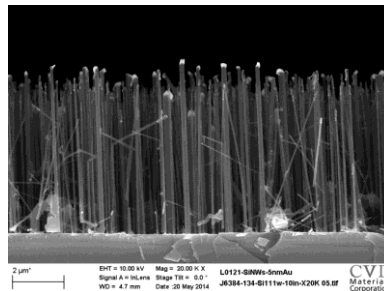
CVD Graphene on Cu foil



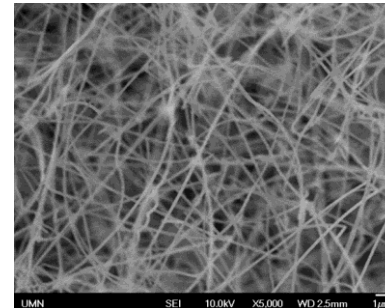
VACNT on SS foil



VASiNW on Si (111)



RASiNW on SS foil



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

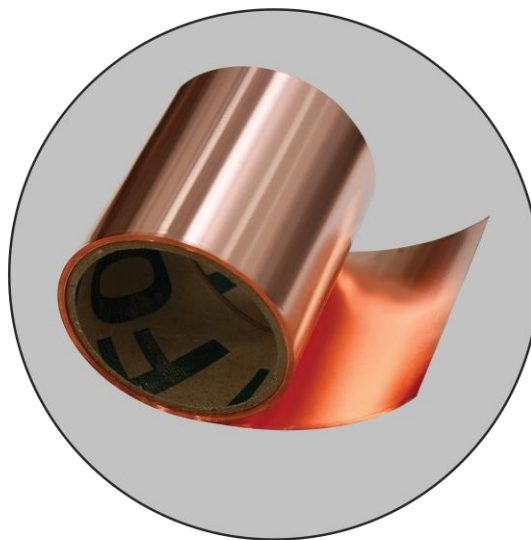
New Archimedes Spiral Batch Process System:

- ✓ < 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

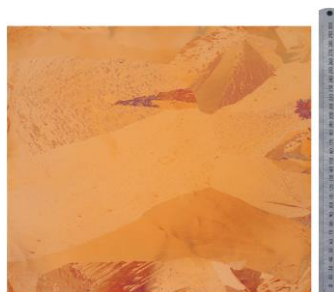


Improvement Potential

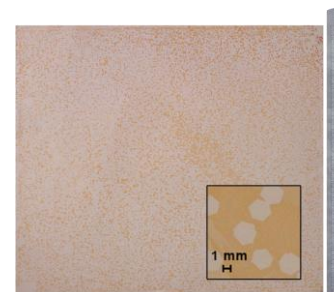
- ✓ 5-9X productivity gain
- ✓ Capital cost: \approx 30%-50%
- ✓ Gas consumption cost: < 50 %
- ✓ AP or LP capable

Possible Applications

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

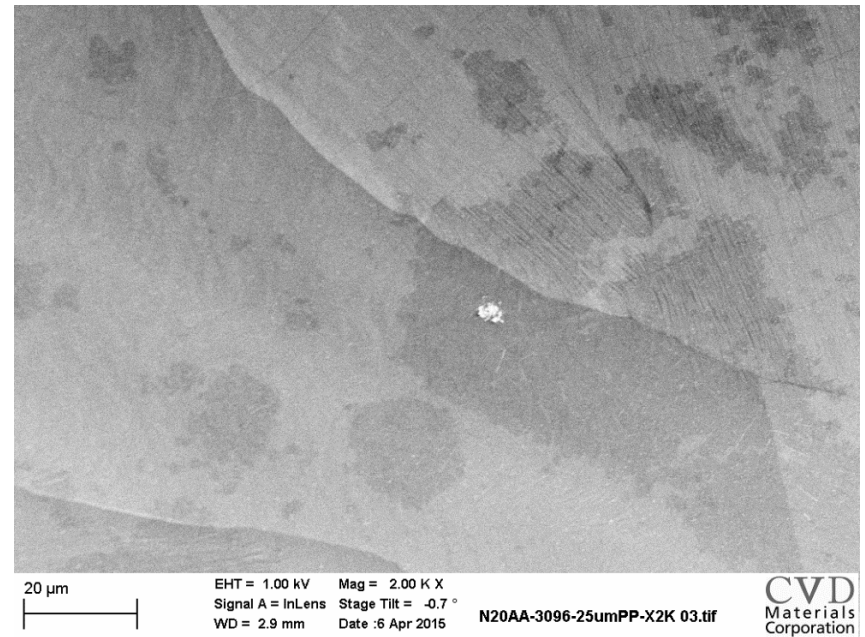
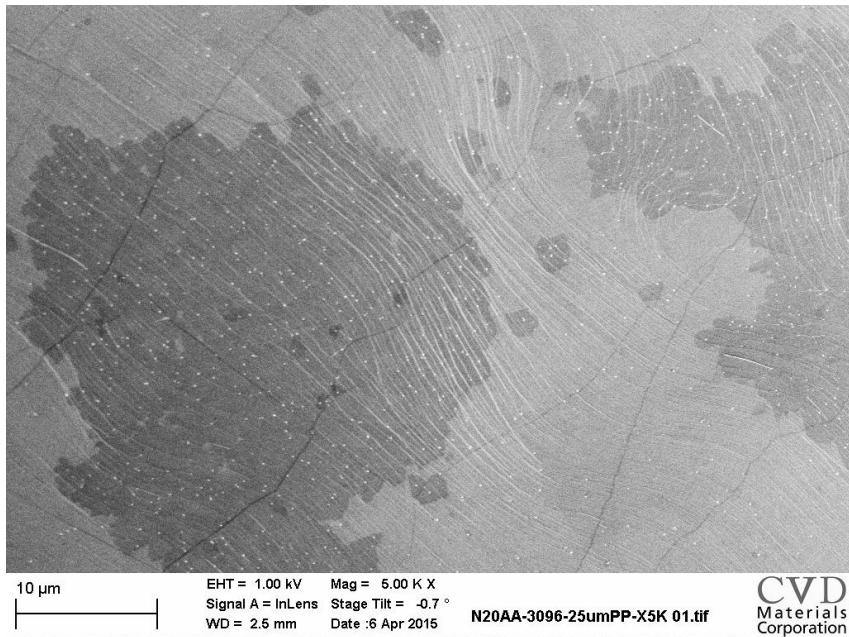


300 mm



300 mm

First Step in Bi-Layer Scale up: duplication of Prior Art paper utilizing Ethanol As C-precursor to make Bi-layer Graphene



(without enclosure box)

> 60% bi-layer coverage

Summary

- ✓ **CVD Equipment Corporation** continues to expand capabilities in:
 - ✓ Equipment design and process control
 - ✓ Process development
 - ✓ Material applications
- ✓ We presented a multipurpose, patent pending, equipment platform that has the potential to be a more universal solution for:
 - ✓ Multipurpose Mono, bi-layer and multi layer graphene growth
 - ✓ Has potential for also other 2D material developments
 - ✓ Can be used for 10 – 100X production quantity improvements
 - ✓ Provides large scale thermal uniformity
 - ✓ Provides vapor pressure control
 - ✓ Enables quality improvement
 - ✓ Provides parallel processing capabilities
- ✓ We collaborate with Startups and Universities to accelerate the Commercialization of CVD graphene and other Nano-structured Materials for a wide range of Applications.

Please contact us with your needs or project ideas!

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

Thank you!