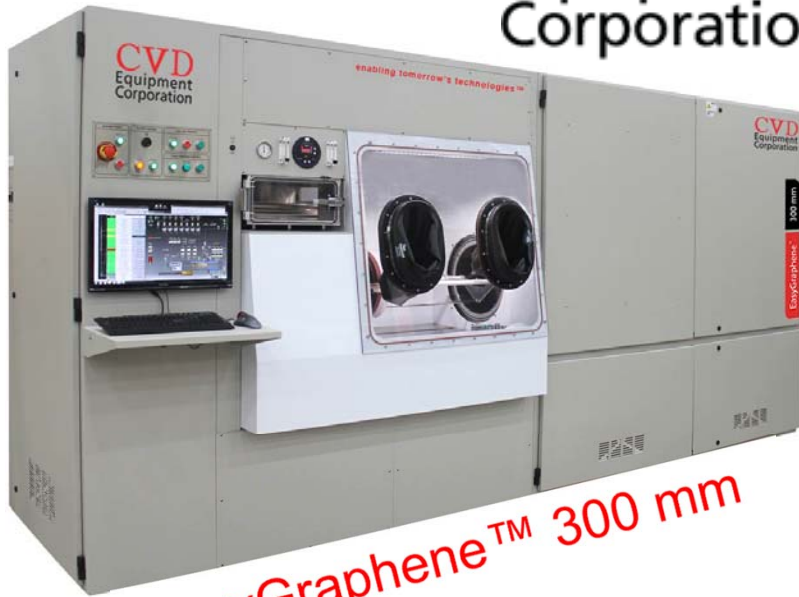


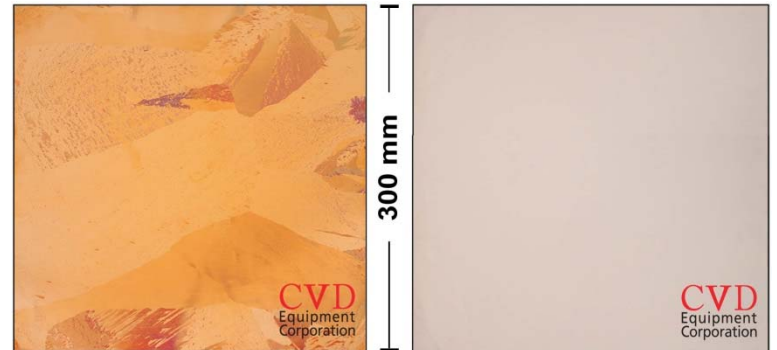
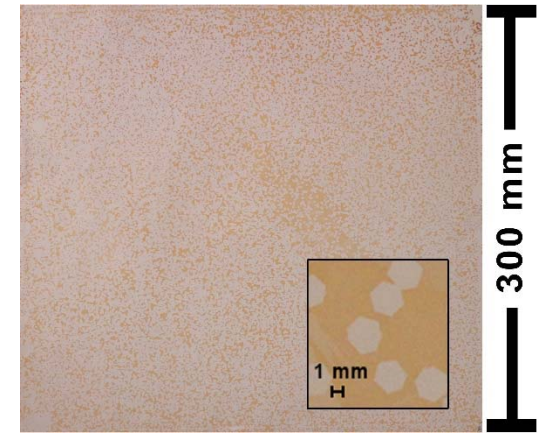
# Novel Tooling for Scaling of High Quality CVD Graphene Production

*Karlheinz Strobl, Mathieu Monville,  
Riju Singhal and Samuel Wright*

CVD  
Equipment  
Corporation



EasyGraphene™ 300 mm



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# Commercialization of Nano Materials



Commercialization

Volume production

Pilot production

R&D

*n*  
firstnano

CVD  
Equipment  
Corporation

Invention

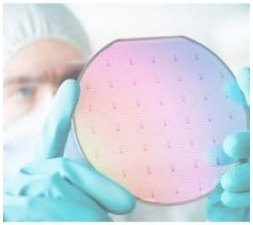
Need

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# CVD Equipment Corporation

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



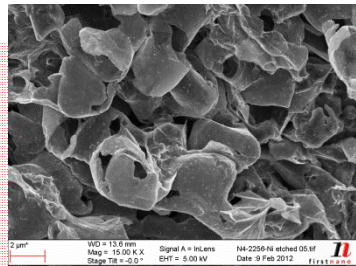
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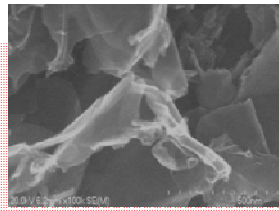
## Operate an Application Laboratory:

- Perform contract process development
- Develop process and equipment for research materials
- Work with researchers to help accelerate the commercialization of nanomaterials

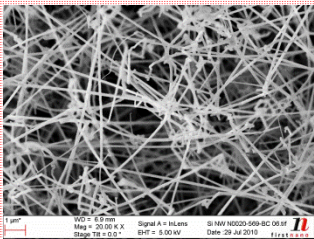
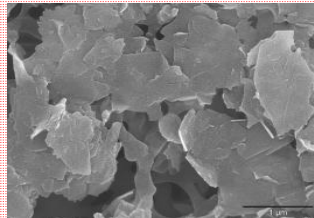
# Novel Nano**to**Macro™ Manufacturing Platform



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

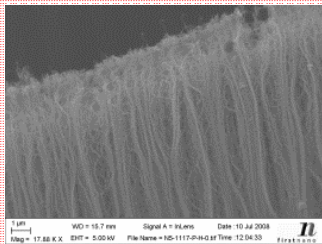


Nano platelets:  
graphene  
vermiculite, clay  
BN, MoS<sub>2</sub>...



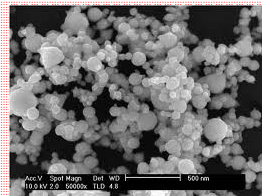
Nanowires:  
Si, GaN, BN,  
TiO<sub>2</sub>...

Nanotubes:  
VACNT, BN NT

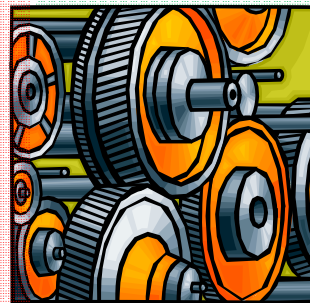


Raw nanomaterial  
manufacturing process

Nanoparticles:  
LiFePO<sub>4</sub>...



## Nano**to**Macro™ 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



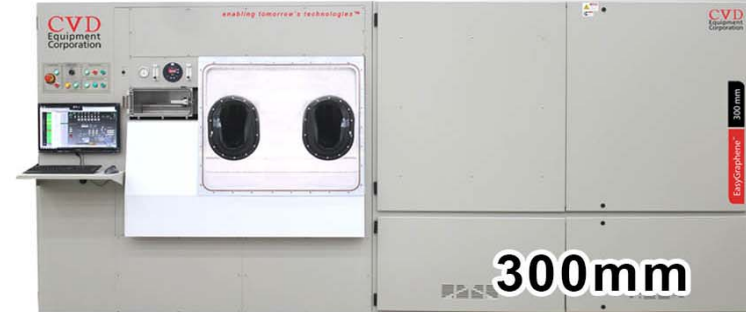
### OPTIMIZED FOR:

- 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.

# NEW EasyGraphene™ CVD graphene growth platform



## EasyGraphene™ Process Solutions



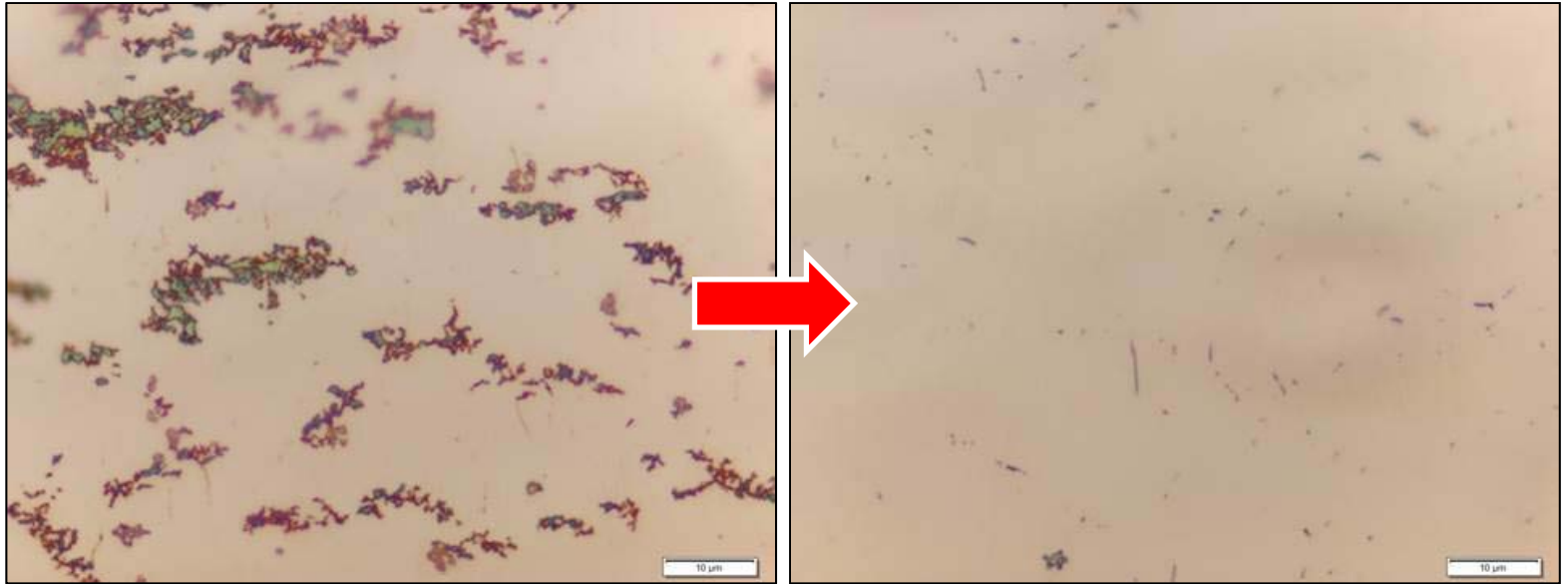
- Scales CVD graphene processes in size and production volume with low execution risk
- Operates with a wider process window to manufacture CVD graphene at lower cost and/or time
- Enables the development of new process windows



# Substrate Preparation of Cu foil is very critical For quality improvement of CVD graphene films



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Regular Cu foils, as received  
from vendor after  
CVD graphene processing  
Viewed at 100 X

Electropolished Cu foils after  
CVD graphene processing  
Viewed at 100 X

Both regular and electropolished Cu foils processed in same CVD graphene process run and removed from oven at 200 °C to increase contrast.

**Further optimization of electropolishing or equivalent chemical etching is needed to further improve surface cleanliness and reduce the number of graphene seeds.**

# EasyGraphene™: Scaling to 300 mm size

Traditional horizontal tube furnace systems can get the Cu foil stuck after 2 hr annealing and 2 hr CVD graphene growth @ 1020 °C and 15 Torr on 18 μm electropolished Cu foil.



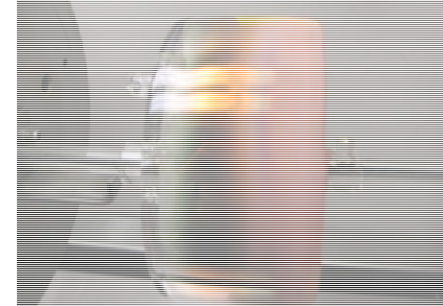
EasyGraphene™ with proprietary processing technology enables **WRINKLE FREE** Cu foil processing even for > 5 hr processing time on 300 mm foils.




# Traditional Systems: Pollution requires frequent maintenance

Traditional horizontal tube furnace systems pollute Cu foil after graphene run: “White dots”.

(see OO 4.06, Isaac Ruiz  
University of California Riverside)



These  $\text{SiO}_2$ ,  $\text{CuO}_x$  and other particles problem requires to clean and/or exchange quartz parts often to get repeatable results.

1  $\mu\text{m}^*$       WD = 8.8 mm      Signal A = InLens      N3-736-C 03.tif  
 Mag = 20.00 K X      EHT = 5.00 kV      Date :1 Feb 2012  
 Stage Tilt = 0.0 °      



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# EasyGraphene™ Processing Technology enables significantly less pollution and maintenance

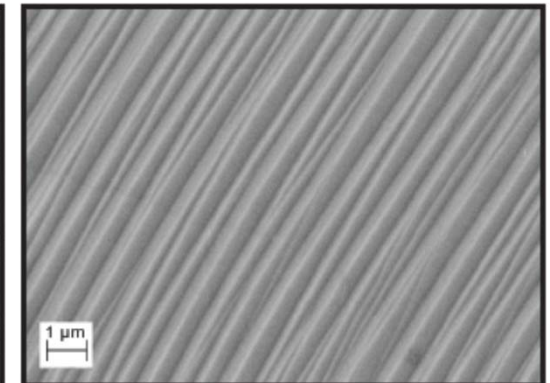
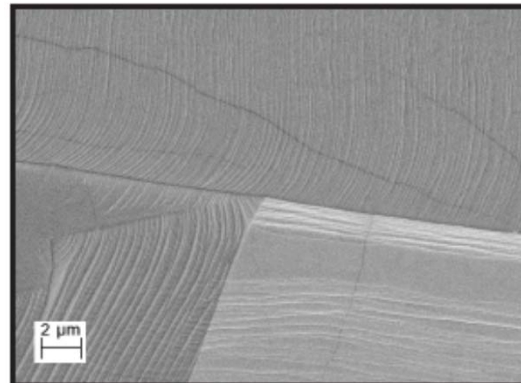
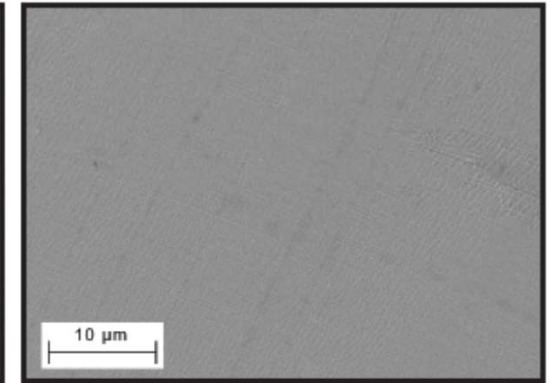
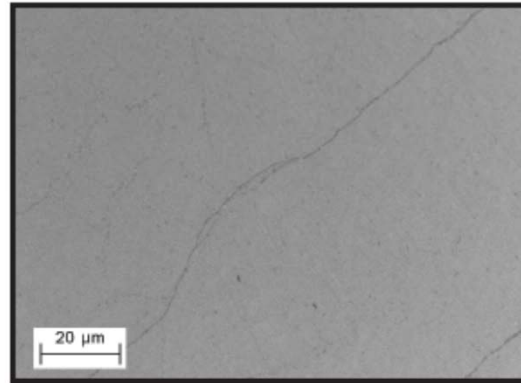
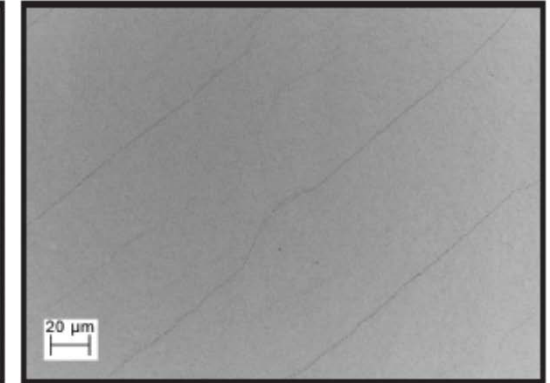
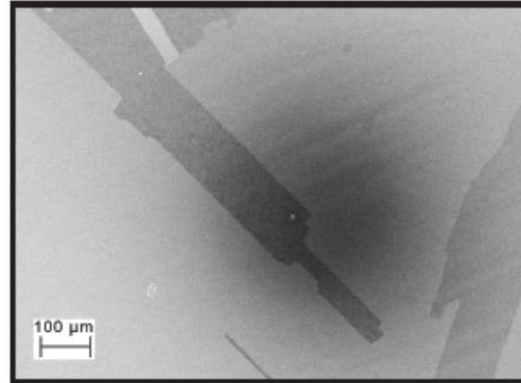


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Reduced Cu deposits on colder parts of the reactor:

- > 1000 X less “white dots”
- 10-100 X less maintenance needed
- SUPER CLEAN CVD graphene surfaces possible with optional hardware and process upgrades



# EasyGraphene™ Processing Technology enables larger Cu grains + smoother Cu foil

In general Cu grains of any Cu foil can be increased 100 – 10,000 X.

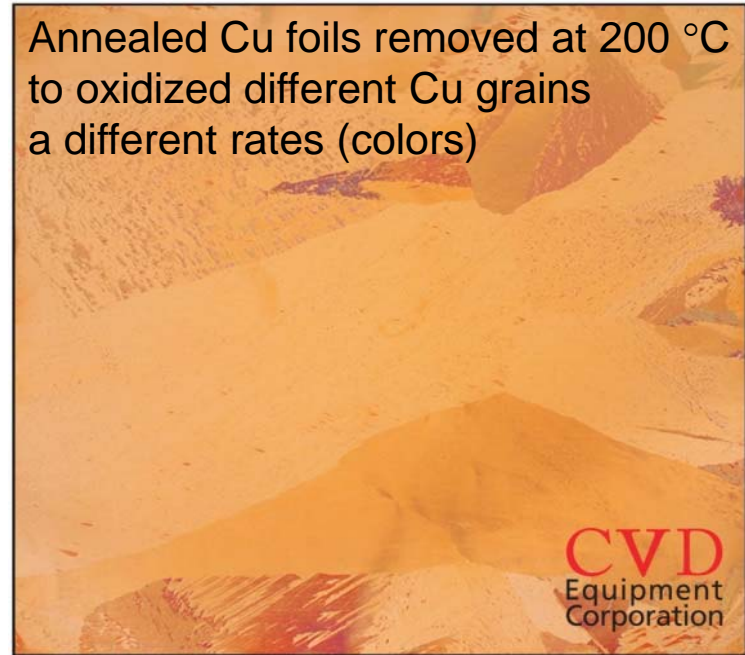
Up to 300 mm Cu grains have been demonstrated depending on process conditions and Cu foil type.

**Cu grain size** is limited by Cu foil type and annealing conditions.

Large Cu grains can be obtained in less time than with traditional CVD graphene systems.

**Large Cu grains enable higher quality CVD graphene due to fewer grain boundaries and larger spatial growth regions of Cu. This can lead to higher conductivity/mobility films.**

Annealed Cu foils removed at 200 °C to oxidized different Cu grains a different rates (colors)



300 mm



200 mm



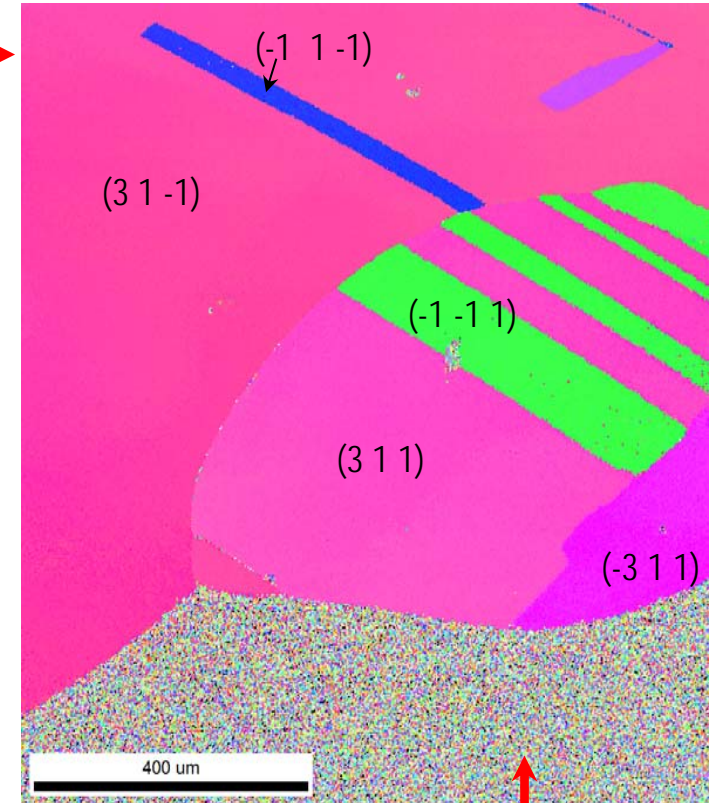
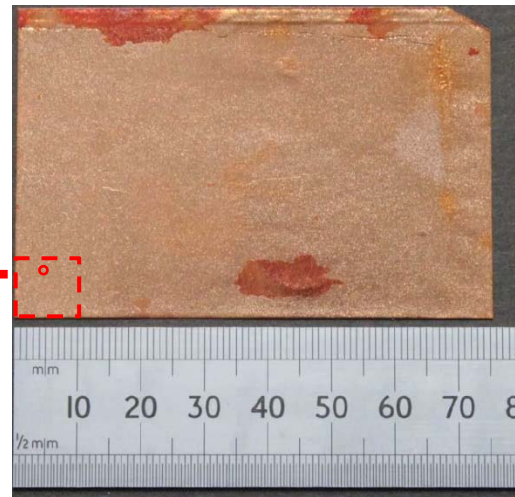
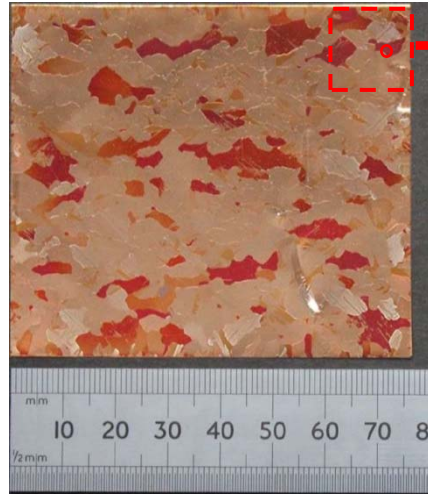
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# EasyGraphene™ Cu grain analysis for different process conditions and Cu foils



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LPCVD



Failed measurement

APCVD can have bigger but rougher Cu grains than LPCVD

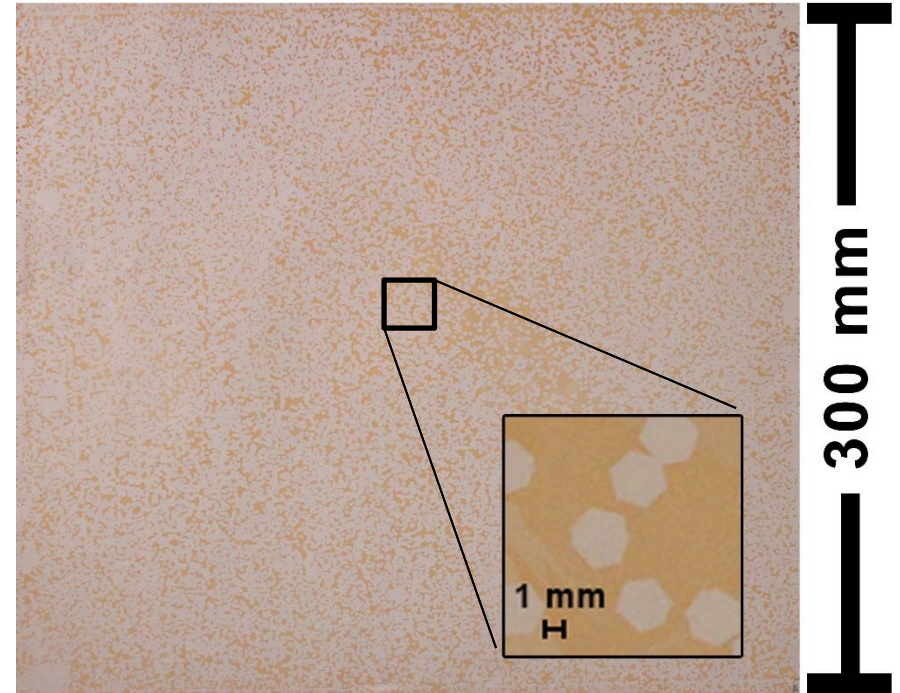
# EasyGraphene™ Processing Technology enables uniform CVD Growth over a large area

Sub-monolayer of CVD graphene film growth, i.e. growth process was terminated before full monolayer coverage.

→ Allows simple process uniformity testing

Image on the right shows 2-3 mm hexagonal CVD graphene grains spread uniformly over 300 mm size Cu foil.

CVD graphene growth uniformity is visible by naked eye - without any instrument.



Sample was automatically offloaded at 200 °C to oxidize the non graphene covered Cu foil increasing the optical contrast between graphene islands and substrate.



## EasyGraphene™ Processing Technology enables a wider CVD graphene growth processing window

Some benefits of patent pending technology that have been demonstrated thus far:

- Operates at low, medium and atmospheric pressure
- Operates at low to high process temperatures
- Substantially independent of total gas flow rate
- Processing cost and time is reduced compared to traditional CVD graphene processes while providing similar results

Sample on the right was done with in 1hr growth time.

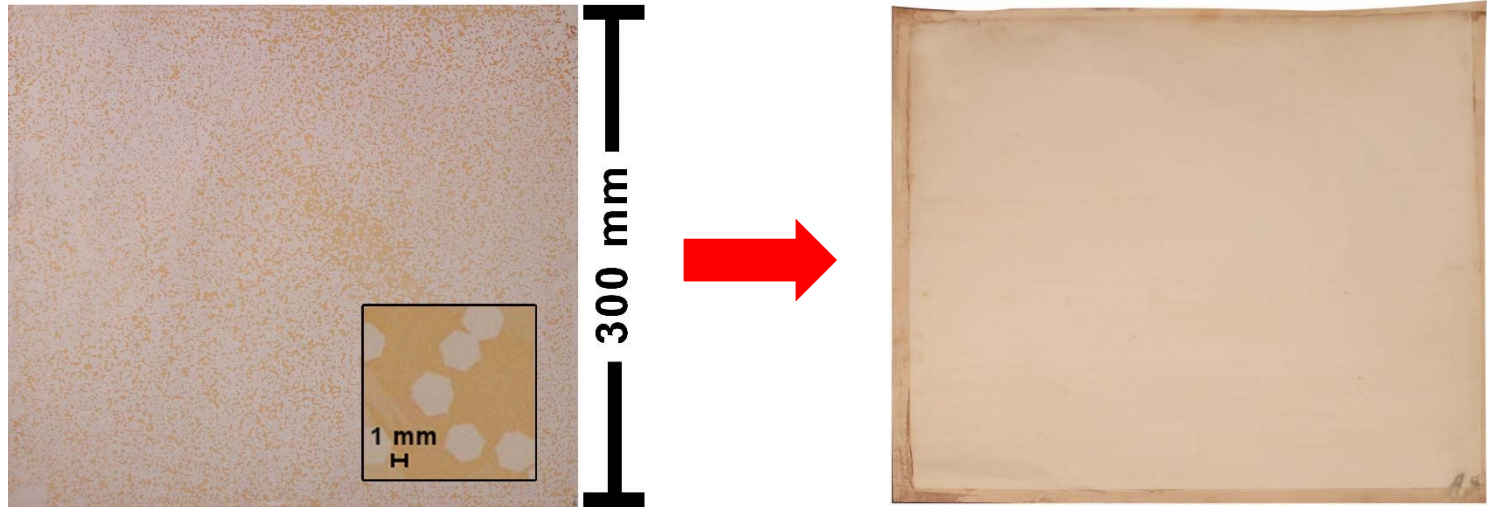
This compares to an equivalent 5-7 hrs growth time with traditional CVD graphene processes.



# EasyGraphene™ Processing Technology enables complete CVD graphene growth



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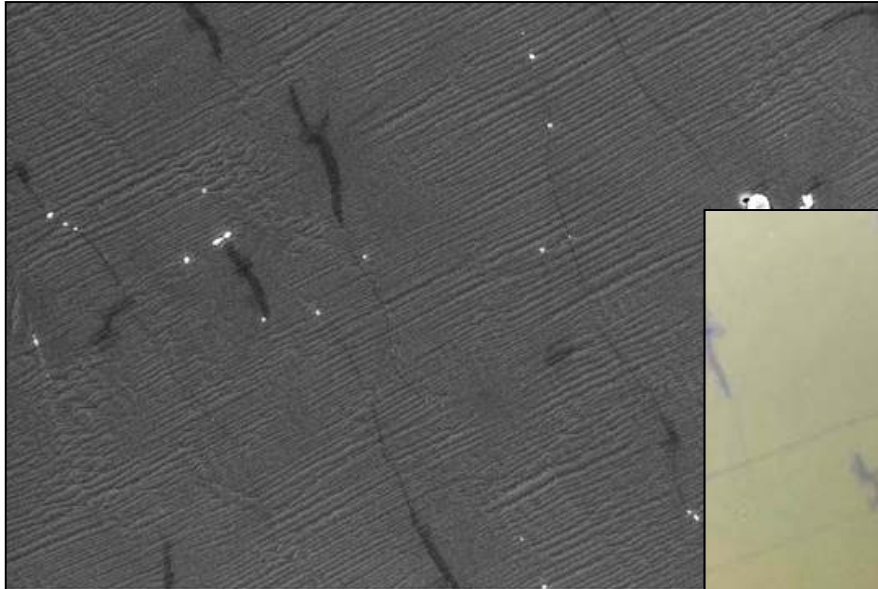
In a first growth step large graphene grains are grown. In additional growth process steps the space between these large grains is closed with a minimum content of multilayer regions:

“Large scale atmospheric pressure chemical vapor deposition of graphene”, Ivan Vlasiouk, et. all, CARBON 54 ( 2013) 58 –67.

# SEM image is a good indication of graphene quality



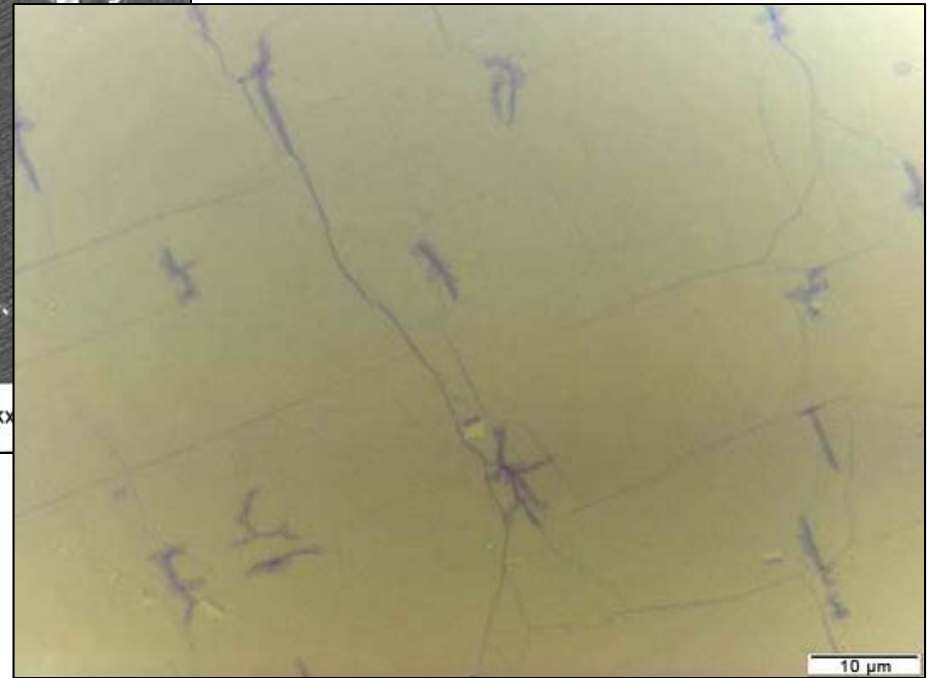
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2  $\mu\text{m}$   
EHT = 10.00 kV Mag = 10.00 K X  
Signal A = InLens Stage Tilt = -0.1 ° N4-2756U-B-75um-EP-10KX  
WD = 4.0 mm Date :5 Feb 2014

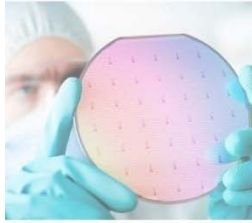
SEM image before transfer

Optical image after transfer



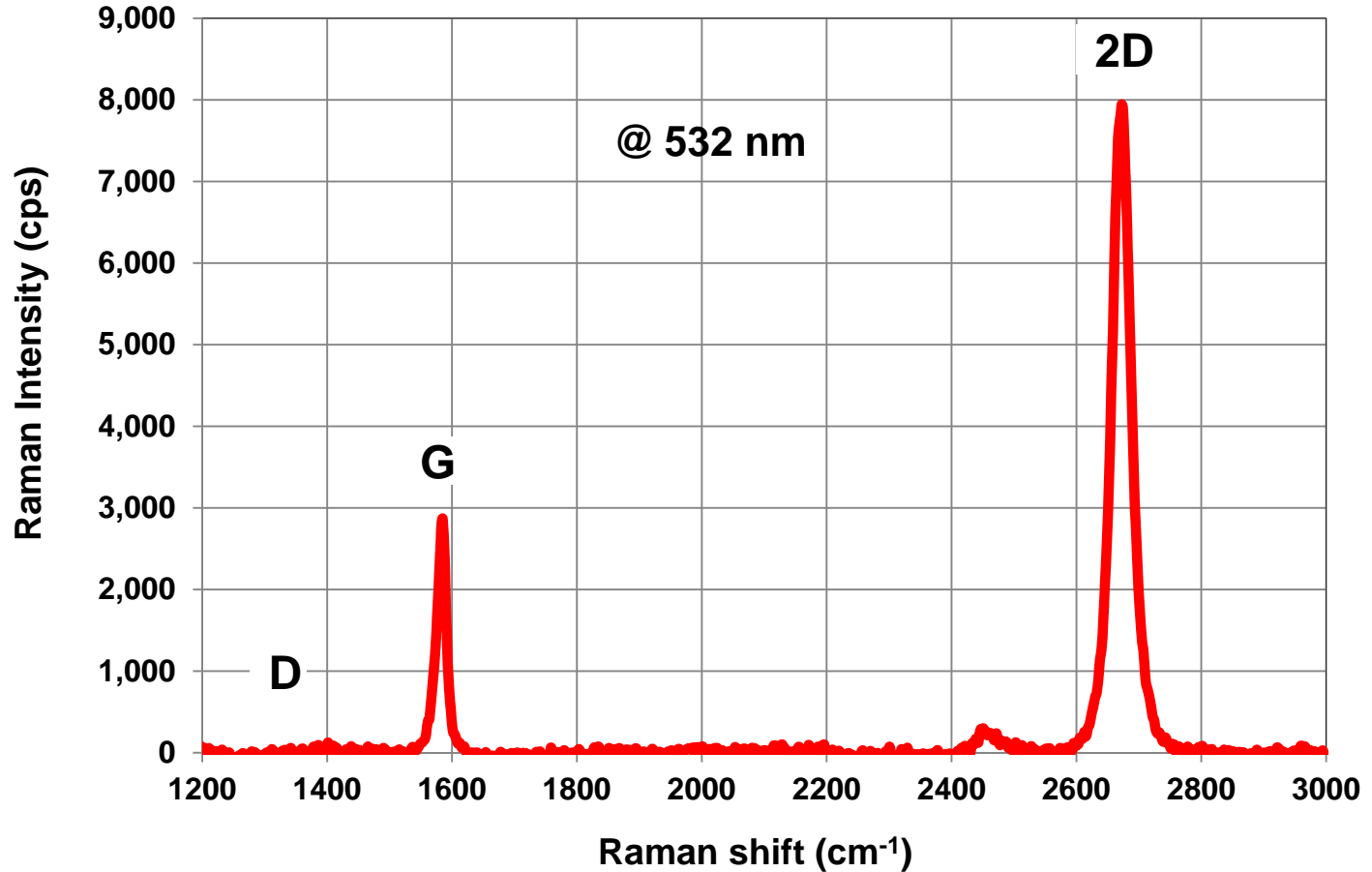
This rejected CVD graphene sample shows similar multilayer regions before and after graphene transfer using a bubbling electrochemical method.

# EasyGraphene™ Raman characterization



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Raman spectrum of CVD graphene transferred onto 280 nm SiO<sub>2</sub>/Si wafer



After transfer CVD graphene film onto glass shows improved 2D/G peak ratio (>2) due to less interference from the flatter Cu foil surface.



## Summary:

- **CVD** Equipment Corporation continues to expand capabilities in:
  - Equipment design
  - 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.
- Our **EasyGraphene™** platform is designed for both R&D and pilot production scale-up development efforts. Together with our patent pending hardware and process solutions it also enables straightforward scaling to higher production quantities.
- Scaling of high quality CVD graphene from 50 mm to 300 mm has been demonstrated.
- We continue to work on further capacity increases and quality.
- We collaborate to accelerate the commercialization of CVD graphene for a wide range of applications.

[www.cvdequipment.com](http://www.cvdequipment.com)

[www.easygraphene.com](http://www.easygraphene.com)

