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Raman Imaging: A Critical Tool for Realizing Graphene and Graphene Composite Materials

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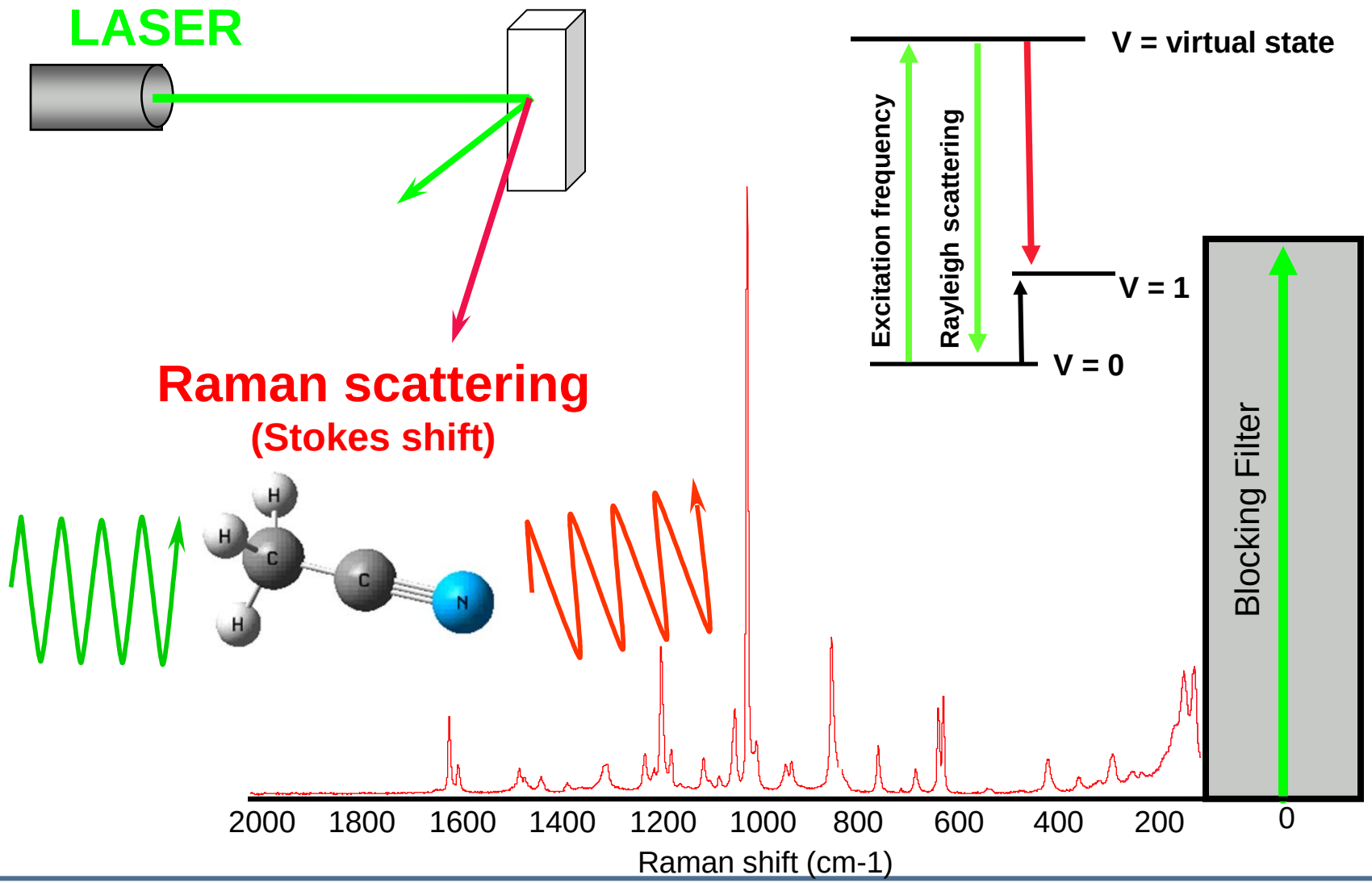
Thermo Fisher Scientific

Overview

- Fundamentals of Raman spectroscopy
- *Mode*rn instrumentation
- The Raman Characterization of graphene
  - Point measurements
  - Mapping and Imaging
- Raman imaging examples
  - Partial growth graphene
  - Graphene as a protective coating material
- Confocal Raman imaging of graphene
  - Cross sectional and Z-stack measurements

Raman spectroscopy



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Modern Raman Instrumentation

- Instruments of the past
  - Large
  - Complex
  - Difficult to maintain
  - Required dedicated operator

- Modern instrumentation
  - Integrated and compact
  - Easy to use
  - Very low maintenance
    - Automated alignment
    - Automated calibration
  - True walk up instruments

Thermo Scientific Family of Dispersive Raman Instruments

Raman Spectroscopy and Graphene Characterization

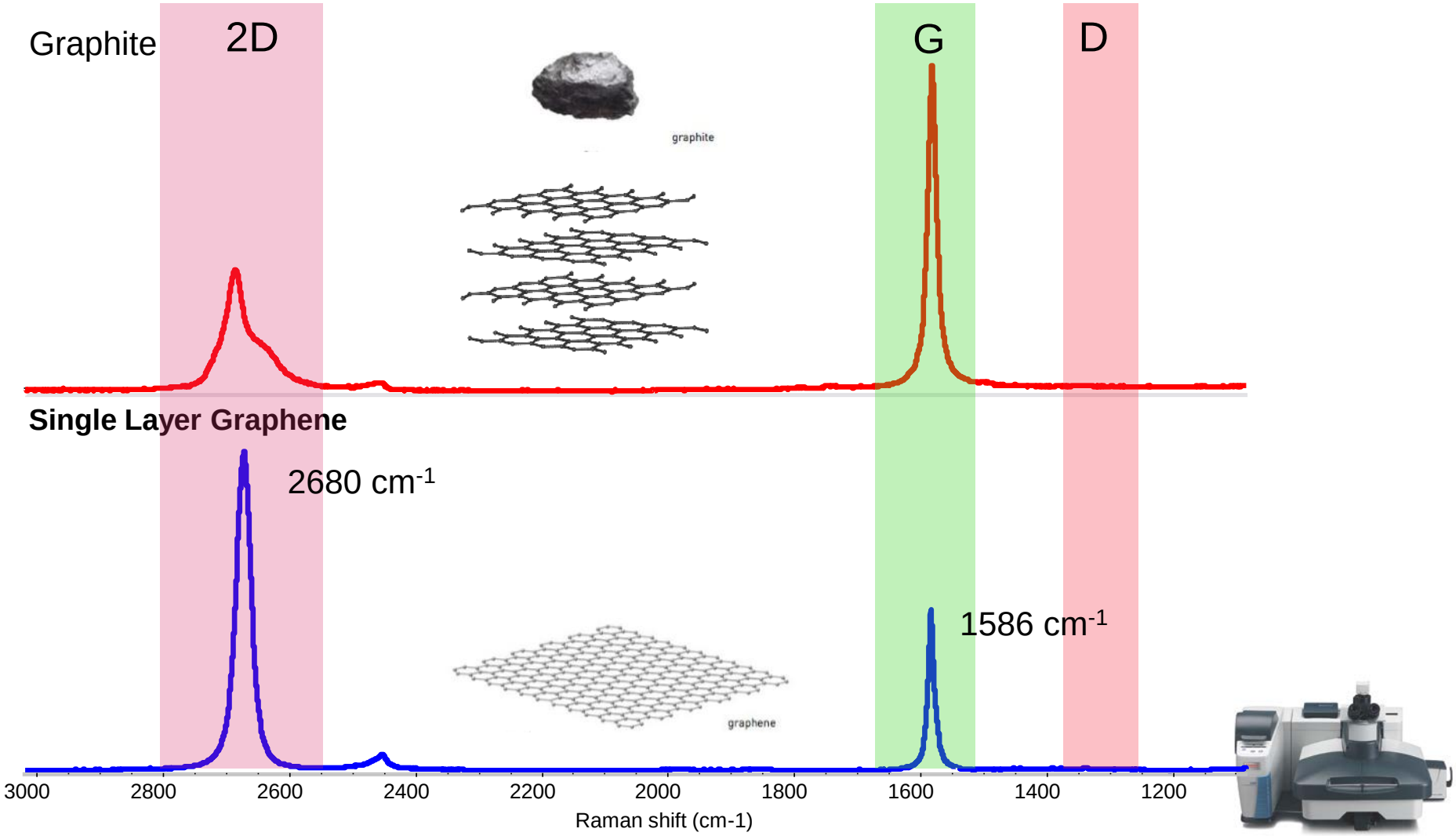
- Techniques used for characterization of graphene
  - SEM/TEM
    - Nanometer scale morphological information
    - Sample preparation needed
    - Detailed elemental information lacking in detailed molecular information
    - Requires vacuum
    - Often destructive measurement
  - XPS
    - Nanometer scale surface information
    - Oxidation state and fuctinalization information
    - Requires vacuum
  - AFM
    - Nanometer scale morphological information
    - Topological, mechanical
    - Lacking in molecular or chemical information

Raman Spectroscopy and Graphene Characterization

- Raman spectroscopy fills the chemical/ molecular “hole”
  - Provides specific and direct chemical information
    - Detailed structural information
    - Sensitive to the local environment
      - Stress and strain
  - No Sample preparation
  - Non destructive
  - No vacuum required
  - Rapid collection times

- Raman microscopy benefits
  - Surface and sub-surface characterization
  - Mapping/imaging capabilites
    - High spatial resolution
      - Sub micron x and y
      - Micron scale in the Z

Graphene: Raman Spectral Features



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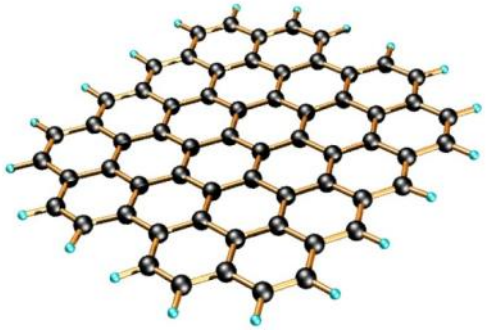
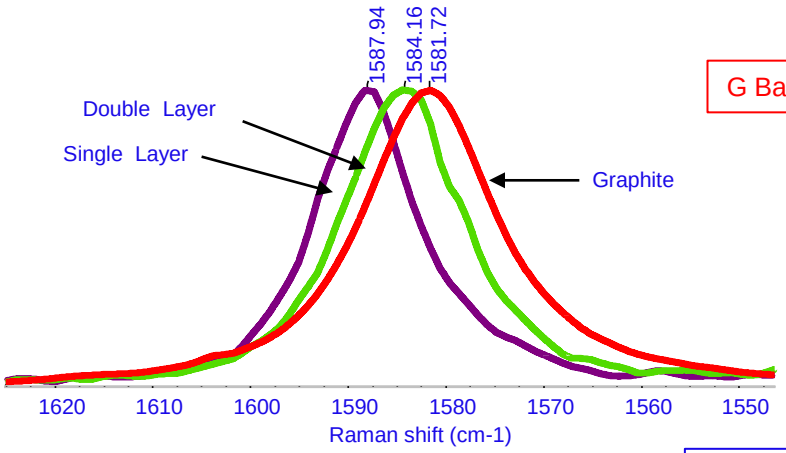
Raman Spectrum of Graphene – Principle Bands

- G band
  - Peak position and relative intensity is sensitive to
    - Layer thickness
    - Doping
    - Strain
- D band
  - Peak intensity is sensitive to
    - Presence of defects or disorder
    - Sampling in proximity of an edge
    - Chemical modification
      - Increase of sp3 hybridized C bonding at the expense sp2 hybridzed C bonding
- 2D band
  - Peak position, band shape, and intensity sensitive
    - Layer thickness and interlayer orientation
    - Strain



Raman Spectroscopy – Graphene Layer Thickness

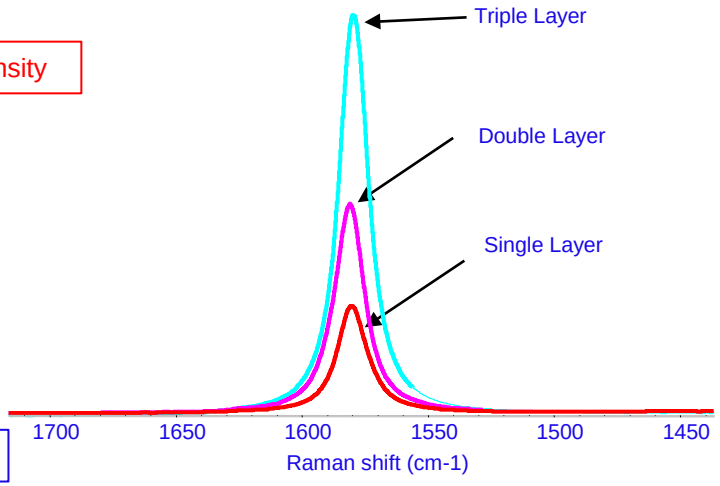
$$\omega_G = 1581.6 + 11/(1 + n^{1.6})$$



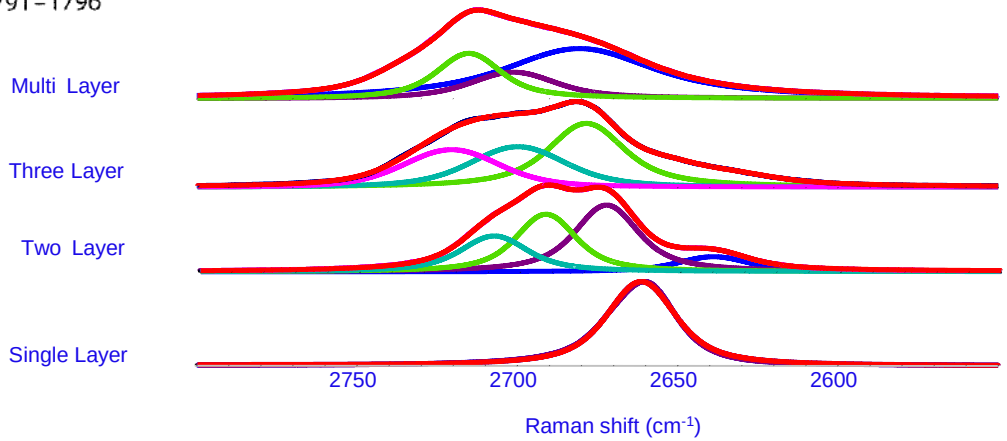
Wang,Hui; Cao,Xuewei; Feng,Min; and Lan,Guoxian
J. Raman Spectrosc. **2009**, *40*, 1791–1796

G Band Position and Intensity

Linear increase in G band intensity with # of layers present



2D Band Shape Analysis



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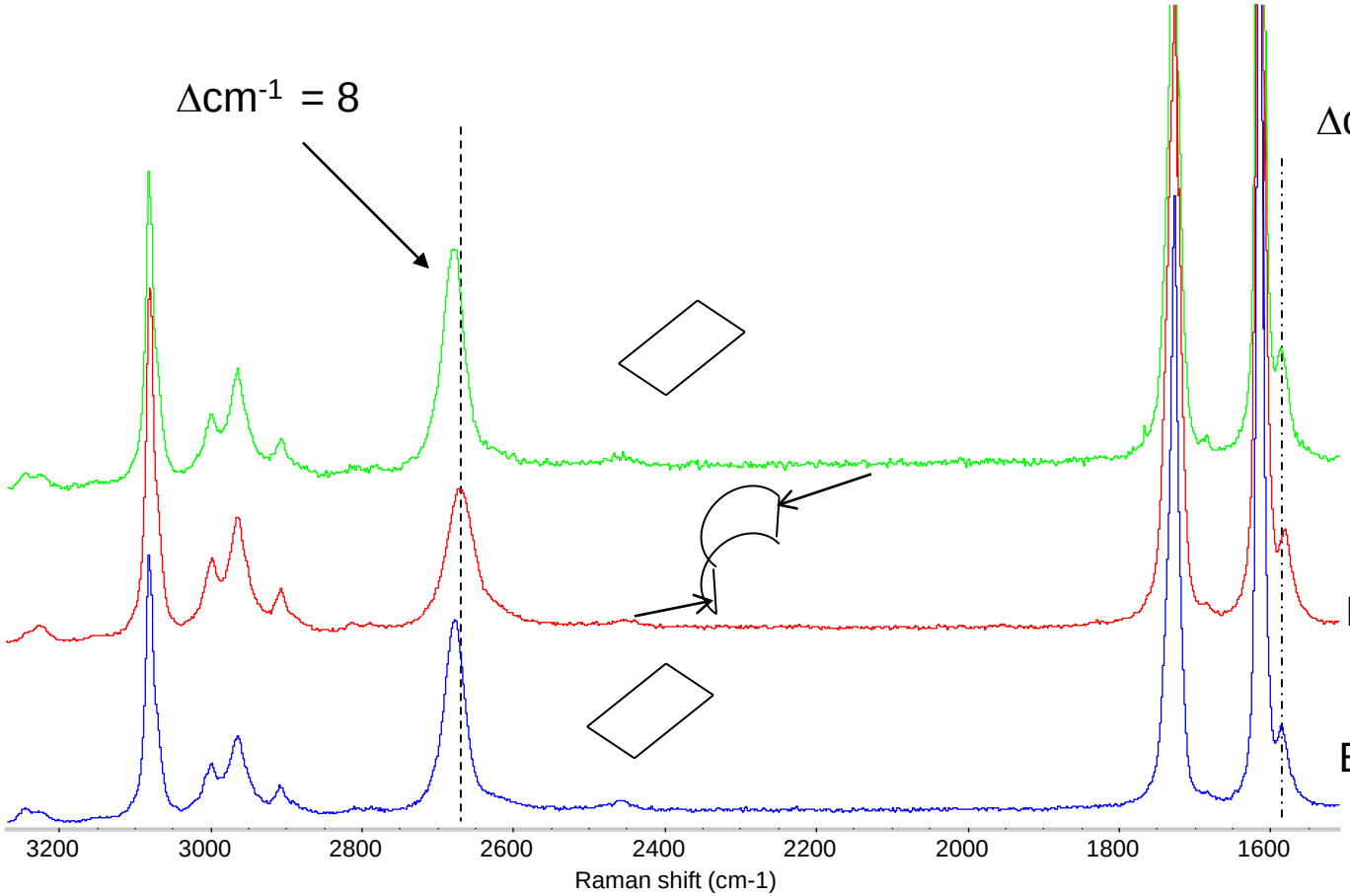
The Effect of Strain on Graphene



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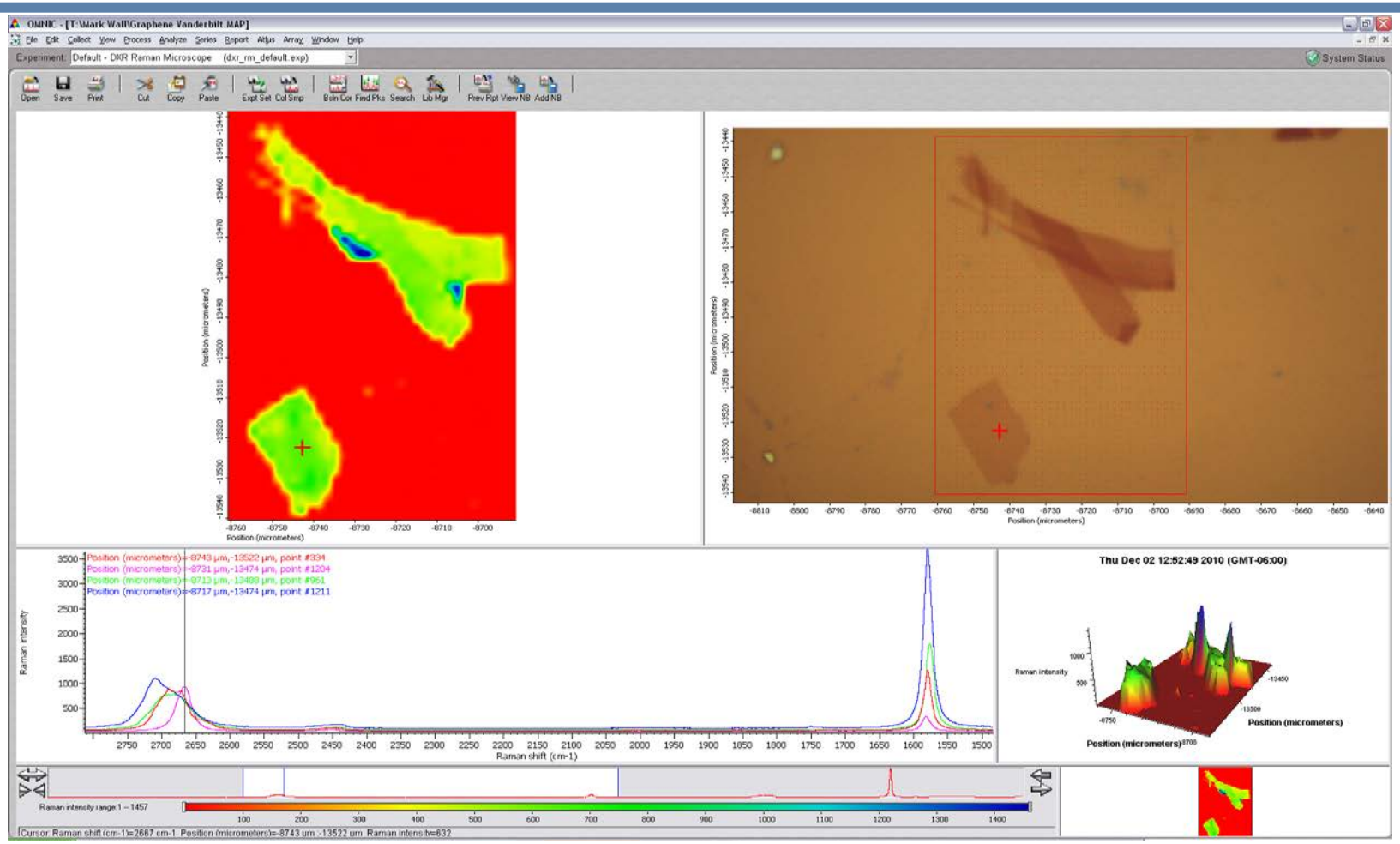
Graphene Characterization – Raman Mapping



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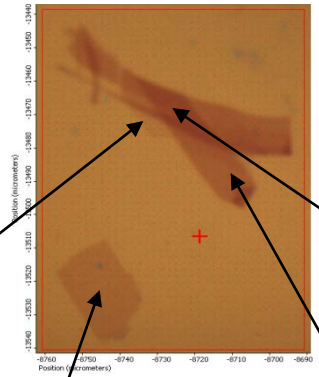
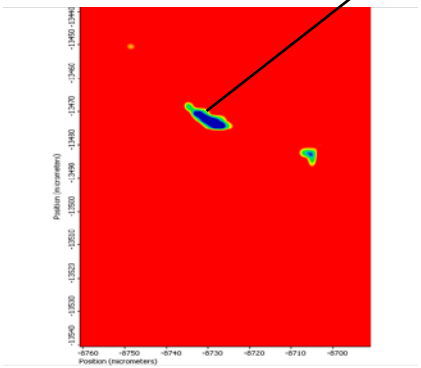
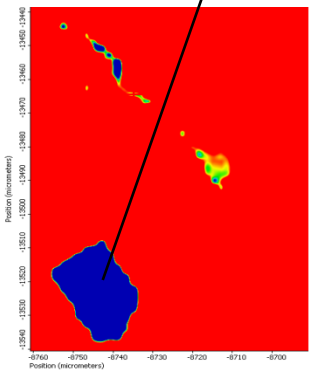
Graphene Characterization – Raman Mapping

- Discriminant analysis results based upon the 2D band

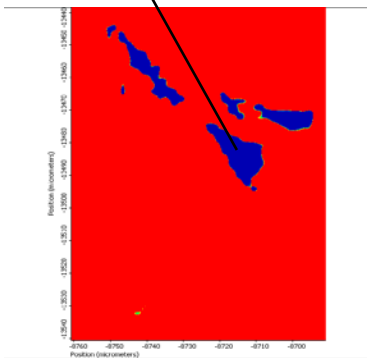




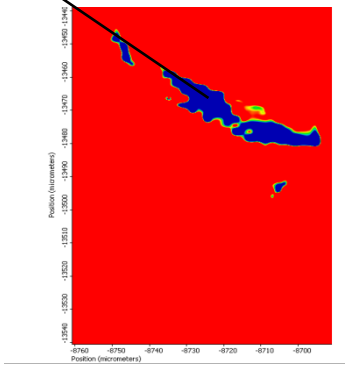
Single Layer



Double Layer



Triple Layer



Multi Layer

TQ Analyst

Chemometrics

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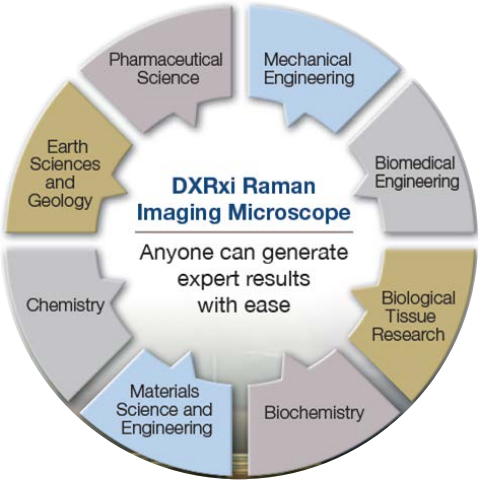
The DXRxi Raman Imaging Microscope

A total imaging system: hardware and software integration combines **powerful performance** with **image-centric** analysis and **ease of use**

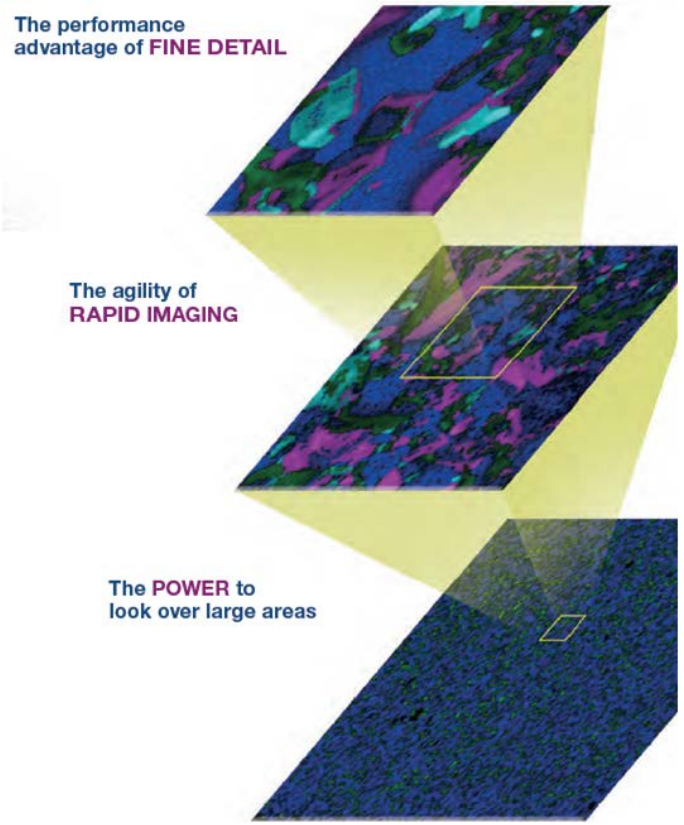
*A completely **new approach** to Raman imaging!*

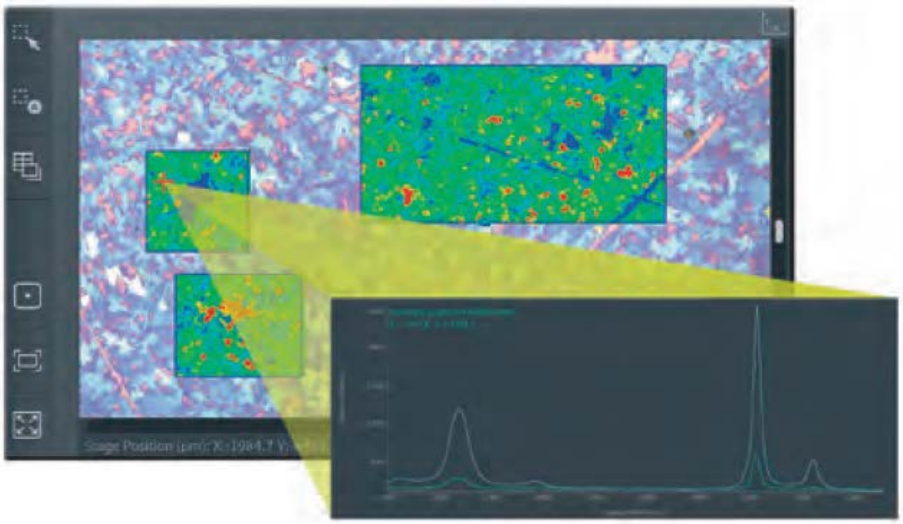
Raman Imaging – A New Tool for Rapid Characterization

The instrument should provide a tool for all users, from basic to advanced



Advanced materials analysis benefits from an image-driven approach





Emphasis on microscopy, powered by spectroscopy keeps the answer in focus

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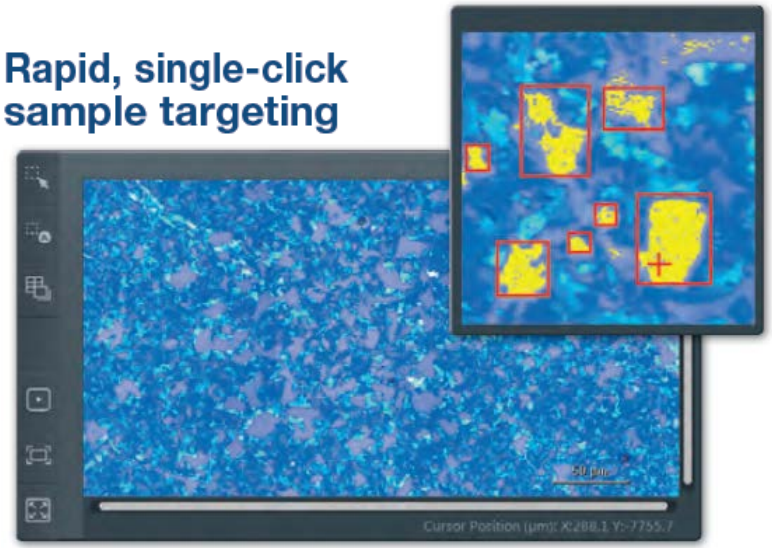
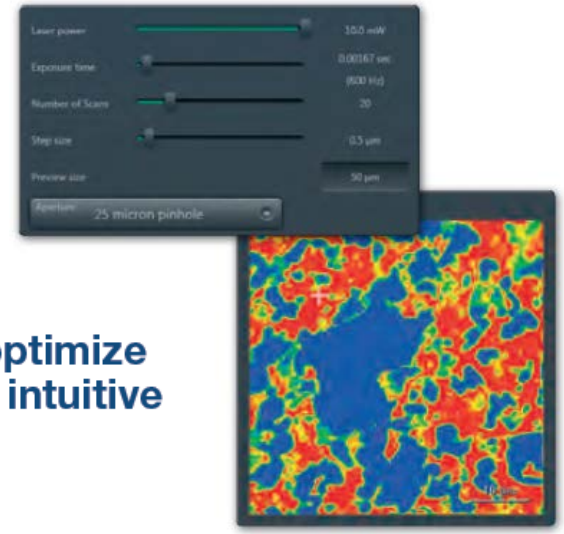
Intelligent Workflow with Excellent Flexibility

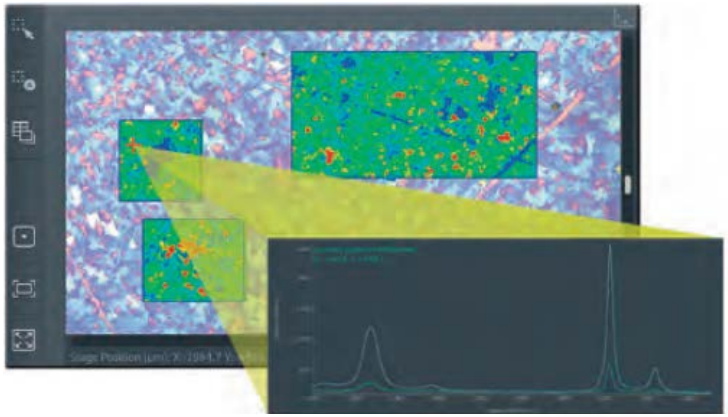
1 Rapid, single-click sample targeting



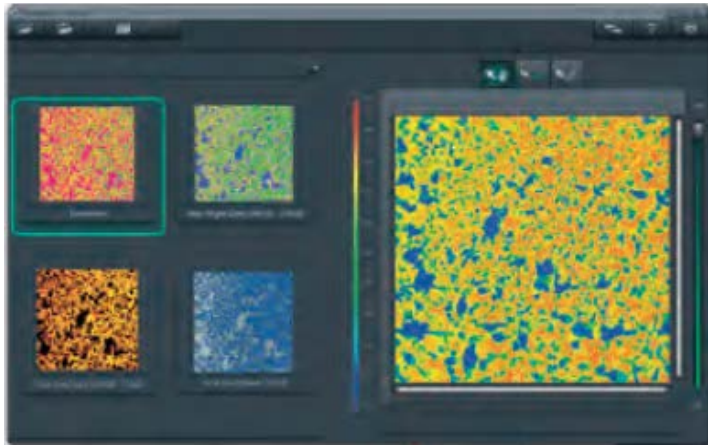


2 Confidently optimize settings with intuitive controls

3 Quickly prioritize multiple regions of interest and run



4 Information-rich images reveal a multitude of material characteristics



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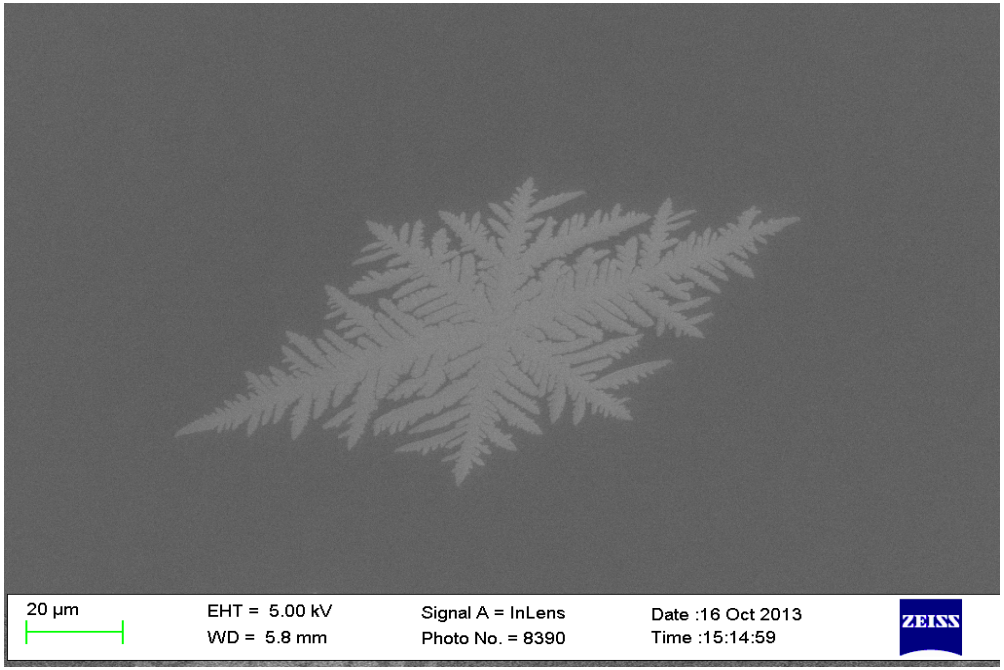
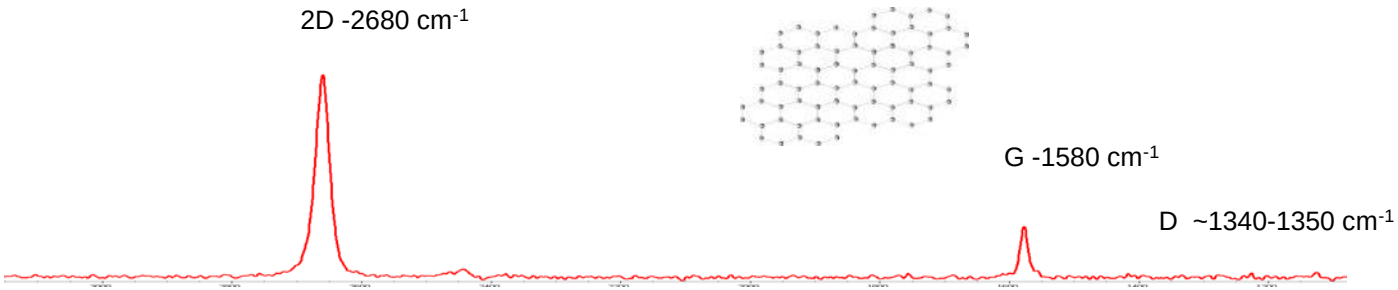
SEM Image of Dendritic Growth Graphene

- SEM illustrates the morphological characteristics that result from particular CVD deposition conditions
- Other techniques are required to obtain deeper insight



Rapid Raman Imaging of Partial Growth Graphene

- Provides vital information to understand growth dynamics
  - Allows determination of number of layers present
  - Provides information about the density of defects during growth
  - Information can be used to understand critical synthesis parameters and mechanisms that govern nucleation and growth of graphene
- Information from Raman can be used to optimize synthesis graphene
  - Minimize defect densities
  - Drive growth towards single crystal graphene
- Rapid imaging allows for bigger areas to be analyzed far faster than ever



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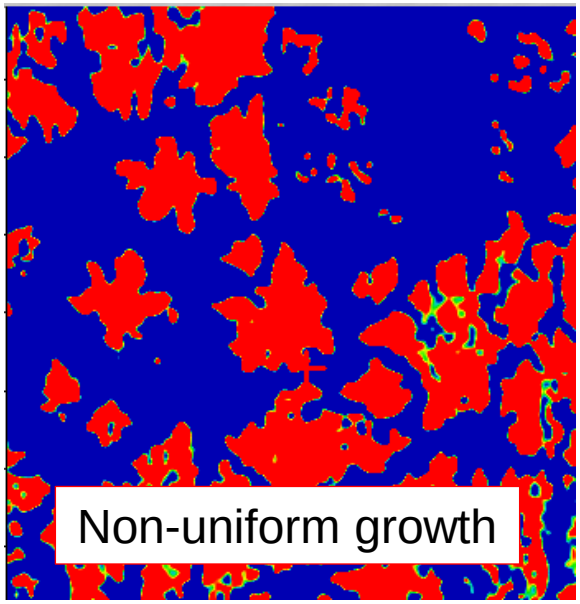
Analysis of Graphene, 532nm laser

Ratio of the 2D to G band of graphene:



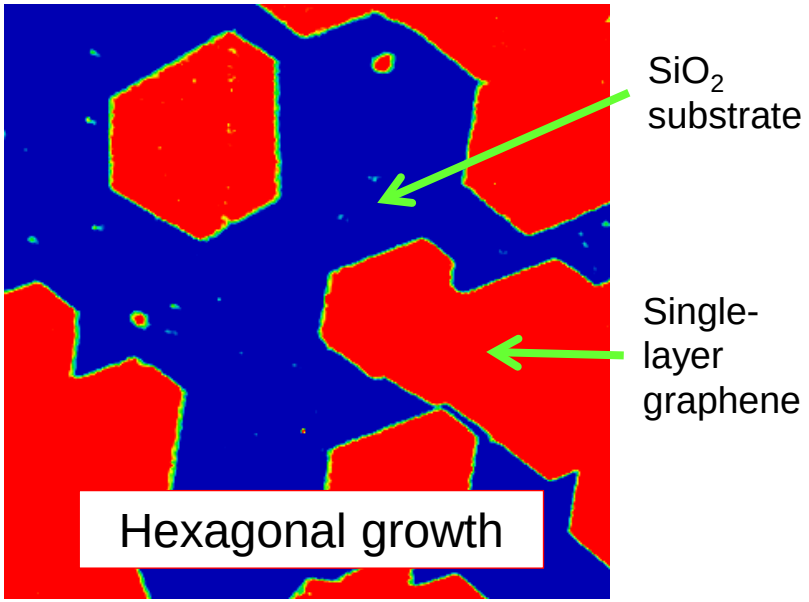
50 x 50 μm surface area

10,000 spectra!!!

Acquisition parameters: 100 Hz (10 ms/spectrum)

~16.7 minute collect time!!

MCR of graphene:



175 x 175 μm surface area

122,000 spectra!!!

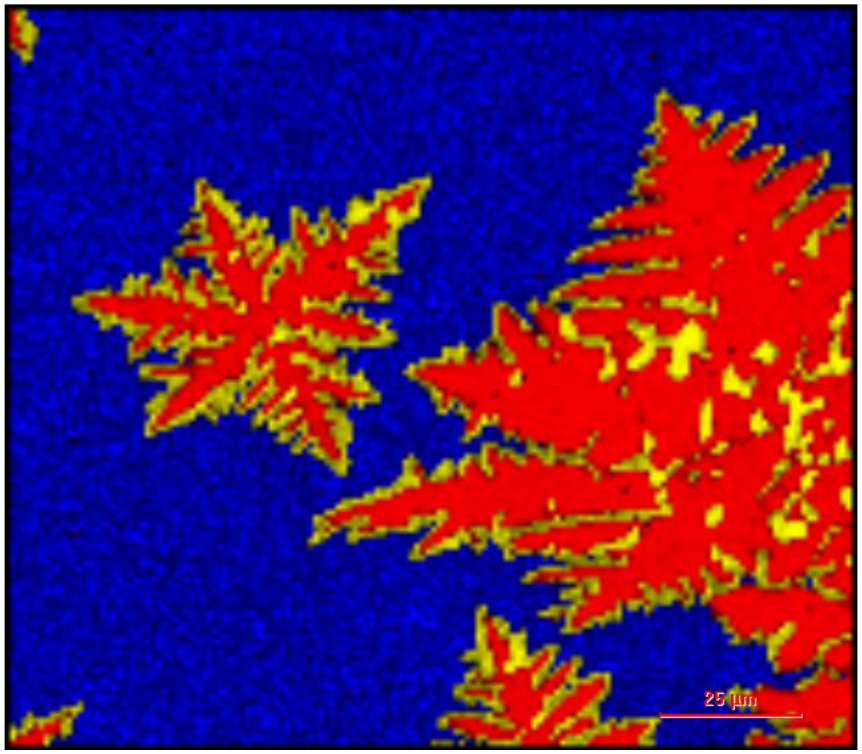
0.5 μm pixel size

Acquisition parameters: 100 Hz, 10 scans

~3.4 hour collect time!!

*Note: This graphene was initially grown on copper and then transferred to a silica substrate because the copper is a significant source of interference

Analysis of Graphene on a Copper Substrate



Graphene grown on copper and analyzed ***on the copper*** with the 455nm laser

$$I_{scatter} \propto \frac{1}{\lambda_{ex}^4}$$

455nm laser
150 x 150 µm surface area
90,000 spectra!!!
2.0 µm pixel size
Acquisition parameters: 100 Hz (10 ms/spectrum), 4 scans

Copper Substrate Oxidized Copper Single-layer graphene

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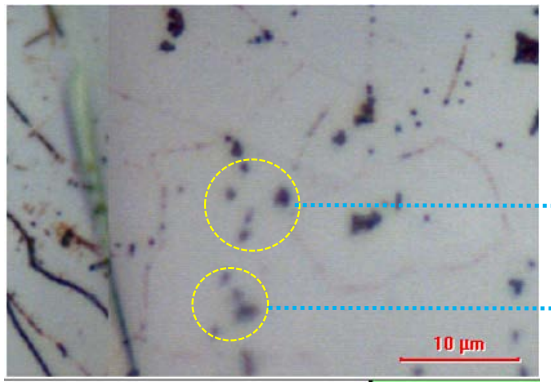
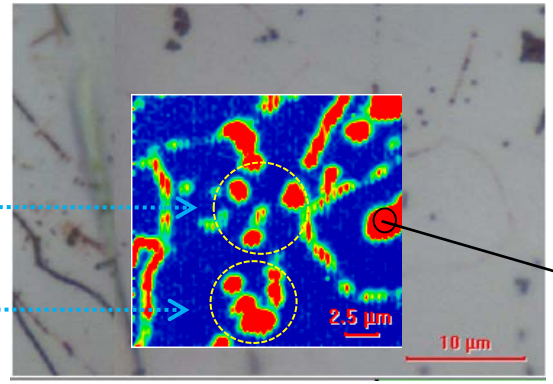
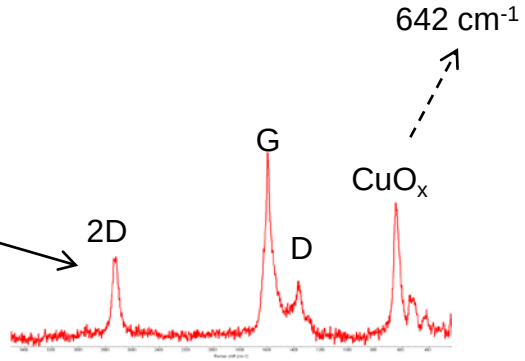
Graphene as a Protective Thin film

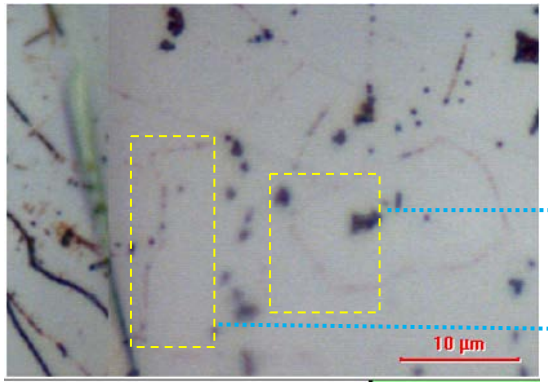
Chemical images based on Intensity of 642cm^{-1} band



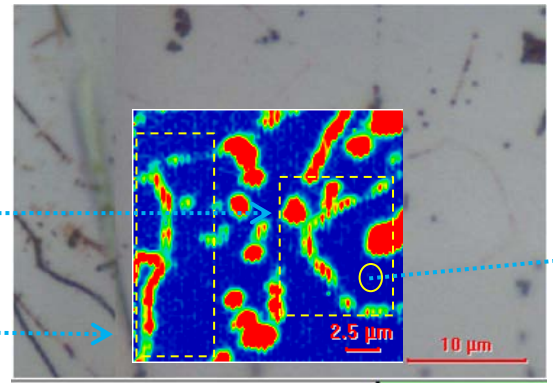




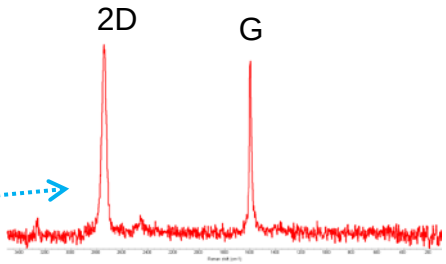
Raman Spectrum Red Area



Optical Image Graphene on Cu



Optical Image/ Chemical Image Overlay Graphene on Cu



Raman Spectrum Blue Area

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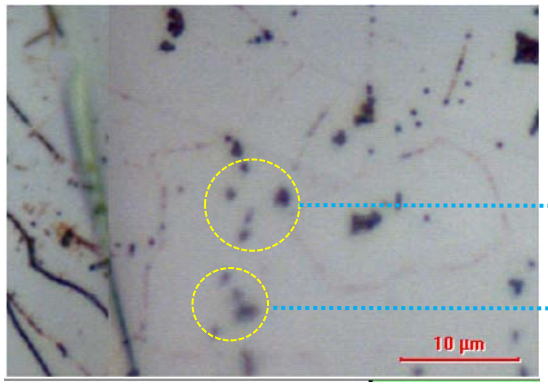
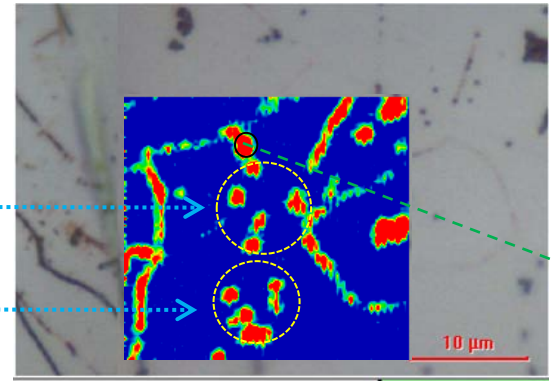
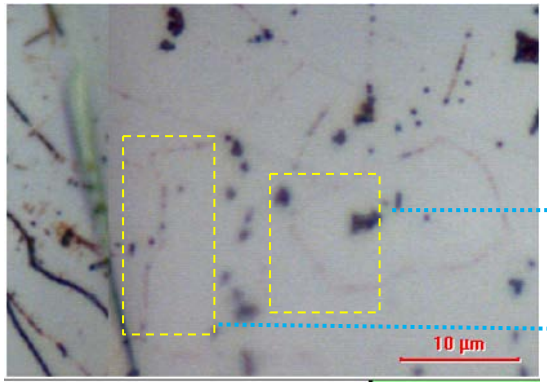
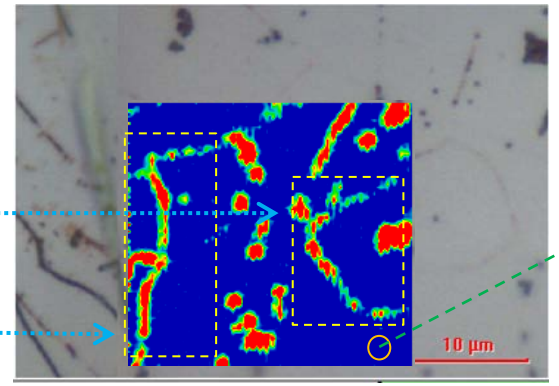
Chemical images based on
Intensity of 1370 cm^{-1} band



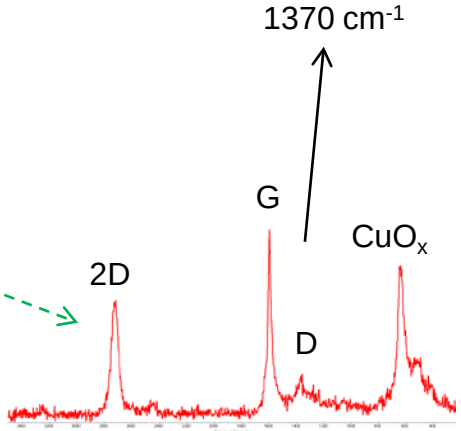




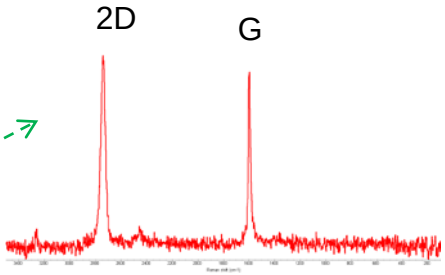


Optical Image Graphene on Cu

Optical Image/ Chemical Image
Overlay Graphene on Cu



Raman Spectrum on Red Area



Raman Spectrum on Blue Area

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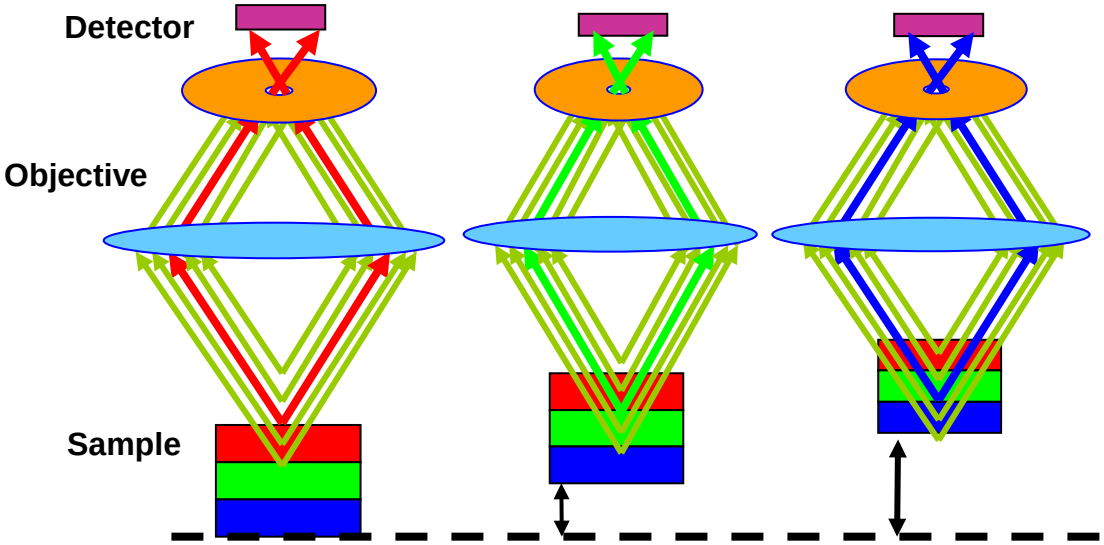
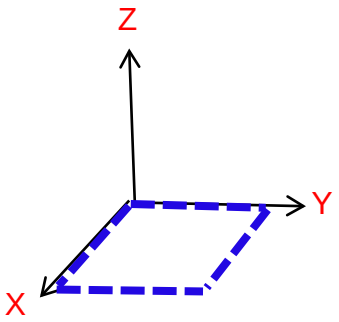
DXRxi Confocal Microscope

- DXRxi is a fully confocal microscope
  - Provides for higher spatial resolution
    - Achieves <1 µm measured x-y resolution
  - Provides for depth profiling of optically clear samples
    - Achieves 2 µm depth resolution
  - Provides for increased rejection of fluorescence from substrate

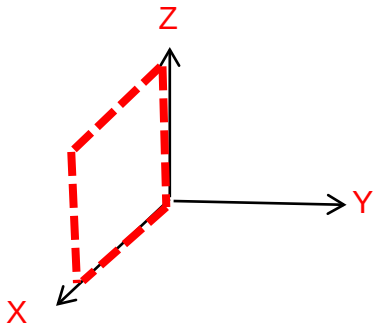


DXRxi Imaging -Sampling

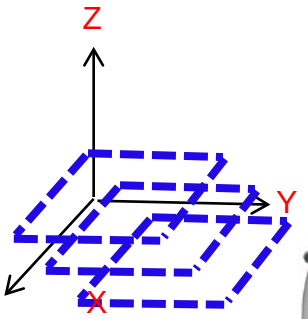
- Raman/Chemical Images – Image Planes
  - XY Image plane
    - Surface image – most common image
    - Subsurface if the z position is below the surface



  - XZ Image plane
    - Confocal
      - Surface and subsurface
      - sample needs to be transparent
    - Also referred to as Cross-section

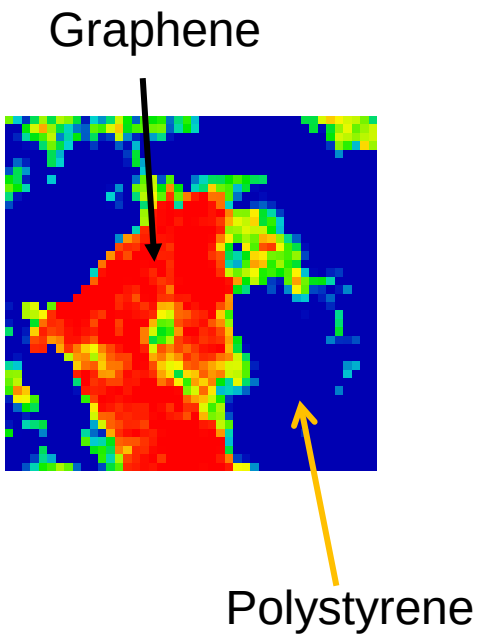


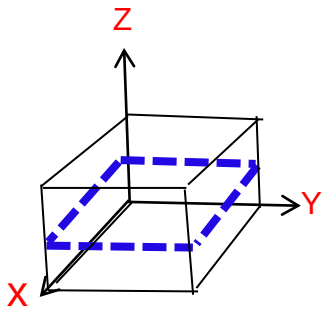
  - Image stack of XY Image planes
    - Confocal – sample needs to be transparent
    - Z axis image stack
      - Volume rendering capable



Confocal Raman Imaging Optical Cross Sectioning

Sub-surface xy Raman Image of Multilayer Graphene Flakes in Polystyrene

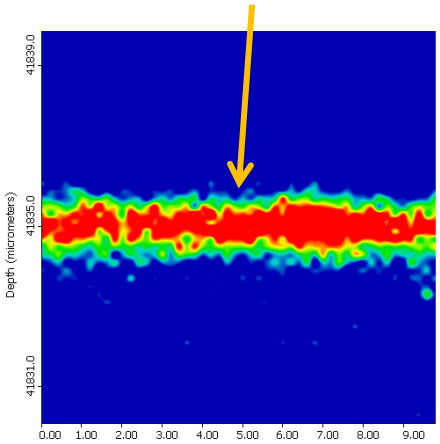




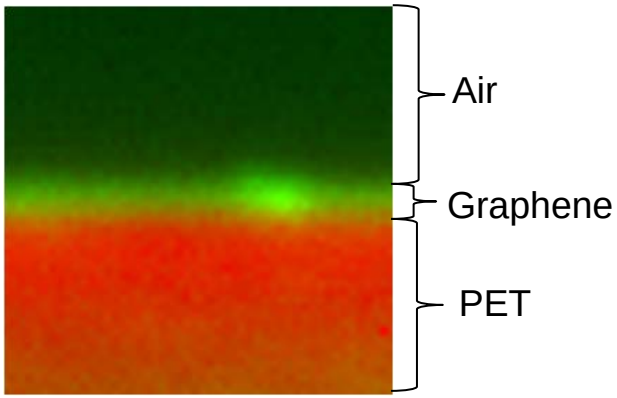
Cross- Section Analysis – Graphene on PET

Sub-surface xz Raman Image of Single Layer Graphene on PET

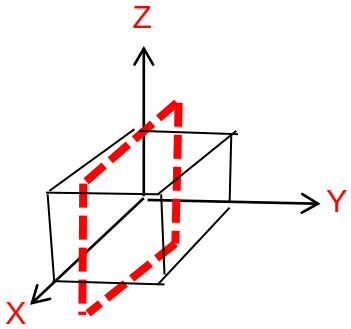
Graphene



Correlation Profile



MCR Profile

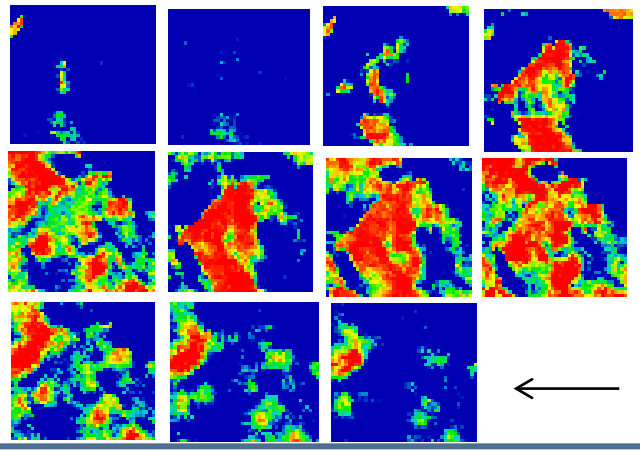


Multilayer Graphene Dispersed in Polystyrene Image Results

- Graphene was dispersed in Polystyrene at 1% w/w
- Confocal Raman images collected on Thermo Scientific DXRxi Raman Imaging Microscope
  - 455 nm excitation 3.7 mW laser power at sample
  - Raman spectra collected at a rate of 35 spectra/sec with 35 co-adds
  - 2 μM x 2μM image pixel size
  - 11 xy chemical image planes (slices) were collected over an area of 82 μM x 86μM - 20,000 spectra for the image stack

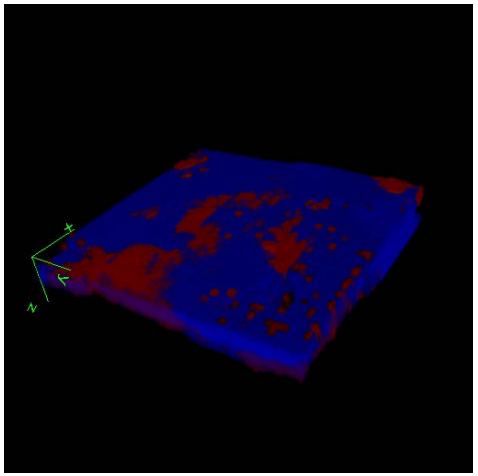
Top Image ⟶

Image Intensity Based on the
2D Band of Graphene at 2711 cm^{-1}



⟵ Bottom Image

Graphene Dispersed in Polystyrene Z –Stack Slices



3D Volume Rendering

Top

Distance between Image Planes is 2 microns

Slice 1

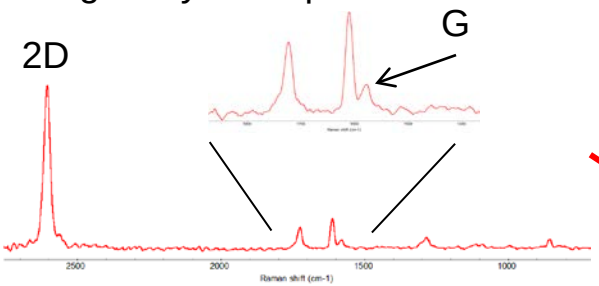
Red – Graphene
Blue - Polystyrene

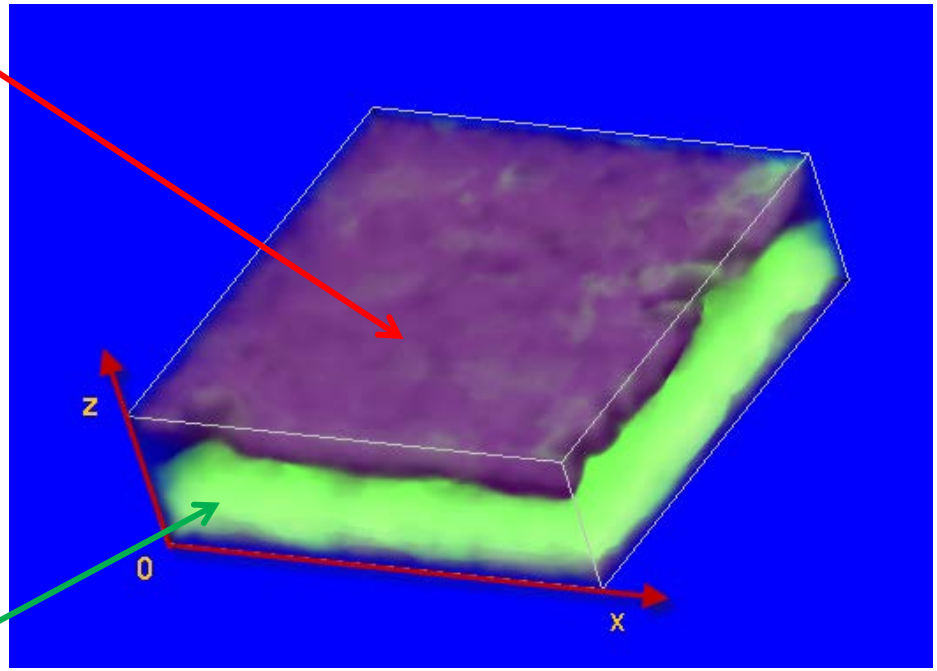
Slice 11

Bottom

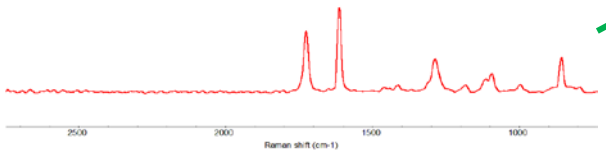
Raman Imaging – Confocal Volume Rendering

Single Layer Graphene





(Poly)ethylene terephthalate



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Summary

- *Raman Spectroscopy was presented demonstrating the usefulness of Raman Spectroscopy for characterizing Graphene*
- *Mode*rn instrumentation was discussed
- Raman imaging examples were presented
  - Partial growth graphene
  - Graphene as a protective coating material
- Confocal Raman imaging of graphene
  - Cross sectional and Z-stack measurements

Questions?

Thank You for our time and attention!

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