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Shedding New Light on Materials Science with Raman Imaging

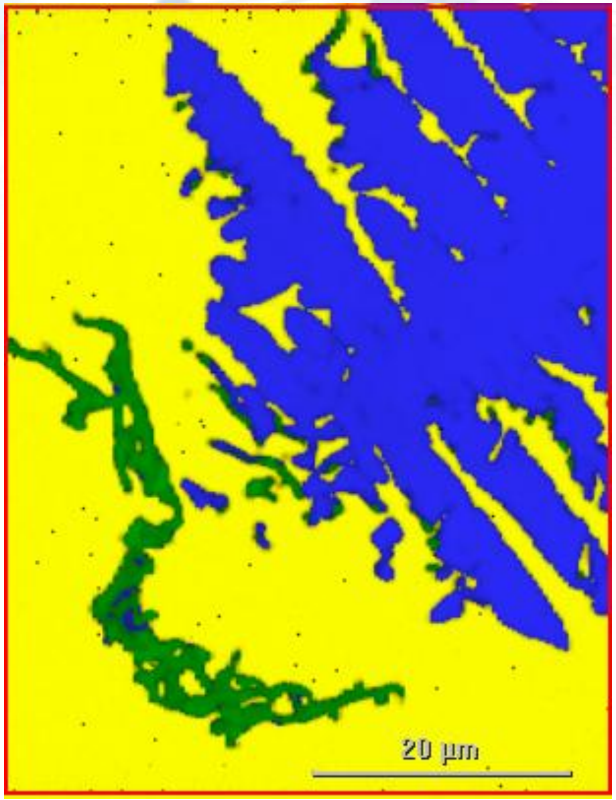
Robert Heintz, Ph.D.
Senior Applications Specialist

PITTCON CONFERENCE & EXPO 2015

The world leader in serving science

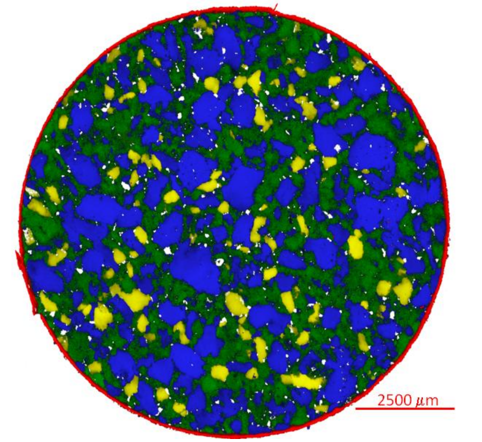
Raman Imaging – Provides More Information

- Microscope problems aren't just about points, they're about areas and images!
- Raman imaging extends the advantages of Raman analysis across the sample
- Raman imaging generates visual images depicting differences in molecular structure and chemical environment
- Raman images provide unique views of the samples that are not always readily apparent in other forms of microscopy



Single Layer Graphene
Multilayer Graphene
Silicon Substrate

Raman Imaging Solves More Problems

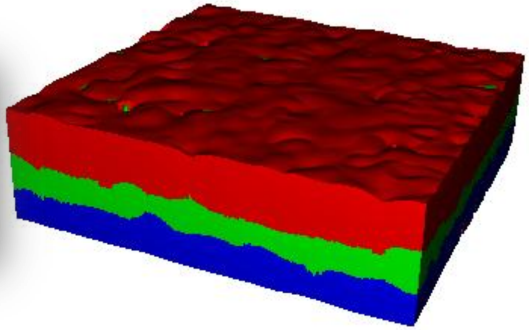


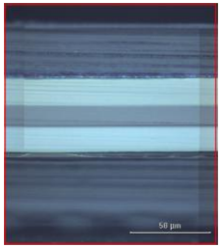
Pharmaceuticals

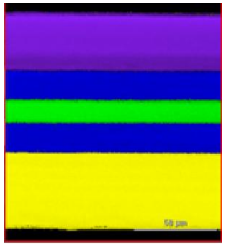
Full tablet imaging for **content uniformity** and formulation analysis

Polymers and Packaging

Subsurface analysis to **identify inclusions ,** **visualize defects,** and **verify layers** without sample preparation

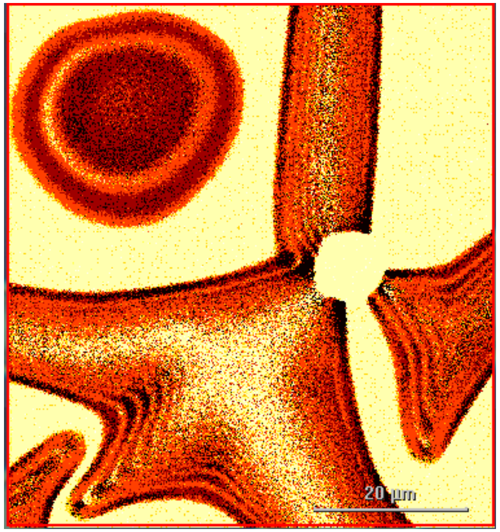




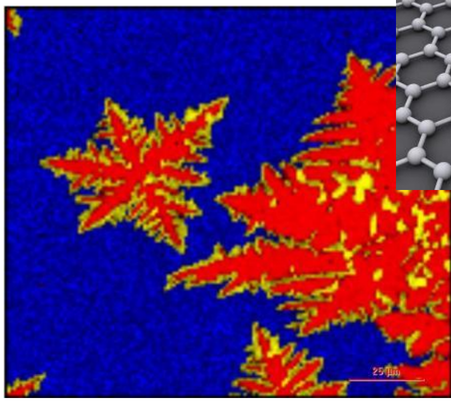


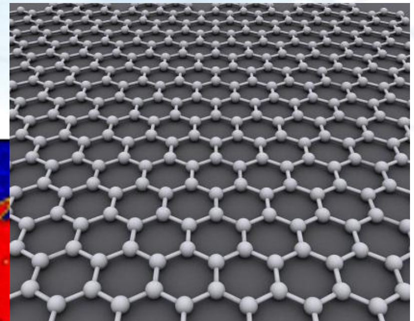
Semiconductors and Thin Films

Reveal variation in **stress distributions and morphology,** identify contaminants and defects



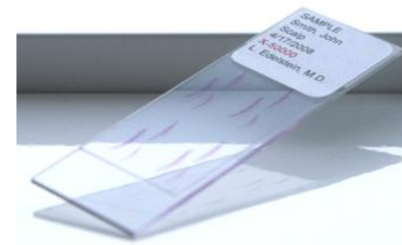
More Raman Imaging Application Areas …





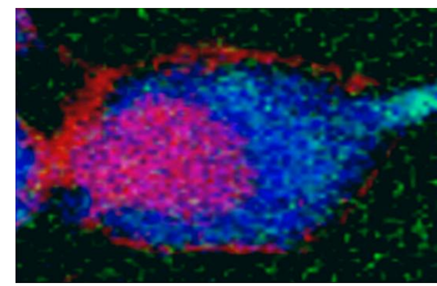
Life Science Applications

Imaging of living cells and spectroscopic staining of cancerous tissue to **visualize components and access differences and distributions**



Carbon Nanomaterials

Analysis of graphene **growth mechanisms and distribution of defects**

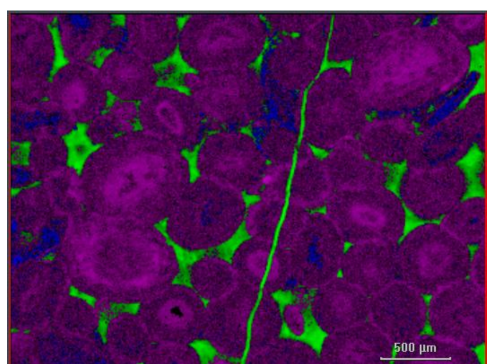


Live cell - RGB Image

- Lipids
- Cytohrome C
- Protein

Geology / Mineralogy

Non-destructive evaluation of inclusions and rapid **identification and distribution of minerals** over large-areas



The Thermo Scientific™ DXR™xi Raman Imaging Microscope

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

This Instrument is easy to operate, allowing researchers to focus on their own area of expertise – not on the technique

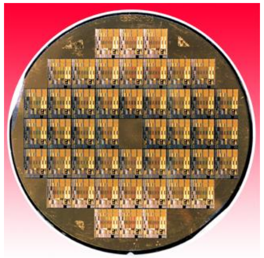
Highlights of the DXRxi Raman Imaging Microscope

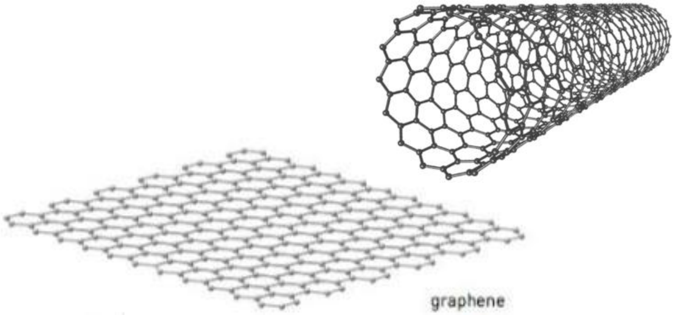
- The software provides a data pipeline that synchronizes the EMCCD detector with a state of the art motorized stage to manage and process the vast amounts of spectroscopic data generated at astounding speed
- This provides for exceptional Raman imaging performance
- The user interface was developed with imaging in mind and is both easy to use and has a clean and uncluttered design
  - Some Software Highlights
    - Sliders allow for easy selection of collection parameters while getting immediate visual feedback on how these selections effect the data
    - A live Raman imaging preview allows for quickly surveying the sample to identify areas of interest and evaluate image quality before investing the time required for imaging the whole area
    - Single and multiple region selection allows the user to define multiple areas of interest and to set the collection parameters independently for each region
    - A range of analysis options allow for generation of informative visual images from the spectroscopic data using a variety of different profile types including MCR (multivariate curve resolution). These profiles are available both live during data collection as well as post collection options

Raman Imaging Provides a Unique View of Materials

- The information obtained from Raman imaging is essential for characterizing many different types of materials.

- Examples of Raman imaging in this presentation include,
  - Lithium ion battery components (phase differences, in situ changes)
  - Carbon based materials such as graphene (defects, number of layers, etc.)
  - Silicon materials (stress and morphology)





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Wide Spread Use of Lithium Ion Batteries

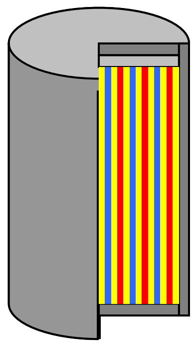
- Portable Electronic Devices
  - Laptops
  - Mobile Phones
  - Tablets
  - DVD Players
  - Digital Cameras

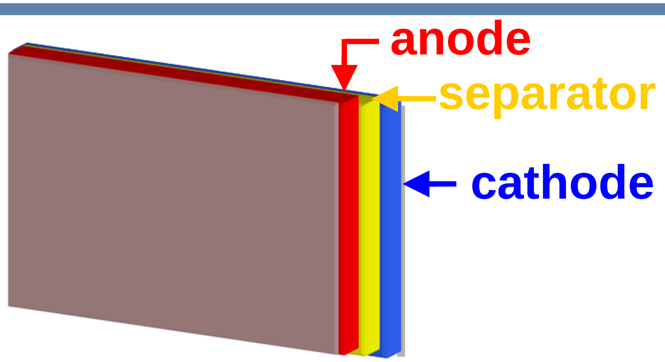
- Cordless Tools
  - Drills, Saws, Sanders

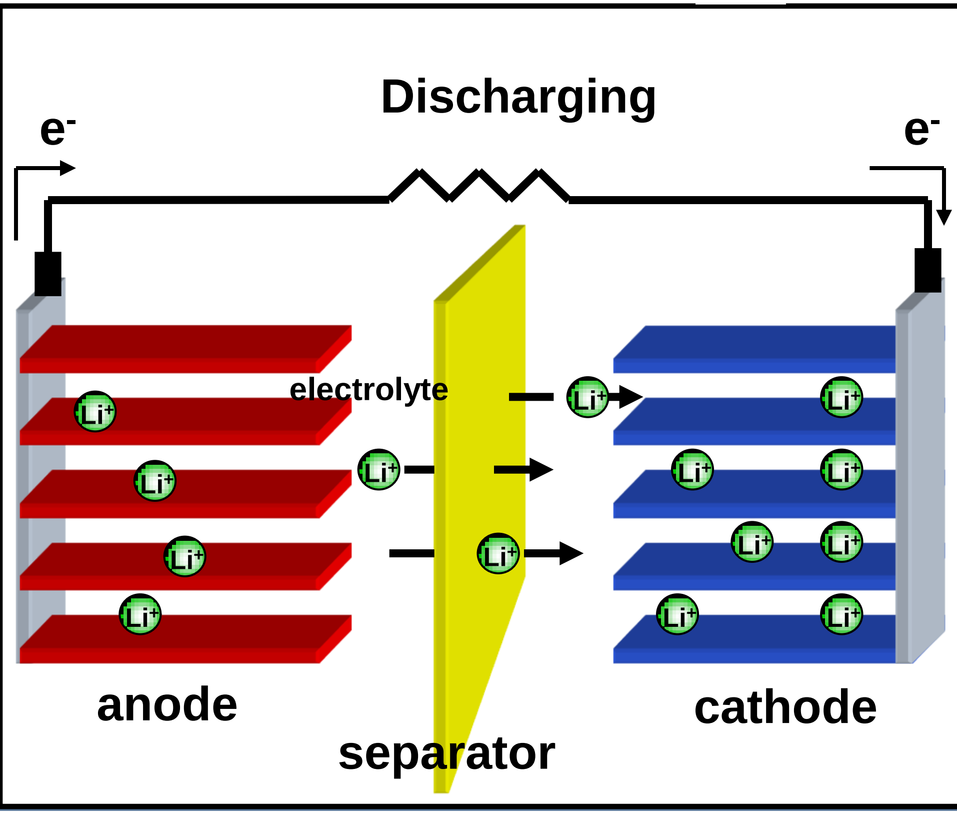
- Automobile*
  - Plug-in Hybrid-Electric Vehicles (PHEV)
  - Electric Vehicles

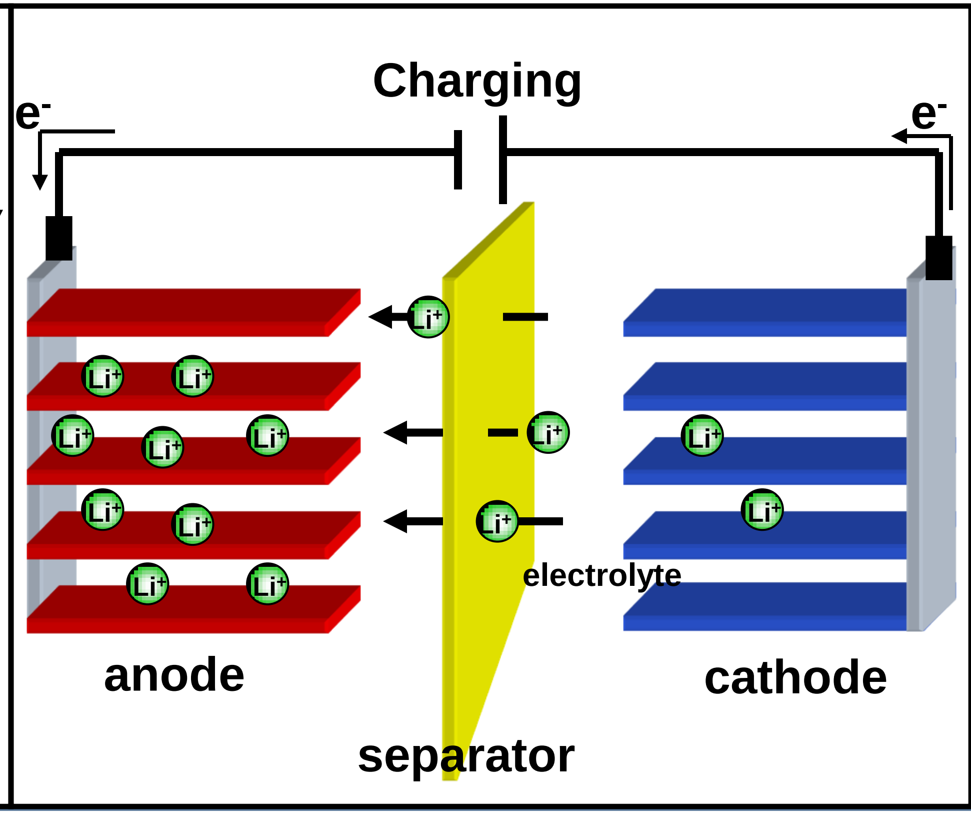
*A substantial growth in lithium ion batteries in transportation is expected $2 billion in 2011 and predicted to grow to $14.6 billion by 2017

Lithium Ion-Battery Components

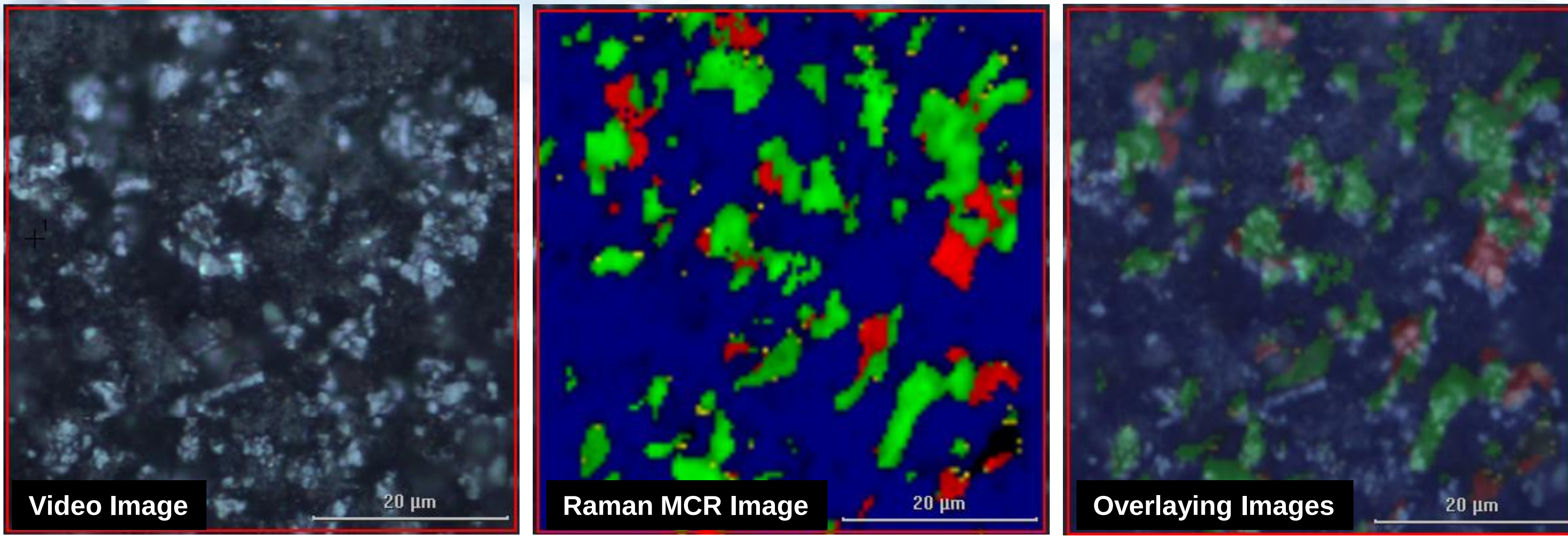


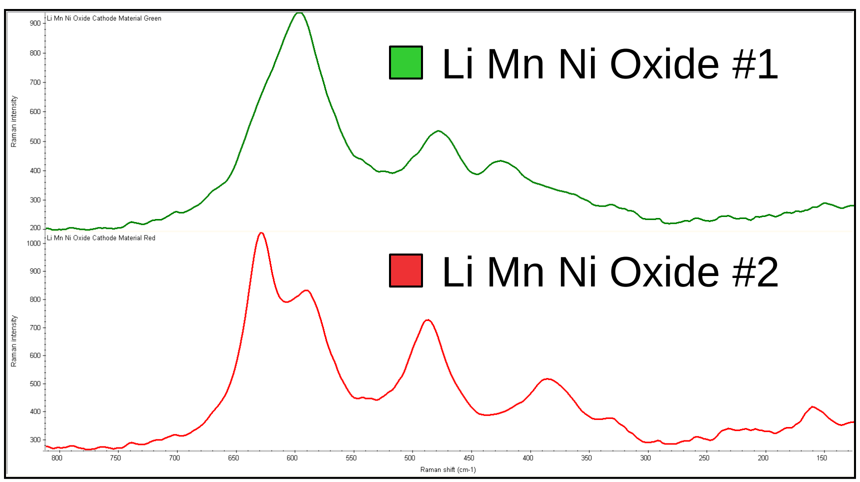






Raman Imaging of a Li Mn_x Ni_y O_z Cathode





- Carbon Black
- Li Mn Ni Oxide #1
- Li Mn Ni Oxide #2

455 nm laser (2 mW)
52.5 x 54 μm^2 area
0.5 µm image pixel size
11554 spectra
0.1 s exposure time
50 scans

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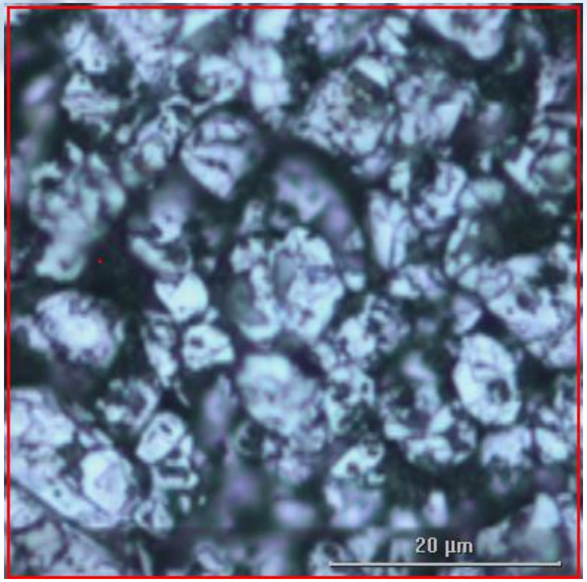
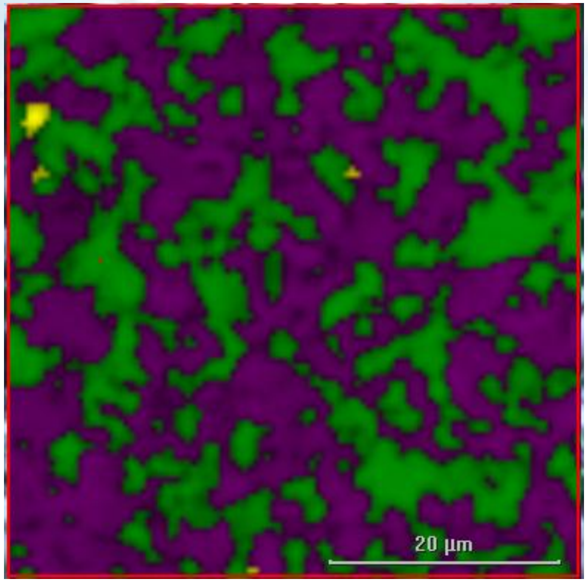
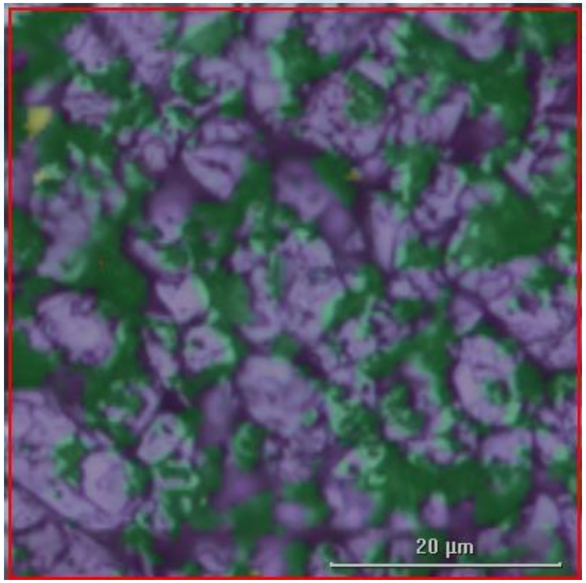
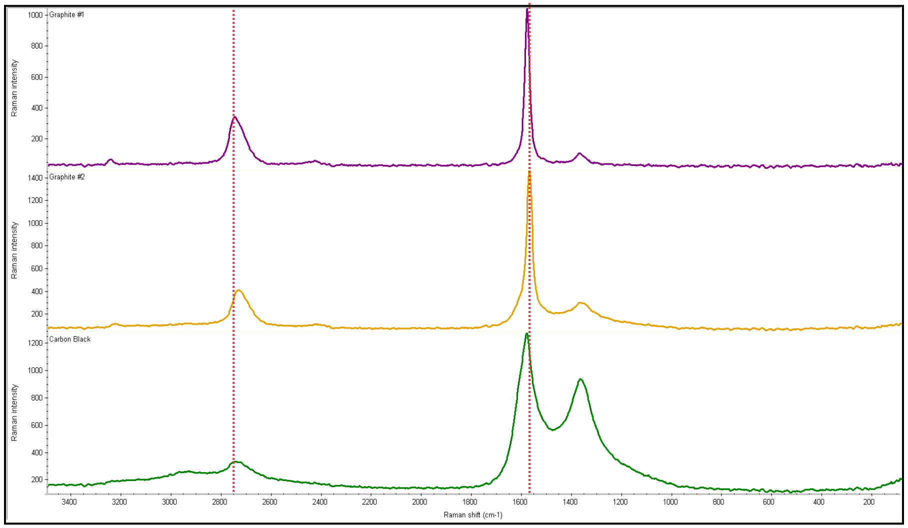
Raman Imaging a Graphite Anode





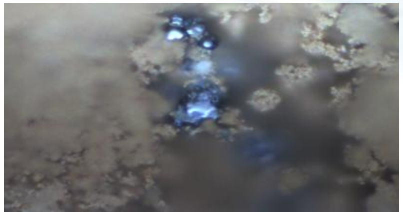


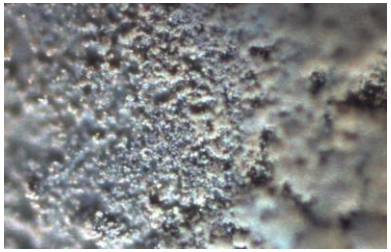


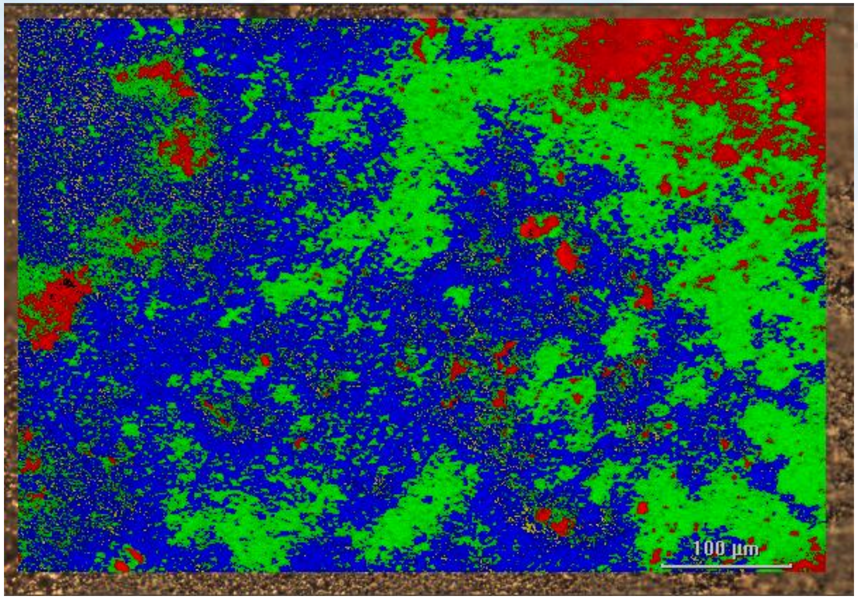
- Graphite
- Graphite (shifted)
- Carbon Black

455 nm laser (2 mW)
50 x 50 µm^2 area
0.5 µm image pixel size
10201 spectra
0.1 s exposure time
50 scans

Nano-Crystalline Silicon Powder for Silicon Anodes

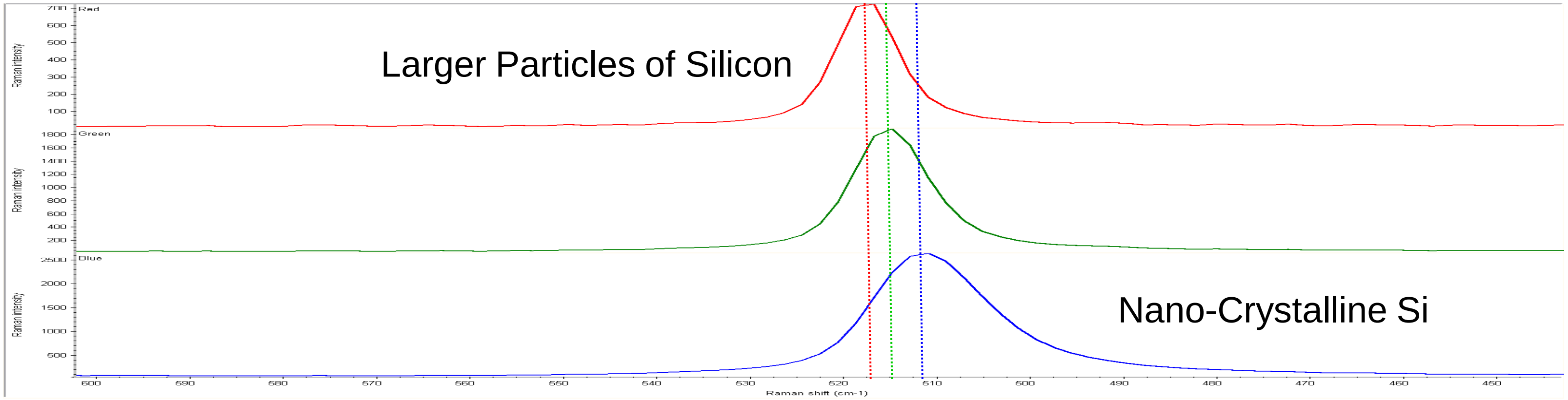






455 nm laser (0.2 mW)
629 x 430 μm^2 area
1.0 μm image pixel size
270500 spectra
0.020 s exposure time
10 scans

Shift in the silicon peak position and change in peak shape with silicon morphology (from crystalline silicon to amorphous silicon)



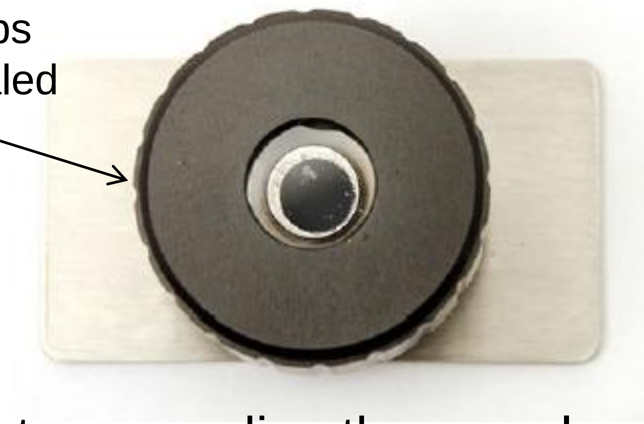
Battery Components can be Sensitive to Atmospheric Exposure

ex situ transfer cell for sensitive materials

O-ring seal maintains inert gas environment

Wide variety of industry standard sample holders also provide compatibility with SEM analysis

Interchangeable caps with a variety of sealed window materials



- Transfer cell maintains an inert environment surrounding the sample so it can be analyzed using instruments outside a glove box

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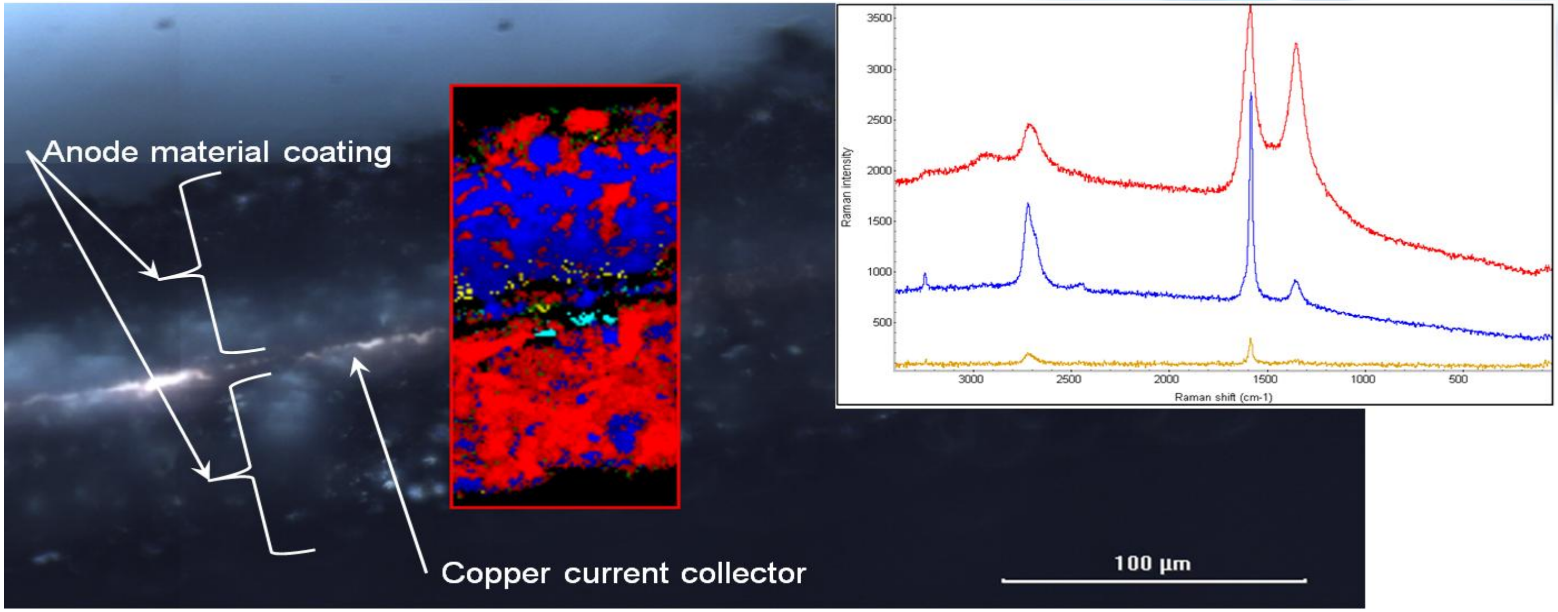
Ex situ Analysis of a Cross-Sectioned Anode Material

Cross-sectioned anode material in the ex situ transfer cell



The red color indicates the presence of carbon black while the blue color represents graphite. The distribution of these materials on the two sides of the electrode is significantly different. The copper current collector is in the center.

50X long working distance objective, 532 nm laser (2.0 mW), area imaged 76 µm x 160 µm, image pixel size 1 µm, 0.2 s exposure time, 4 scans

Slide content courtesy of Dick Wieboldt , Thermo Fisher Scientific, Madison, WI USA

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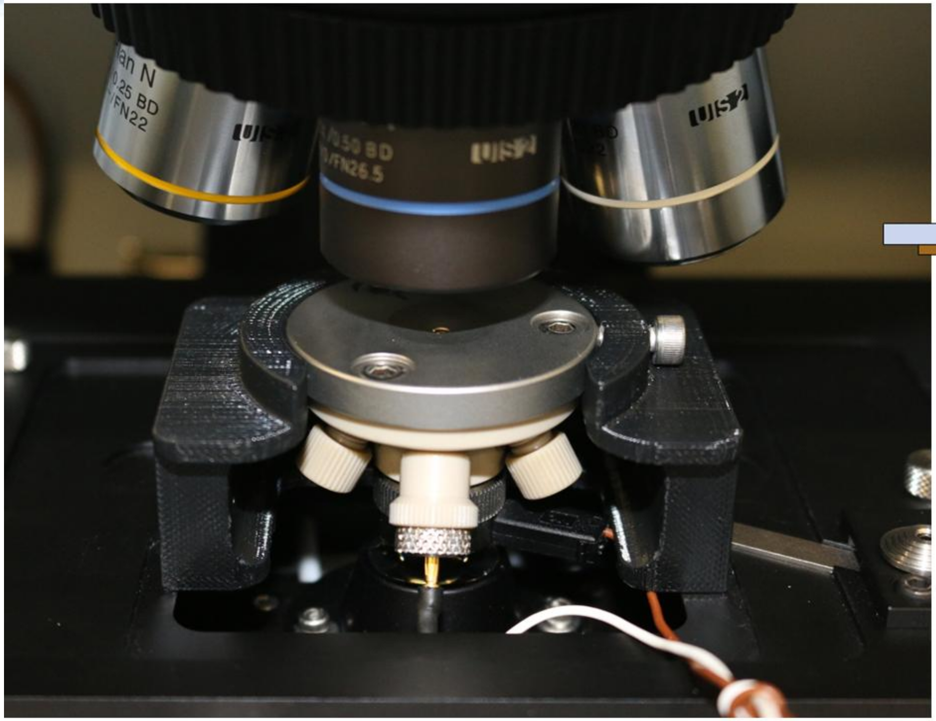
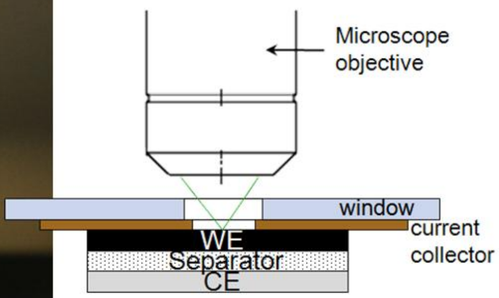
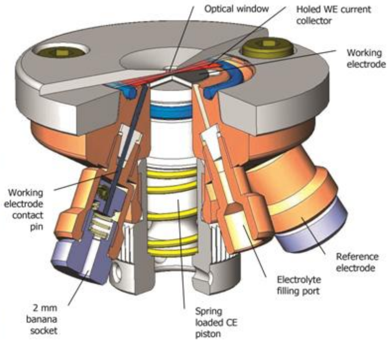
Raman Imaging of Components in a Working Cell



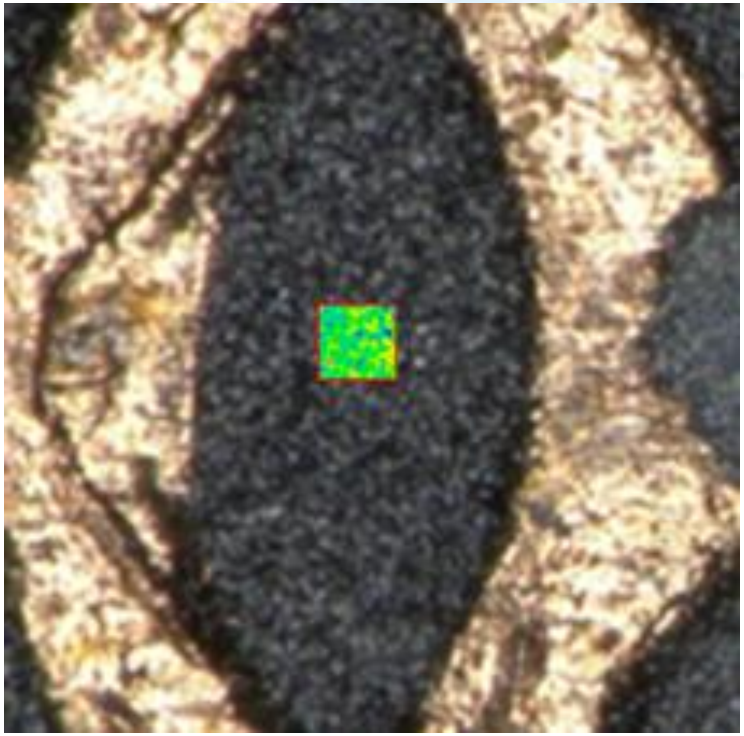




<u>in situ cell</u>

- Raman imaging of components in a working cell
- Monitor changes during charging and discharging cycles
- Electrode material was deposited on the copper mesh current collector

In situ Raman Imaging: Lithiation of Graphite



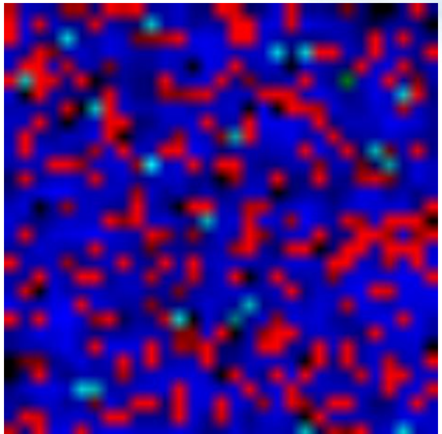
- Graphite coated on wire mesh current collector
- Representative area examined by Raman imaging
- Raman images were collected during the charging cycle
- Looking at changes in the graphite anode material that occur with the intercalation of lithium ions that takes place during charging
- Intercalation of lithium ions causes an expansion of the graphite layers

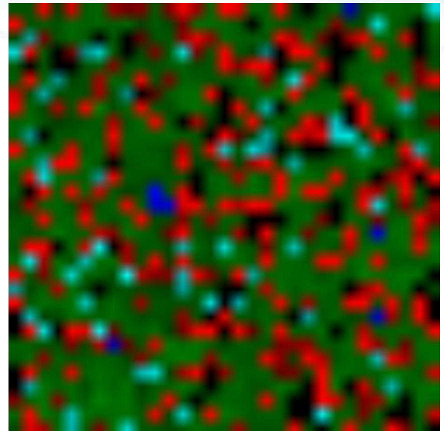
532 nm laser (2 mW), 30 x 30 μm^2 area, 1 μm image pixel size, 0.01 s exposure time, 50 scans, Raman images were collected during the charging cycle (8 hours) of the cell.

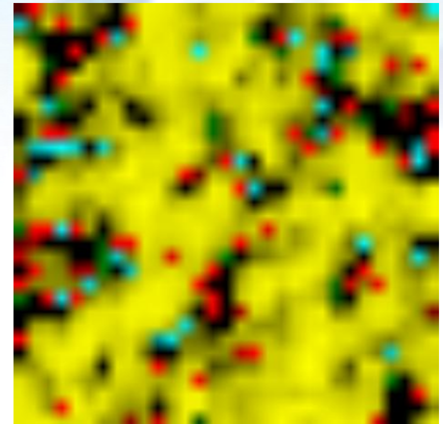
Slide content courtesy of Dick Wieboldt , Thermo Fisher Scientific, Madison, WI USA

Changes in the Anode are Reflected in the Raman Images

The change from blue to green is the shift in the graphite peak from1580 to 1590 cm^{-1}



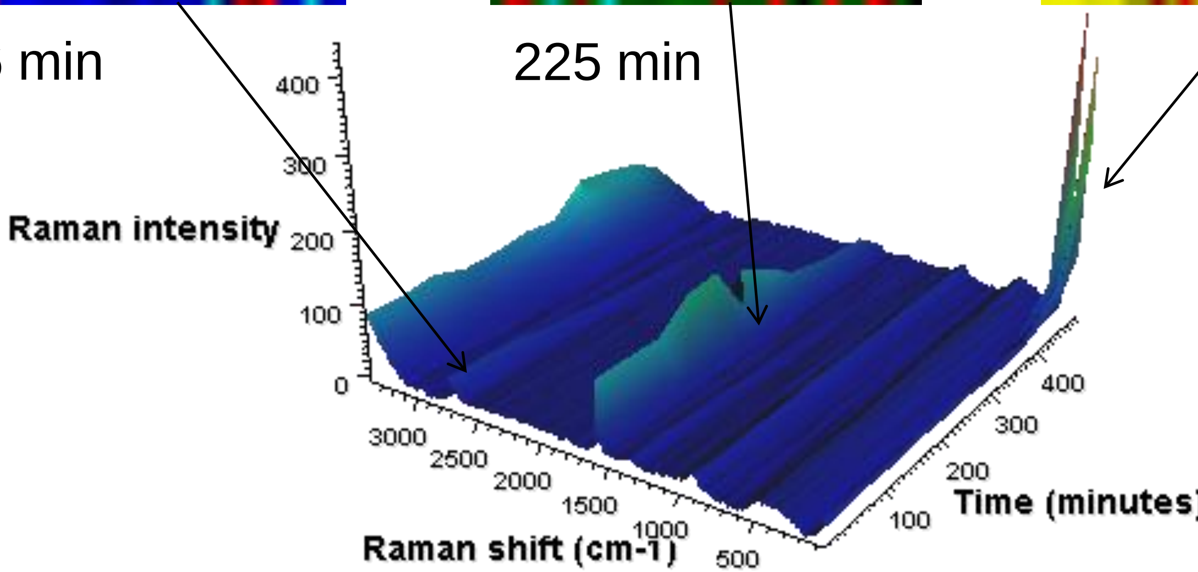




36 min

225 min

496 min

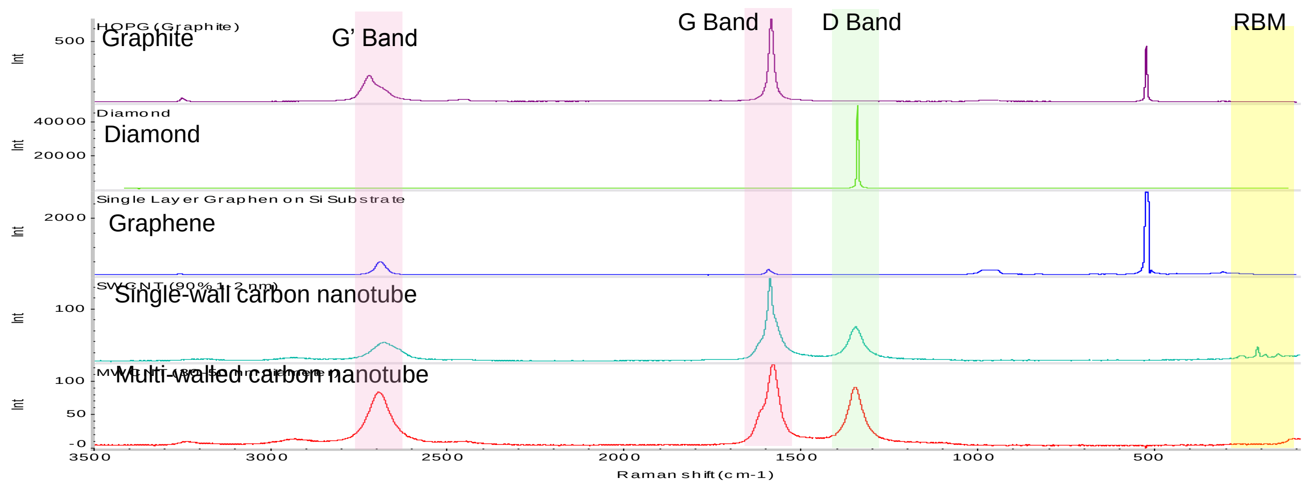


The shift to yellow indicates the appearance of a peak at 154 cm^{-1}

Slide content courtesy of Dick Wieboldt , Thermo Fisher Scientific, Madison, WI USA

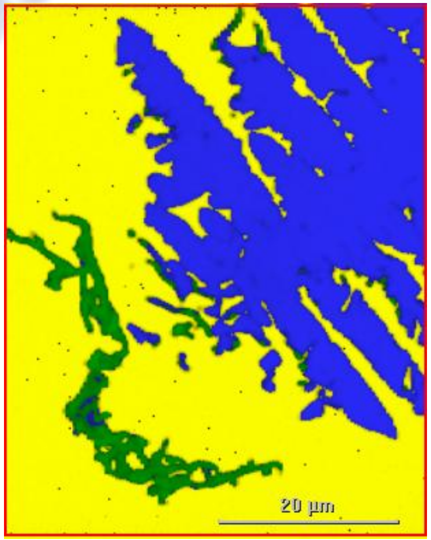
Raman Imaging of Carbon Based Materials

- Raman imaging is an excellent choice for the analysis of carbon based materials.
- Raman analysis provides information on molecular structure (defects, grain boundaries, number of layers in graphene materials, diameters of single walled carbon nanotubes, etc.).
- Many different types of applications including, but not limited to,
  - Monitoring the results of the growth of CVD deposited graphene films
  - Evaluating thin graphene films (defects, number of layers, etc.)
  - Assessing graphene films as protective barriers

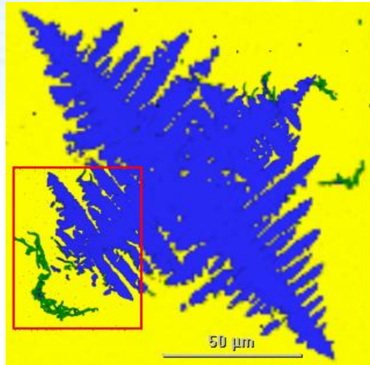


Monitoring the Growth of CVD Graphene Films

Dendritic Growth



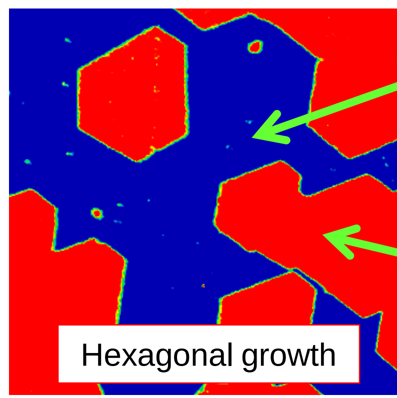
47 x 61 μm^2, 0.2 μm image pixel size,
72216 spectra, exposure time 0,0033 s,
2 scans, 9 minutes



- Single Layer Graphene
- Multi - Layer Graphene
- Silicon Substrate

133 x 138 μm^2, 1 μm image pixel size,
18626 spectra, exposure time 0,0033 s,
2 scans, 3 minutes

MCR Image

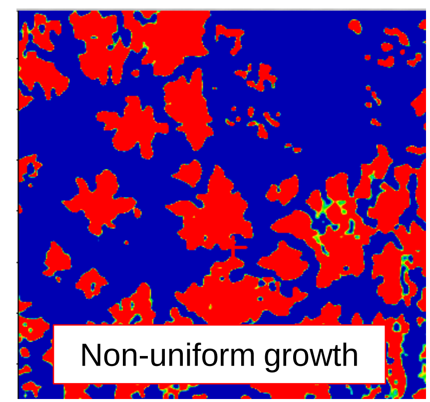


SiO_2 substrate

Single-layer graphene

175 x 175 μm^2 area
0.5 μm pixel size, 122,500 spectra,
exposure time 0.010 s, 10 scans
(approximately 3.4 hour collect time)

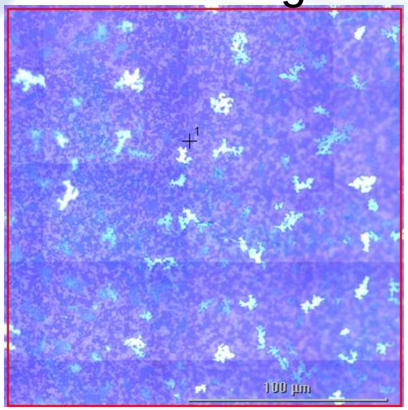
Ratio of the 2D to G band of graphene:



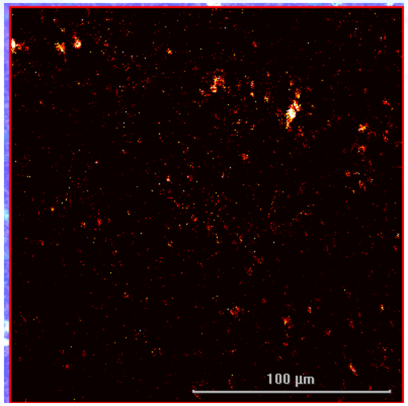
50 x 50 μm^2 area
0.5 μm image pixel size,10,000 spectra,
exposure time 0.010 s, 10 scans
(approximately 17 minute collect time)

Raman Imaging of a Multilayer CVD Graphene Film

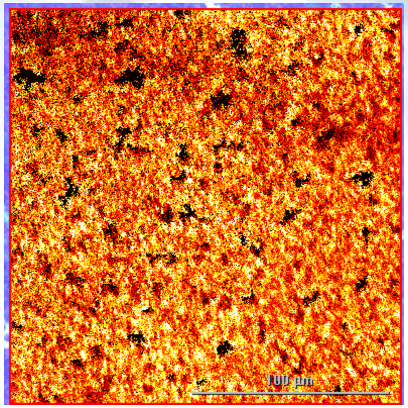
Video Image

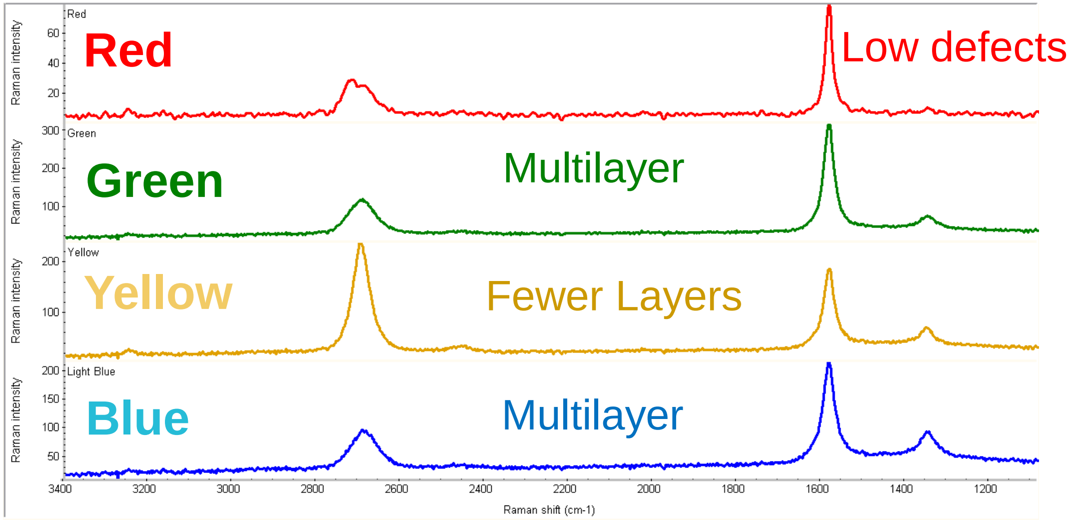


2D/G Ratio

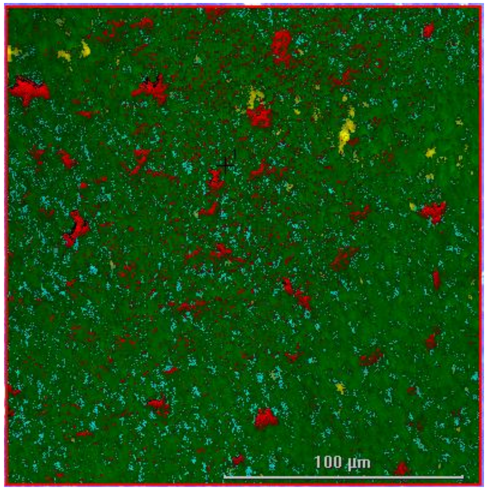


D/G Ratio





MCR Image



532 nm laser (10 mW), 100X objective, 200 x 201 μm^2 area, image pixel size 0.5 μm, 162000 spectra, exposure time 0.01 s, 5 scans, 154 minute collection time

Graphene as a Protective Coating

- Single layer graphene exhibits superior barrier properties
  - Impermeable to particles as small atomic He
  - Potential to inhibit corrosion or degradation of a variety of materials
  - Optically transparent
  - Ideal as protective film for Photovoltaic/solar cells

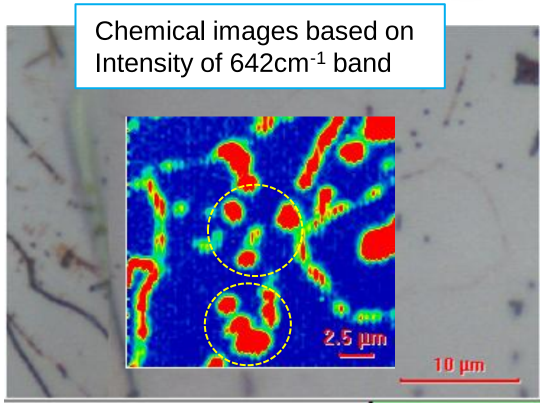
- Challenges to realize potential of graphene as a protective thin film
  - Defects are often present
  - Defects often lead to leaks which in turn leads to oxidation (decomposition)
  - Concentration and distribution of defects depends on growth conditions

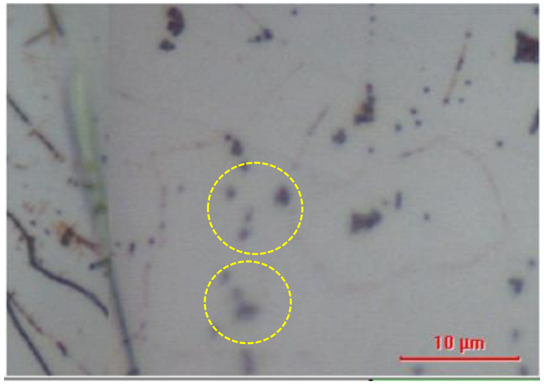
- Imaging Raman microscopy can be used to evaluate the quality of the coatings as well as detecting the results of the failure of the coatings

Roy, S. S; Arnold, M. S.: Adv. Funct. Mater. ***2013,*** DOI: 10.1002/adfm.201203179

Defects in the Coating Allows Oxidation of the Copper

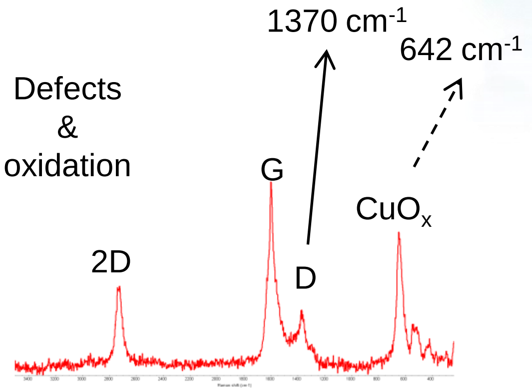
Distribution of copper oxide formed on the copper surface



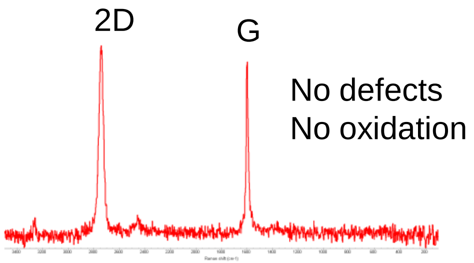


Optical Image – Discolored Points
Graphene on Cu

One analysis Two parts of the puzzle

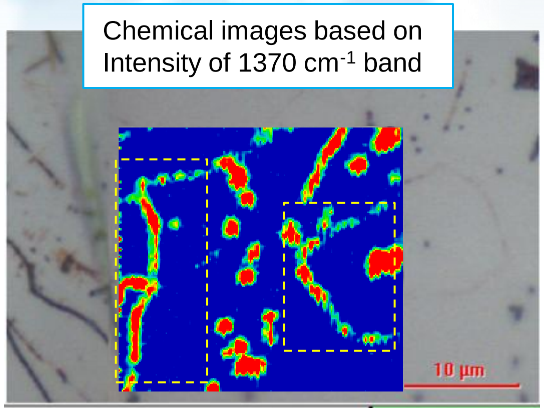


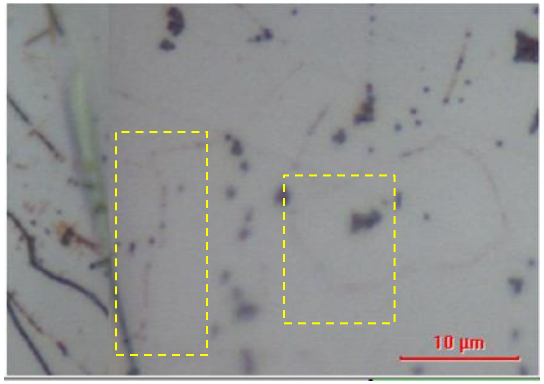
Raman Spectrum Red Area



Raman Spectrum Blue Area

Distribution of defects in the graphene films





Optical Image/ - Discolored Lines
Graphene on Cu

455 nm laser (2 mW), 100X objective, image pixel size 0.25 µm, 10000 spectra, 50 minute collection time

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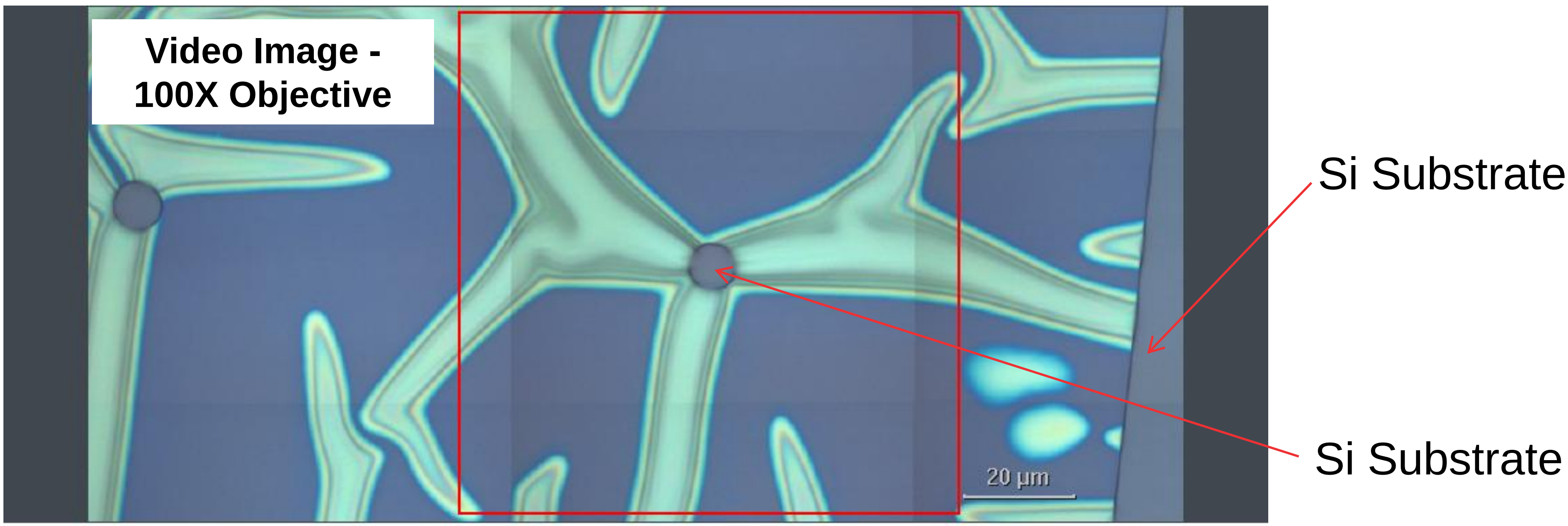
Raman Imaging of Stress in Silicon Samples

Induced Stress in Si Epilayer
Larger Lattice for Si/Ge alloy
Lattice mismatch causes stress



Sample courtesy of Jose R. Sanchez-Perez (Professor Lagally's Group), Department of Materials Science and Engineering, University of Wisconsin Madison

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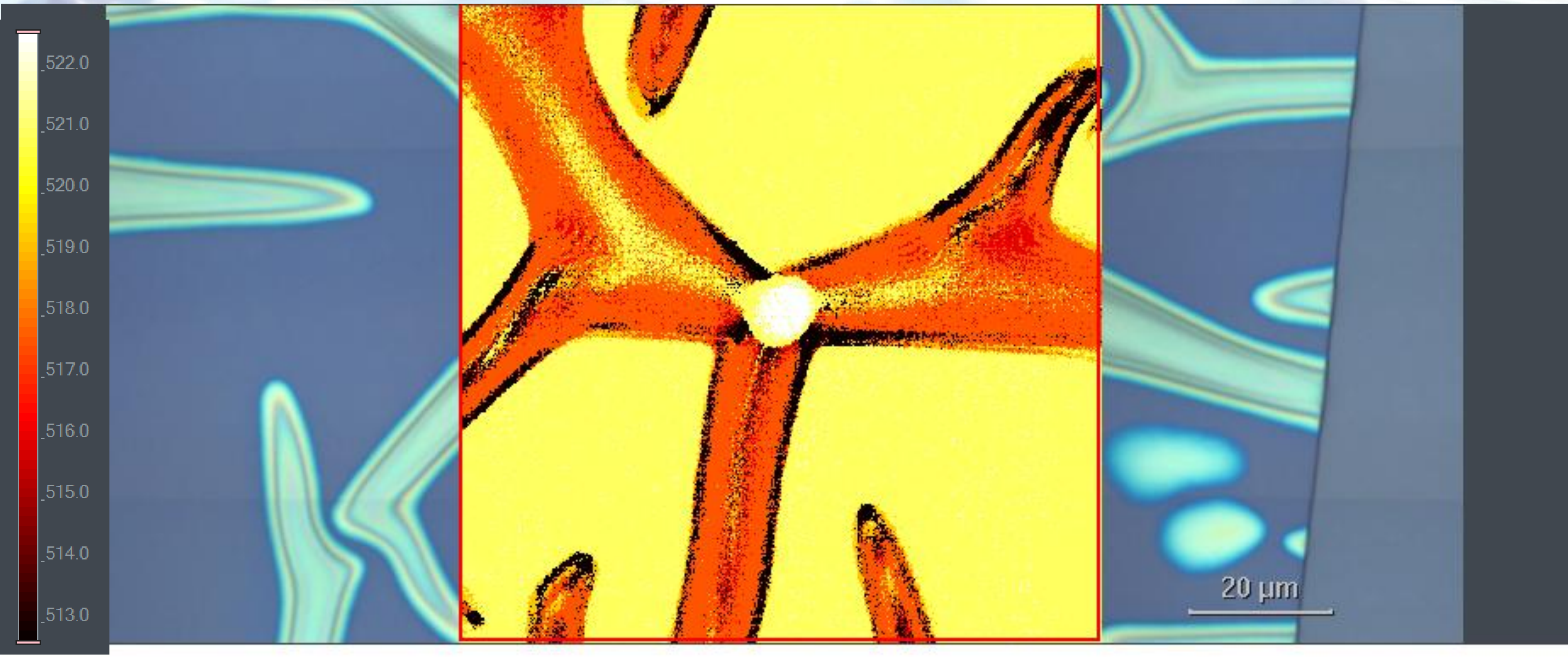
Stress Image – Shift in the Silicon Peak



- Colors represent a shift in the location of the silicon peak for the Si epilayer
- White corresponds to the location of the Si substrate peak
- The darker the colors the more the peak has shifted to lower wavenumbers.
- The greater the shift the greater the stress

455 nm laser (1 mW), 91 x 91 μm^2 area, 0.2 μm image pixel size, 207025 spectra, exposure time 0.020 s, 20 scans

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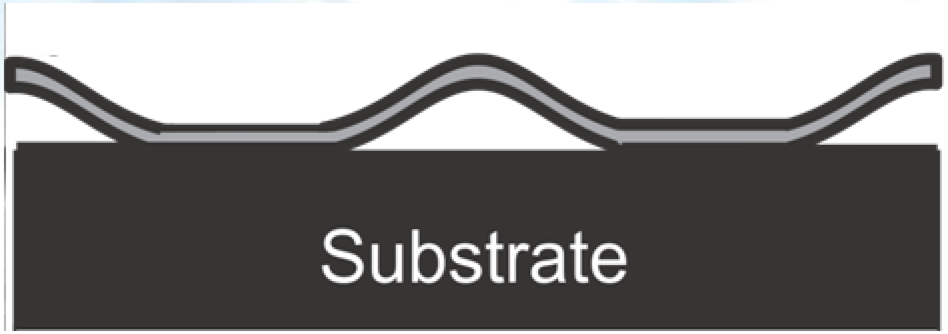
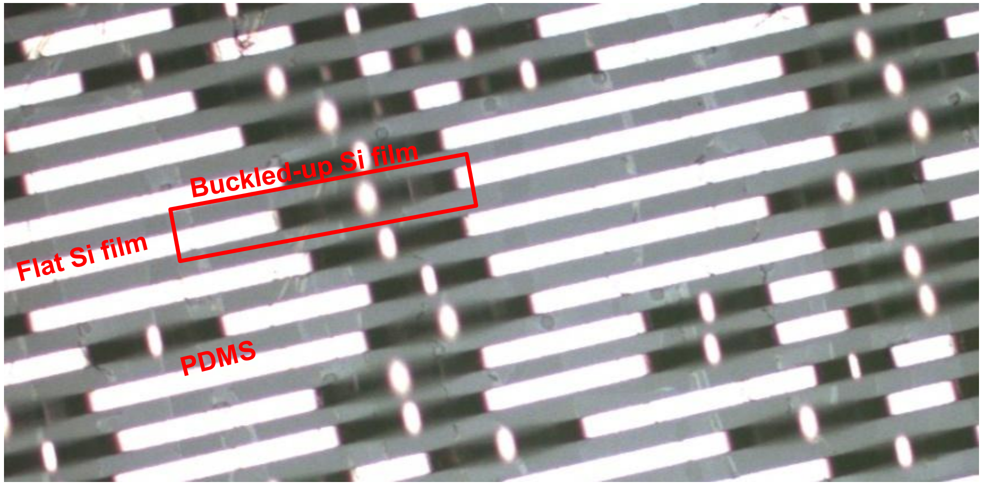
Imaging of Silicon Nano-ribbons



220 nm thick Si nano-ribbon buckled-up on PDMS.



Sample courtesy of Dr. Francesca Cavallo (Professor Lagally's Group), Department of Materials Science and Engineering, University of Wisconsin Madison

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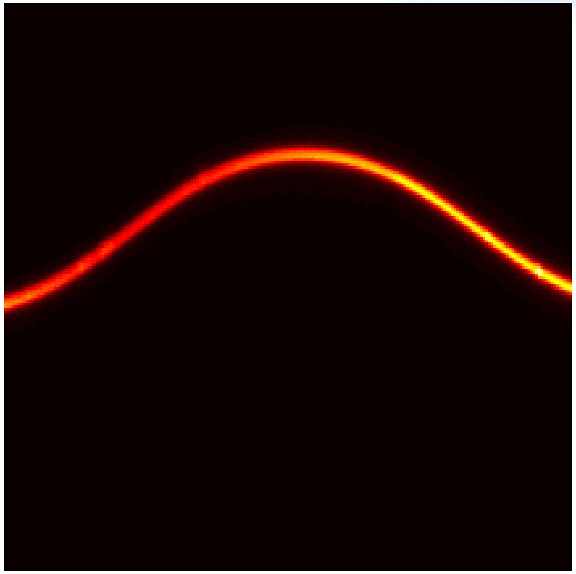
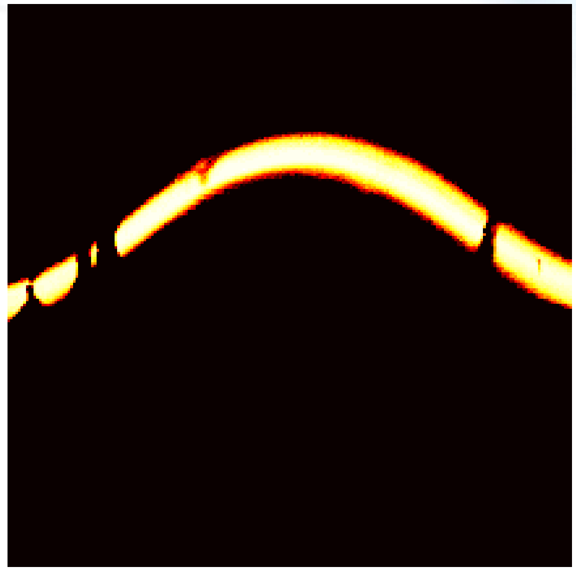
Raman Imaging - Silicon Nano-ribbons

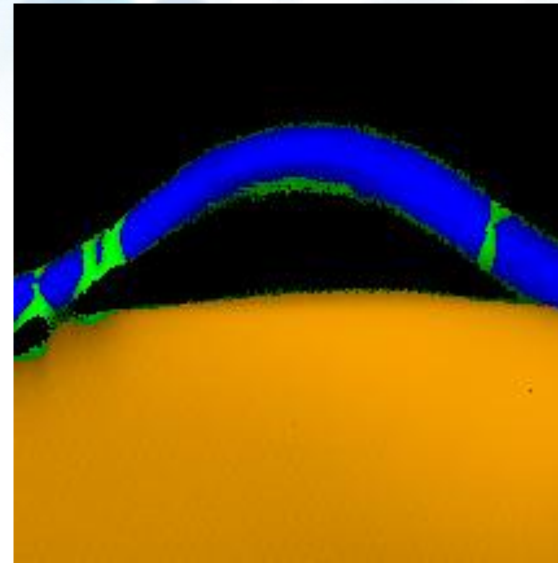
Confocal depth profiling cross-sections of the silicon ribbons



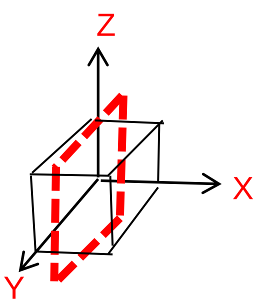
Peak Height



Correlation



MCR



- PDMS
- Si
- Si + Fluorescing Material

455 nm laser (1 mW), 128 x 128 μm^2, 1 μm image pixel size, 0.010 s exposure time, 16384 spectra, 10 scans

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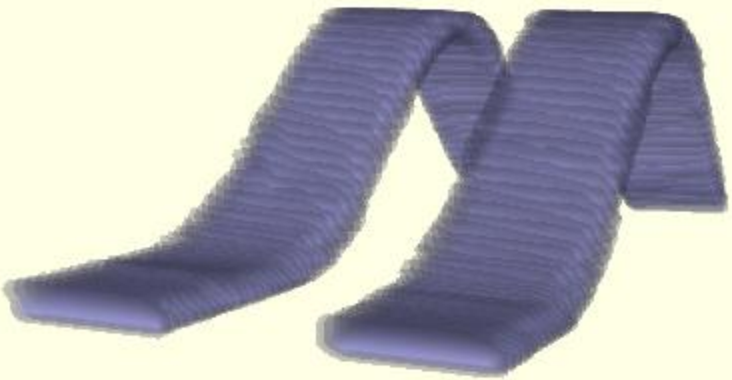
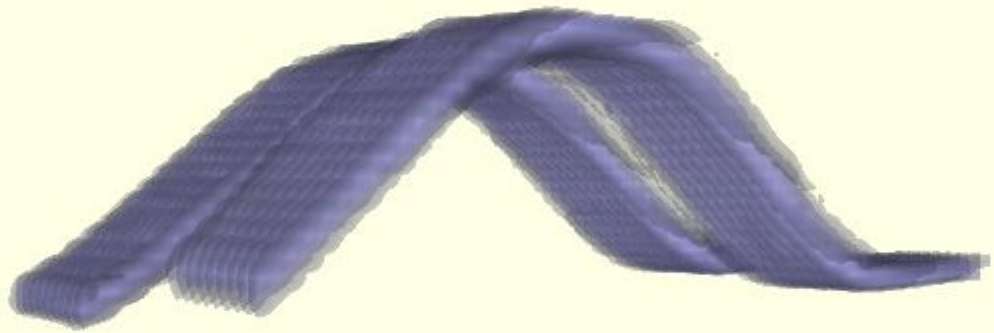
3-D Raman Images of Silicon Nano-ribbons

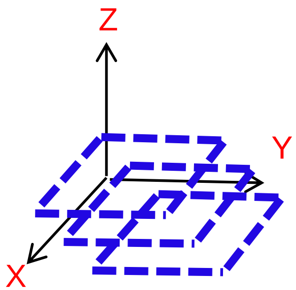
455 nm laser (1 mW), 72 x 157 μm^2, 1 μm image pixel size, 11304 spectra per region, 0.010 s exposure time, 10 scans, 40 slices, 1 micron spacing, 452160 spectra

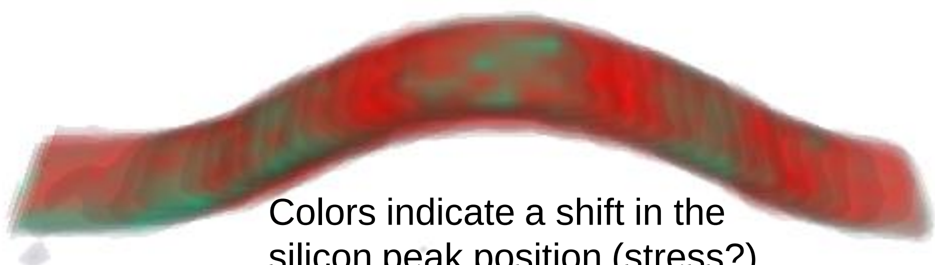
3-D Images of Si Ribbons Based on the Silicon Peak





3-D Images of Si Ribbons Showing a Shift in the Silicon Peak Position





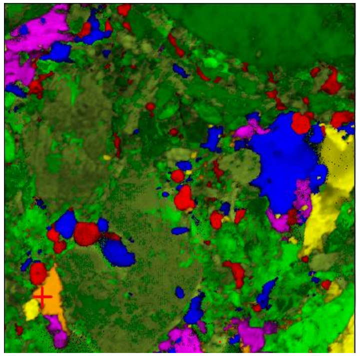
Colors indicate a shift in the silicon peak position (stress?)

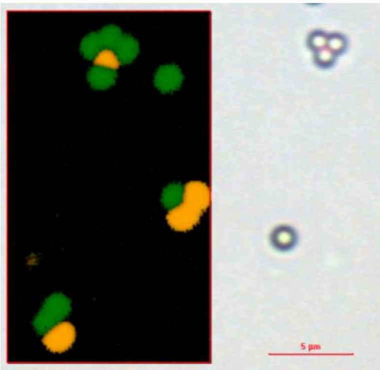
Shift in Si peak (stress?)

455 nm laser (1 mW), 36 x 168 μm^2, 2 μm image pixel size, 1615 spectra per region, 0.020 s exposure time, 100 scans, 41 slices, 1 micron spacing, 66215 spectra

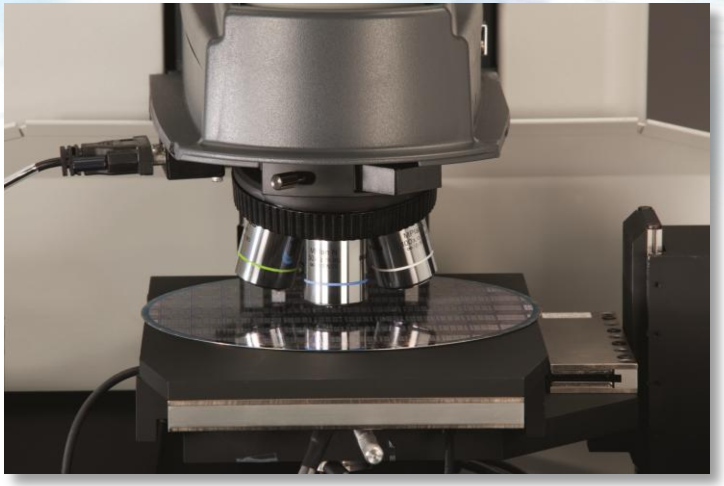
Raman Imaging Provides a Unique View of Materials

- Microscope problems are typically not just point analysis problems
- Imaging adds context and distribution information
- Raman imaging extends all the advantages of Raman spectroscopy across sample surfaces.
- Raman imaging not only provides a quick and efficient way to identify components and evaluate their spatial distribution but also can provide information on molecular structure and chemical environment (examples: morphology and stress)
- Vast amounts of data are generated very quickly and easily converted into visually stunning and informative images
- Many different applications can benefit from the power of Raman imaging





The DXRxi Raman Imaging Microscope



Accelerate your work

Visualize your answers