Raman Imaging for Visualizing Structural Variations in Advanced Materials

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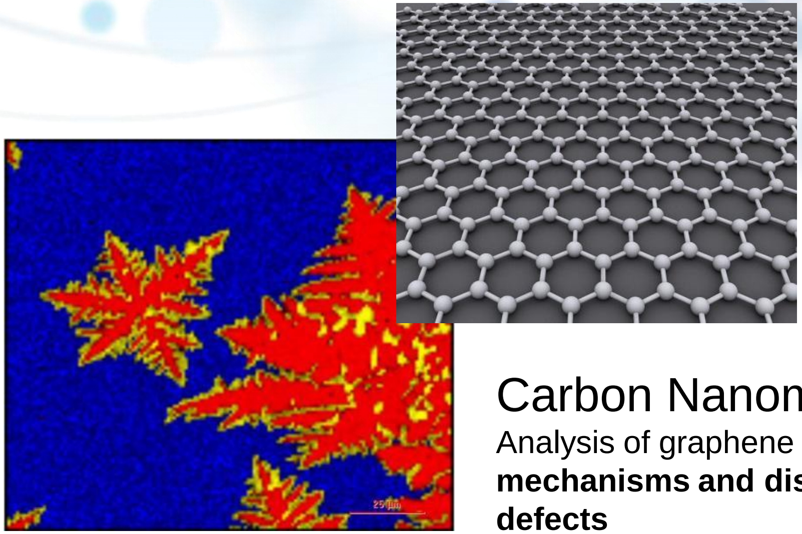
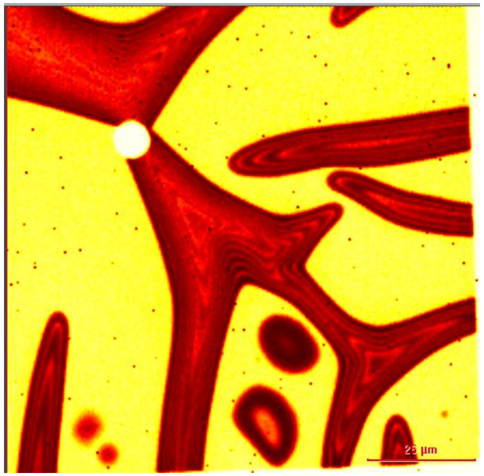
Raman Imaging Applications

- 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



Carbon Nanomaterials

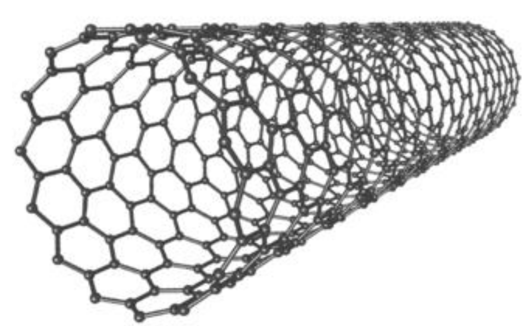
Analysis of graphene **growth mechanisms and distribution of defects**



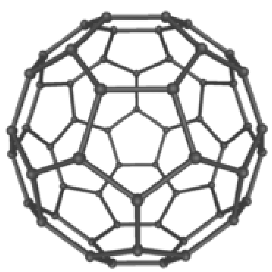
Semiconductors and Thin Films

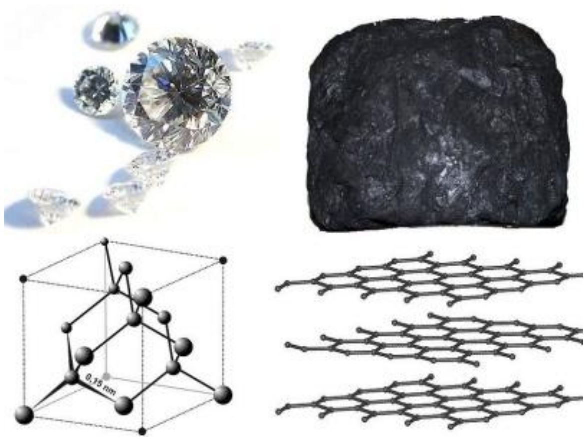
Variation in **stress distributions and crystallinity** across a sample area

ThermoFisher SCIENTIFIC

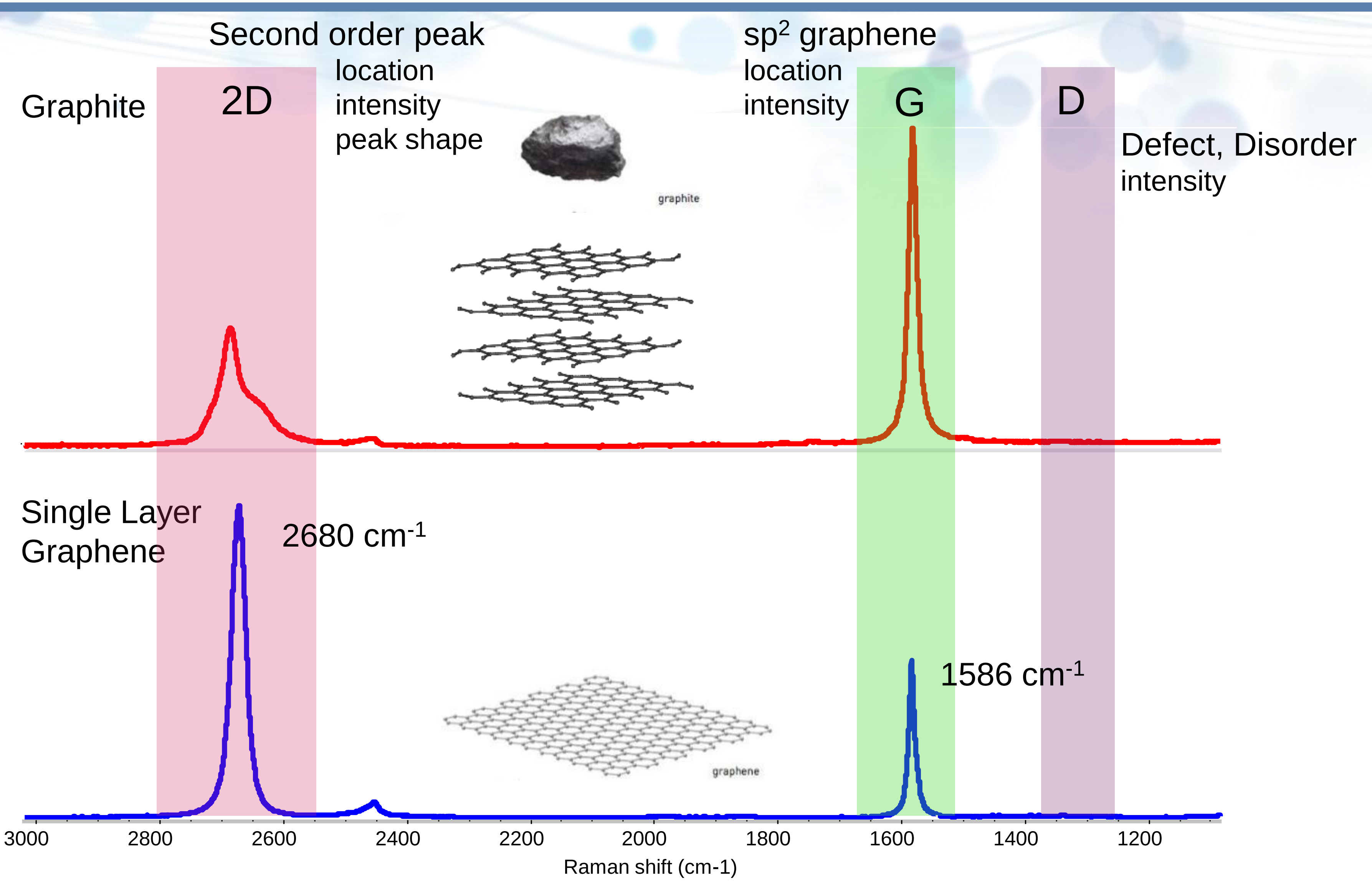


Raman Imaging of Carbon Materials



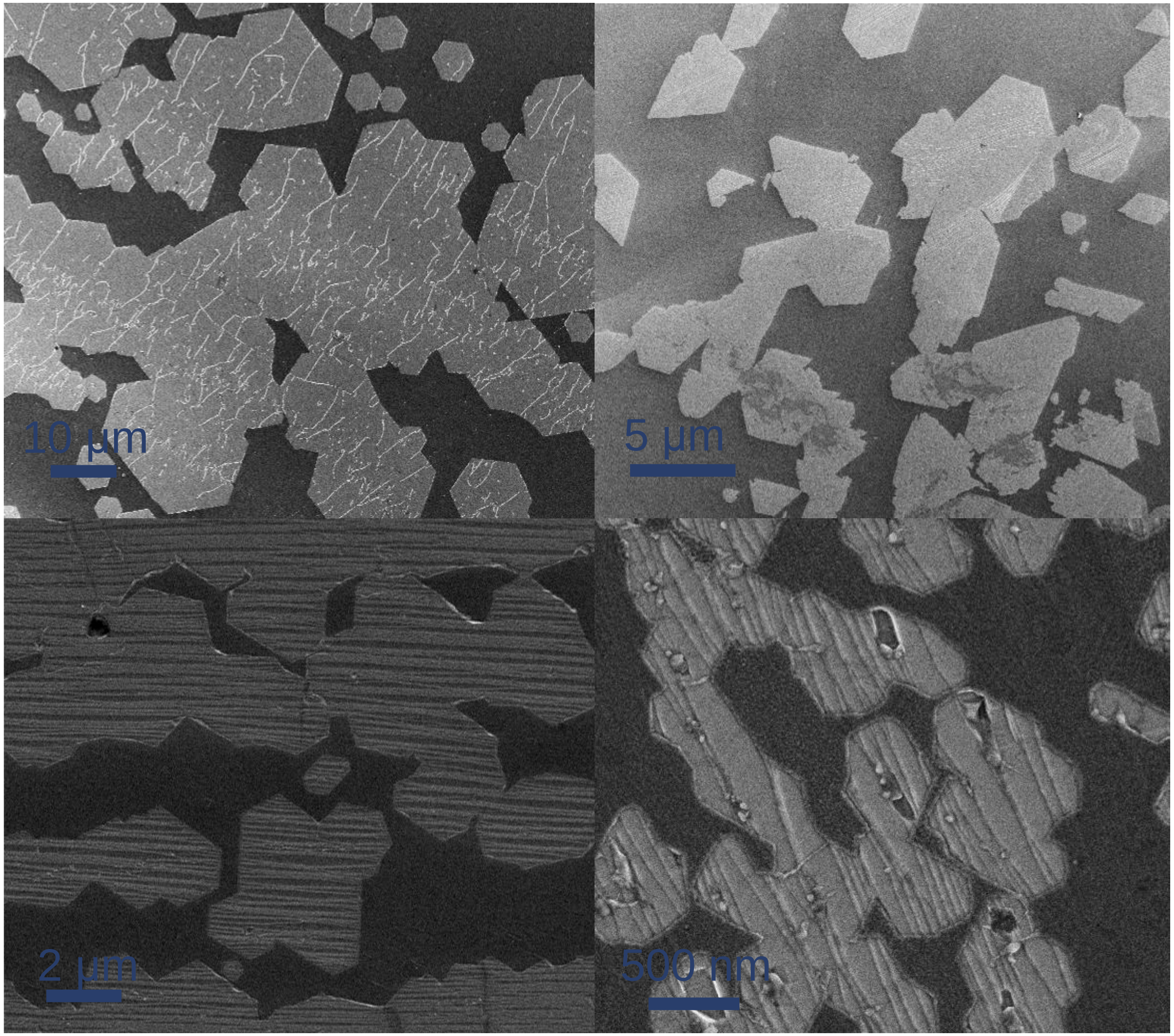


Graphene: Raman Spectral Features



CVD Growth of Graphene

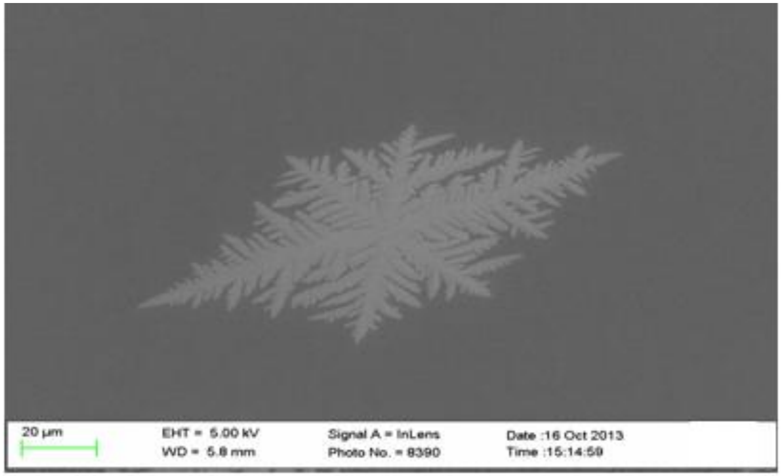
- Morphology of graphene films depends on the deposition conditions
- Monolayer as well as multilayer films can be grown
- Grain boundaries and defects concentrations will depend on the deposition conditions
- Raman imaging can be used to visualize the distributions of defects and assess the quality of the graphene films.



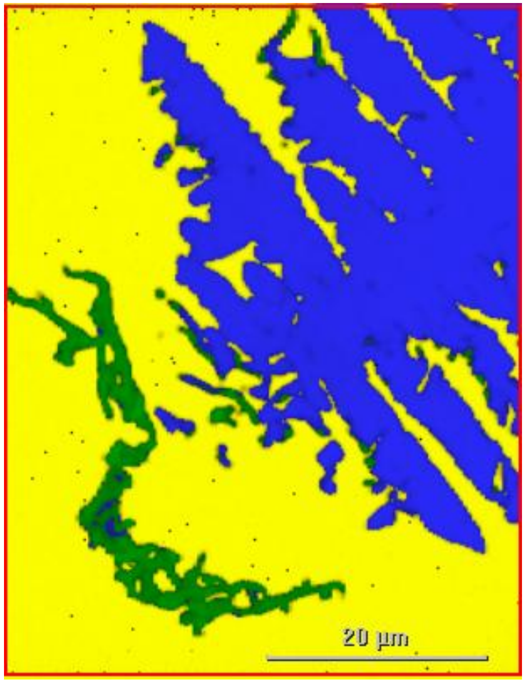
Growth of Graphene Films – Dendritic Graphene

- SEM illustrates the morphological characteristics that result from particular CVD deposition conditions
- Raman imaging can distinguish structural differences

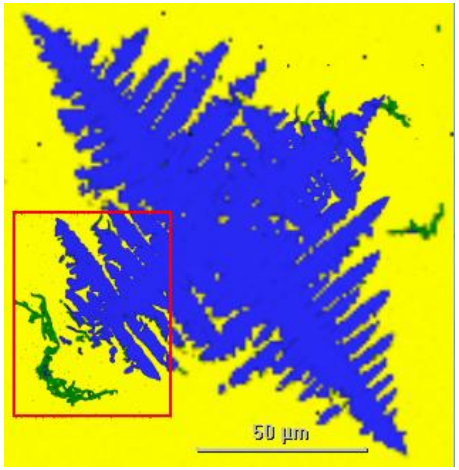
SEM Image



Raman Images



532 nm laser (10mW), 47 x 61 μm^2, 0.2 μm image pixel size, 72216 spectra, exposure time 0,0033 s, 2 scans, 9 minutes

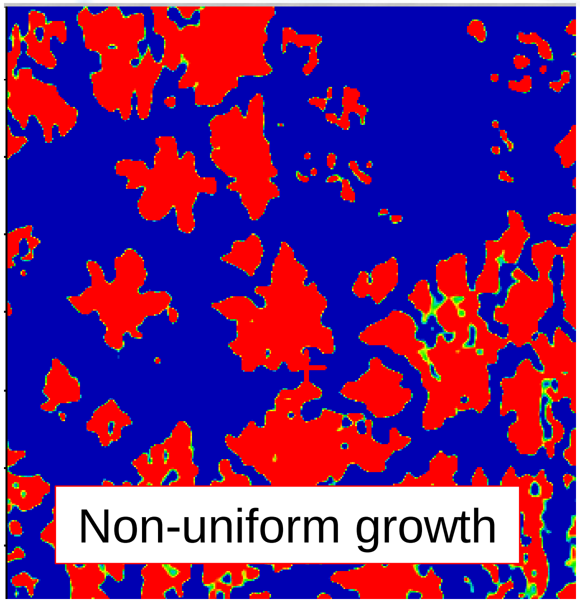


532 nm laser (10mW), 133 x 138 μm^2, 1 μm image pixel size, 18626 spectra, exposure time 0,0033 s, 2 scans, 3 minutes

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

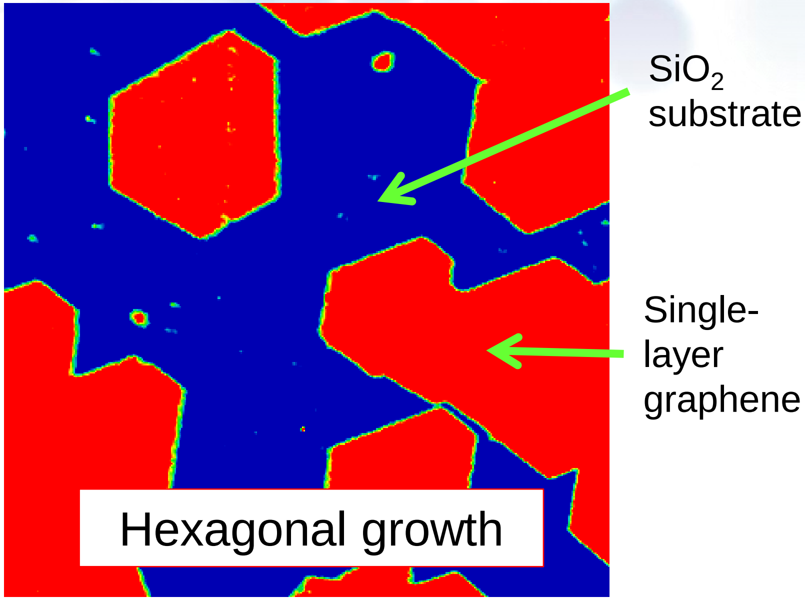
Growth of Graphene – Domain Sizes

Ratio of the 2D to G band of graphene:



532 nm laser, 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)

MCR Image

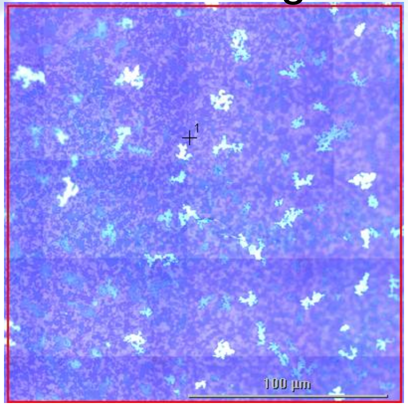


532 nm laser, 175 x 175 μm^2 area
0.5 μm image pixel size, 122,500 spectra,
exposure time 0.010 s, 10 scans
(approximately 3.4 hour collect time)

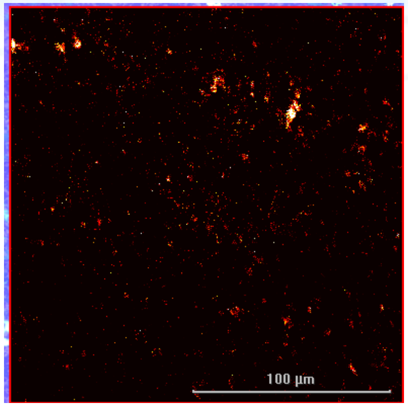
*Note: This graphene was initially grown on copper and then transferred to a silica substrate because the copper is a significant source of interference

Raman Imaging of a Multilayer CVD Graphene Film

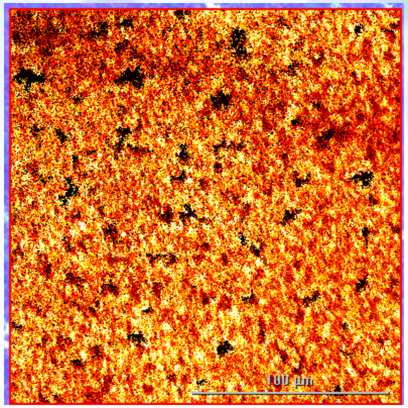
Video Image

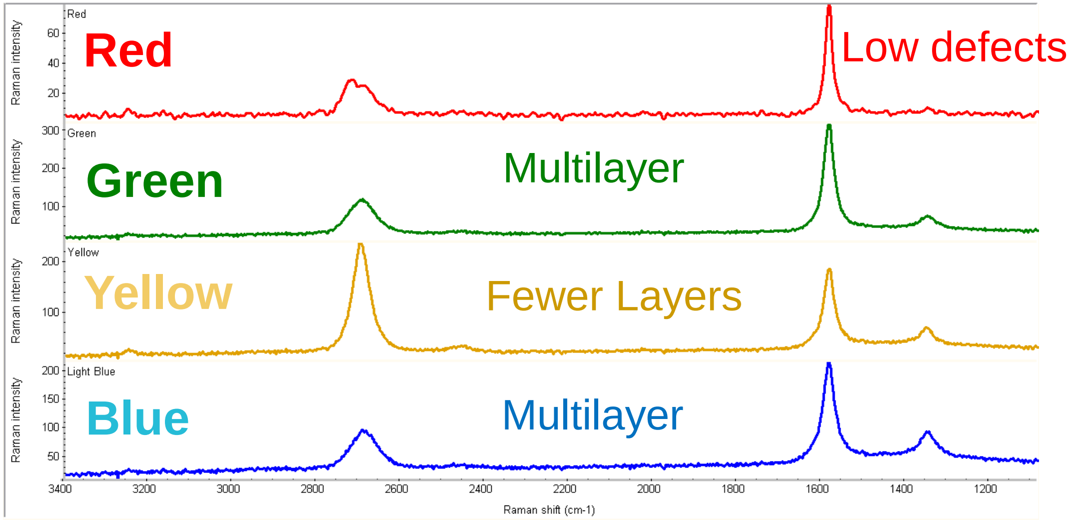


2D/G Ratio

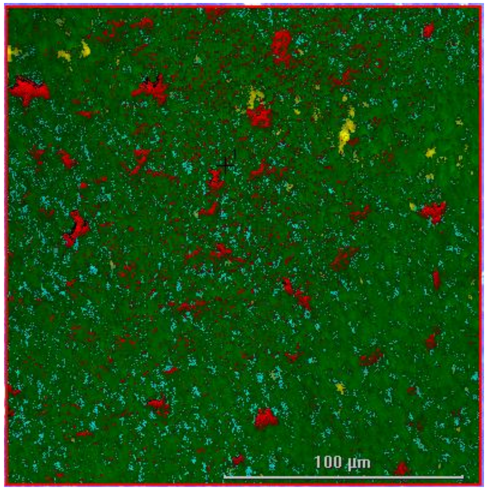


D/G Ratio





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

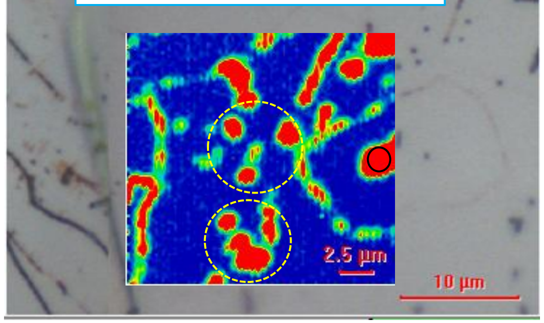
- Imaging Raman microscopy can be used to evaluate the quality of the coatings as well as detecting the results of the failure of the coatings

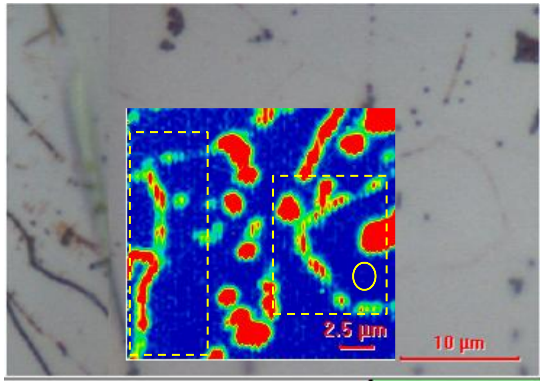
Roy, S. S; Arnold, M. S.: Adv. Funct. Mater. ***2013,*** DOI: 10.1002/adfm.201203179

Defects in the Coating Allows Oxidation of the Copper

Distribution of copper oxide formed on the copper surface

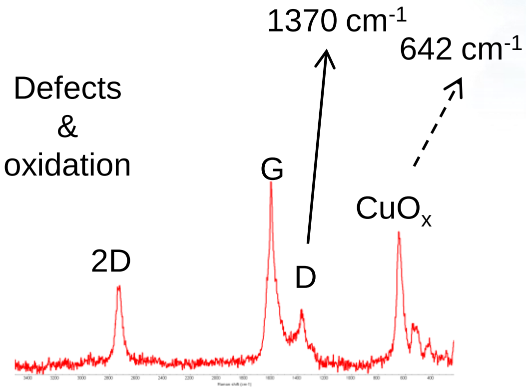
Chemical images based on Intensity of 642cm^{-1} band



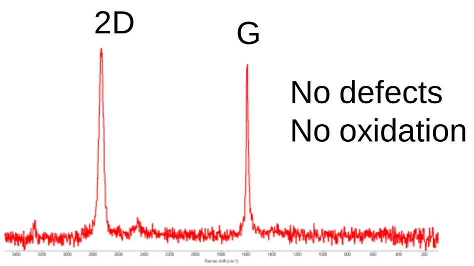


Optical Image/ Chemical Image Overlay Graphene on Cu

One analysis Two parts of the puzzle



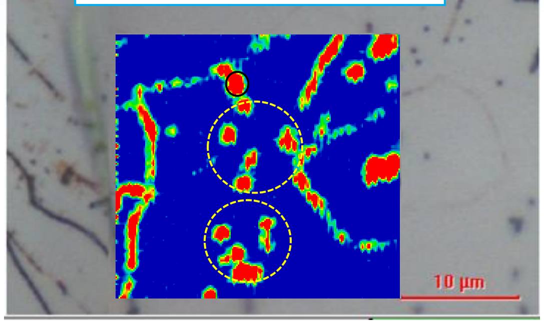
Raman Spectrum Red Area

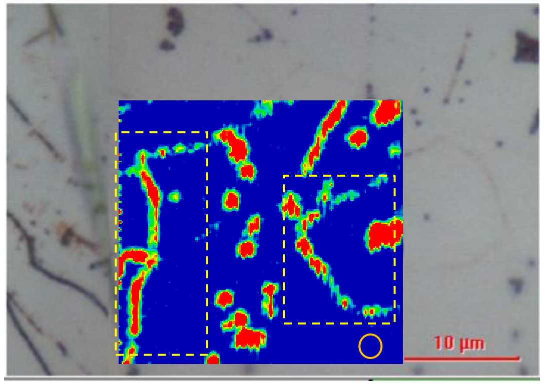


Raman Spectrum Blue Area

Distribution of defects in the graphene films

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





Optical Image/ Chemical Image Overlay Graphene on Cu

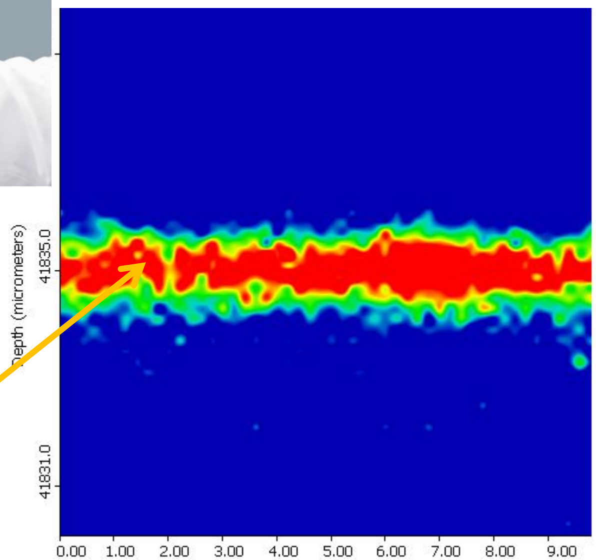
455 nm laser (2 mW), 100X objective, image pixel size 0.25 µm, 10000 spectra, 50 minute collection time

Single Layer Graphene on a Flexible Polymer Substrate

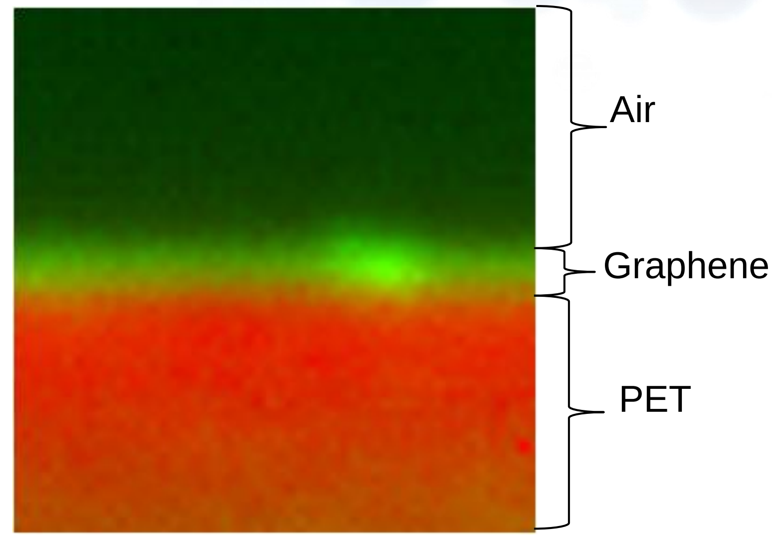
Raman Imaging of Single Layer Graphene on PET

Cross-Sectional Image

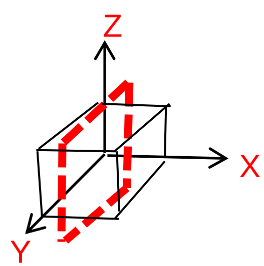
Graphene



Correlation Profile

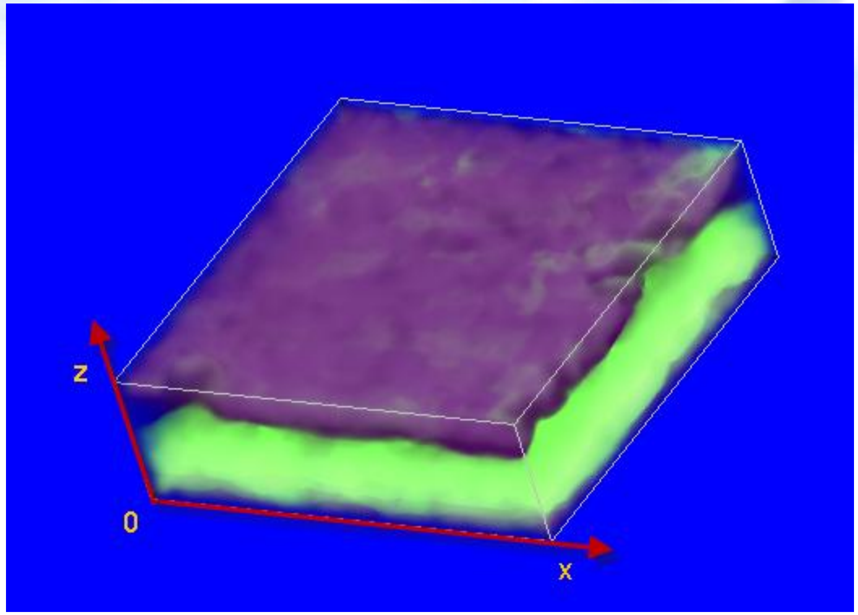


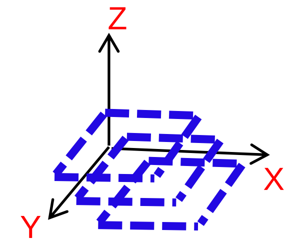
MCR Profile

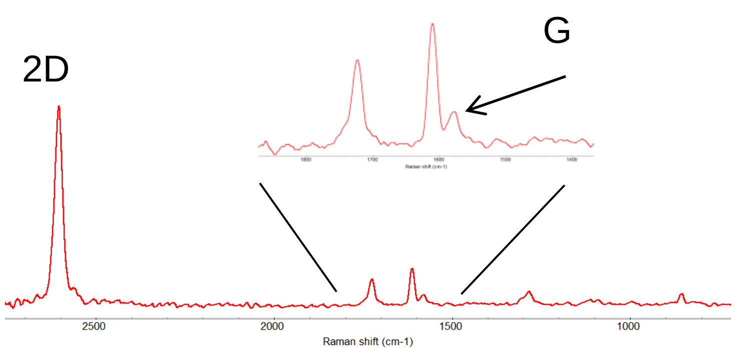


Raman Imaging of Single Layer Graphene on PET

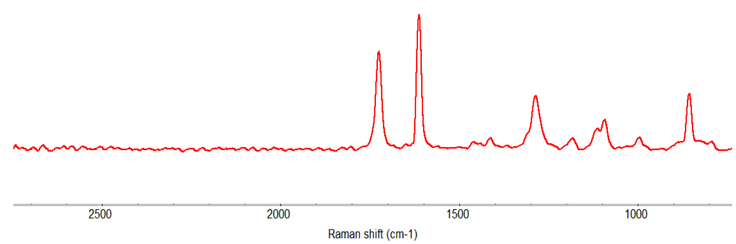
3-D Volume Raman Image



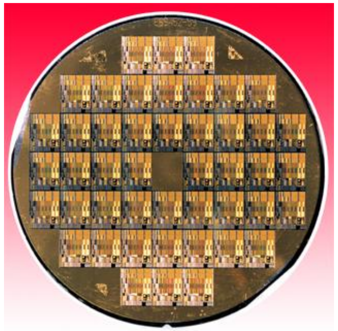




Single Layer Graphene



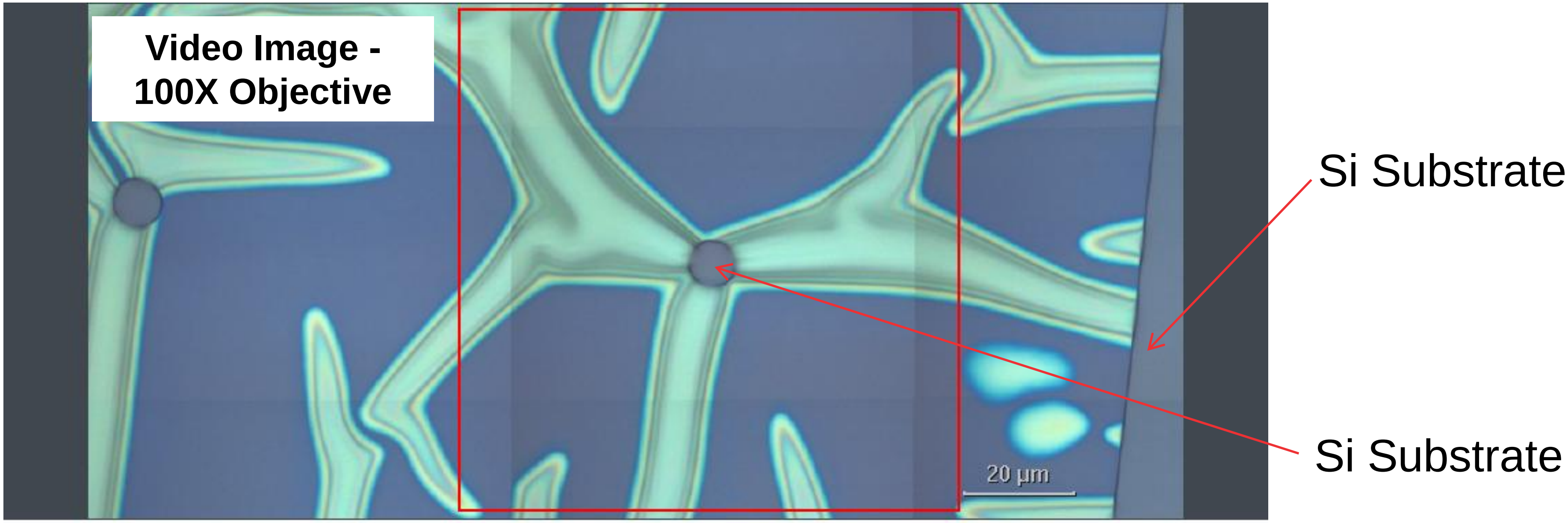
(Poly)ethylene terephthalate



Raman Imaging of Silicon Materials

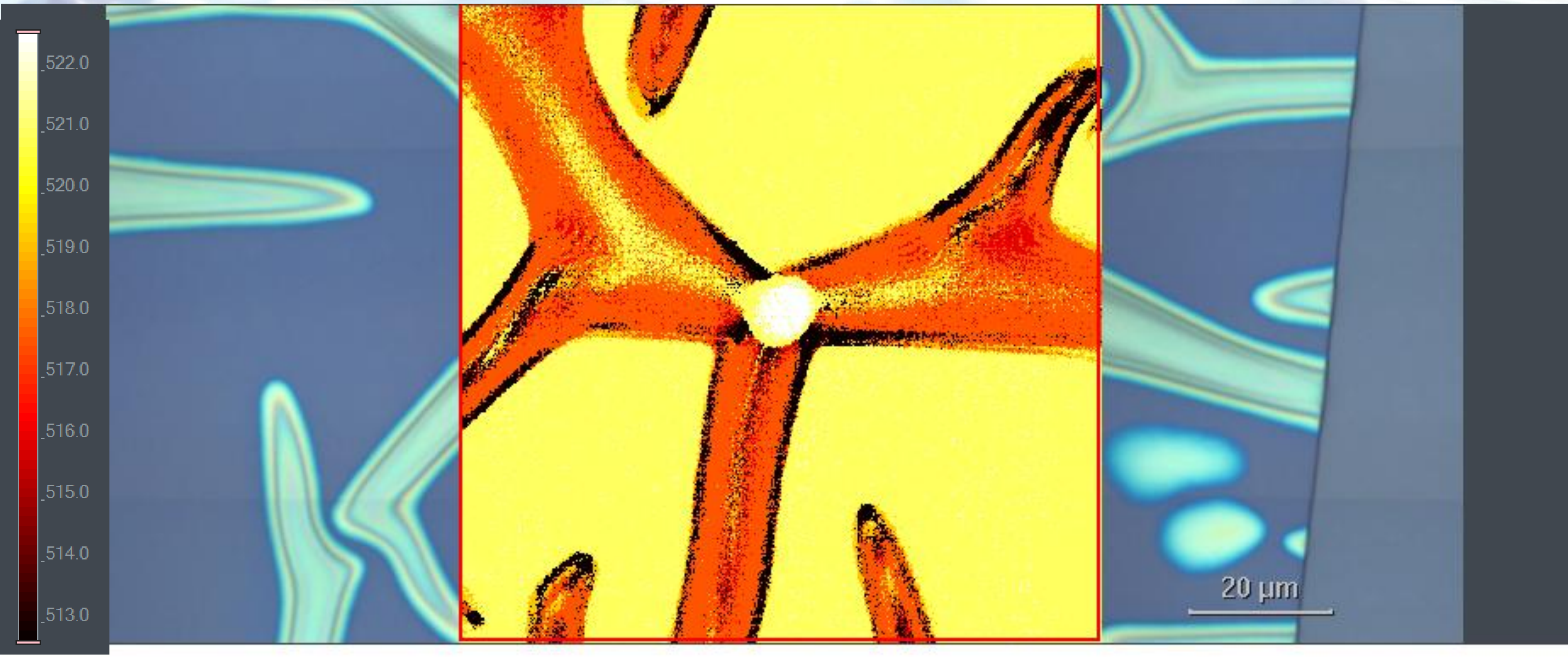
Raman Imaging of Stress in Silicon Samples

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

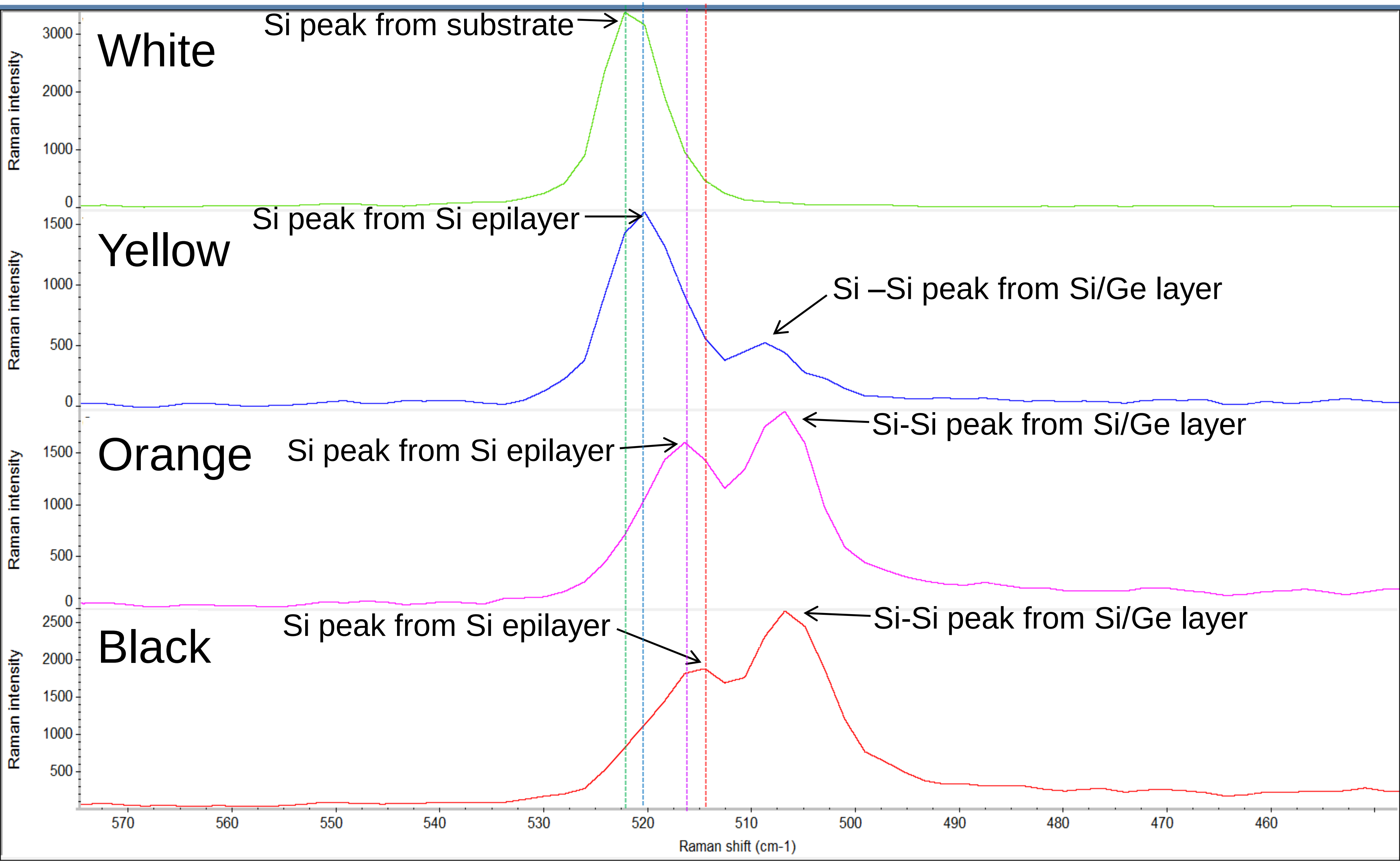
Stress Image – Shift in the Silicon Peak



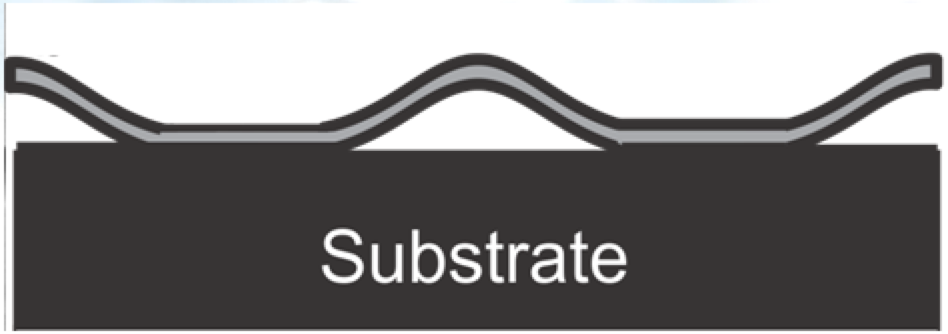
- Colors represent a shift in the location of the silicon peak for the Si epilayer
- White corresponds to the location of the Si substrate peak
- The darker the colors the more the peak has shifted to lower wavenumbers.
- The greater the shift the greater the stress (red shift up to 8 cm^{-1})

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

Representative Raman Spectra

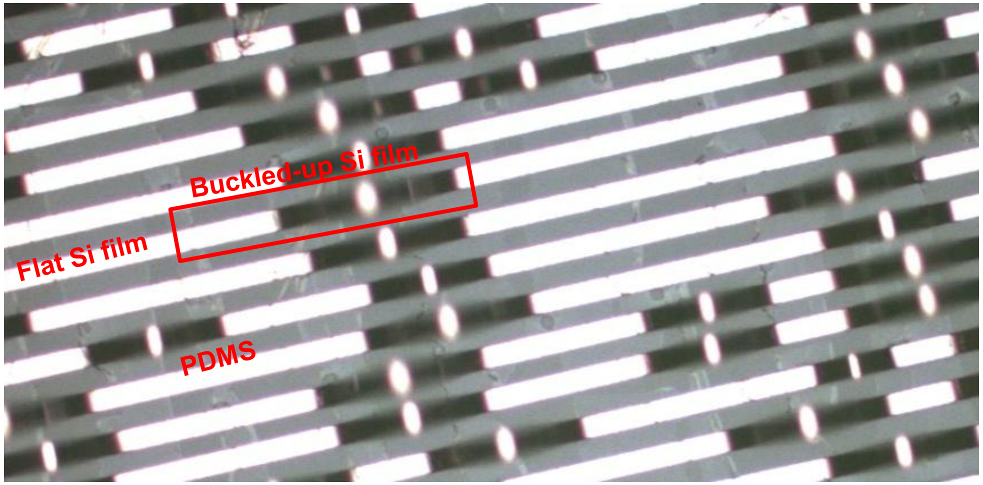


Imaging of Silicon Nanoribbons



Diagram

220 nm thick Si nanoribbon buckled-up on PDMS.

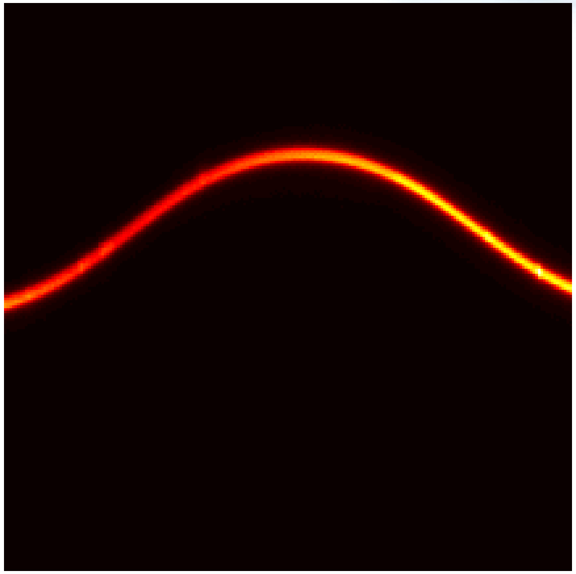


Visible Image

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

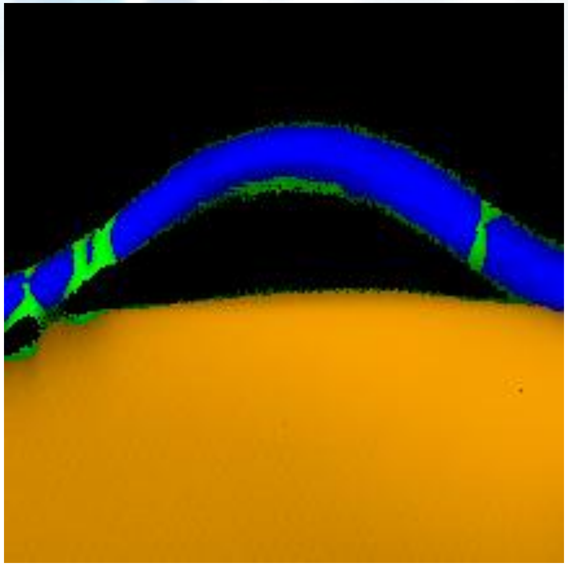
Raman Imaging - Silicon Nano-Ribbons

Confocal depth profiling cross-sections of the silicon ribbons

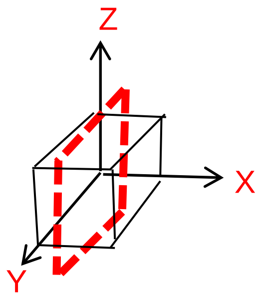


Peak Height

Correlation



MCR

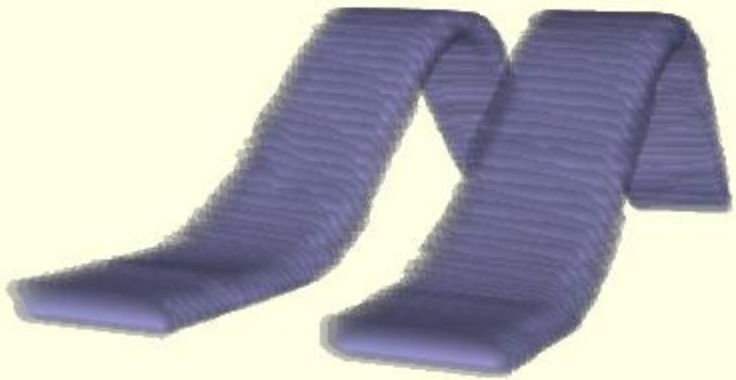


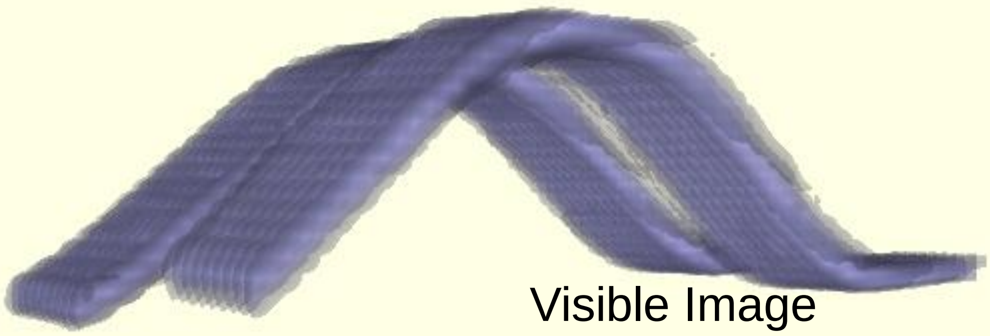
455 nm laser (1 mW), 128 x 128 μm^2, 1 μm image pixel size, 0.010 s exposure time, 16384 spectra, 10 scans

3-D Raman Images of Silicon Nano-ribbons

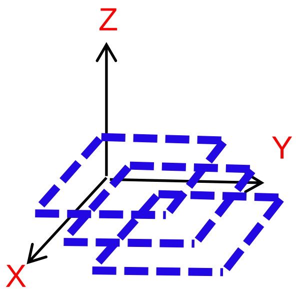
455 nm laser (1 mW), 72 x 157 μm^2, 1 μm image pixel size, 11304 spectra per region, 0.010 s exposure time, 10 scans, 40 slices, 1 μm steps between x-y planes, 452160 spectra

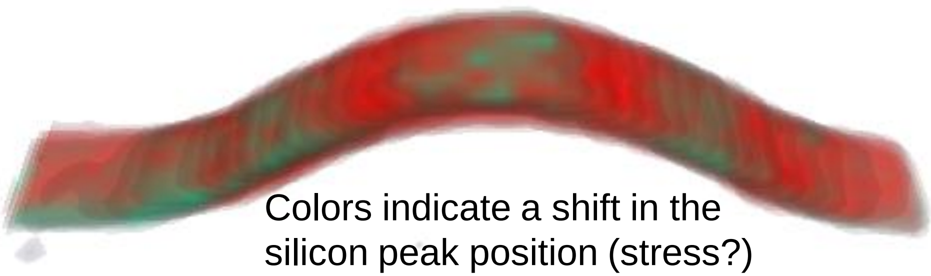
3-D Images of Si Ribbons Based on the Silicon Peak





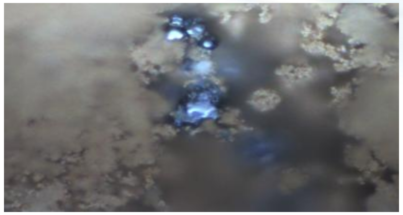
3-D Images of Si Ribbons Showing a Shift in the Silicon Peak Position

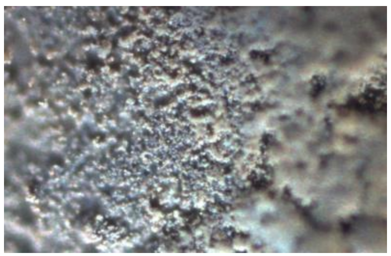


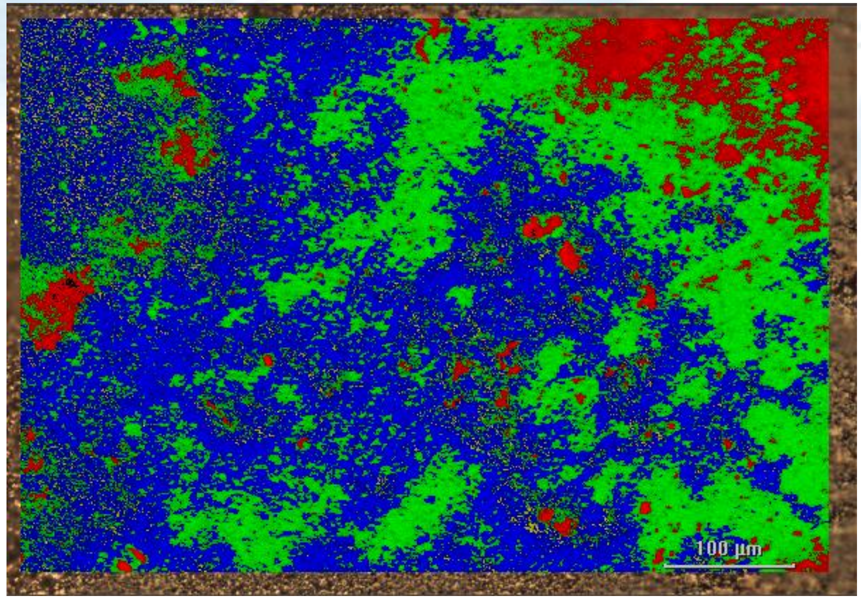


455 nm laser (1 mW), 36 x 168 μm^2, 2 μm image pixel size, 1615 spectra per region, 0.020 s exposure time, 100 scans, 41 slices, 1 μm steps between x-y planes, 66215 spectra

Nano-Crystalline Silicon Powder for Silicon Anodes

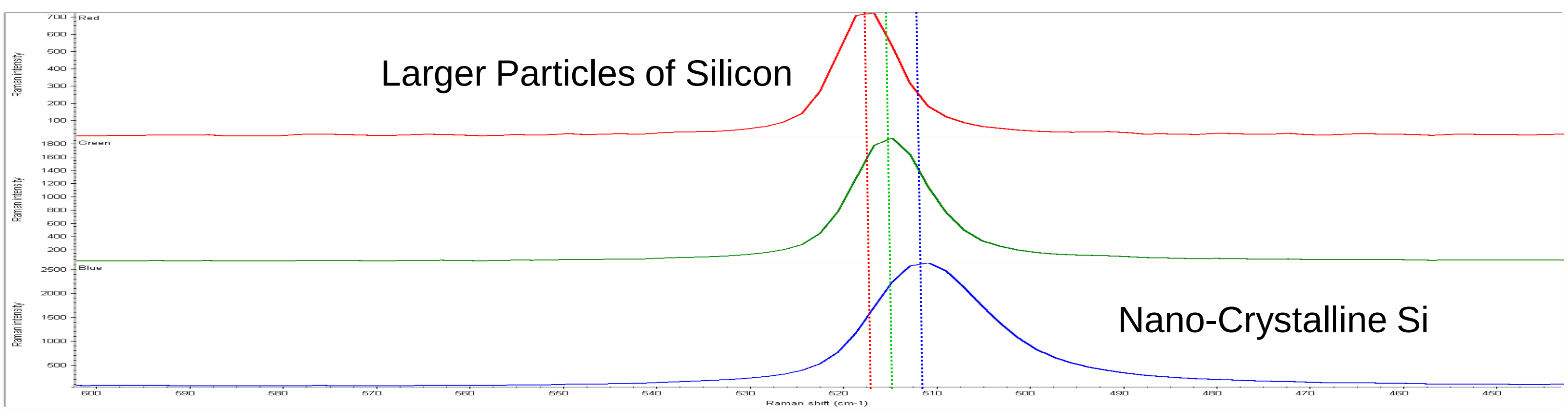






455 nm laser (0.2 mW)
629 x 430 μm^2 area
1.0 μm image pixel size
270500 spectra
0.020 s exposure time
10 scans

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



Conclusions

- Raman imaging can be used for a wide variety of different applications including, but not exclusive to,
  - Graphene
  - Silicon
- Raman imaging not only can be used to identify unknown materials but it also provides information on molecular structure and sample morphology
  - Evaluation of graphene film quality – number of layers and defects
  - Visualizing stress in silicon – shift in silicon peaks
  - Distributions of sample morphologies in silicon -peak shape and position
- Raman Imaging provides distribution and context information for areas of interest.
- Raman imaging presents the vast amounts of spectroscopic data generated as informative visual images