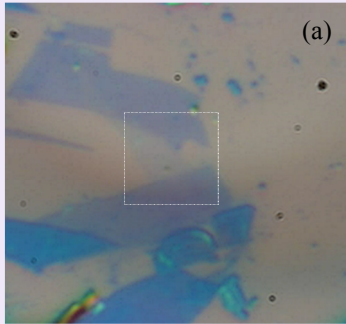


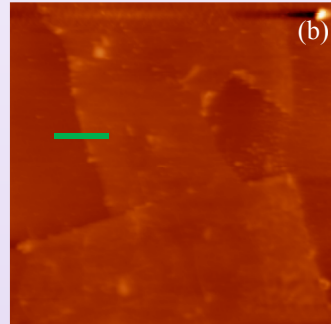
Graphene

Transparent On-line AFM & Raman Integration Without Top or Bottom AFM Optical Interference Investigation of Graphene on Silicon

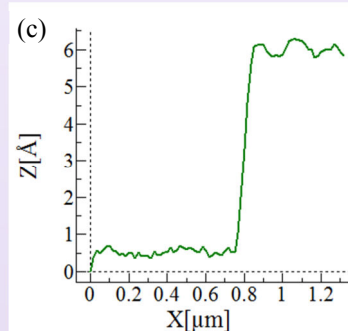
Online AFM/Raman Imaging



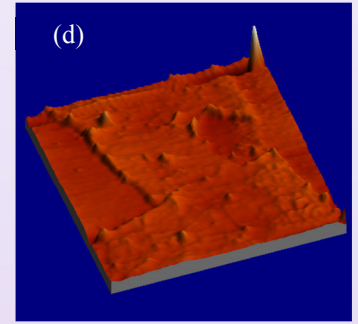
Optical top-view of Graphene flake on Silicon performed with 100x objective (NA=0.75) of an upright microscope during AFM/Raman imaging.



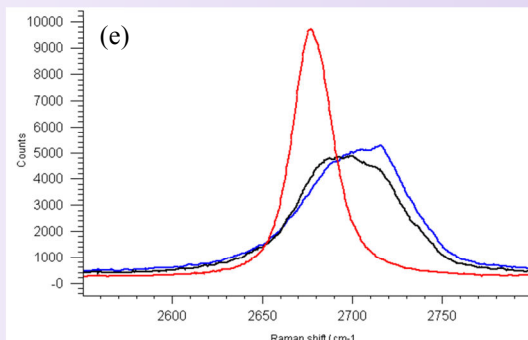
10x10 μm AFM Height image of single and double layer of Graphene.



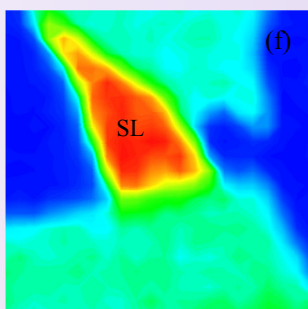
Height line profile at the green line shown in (b) of the Graphene single layer.



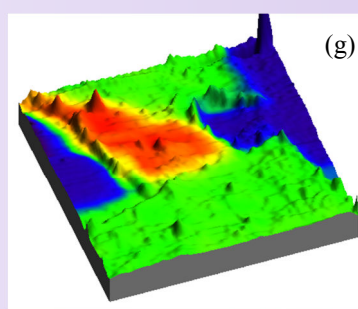
AFM 3D Image of Graphene.



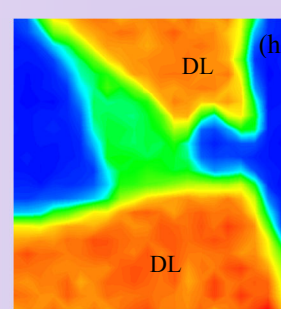
(e) Graphene Raman spectra of Single Layer (Red), Double Layer (blue and black) at the marked area on (a). The red spectrum corresponds to the single layer graphene shown in (b). Blue and black corresponds to double & multilayers on the red area of map (c). The 2700cm^{-1} peak alteration in this area are due to alterations in numbers of layers of graphene.



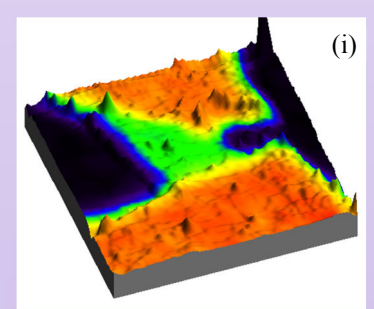
Raman Intensity map of the 2676cm^{-1} 2D single layer band. The map was obtained during online AFM Raman image with full correlation to the AFM image presented on (b)



AFM/Raman Collage image showing the 2676cm^{-1} band's intensity merged with the AFM topography. The colors represent the Raman intensities where red is the highest.



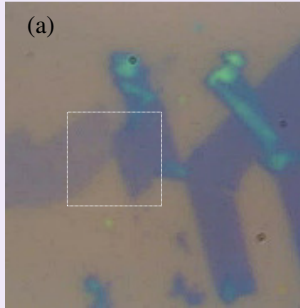
Raman Intensity map of the 2700cm^{-1} double layer band. The map was recorded during online AFM Raman scan with full correlation to the AFM image presented on (b)



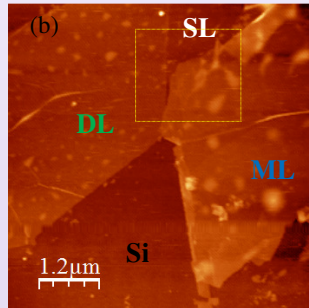
AFM/Raman Collage image showing the 2676cm^{-1} band's intensity merged with the AFM topography. The colors represent the Raman intensities where red is the highest.

Transparent AFM & Raman Integration Without Top or Bottom AFM Optical Interference Investigation of Graphene on Silicon

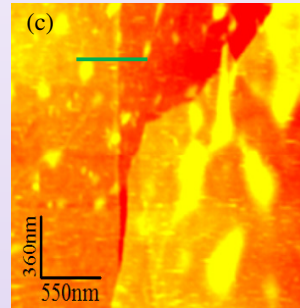
Graphene Online AFM/Raman Imaging



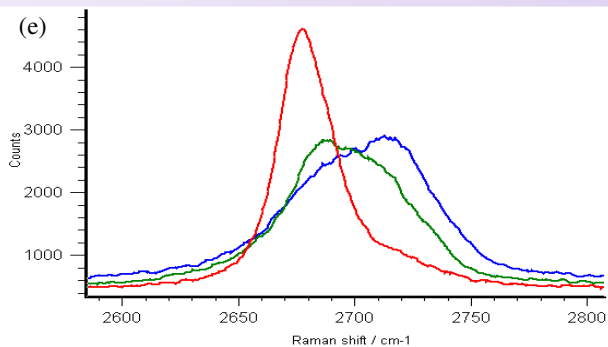
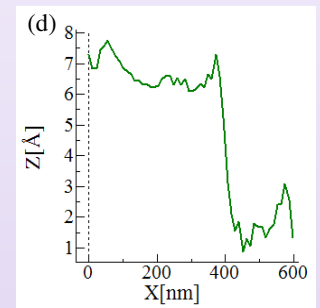
Optical top-view picture of Graphene flake on Silicon performed with an upright microscope 100x objective (NA=0.75) during AFM/Raman imaging.



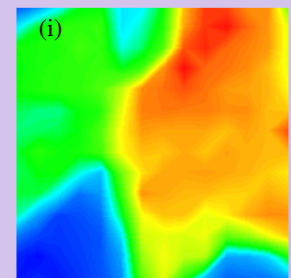
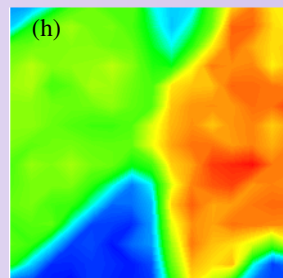
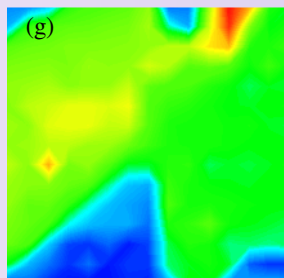
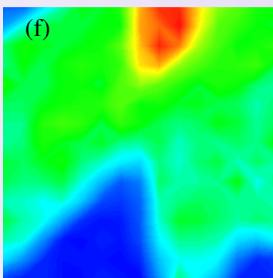
AFM topographic image of Graphene performed at the marked square in (a) showing single, double and multi layers of Graphene.



Zoom of the AFM image (b) of the single layer area marked by a yellow square in (b). The presence of a Single Graphene Layer is clearly seen through the height line profile (d) and the subsequent Raman maps.



Selected Graphene Raman spectra of Single Layer (Red), Double Layer (Green) and Multi Layer (Blue) at the marked areas on the AFM image (b) above) acquired during AFM/Raman imaging. Corresponding Raman maps for intensities of the single layer (f), double layer (g) multi layer (h) bands are presented below. The map in (i) shows the Intensity of and the 1582 cm^{-1} G band where the single layer contribution is minimum compared to the double and multi layers. Red refers to higher intensities and blue to lowest ($6 \times \mu\text{m}$ area)

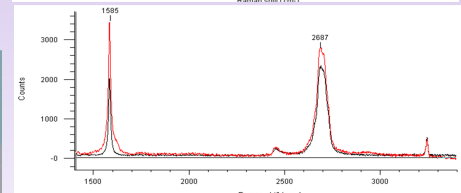
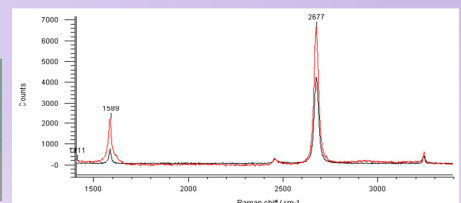
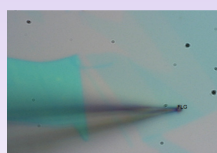
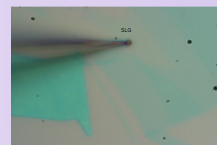
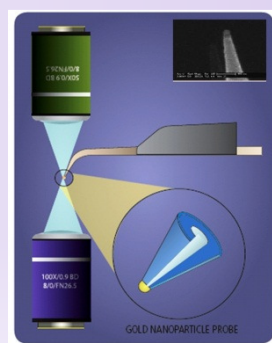


Graphene Tip Enhanced Raman Spectroscopy (TERS)

Left: Gold nanoparticle probe illustration for Tip Enhanced Raman Spectroscopy with high dielectric contrast & well-defined plasmon resonance provides clear optical axis from below and above.

Middle: On-line optical microscope top view of TERS Probe in contact with single layer Graphene.

Right: Raman spectrum of Graphene (black) and enhanced Raman spectrum (red) correlated with the optical microscope images (middle).

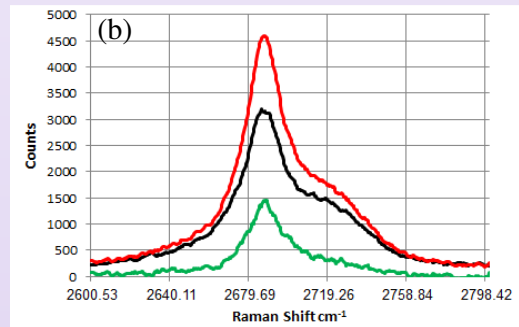
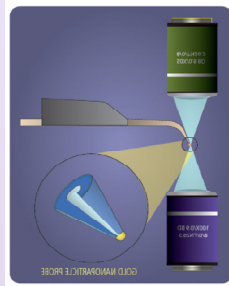
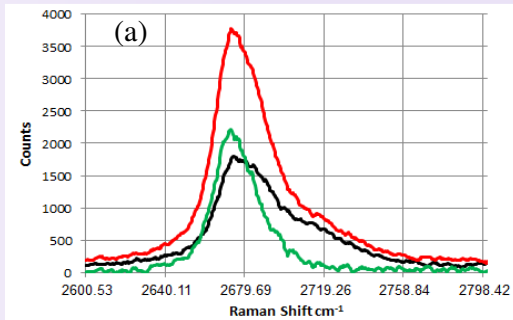


TERS of Graphene On Insulating Silicon Oxide

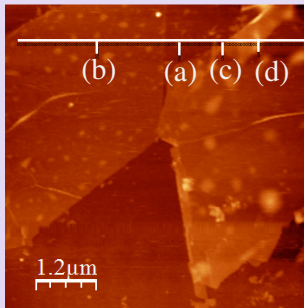
Unique High Dielectric Contrast Optically Friendly & Raman Background Free NanoParticle Probes

Tip Enhanced Raman Spectroscopy (TERS) of a Graphene Flake on Insulator Critical Issues:

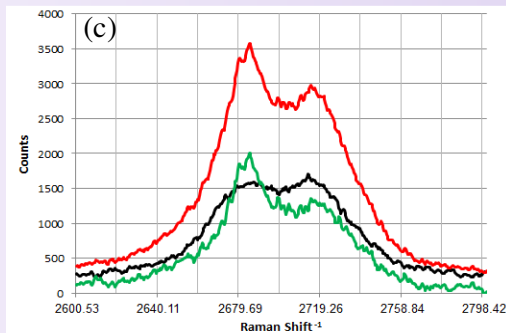
- **TERS Probe:** Unique high dielectric contrast gold nanoparticle probe with defined plasmon resonance
- **Independent Tip and Sample Scanning AFM Head:** Tip piezo scanning allows for maximizing Z polarization excitation even when using conventional Raman excitation with a Gaussian focused laser beam. In addition, Tip scanning is required for Difference Raman Protocols where the TERS signal is evaluated as a difference between the Near-field signal (when the tip is in feedback with the surface) and the far-field signal (when the tip is retracted). Sample scanning on the other hand is required not only for Raman data acquisition but also for feedback to keep the sample-lens distance identical for each pixel in the Raman image with *on-line* AFM autofocus the best method for insuring true chemical contrast without sample topography or less than parallel sample placement
- **Free Optical Axis AFM/Raman TERS:** For maximizing signal with high numerical aperture conventional top down illumination critical for opaque grapheme on silicon samples



TERS measurement performed at the single layer area indicated as (a) in the middle AFM image. Black is the far-field Raman spectrum. Red the enhanced spectrum when the TERS tip is in contact. Green is the difference of these two spectra. Note the width of the difference signal. The single layer is principally responsible for the enhancement even though the laser excites this point & the surroundings



TERS measurement performed at the double layer area indicated as (b) on the middle AFM image. Black is the far-field Raman spectrum. Red is the enhanced spectrum when the TERS tip is in contact. Green is the calculated difference of these two spectra. Note that the principal enhancement is from the top layer in spite of the presence & the illumination of the bottom layer.

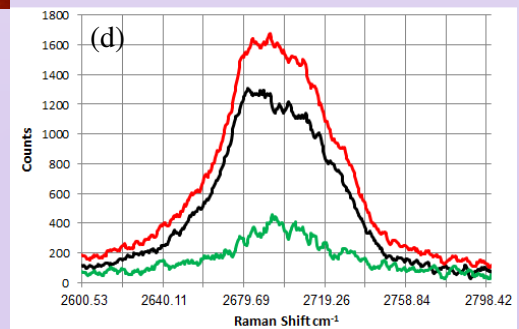


AFM Height image of Graphene flake.

TERS measurements were performed at each of the alphabetically indicated points.

The results are shown and described for each of the spectra.

TERS measurement performed in the three (or four) layer area indicated as (c) in the AFM image (middle). Black is the far-field Raman spectrum. Red the enhanced spectrum when the TERS tip is in contact. Green is the difference of these two spectra. Note that the principal enhancement is from the top layer (left peak) in spite of the presence & the illumination of the bottom layers.



TERS measurement performed at the multiple layers area indicated as (d) in the AFM image (middle). Black is the far-field Raman spectrum. Red the enhanced spectrum when the TERS tip is in contact. Green is the difference of these two spectra.