Application Note

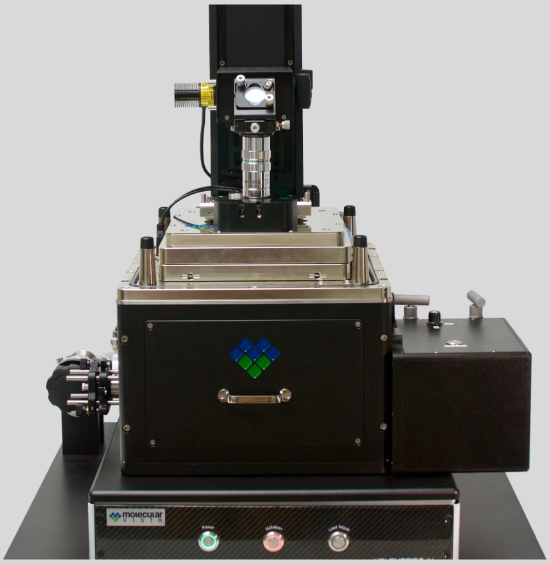
AFM-IR-Raman: Using Three Techniques for Better Nano-Chemical Analysis

Background

Raman microscopy is becoming increasingly popular, and companies are creating new products that combine Raman with other techniques to analyze samples more efficiently. Some of these products can take co-located Raman and FTIR data, while others combine Raman with optical or topographic information. By having a variety of data types all taken in precisely the same spot, researchers can make more informed decisions. Molecular Vista primarily focuses on photo-induced force microscopy (PiFM). This technique can simultaneously measure the topography with AFM and the surface chemistry through PiFM with a lateral resolution of better than 5 nm. However, these PiFM instruments also support other optical AFM imaging techniques such as Raman spectroscopy (RS) or photoluminescence (PL). IR PiFM can provide infrared (IR) data at higher resolutions than any other technique. However, depending on the sample, IR spectroscopy is not always the best choice.
For instance, IR spectroscopy probes vibrational modes which is great for many molecules but is not effective on metals. Also, PiFM is excellent in detecting absorption of photons via force measurement, however, emission of photons in processes such as Raman and photoluminescence cannot be converted to force for detection.

About Molecular Vista

Molecular Vista designs, develops, and provides tools that allow its customers to probe and understand matter at the molecular level through quantitative visualization. Molecular Vista was founded by two industry veterans, Prof. Kumar Wickramasinghe (UC Irvine and formerly with IBM Research) and Dr. Sung Park (co-founder of Park Scientific Instruments).



Principles of PiFM vs Raman & PL

Raman, PL, and PiFM can be done on the same instrument. However, it is important to understand the differences in how the signals are measured so that each technique can be applied properly. PiFM achieves its impressive resolution and sensitivity by measuring attractive forces between the tip and the sample. Because the optical response of the sample is measured mechanically via force interactions, all of the far-field response from the IR excitation is excluded from the measurement. Instead, just the local near-field response is measured by the AFM tip. This is why such high resolution and sensitivity is possible. However, this only works on samples that are active in the IR region. Raman and PL on the other hand can measure some samples that are not IR-active. However, the resolution, sensitivity, and SNR will be far inferior to PiFM. When Raman spectroscopy or PL is combined with an AFM, there will be both a far-field response from the sample that is excited by the laser spot as well as a more localized near field response from light enhanced by the AFM tip. Both the far-field and near-field optical responses must be measured by collecting the photons using a parabolic mirror and diverting that light to a spectrometer using a dichroic filter [Figure 1]. Because Raman and PL use an optical detection scheme, the sensitivity and resolution will be quite poor unless the near field signal can be isolated from the far field signal. Near-field optical detection has been done with tip-enhanced Raman spectroscopy (TERS) or tip-enhanced photoluminescence (TEPL), but the field enhancement required makes these techniques impractical. The difference in signal strength between the near and far field responses is related to the volume probed. Assuming a tip-enhanced spot size of 10 nm and a far-field focal spot size of 500 nm, far-field probes 2500x and 125000x larger amount for 2D and 3D samples, respectively. Under ideal conditions a wide AFM tip with a single plasmonic ellipsoid particle isolated at the tip could produce a field-enhancement of about 50. This enhancement would produce 1:1 ratio of near and far field responses in a 2D material. However, for a real-world goldcoated AFM tip, the enhancement factor is about 4 because a long gold ellipsoid suffers phase retardation which severely diminishes the plasmon resonance [1]. The result is that on most samples other than 1D samples such as carbon nanotubes, the TERS/TEPL signal will be completely buried within the far-field signal, and so Raman and PL cannot achieve the resolution possible with PiFM.

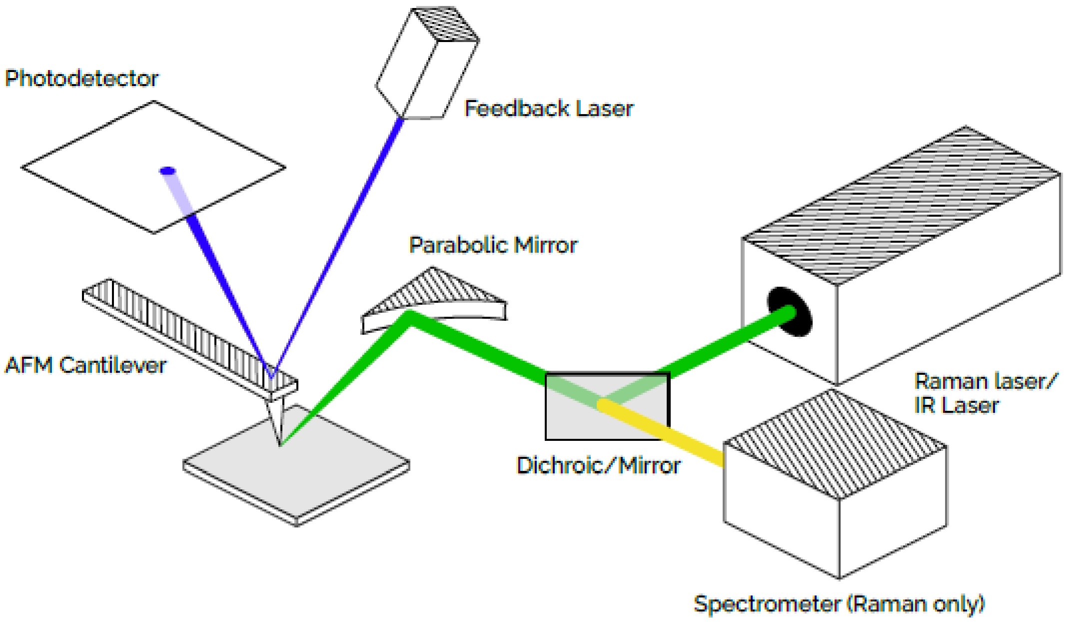


Figure 1. A Raman (or PL) laser focused on the apex of the AFM tip excites the sample. Scattered photons are collected by the parabolic mirror and separated from the excitation laser with a dichroic where it is then passed to a spectrometer. Switching the dichroic for a mirror will make the system ready for IR PiFM.

Combining PiFM and Raman

PiFM is fast, extremely sensitive, and extremely high-resolution, so how can one get these features when working with materials that are not IR active? One way would be to use Raman, but that takes too long and has poor spatial resolution. Therefore, a practical approach would be to use Raman to calibrate a tip so that PiFM can be used instead. This unconventional approach may not seem obvious, but it has many practical benefits. When PiFM is performed on a sample that is not IR active, there will still be some contrast in the IR image. Regardless of whether or not the sample is IR-active, there will still be an enhanced field created by the AFM tip. If the magnitude of this enhancement changes, then that will change the forces acting on the AFM tip and create contrast in the PiFM image. Therefore, while PiFM cannot do spectroscopy on IR-inactive samples, it can still measure changes in the field enhancement that are mediated by the sample material below it. This field enhancement measurement technique can be further amplified by using a reporter molecule. If the apex of the AFM tip has a material, say PDMS, that is very sensitive to IR excitation, then this reporter molecule will respond to changes in the field enhancement and act as an amplifier. This patented technique means that PiFM can measure the field-enhancement changes on a sample with incredible resolution and sensitivity even when the sample is not IR active. If one uses Raman or PL on a Vista instrument first, they can perform some low-resolution spectroscopy and mapping to understand the composition of a surface. Then, the instrument can be configured for PiFM in seconds by removing the dichroic and switching to an IR laser via software [Figure 1]. IR data taken with the same tip will map the sample-mediated field enhancement. Then the PiFM data can then be correlated with the Raman or PL data to get an extremely detailed understanding of the sample. This approach also saves a significant amount of time since all this data can be collected on the same instrument where Raman, PL, AFM, and PiFM data can all be co-located to exactly the same region of the sample's surface.

Examples

SiGe strain

Figure 2 shows a sample where both Raman and PiFM can analyze the SiO2 lines in a SiO2/SiGe sample; however, only Raman can analyze the SiGe lines albeit with much worse spatial resolution. In this example, AFM topography and hyperspectral Raman data are collected at the same time. Two wavenumbers associated with unstrained silicon signal and the strained silicon Raman signal are used to highlight the SiO2 and SiGe lines, respectively [Figure 2, top images]. At the bottom, the optical image of the sample as seen in Vista One is shown [Figure 2, bottom left] with the location from where the Raman data are collected [Figure 2, top left]. From the AFM/Raman image, a 10 micron × 10 micron region (as shown by the red square) is analyzed by PiFM to acquire the SiO2 lines [Figure 2, bottom right] with much higher spatial resolution along with the corresponding topography [Figure 2, bottom center]. Figure 3 shows the topography and PiFM image at 1122 cm−1 at a region with much smaller pitch, where we can see the IR signal due to SiO2 is depleted at the SiGe layer and gradually increases as it moves away from the interface; the effect of strain is completely gone about 400 nm away from the SiGe line. In between two SiGe lines, PiFM image clearly shows that the strain is frozen in since the distance between the two SiGe lines is much less than 400 nm. This is a good example where optical microscopy, AFM topography, co-located Raman, and IR PiFM are realized in the same sample with progressively higher spatial resolution.

Counting layers in 2D materials

Another way PiFM can be effectively utilized with 2D materials is to use PiFM to monitor N-dependent optical absorption (N = number of 2D layers) and defects with high resolution (100x better spatial resolution compared to Raman and PL) while using Raman/PL data to calibrate the PiFM signal. Figure 4 shows a graphene sample that was transferred onto a quartz substrate. Raman spectra and map at 1590 cm−1 clearly identifies the monolayer regions of the sample albeit with poor spatial resolution and slow acquisition time (13 µm × 13 µm, 32 × 32 pixels, ~ 20 minutes). A similar region imaged with PiFM at 800 cm−1 shows the graphene layers with N = 1 and 2 with much higher spatial resolution and faster acquisition time (8 µm × 8 µm, 256 × 256 pixels, ~ 5 minutes). When we zoom into a 2 µm region, PiFM image clearly shows contrasts due to defects within the monolayer region; notice the strong contrast in the PiFM image compared to the topography.

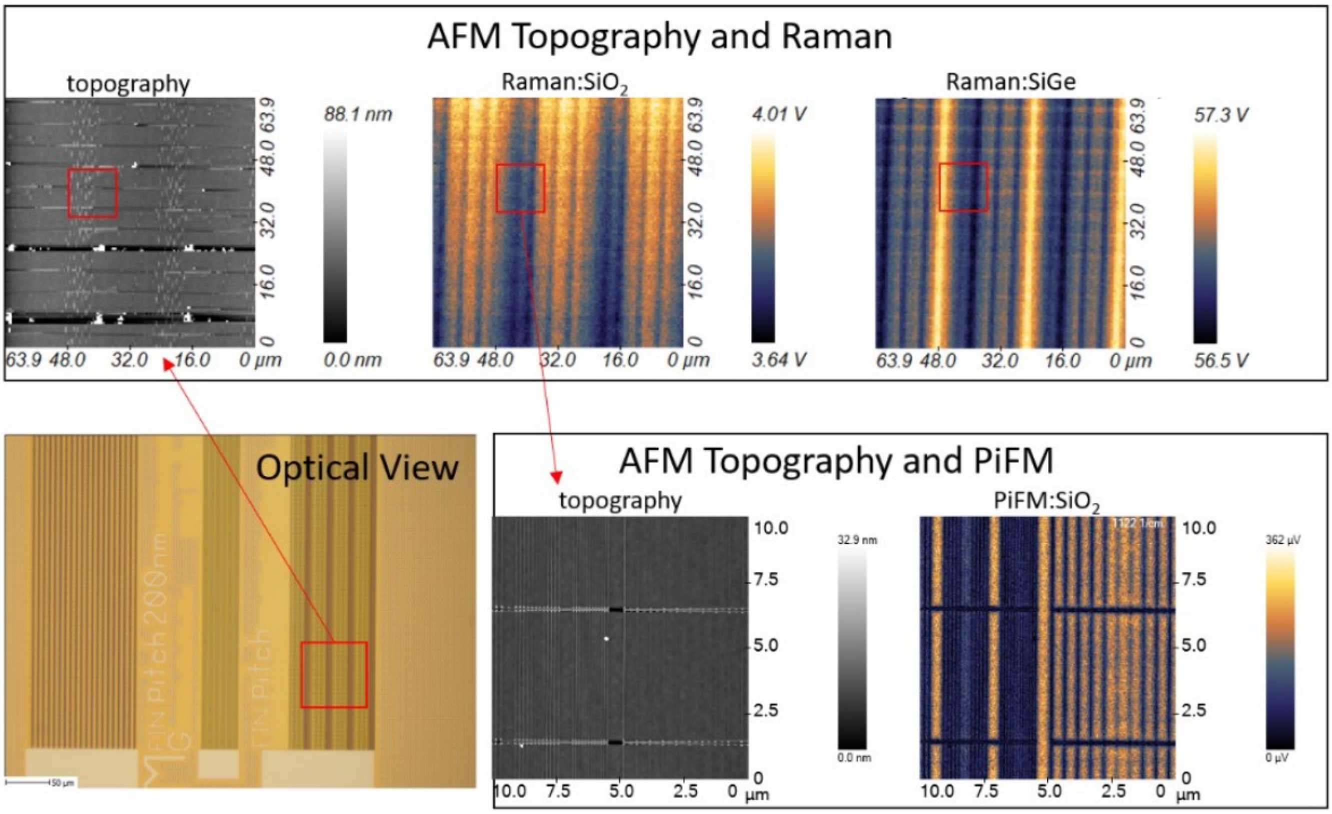


Figure 2. Analyzing strain in a SiO2/SiGe test sample using optical microscopy, AFM topography, Raman and PiFM.

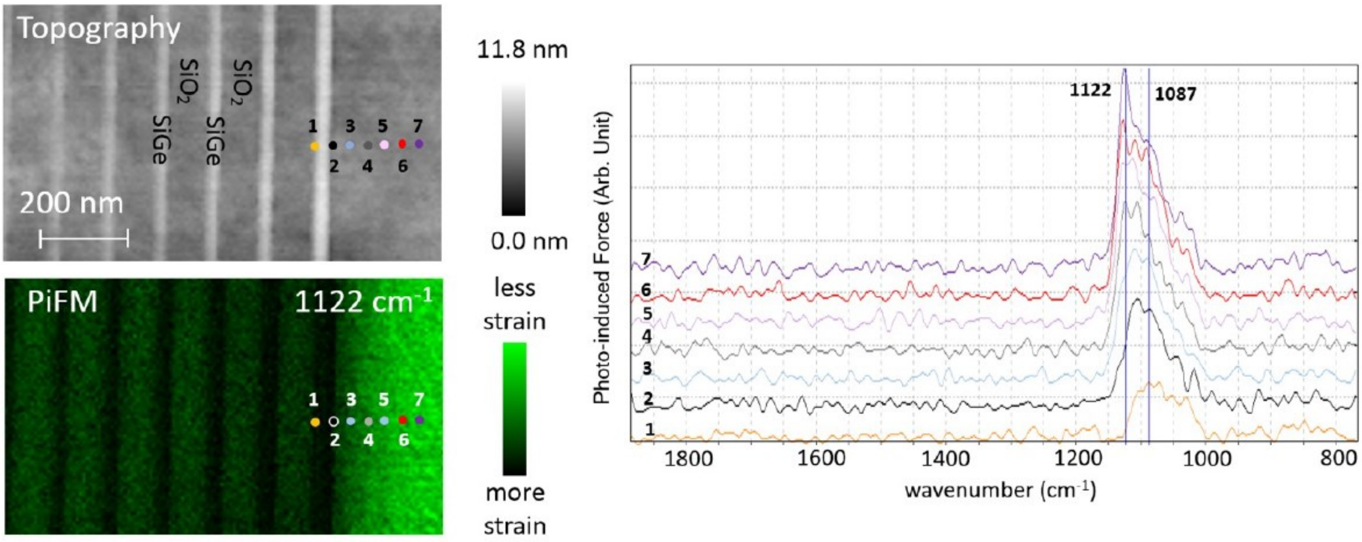


Figure 3. Analyzing strain in a SiO2/SiGe test sample using PiFM. SiO2 is IR active, so the PiF-IR spectra show a peak shift from 1122 cm−1 to 1087 cm−1 as the strain from the SiGe increases.

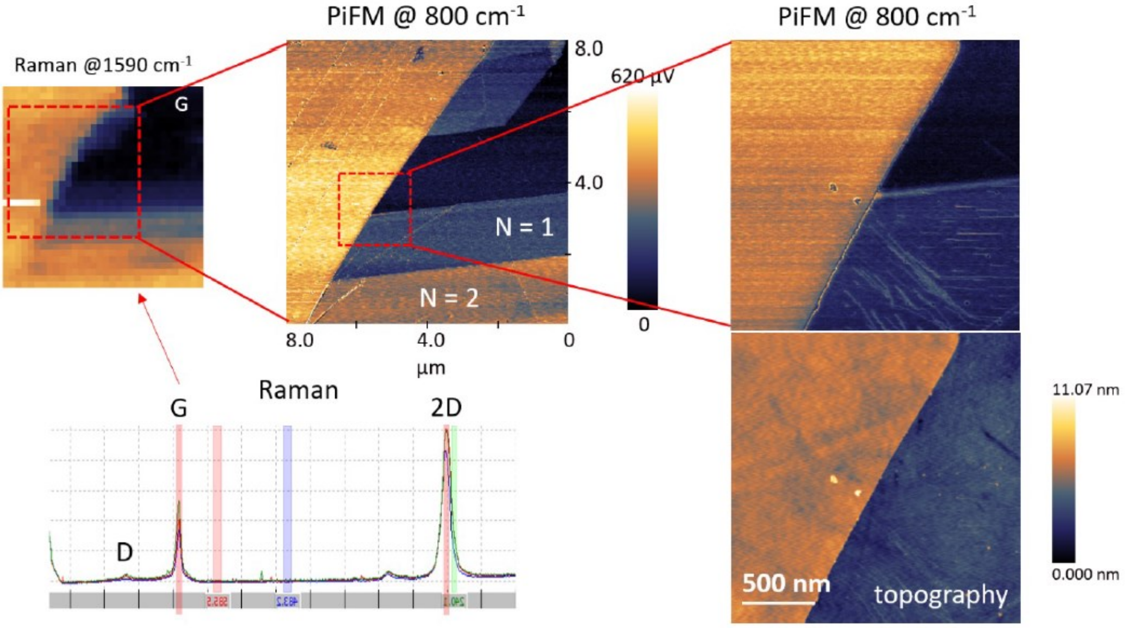


Figure 4. Raman spectroscopy can be used to identify regions with N-number of graphene layers. Then, PiFM can be used to analyze the same region with much higher resolution. The PiFM image shows the different number of graphene layers because the strength of the tip-enhanced field is mediated by the sample below. 800 cm−1 is chosen since that corresponds with the reporter molecule used.

Figure 5 shows the results acquired on an exfoliated MoS2 that is transferred onto a quartz substrate. The photoluminescence (PL) spectra provided by the customer identifies the regions of different number of layers on the optical image; the colored number refers to the number of layers inferred by the PL data. While the topography is quite messy due to the transferring process using PDMS, PiFM (at the excitation λ = 488 nm) image provides high resolution image that clearly delineates regions of different number of layers. Using the rainbow scale, it is clear that each layer increases the PiFM signal roughly by the same magnitude; this is due to the N-dependent absorption, which is expected with many 2D materials.[2] The PiFM signal alone cannot determine the layer-number since its magnitude will change with different tips. However, once the PiFM signal is calibrated by PL (or Raman), then PiFM can be used to identify the regions of different N with much higher spatial resolution and clarity; see the region encircled by the dotted ellipse in the PiFM image where the small neighboring regions of N=1 (orange colored) and N=2 (yellow colored) are clearly identified.

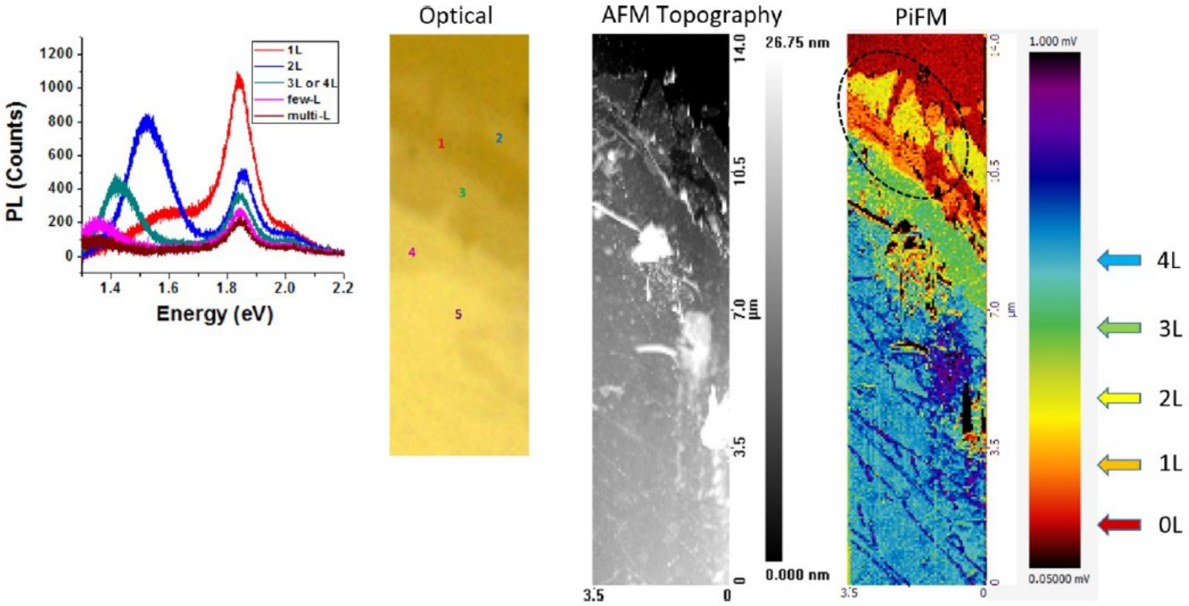


Figure 5. Photoluminescence and PiFM work together to analyze the number of layers in this MoS2 sample.

Summary

In summary, Raman and PL alone cannot provide the resolution or sensitivity researchers want for analyzing 2D materials at extremely high resolutions. PiFM has these capabilities, but it is most effective on materials active in the IR. By adding Raman or PL capabilities to a Vista instrument (AFM-IR), one can extend the relatively fast and high-resolution imaging capabilities of PiFM to the characterization of 2D materials.

References

1. [Nanoscale chemical imaging by photoinduced force microscopy. Derek Nowak, et. al., Sci Adv. 2 (3), e1501571 (2016)

2. Strength of the electric field in apertureless nearfield optical microscopy. Yves C. Martin, et. al., J. of Appl. Phys. 89(10), 5774 (2001)

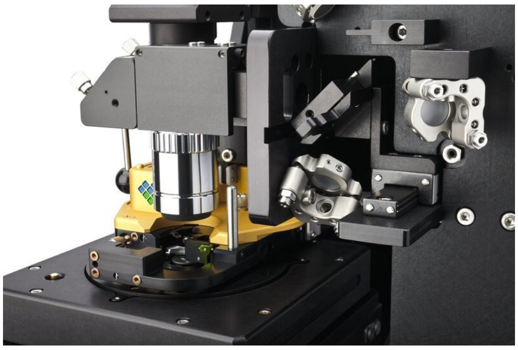
3. Layer-number Dependent Optical Properties of 2D Materials and Their Application for Thickness Determination. Xiao-Li Li, et. al., Adv. Func. Mater. 1604468 (2017)

Suggested instrument for similar testing technique:

Vista One

The Vista One is the original tool that combines AFM with IR (AFM-IR) spectroscopy to provide IR spectral imaging with unprecedented sub-5 nm spatial resolution. Its unique, patented photo-induced force microscopy (PiFM) measures the near-field optical response of the sample via mechanical force detection, making the technique robust and easy-to-use. Reliable and repeatable measurements in the sub 5-nm region provide a nano-FTIR spectrum in less than a second, comparable to regular FTIR spectra in your usual FTIR database.’

Vista 75



The Vista 75 is the next generation AFM-IR instrument, combining AFM with IR (AFM-IR) spectroscopy to provide IR spectral imaging with unprecedented sub-5 nm spatial resolution. Building on the patented photo-induced force microscopy (PiFM) technology of the Vista One, the Vista 75 is the latest instrument from Molecular Vista’s proven AFM-IR line-up. Reliable and repeatable measurements in the sub 5-nm region provide a nano-FTIR spectrum in less than a second, comparable to regular FTIR spectra in your usual FTIR database, now on even larger samples, in a more compact design.