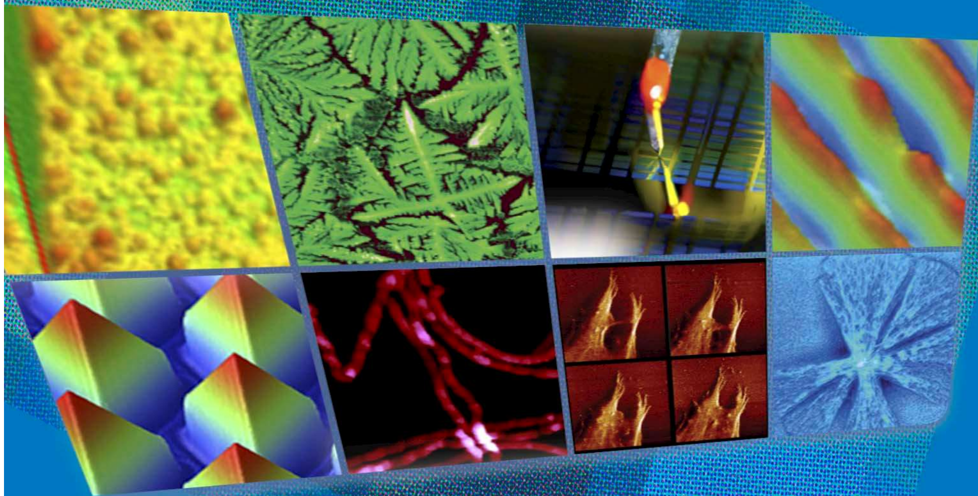
Quantitative Nano-Mechanical/Nano-Electrical Properties Measurement

Wanxin SUN, Bruker Nano-Surface (wanxin.sun@bruker.com)



Atomic Force Microscopy
3D Optical Microscopy
Tribology
Automated AFM
Stylus Profilometry
Mechanical Testing,
Nano Indentation

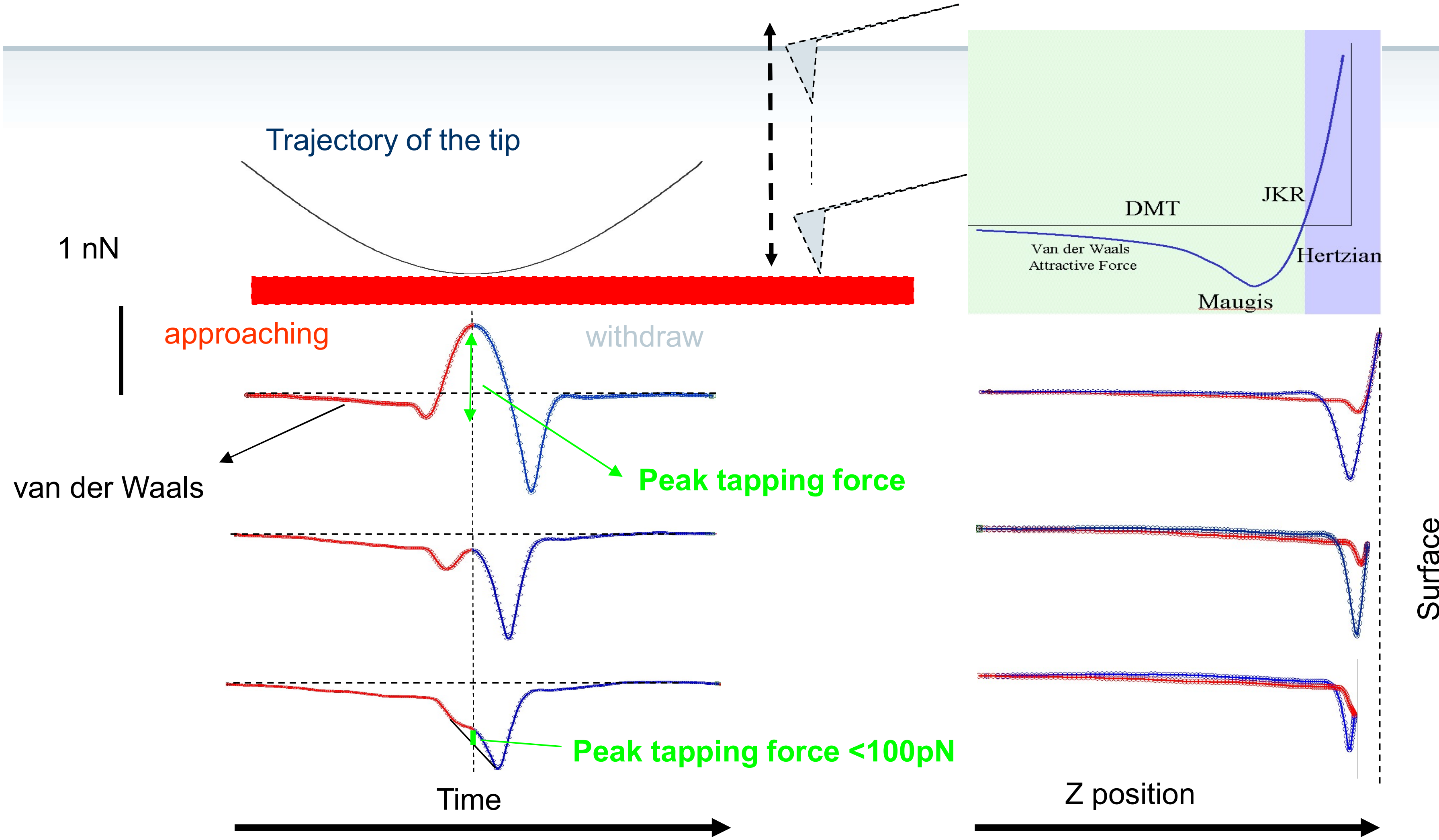
Bruker Nano Surfaces Division

Innovation with Integrity

Outline

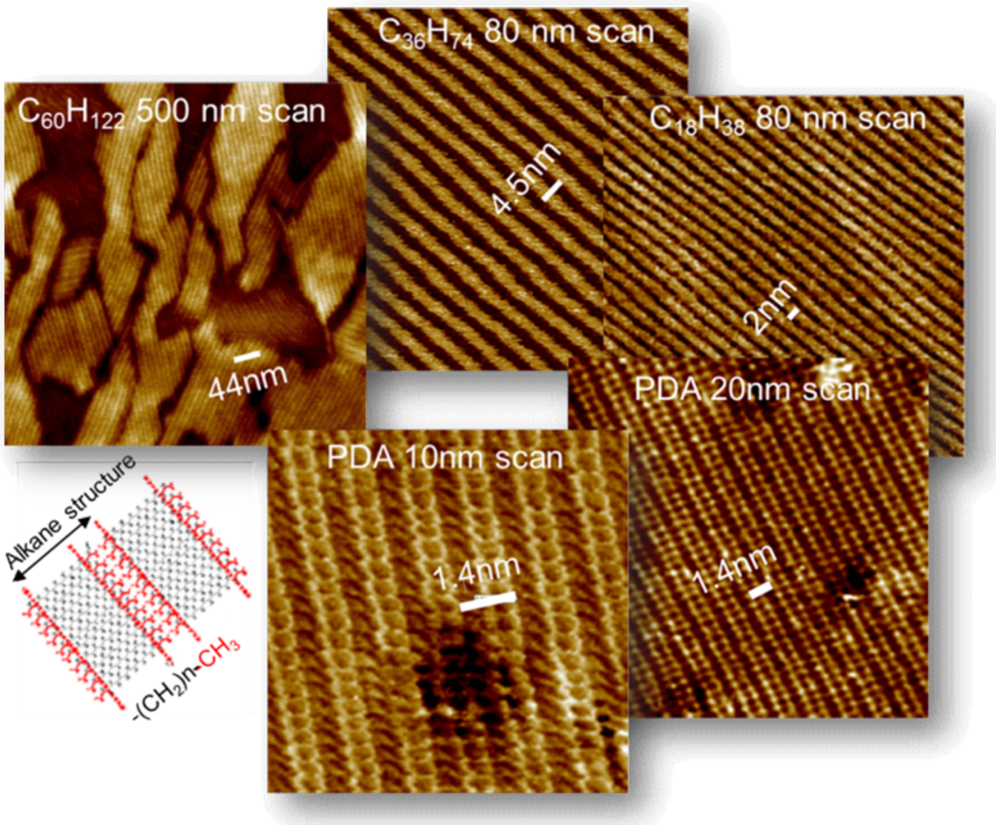
- Quantitative Nano-mechanical Measurement
  - Modulus measurement
  - Molecular recognition
- Force Volume
  - Mechanical mapping mode
- Contact Resonance AFM
  - Elasticity and Viscoelasticity Characterization
- KPFM Development
  - PF and FM make KPFM more sensitive

PeakForce Tapping



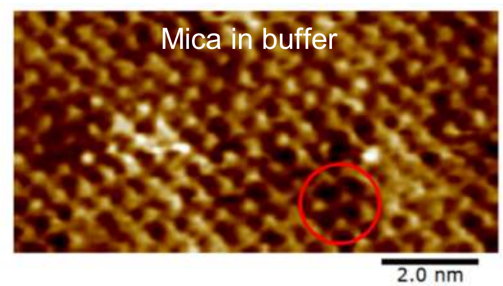
TESP (42 N/m) on Si, MM8

High Resolution Easily Achieved due Superior Force Control

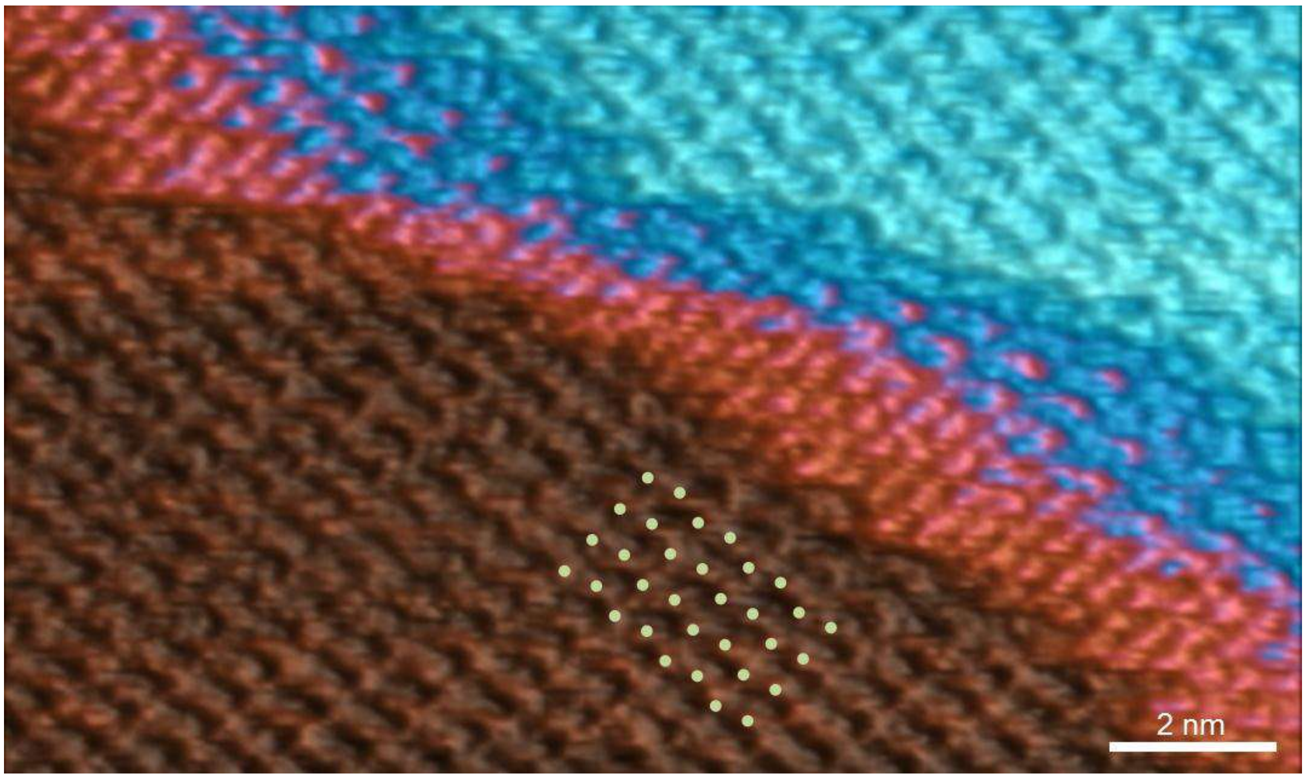


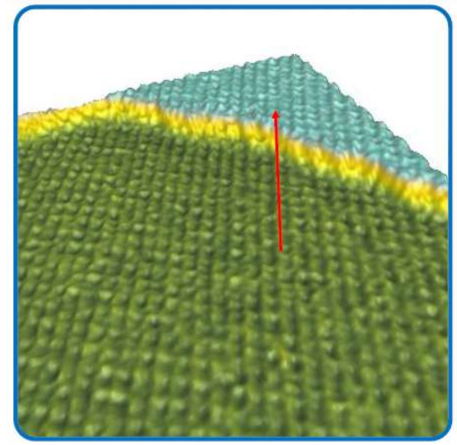
- Topography down to atomic resolution!
- Resolving single atomic and molecular defects

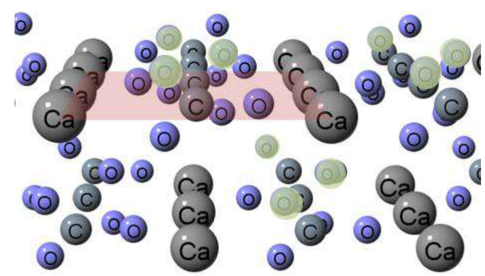
Enabled by PeakForce Tapping™



Oxygen Atoms of Calcite Dissolution Crystal Plane



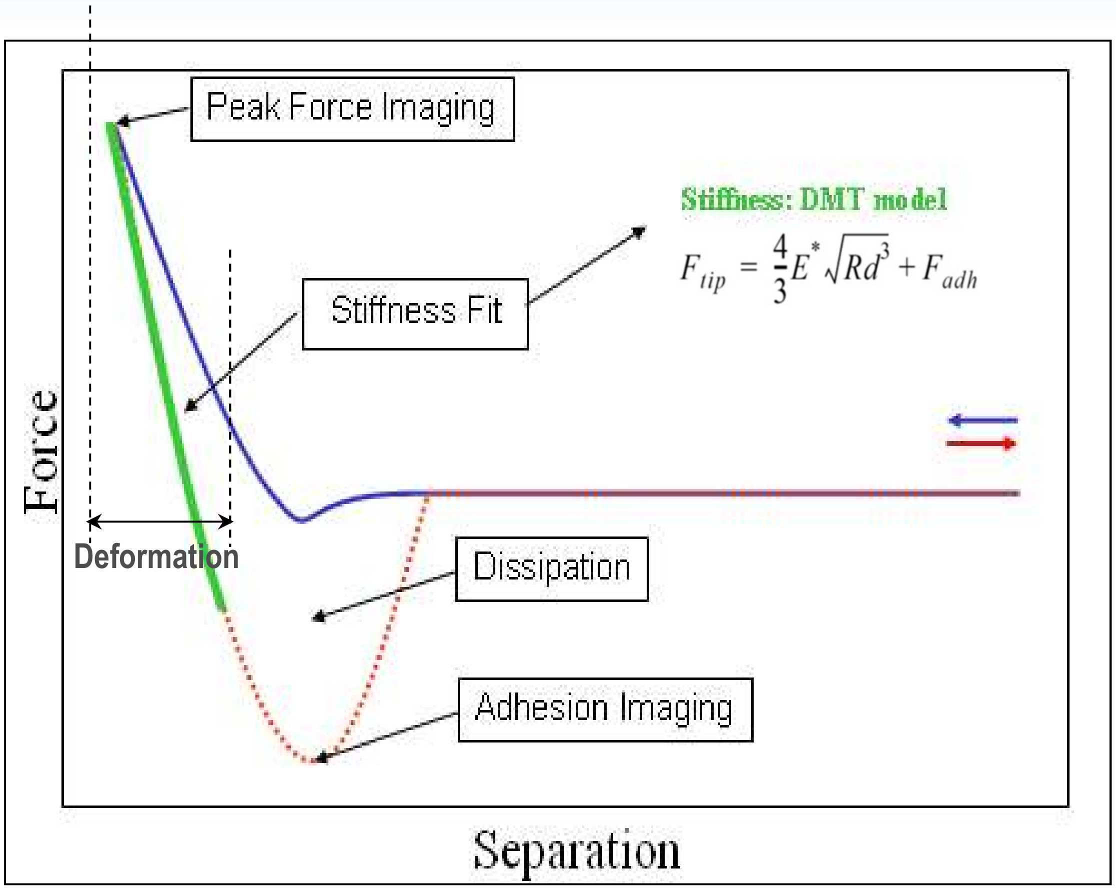




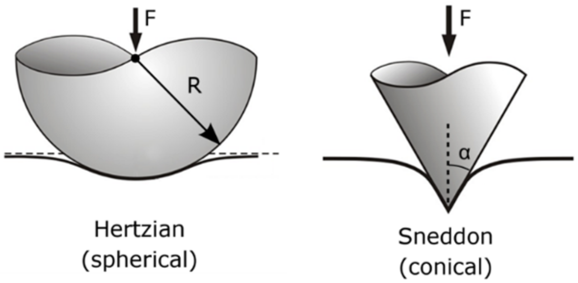
- Dissolution plane interface shows expected offset in crystal planes.

PeakForce QNM

Quantitative Nanomechanical Property

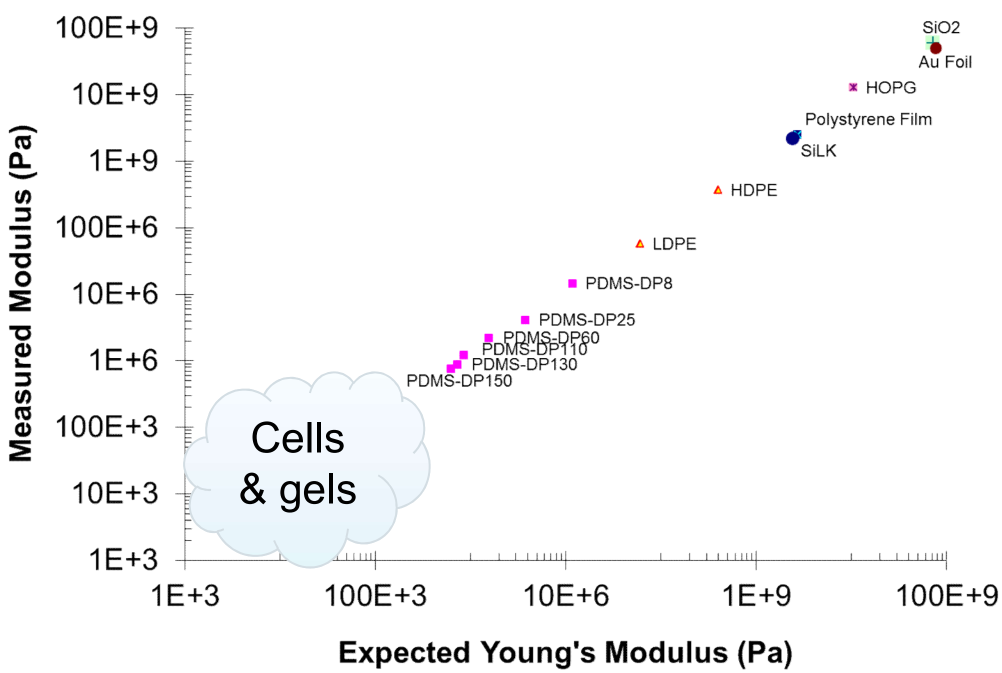


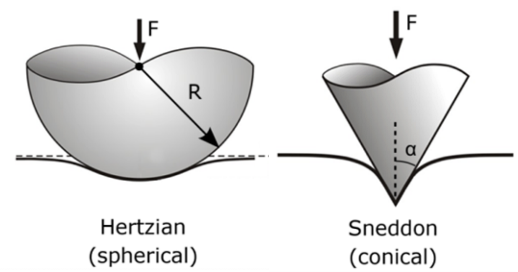
- Simultaneously obtain quantitative data:
  - Topography
  - DMT Modulus ~1MPa – 100GPa
  - Adhesion
  - Energy Dissipation
  - Deformation

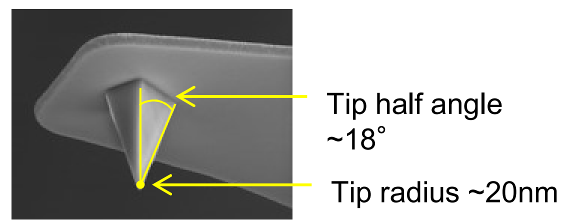


Expanded PeakForce QNM Capabilities

Softer samples & wider range of frequency



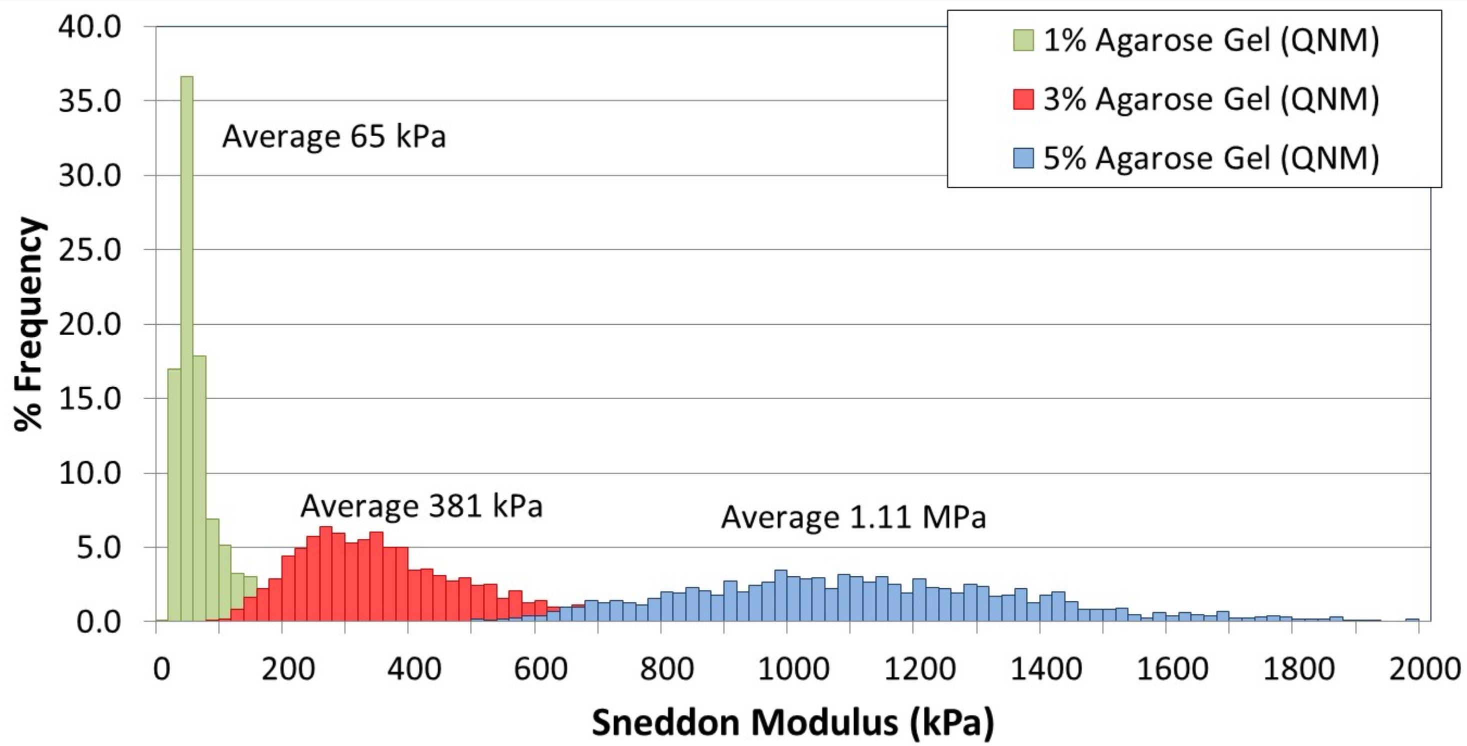




Real AFM tip

- Multiple probes allow wide range of property measurement
- New models: more precise representation of tip shape, adhesion
- New properties: Wider range of ramp size and frequency, study deformation at different rates

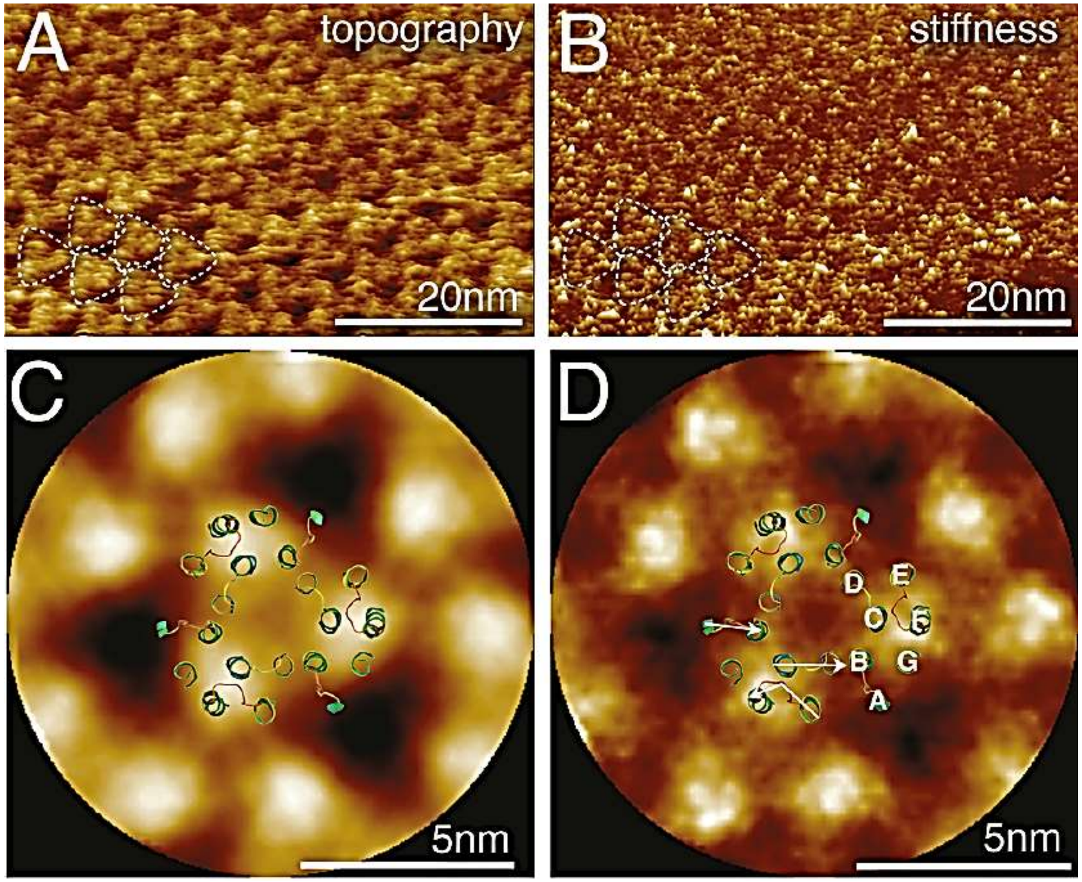
Sneddon Model



- Sneddon model works well over the biologically relevant kPa-MPa range
- Agarose gels measured with PeakForce QNM (Sneddon model, MLCT-E probe)

Molecular Resolution Mapping

Mechanical Mapping of Single Membrane Proteins (bacteriorhodopsin) at Submolecular Resolution



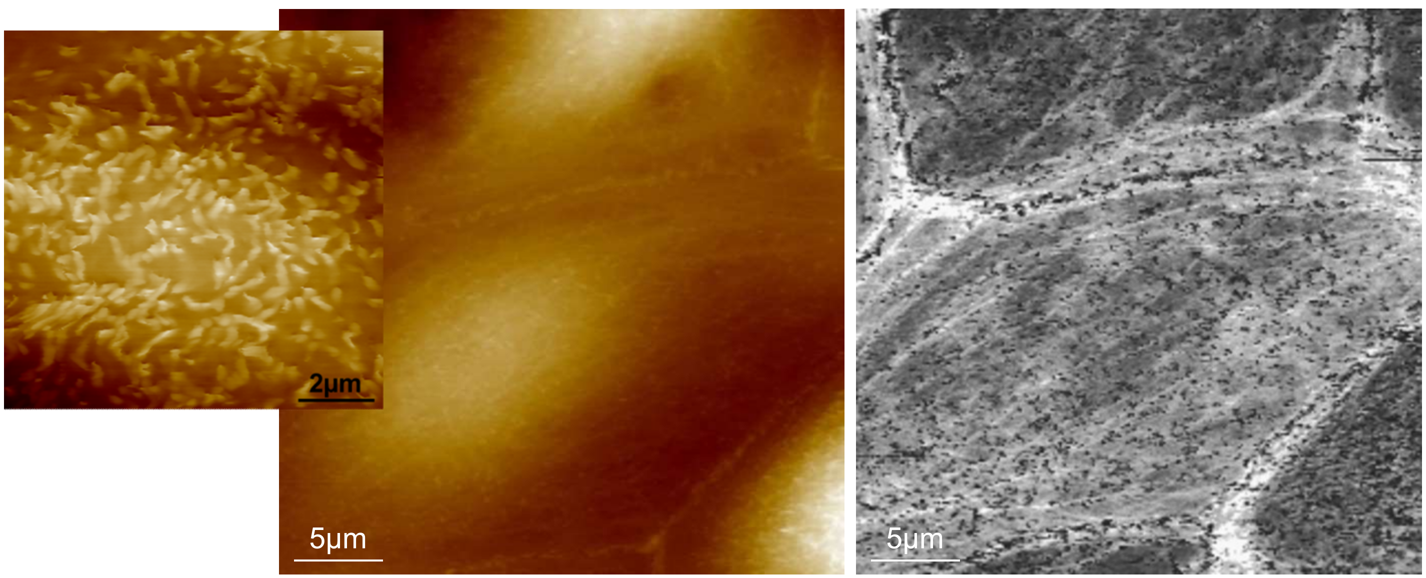
- Flexibility of individual membrane proteins determines their ability to undergo conformation changes
- α-helices are stiff structures contributing to the mechanical stability of membrane proteins, while iterhelical loops appearing more flexible to allow conformational changes

Rico et al, Nano Letter, 2011

PeakForce QNM for Live Cell Imaging

High Resolution Mechano-Biology with BioScope Resolve

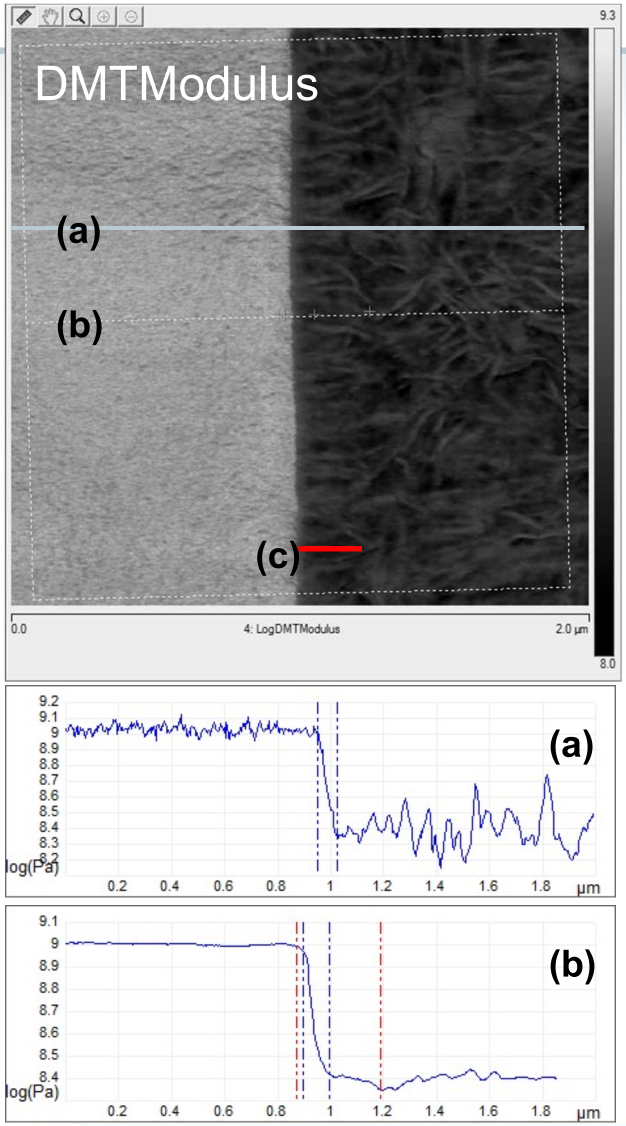
- PeakForce QNM property mapping of live cells provides:
  - Fast acquisition of high-resolution mechanical property maps (up to 1kHz in fluid)
  - Quantitative and highly repeatable modulus/adhesion measurements
- Achieved Through:
  - Unique instrument design including very stable sample clamping
  - Bruker PeakForce QNM Live cell probe (17µm tip, k ~0.08N/m)

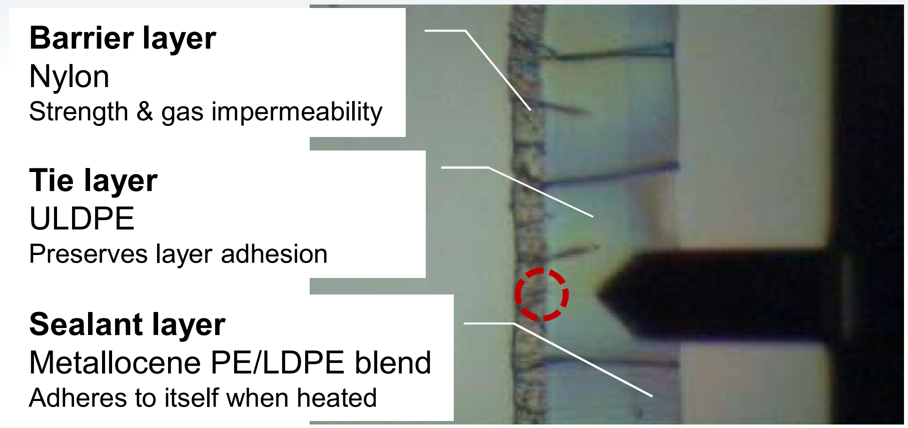


PeakForce QNM topography image (left) and corresponding modulus image (right) of living MDCK cells. Cell structures corresponding to actin fibers show higher modulus (lighter) while cell surface features, believed to be microvilli, appear softer (darker) than the cell membrane itself.

High Resolution PF-QNM

New information revealed

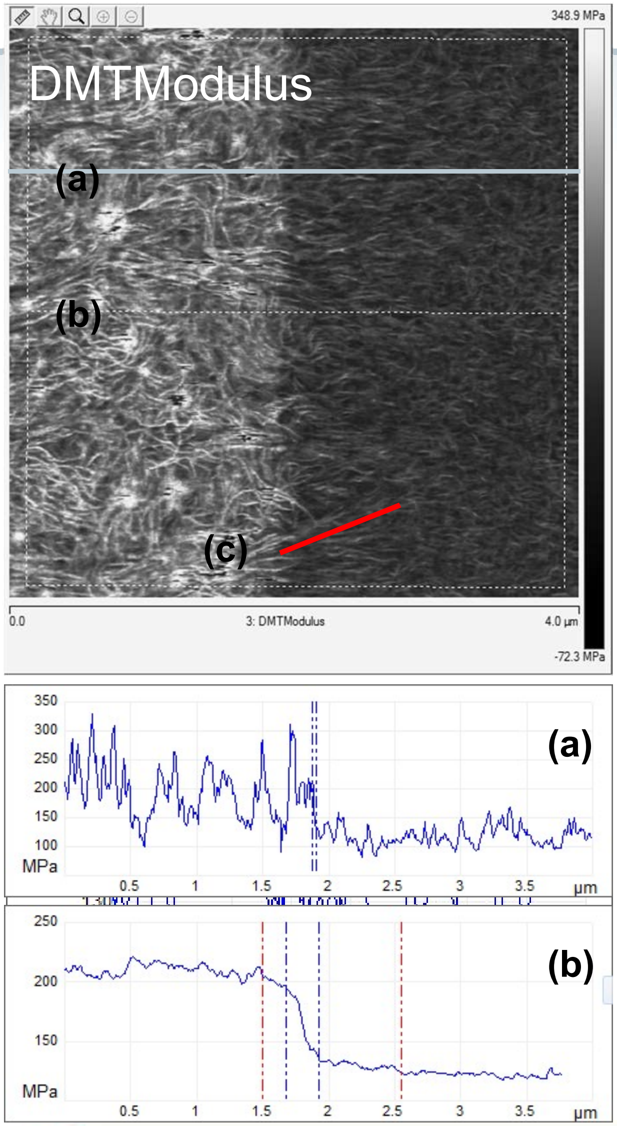


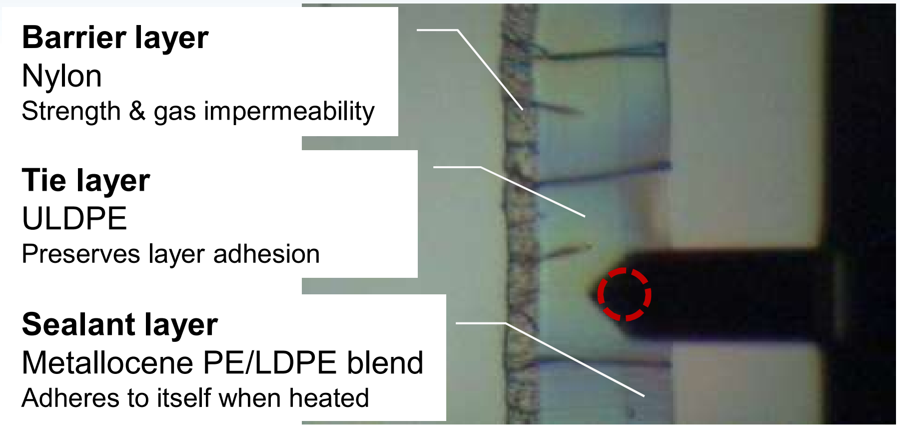


- Heat sealed bag: Barrier and Tie layers are incompatible, so we expect a relatively abrupt interphase.
  - Single scan line has a clear step in modulus over a distance of ~75nm.
  - Lamella do not cross the interface, but grow epitaxially from the Barrier layer – can see in averaged profile.
  - Lamella are highly ordered and perpendicular to interface ~250nm into the Tie layer.

High Resolution PF-QNM

New information revealed

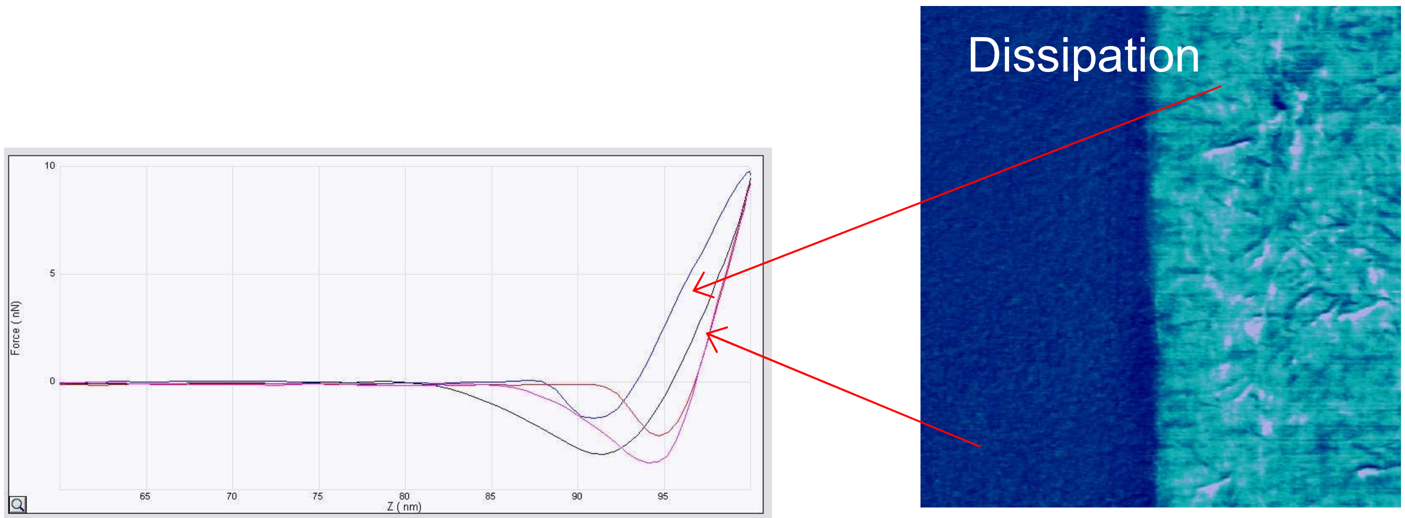




- Tie and Sealant layers are relatively compatible = wider interphase.
  - Single scan line: the variation in modulus is dominated by individual lamella.
  - Collectively: modulus varies over a much wider range ~250nm to ~1um.
  - Lamella from Tie layer act as nucleation sites or penetrate into the Sealant: more ordered region to ~1um from the interface.

Variation in viscoelastic response

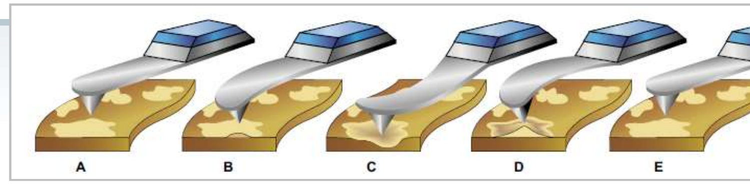
Visible in Dissipation map



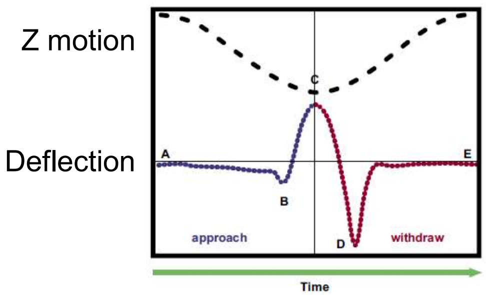
- Dissipation in Barrier<Tie
  - Demonstrated both by images and simultaneous force curves extracted from HSDC
- Hysteresis in contact part of force curves suggests an inelastic deformation mechanism is active

PeakForce QNM and Force Volume

Mechanical Property Mapping Modes

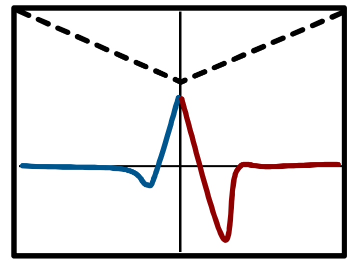


PeakForce Tapping (PF-QNM)



- Sinusoidal ramping (not linear): no piezo resonance, no overshoot
- Real feedback loop force control: benefits from prior curves
- Fast ramping (~kHz): faster images, even with more pixels

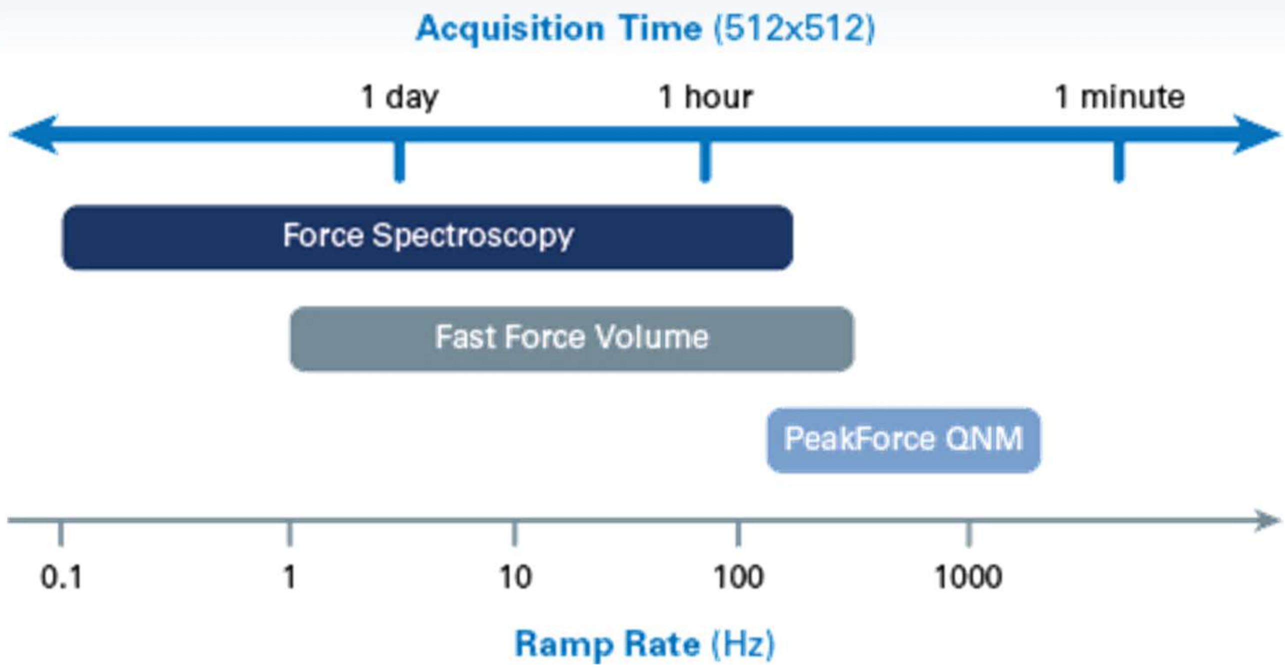
Force Volume (FV)



- Linear ramping: abrupt turn-around at high speed -> ringing, overshoot
- Discrete force triggers at each ramp: attempts to turn around at trigger. At high speeds, it can't reverse fast enough, so it overshoots.
- Ramping rate is limited (~.1kHz)

Expanded Frequency Ranges

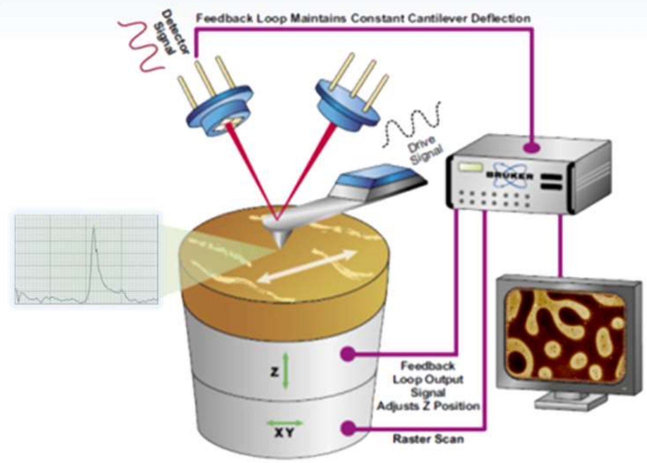
Easy comparison of Force Volume & PeakForce QNM with expanded frequency ranges (Nanoscope v9.20)

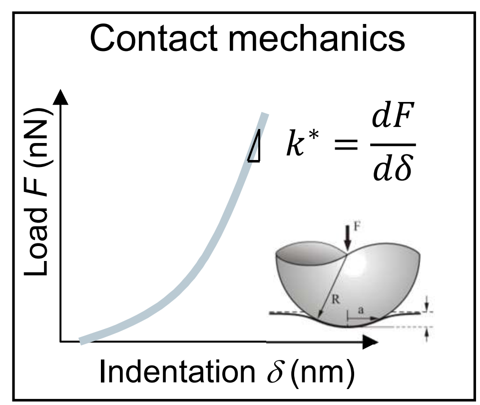


- Closed the gap in frequency between Force Volume and PeakForce QNM
  - PeakForce QNM minimum frequency now 125Hz; FV max at 300Hz
- Improves productivity and makes high-resolution FV maps practical
- Allows investigation of time dependent material property maps

Introduction to Contact Resonance AFM

- Benefits
  - Better sensitivity for stiff samples (10-500GPa)
  - Provides storage & loss modulus
    - But only at discrete (high) frequencies
- Method
  - Excite sample (AFAM) mechanically at contact resonance freq
  - Measure fcr, Qcr (don't need to calibrate amplitude!)
- Challenges:
  - Preserving the tip (repeatability)
  - Modeling the cantilever dynamics (fcr -> k*)
  - Modeling the contact mechanics (k* -> E*)
  - Calibrating all of the parameters (accuracy)



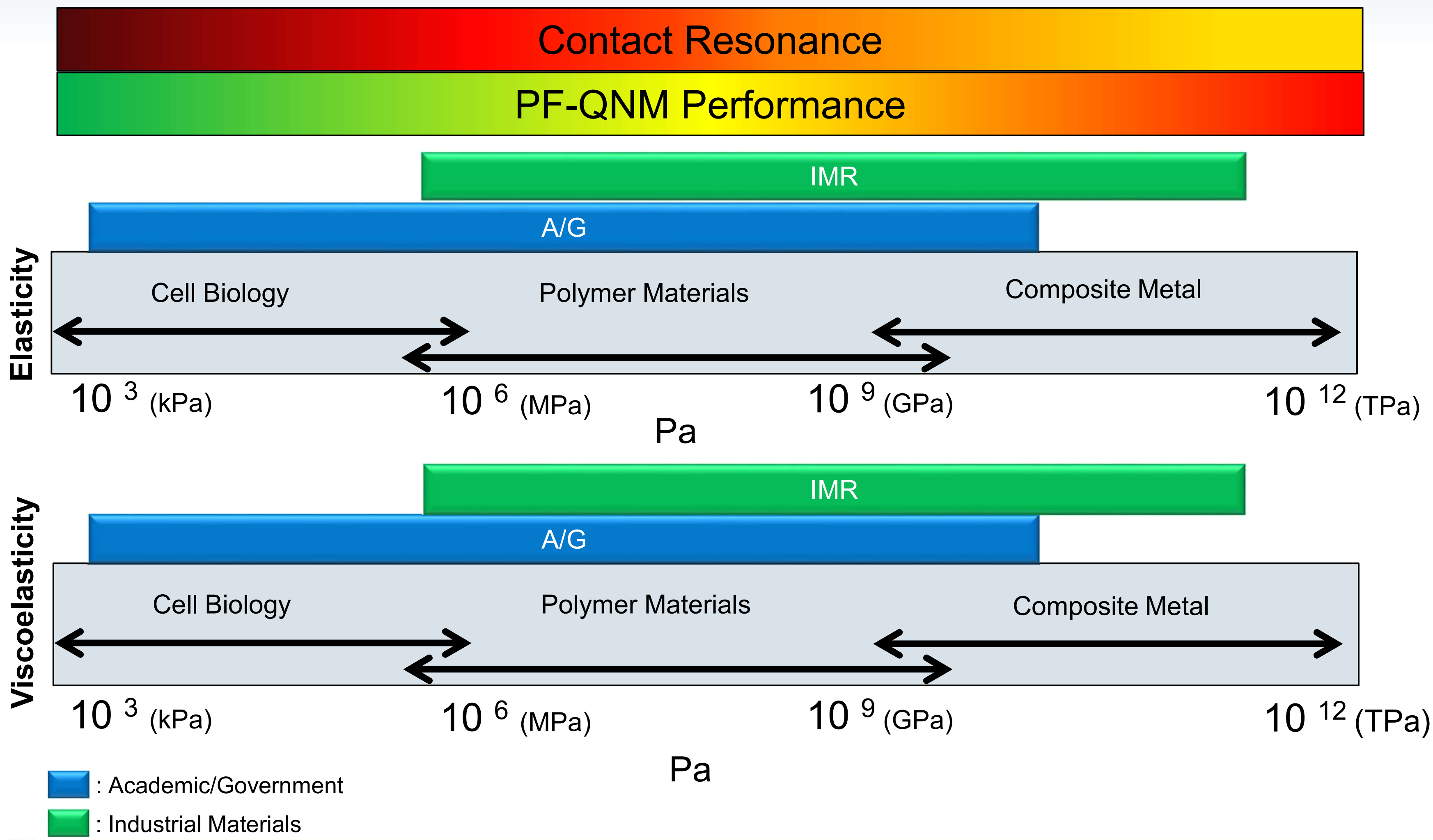


Elasticity and Viscoelasticity Characterization

Accurate Measurements of Materials 1kPa to 300+ GPa

BRUKER

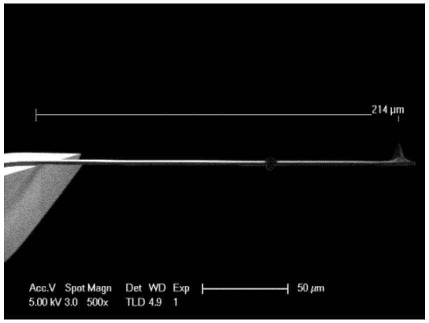
Complete Solution for Nanomechanical Characterization

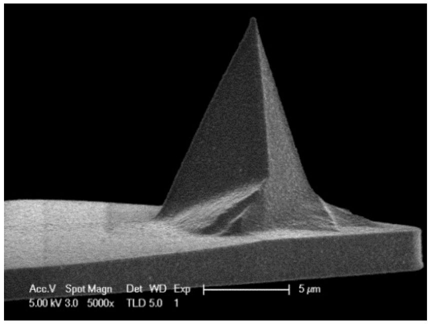


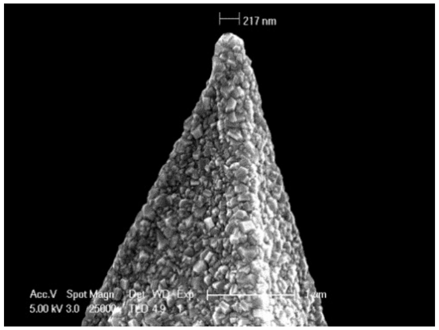
Contact Resonance Probes and Samples

- Probes and reference samples
  - 3-probes types diamond coated with various spring constant cover modulus range from 1 GPa to 300+ GPa.
  - 7-reference samples including HOPG, Mica, Fused Silica, Al (50nm film), Si, Cr (50nm film), and Sapphire.

  - Note: During development engineering used 6 probes collected over 2.7 million CR curves and lasted 257 hours of CR operation.



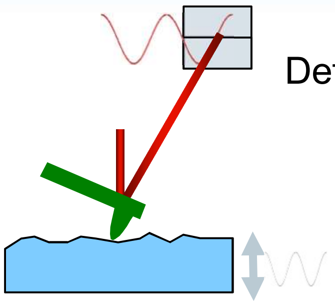


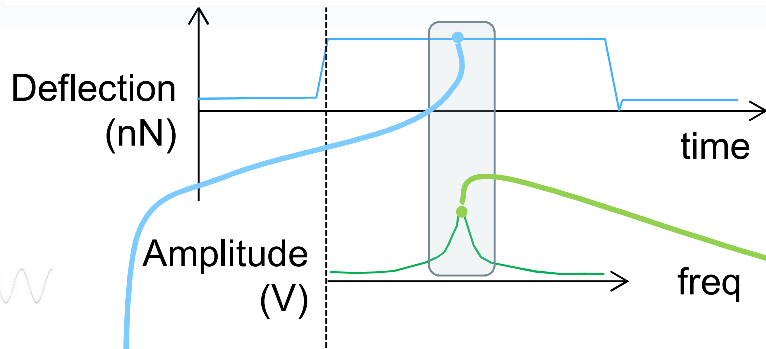


Explaining Contact Resonance

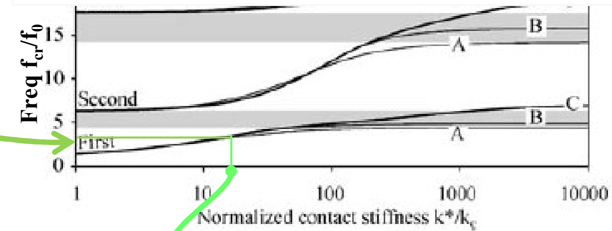
From Frequency and Deflection to modulus

1. Measure frequency (fcr) & Deflection





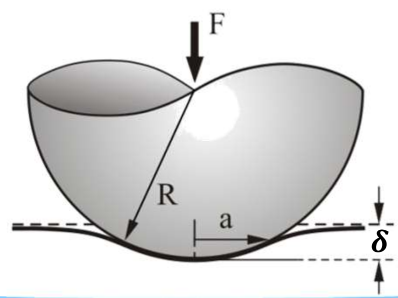
2. Apply cantilever dynamics to calculate k*/kc from fcr/f0



3. Convert Deflection to Force using deflection sensitivity & spring constant (kc)

4. Apply Contact Mechanics to calculate E* from Radius (R), Force (F) and contact stiffness (k*)

Hertzian Contact

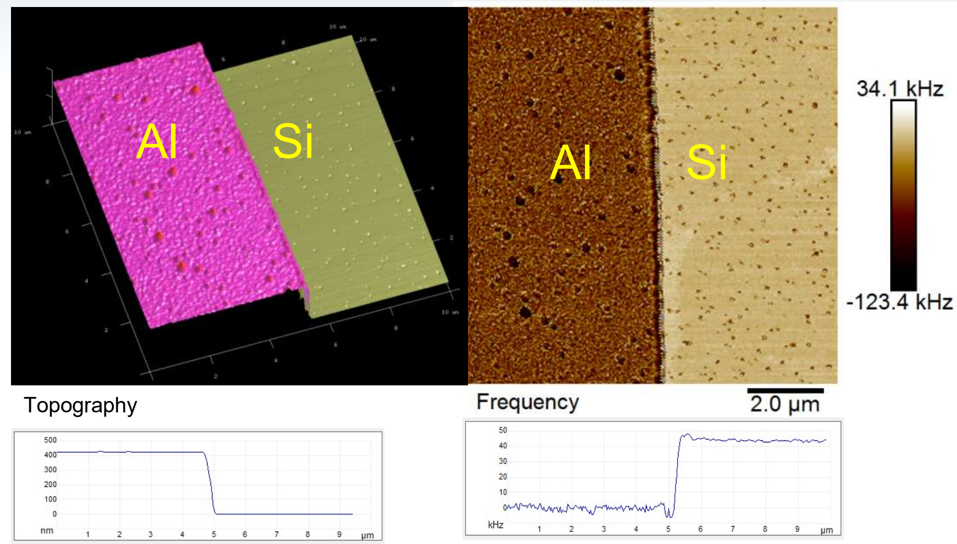


$$E^* = \sqrt{\frac{k^{*3}}{6RF}}$$

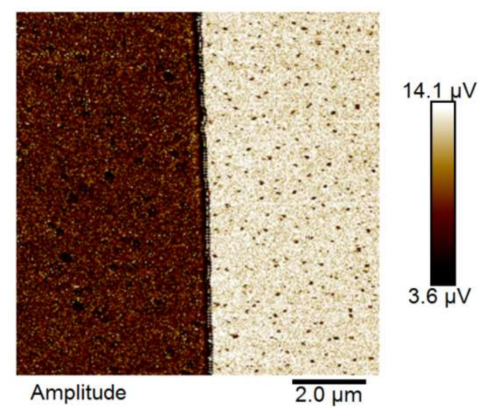
Contact Resonance Mapping

Al Film on Si
Force Volume Image 10um 256x256 Force Curves

- FastForceVolume “Big Data” every force curve, 4-channels
- High resolution FV mapping
  - (256x256)x2048
  - Max pixels now (956x956)x256
- FV Mapping with more than 15 data types: Frequency, Amplitude, Q, Modulus, R2



Slice
Modulus
Log Modulus
Stiffness
Adhesion
Force Section
Real Height
Height Sensor
CR Frequency
CR Q
CR Amplitude
CR R^2
CR Stiffness (k*/kc)
CR Damping (p)
CR Radius
CR Storage Modulus
CR Loss Modulus

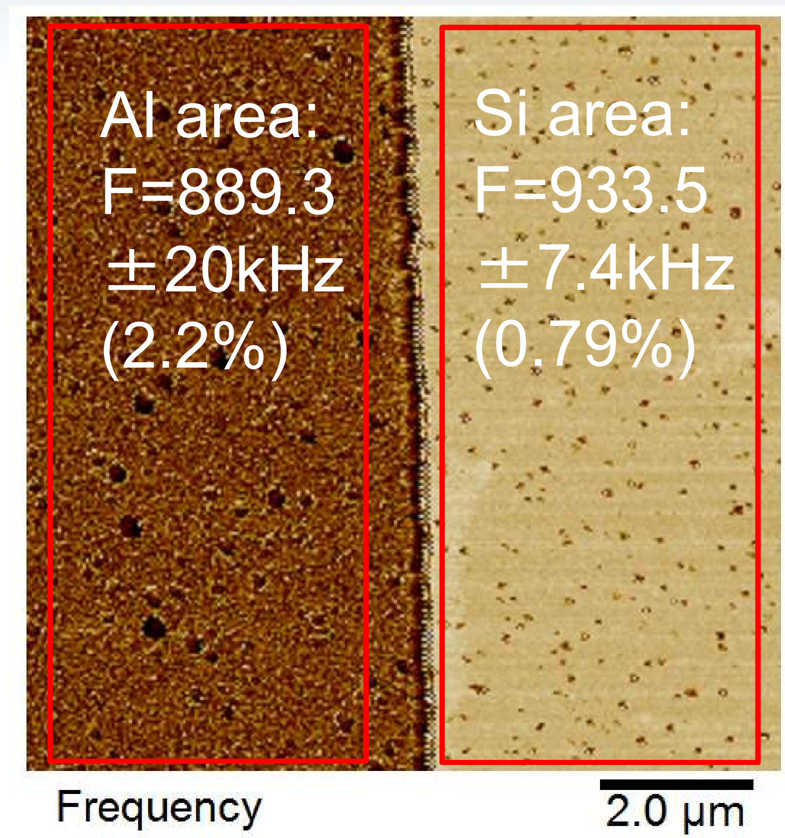


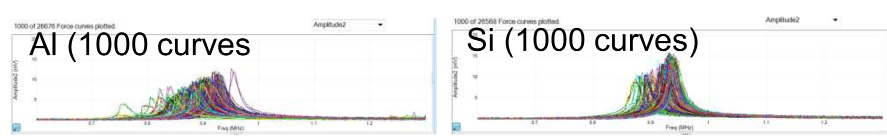
Contact Resonance Mapping

Al Film on Si

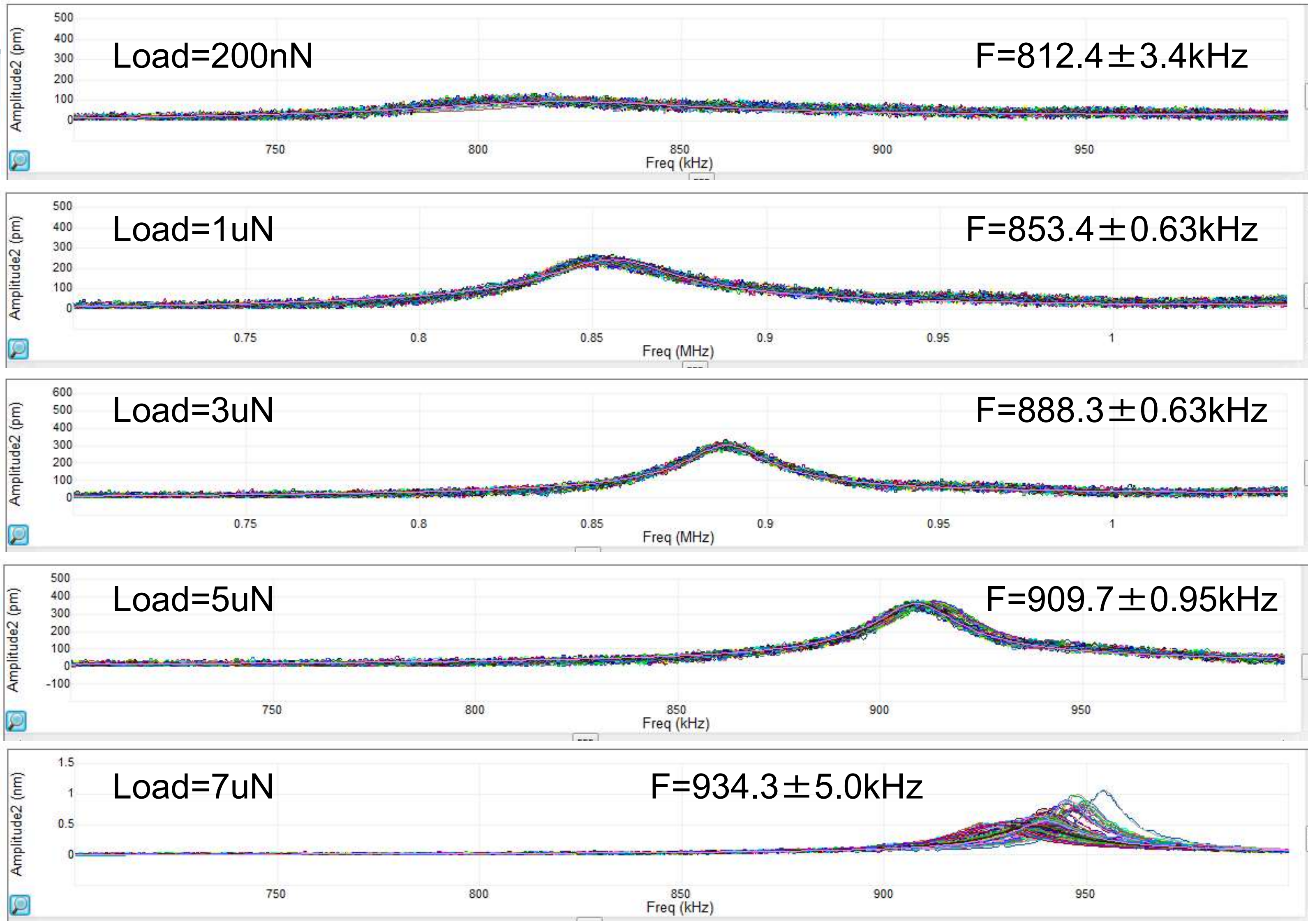
Force Volume Image 10um 256x256 Force Curves

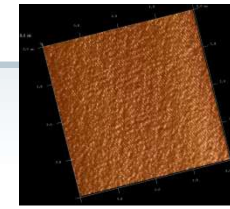
- Exceptional Sensitivity
- Exceptional Repeatability
- Bruker Diamond coated Probes
- Dimension Platform for efficiency in measurements

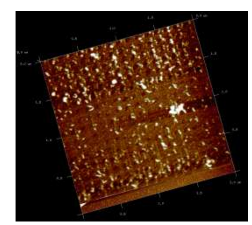




Precise Force Control
Enables Measurement Optimization



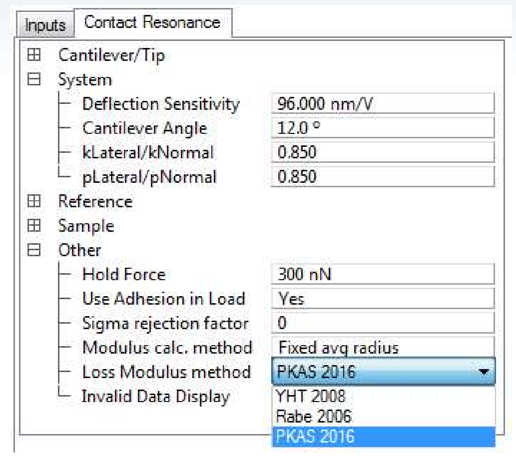




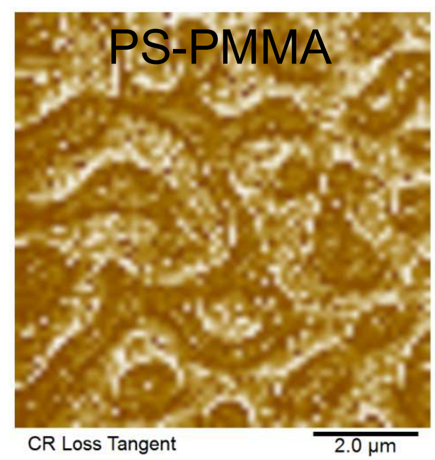
Loss Modulus Accuracy
and loss tangent…

- Loss modulus can be calculated from the Q of the CR peak
- Research community lacks consensus about the best way to do this, so we implemented three algorithms
  - YHT 2008 and Rabe 2006 are very similar and both require the reference sample to have a known loss modulus
  - PKAS 2016 does not require a reference sample with known loss modulus

- Accuracy of Loss Modulus and Loss Tangent is viewed with skepticism, yet lots of traction in materials research.
  - Our competition is just using the YHT model, we are providing more flexibility…



$$\tan\delta = \frac{E''}{E'}$$

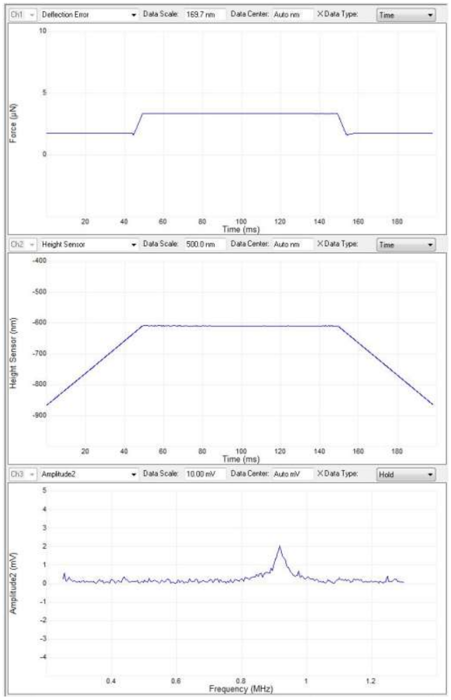


CR Loss Tangent

Bruker Contact Resonance Key Features

Nanomechanics Expansion

- More repeatable: lateral force on tip is minimized, reducing tip wear
  - New diamond coated probes further stabilize the measurement
  - Stage allows automatic re-checking of reference sample
- More information: whole force curve is collected at every pixel, including Adhesion force
  - Allows better contact mechanics modeling
  - Comparison with Force Distance data
- Real-time maps of both raw data and mechanical props
  - f, Q, A, k*/k, E’, E’’, loss tangent, etc.
- Whole sweep is saved, allowing detection of artifact peaks, etc. (unlike freq tracking methods like DART)



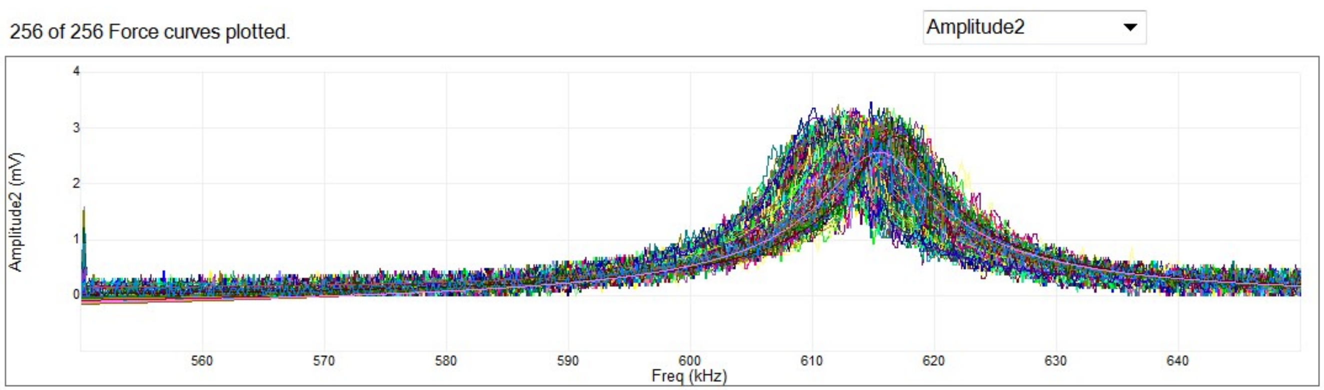
Contact Resonance FASTForce Volume

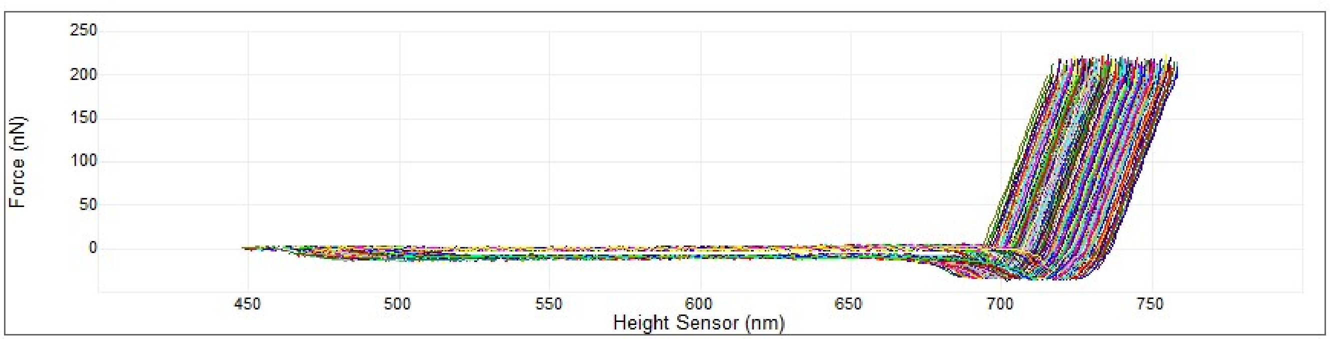
Full Compliment of nanoMechanical information

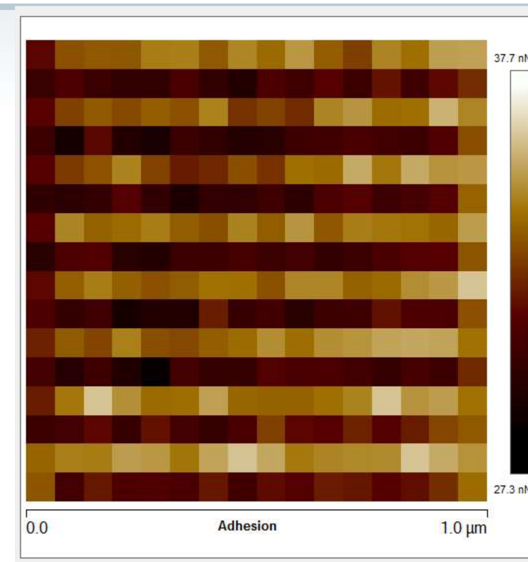
Ramp Rate=122Hz

Average = 613.58kHz

Std Dev = **1.62kHz**





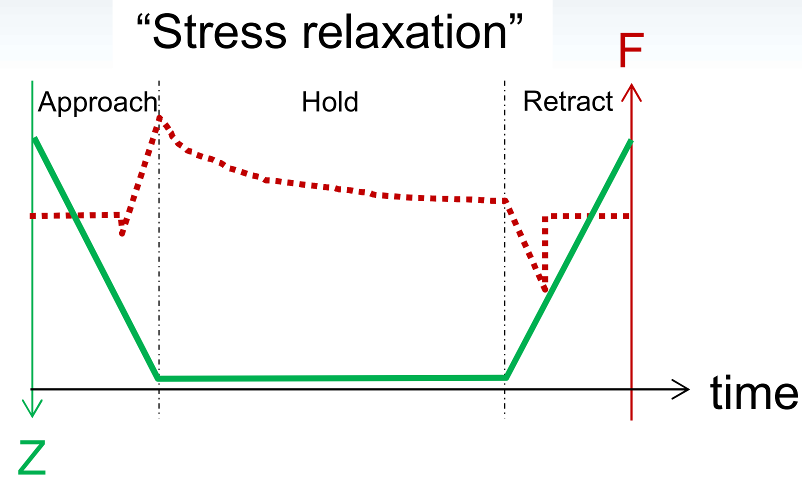


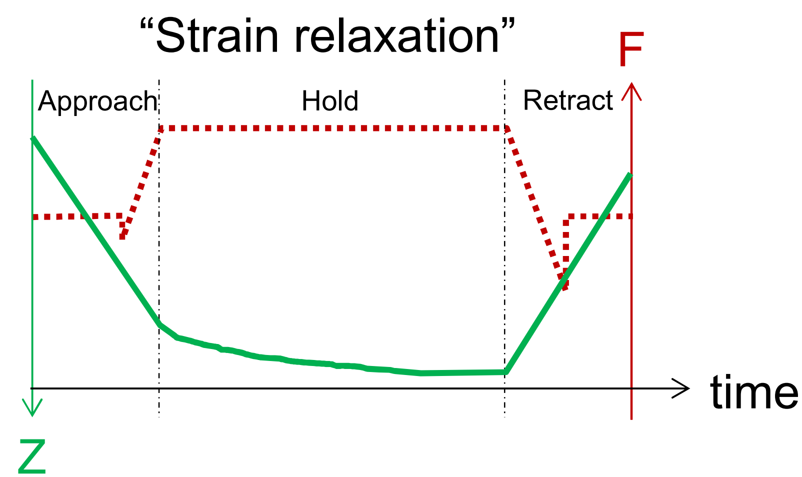
- 1 µm Scan
- 16x16 points
- Adhesion=32.4nN
- Rq=1.8nN

Ramp&Hold Z or Force

Stress or Strain Relaxation

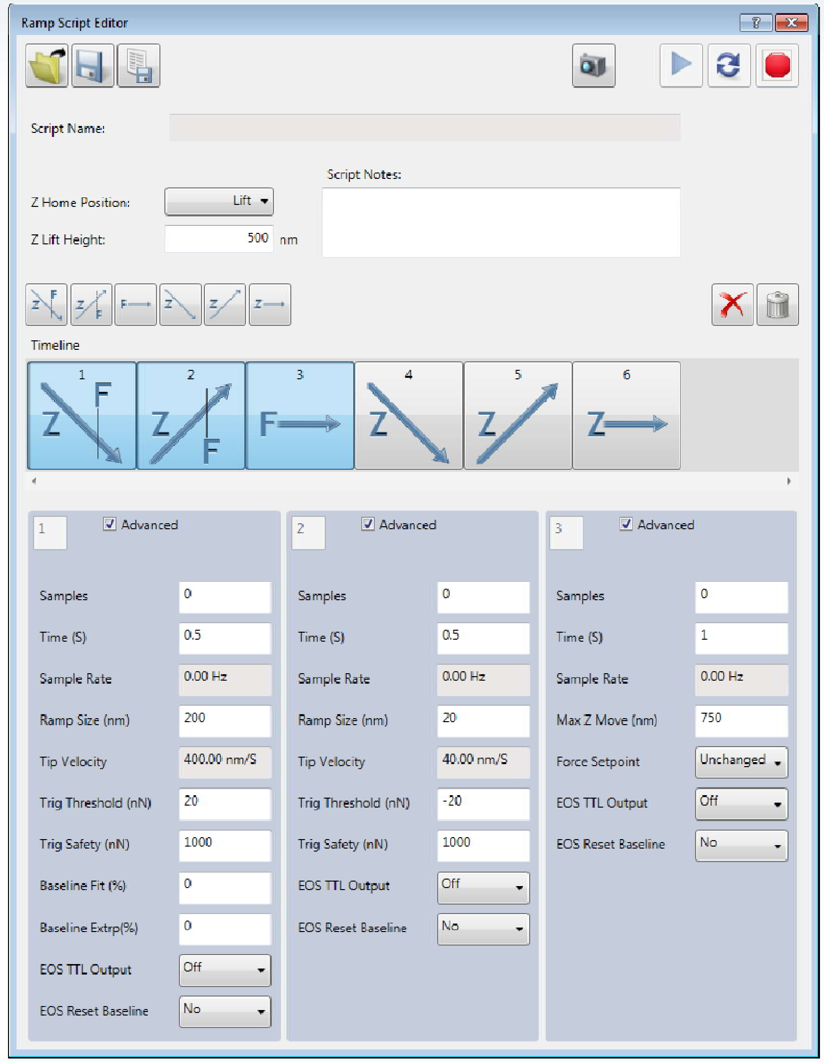
- Hold Z, hold trigger force, or hold user defined force
- Integrated with Force Volume
- Easy: similar to ramp mode
  - Typical ramp time~0.1-10sec
  - Typical Hold time ~1-5000sec.
  - User definable sample rates
- For Ramp&Hold>a few sec, the plot is updated during acquisition and can be cancelled
- Offline analysis





RampScript Editor

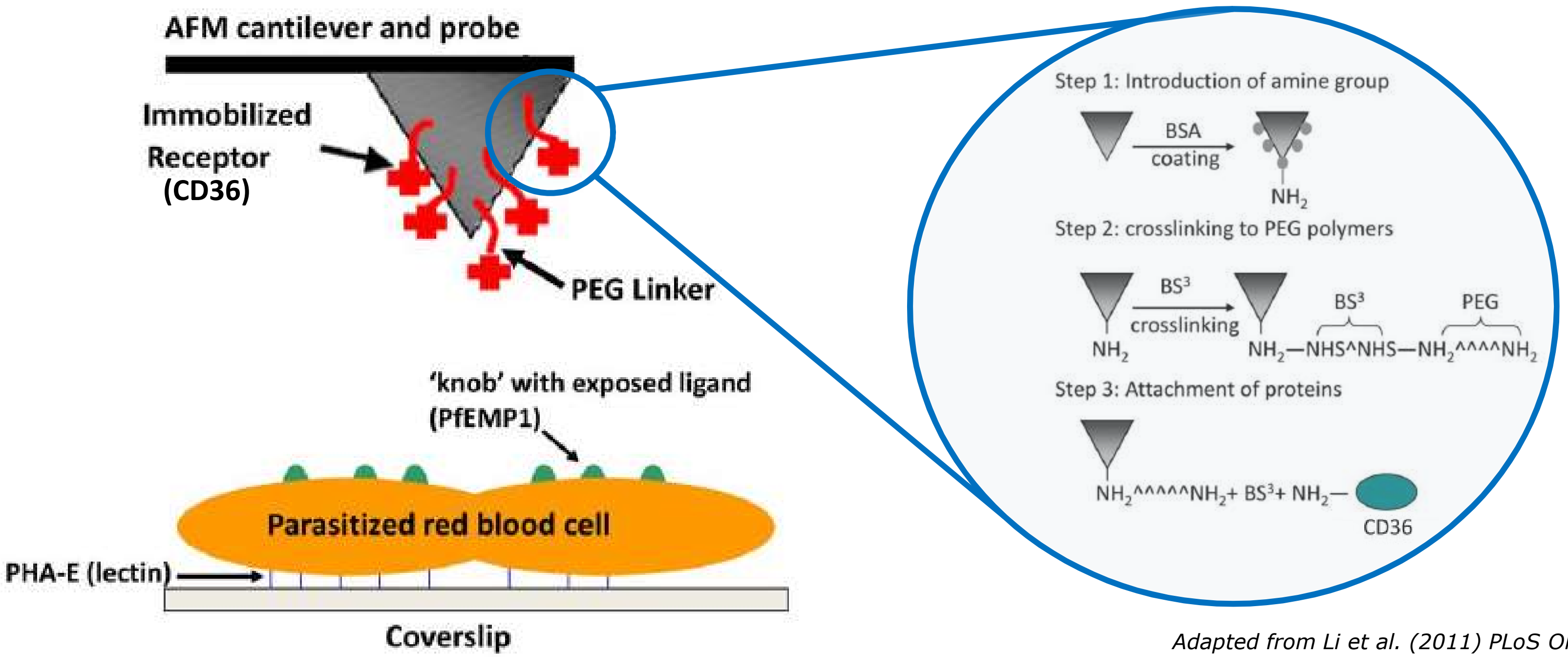
- Multi-segment types and control in a single script.
- Force Ramps and Frequency Sweeps.



The Biological Question:

Can we map the distribution of cytoadherent molecules to specific cell surface structures?

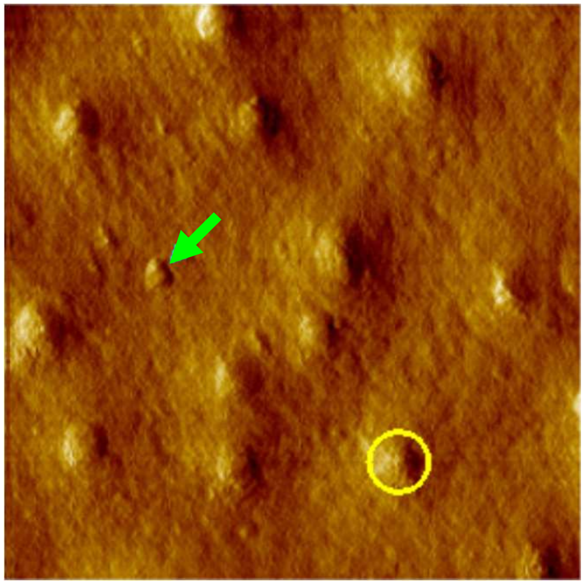
- AFM probes were functionalized with endothelial surface receptor CD36.
- Used PeakForce QNM with functionalized probe to obtain 2D map of the distribution of CD36 molecular binding sites on IE.



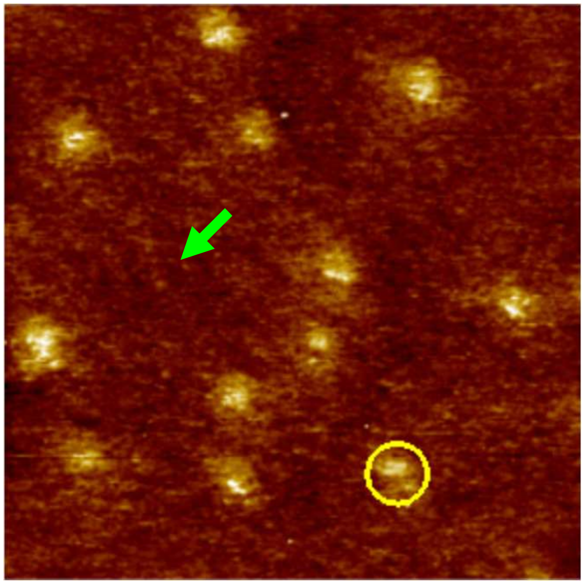
Adapted from Li et al. (2011) PLoS ONE 6: 1-10.

Molecular Recognition Mapping with PeakForce QNM and Functionalized Probes

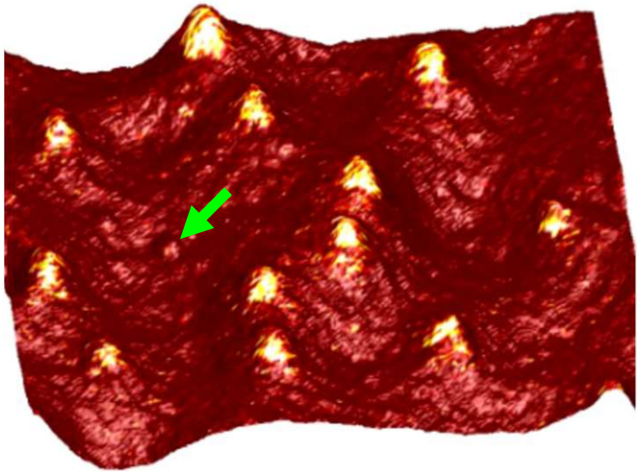
- Malaria infected red blood cells were imaged with probes functionalized with endothelial surface receptor protein CD36, which is implicated in the adhesion of infected blood cells to blood vessels and the resulting blockage of those vessels.
- Infection results in the appearance of knob-like bumps on the blood cell surfaces
- Many of these knobs are shown to be CD36 binding sites (e.g. yellow circle)
- Recognition is not an artifact of topography though, as some knobs show no adhesion (green arrow)



Height (topography)



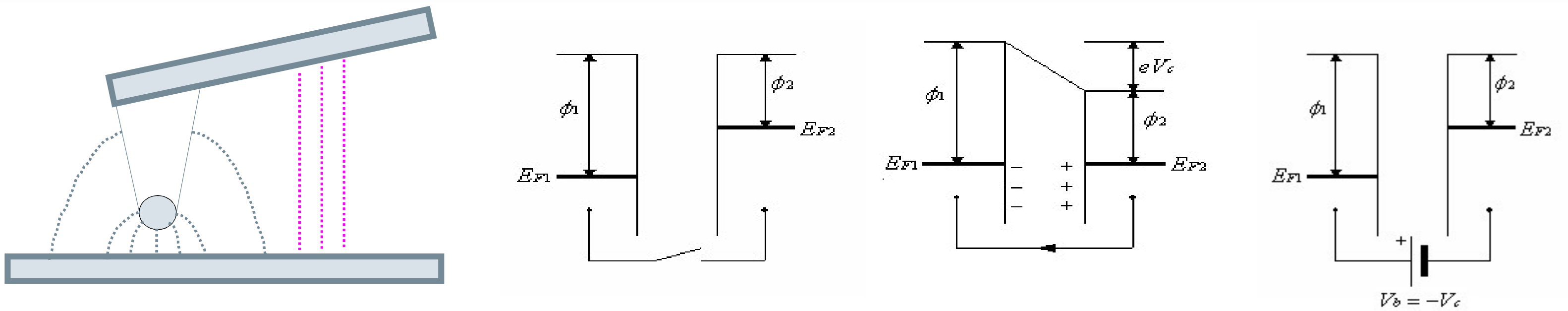
Adhesion (recognition map)



3D topography painted with adhesion data skin

Li et al. 2010 Proceedings of the World Congress on Biomechanics

KPFM: work function measurement



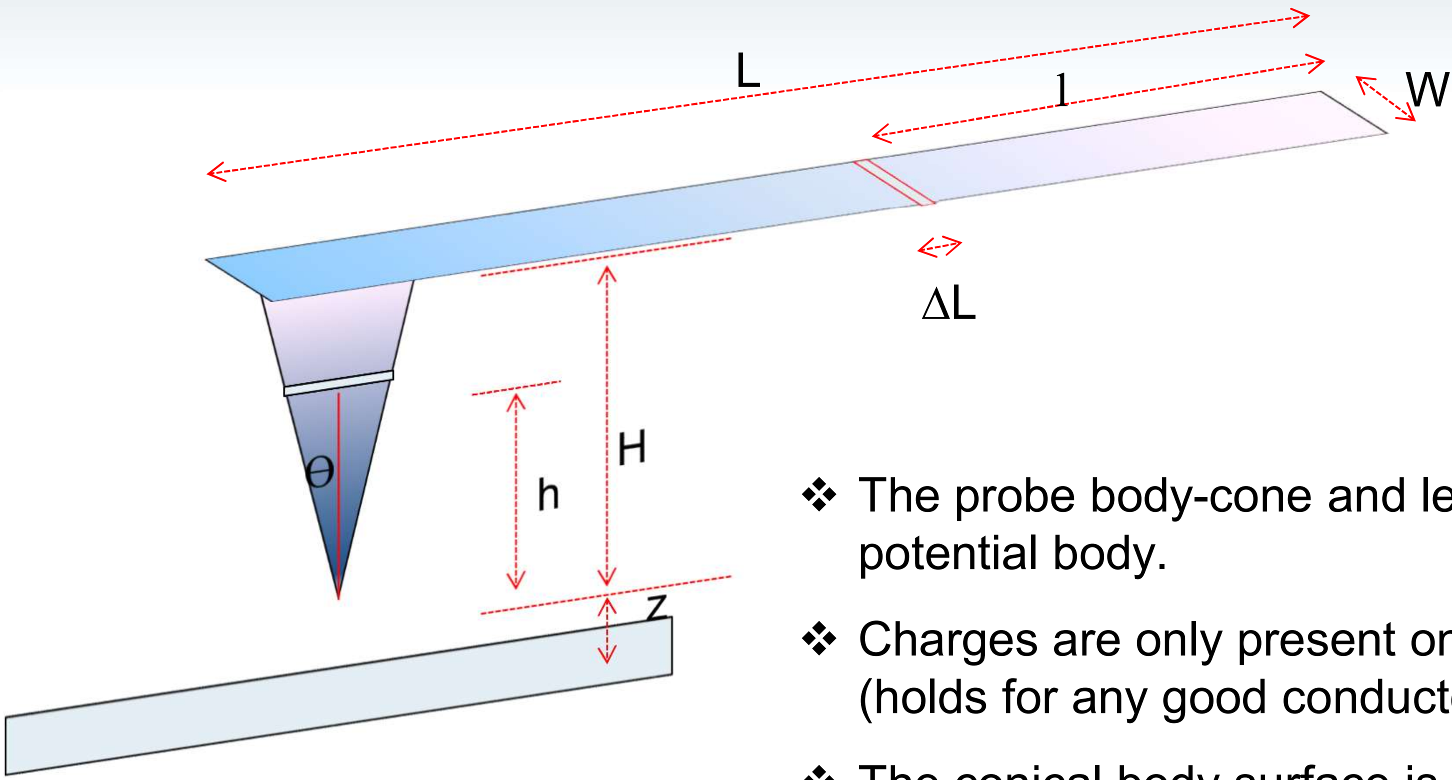
KPFM measures the work function difference of tip/sample.

AM	Amplitude-Modulation
FM	Frequency-Modulation ✓ Better spatial resolution ✓ Better accuracy

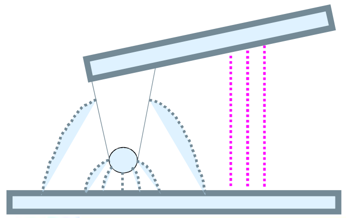
Physical Review B 2005, 71(12) 125424

Probe Modeling and Assumptions

Electrostatic Forces are Long Range - cantilever geometry matters

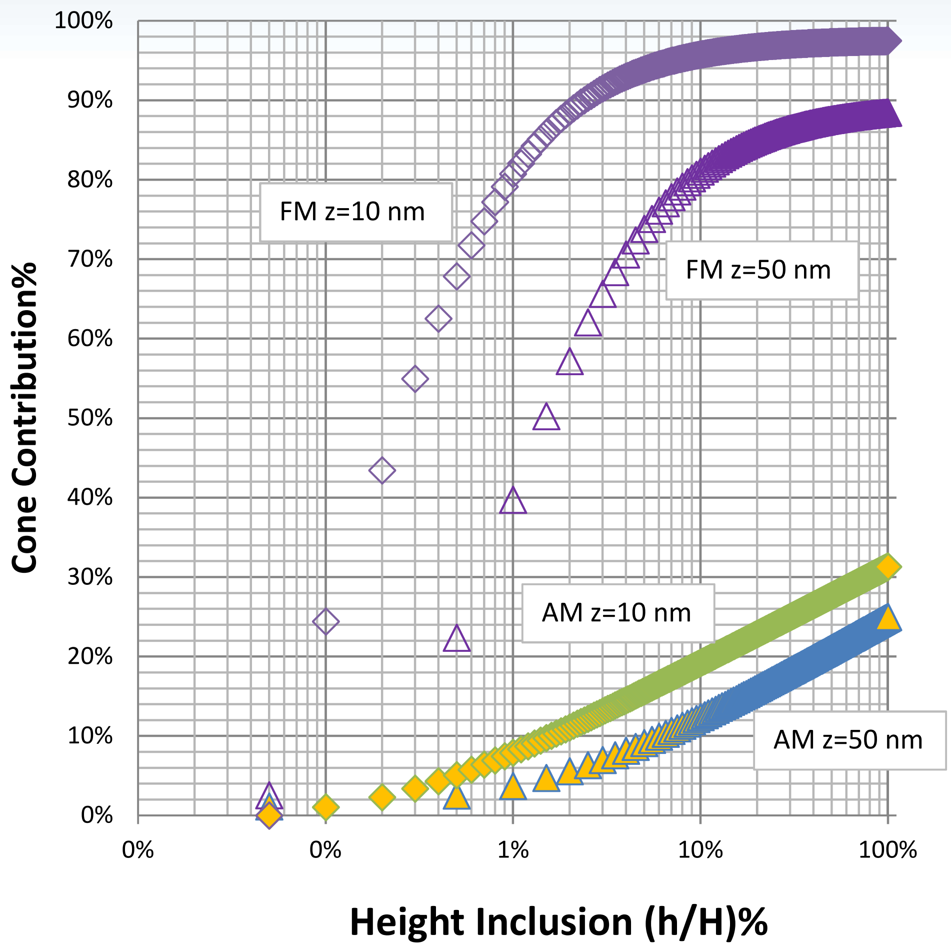


- The probe body-cone and lever-is an equal potential body.
- Charges are only present on the surface (holds for any good conductor).
- The conical body surface is a stack-up of rings, each ring contributes to the total electric field in proportion to their capacitance (assumption).



Tip Cone Contribution in KPFM

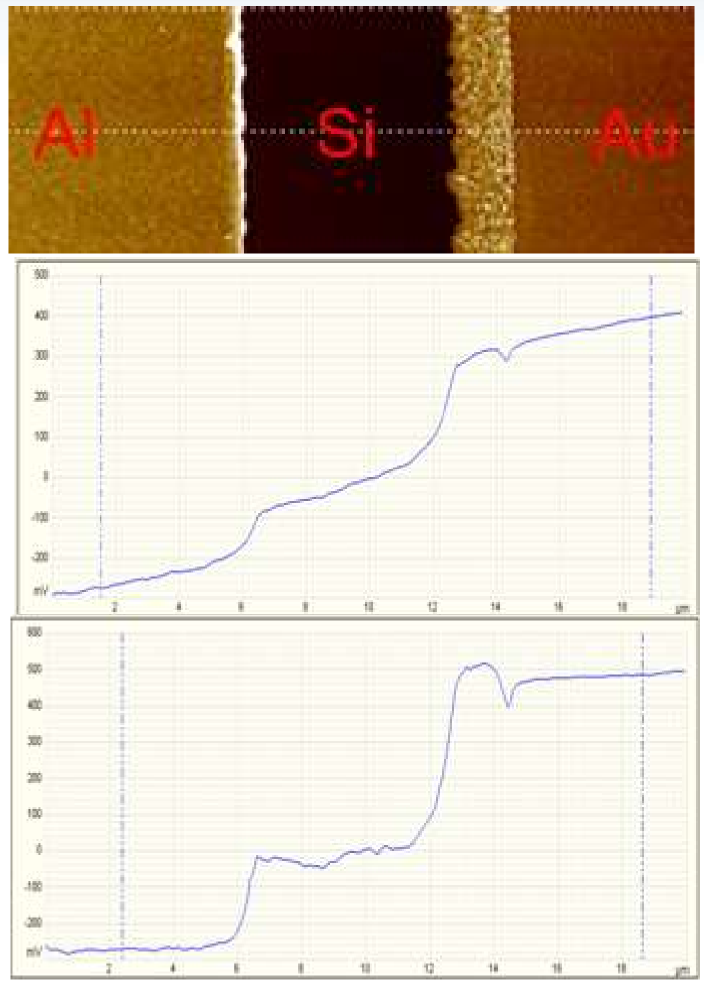
FM gradient detection isolates contribution from tip



Based on SCM-PIT Geometry:
W=30um, L=225um, H=10um, Cone Angle=45

- FM-KPFM:
  - The foremost **0.3%** of the tip cone accounts for half of the signal in.
  - FM can achieve a lateral resolution better than 50nm.
- AM-KPFM
  - The contribution from the tip cone never reaches 50%.
  - Its lateral resolution is dictated by the um-scale lever.

PeakForce KPFM Retains FM-KPFM’s High Resolution



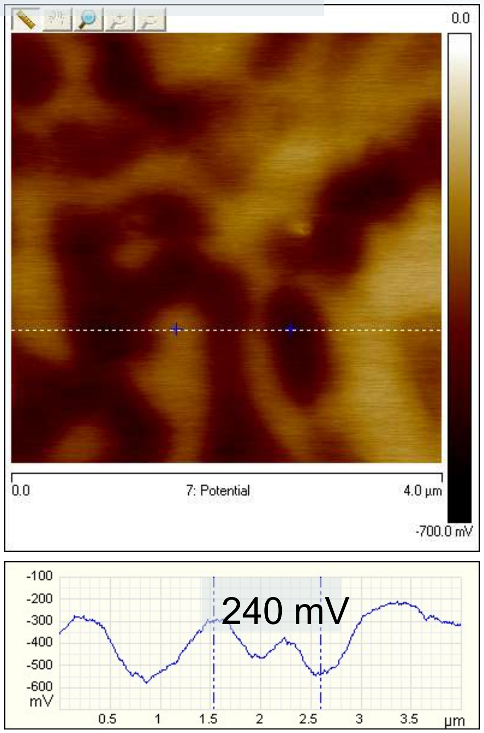
PeakForce KPFM-AM

PeakForce KPFM

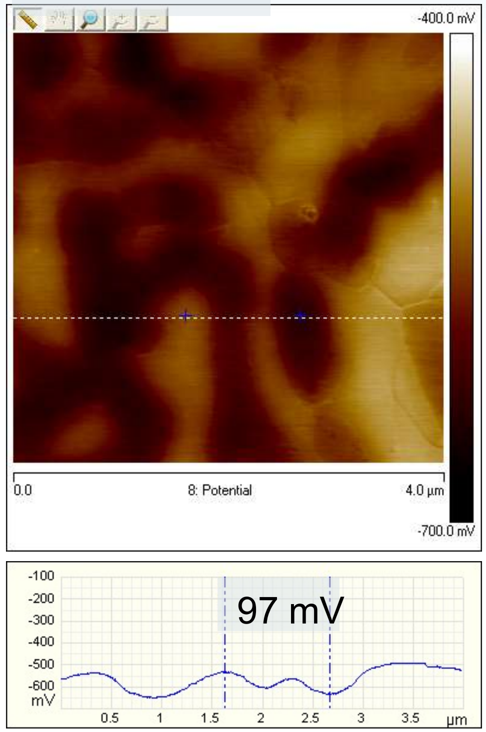
PeakForce KPFM *vs* FM-AM

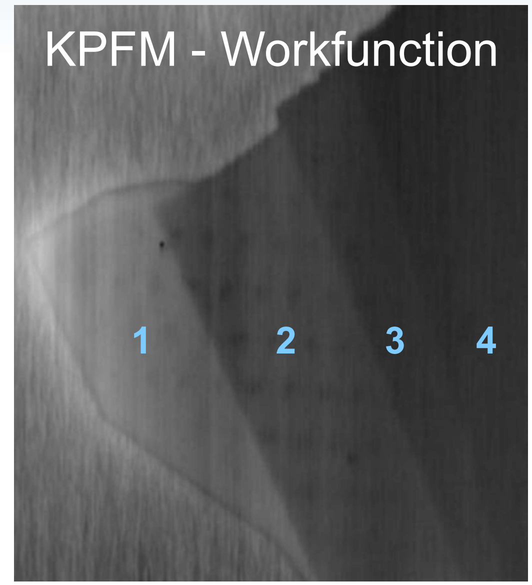
FM detection advantage maintained

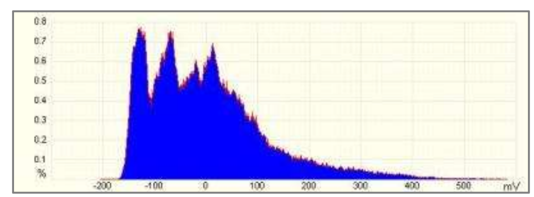
PeakForce KPFM



AM detection







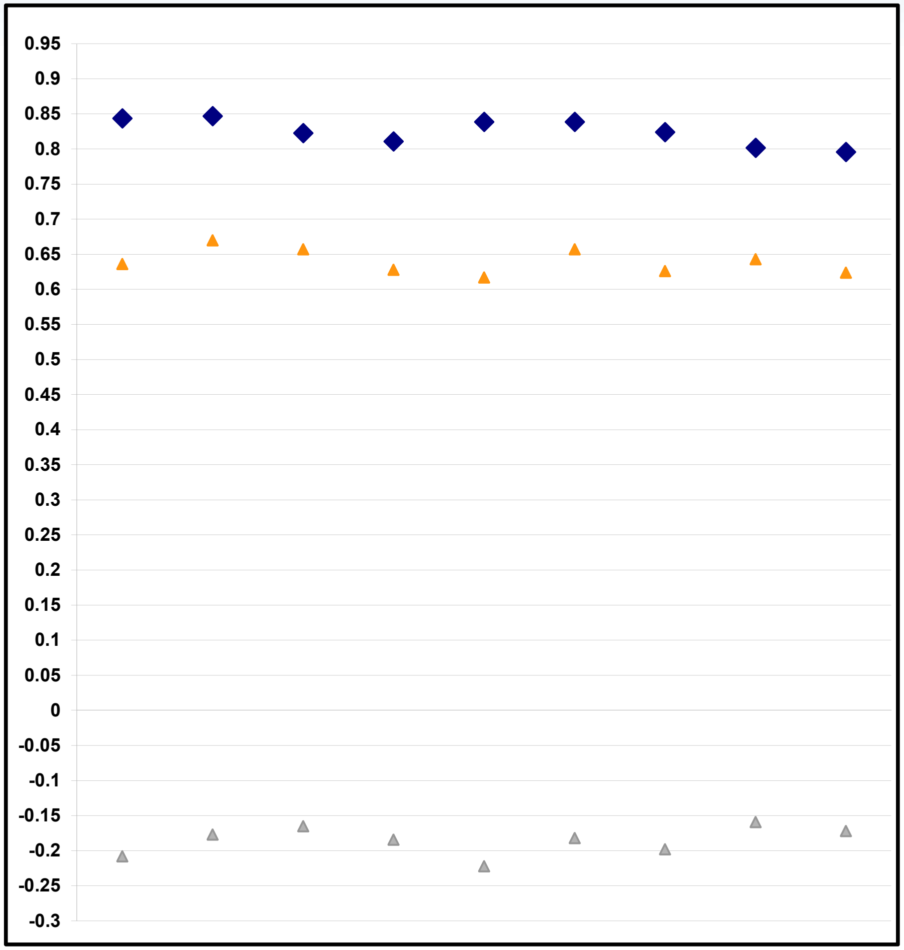
$Sn_{60}Pb_{40}$ Alloy

FM sees larger and more localized contrast leading to **better accuracy.**
AM contrast smaller and more convoluted.

Work functions: Sn 4.42 eV; Pb 4.25 eV

PeakForce KPFM Repeatability

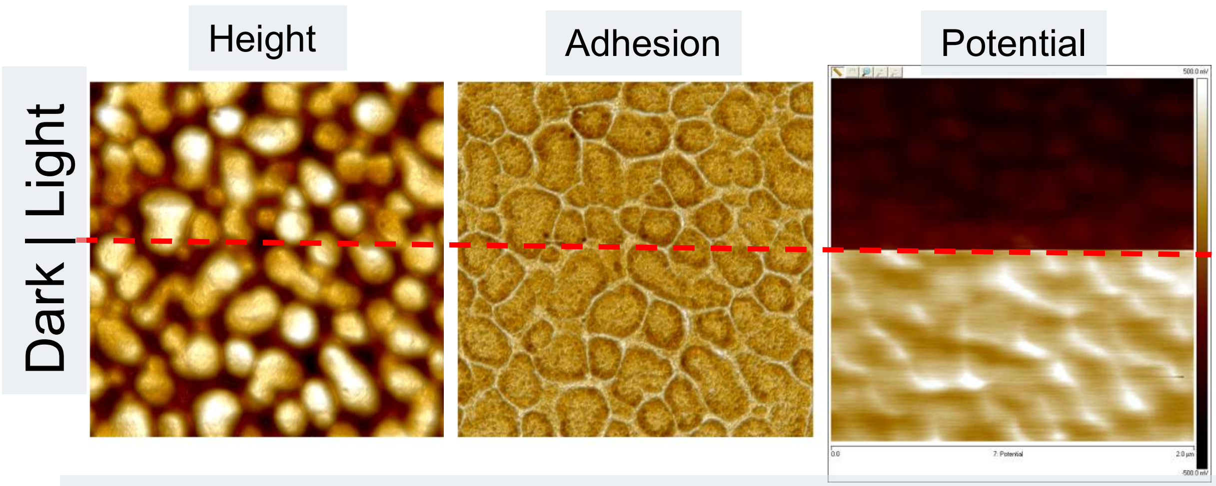
5x improvement over traditional KPFM

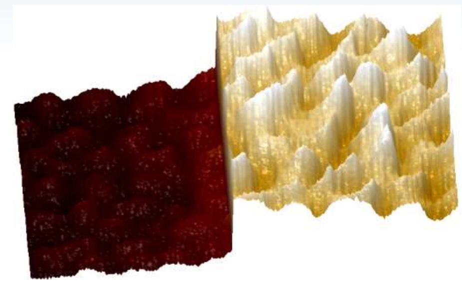


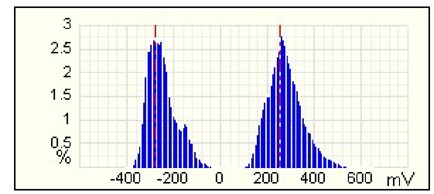
	Average	**Std Dev**	Maximum	Minimum
Au-Al	0.825	**0.019**	0.847	0.796
Au	0.639	**0.018**	0.617	0.670
Al	-0.185	**0.020**	-0.159	-0.222

9 KPFM Porbes

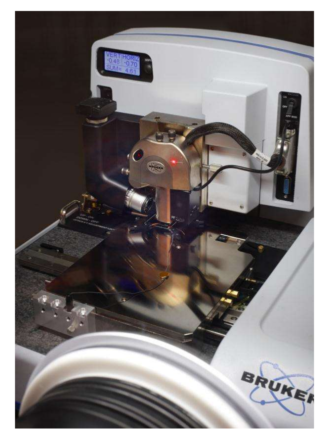
Organic Photovoltaic Applications:
PCBM Crystals on MDMO-PCBM Matrix







Particles are PCBM crystals on matrix of MDMO-PCBM blend, ITO substrate.
Sample courtesy of Dr. Philippe Leclere, University of Mons



Work function downshifts 535 mV under 300-sun illumination.

Scaling Topography and Potential

$$KPFM\ Sensitivity \quad \propto \quad \frac{Q}{k}$$

- But Tapping Mode Requires :
  - k to be not too small
  - Q not to be too big

  Tapping and KPFM scaling in conflict.

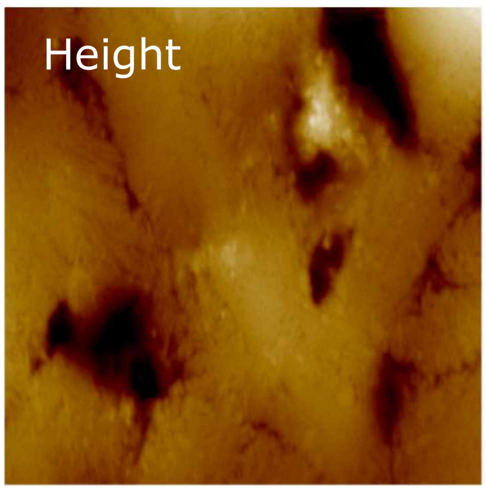
- Peak Force Tapping Mode Allows Freedom to use:
  - Smaller k (10x or more)
  - Big Q (10x or more)

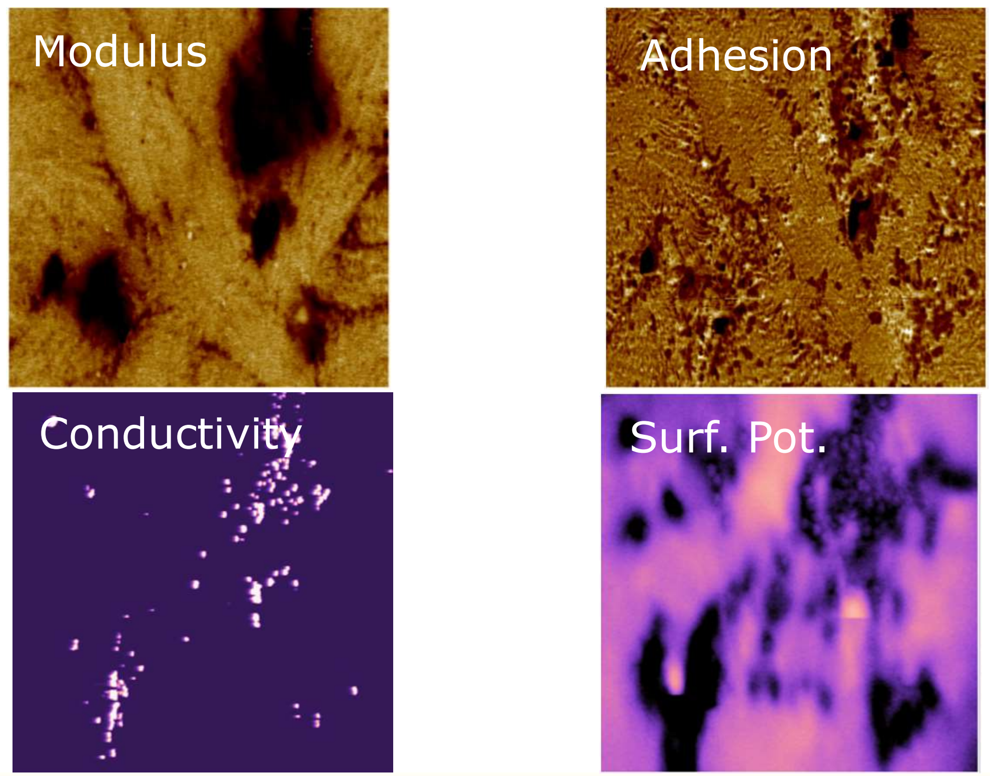
  PeakForce Tapping and KPFM scaling aligned.

Multi-Dimensional Information Obtained

BRUKER

- Mechanical property mapping is natural for AFM (PeakForce QNM®)
- Extensions to electrical properties are straightforward
- Correlated measurements with PFTUNA, PFKPFM





3 um scan of a thermoplastic vulcanizate comprised of Polypropylene, modified rubber, and carbon black particles

www.bruker.com