Rebirth of Force Spectroscopy: HybriD AFM Mode

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NT-MDT Spectrum Instruments, Moscow, Russia

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Agenda

Introduction

HybriD (HD) mode working principle

Fast quantitative nanomechanical studies

New generation of HybriD mode control electronics

Recently developed HybriD-based modes:

- Piezoresponse force microscopy (HD PFM)
- Scanning thermoelectric microscopy (HD SThEM)
- Scanning thermal microscopy (HD SThM)
- Conductivity studies (HD C-AFM)
- Vacuum and Liquid measurements (Vacuum HD & Bio HD)
- AFM+Optical: HD TERS and HD s-SNOM

Conclusion

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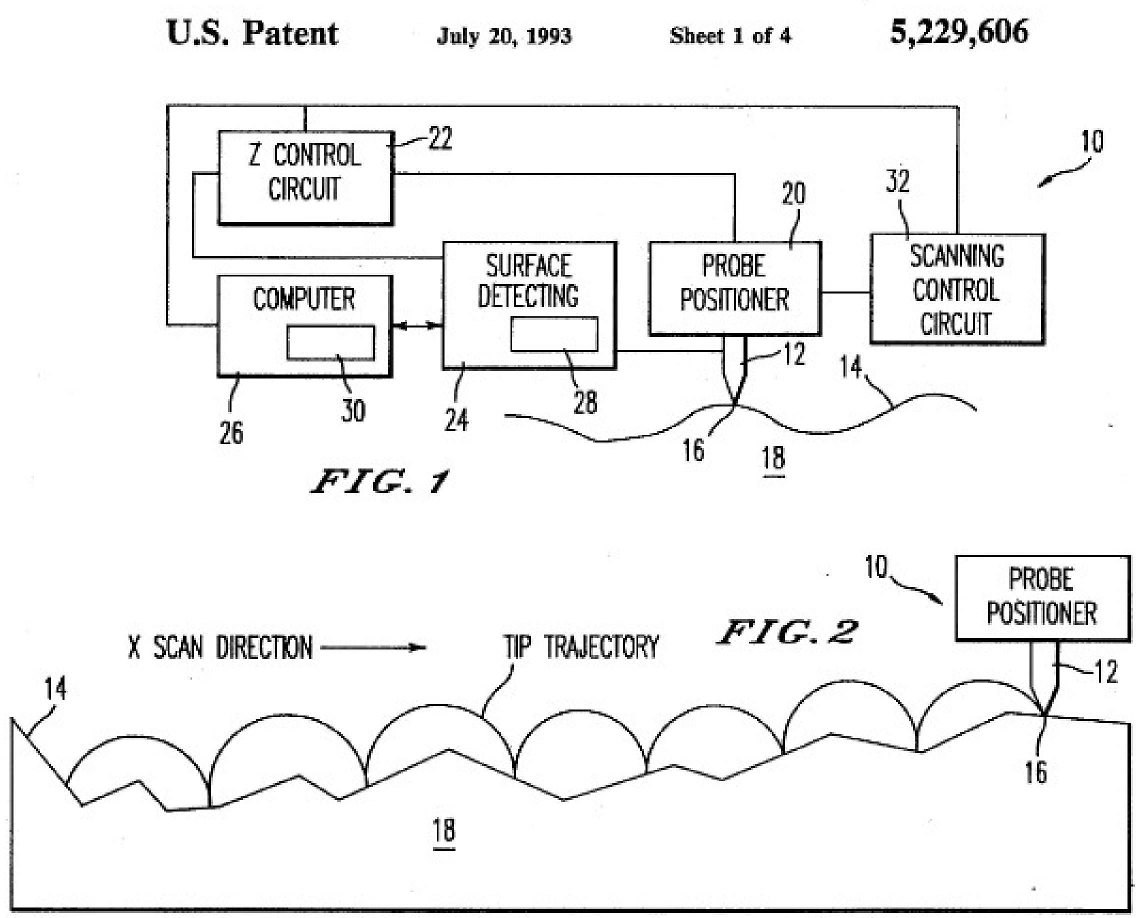
History: Jumping mode AFM



Patent US 5229606 "Jumping probe microscope"
Applied in 1989 by Virgil B. Elings, John A. Gurley

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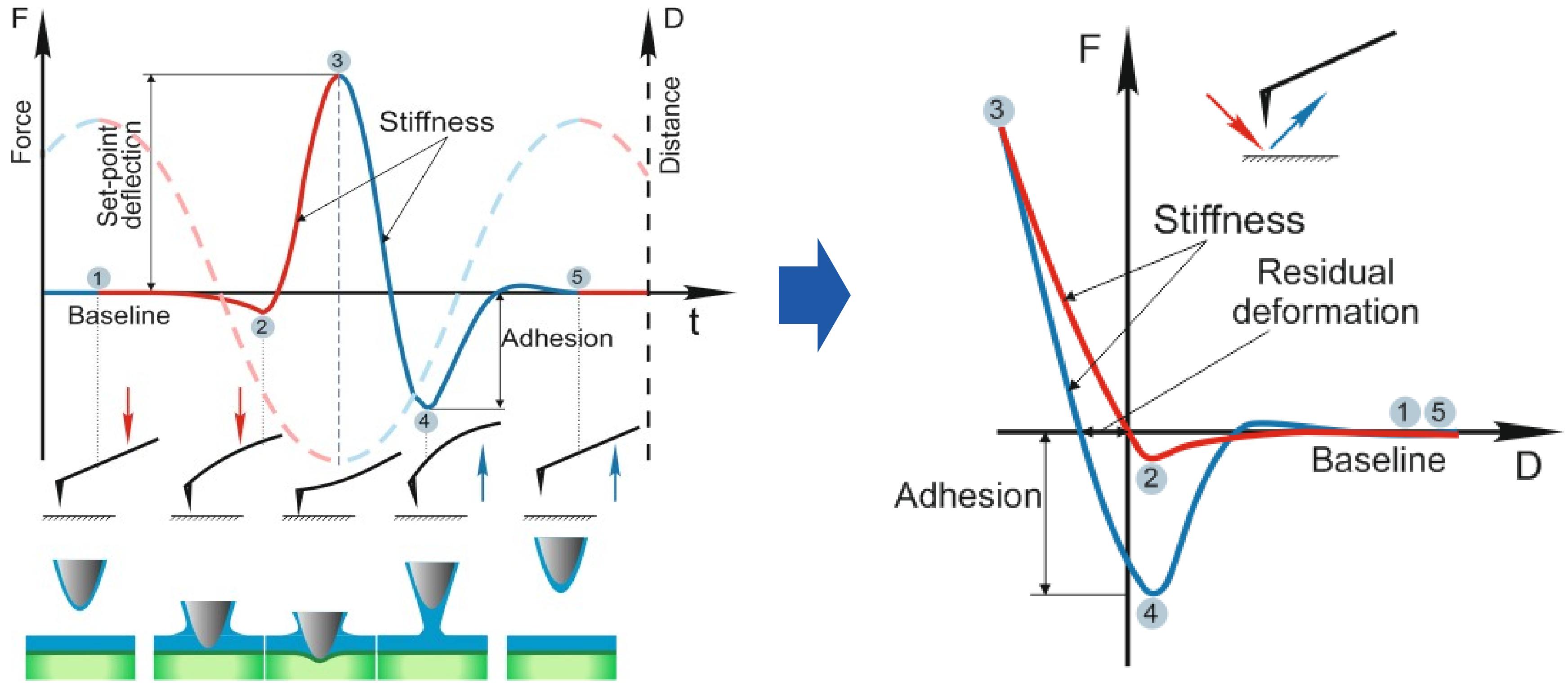
HybriD Mode working principle

HybriD mode (HD mode) – scanning technique based on fast force-distance curves measurements with real-time processing of the tip response.

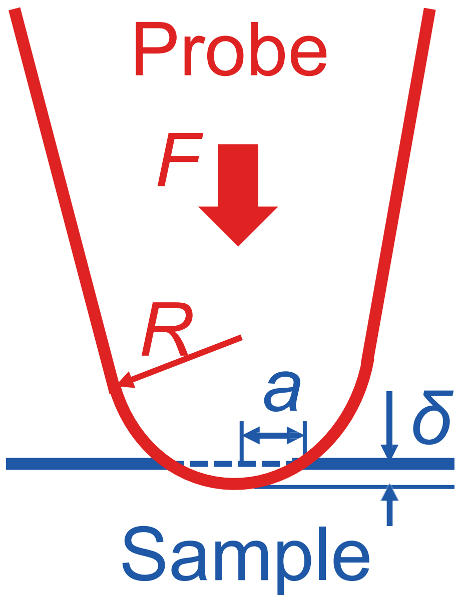


HybriD mode working principle

S. Magonov, S. Belikov, J. D. Alexander, C. G. Wall, S. Leesment, and V. Bykov, "Scanning probe based apparatus and methods for low-force profiling of sample surfaces and detection and mapping of local mechanical and electromagnetic properties in non-resonant oscillatory mode,"US9110092B1.

HD QNM
Quantitative nanomechanical measurements

Most used models of contact mechanics

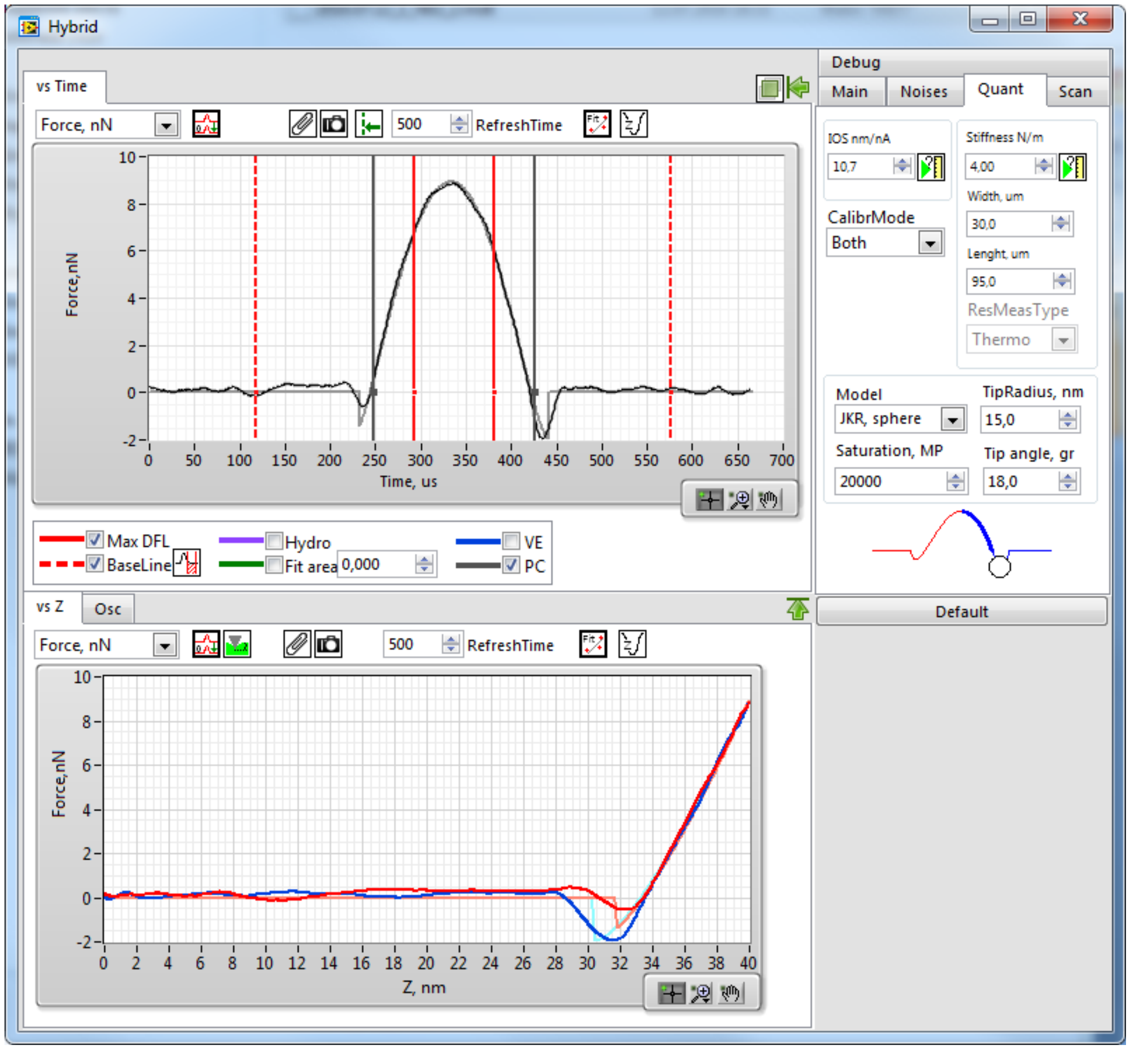


Tip-sample interaction model

Model	Approximation
Hertz model	• Large tip radius (a/R<<1) • No adhesive and capillary forces
Derjagin-Muller-Toropov model (DMT)	• Sharp tip (a≈R) • Low adhesive and capillary forces • Stiff samples
Johnson-Kendall-Roberts model (JKR)	• Large tip radius (a/R<<1) • High adhesion

Quantitative nanomechanical measurements

Real-time approximation of the force curves



HybriD mode software

Quantitative nanomechanical measurements

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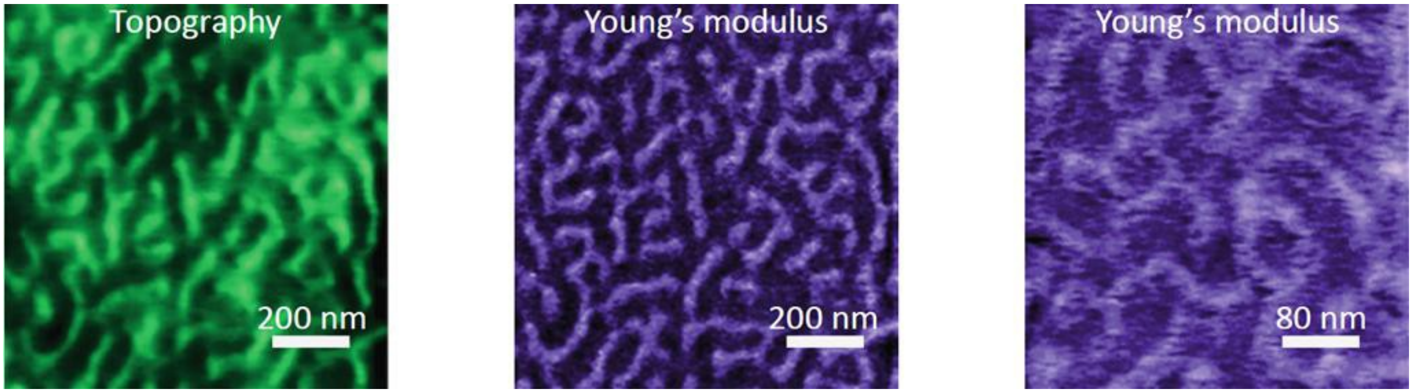
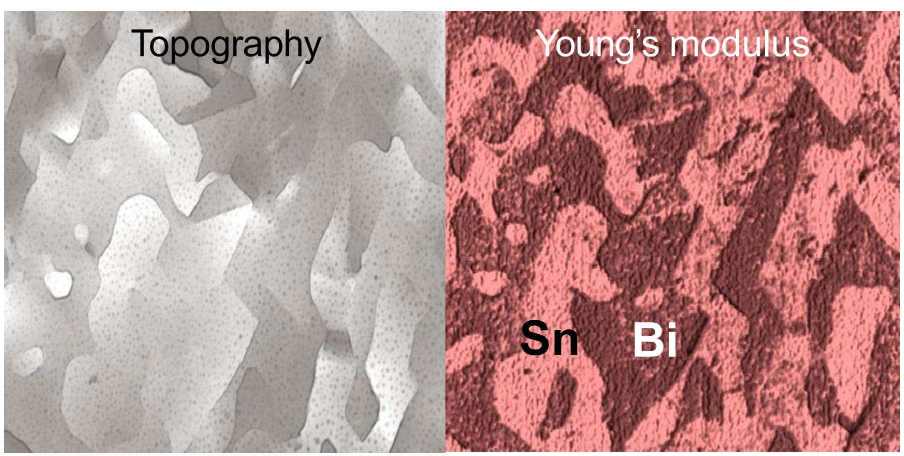
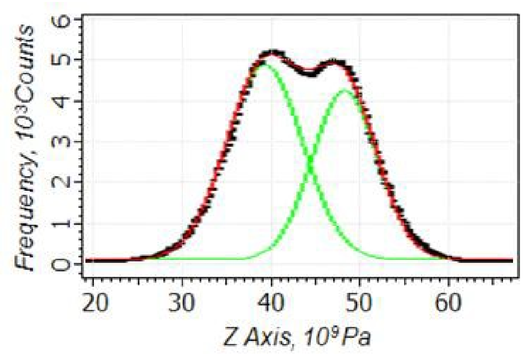
Ultimate spatial resolution



HD QNM study of PS-b-PMMA. Right image demonstrates around 10 nm spatial resolution.

Braking the force limit





Young's Modulus:

Si: 70 GPa

Tin: 50 GPa

Bismuth: 32 GPa

HD QNM study of Tin-Bismuth alloy. Scan size: 10×10 µm.

HD 2.0
New generation of control electronics

HybriD 2.0 Control Electronics

Hew generation of control electronics for HybriD mode

2012: HD Control electronics

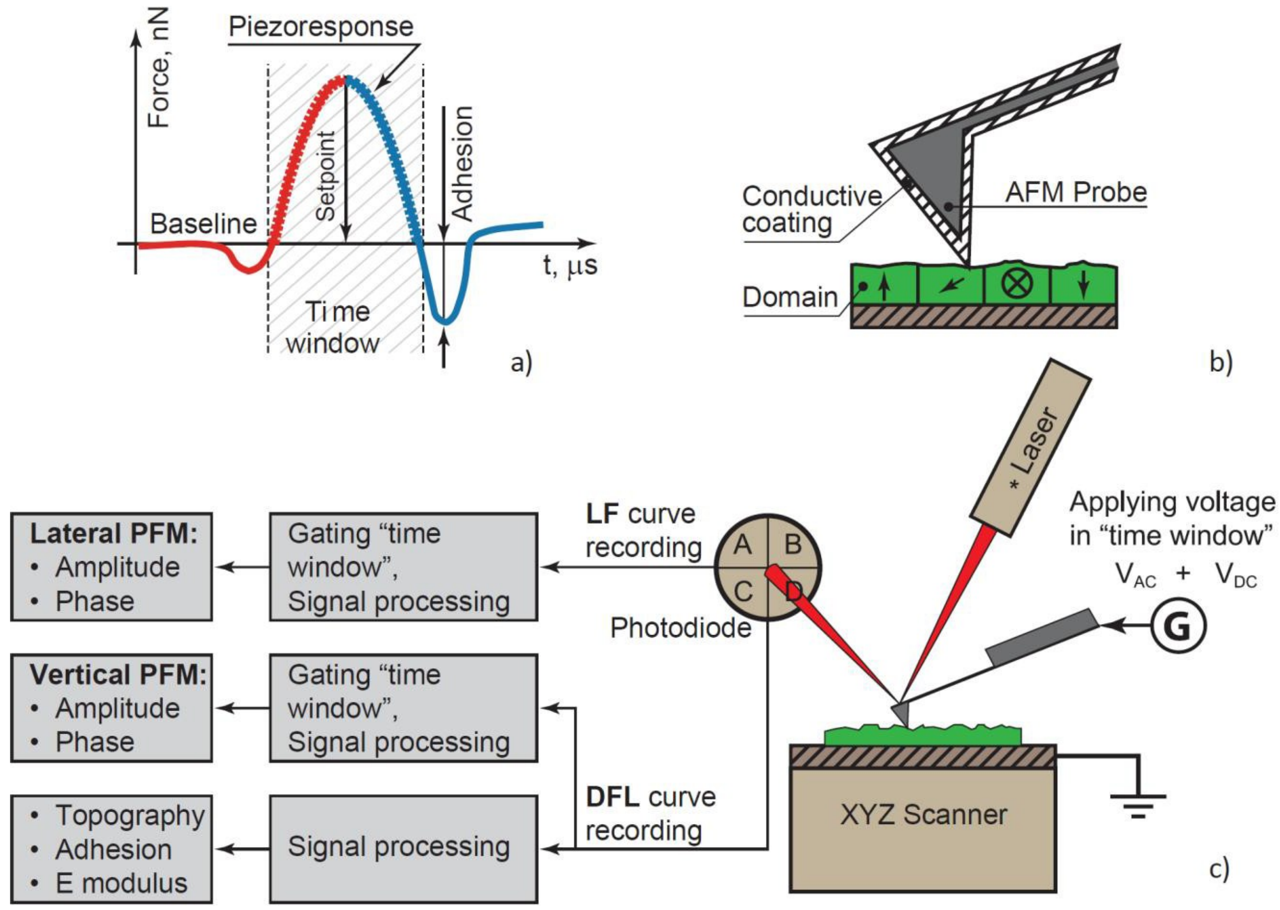
2017: New HD 2.0 Control electronics

- 4x faster FPGA and DSP
- 2x faster ADCs
- High-speed digital LIAs and generators
- Build-in 150V AC and DC voltage extension for PFM measurements

HybriD Piezoresponse Force Microscopy

HybriD Piezoresponse Force Microscopy

In HD PFM an AC voltage is applied to the conductive coating of the AFM cantilever when the tip comes in contact with the sample during each fast force spectroscopy cycle.



HD PFM working principle: a) an idealized temporal deflection curve during an oscillatory cycle, b) tip-sample interaction in "time window", c) measurement scheme

HybriD Piezoresponse Force Microscopy

Key advantages of HD PFM compared to the contact mode PFM:

1. **The ability of piezoresponse study of soft, loose and fragile samples**: since the AFM tip retracts from the surface in each scanning point, the lateral tip-sample interaction force is significantly reduced in comparison to the conventional contact PFM technique.

2. **Simultaneous Quantitative Nanomechanical measurements**

3. **Simultaneous** double-pass resonant electrostatic measurements: **Kelvin Probe Microscopy** or **Electrostatic Force Microscopy.**

4. Automatic compensation of the thermal drift of the AFM probe at each scanning point for the **real-time PFM studies under varying temperature.**

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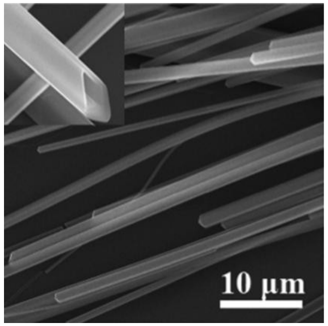
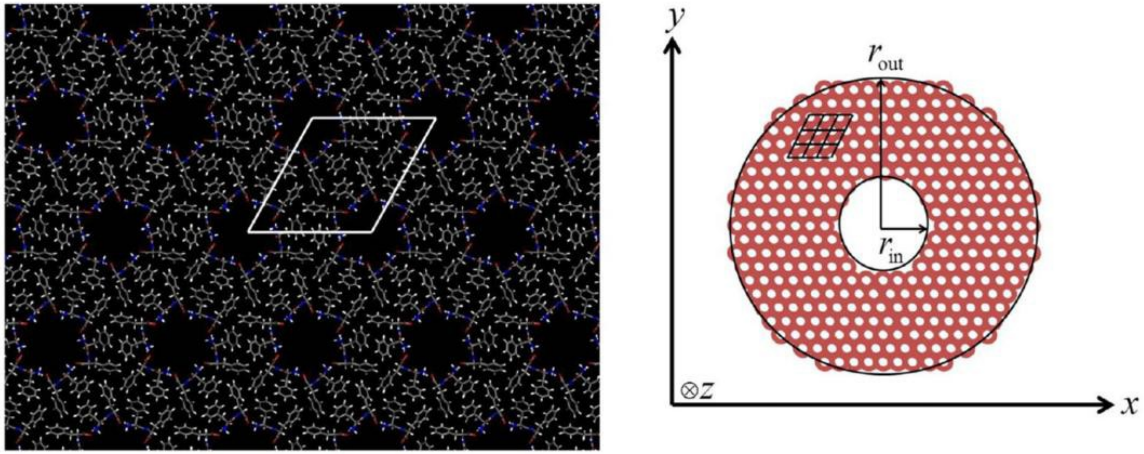
HybriD Piezoresponse Force Microscopy

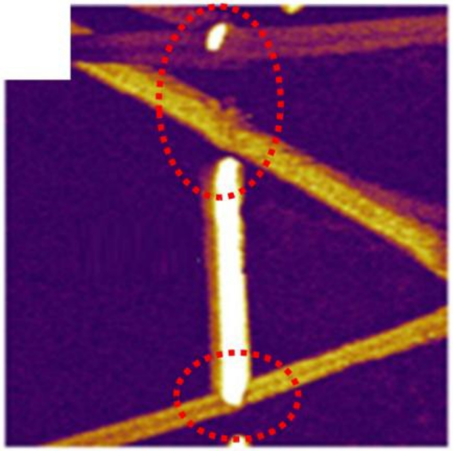
Motivation for the development: diphenylalanine peptide nanotubes



d_{15} = 60 pm/V[1]
E modulus = 19÷32 GPa



Molecular structure of diphenylalanine peptide nanotubes[1]

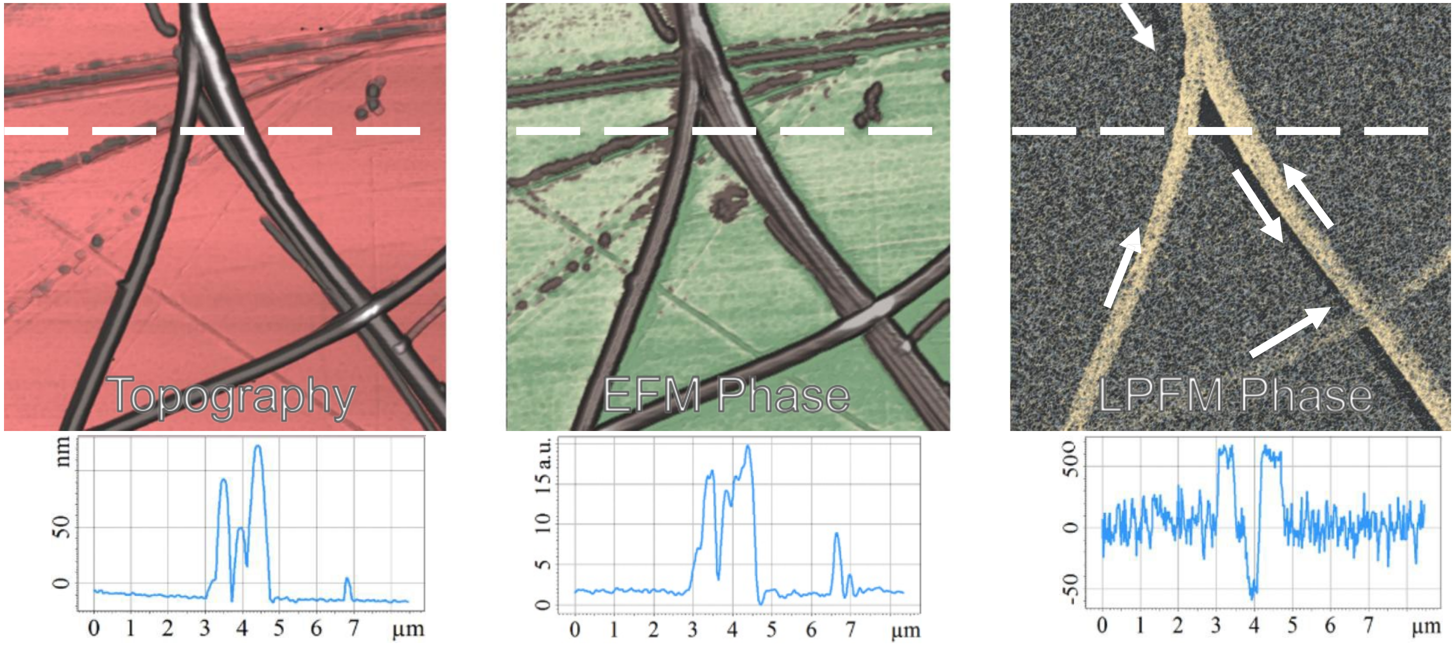


Contact PFM image[2]

[1]Kholkin, A., Amdursky, N., Bdikin, I., Gazit, E., & Rosenman, G. (2010) ACS nano, 4(2), 610-614.
[2]Ivanov, M., Kopyl, S., Tofail, S. A., Ryan, K., Rodriguez, B. J., Shur, V. Y., & Kholkin, A. L. (2016) In Electrically Active Materials for Medical Devices (pp. 149-166).

HybriD Piezoresponse Force Microscopy

For the first time HD PFM mode allowed non-destructive piezoresponse study of diphenylalanine peptide nanotubes – a very prospective material for biomedical applications.



Non-destructive electromechanical study of diphenylalanine peptide nanotubes. Scan size: 8×8 μm, nanotubes diameter: 30÷150 nm[1]. Sample courtesy: Dr. A. Kholkin, University of Aviero

[1] A. Kalinin, V. Atepalikhin, O. Pakhomov, A. Kholkin, A. Tselev. An Atomic Force Microscopy Mode for Nondestructive Electromechanical Studies and its Application to Diphenylalanine Peptide Nanotubes. To be published in Ultramicroscopy

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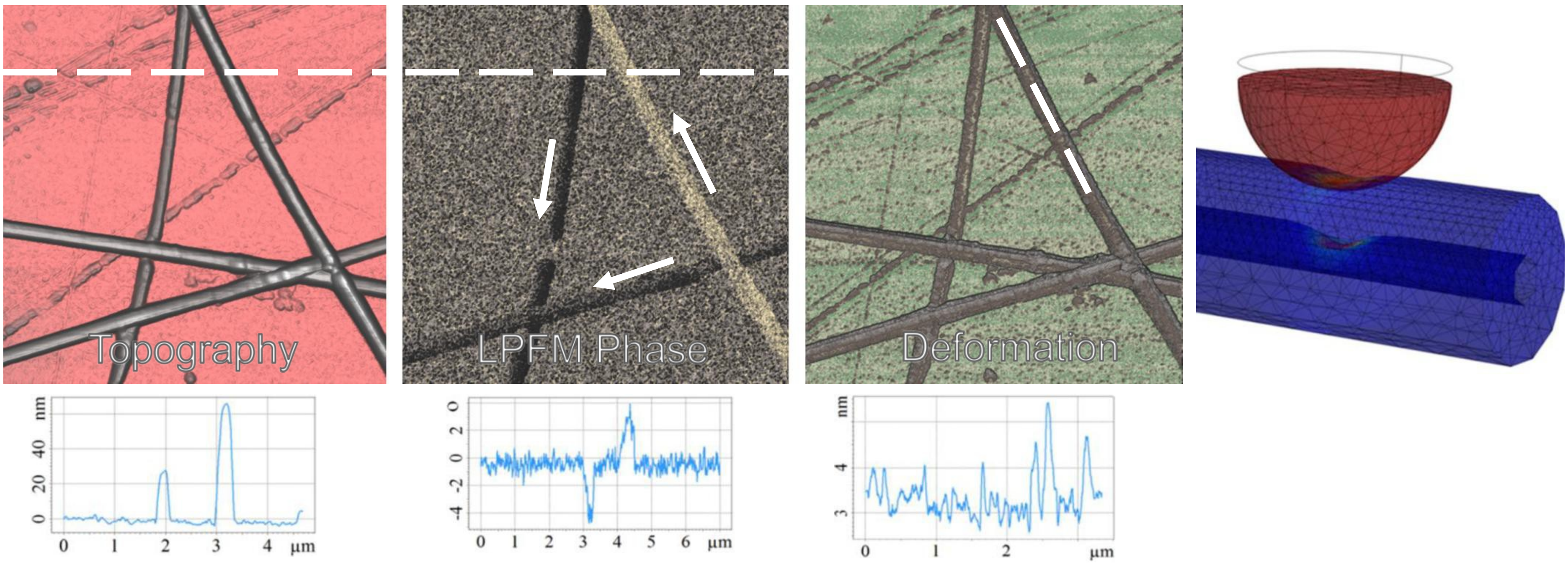
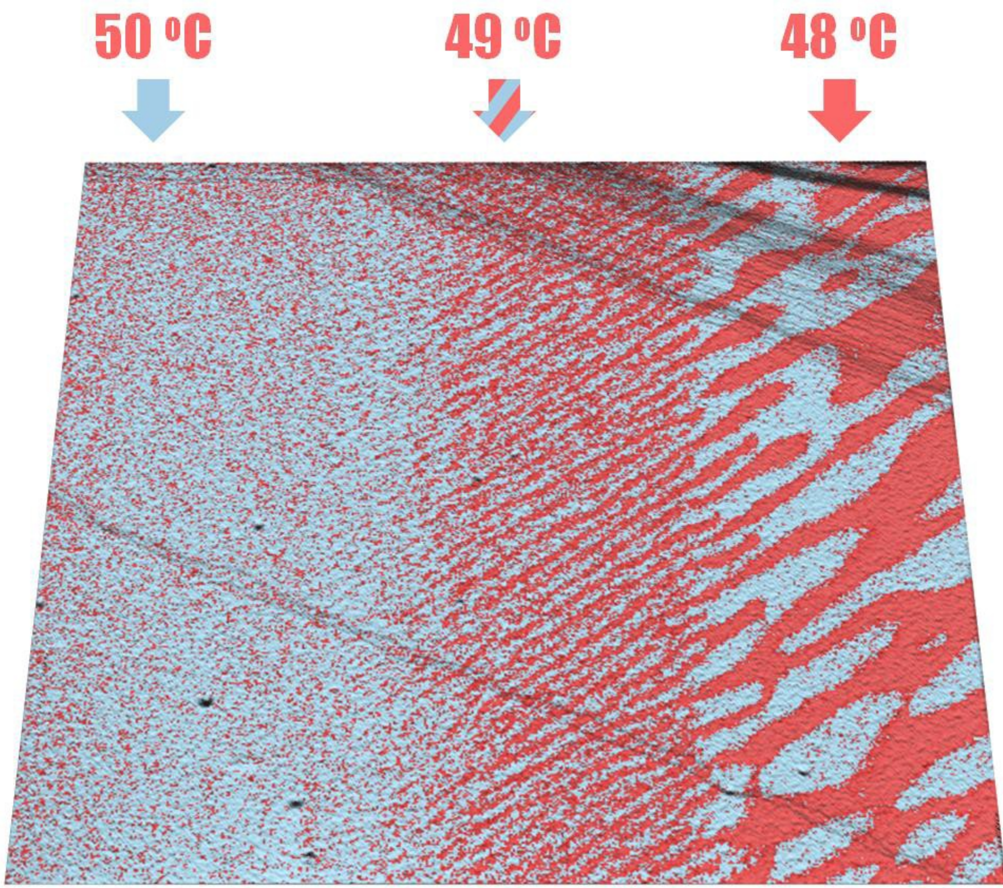


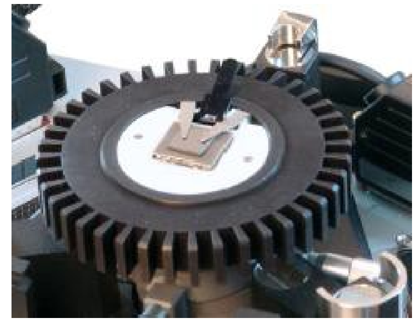
Non-destructive electromechanical study of diphenylalanine peptide nanotubes. Scan size: 7×7 µm, nanotubes diameter: 70÷100 nm[1]. Sample courtesy: Dr. A. Kholkin, University of Aviero

[1] A. Kalinin, V. Atepalikhin, O. Pakhomov, A. Kholkin, A. Tselev. An Atomic Force Microscopy Mode for Nondestructive Electromechanical Studies and its Application to Diphenylalanine Peptide Nanotubes. To be published in Ultramicroscopy

HybriD Piezoresponse Force Microscopy

Continuous PFM studies under varying temperature

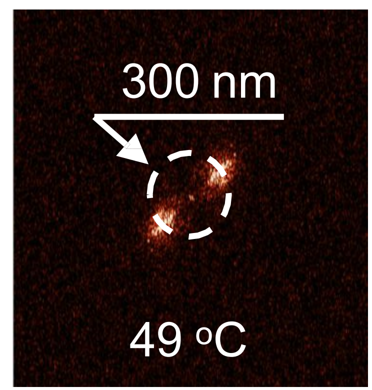


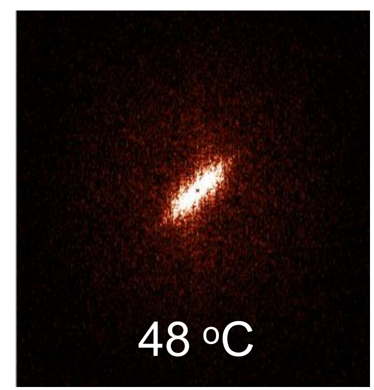


RT÷300 °C

-30÷120 °C

NT-MDT S.I. accessories for sample temperature control



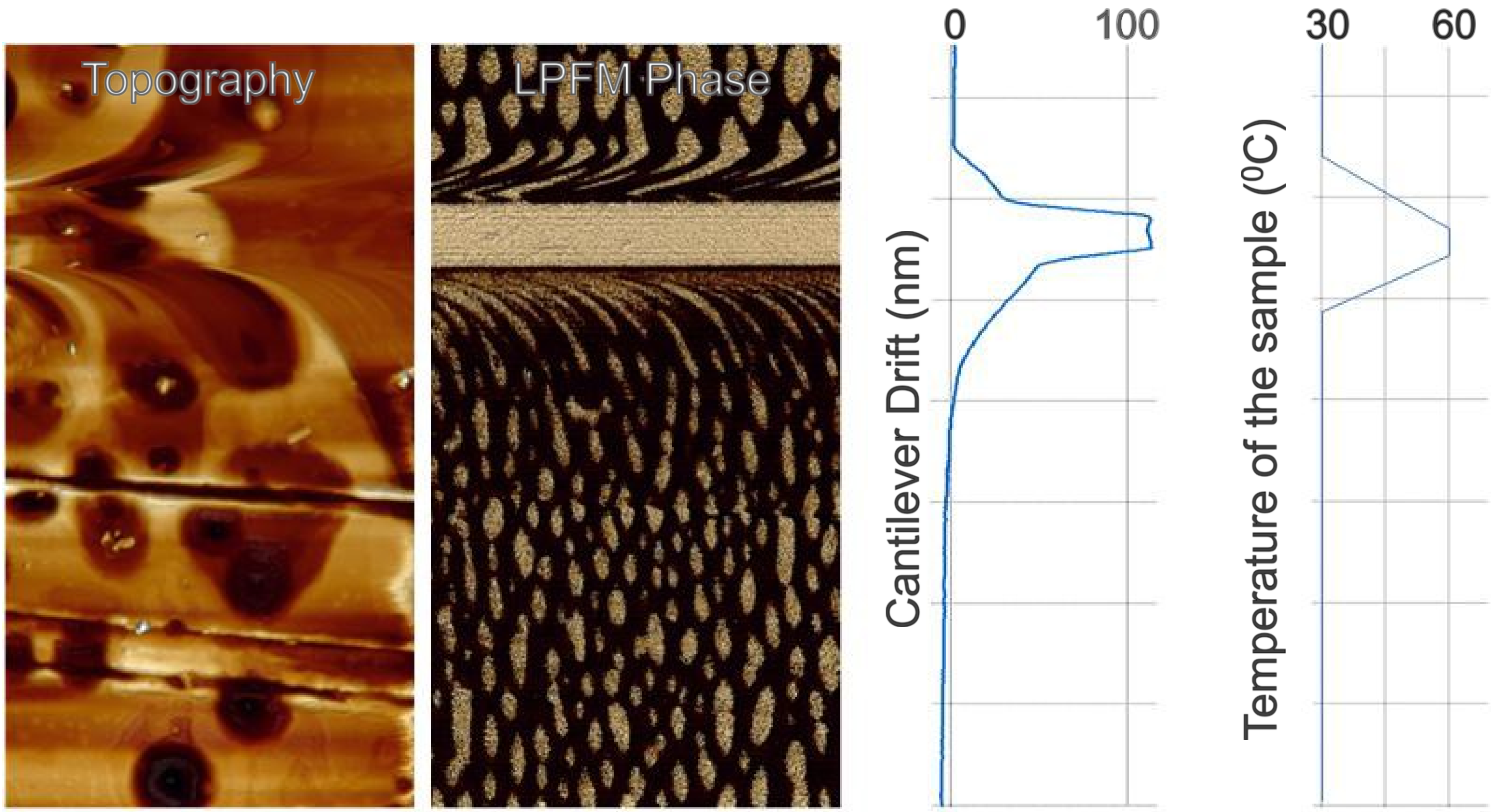


In-situ HD PFM study of second-order phase transition of triglycine sulfate crystal. Scan size 15×15 µm. Sample courtesy: Dr. R. Gainutdinov, IC RAS

HybriD Piezoresponse Force Microscopy

Continuous PFM studies under variable temperature

>0.1 °C/sec temperature change



In-situ HD PFM study of second-order phase transition of triglycine sulfate crystal. Scan size 15×15 µm. Sample courtesy: Dr. R. Gainutdinov, IC RAS

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HybriD Piezoresponse Force Microscopy

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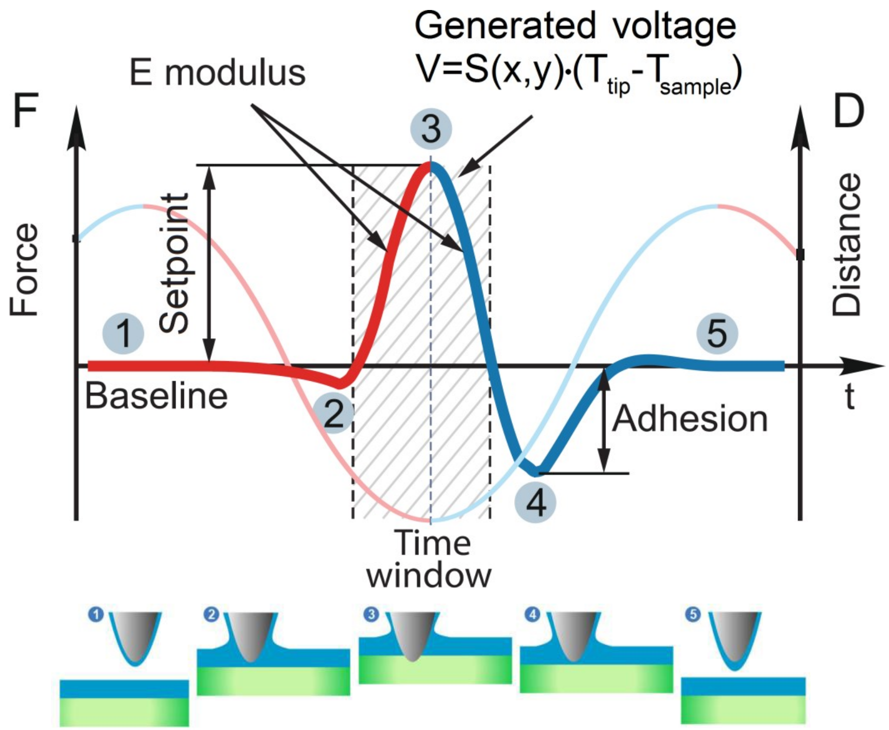
4. Automatic compensation of the thermal drift of the AFM probe at each scanning point for the **real-time PFM studies under varying temperature.**

HybriD Scanning Thermoelectric Microscopy

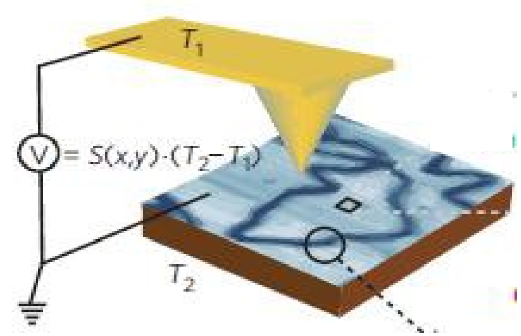
HybriD Scanning Thermoelectric Microscopy

HD SThEM working principle is based on direct measurement of generated voltage when conductive tip and sample under different temperatures contact each other (Seebeck effect) during fast force spectroscopy measurements



HD SThEM working principle

NT-MDT S.I. insert for SThEM measurement



S. Cho et al “Thermoelectric imaging of structural disorder in epitaxial graphene” Nature Materials, 2013.

J.C. Walrath *et al*, Quantifying the local Seebeck coefficient with scanning thermoelectric microscopy, Appl. Phys. Lett. 103 (2013) 212101.

HybriD Scanning Thermoelectric Microscopy

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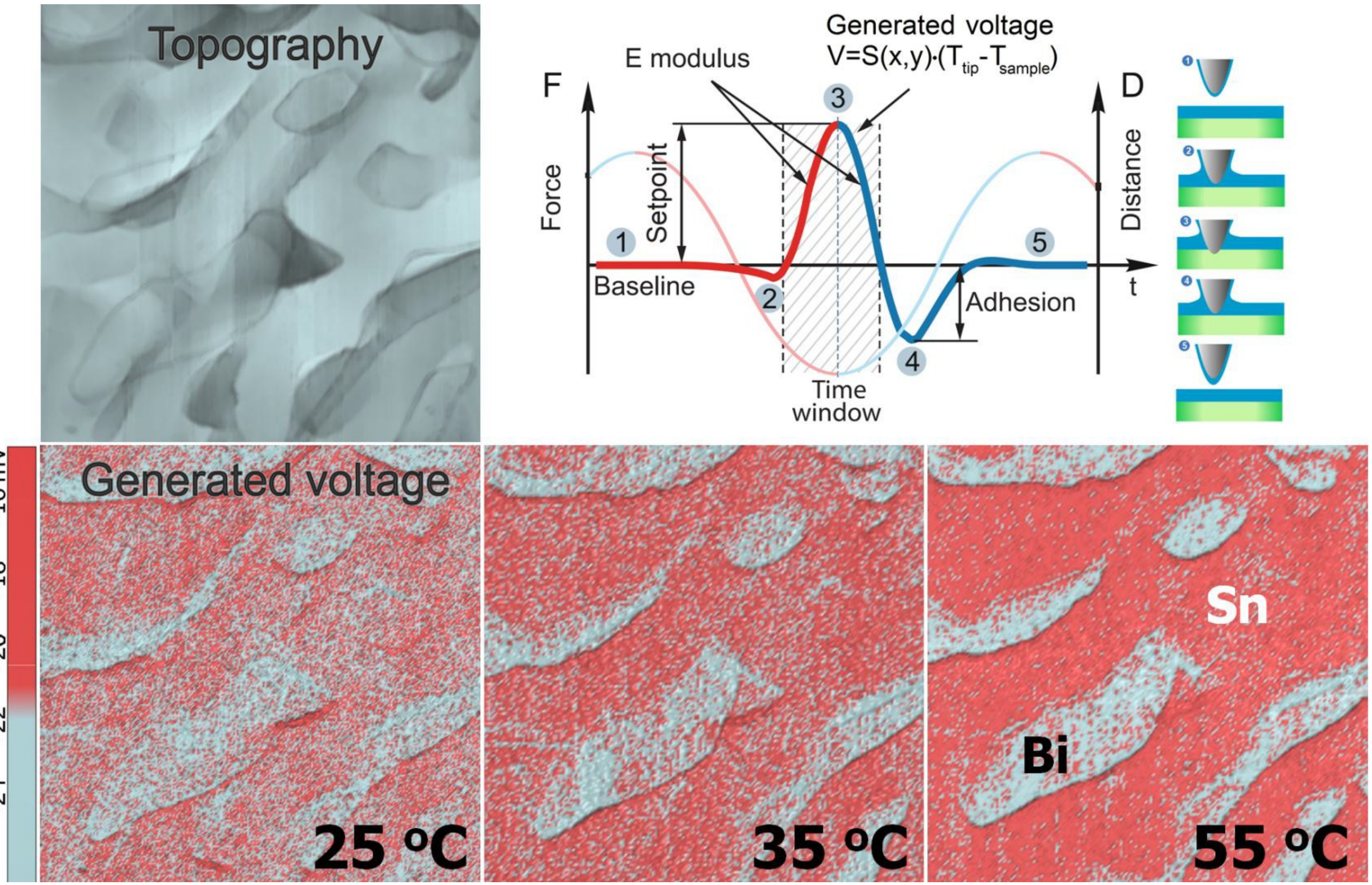


HD SThEM study of Tin-Bismuth alloy. Seebeck coefficient, S: Bi -72 mV/C, Sn -1.5 mV/C. Scan size: 7×7 µm.

HybriD Scanning Thermoelectric Microscopy

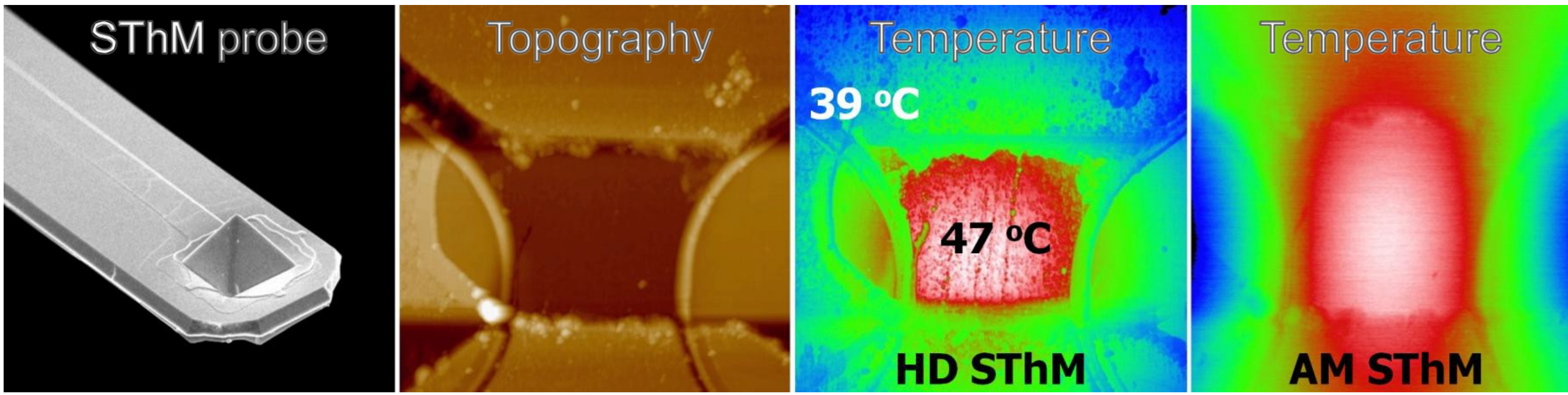
Key advantages of HD SThEM:

1. **The first commercially available SThEM equipment.**
2. **The ability of thermoelectric study of loose and fragile samples**: since the AFM tip retracts from the surface in each scanning point, the lateral tip-sample interaction force is significantly reduced in comparison to the conventional contact PFM technique
3. **Simultaneous nanomechanical** and double-pass resonant electrostatic measurements: **Kelvin Probe Microscopy** or **Electrostatic Force Microscopy** studies**.**

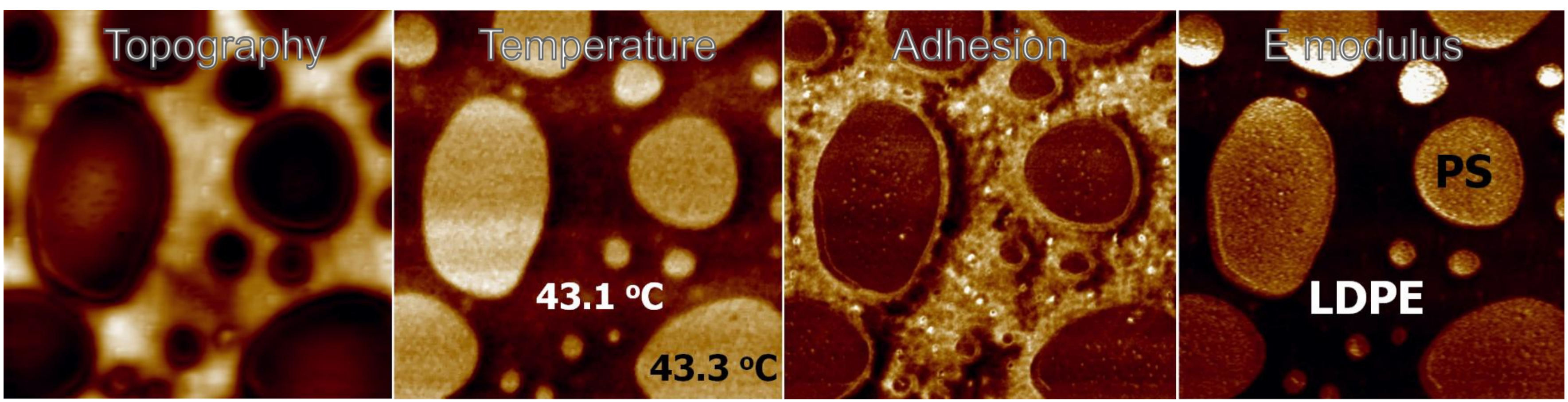
HybriD Scanning Thermal Microscopy (HD SThM)

HybriD Scanning Thermal Microscopy

HD Scanning Thermal Microscopy (HD SThM) allows studying local thermal properties – temperature and thermal conductivity – simultaneously with QNM measurements.



SEM image of AppNano VertiSense™ thermocouple probe and comparison of HD SThM and AM SThM techniques. Scan size: 17×17 µm.



HD SThM study of PS-LDPE. Scan size: 10×10 µm.

HybriD Scanning Thermal Microscopy

Key advantages of HD SThM:

1. **The ability of thermal studies of soft, loose and fragile samples**: since the AFM tip retracts from the surface in each scanning point, the lateral tip-sample interaction force is significantly reduced in comparison to the conventional contact SThM technique.

2. **Increased spatial resolution** compared to AM SThM where tip-sample contact time is dramatically short.

3. **Simultaneous** nanomechanical studies.

HybriD Conductive-AFM

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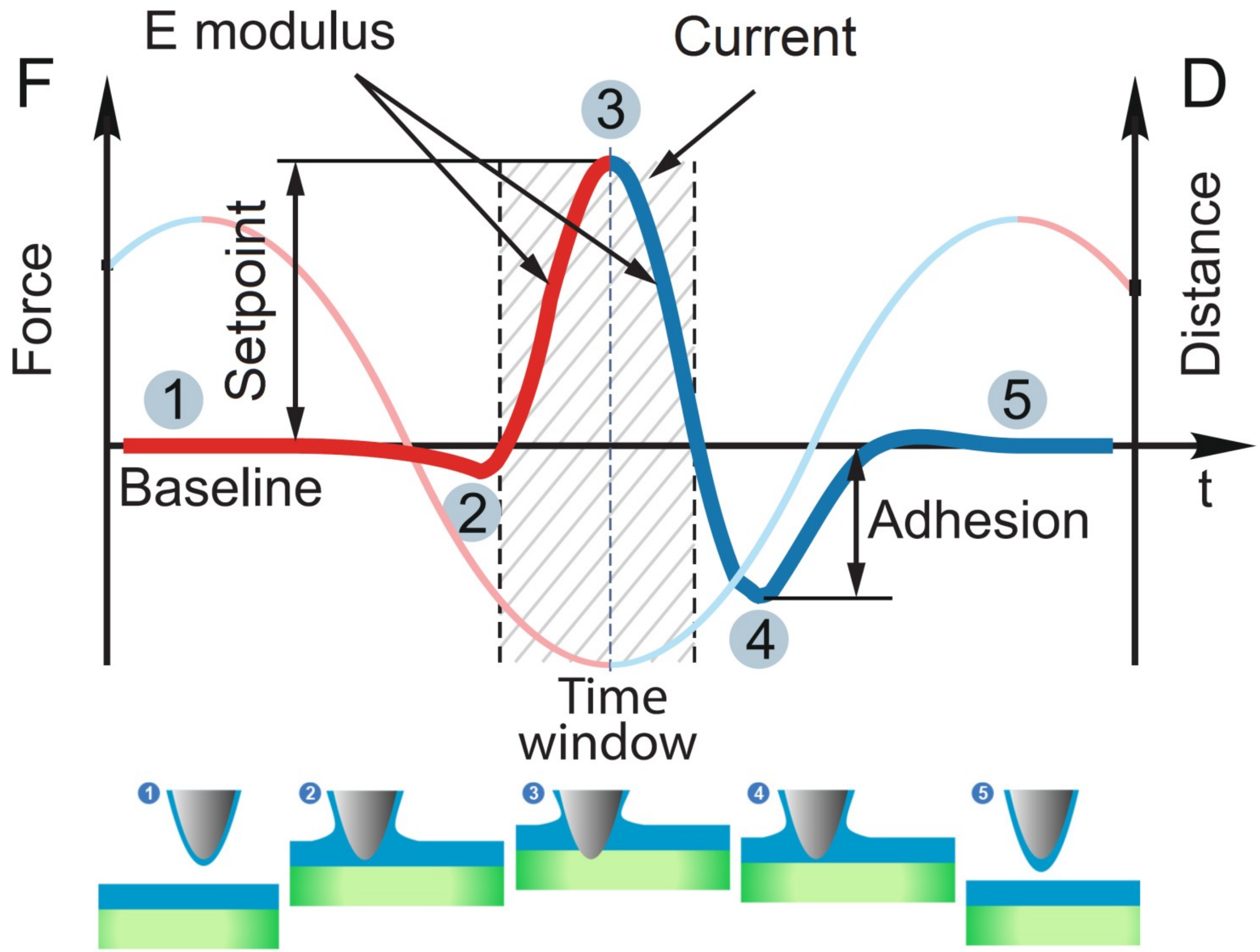
HybriD Conductive AFM

Conductivity mapping while fast force spectroscopy measurements



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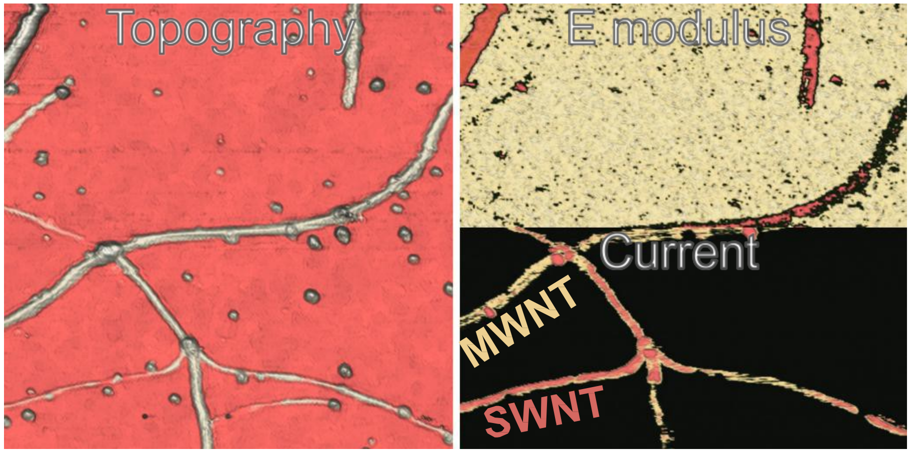
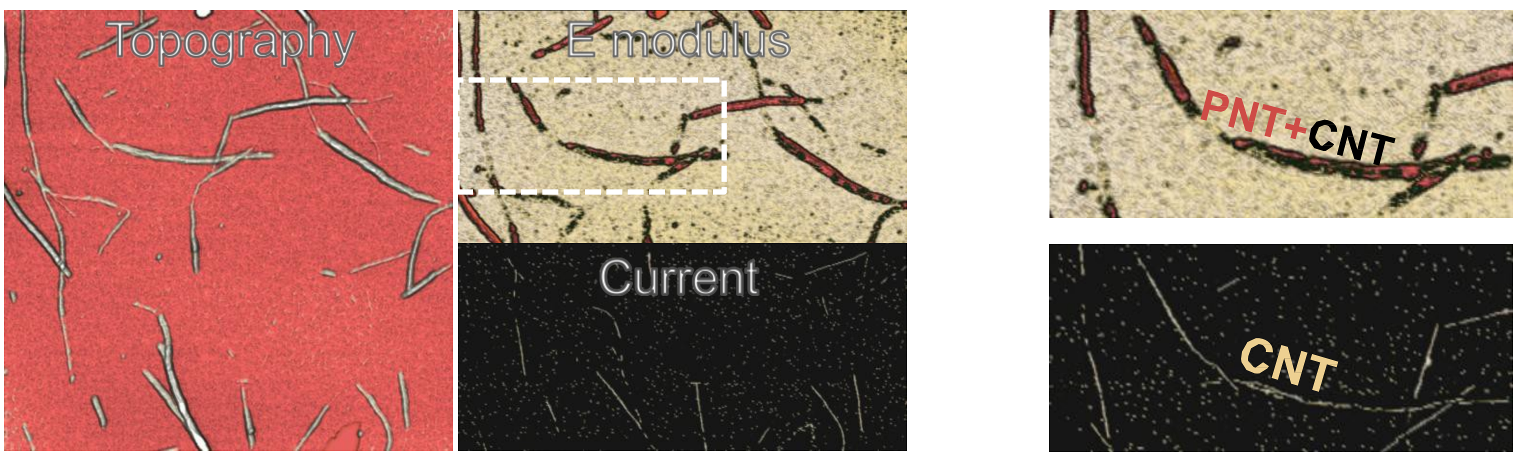
HybriD Conductive AFM

HybriD Mode drastically decreases the impact of lateral forces and simplifies C-AFM experiments



HD C-AFM study of carbon Nanotubes on Silicon.

Scan size: 1×1 μm.



HD C-AFM study of coupled carbon and peptide Nanotubes. Sample courtesy: Dr. J. Montenegro, University Santiago de Compostela. Scan size: 3×3 μm[1].

[1] J. Montenegro, C. Vázquez-Vázquez,A. Kalinin, K.E. Geckeler, J.R. Granja, Coupling of carbon and peptide nanotubes, J. Am. Chem. Soc. 136 (2014)2484–2491

HybriD Conductive AFM

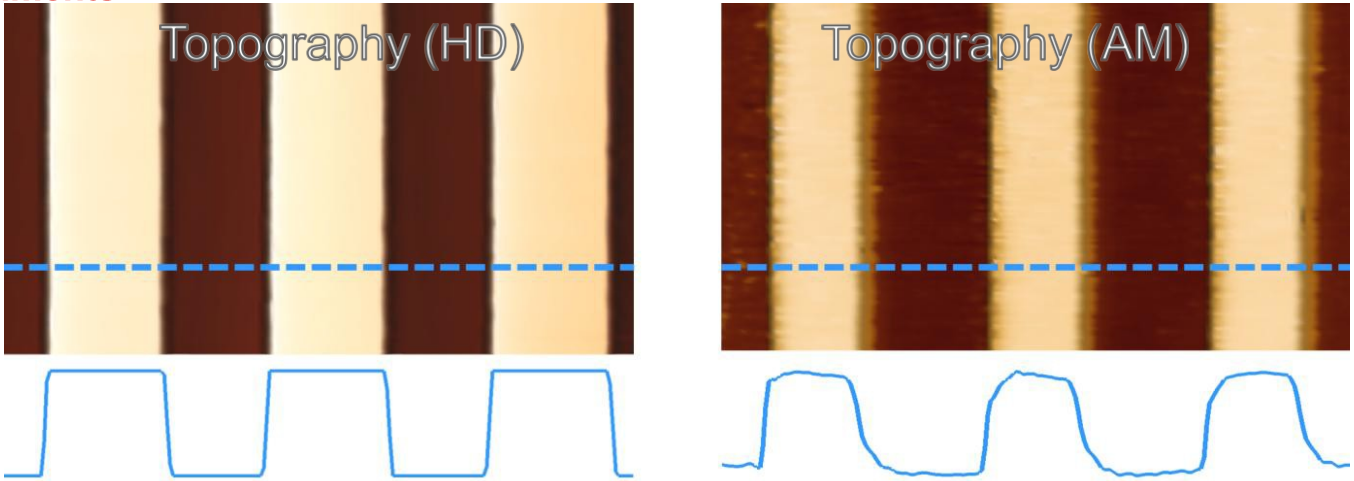
Key advantages of HD C-AFM:

1. **The ability of conductivity studies of soft, loose and fragile samples**: since the AFM tip retracts from the surface in each scanning point, the lateral tip-sample interaction force is significantly reduced in comparison to the conventional contact SThM technique.

2. **Simultaneous** nanomechanical studies**.**

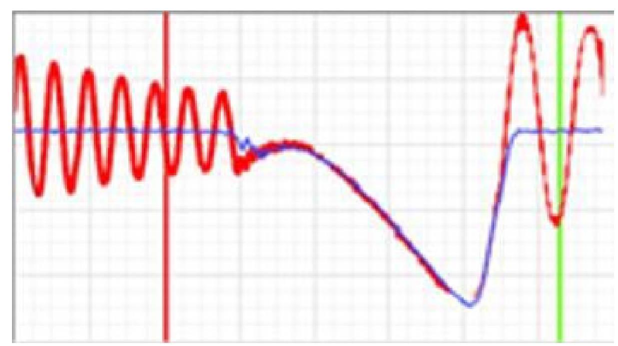
Advanced environmental studies:
Vacuum HD, Bio HD

Vacuum HD measurements



Topography of TGZ2 calibration grating measured in vacuum with use of HD and AM modes. Scanning speed is 1Hz. Grating period is 3 μm, height is 100 nm.

Vacuum AFM
NTEGRA Aura



Example of filter operation.
Red – before, blue – after filter is appliedd

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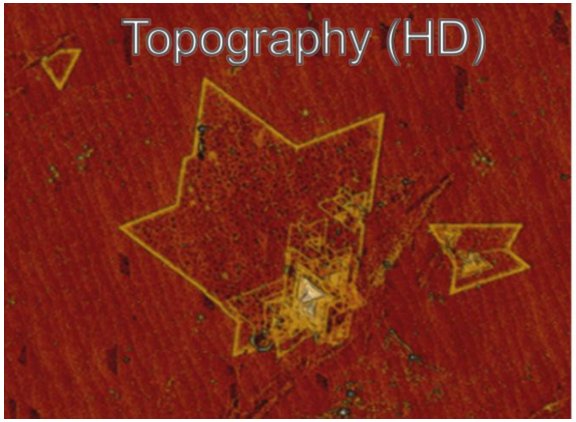
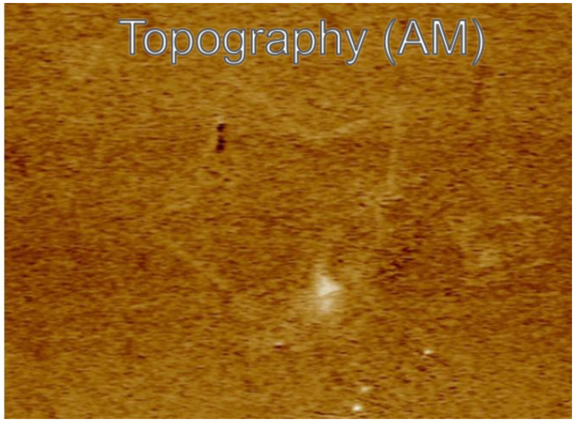
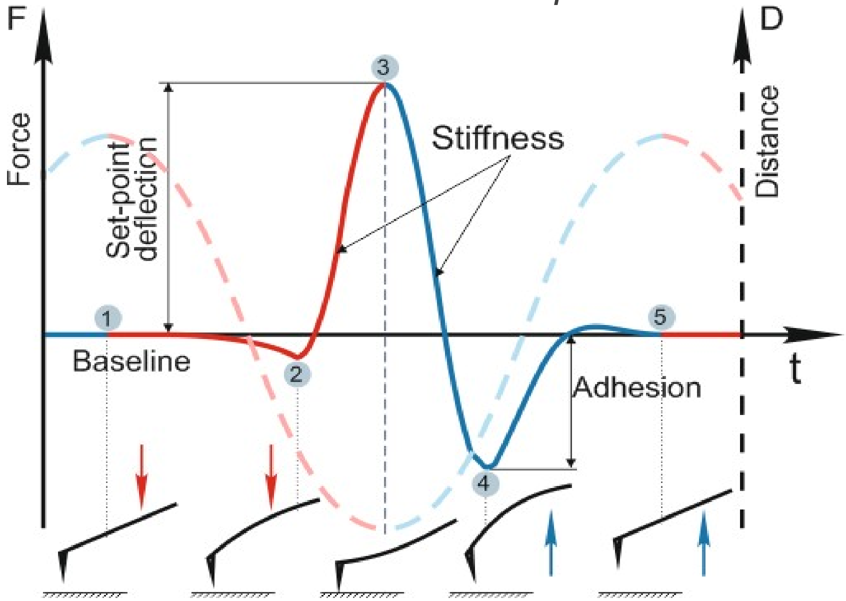
Vacuum HD measurements





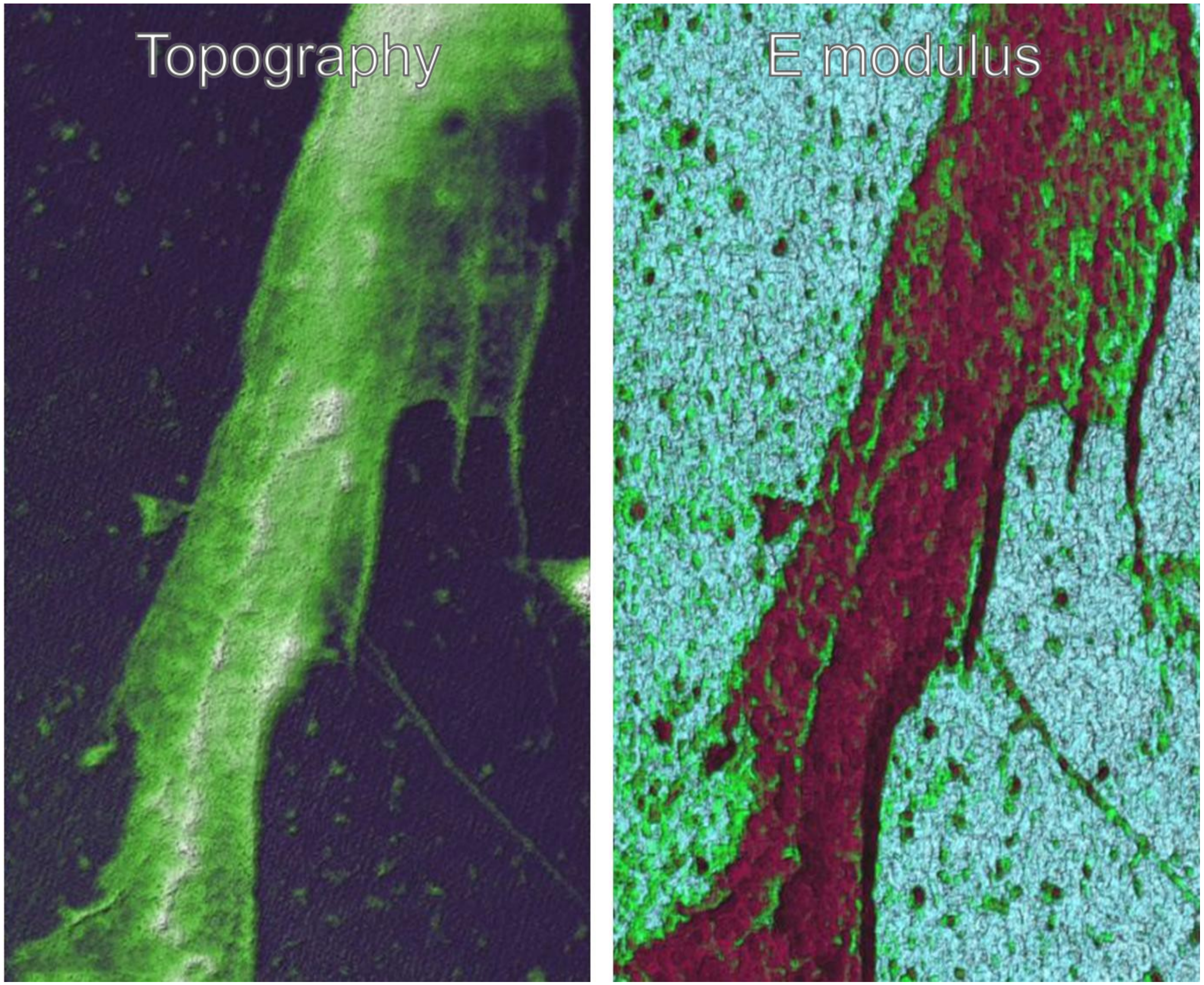
WS_2 monolayers grown on epitaxial graphene measured in vacuum with use of HD and AM modes. The influence of electrostatic forces is demonstrated. Scan size: 14×14 μm

Vacuum AFM NTEGRA Aura



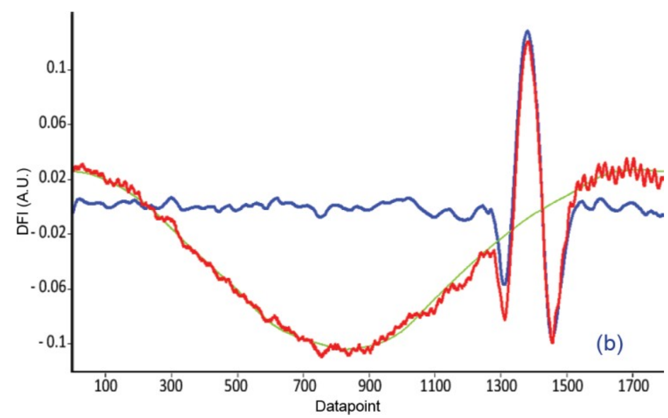
Set-point calculation principle eliminating electrostatic force gradient

Liquid HD measurements



Bio HD study of Stem Cell fragment in Liquid. Elastic Modulus range: 0.2-1.5 kPa. Scan size: 18×30 μm

NT-MDT S.I. accessories for liquid measurements



Example of filter operation

Advanced combined AFM-Optical modes:
HD TERS, HD SNOM

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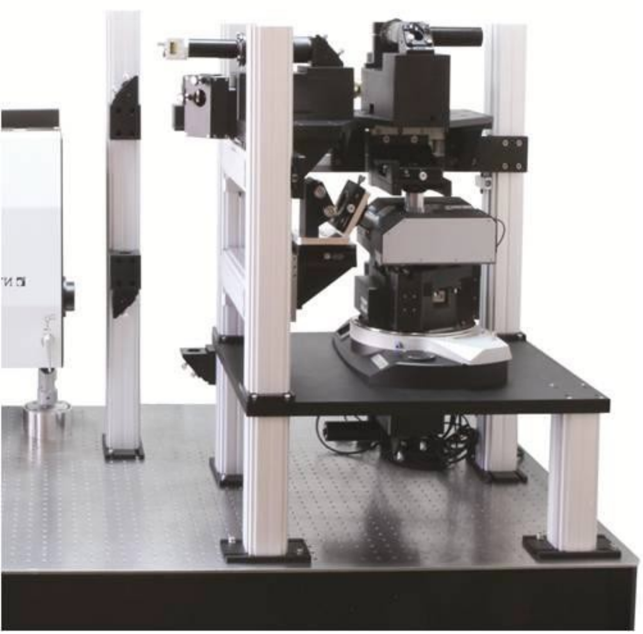
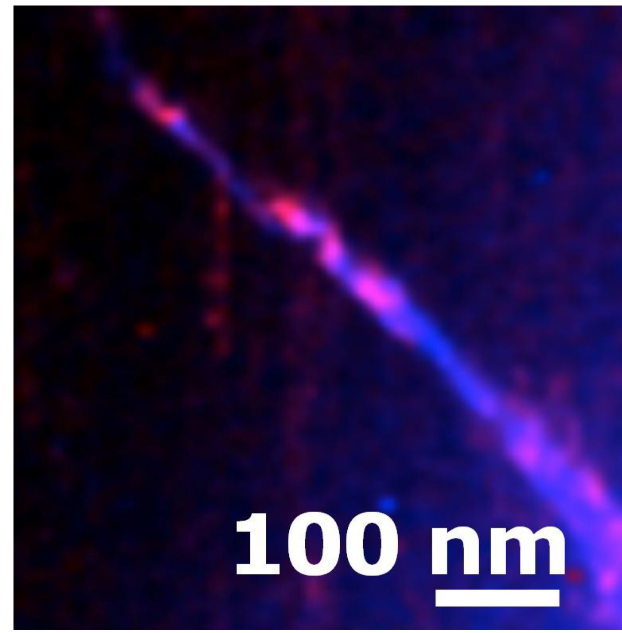
HybriD Tip-Enhanced Raman Scattering

Using HybriD mode for TERS imaging dramatically increases the life time of the probe and allows non-destructive studies



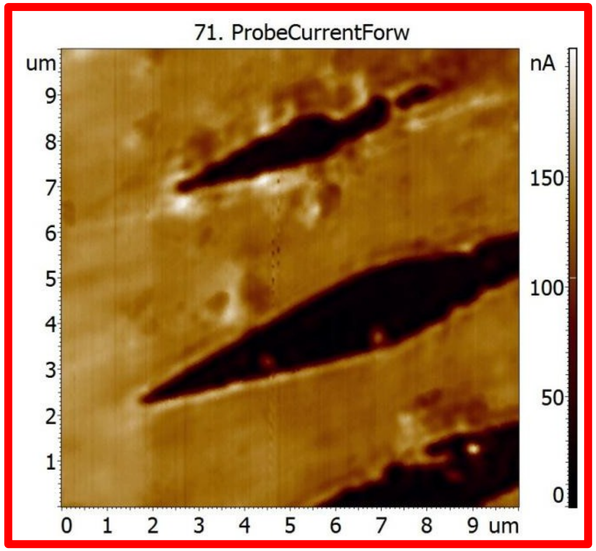
Versatile automated AFM-Raman, SNOM and TERS system NTEGRA SPECRTA II

NT-MDT S.I. commercially available TERS probes

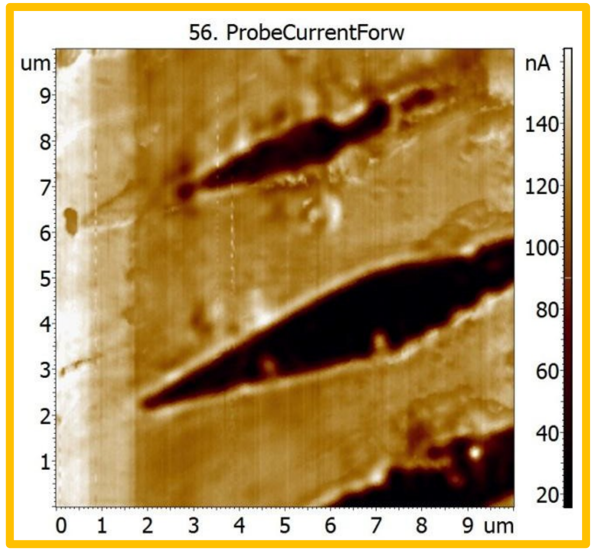


High resolution TERS map of carbon nanotubes on Au substrate. Resolution: ~10 nm. Overlay of G-band (blue) and D-band (red).

HybriD Scanning Near-field Microscopy



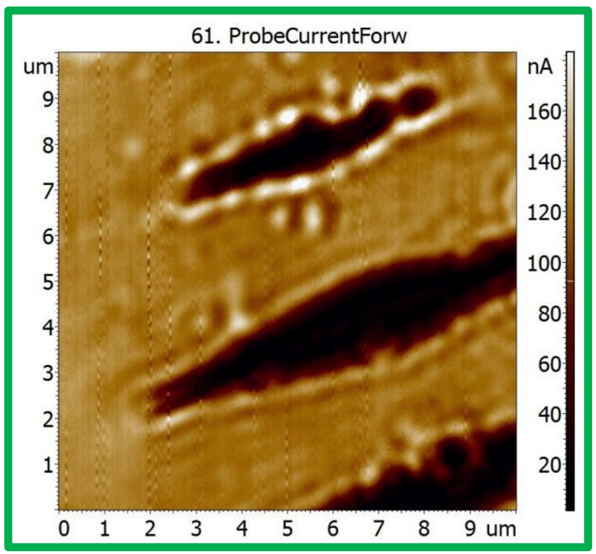
SNOM in contact



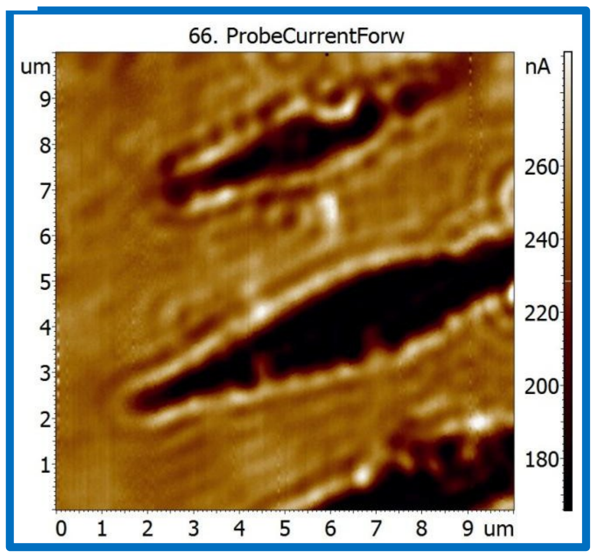
SNOM at 100 nm from surface

Aperture AFM SNOM probe

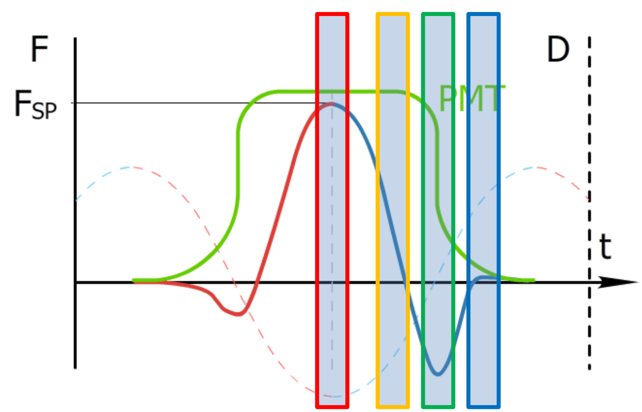
PMT signal per one cycle



SNOM at 220 nm from surface



SNOM at 290 nm from surface



Schematic force curve and optical curve

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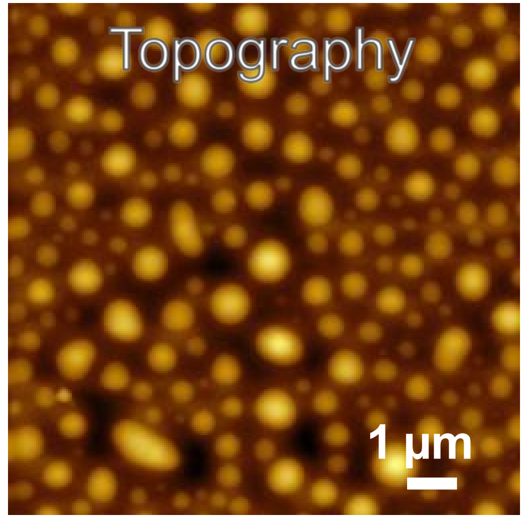
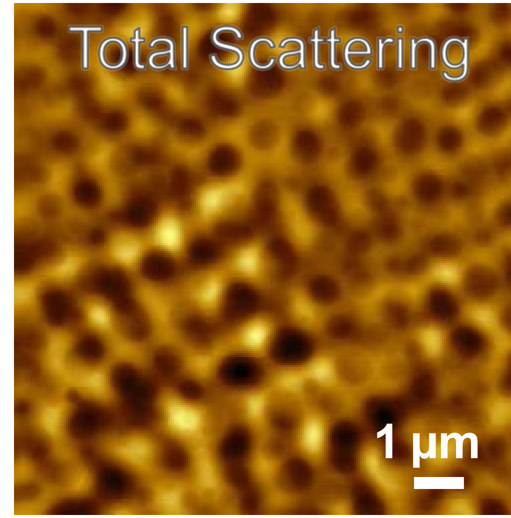
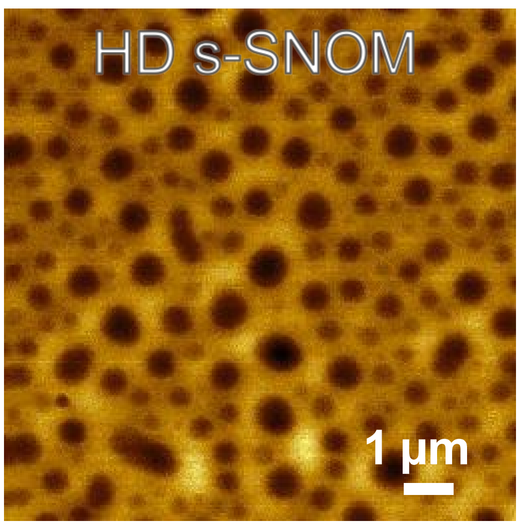
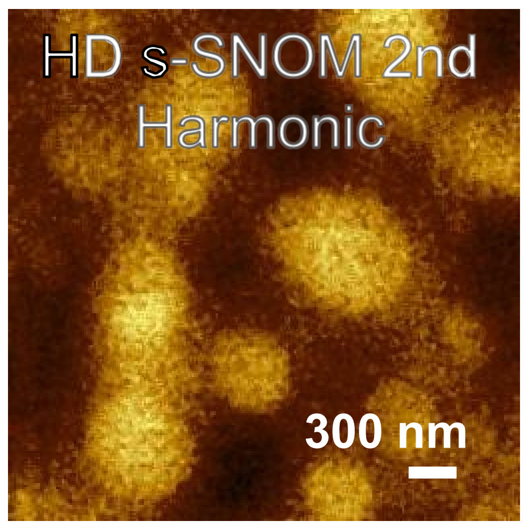
HybriD Scattering Scanning Near-field Microscopy

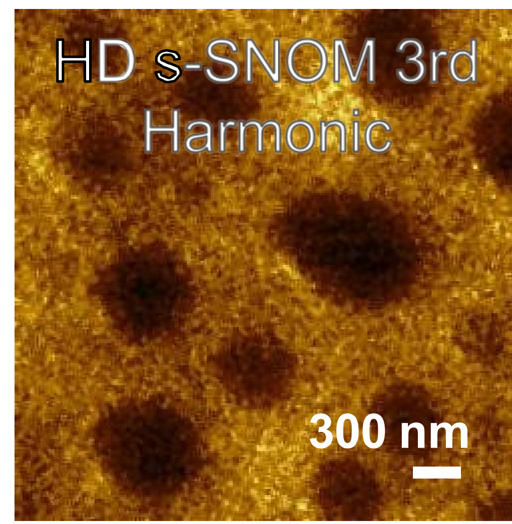
PMT signal per one cycle – "optical curve"











HD s-SNOM study of PS/PBD film demonstaring better than 100 nm optical resolution

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HD TERS, HD SNOM Microscopies

Key advantages of HD TERS, HD SNOM:

1. Non-destructive TERS imaging with use of commercially available cantilever-type probes

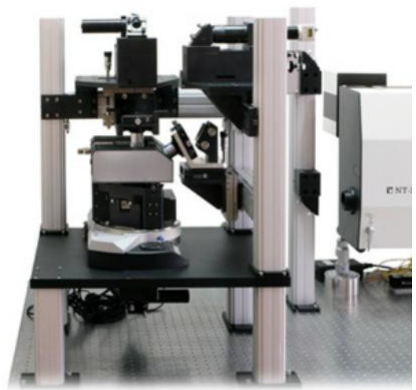
2. Ability to separate far- and near-field component of optical response and measure s-SNOM at 2^{nd} and 3^{d} harmonics

3. Simultaneous nanomechanical measurement

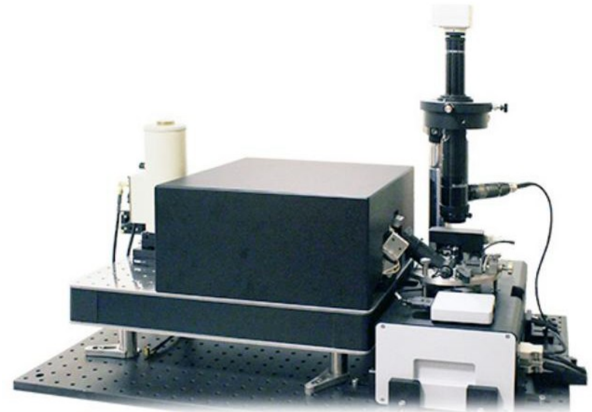
Conclusion

HybriD mode and HD 2.0 Control Electronics are compatible with all the product line of NT-MDT Spectrum Instruments

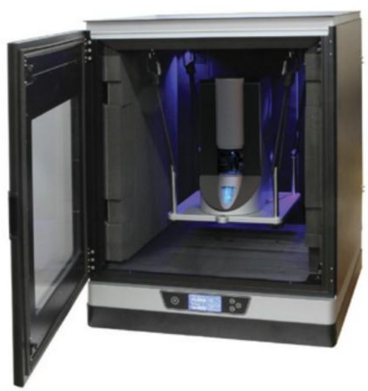
Modular SPM NTEGRA



Automated AFM-Raman, SNOM and TERS system NTEGRA SPECRTA II



AFM-IR & sSNOM system NTEGRA Nano IR



Ultra-low-drift automated SPM Titanium

Practical AFM Solver NANO

Automated SPM NEXT

Automated large-sample AFM VEGA

Conclusion

Your questions

Visit us at MRS FALL MEETING & EXIBITION!

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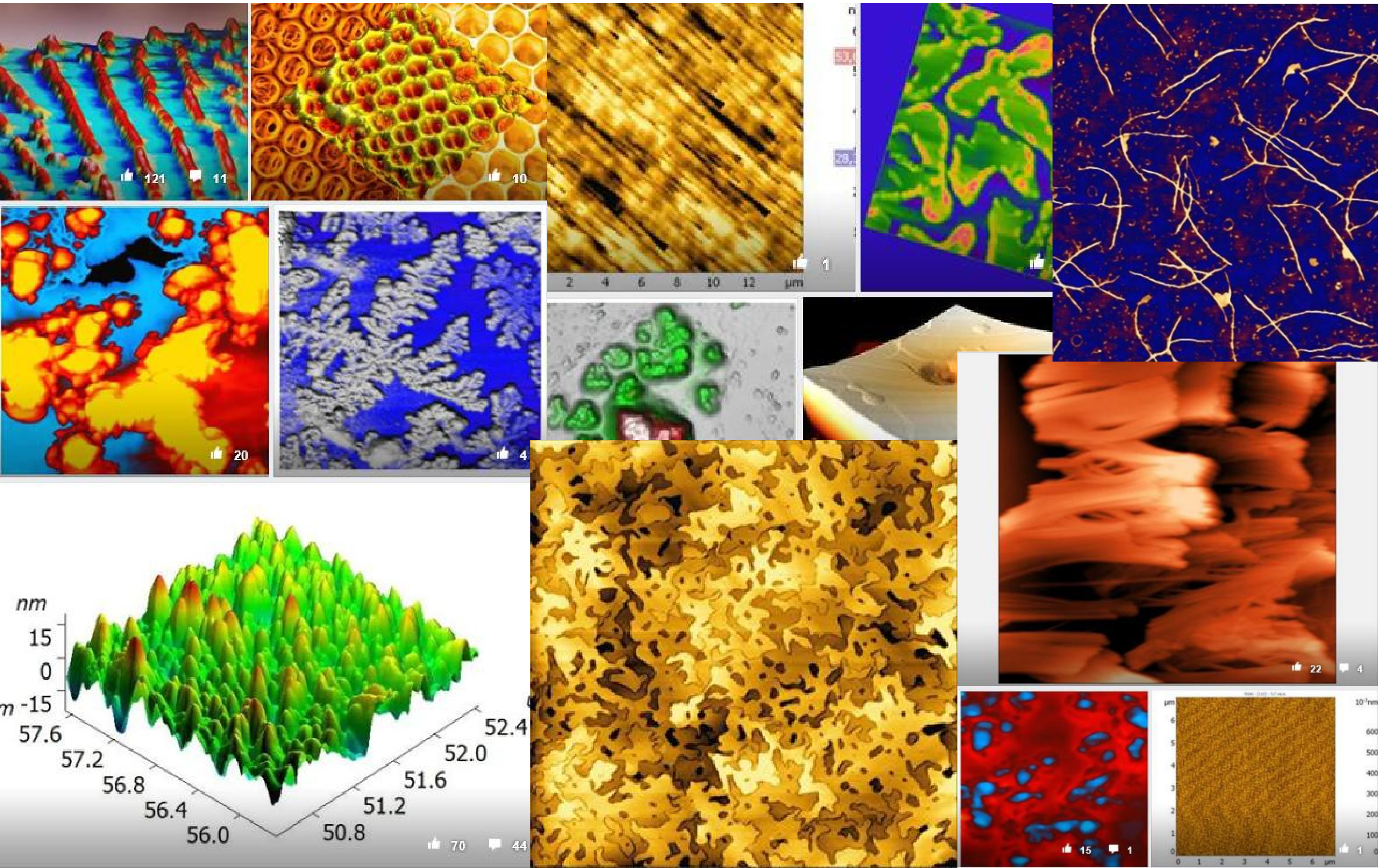
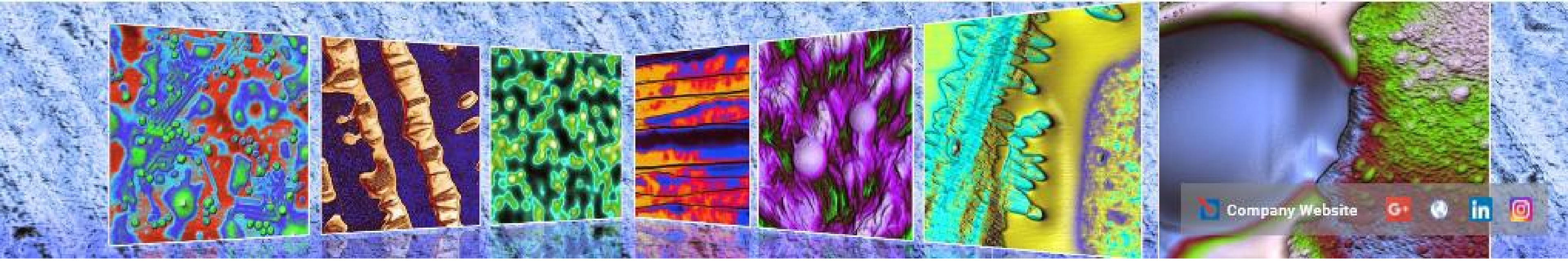
NT-MDT Image Contest 2017





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