Some current challenges in materials measurements

An industrial perspective

Roger Proksch

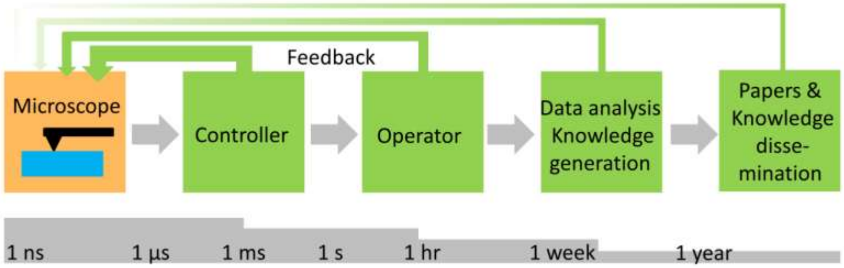
CTO, Oxford Instruments

Measuring materials on the nanoscale

Presentation Outline

- Brief intro to Oxford Instruments
- Currently: No fast ML, typically remote, after acquisition
  - Commercial requirements are different from research
- Goal: Get rid of the domain experts – self driving instruments
  - Ease of use – Confocal and EBSD examples
  - Atomic Force Microscopy
    - Parameter estimation and process control
      - VRS – video rate AFM imaging
    - Hyperspectral measurements
      - Correlative topographic, chemical and nanomechanical imaging

Kalinin, Strelcov et al. 2016



“The first commercially successful spin-out from Oxford University”

Our business

Addressing some of the world's most pressing challenges

Materials & Characterisation

Products and solutions that enable the fabrication and characterisation of devices down to the atomic scale.

PLASMA TECHNOLOGY

Leading provider of etch and deposition processing solutions and recipes

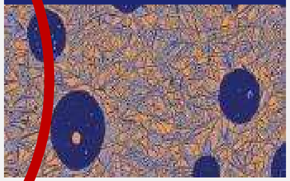
MAGNETIC RESONANCE

Leaders in benchtop Nuclear Magnetic Resonance (NMR) instruments

NANOANALYSIS

Leaders in sample characterisation and manipulation in electron microscopes

ASYLUM



Leader in development & manufacture of Atomic Force Microscopy (AFM)

WITEC

Leading provider in Raman spectroscopy and imaging

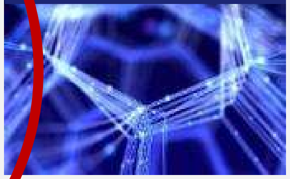
Research & Discovery

Provides advanced solutions that create unique environments and enable imaging and analytical measurements down to molecular and atomic levels.

ANDOR

Development & manufacture of high performance scientific digital cameras and light microscopes

NANOSCIENCE



Enabling quantum technologies, nano technology research, advanced materials & nano device development

X-RAY TECHNOLOGY

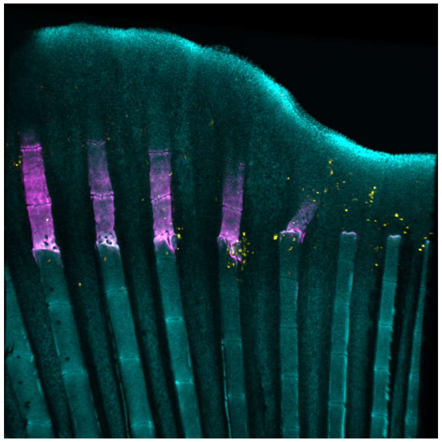
Leading manufacturer of x-ray tubes, power supplies & integrated x-ray sources

Image classification – optical fluorescence microscopy

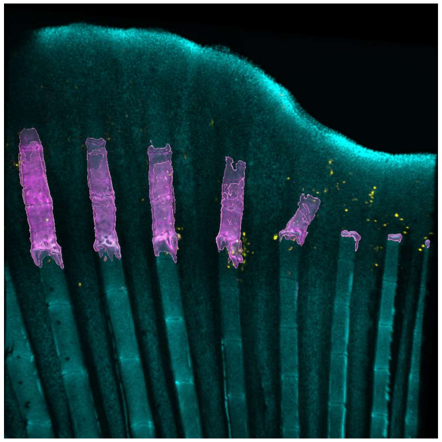
- BC43 – Benchtop Confocal microscope from Andor
    - Extremely rapid 3D fluorescence MPixel optical slicing with sub-micron resolution
    - Data sets can be 1-10s of GB

BC43 Zebrafish workflow with Imaris 9.9

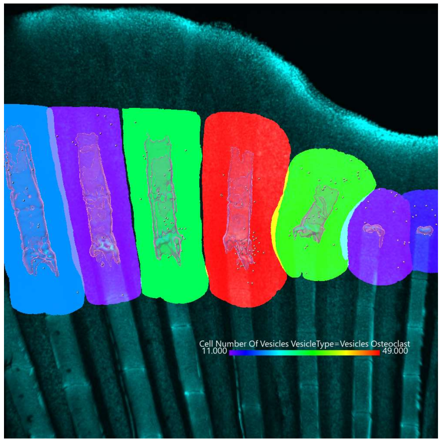
Segmentation via machine learning



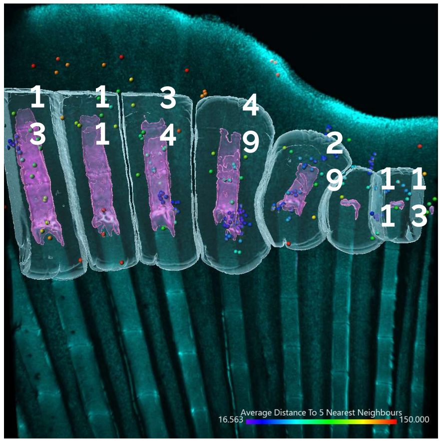
Raw microscopy image



Newly formed bone tissue (magenta) segmented with machine learning pixel classifier



Envelopes coloured by the number of osteoclasts inside (11- purple, 49 – red)



Envelopes created with machine learning pixel classifier which are created based on distance from the newly forming bones

Zebrafish fin in the process of bone regeneration. Image shows the perfect stitching of 4 imaging fields, using three channels and 51 stacks for each field, covering a Z range of 174 µm.

Magenta - Newly formed bony tissue (calcein staining)
Yellow - cathepsin k+ cells (the osteoclasts)
Cyan -DNA.

Image credits: Alessio Carletti, Universidade do Algarve

Osteoclasts seem to be required for active bone regeneration

https://imaris.oxinst.com/newrelease

Characterisation of Metals and Alloys using EM

Composition
Grain size
Texture
Phase fraction
Phase distribution

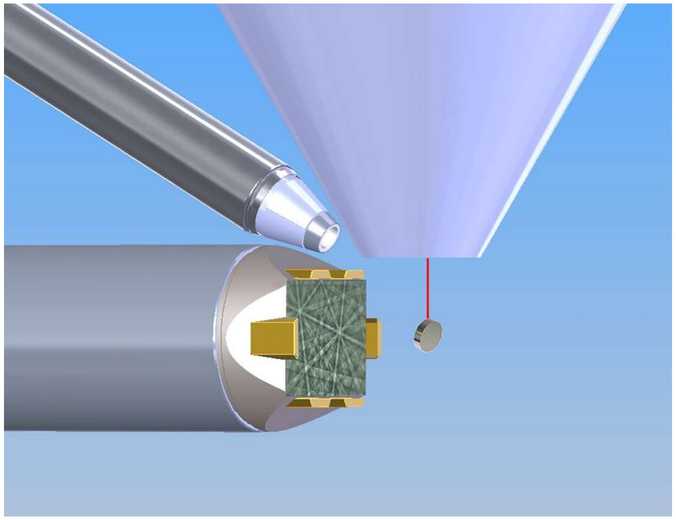
Cleanliness
Boundary population
Boundary precipitation
Deformation / strain

EDS – Energy Dispersive X-ray Spectrometry

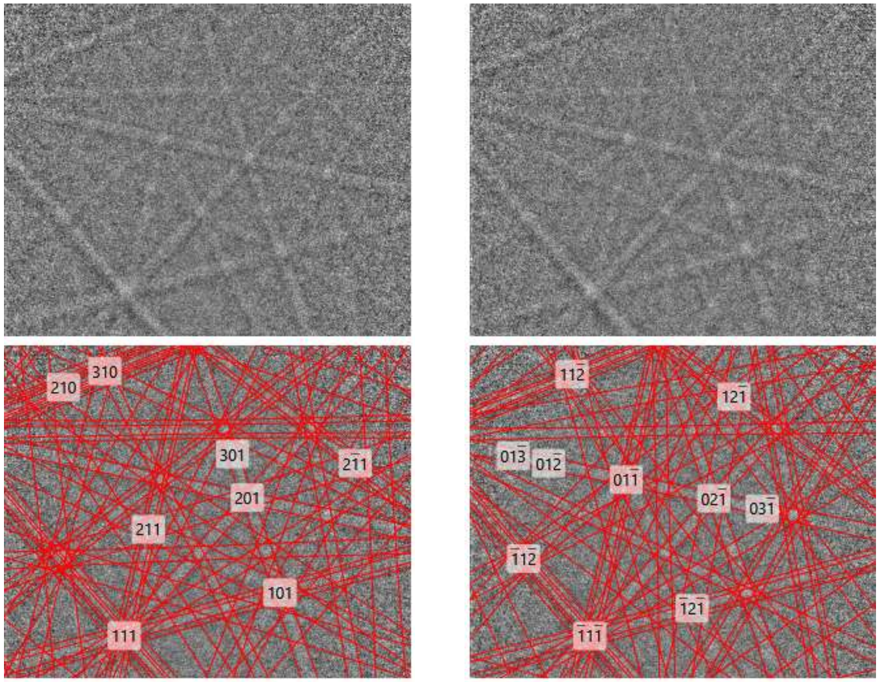
EBSD – Electron Backscatter Diffraction

Crystallographic orientation

Electron backscatter diffraction (EBSD)



Oxford Instruments
http://www.ebsd.com/10-ebsd-explained



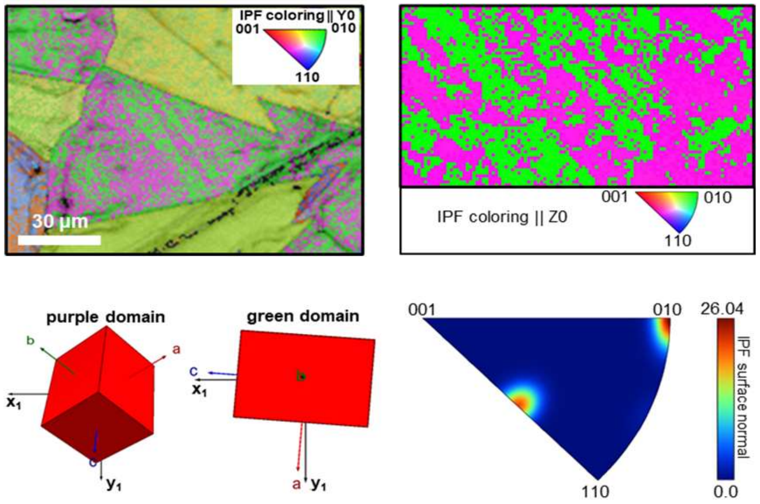
<030> II Z

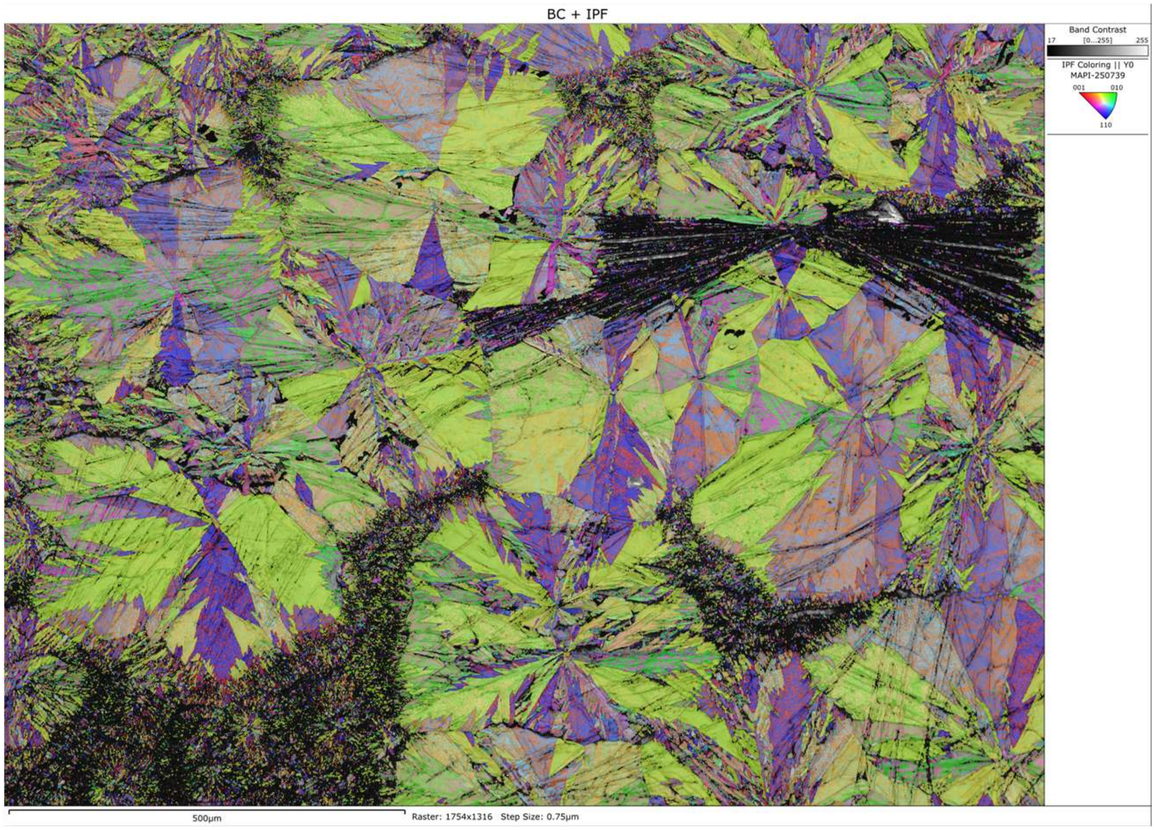
<111> II Z

- ☐ Liu, Yongtao, et al. "Correlating Crystallographic Orientation and Ferroic Properties of Twin Domains ain Metal Halide Perovskites." ACS nano (2021).

- Example Kikuchi patterns of MAPbI3 show the similarity of patterns from domains with either the <030> or the <111> directions normal to surface.

Crystallographic orientation – MAPI solar cell material

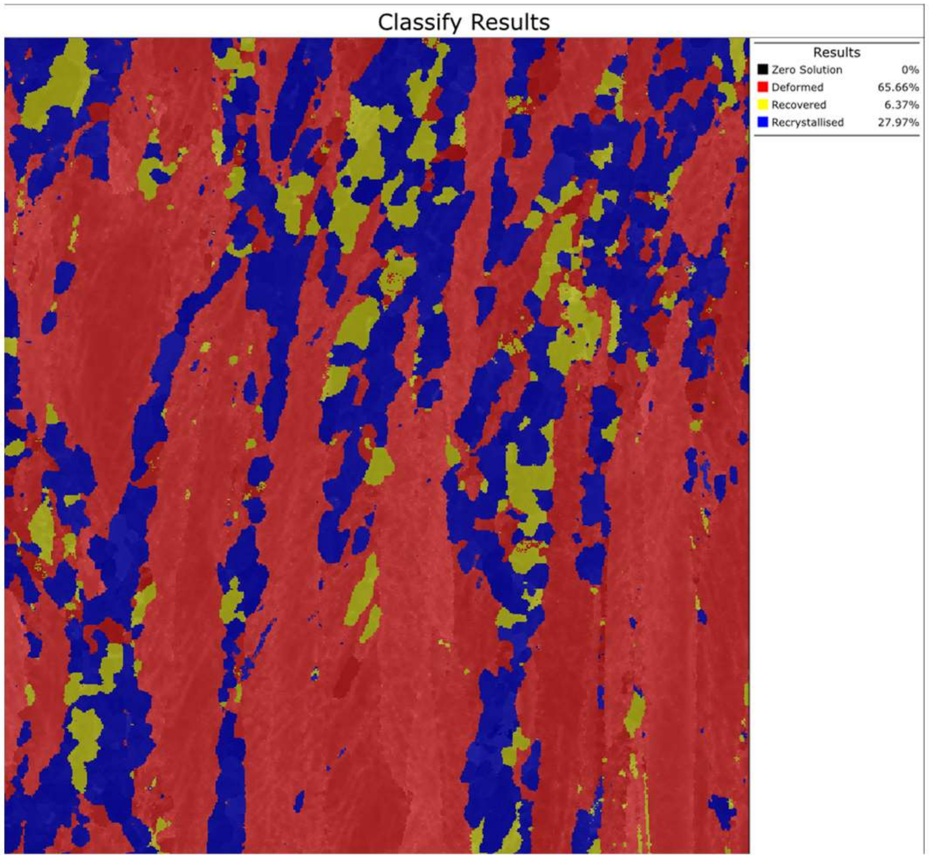




- EBSD orientation maps for the first time identify twin domains, 90° rotated around the $\langle \bar{1}\bar{1}0 \rangle$ orientation
- schematic unit cell orientations show the crystallographic orientation of the purple and the green domains
- Inverse pole figure (surface normal direction) shows the clear alignment with the ⟨030⟩ and ⟨111⟩ directions

How does it classify?

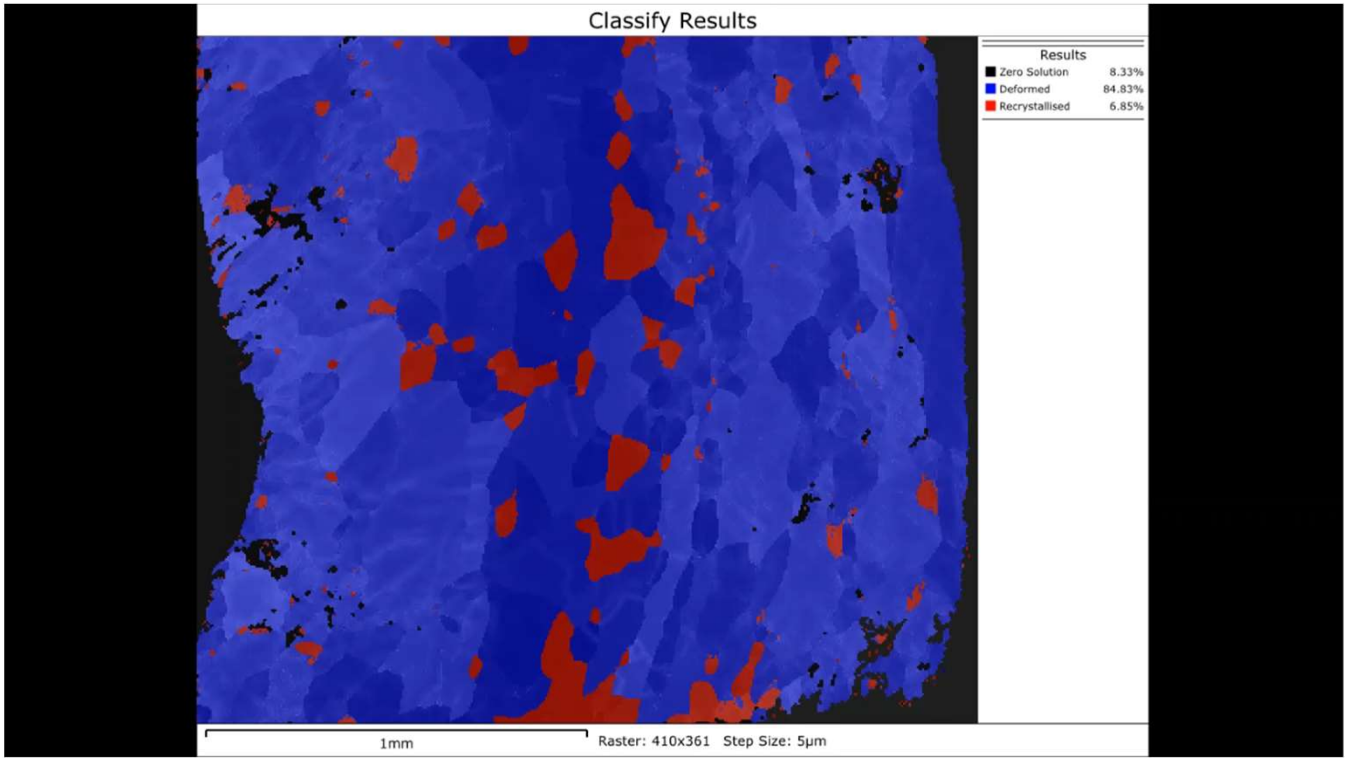
- An n-dimensional space is created, with each chosen parameter represented as an axis
- Parameters rescaled to fit into a range of 0-39
- In each of the 40^n cells there is a table set up with class "votes"
- During training, the vote count for the allocated class is increased by 1 in the cell corresponding to the parameter values at each position
- Each cell is assigned the class with the most counts
- Unassigned cells are given a class using a nearest neighbour algorithm
- In the map, the parameter values at each point are used to determine the corresponding cell in parameter space, and thus the correct class



Results	
■ Zero Solution	0%
🟥 Deformed	65.66%
🟨 Recovered	6.37%
🟦 Recrystallised	27.97%

Martensitic steel heating - Classification

- Training on one image allows many to be estimated: deformed (blue) recrystallised (red)



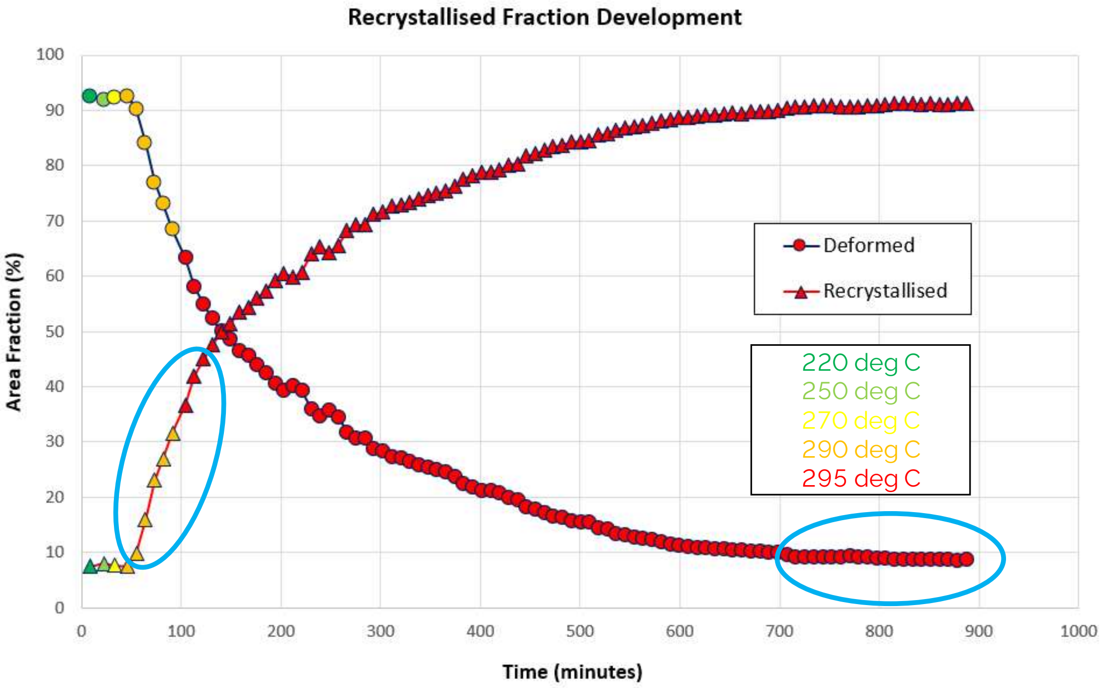
Classify Results

Results	
■ Zero Solution	8.33%
🟦 Deformed	84.83%
🟥 Recrystallised	6.85%

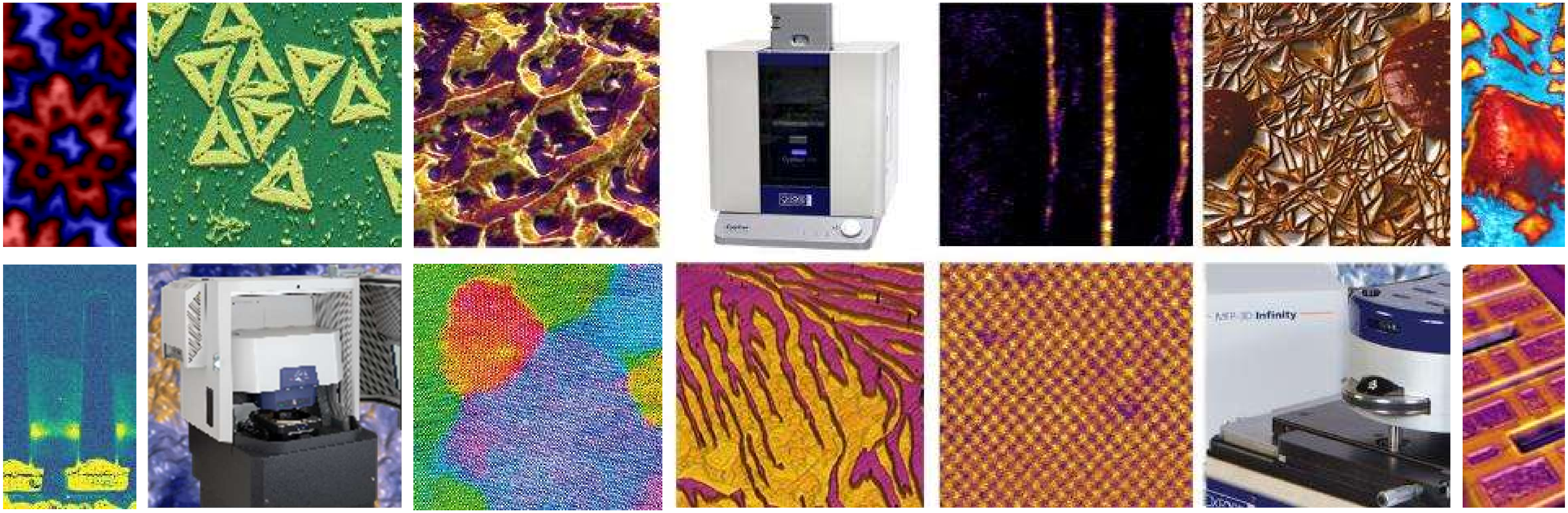
Raster: 410x361 Step Size: 5µm

In-situ recrystallisation summary

- Results show the progressive recrystallisation during the experiment
- High recrystallisation rates occurred early at 290-295 °C
- Some residual deformation within grains retained even after 15 hours
- Full data processing for all 100 maps (including multiple maps and grain size data) completed in under 2 hours



Atomic Force Microscopy



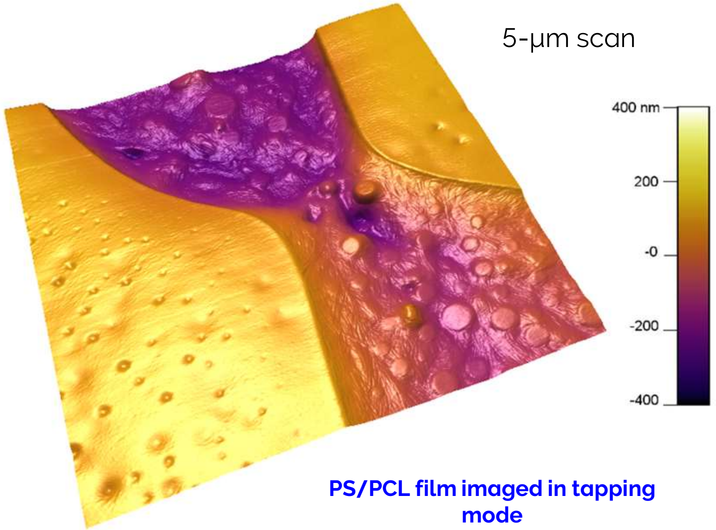
Surface Visualization Tool

AFM is a **visualization tool** for

Surface topography

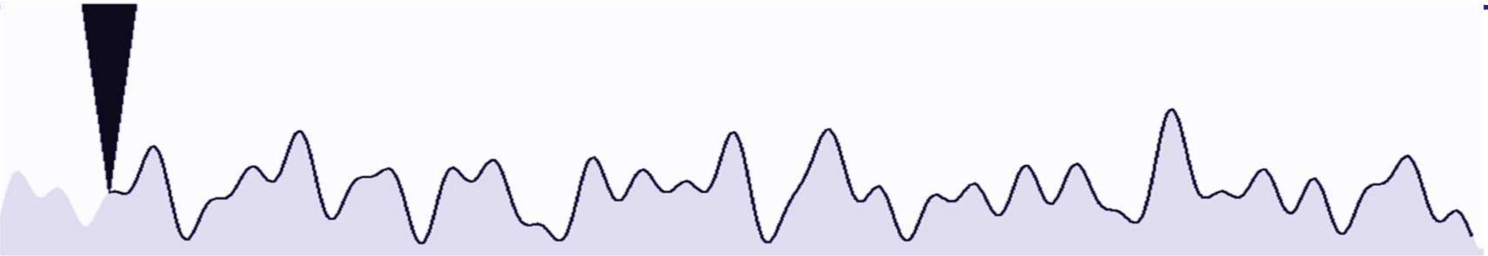
“Touches” surface with a **mechanical probe**

- Cantilever & tip (sharp stylus)
- Lateral Resolution
  - depends on tip radius (usu. <10 nm)
- Height Resolution
  - depends on Z-noise (can be <15 pm)
- Force sensor
  - pN to µN
  - kPa to GPa
- Surface modification
  - scratch, bias, heat, dip-pen lithography



PS/PCL film imaged in tapping mode

Material Characterization Tool

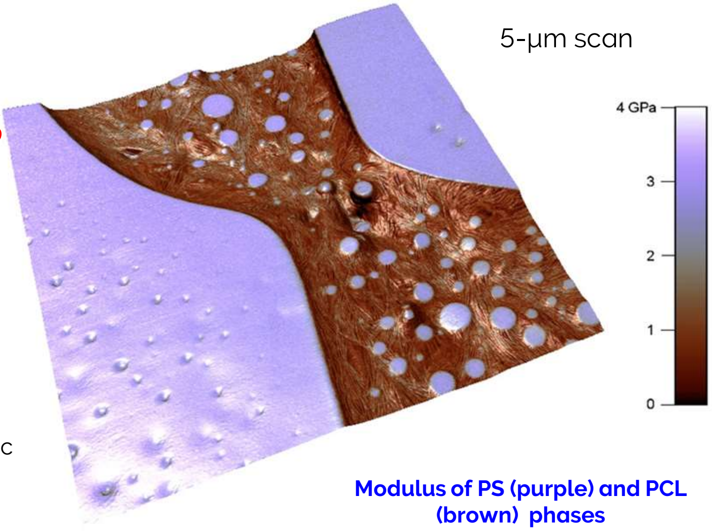


Contact/proximity to the surface **also** allows probing

Local material properties

Strength: **materials characterization**

- **Mechanical properties**
    - stiffness, modulus, dissipation, adhesion
- **Thermal properties**
    - phase transitions, thermal conductivity
- **Electrical/magnetic properties**
    - current, surface potential, electrostatic charge, magnetic fields, capacitance, resistance
- Mapped (located) on nanoscale topographic contours



5-µm scan

Modulus of PS (purple) and PCL (brown) phases

What Can We Measure?

AFM as a Materials Characterization Tool

Mechanical

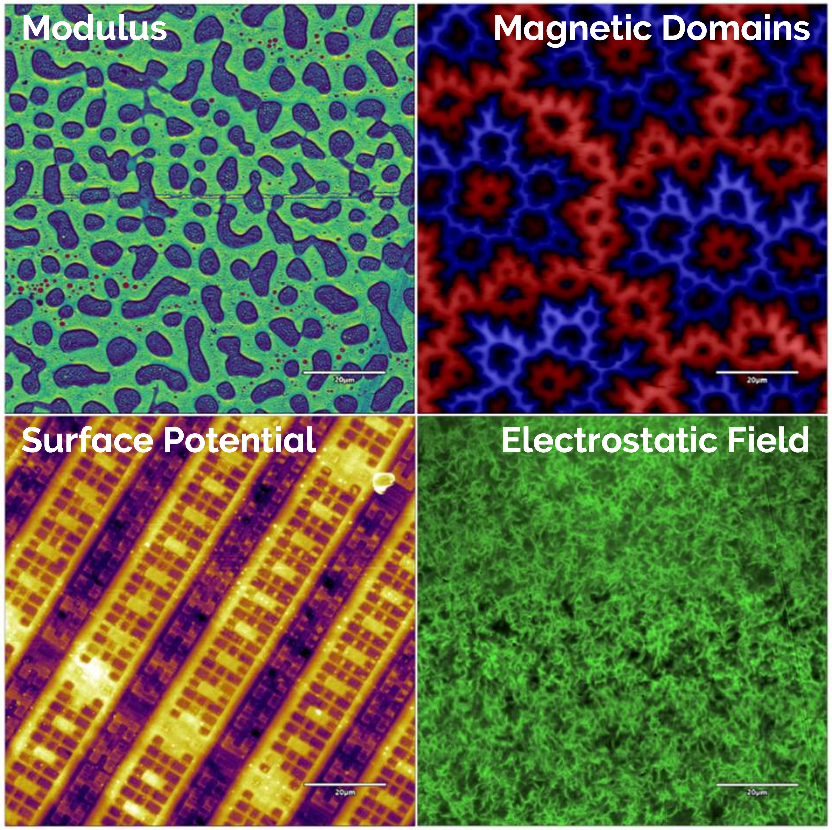
- Young's Modulus
- Adhesion (pull-off force)
- Dissipation
- Loss Tangent (tan δ)
- Store and Loss Moduli
- Friction Loops

Thermal

- Thermal conductivity
- Melting point (phase transitions)

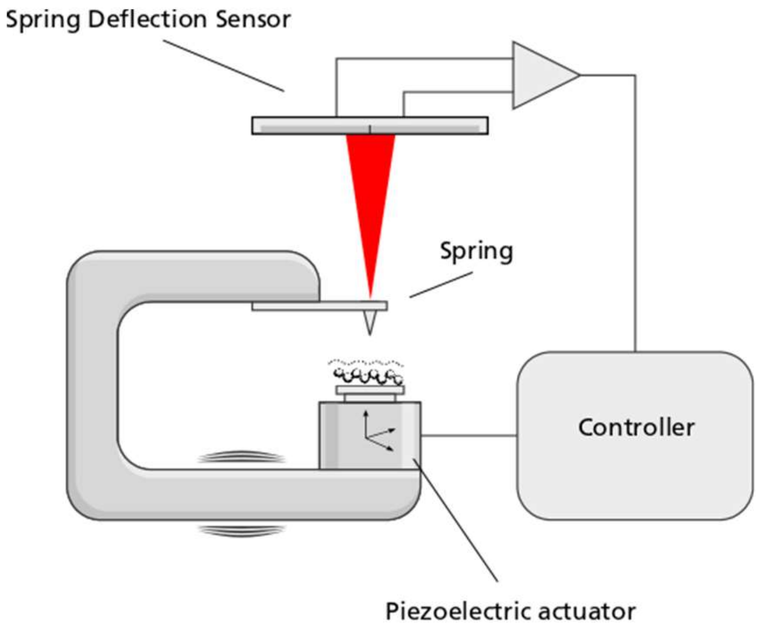
Electrical/Magnetic

- Current, Photocurrent
- Capacitance and Resistance
- Permittivity and Conductivity
- Magnetic Force Gradient
- Electrostatic Force Gradient
- Surface Potential
- Work Function
- Piezoelectric Coefficient
- Hysteresis Loops

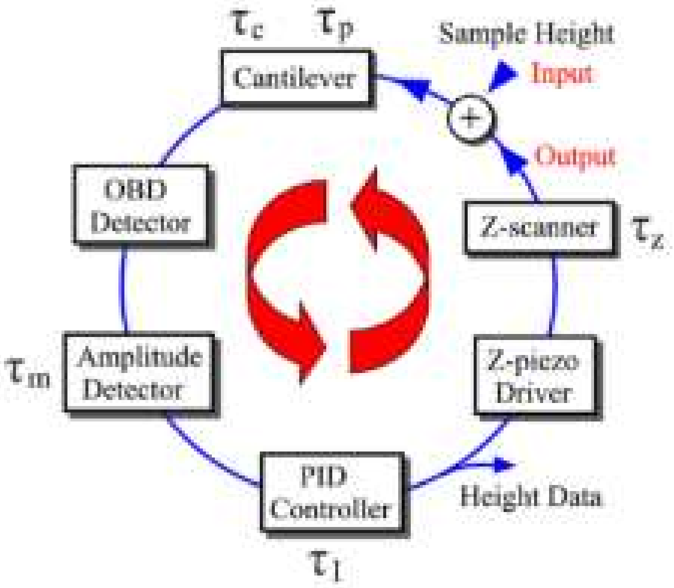


100 x 100 µm scan on Jupiter XR

What about temporal resolution?



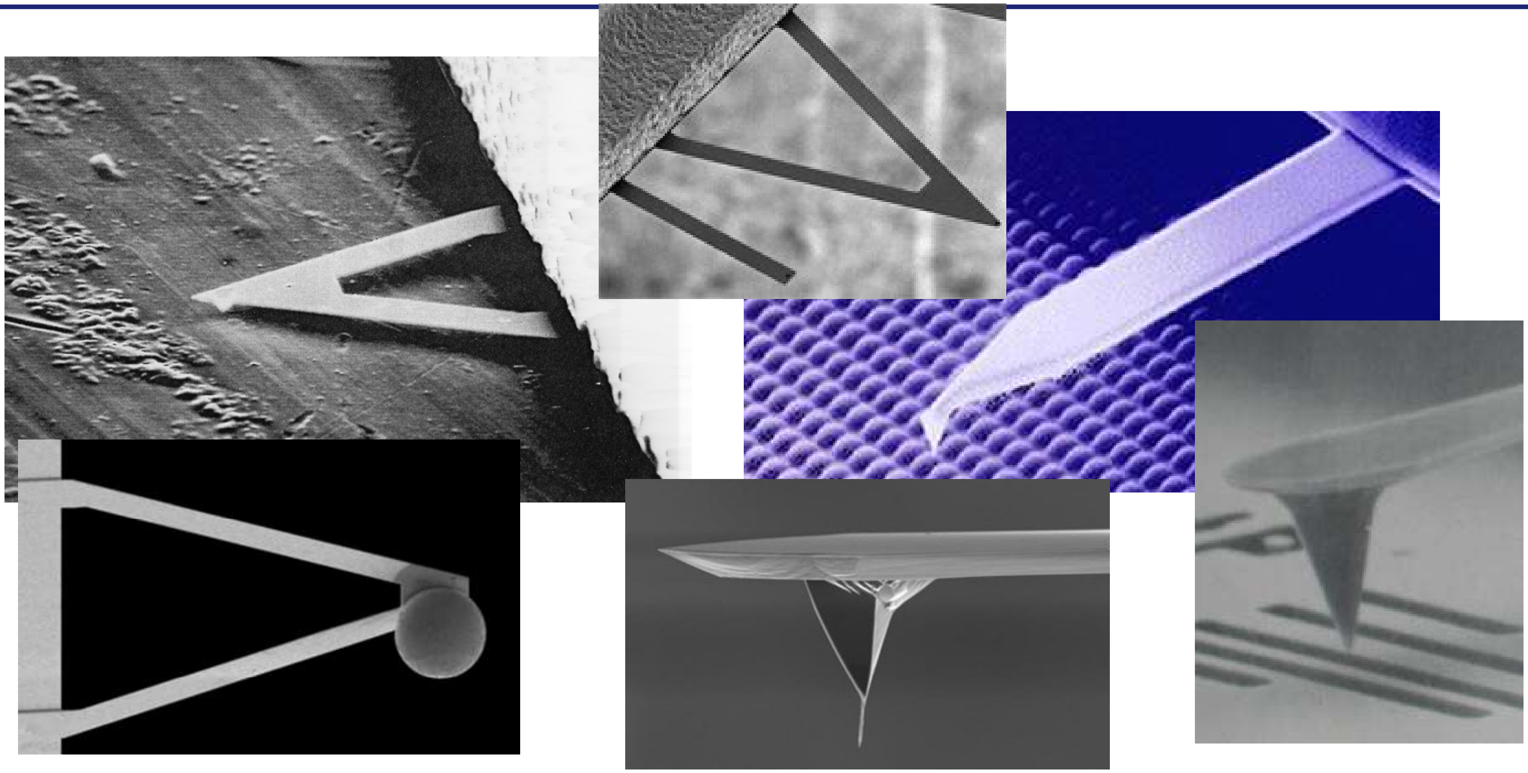
Control loop



Need very low latency on every step

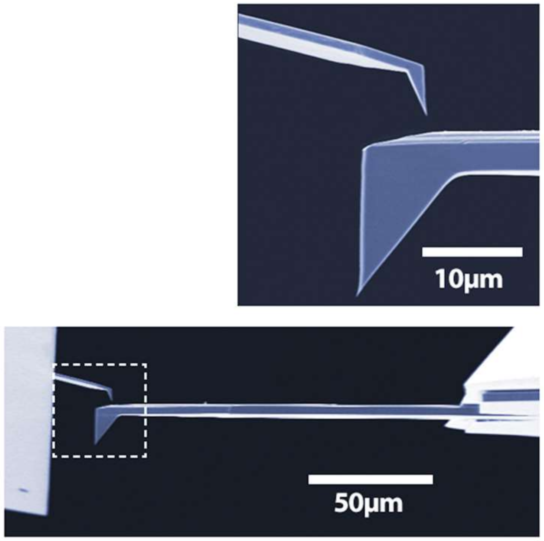
Ando, T. (2012). High-speed atomic force microscopy coming of age. *Nanotechnology,23*(6), 062001.

Commercial levers: 1990-2008



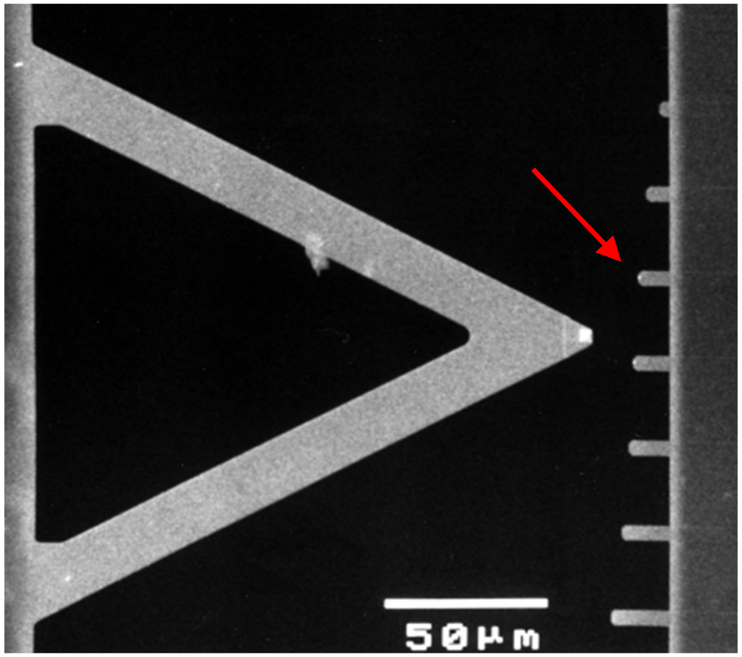
Lots of variety in styles developed, but for the most part, lever sizes remained in the 100 µm to 500 µm sizes pioneered by Cal Quate's group in 1990.

Evolution towards smaller levers



$k's \approx 2.5N/m$

$k's \approx 0.3N/m$



Why go small?

Fluctuation-dissipation and SHO dynamics

$$-kz - b\frac{dz}{dt} = m\frac{d^2z}{dt^2}$$

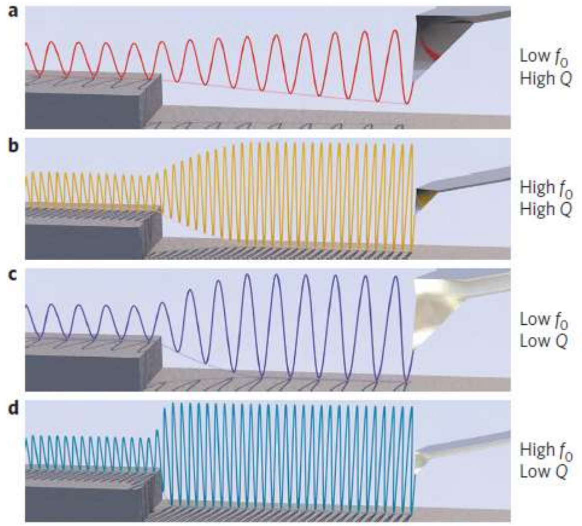
Eur Biophys J (1998) 27: 75–81

BIOPHYSICS LETTER

Frederick Gittes · Christoph F. Schmidt

Thermal noise limitations on micromechanical experiments

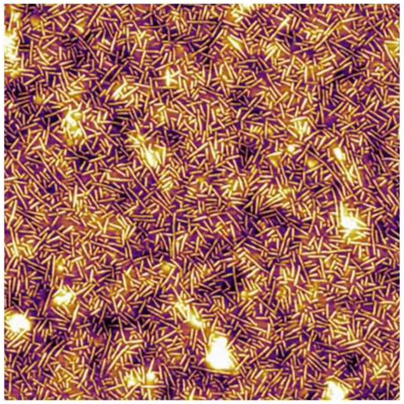
- Drag coefficient and force noise $\Delta F_{rms} = \sqrt{4BWk_BTb}$
  - Just like Johnson noise in resistors
  - Smaller objects have smaller drag coefficients so **smaller is quieter!**
    - Note, for SHOs, can estimate $b = \frac{k}{\omega_0 Q}$
- For a cantilever, $\omega_0 \approx \sqrt{\frac{k}{m_c + 0.24m_t}}$.
  - Smaller = less mass, so **smaller is also faster!**
- Damping effects $\tau = \frac{\pi Q}{f_0}$.
  - More damping = smaller Q, **fluid is faster!**



Jonathan D. Adams et al., Nature Nanotechnology, vol. 11 147 (2016).

How fast is AFM?

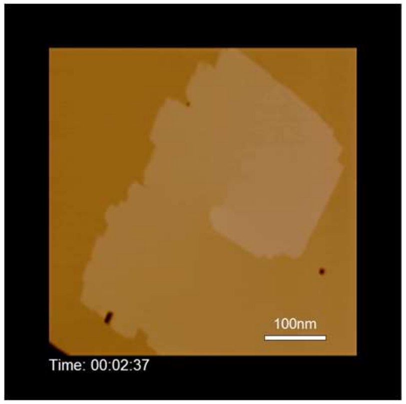
Conventional Speed AFM



Imaged on a MFP-3D with 256×256 pixels at 1 Hz line rate (0.004 fps). Playback at ~900X real-time.

- Still typical of most AFMs
- Each image takes several minutes to capture
- Only static samples can be imaged. Any dynamics distort the images.

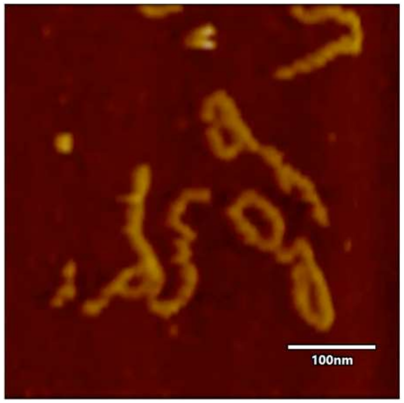
Fast Scanning AFM



Imaged on a Cypher ES with 256×128 pixels at 19.5 Hz line rate (0.15 fps). Playback at ~50X real-time.

- First available in 2008 on the Cypher S AFM. Typical line scan rates 10-20 Hz.
- Though some dynamics are within the temporal resolution, <u>primary benefit is improved productivity</u>.

Video-Rate AFM

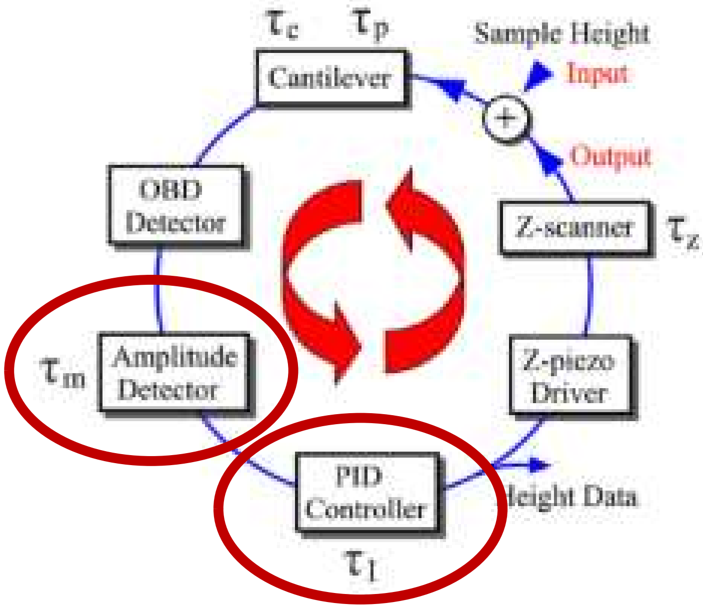


Imaged on a Cypher VRS with 320×64 pixels at 625 Hz line rate (8.7 fps). Playback in real-time.

- Only lab-built units until the 2017 release of Cypher VRS
- Far faster scanning captures video instead of images. <u>Primary purpose is to capture nanoscale dynamics</u>.

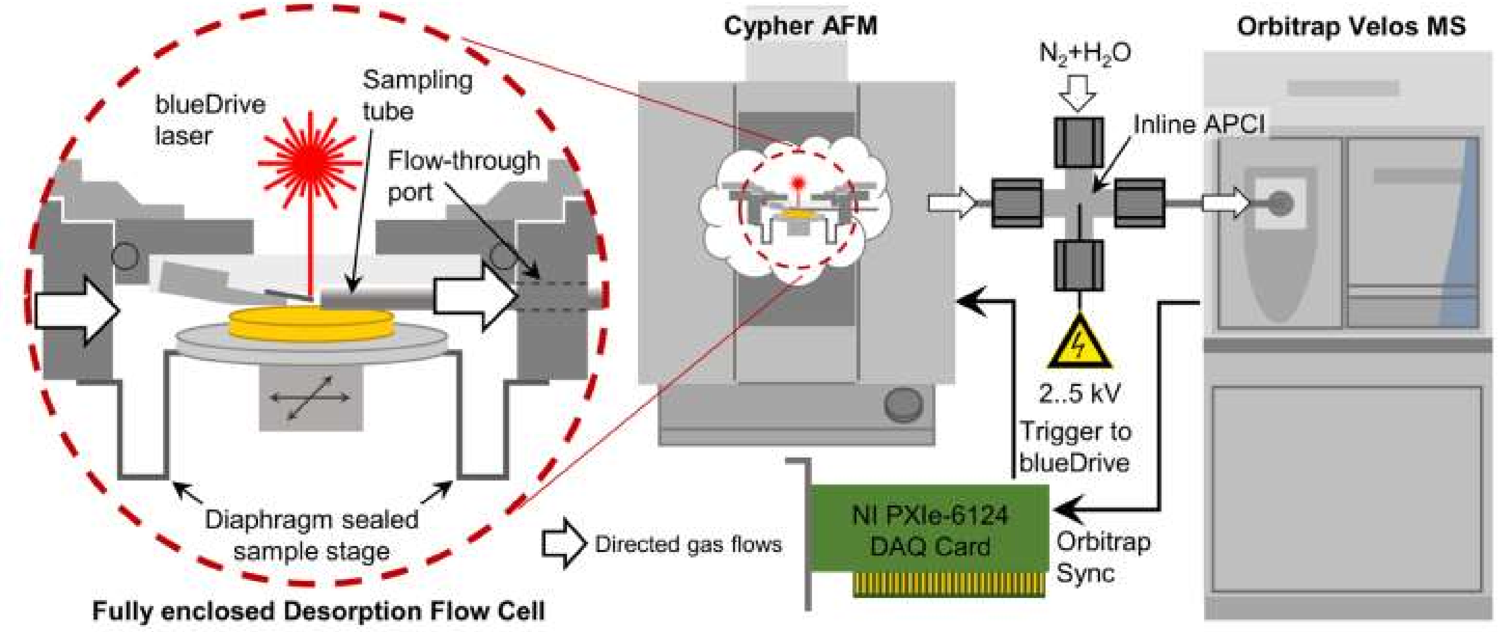
Some ML opportunities in video rate AFM…

- Approaching the limit for practical cantilever dimensions (few microns).
  - To date, AFM has generally assumed steady state amplitude measurements (lockin amplifier)
    - Sub-relaxation time ($\tau < \frac{\pi Q}{f_0}$) amplitude estimation
    - Sub-period sampling – inferring amplitudes from less than a full oscillation of the cantilever
  - Feedback optimization – PID controllers are not fast enough
    - Feed forward for scanning control
    - Cantilever-tip FB loop should be faster
  - Beyond simple topography
    - Physics-based material properties (modulus, adhesion…)



Kodera, Sakashita et al. 2006, Umeda, Okamoto et al. 2021

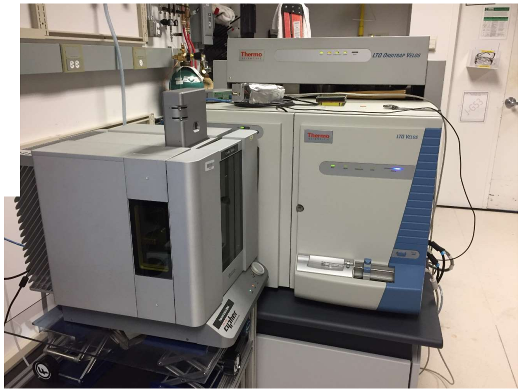
Chemical and AFM imaging with a Mass Spec



Nanoscale Mass Spectrometry Multimodal Imaging *via* Tip-Enhanced Photothermal Desorption

Matthias Lorenz,* Ryan Wagner, Stephen Jesse, Jennifer M. Marsh, Marc Mamak, Roger Proksch, and Olga S. Ovchinnikova*

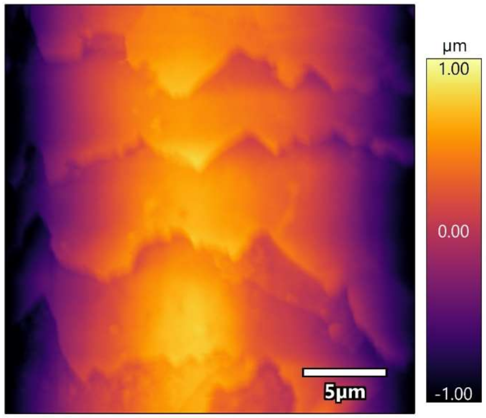
Cite This: *ACS Nano* 2020, 14, 16791−16802 Read Online



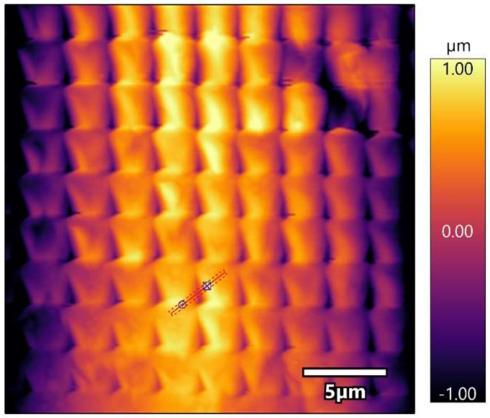
Imaging and Thermal Desorption of Washed Hair

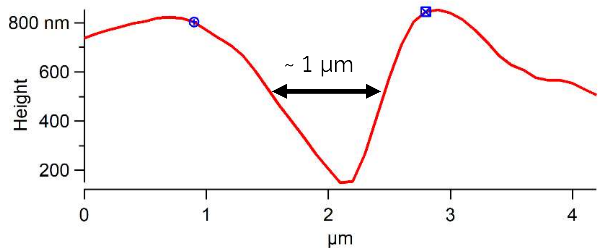
Question: Where does this stuff go?

Topography before thermal desorption

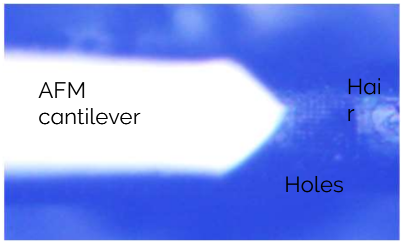


Topography after thermal desorption



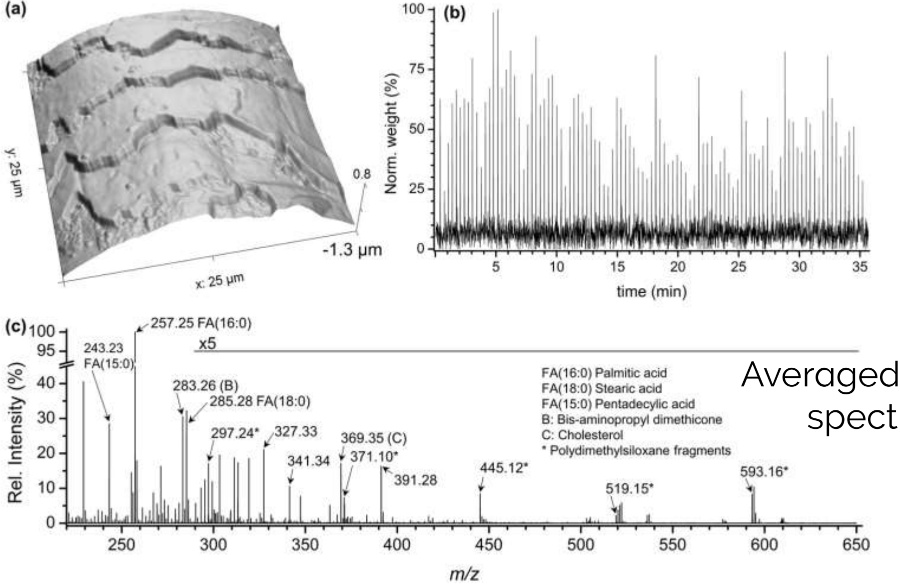


Optical View



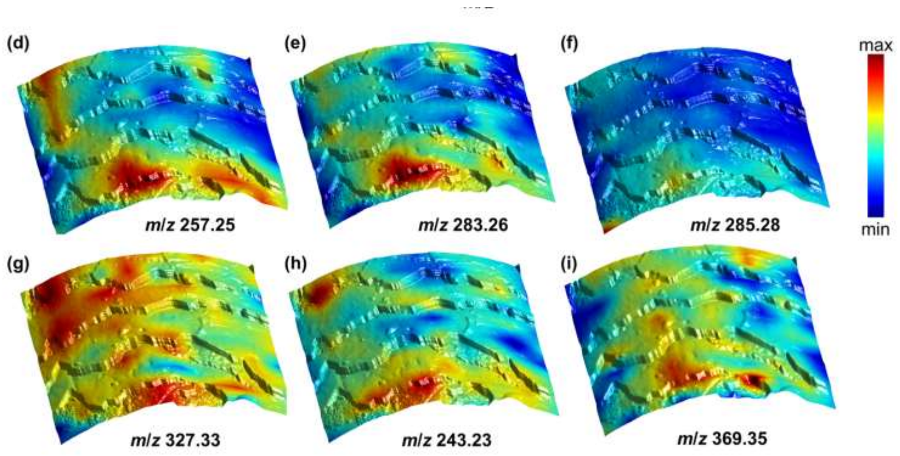
Chemical Imaging of Treated Hair

Thermal Desorption Events

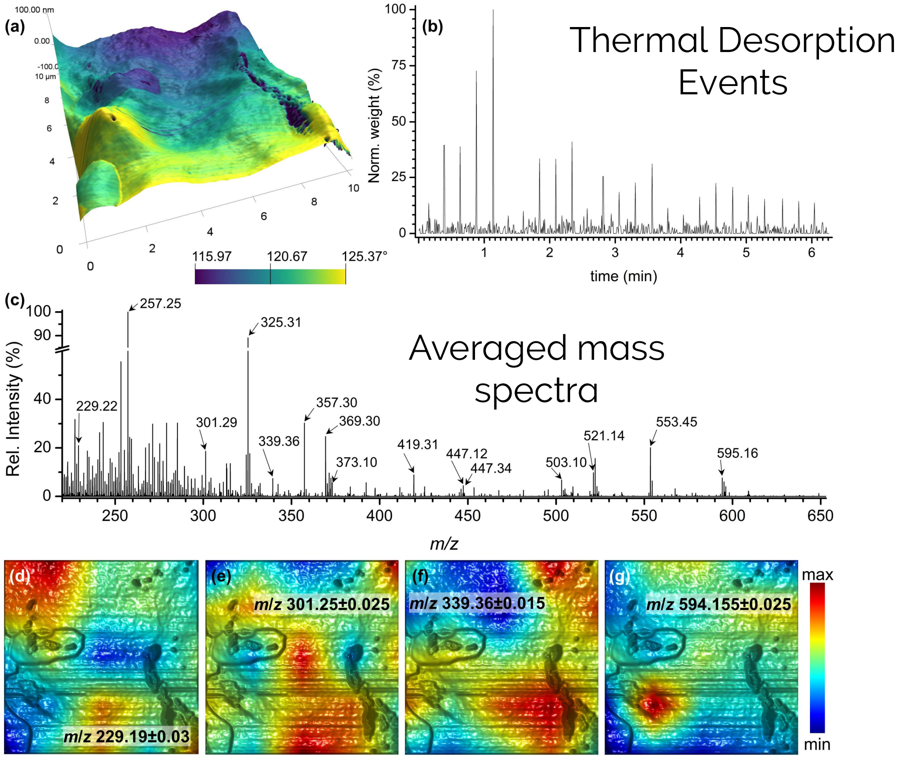


Averaged mass spectra

m/z components painted on topography



Chemical and Mechanical Mapping of Adhesive



Thermal Desorption Events

Averaged mass spectra

Mechanical map and chemical maps overlaid on topography for sticky note adhesive.

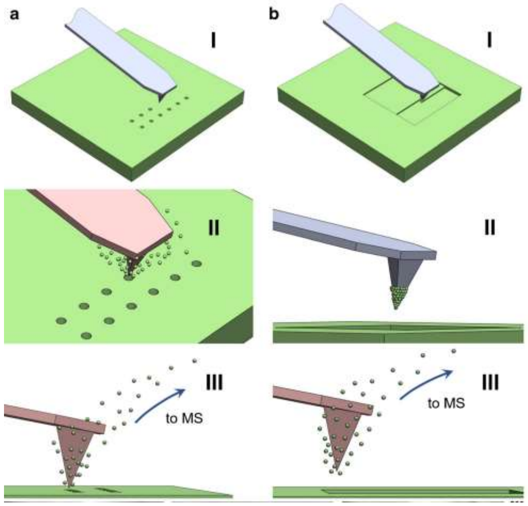
Weak signals, low concentrations: “Scratch and Sniff”

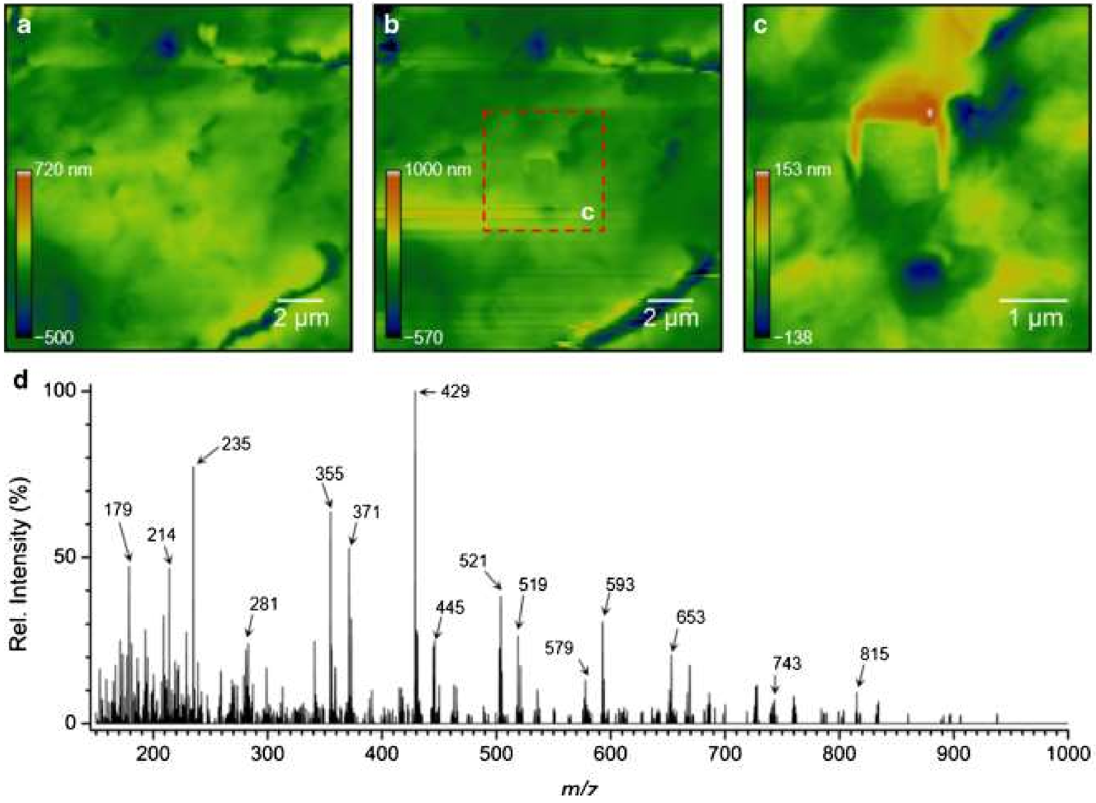
Analytical and Bioanalytical Chemistry (2021) 413:2747–2754
https://doi.org/10.1007/s00216-020-02967-0

RESEARCH PAPER

Nanomechanical sampling of material for nanoscale mass spectrometry chemical analysis

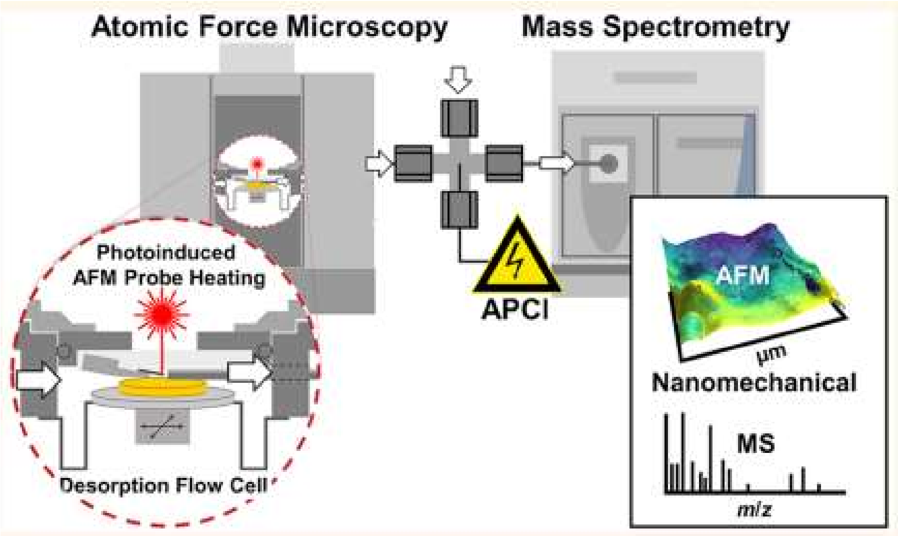
Olga S. Ovchinnikova[1] · Matthias Lorenz[1,2] · Ryan B. Wagner[3] · Ron M. A. Heeren[4] · Roger Proksch[5]





Some ML opportunities in Chemical AFM…

- Discovery mode (when you don't already know what to look for):
  - Mass Spec spectra are complicated, signals are small (already used NMF for the data here)
  - Data sets are enormous
- Operation is non-trivial
  - Lots of things need to work and work together!
    - AFM
    - Thermal desorption
    - Plume collection
    - Atmospheric pressure ionization
    - Mass Spec



Thanks!

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