Recent Advancements in Nanoscale IR Spectroscopy and Imaging

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Atomic Force Microscopy
3D Optical Microscopy
Fluorescence Microscopy
Tribology
Stylus Profilometry
Nanoindentation

Bruker Nano Surfaces Division
Outline

- Company Background
- Introduction to AFM-IR
- Latest AFM-IR Advancements
  - Resonance Enhanced AFM-IR
  - HyperSpectral Imaging/Spectroscopy
  - Tapping AFM-IR Imaging/Spectroscopy
    - Technical Overview
    - Applications
- s-SNOM Technology and Applications
- Tunable IR Laser Options
- Summary
Bruker Nano Acquires Anasys Instruments

Anasys joins Bruker Nano Surfaces Division

Strengthening the world of nanoanalysis and nanomechanical materials characterization— together

- Bruker Nano Surfaces Division acquired Anasys Instruments Corp on April 10th 2018
- All nanoIR products are now integrated into the Bruker Nano Product Support
Nanoscale IR spectroscopy

2010
nanoIR™
1st Generation AFM-IR

2014
nanoIR2™
2nd Generation AFM-IR
Top Down Configuration & Resonance Enhanced

2015
nanoIR2-s™
Combined IR s-SNOM & AFM-IR

2016
nanoIR2-FS™
3rd Generation
FASTspectra

2017
Tapping AFM-IR
HYPERspectra

2018
NEW
nanoIR3™
Latest Generation
nanoIR platform with Tapping AFM-IR
Power and Limitations of Infrared Microspectroscopy

FT-IR microscope

Multilayer film, courtesy of Dr. Curtis Marcott

IR spectra

Chemical Image

IR microspectroscopy applications
• Materials Science
• Consumer products
• Pharmaceuticals
• Life sciences
• Health & beauty
• Forensics

Sampling Method | Diffraction limited resolution* | Practical resolution limit
--- | --- | ---
Transmission | 2λ | ~10-30 μm
ATR | 0.5λ | ~3-10 μm

Abbe diffraction limit: Practical resolution many microns
AFM-Based IR Spectroscopy (AFM-IR)


Alexandre Dazzi
2014 Ernst Abbe Award

Ernst Abbe
nanoscale infrared imaging & spectroscopy capabilities

Nanoscale IR chemical analysis

Chemical composition & nanoscale property mapping

Rich, interpretable spectra directly correlates to FTIR

Monolayer sensitivity & high spatial resolution
### Broad range of nanoIR applications

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*Bruker Confidential*
Resonance Enhanced Mode

Demonstrated by Pr. Belkin team in 2011 (Opt. Express)

Cantilever deflection detection

Pulsed tunable IR source

Contact Resonance

Sensitivity limit 2-5 nm
Resonance Enhanced Mode

![Diagram showing deflection and laser signals over time](image-url)
Forced resonance makes AFM-IR more sensitive

Laser repetition rate
Single Monolayer Sensitivity

Resonance enhanced AFM-IR of PEG monolayer

Topography

IR image at 1340 cm\(^{-1}\)

- CH\(_2\) wag
- CH\(_2\) scissor
- C-O-C Asym

IR-amplitude vs. Wavenumber (cm\(^{-1}\))

- PEG/gold
Purple Membrane (Resonance Enhanced AFM-IR)

Halobacterium Salinarum deposited on a Au substrate

Amide I

Amide II

IR Image at 1540 cm⁻¹

3 x 4 μm

Topography

Template-stripped Au
QCLs are getting faster!

Single spectrum, 400 msec sweep, 0.2 msec time constant, no averaging
Figure 5. Illustration of the hyperspectral image cube. High speed AFM-based IR spectroscopy allow for the first time practical hyperspectral imaging, i.e., where spectra are mapped at matrix of XY points. One can extract segments of the hyperspectral cube to obtain (A) chemical maps that show spatial variation in absorption at a given wavelength, (B) spectral line maps showing the variation in spectra in one direction, or (C) individual spectra at any X,Y location.
Hyperspectral animation

5-μm x 5-μm, 50 x 50 spectrum array on PS/PMMA/epoxy blend

Move cursor onto above image and click on arrow to start animation
Hyperspectral array PCA weight maps

5-μm x 5-μm, 50 x 50 spectrum array on PS/PMMA/epoxy blend

AFM image
PS
PMMA
Epoxy

- New hyperspectral imaging provides point by point spectra over a large number of data points to provide an array of spectra and chemical images at specific wavenumbers
- Principle component analysis can be applied to identify specific chemical components and their spatial distribution
**NEW nanoIR3 platform configurations**

**nanoIR3™** - Latest Generation nanoIR platform with Tapping AFM-IR
- Highest performance nanoIR spectra with AFM-IR
- Sub-10nm resolution IR chemical imaging with Tapping AFM-IR
- Correlates to FTIR & industry databases
- Easy to use for fast, productive measurements

**nanoIR3-s™** High Performance IR nano-spectroscopy
- Complementary s-SNOM & Tapping AFM-IR
- Highest Performance IR nano-spectroscopy
- Broadband Spectroscopy & Chemical Imaging
- Nanoscale property mapping
- Versatility & Easy to Use

**nanoIR3-s™ S-SNOM** - High Performance s-SNOM Imaging
- IR s-SNOM platform for optical & chemical Imaging
- Supports multiple laser types, visible, nearIR
- Electrical nanoscale property mapping
- Upgradeable to nanoIR-spectroscopy

**nanoIR Spectroscopy of Polyethersulphone (PES)**

**Plasmonic Imaging on Graphene with Tapping AFM-IR & s-SNOM**

**s-SNOM imaging**
Phase and Amplitude on HbN
Sample Environmental Control

**Humidity control & heater & cooler**
- For control of humidity/gas & temperature for in-situ AFM-IR
- 4% to 95% non-condensing
- 4°C to 80°C heating and cooling

**Sample transfer port for nanoIR3-s**
- Protects sample in controlled gas environment from glove box to nanoIR system to protect
- Includes integrated humidity sensor with optional high sensitivity humidity and oxygen sensors
IR Polarization Control & extended IR range

**Polarization control**
Allows users to study molecular orientation with nanoscale spatial resolution by changing the input polarization of the IR light while studying the associated changes in the nanoscale IR spectra and/or chemical maps at a certain wavenumber.

**Polarizer Option**
Optional & upgradeable

![Graph showing IR absorption spectra](image)

(L) AFM-IR spectra on electrospun PVDF fibers under two different IR polarizations. (R) IR absorption image at 1404 cm\(^{-1}\) of crossed PVDF fibers under polarized illumination (polarization direction shown by arrow).

**FASTspectra- OPO mid-IR laser**
The new high pulse rate OPO laser extends the wavelength range of Resonance Enhanced AFM-IR to cover the 2700 to 3600 cm\(^{-1}\) wavenumbers, extending capability to important spectroscopic regions and addressing wider range of applications, while still providing direct correlation to FTIR at the nanoscale.
nanoIR nanoscale property mapping modes

**Conducting AFM (CAFM):**
(Application Module)
Allows the user to obtain simultaneous height and current flow maps of the sample surface. Available on all Anasys systems.

**Kelvin Probe Force Microscopy (KPFM):**
(Application Module)
Allows the user to obtain surface potential measurements. Available on all Anasys systems.

**Lorentz Contact Resonance mode**

LCR composite image made by overlying the LCR amplitudes collected at three different contact resonances. These resonances were selected to highlight the varying ratios of the lignin and cellulose which compose the sample.

**Nano thermal analysis**

Nanoscale thermal analysis of a PS-PMMA blend deposited on glass. A scan (left) shows indent in the surface caused by temperature ramps (right). The data from the PS (red) and PMMA (green) clearly differentiate the two materials. Also shown in data from a thin film of PS on PMMA (blue) showing the initial penetration of the PS, followed by the melting of the PMMA.
**Tapping AFM-IR: Technical Overview**

**Concept**

- **$Z_t$: Distance of the Tip**
- **$Z_s$: Sample expansion (photothermal)**
- **$k/\gamma$: Linear/non-linear force constant**
- **$a_s$: Absorption coefficient**
- **$a_t$: Tip oscillation amplitude**
- **$\omega_p$: Laser pulse rate**
- **$\omega_n$: cantilever eigen mode frequency (n=1,2,3...)**

**Resonance Condition:**

\[ \omega_1 + \omega_p = \omega_2 \]

**Equations:**

\[ F = k \cdot (z_t - z_s) + \gamma \cdot (z_t - z_s)^2 \]

\[ z_s = a_s(\lambda) \cos(\omega_p t) \]

\[ z_t = a_t \cos(\omega_n t) \]

\[ F \sim 2\gamma a_t a_s(\lambda) \cos(\omega_n t) \cos(\omega_p t) \]

\[ F \sim \gamma a_t a_s(\lambda) \left[ \cos(\omega_n + \omega_p) t + \cos(|\omega_n - \omega_p|) t \right] \]

- **Fundamental mode**
- **Pulse rate**
- **2nd Eigen mode**
Heterodyne Force Microscopy

* M.T. Cuberes, J. Nanomater., 2009

Resonance Condition:

\[ \omega_1 + \omega_p = \omega_2 \]
Tapping AFM-IR: Key features

- **Broad Application range:**
  - Hard/soft sample, Adhesives, Membranes, Particulates
  - Minimal sample/tip degradation due to absence of lateral forces

- **Improved Sensitivity:**
  - Sensitivity enhanced by cantilever Q-factor – new probes
  - AFM detector with higher sensitivity
  - Efficient optical beam delivery optics with minimal loss

- **High Spatial Resolution:**
  - Spatial resolution extends to ~10 nm or better

- **Multimodal Imaging:**
  - Simultaneous chemical and viscoelastic property (Tapping Phase) imaging
Tapping AFM-IR: Applications
Polymer 01: PEMA/PMMA Blend

Sample courtesy: University of Minnesota
Tapping AFM-IR: Applications
Polymer 02: PS/PMMA block copolymer

Sample courtesy: CEA-Leti

Tapping AFM-IR image at 1730 cm\(^{-1}\) highlights PMMA spheres embedded in PS matrix

Observed spatial resolution ~5 nm

2 x 2 \(\text{um}^2\)

Tapping IR Image at 1730 cm\(^{-1}\)
Tapping AFM-IR: Applications

Bio-pharmaceuticals 01: Skin/Dexamethasone

- Tapping AFM-IR image ratio at 1456/1740 cm\(^{-1}\) highlights the relative abundance of the drug in the lipophilic regions (bright yellow).

Optical

Amide I & II bands from Proteins

Ester C=O in the lipids

-CH\(_2\) bending

Present in both drug and long chain lipids

Sample courtesy: FU Berlin
Paclitaxel, a powerful anti-cancer drug, suffers from low efficacy and side effects due to low water solubility/recrystallization.

Recent study by Centrone and coworkers highlights the use of Tapping AFM-IR technology to explore the effect of different encapsulations in drug delivery.

High resolution compositional sensitivity of this technique unfolds new developments of lipid-polymer hybrid films in drug delivery applications.

Tapping AFM-IR: Applications
Organic Photovoltaics: TQ1/PC$_{70}$BM Blend

- Tapping AFM-IR spectra and images highlights the polymer rich matrix and PC$_{70}$BM rich domains

Sample courtesy: Karlstad University
Tapping AFM-IR: Applications
2D Materials: Graphene/Graphene Oxide

- Tapping AFM-IR spectra and images show sensitivity to monolayer Graphene and Graphene Oxide

Liu et al., *Carbon*, 2018, 127, 141-148

Manuscript in prep
Tapping AFM-IR: Applications
Failure Analysis: Organic Nanocontaminations

“…Knowing why devices fail is a must when designing next-generation products..”

V. Lakshminarayanan
www.rfdesign.com, 2011

- AFM-IR technology complements traditional analytical tools used for failure analysis in nanoscale semiconductor devices/architectures
- Enhanced sensitivity extends to samples with thickness <20 nm
- Tapping AFM-IR technology demonstrates positive identification of nanoscale organic contaminants on Silicon wafer
Tapping AFM-IR Measurements on nanocontaminant sample

- Each spectrum is an average of 5 measurements, **NOT** smoothed
- Tapping AFM-IR spectra show absorption bands consistent with earlier measurements performed onsite – contamination is most likely synthetic polyester (PET/PBT)
- IR signal **sensitivity goes down to 3 nm thick residue** (bright green)
Tapping AFM-IR of a Biological Membrane
Polymeric Nanoparticles for drug delivery

FTIR spectra of products

Antibiotic = pipemidic acid
Polymeric Nanoparticles for drug delivery

PLA/PVA nanoparticle
Mapping at 1760 cm$^{-1}$ center on ester carbonyl band of PLA

Tapping AFM-IRode
Polymeric Nanoparticles for drug delivery

PLA/PVA nanoparticle

Mapping at 1425 cm\(^{-1}\) center on absorption band of PVA
PLGA/PVA nanoparticles with antibiotic
Benefits of Tapping AFM-IR approach

- Better spatial resolution/softer samples via tapping AFM
- Improved chemical imaging via heterodyne detection
  - Insensitive to non-local background forces
- Material selectivity via resonance tuning
Sensitivity of AFM-IR and s-SNOM

![Graph showing sensitivity comparison between Organics and Inorganics for various materials including protein, PMMA, polycarbonate, low k materials, Au, SiO2, graphene, and SiC. The x-axis represents different materials, and the y-axis represents AFM-IR signal strength.]
s-SNOM: complex optical property

Metal coated tip acts like an antenna to enhance and localize the light.

Spatial resolution: tip radius 10~20 nm
Disadvantages: slow, limited spectral resolution

Disadvantages: can’t do narrowband imaging (e.g. for compositional mapping)
Application: Fano-resonance Bilayer Graphene

AFM height

sSNOM 1580 cm\(^{-1}\)

sSNOM 1600 cm\(^{-1}\)

Graphene 2, 38727 (2013)
s-SNOM with a broadband laser source
nanoIR Laser Options

- AFM-IR lasers (Pulsed tunable OPO & QCL) can provide both spectroscopy & wavelength specific imaging
- Only CW/P QCL (tunable) lasers provide spectroscopy & wavelength specific imaging for s-SNOM
- nanoFTIR lasers only provide spectroscopy & imaging capabilities (AFM-IR&s-SNOM)
Additional Applications – from 2017-2018 publications

- **Life Science**
  - Recent paper in Cell – Simone Ruggeri, Tuomas Knowles (Cambridge)
  - AFM-IR in Fluid – Andrea Centrone (NIST)
  - Malaria Infected Red Blood Cells – Bayden Wood (Monash)
  - *In vivo* AFM-IR of Bacteria – Bayden Wood (Monash)

- **Materials Science**
  - Deuterium-labeled polyolefin copolymer blend - Dow
  - Core/Shell effect in electrospun PHB copolymer fibers – Delaware
  - Functionalized graphene - Manchester
  - Geoscience - Schlumberger & USGS
Additional Applications (continued)

- Atmospheric Aerosols – Mark Banaszak Holl (Michigan/Monash)
- Polarized AFM-IR – Karsten Hinrichs (ISAS)
Recent Technological Advancements in nanoscale IR Technology offers

• Unmatched sensitivity for nanoIR spectroscopy & chemical imaging
• <10nm resolution chemical imaging
• Point spectroscopy in 1-2 secs
• HYPERspectral imaging/Spectroscopy for robust statistical analysis
• Easy to use, high performance AFM imaging with improved noise and sensitivity