ISIT祭り IN SRP ～半導体産業で広がるDX・GX～

ナノの世界を見る・触る・化学する

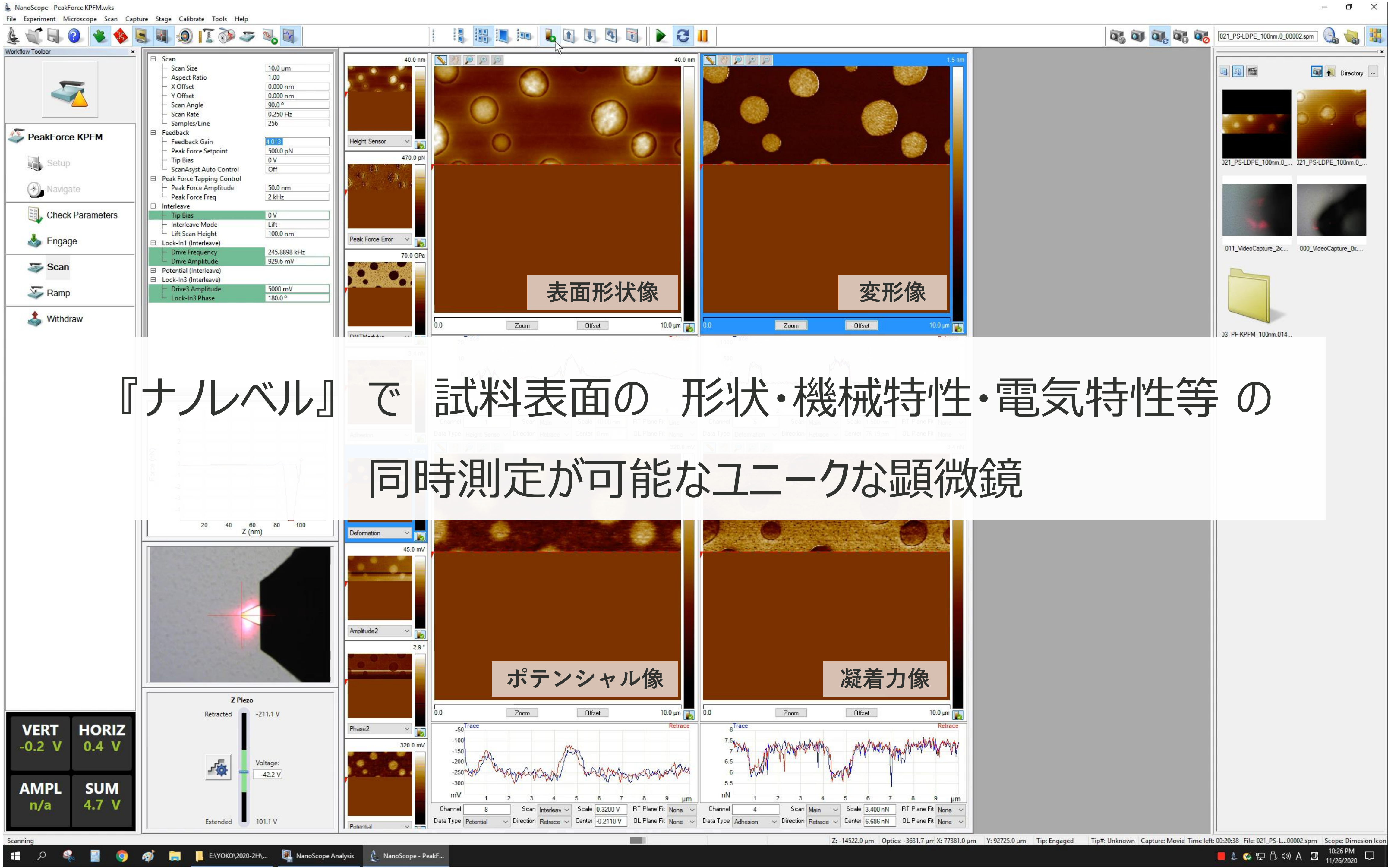
～ 材料研究における AFM 技術の多様性と可能性 ～

Meet the Bruker Team:

2024-11-15

Dr. Masatoshi Yokokawa, Application Scientist
E-mail: Masatoshi.Yokokawa@bruker.com

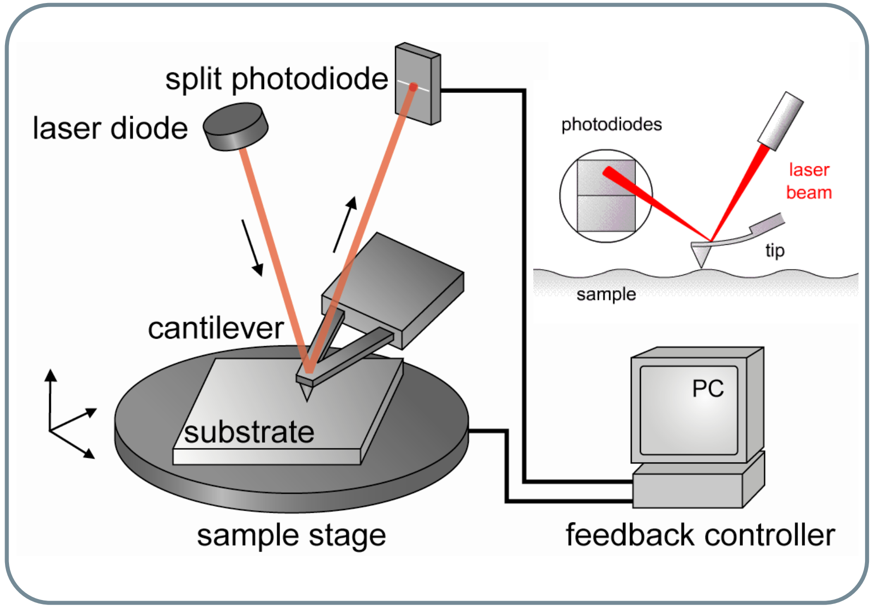
AFMってどんな装置？



『ナノレベル』で　試料表面の　形状・機械特性・電気特性等 の

同時測定が可能なユニークな顕微鏡

原子間力顕微鏡 (AFM) とは？

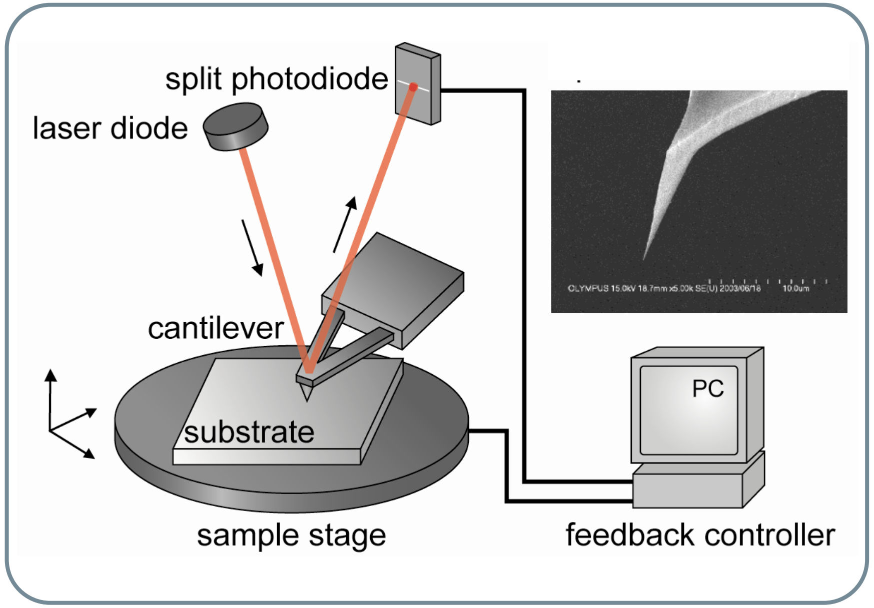


ナノレベルまで先鋭化した探針を用いて試料表面をなぞることで，高い空間分解能でその表面形状を捉える顕微鏡

(Scanning Probe Microscope)

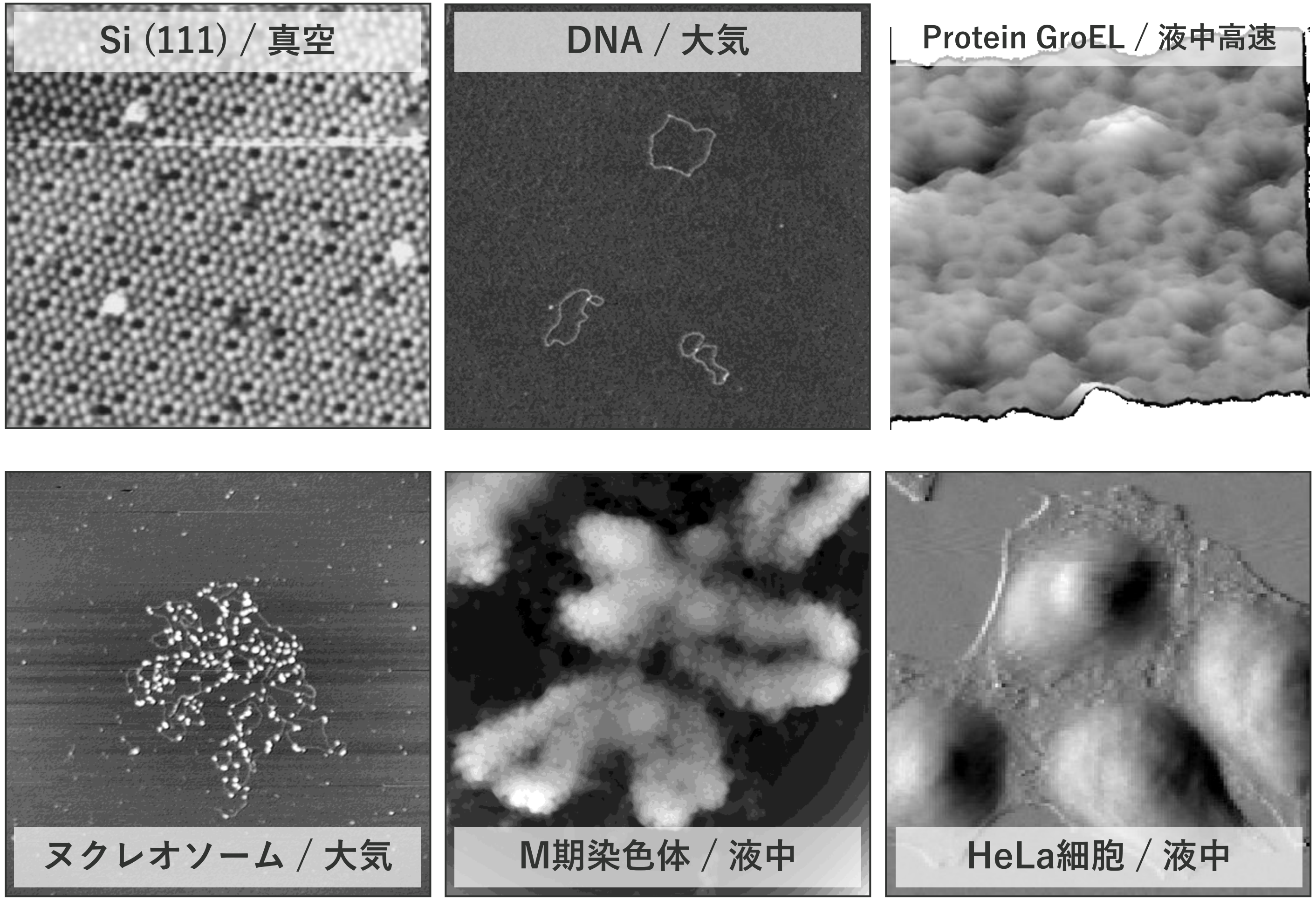
Bruker 製高性能 AFM Dimension Icon

原子間力顕微鏡 (AFM) とは？



AFMの特徴

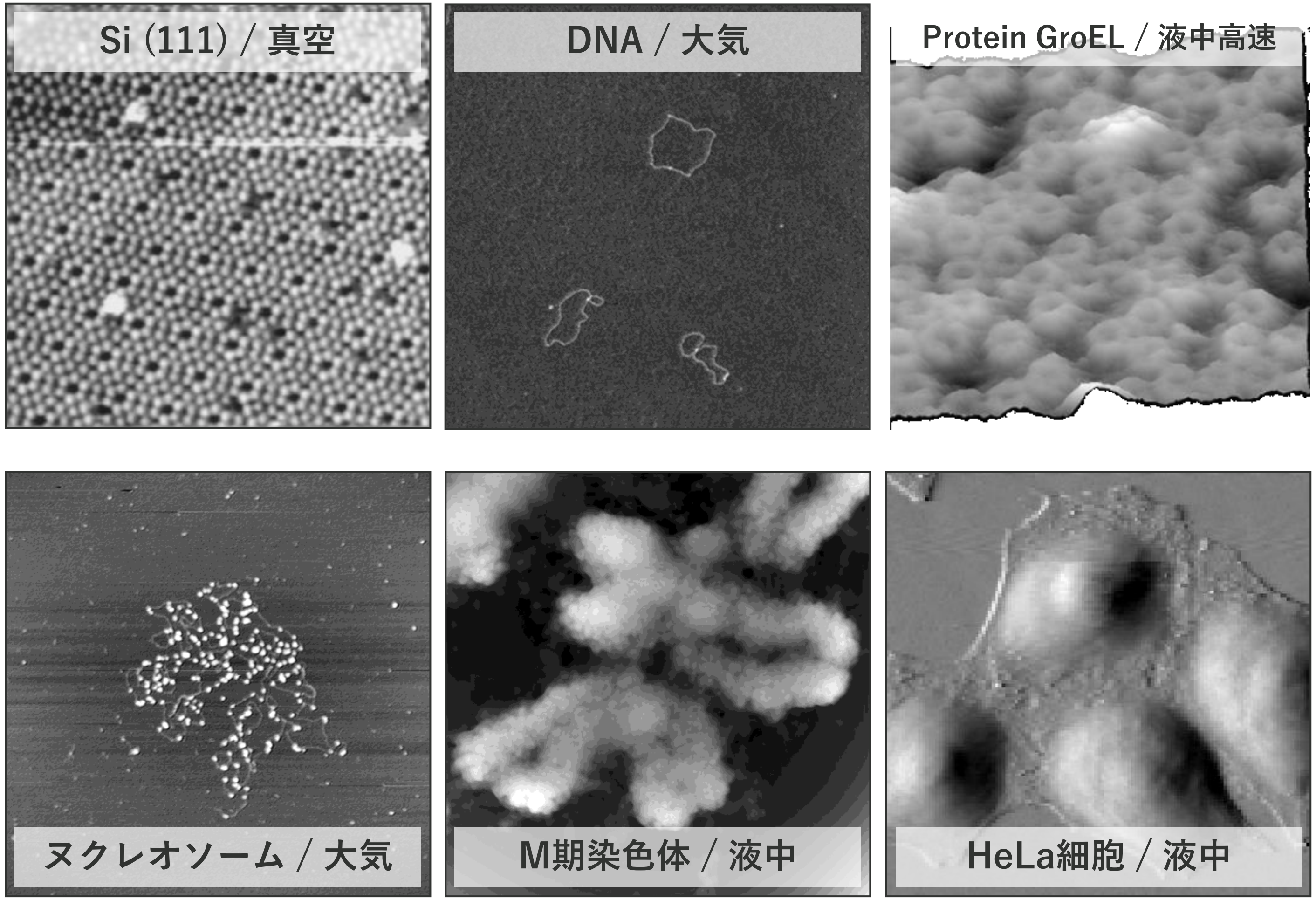
- 簡単に高分解能の表面観察が可能
- 試料の染色・固定化・乾燥が不要
- あらゆる環境下で利用可能



原子間力顕微鏡 (AFM) 技術の進展

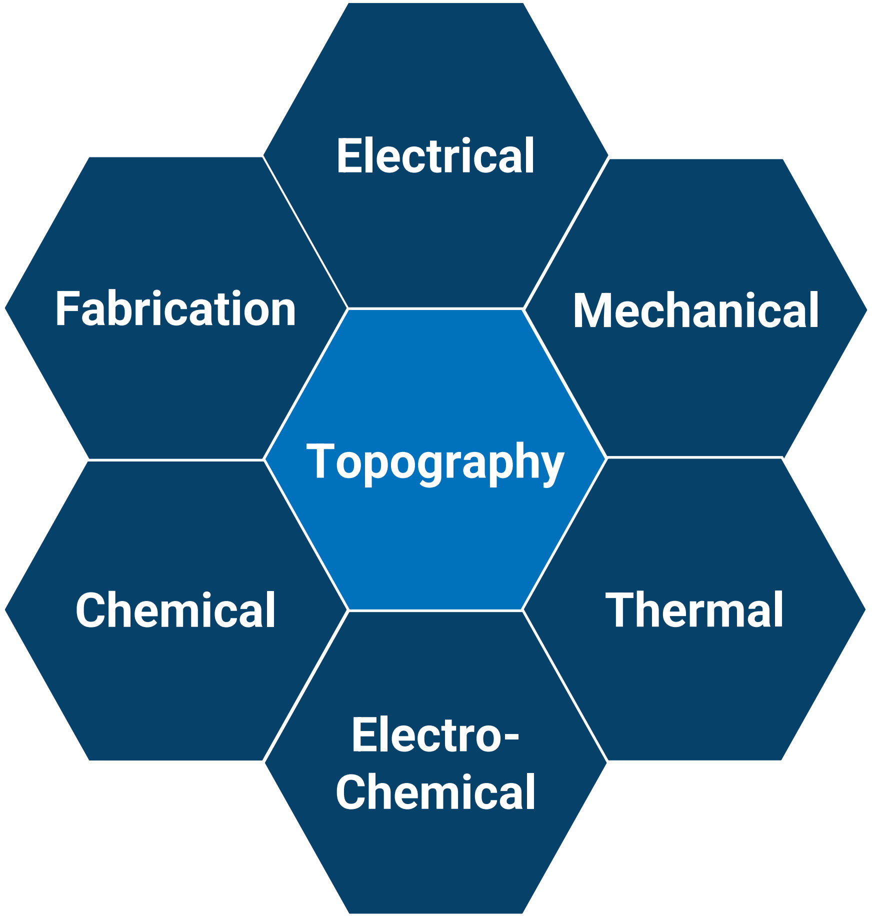
Mapping Topography

Topography

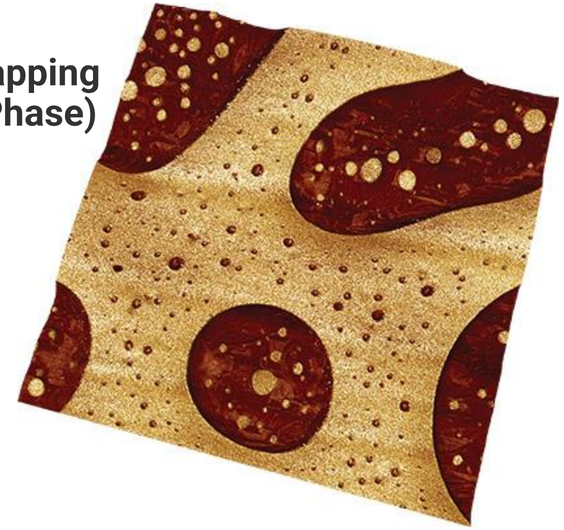


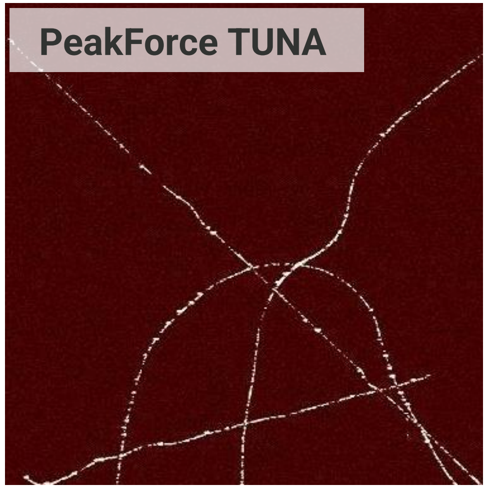
原子間力顕微鏡 (AFM) 技術の進展

Mapping Topography -> More Information!

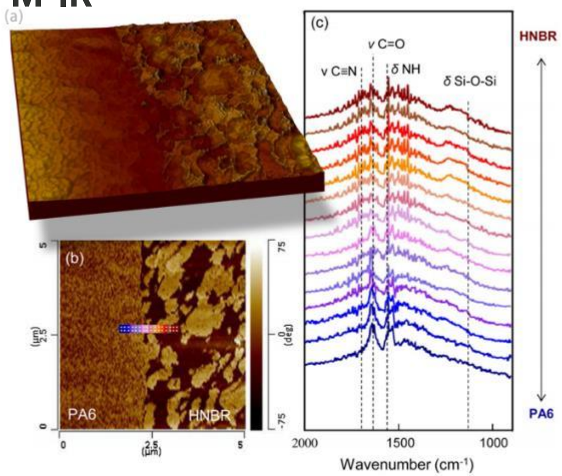


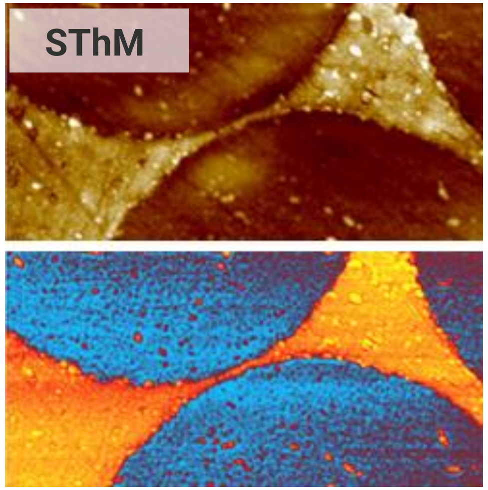
Tapping (Phase)





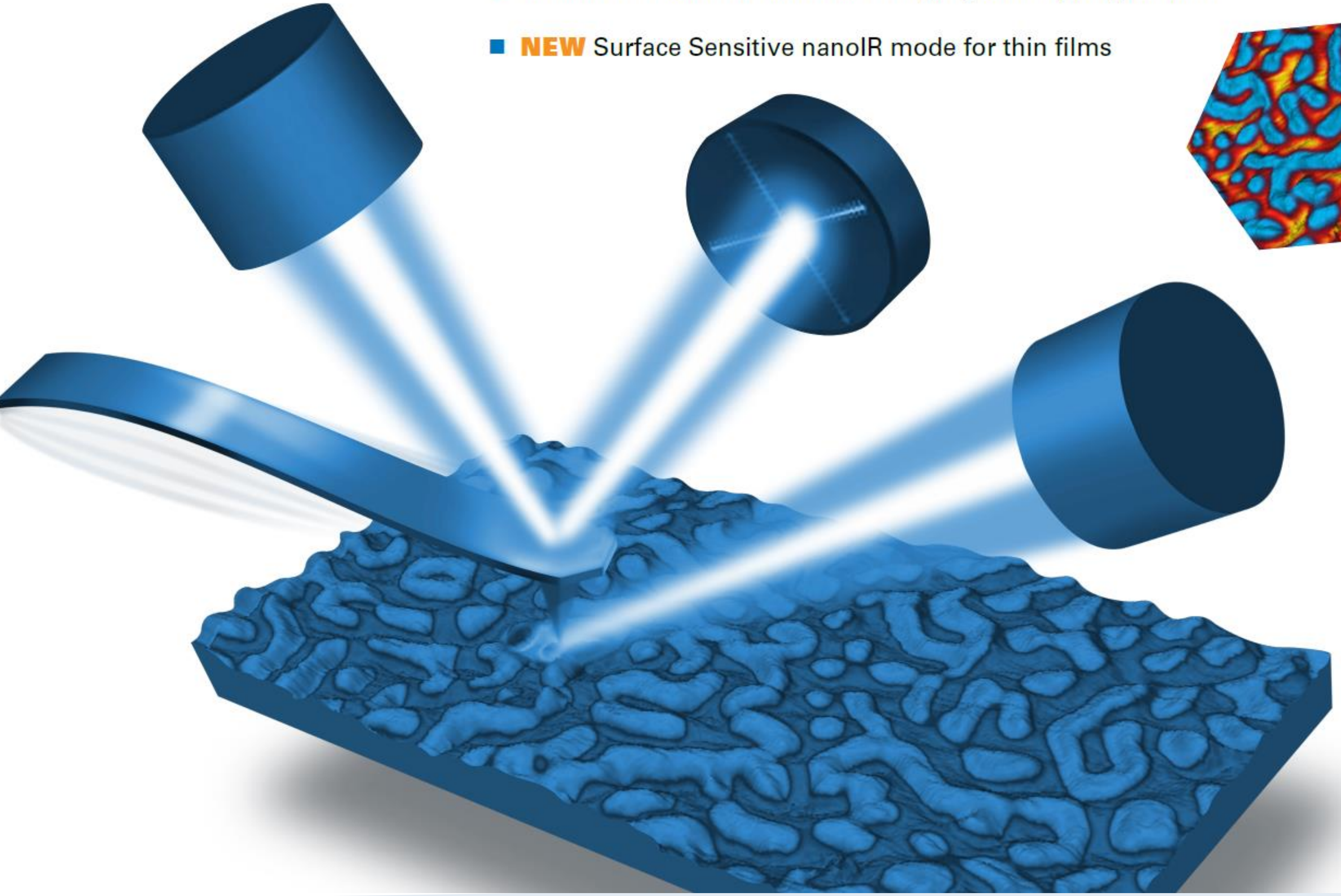
AFM-IR

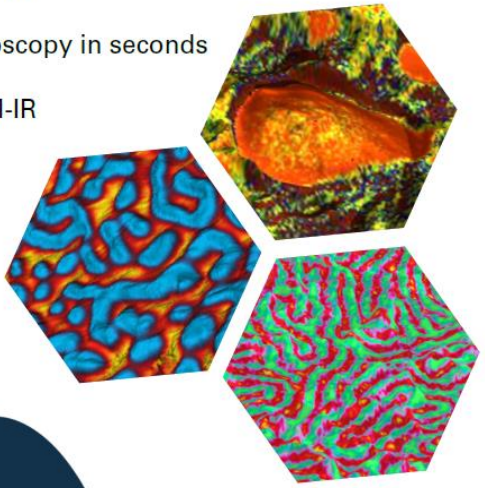


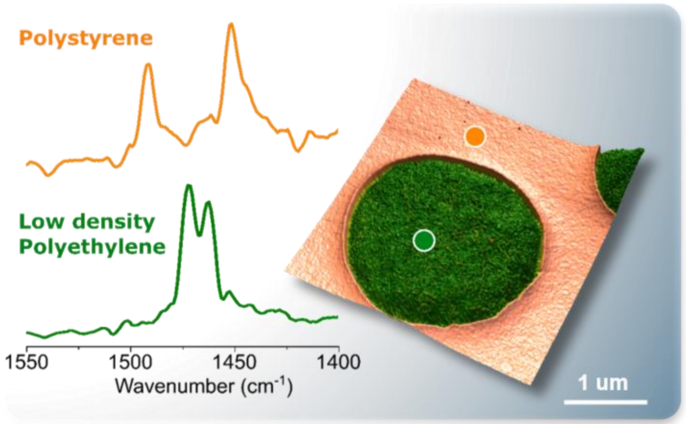


Nanoscale IR Spectroscopy

- Rich, interpretable nanoIR spectra directly correlated to FTIR
- Hyperspectral AFM-IR for high-resolution, nanoIR spectroscopy in seconds
- Sub-10nm resolution chemical imaging with Tapping AFM-IR
- **NEW** Surface Sensitive nanoIR mode for thin films





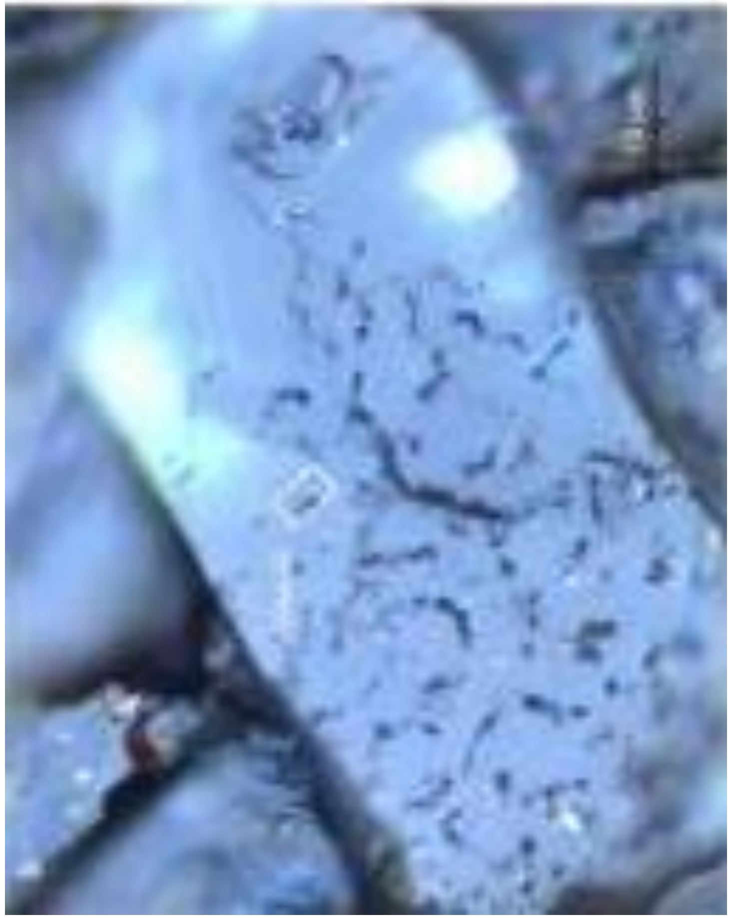


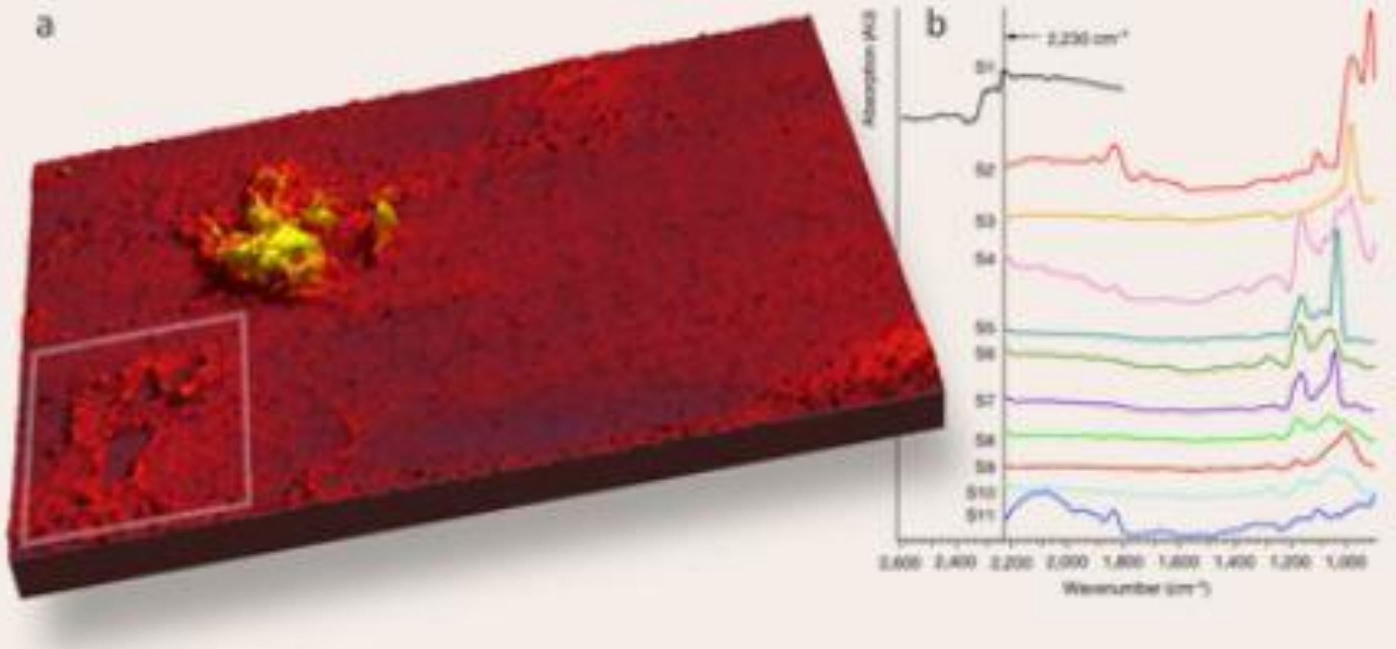
AFM-IR:

AFM based InfraRed spectroscopy

AFM ベースの赤外分光技術

化学的生命の誕生：
鉱物の包含物中に封入された原始生代の生命構成元素分析



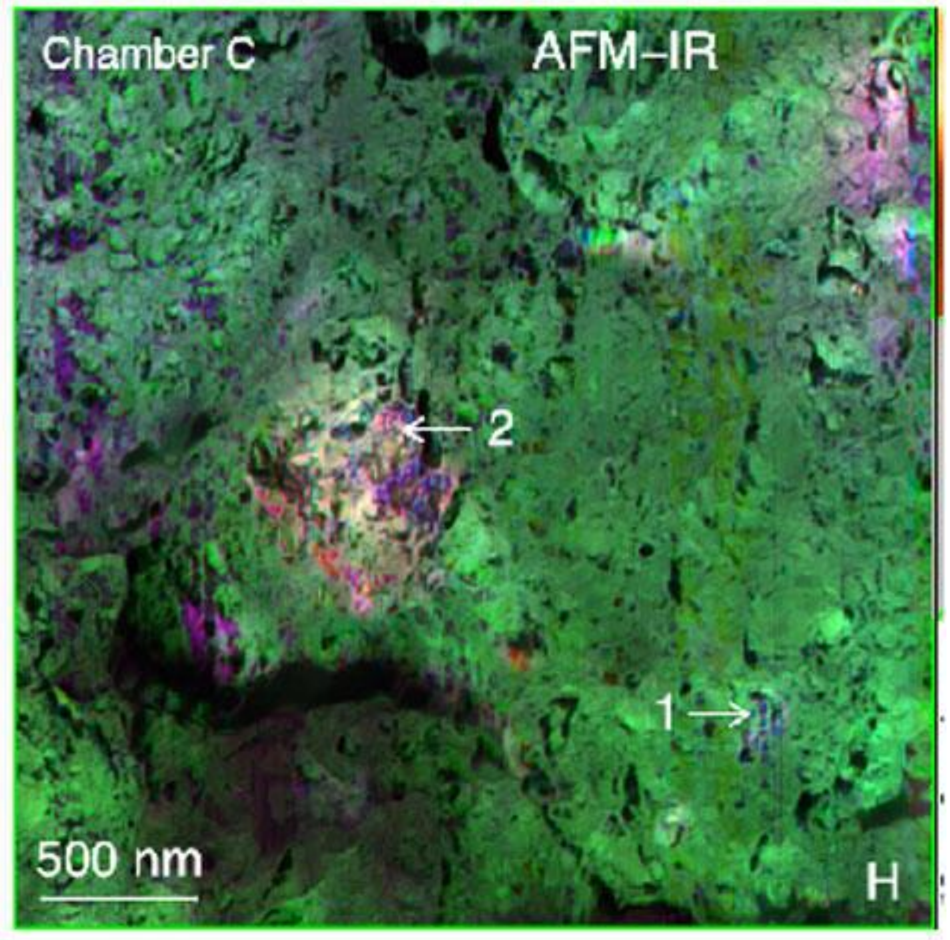


(a) IR chemical image of the absorption intensity at 2,230 cm-1 and (b) IR absorption spectra from 900 to 2,235 cm-1, indicating the presence of organic matter embedded in meteorites.

T. Hassenkam, et.al., *Nature*, **548**, 78–81 (2017)

37億年前の岩石中の **ナノ赤外分析** から，原初の有機生命体の痕跡を発見

小惑星探査機「はやぶさ２」初期分析　固体有機物分析チーム 研究成果の科学誌「Science」論文掲載について



非処理のリュウグウ試料のAFM 赤外顕微鏡観察で取得された各官能基の赤外吸収に基づくマップ

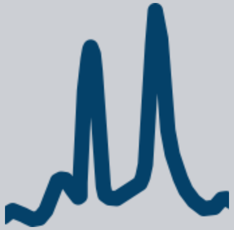
赤：C=O (1,720 cm^{-1})、青：C=C (1,600 cm^{-1})、緑：Si-O（1,020 cm^{-1})。層状ケイ酸塩と有機ナノ粒子（赤、紫）が共存している。濃緑色の領域は、薄く広がった有機物と推測される。

H. Yabuta, et.al., *Science*, **379**: eabn9057 (2023)

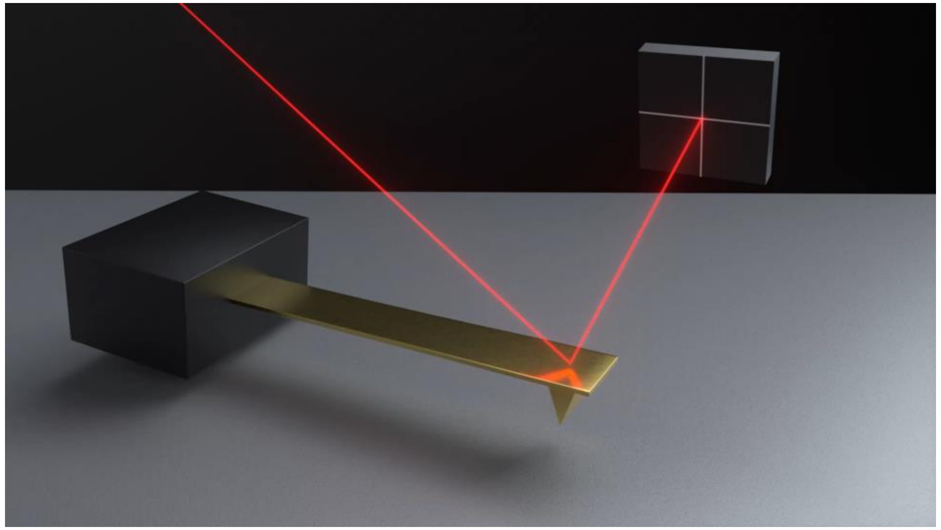
Intro to AFM-IR - the AFM probe is the IR detector

❶ An IR pulse arrives on the sample surface

❷ The sample absorbs the IR pulse, heats up and expands, applying a mechanical force on the AFM probe



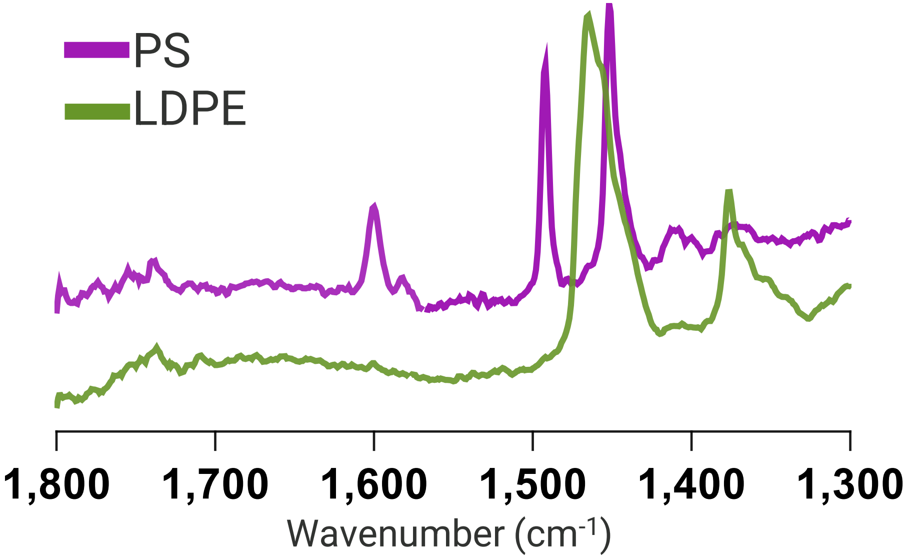
❸ The magnitude of this force is proportional to the absorption coefficient and so the FTIR response



Spectroscopy and Imaging

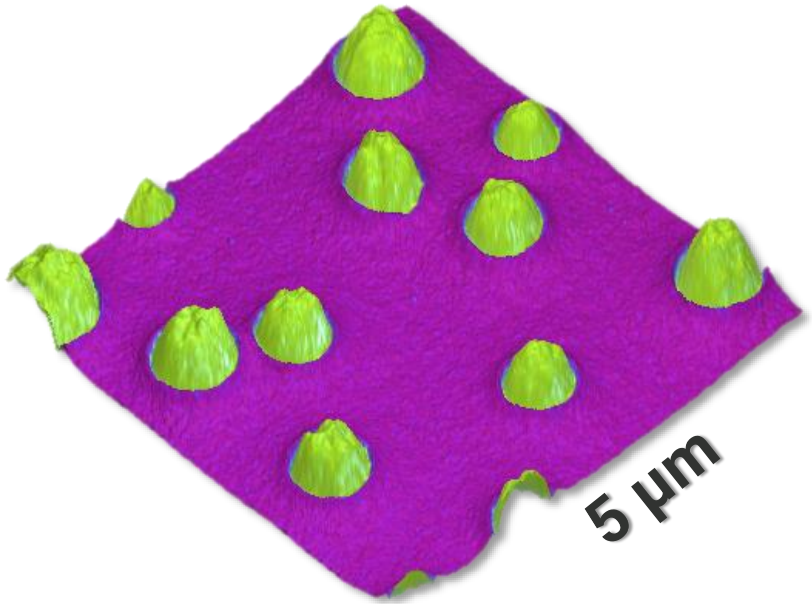
Spectroscopy

- Keep the probe fixed in space and scan the IR wavelength.
- **IR spectroscopy at the nanoscale**



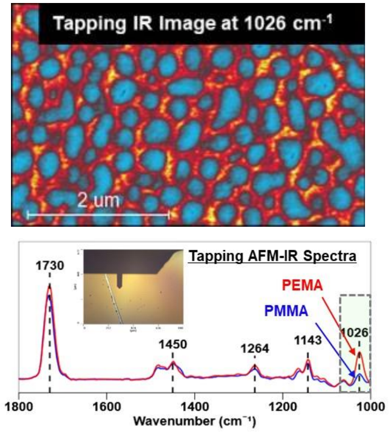
Imaging

- Keep the IR wavelength fixed and scan the probe in space.
- **Simultaneous topography and IR chemical mapping**

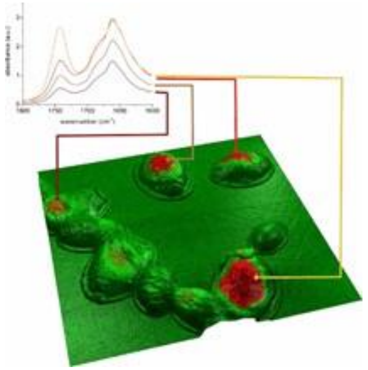


Photothermal AFM-IR: Applications Overview

Polymers
Multilayer Films
Blends
Fibers

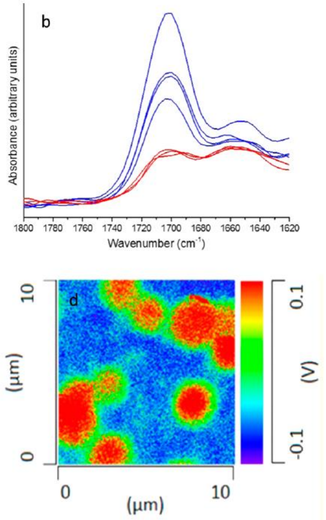


Life Science
Cells
Proteins
Tissues

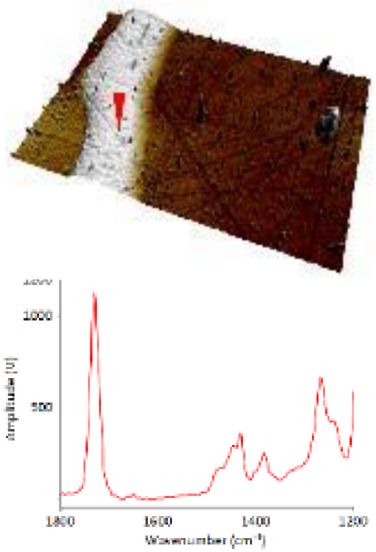


Environmental
Geoscience
Bitumen Cultural Heritage

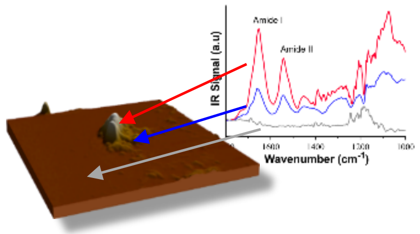
Pharmaceutical Science
Drug Formulation
Drug Delivery



Material Research
Thin films
Solar Cells

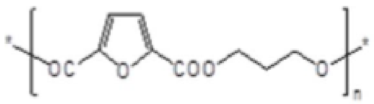


Microelectronics / Semiconductor
Nano-contaminants
Devices

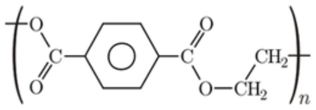


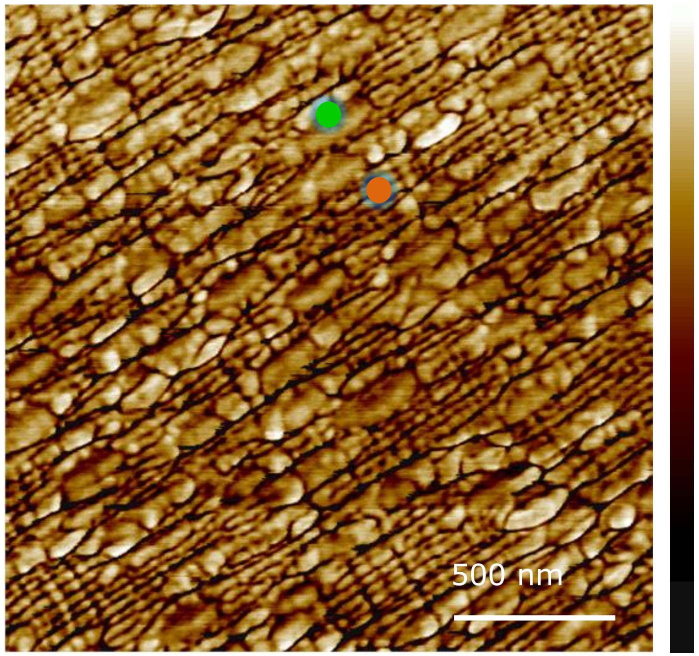
① ポリマーアロイの高分解能 AFM-IR 分析
--- PET / PTF ポリマーブレンド ---

PTF (Domains)

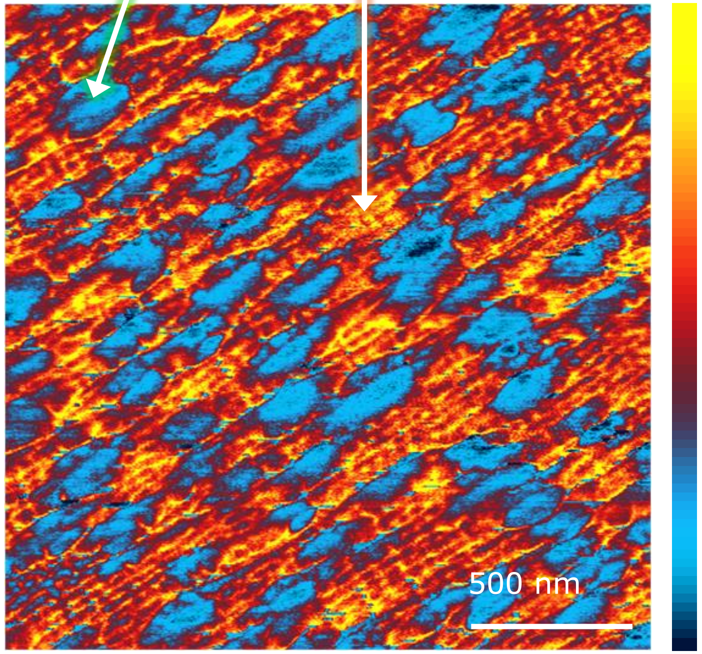


PET (Matrix)

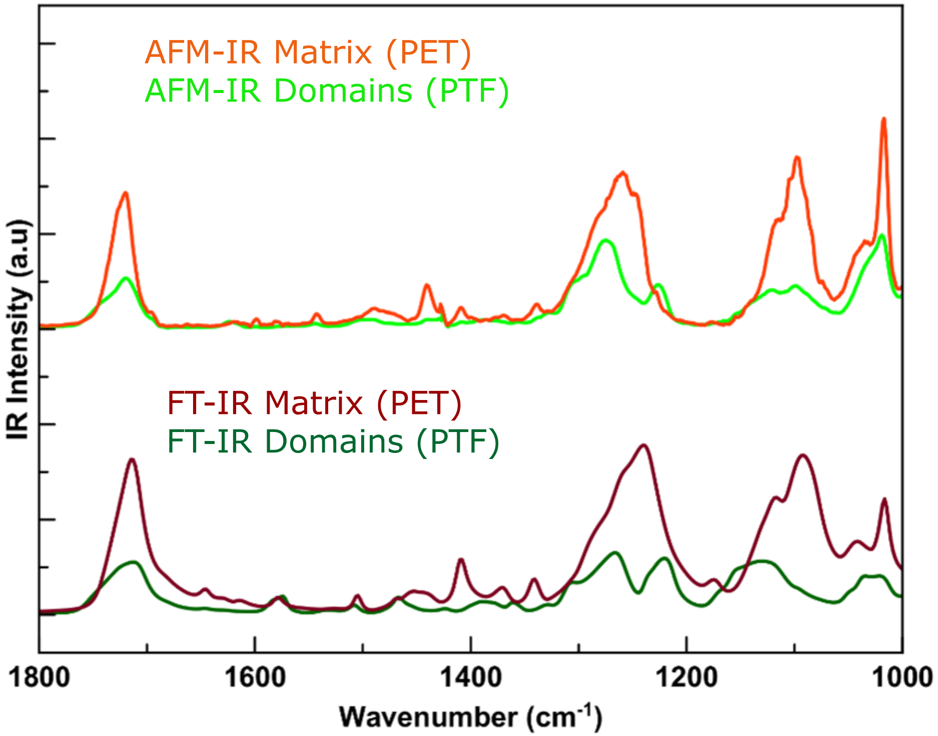




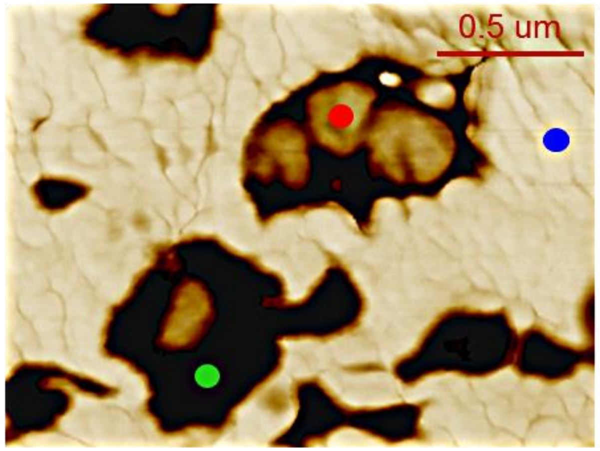
Phase image

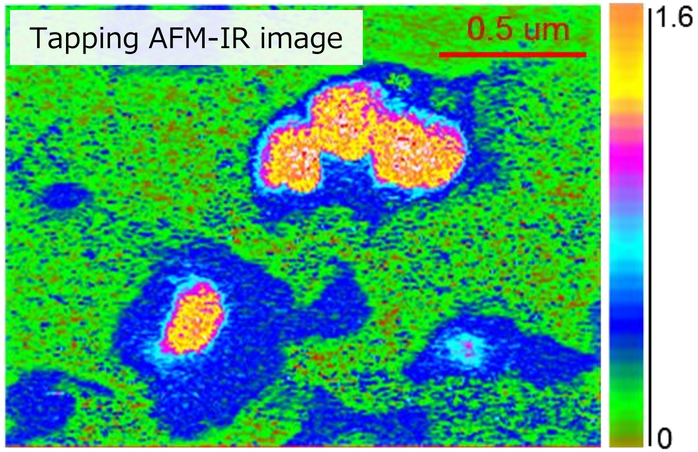


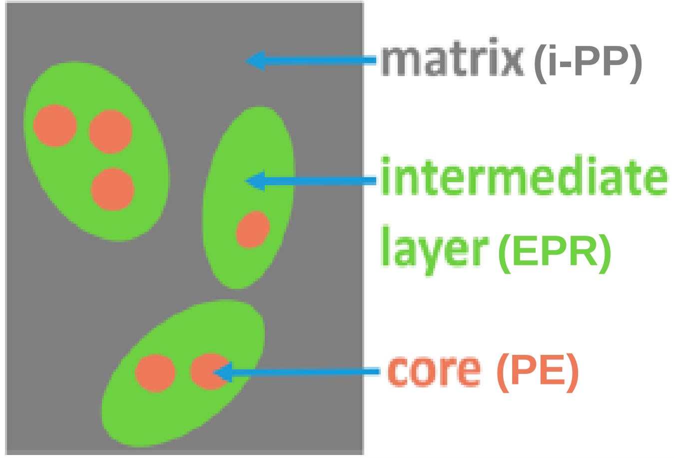
Tapping AFM-IR Image at 1100 cm^{-1}

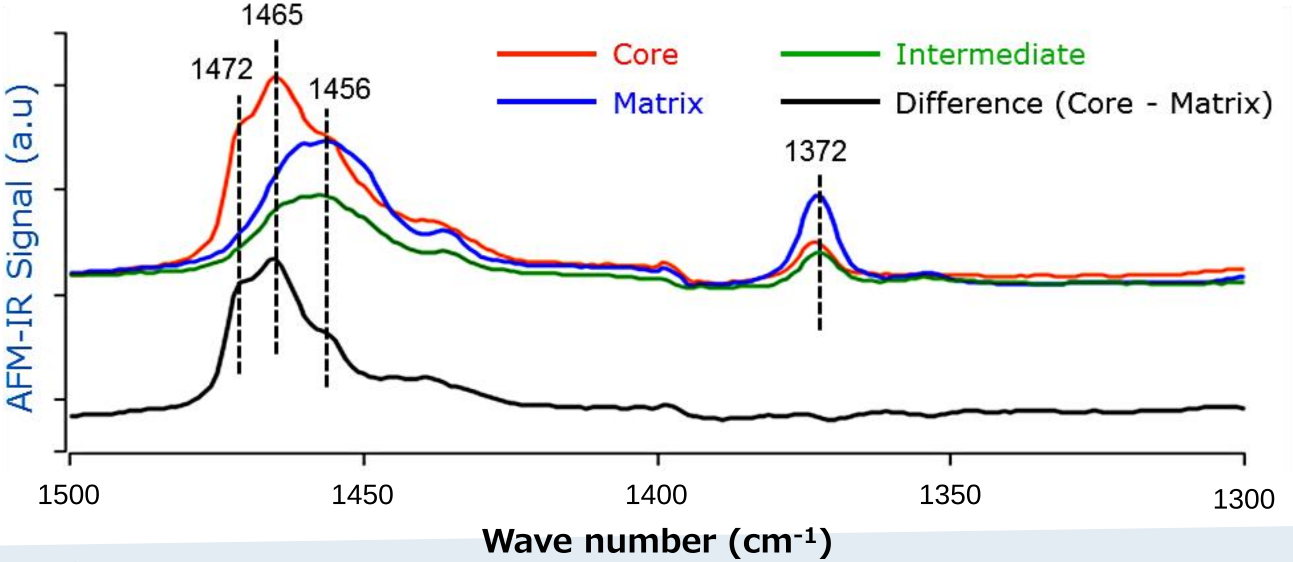


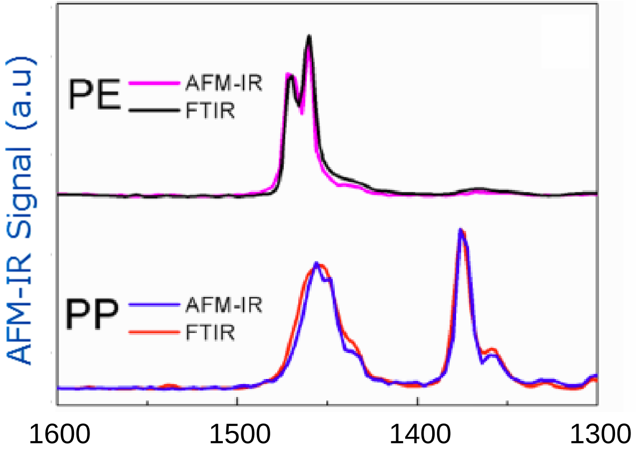
② ポリマーアロイの主成分分析
--- 高耐衝撃ポリプロピレン (HIPP) ---











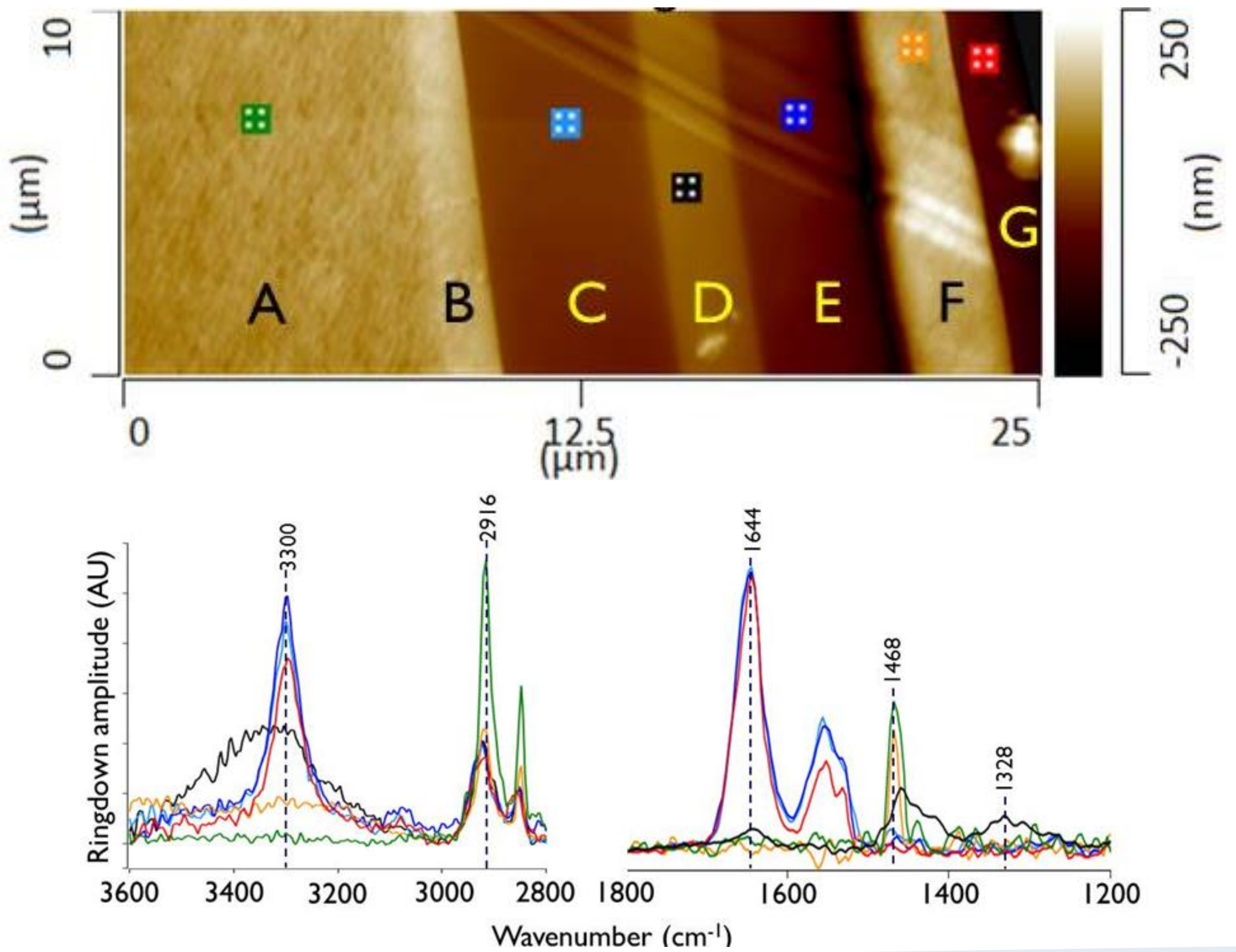
F. Tang, et al., *Polymer*, **142**, 155–163 (2018)

③ ポリマーフィルム 界面の化学

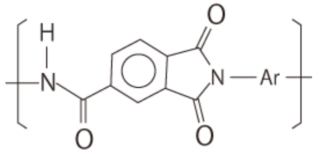
--- PA / EVOH / PE 多層高バリアフィルム ---

AFM image

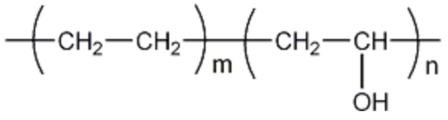
AFM-IR spectra



PA: Polyamide



EVOH: Ethylene-vinyl alcohol copolymer



PE: Polyethylene

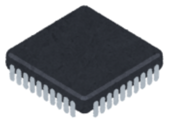
-[-CH2-CH2-]n-

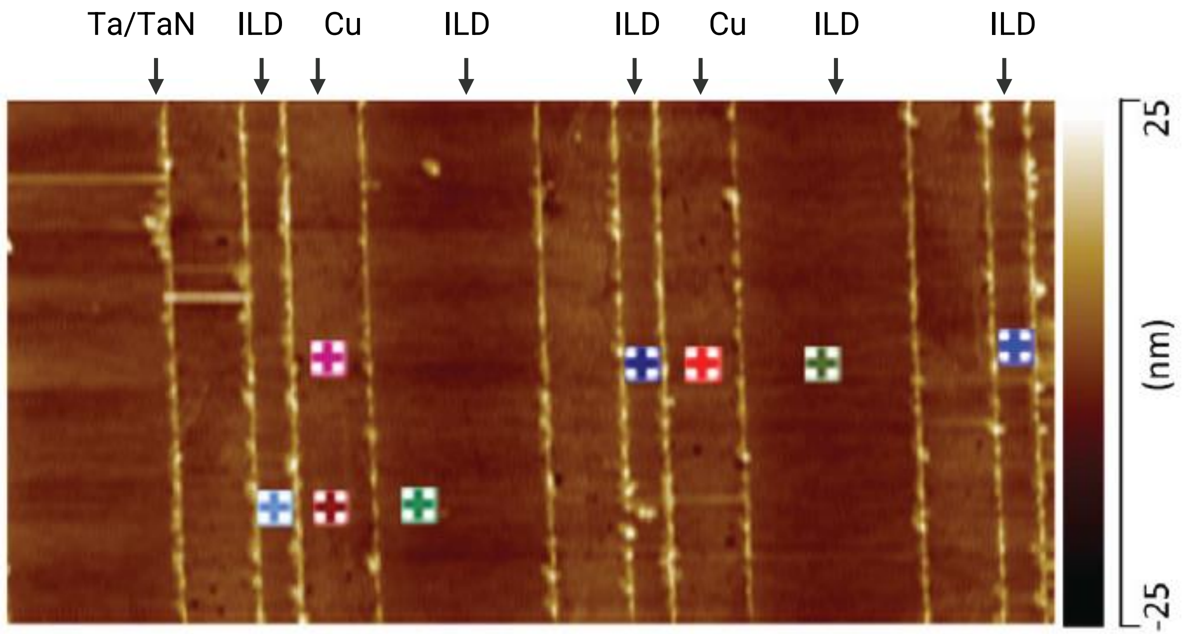
個々のフィルムの成分として PA, EVOH, PE を分光学的に識別

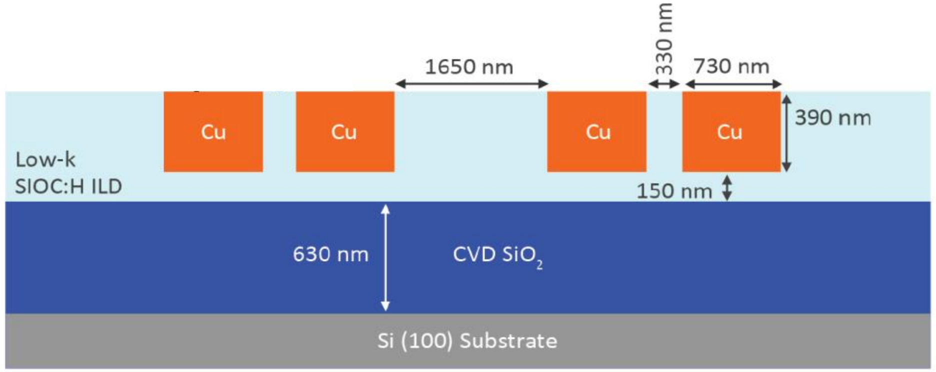
Vib. Spectrosc., 82, 1015 (2016)

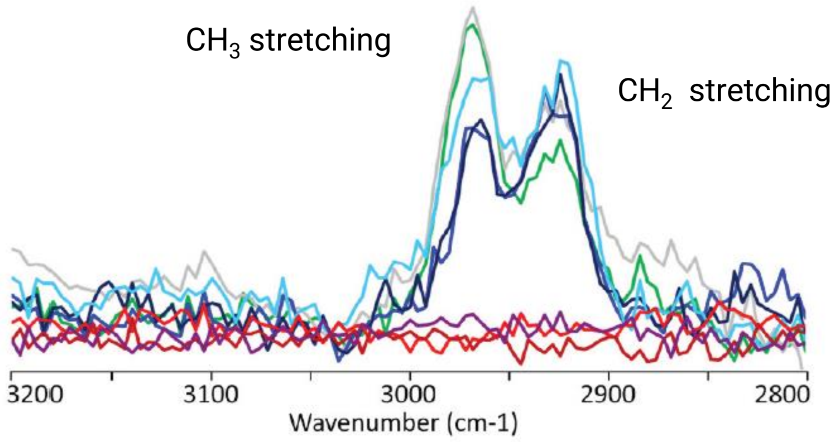
④ 半導体材料のナノ欠陥解析

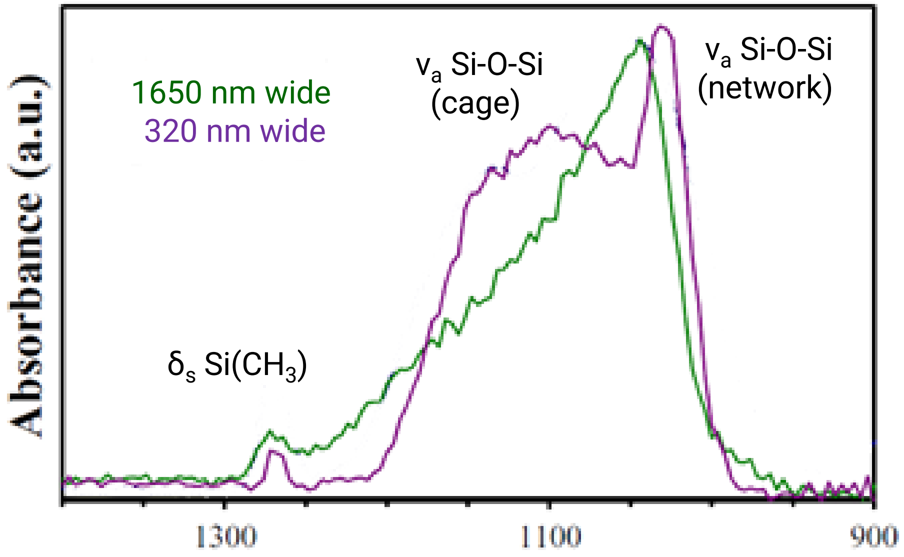
--- プロセス誘起欠陥の解析 ---







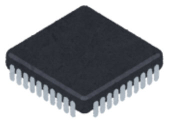




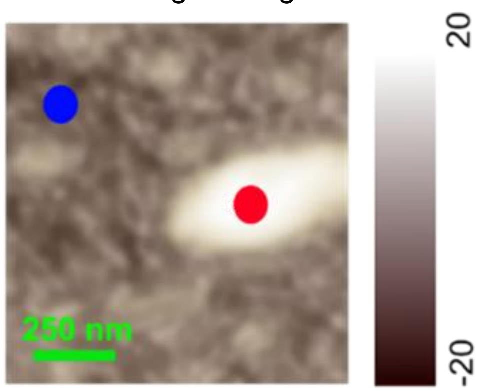
ECS J. Solid State Sci. Technol. 2016, 5 (4), P3018-P3024

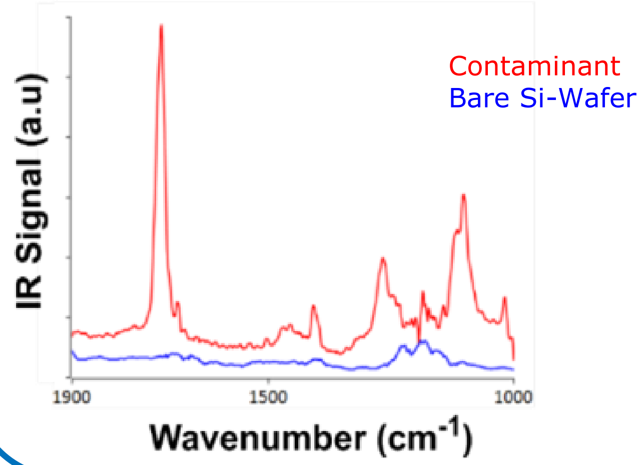
⑤ 半導体材料のナノ欠陥解析

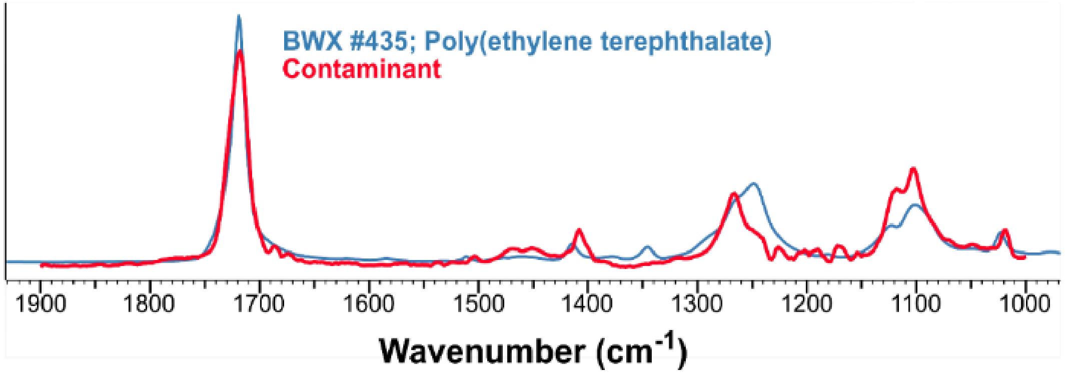
--- シリコン基板上の異物解析ワークフロー ---



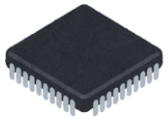
異物発見 → スペクトル測定 → FTIR ライブラリサーチ







Micro and nanocontaminants
Case Study with Intel for SPIE Photomask



Paper 13216-28

AFM Nano-IR for photomask in-line defect characterization

1 October 2024 • 11:15 AM - 11:30 AM PDT | Monterey Conf. Ctr., Steinbeck 2

Add to My Schedule

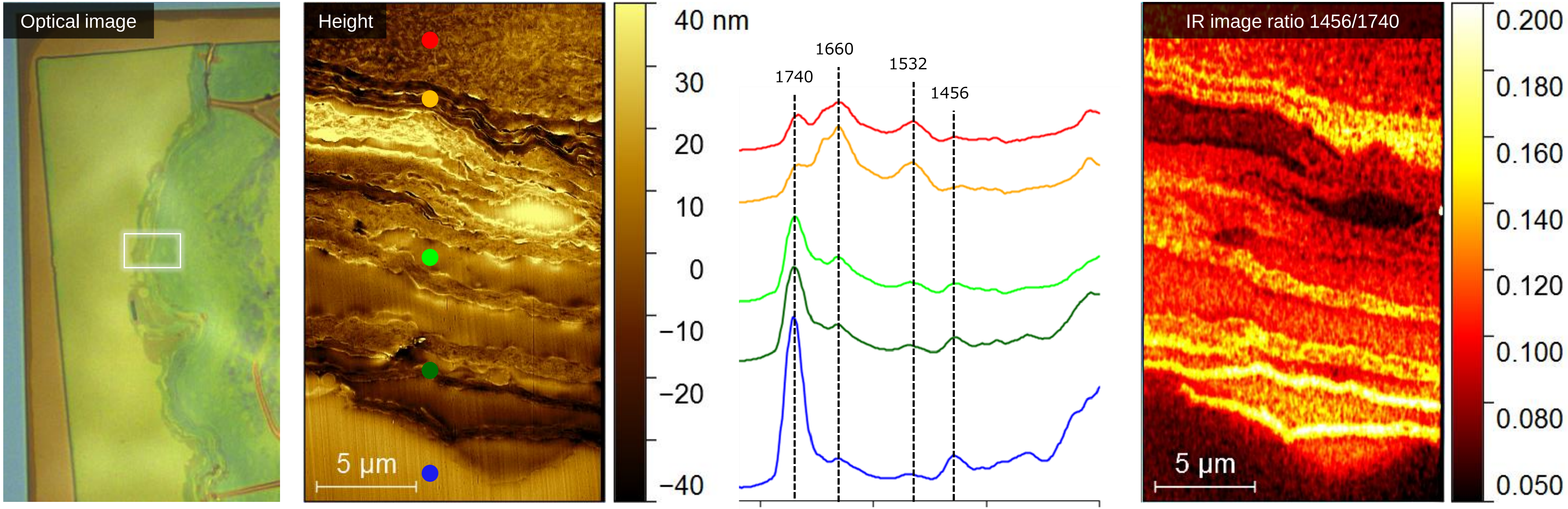
Abstract **Authors**

As HVM of photomasks of various types and processes expands, defects and their origin are of particular concern. Organic materials are present in many aspects of a photomask's lifecycle, from carriers and tool hardware to resists and chemical residues. With the emergence of AFM-NanoIR failure analysis techniques, distinguishing organic defects and thin films with high resolution is limited only by the size of the AFM probe. Using Bruker's Icon-IR lab AFM, we collect IR spectra of many common materials found in our process to build a database, allowing future defects to be matched to our known materials and general external IR databases. To expand our capabilities, an in-line automated AFM with spectra acquisition capability is required, with cleanliness and recipe reliability required for factory use. To support this automated toolset, an automated reporting function has been developed to quickly provide customers with a complete picture of a defect, from AFM scan to IR spectra, complete with IR imaging at wavelengths of interest. This paper seeks to decode the nature of AFM Nano-IR and its place as an essential in-line defect analysis technique.

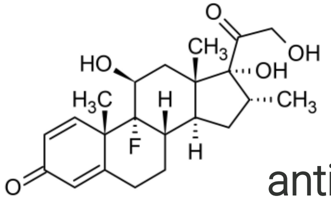
Paper 13216-28, AFM Nano-IR for photomask in-line defect characterization
https://spie.org/photomask-technology/presentation/AFM-Nano-IR-for-photomask-in-line-defect-characterization/13216-28

⑥ 医療応用

--- ステロイド系抗炎症薬 (Dexamethasone) ---



脂質膜領域における薬剤の蓄積が示されている

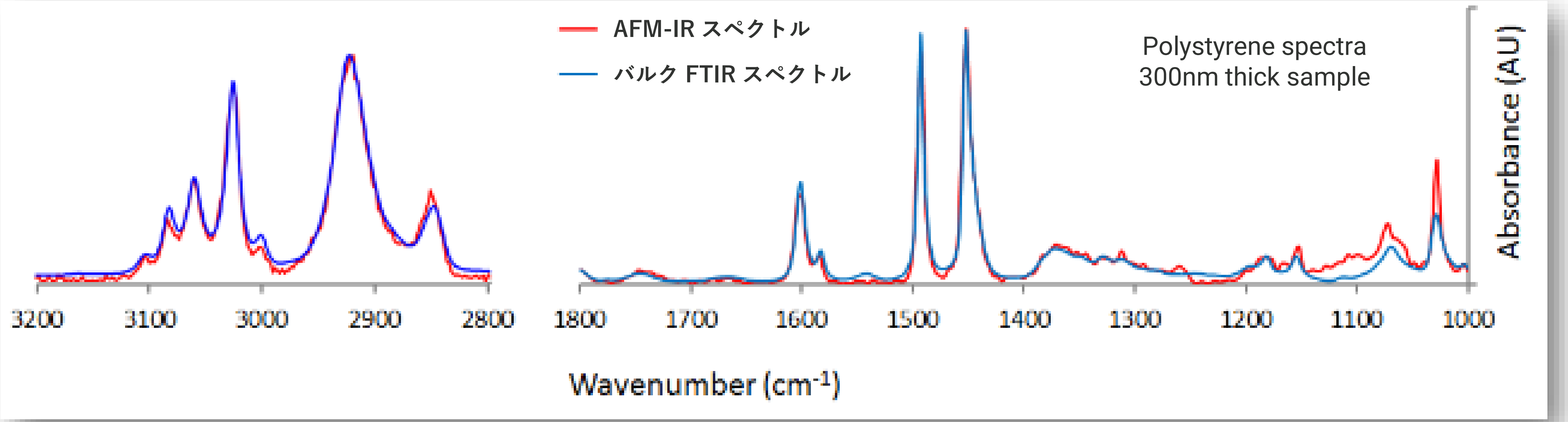


Dexamethasone,
anti-inflammatory glucocorticoid

Sample courtesy: FU Berlin

State of the Art for AFM-IR

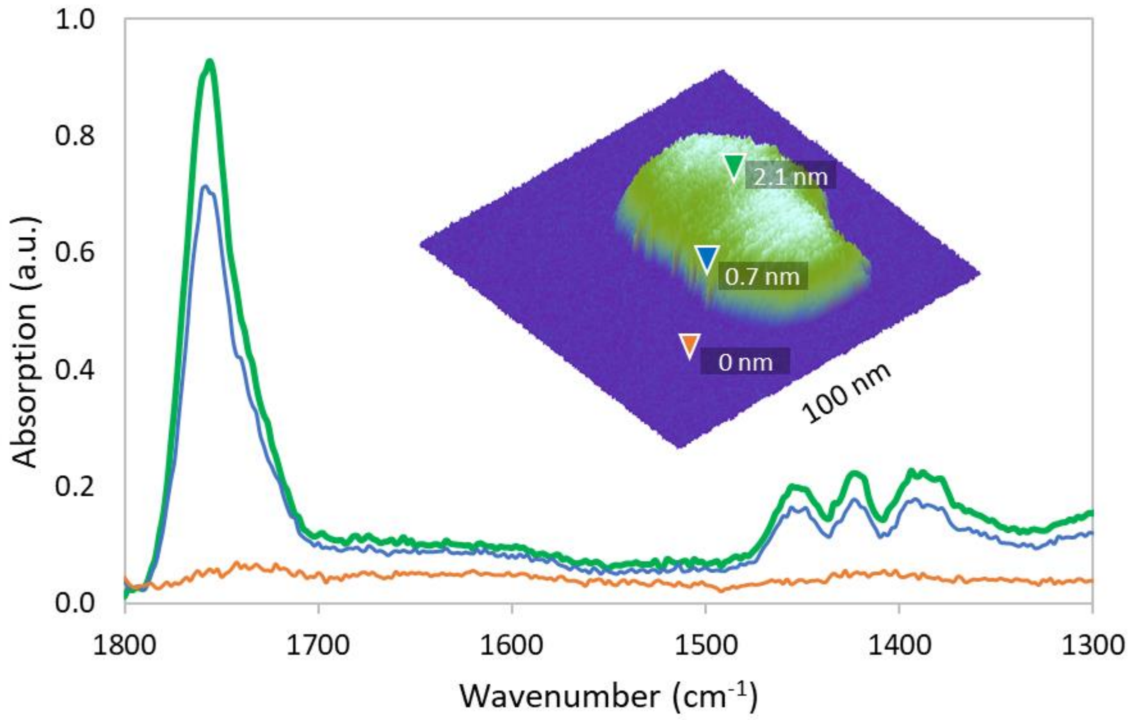
1. Access to True Chemical Selectivity with Easy Data Interpretability



- **AFM-IR では光の吸収現象を直接検出する** ため，得られた AFM-IR スペクトルデータをそのまま従来の赤外分光データと比較し，物質の定量・同定を行う事が可能です

State of the Art for AFM-IR

2. High Sensitivity (< 1 nm)



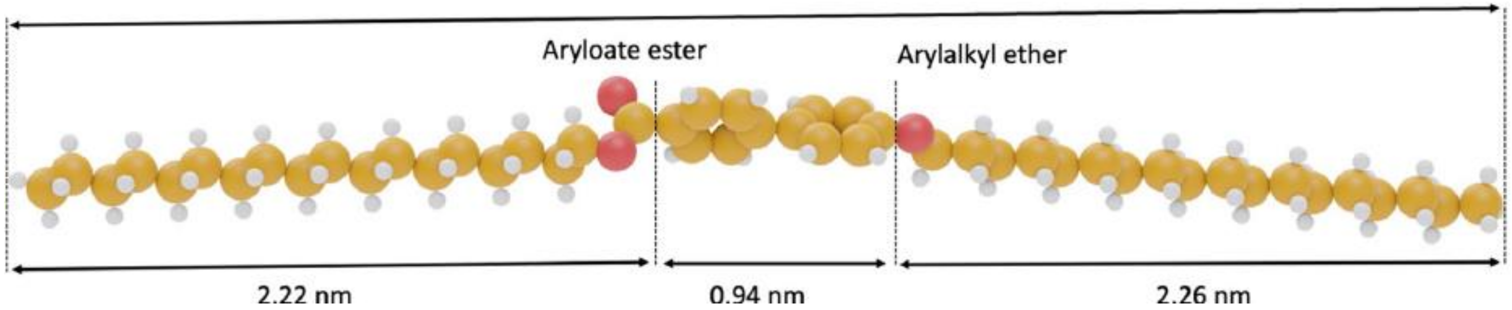
High Performance Tapping AFM-IR

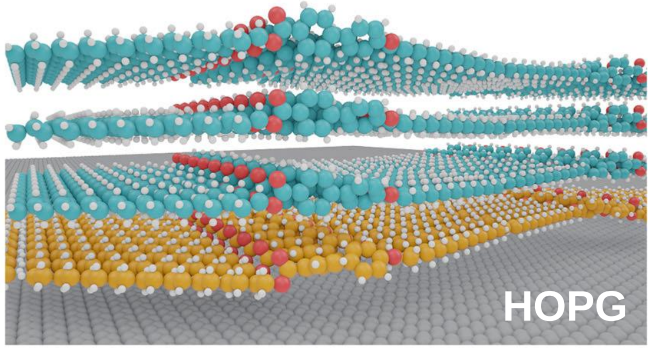
- **High sensitivity:** <1 nm on non-metal substrate
- **High spatial resolution:** <2 nm
- **Controlled probing depth and surface sensitivity**
- **High measurement speed:**
  High IR imaging rate; fast spectroscopy /hyperspectral
- **Artifact-free:** Mechanical compensation with PLL

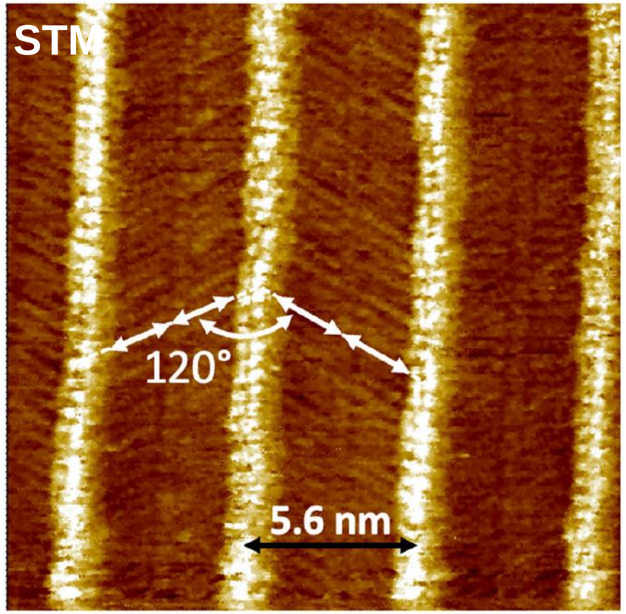
- **Tapping AFM-IR spectra and image of a <u>thin PLA film sample on mica</u>, courtesy of EAG Laboratories**

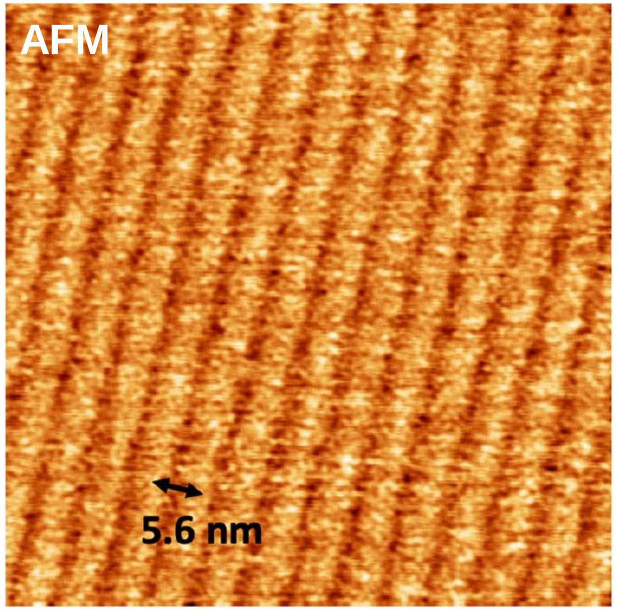
State of the Art for AFM-IR

2. High Sensitivity (monolayer sensitivity on HOPG)

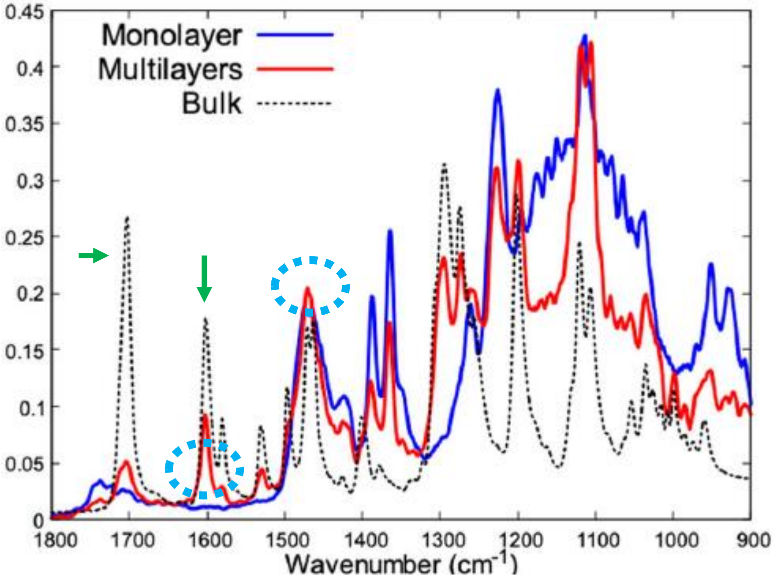








(PeakForce Tapping, PEAKFORCE-HIRS-SSB)

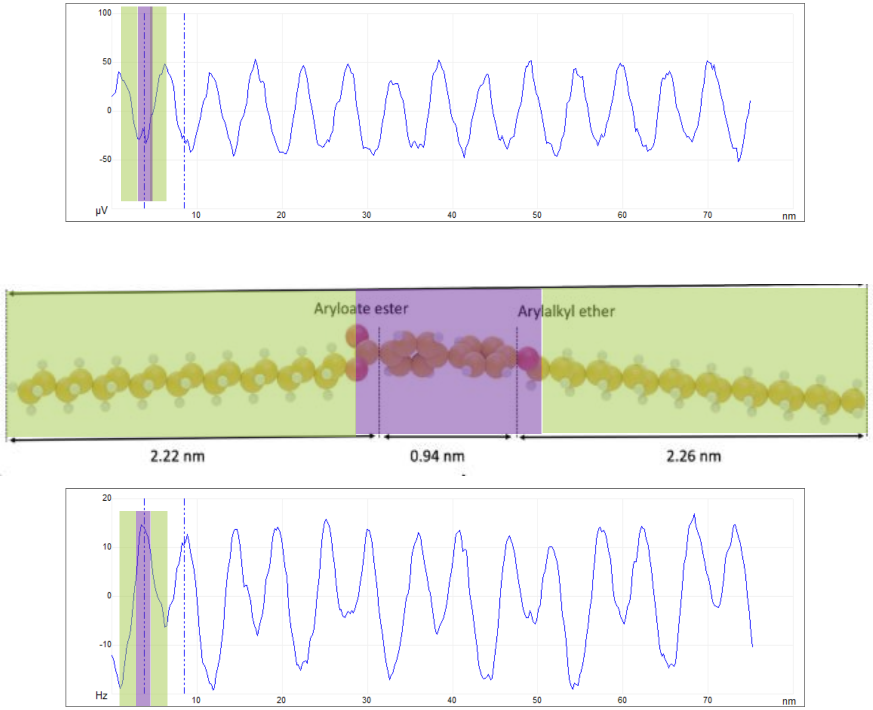


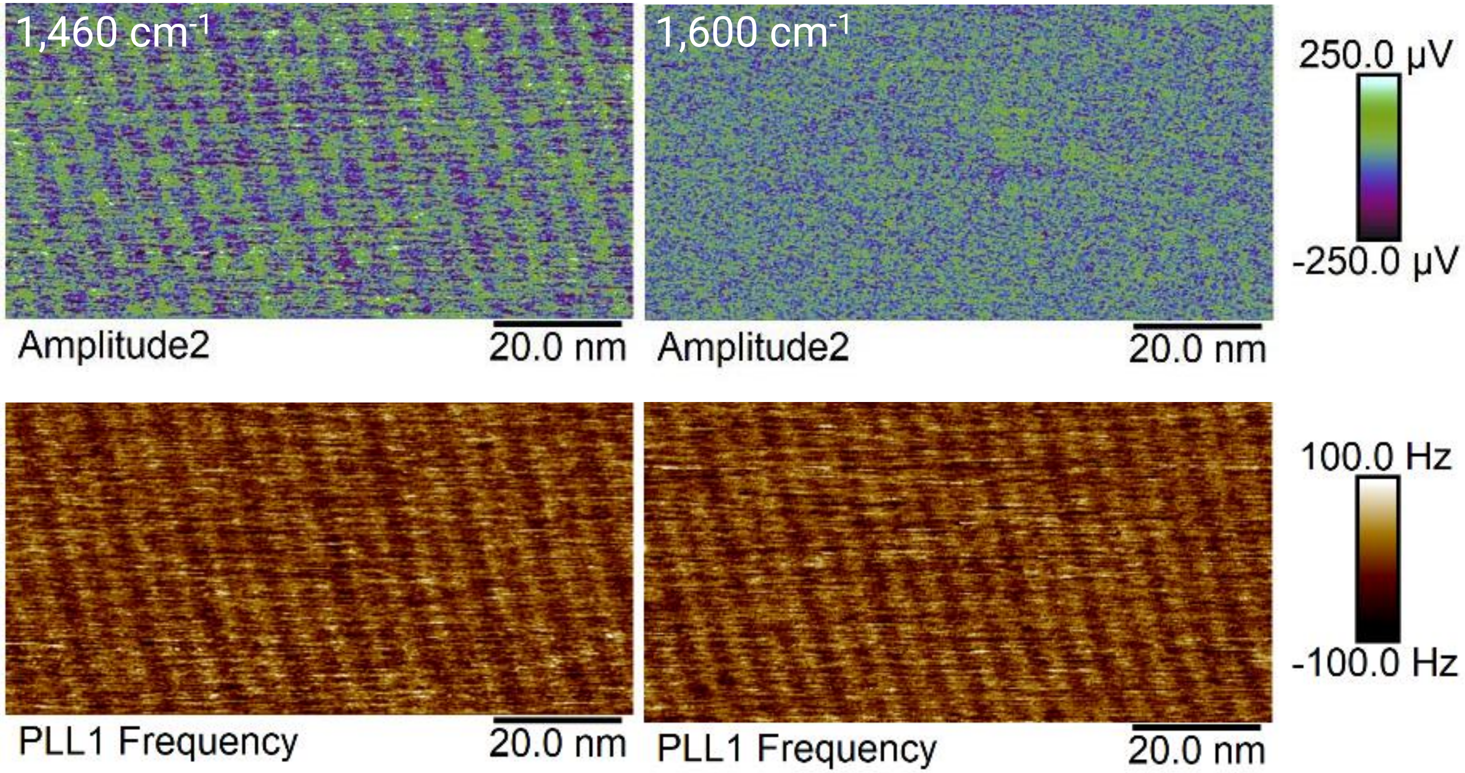
A. Hamadeh, et.al., *Communications Chemistry*, 6, 246 (2023)

State of the Art for AFM-IR

3. High Resolution (molecular resolution: 1-2 nm)

- **Resolution: 1-2 nm (10-90% ‘level’)**
- **Monolayer (0.8 nm) sensitivity on HOPG**





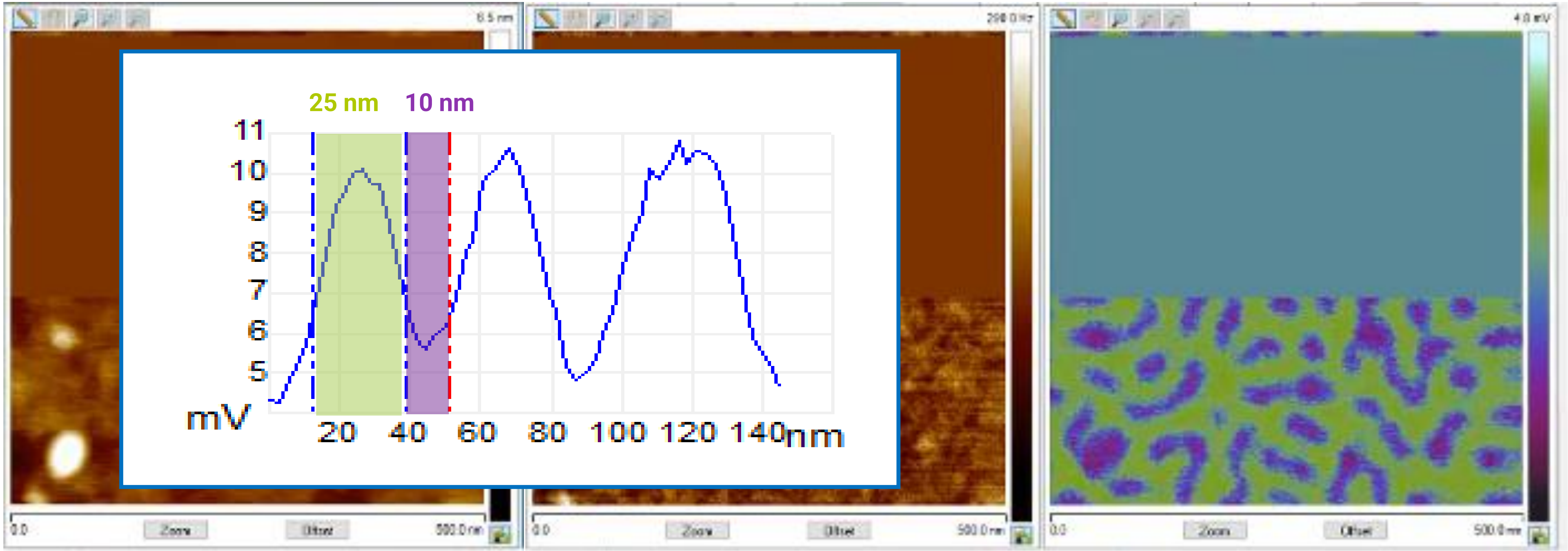
Unpublished data

Collaboration with Pr. Alexandre Dazzi (Université de Paris-Saclay),

Pr. Frank Palmino (Université de Franche-Comté, FEMTO-ST), Pr. Frédéric Chérioux (CNRS, FEMTO-ST)

State of the Art for AFM-IR

4. High Through-put: Scanning speed of 8 Hz (small, hi-res scans)



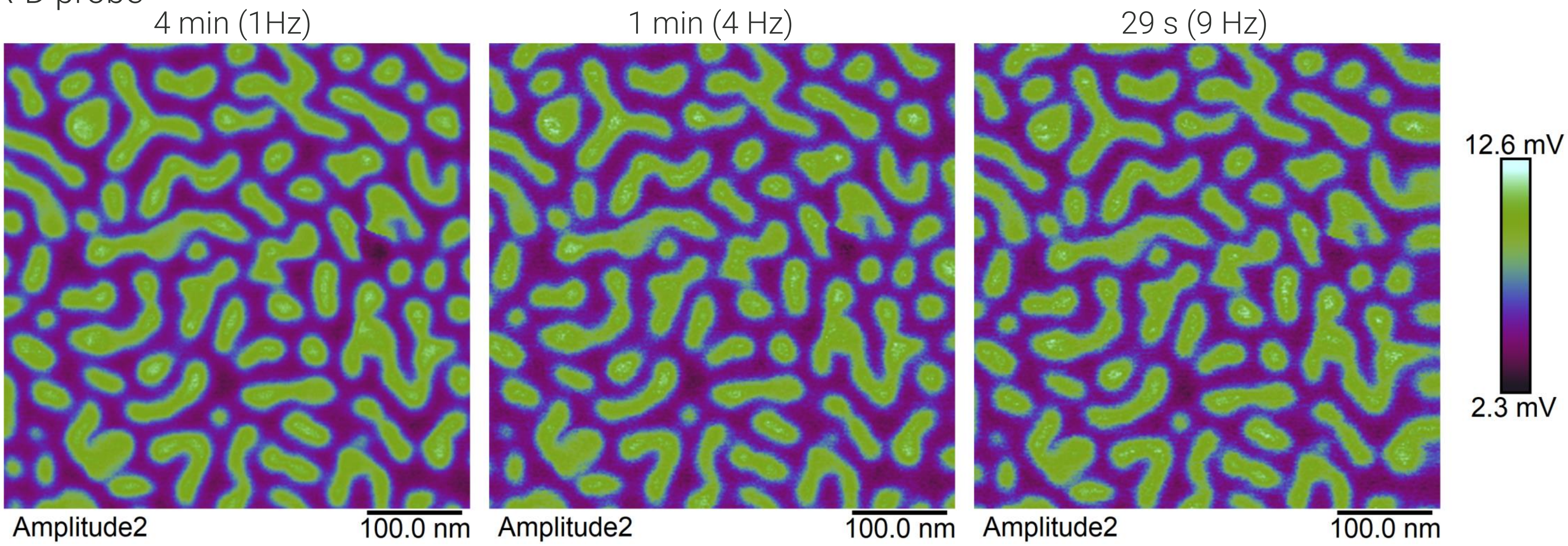
Height Sensor | PLL Frequency | Amplitude (IR)

- **Tapping AFM-IR @ 8.79Hz line rate (500 x 500 nm^2, 256 x 256 px), PS-PMMA sample @ 1,728 cm^{-1}**

State of the Art for AFM-IR

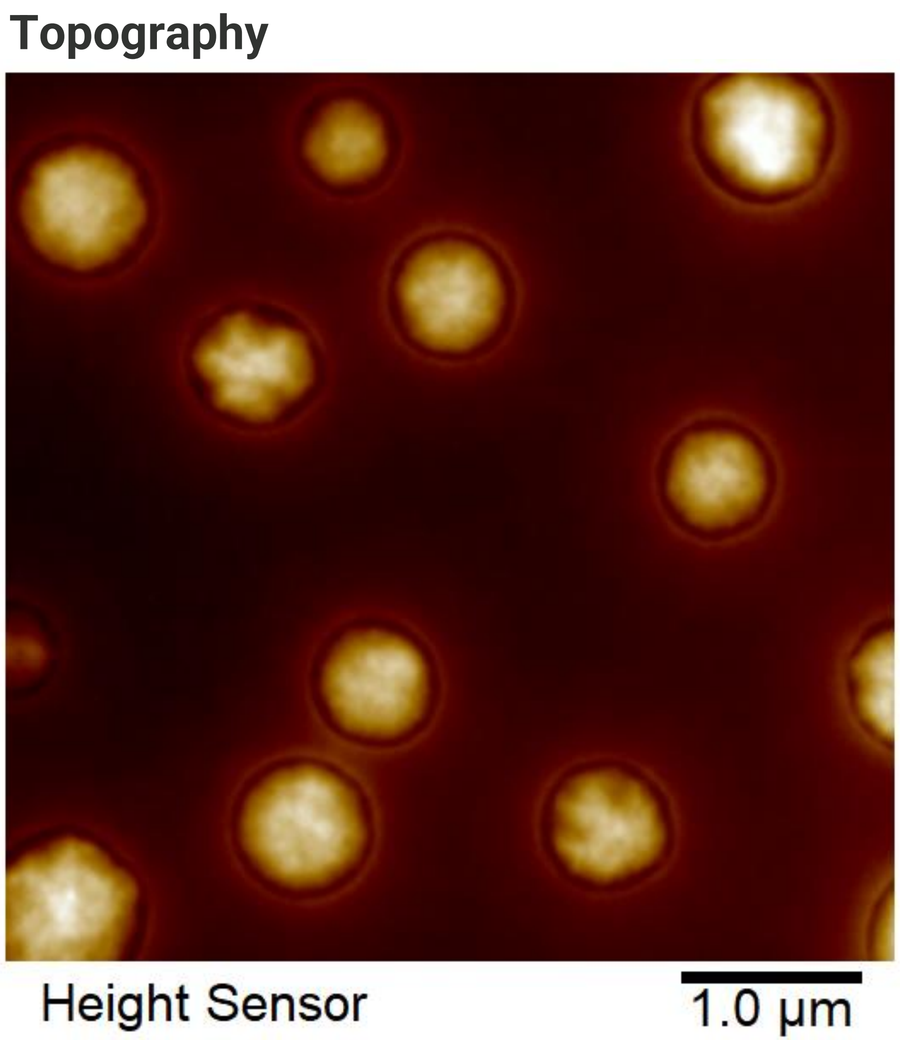
4. High Through-put: Scanning speed of 8 Hz (small, hi-res scans)

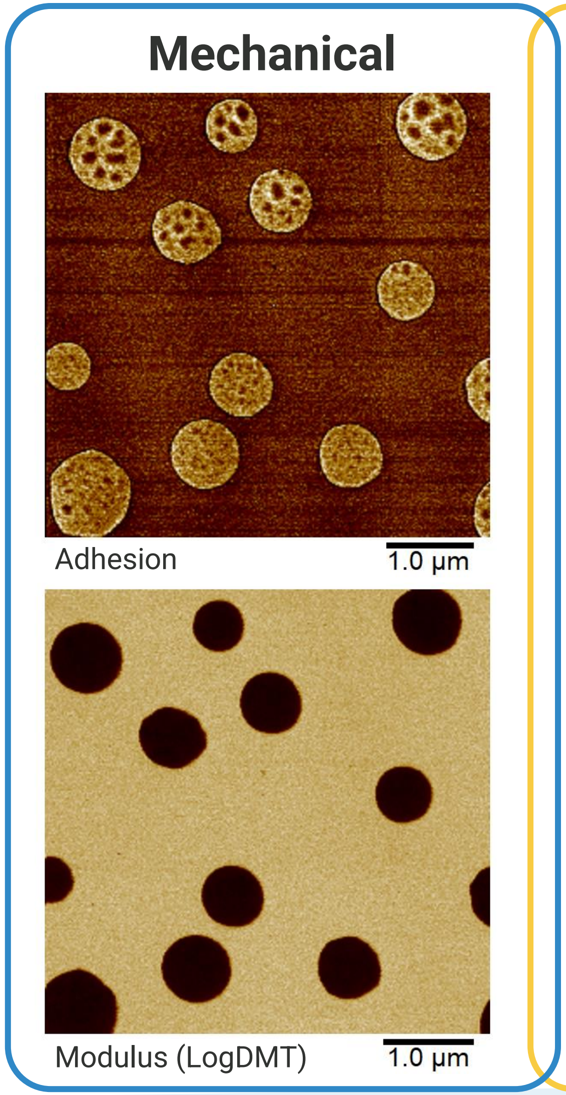
- PS-PMMA block co-polymer, mapping at 1730 cm^{-1}, roughness 0.5 nm, 500x500 nm, 256x256 pixels
- TNIR-D probe

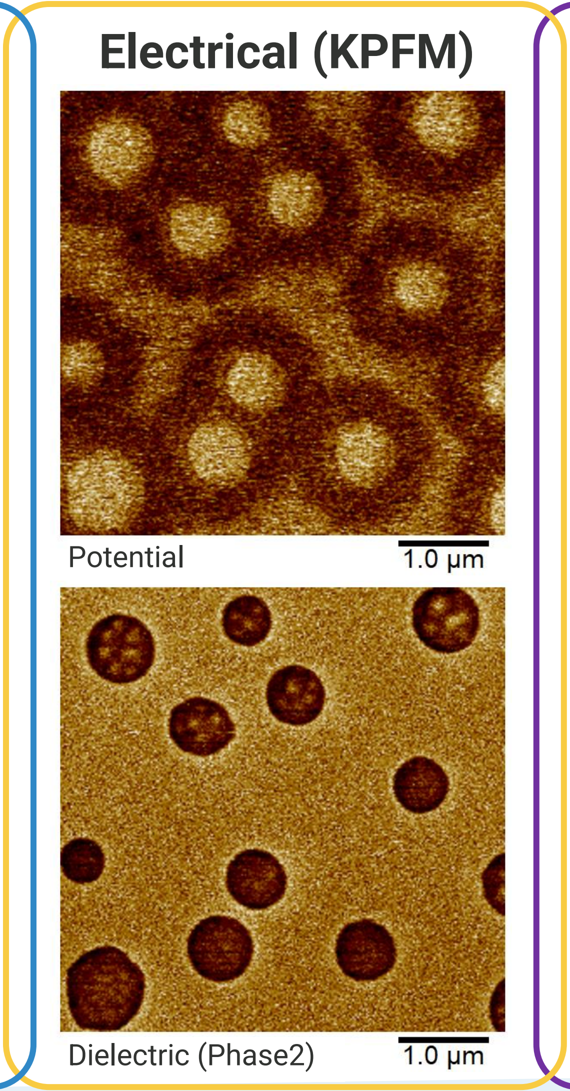


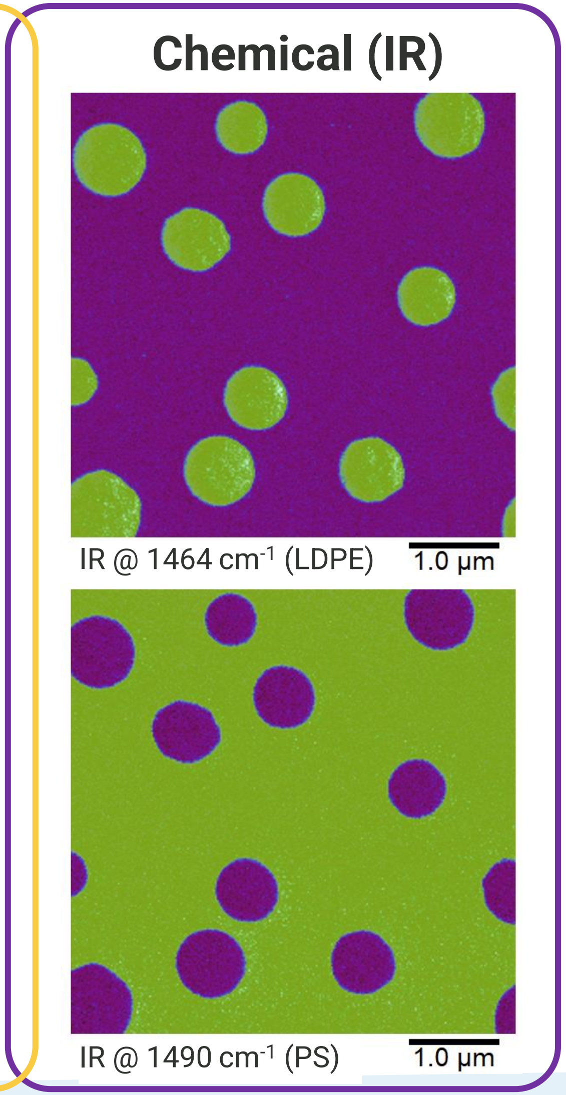
State of the Art for AFM-IR

5. Nanoscale Correlative Imaging - How They Work Together



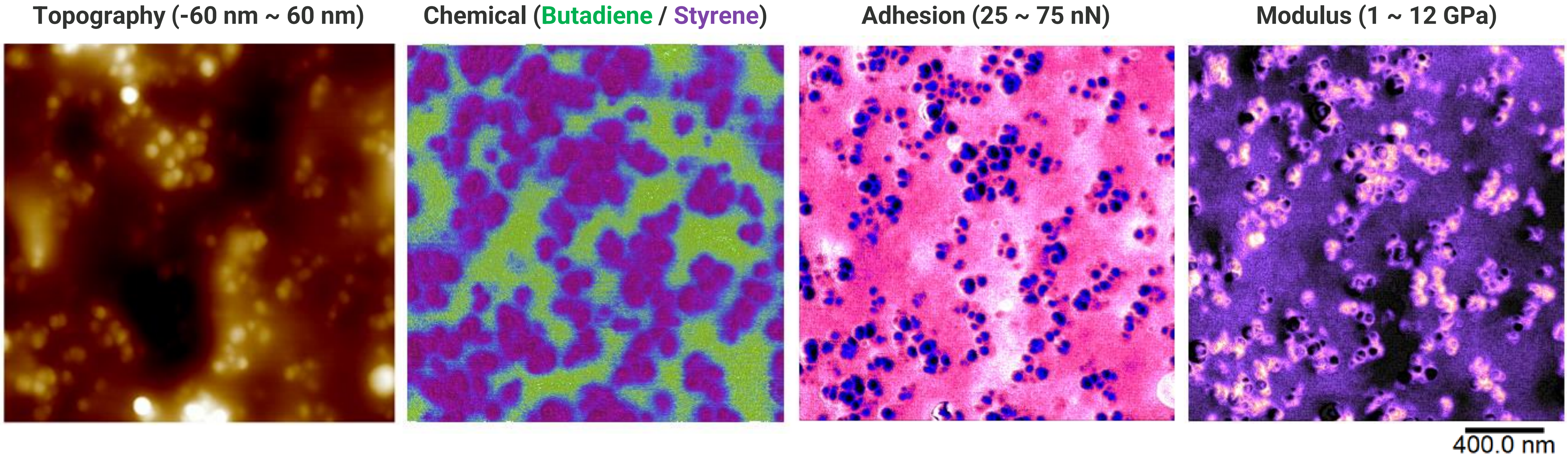






State of the Art for AFM-IR

5. Nanoscale Correlative Imaging - How They Work Together

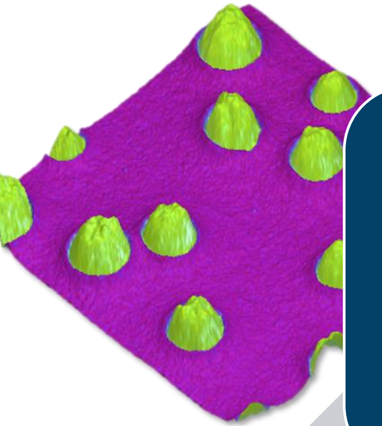


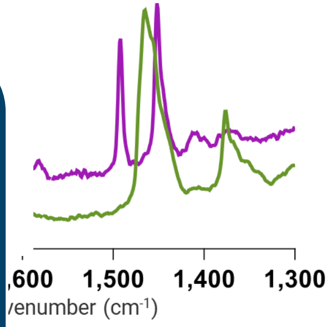
Topography *Chemistry* *Functions（NanoMechanics）*

Styrene-butadiene rubber with a carbon black filler

<< Tapping AFM-IR + PeakForce QNM >>

試料表面の ナノ形状，機械・物理特性，化学構造解析 から総合的に材料評価を行う新しい分析装置



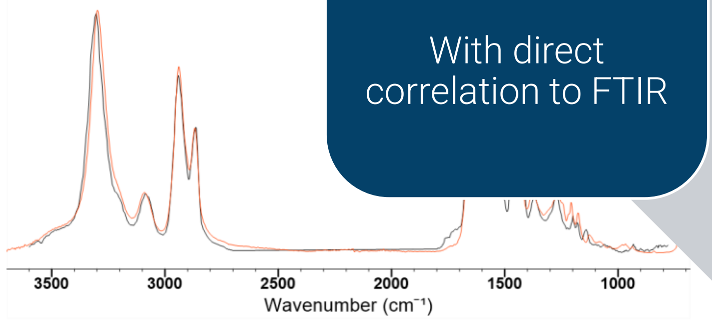


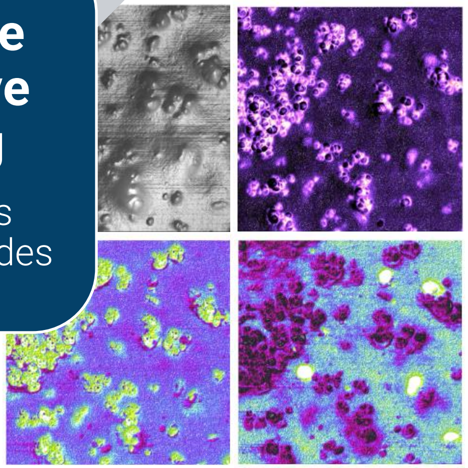
Nanoscale Imaging
With the best nanoIR sensitivity

Nanoscale Spectroscopy
With highest lateral resolution

Nanoscale Chemical ID
With direct correlation to FTIR

Nanoscale Correlative Mapping
With Bruker's PeakForce modes





今回ご紹介した装置が利用できる施設

福岡市産学連携交流センター
Fukuoka industry-academia Symphonicity

分析機器室にて利用可能

- Bruker 製 ナノ赤外分光装置 Dimension IconIR

Thank you!

BRUKER

Innovation with Integrity