# PiFM Nanoscale Chemical Probe for Novel Patterning Applications

Sung Park, D. Nowak, and T. R. Albrecht

*Molecular Vista, Inc.*

# Outline

- Introduction to PiFM
- Applications to Area Selective Deposition
- Applications to Sequential Infiltration Synthesis
- Applications to EUV Exposure Characterization
- Applications to Cross-section and Defect Analysis
- Summary

# Chemical Mapping

Atomic Resolution Elemental Mapping on SrTiO3 crystal by Super X EDS (EDX) system on Titan 80-300 Aberration Corrected Scanning Transmission Electron Microscope

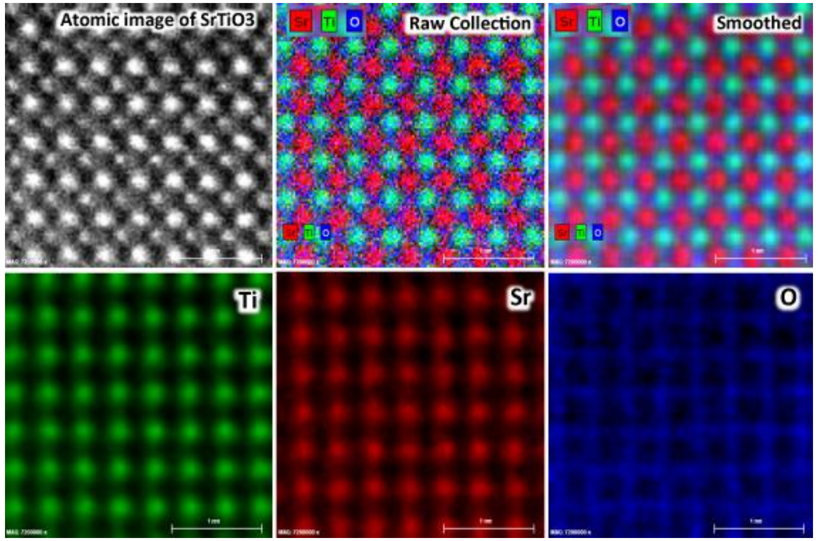



Image credit: North Carolina State Univ. Analytical Instrumentation Facility

https://www.aif.ncsu.edu/tem-lab/

Elemental mapping of a device structure by EDS (EDX)

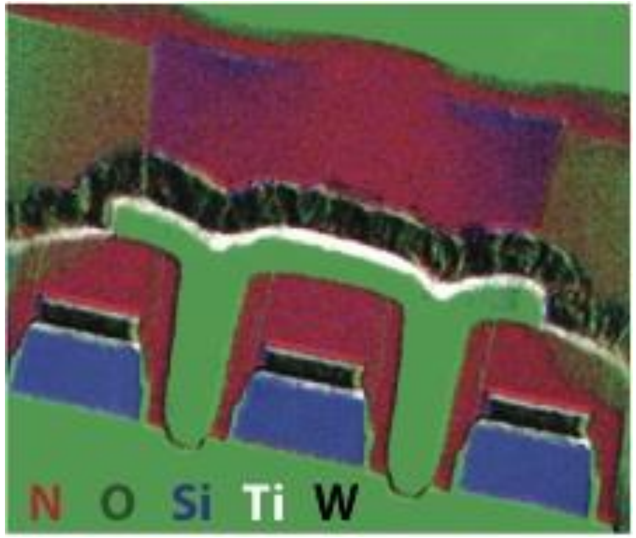



Image credit: Nanolab Techologies

http://www.nanolabtechnologies.com/TEM-STEM-EELS-EDS

- Advanced capability exists for elemental mapping (but fairly limited for organics)
- Wouldn't it be nice to have similar capability for molecular materials?

# FTIR: Infrared absorption "chemical fingerprint" spectrum

FTIR apparatus

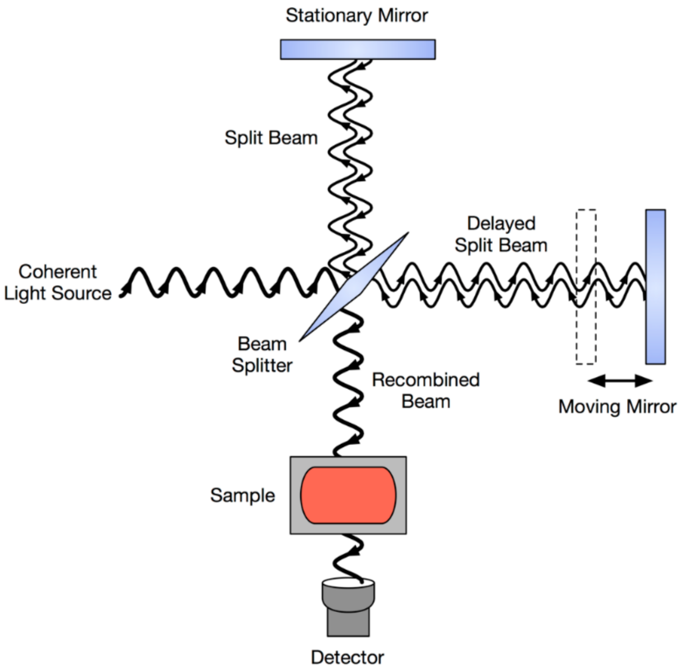



Image credit: Wikipedia

https://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy#/media/File:FTIR_Interferometer.png

Detailed absorption spectrum – chemical "fingerprint"

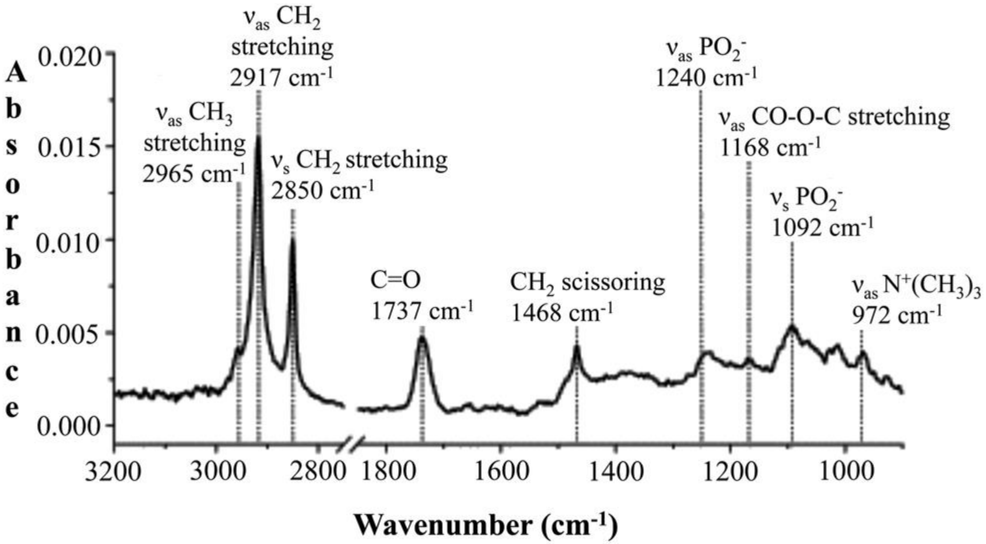


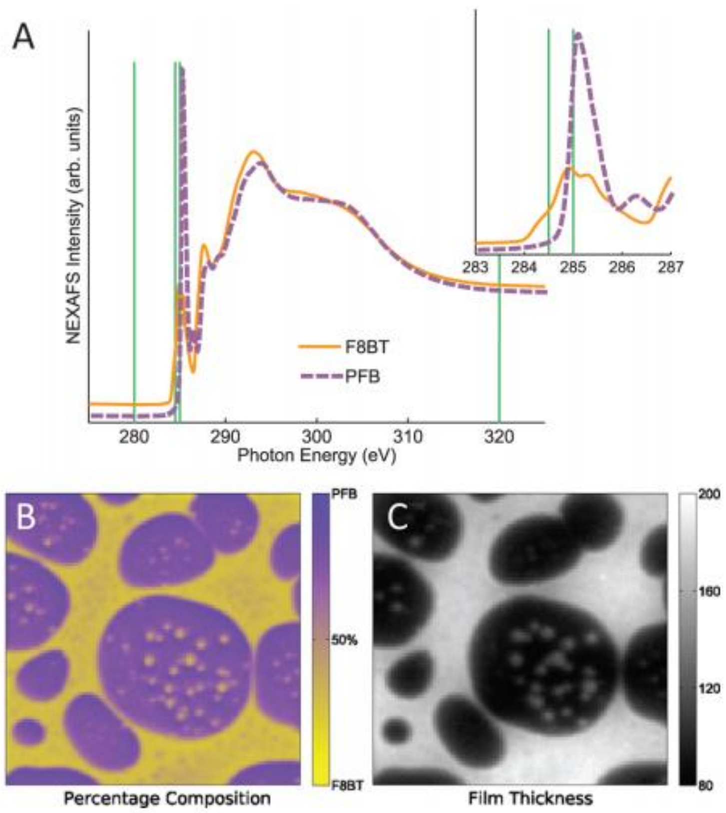

Image credit: Mudunkotuwa et al., Analyst 139, 870-881 (2014).

- Detailed spectra for analysis and identification of molecular materials
- Spatial mapping resolution limited by optical diffraction limit (> 1 $\mu$m)

# Tools for High Resolution Structural Characterization of Polymers

- X-ray Techniques
  - Wide-Angle X-ray Scattering (WAXS)
  - Small-Angle X-ray Scattering (SAXS)
  - Resonant Soft X-ray Scattering (r-SoXS)
- Neutron Techniques

Scanning Transmission X-ray Microscopy (STXM)




PFB

F8BT

10 x 10 μm

Image credit:
Watts, B.; McNeill, C. R.; Raabe, J. Synth. Met. 2012, 161, 2516.

- Polymers prone to damage to X-ray
- Synchrotron sources are not easily accessible

# PiFM: Detecting local effective polarizability via force

APPLIED PHYSICS LETTERS **97**, 073121 (2010)

## Image force microscopy of molecular resonance: A microscope principle

I. Rajapaksa, K. Uenal, and H. Kumar Wickramasinghe[a)]
*Department of Electrical Engineering and Computer Science, University of California, Irvine, California 92697, USA*

(Received 3 June 2010; accepted 12 July 2010; published online 20 August 2010)

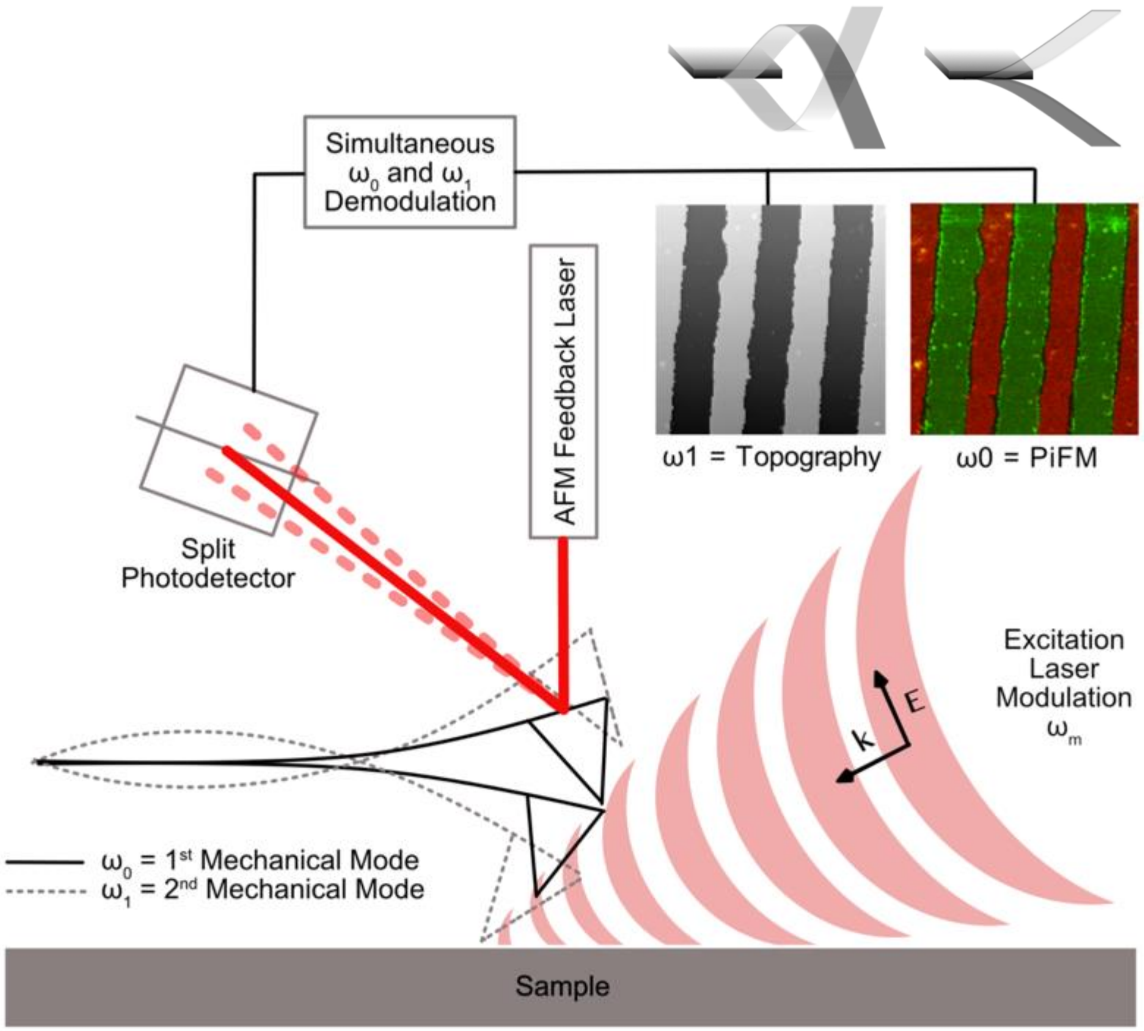
We demonstrate a technique in microscopy which extends the domain of atomic force microscopy to optical spectroscopy at the nanometer scale. We show that molecular resonance of feature sizes down to the single molecular level can be detected and imaged purely by mechanical detection of the force gradient between the interaction of the optically driven molecular dipole and its mirror image in a platinum coated scanning probe tip. This microscopy and spectroscopy technique is extendable to frequencies ranging from radio to infrared and the ultraviolet. © *2010 American Institute of Physics*. [doi:10.1063/1.3480608]

Atomic force microscopes (AFM) have been successfully applied to nanometer scale imaging of chemical,[1] magnetic,[2,3] and electrostatic[4,5] properties of surfaces. These microscopes rely on probe tips (typically silicon) suitably modified to detect the specific property of interest and to translate it into a detectable force. However, except for the magnetic resonance force microscope[6] which has been used

optical power at the entrance pupil of the objective was adjusted to be 100 $\mu$W. We used a cantilever with stiffness constant k=3 n/m and first mechanical resonance $f_0$ =65 kHz. We chose a laser modulation frequency $f_m$ =360 kHz and the frequency at the upper sideband $f_0+f_m$ was detected at 425 kHz.

In the first experiment, we pipetted a 100 $\mu$L drop of

# PiFM – Multimodal AFM detection




$\omega_1$ = dynamic AFM topographic imaging with ~ 1 nm amplitude

$\omega_m$ = Laser modulation ($\omega_m = \omega_1 - \omega_0$)

$\omega_0$ = PiFM Response

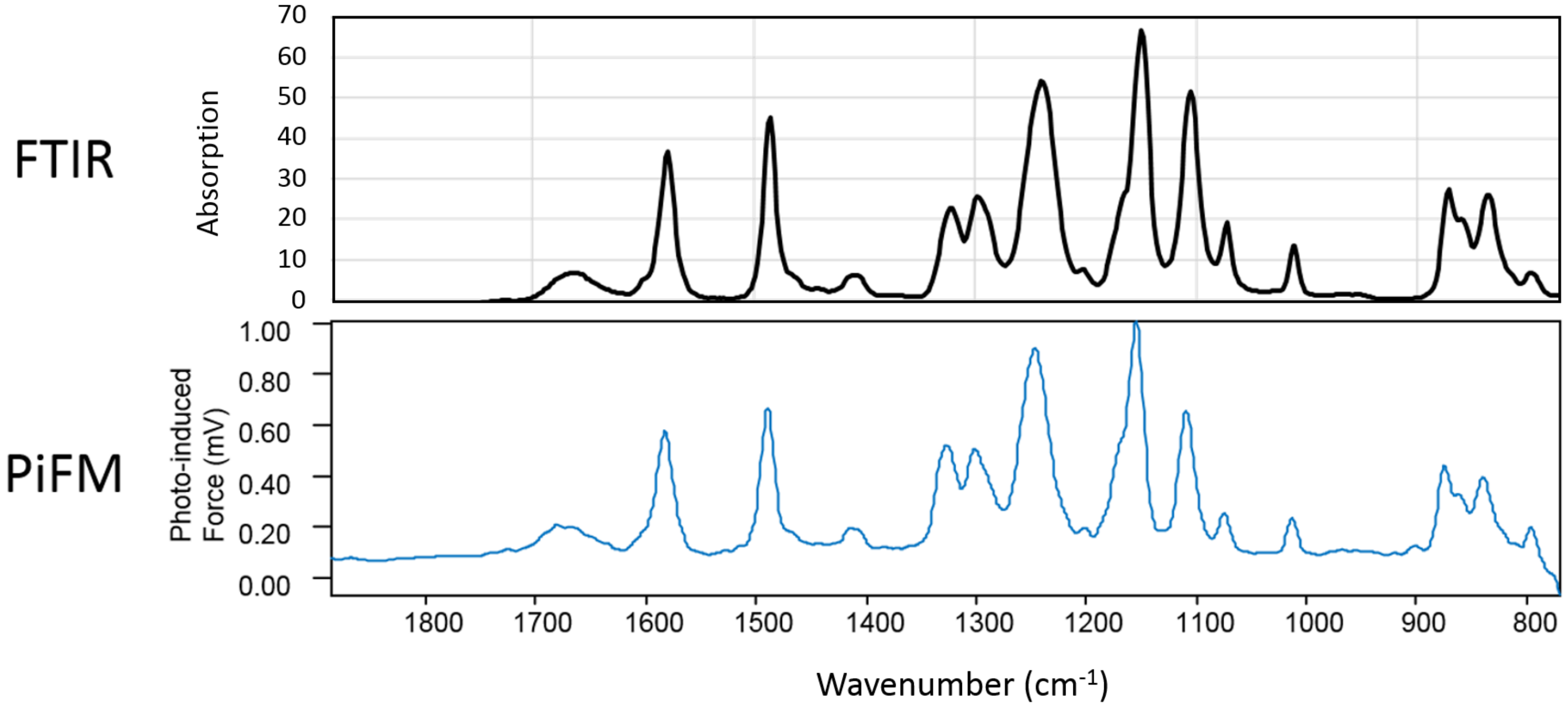
Two modulations on the Van der Waals force at $\omega_1$ when laser shines on the sample at $\omega_m$ :

1. Induced dipole force
2. van der Waals mediated force

Use tunable IR laser sources to generate spectrum as well as spectral images

# Agreement between PiFM and conventional IR spectra

- Good correlation with bulk FTIR spectra – comparison on PES (polyethersulfone ) shown below
- Many times, slight shifts in peak wavenumber and amplitude are observed in PiFM spectra, due to the response from extremely small and localized populations of molecules
- One strength of the PiFM method is capturing the behavior of materials in very small amounts and in confined spaces –environments that can differ greatly from samples on larger scales



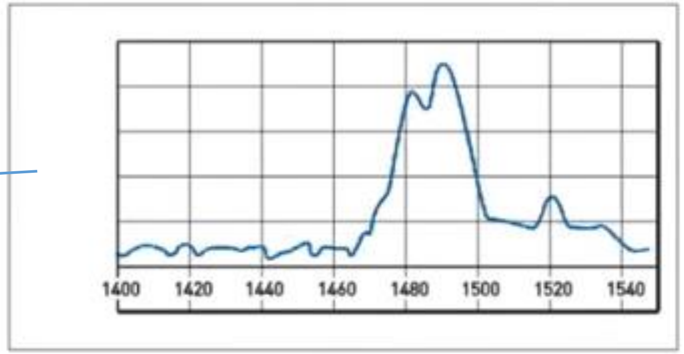
# hyPIR™ - PiFM based hyperspectral imaging

**hyPIR (hyperspectral infrared PiFM)** images consists of (n x n) pixels of PiFM spectra.

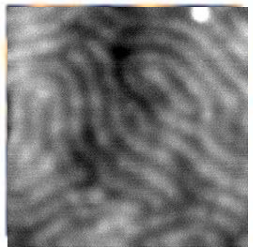
A nano scale hyPIR image can be generated in less than an hour for a 128 x 128 pixel image.

hyPIR Image


Spectrum from one pixel




Topography

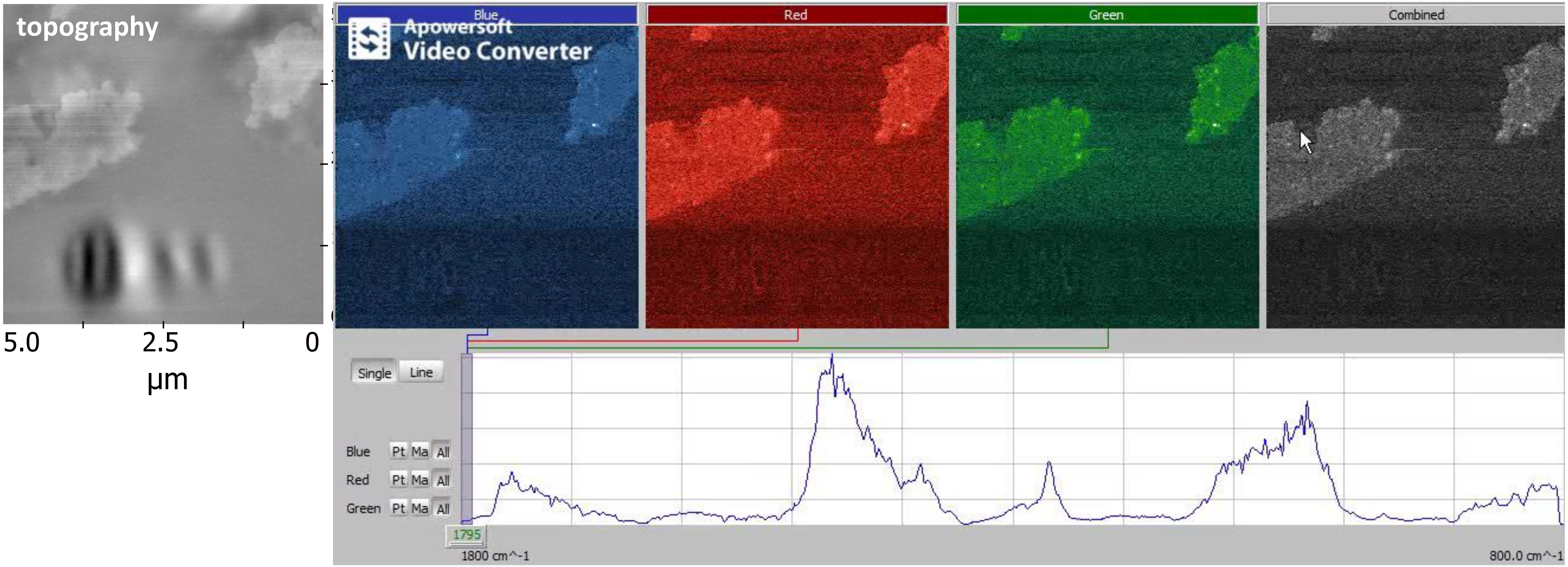


More information and a video demonstrating the hyPIR is available on Molecular Vista YouTube site.



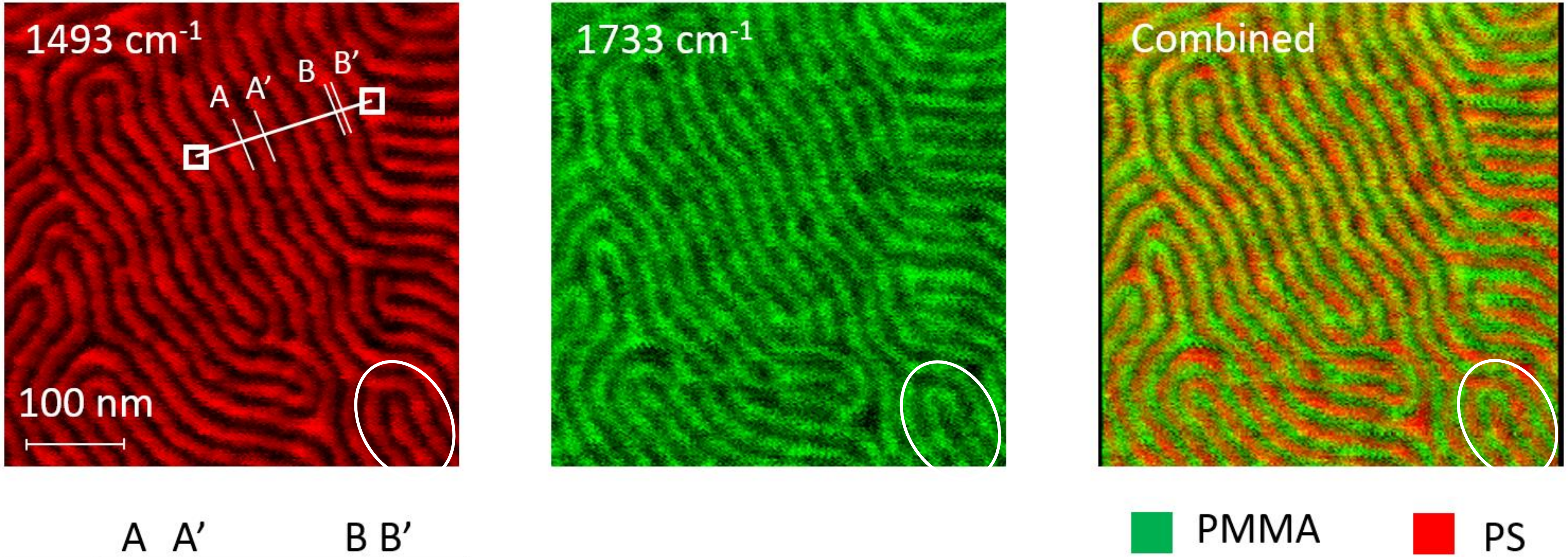
# hyPIR™: A Spectrum at Each Pixel – Asphalt Binder

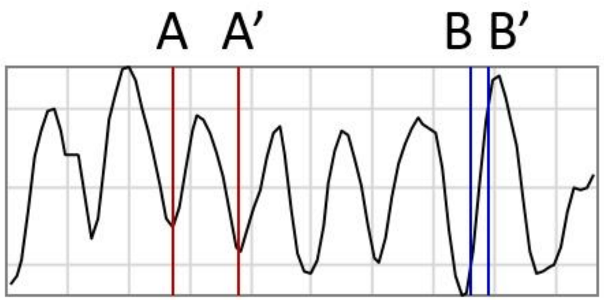



**WPI**: Xiaokong Yu and Nancy Burnham

# Exceptional Spatial Resolution in Chemical Mapping

Ps-*b*-PMMA Block Copolymer, $L_0$ = 22 nm




A-A’: 21 nm
B-B’: 6.5 nm

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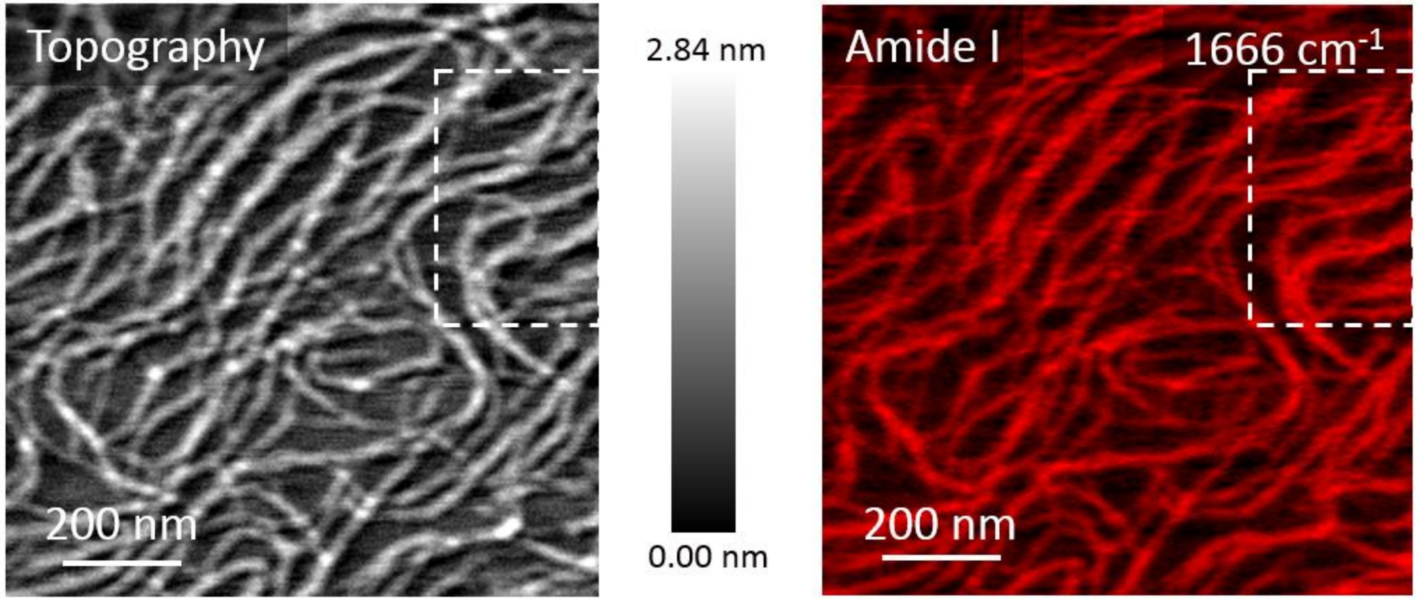
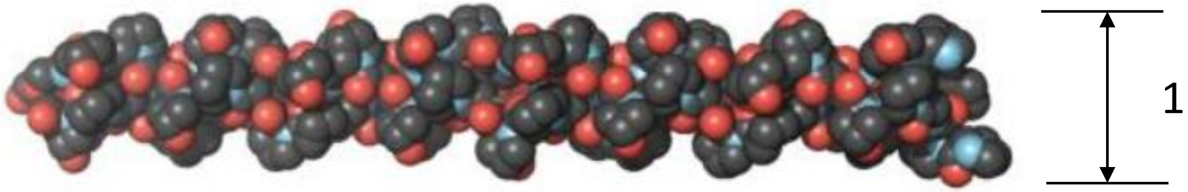
# Surface Sensitivity

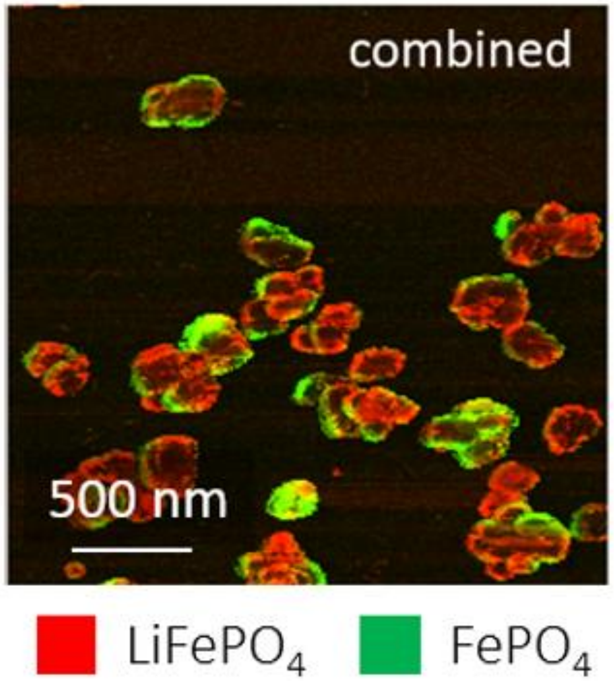


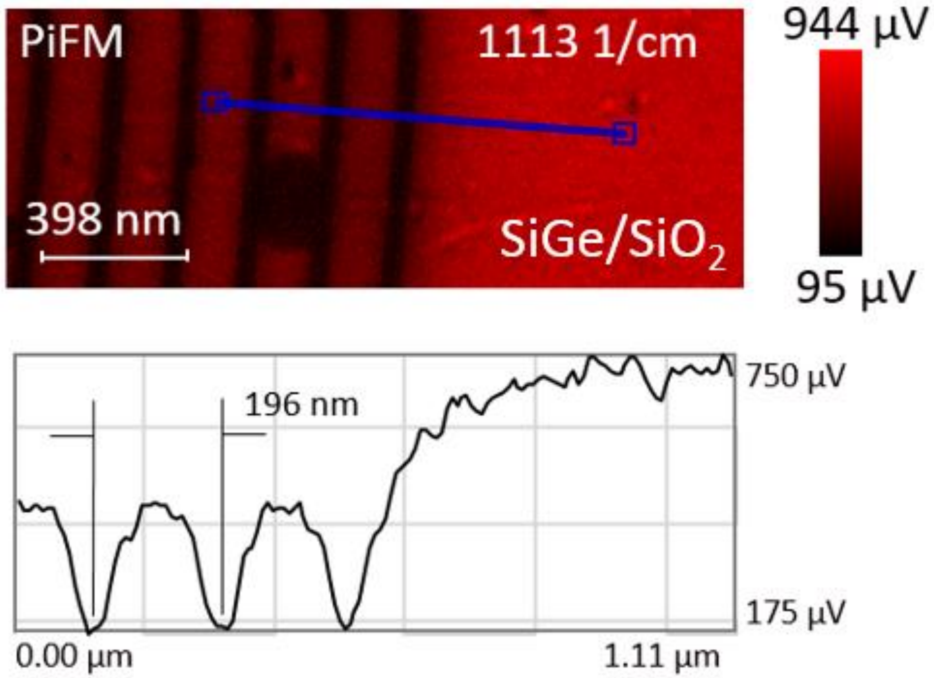



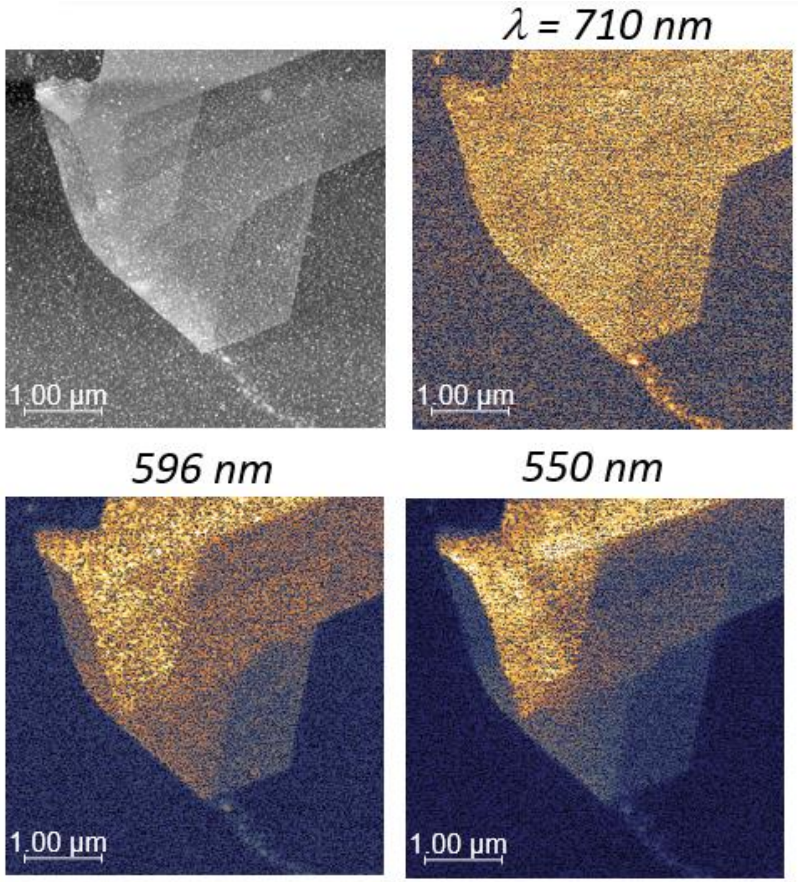

triple helix collagen

Sample: Courtesy of Jinhui Tao, PNNL

# Broad Applicability (Inorganic, Organic, 2D, Strain, Visible, etc.)




$MoS_2$

# Complements other Analytical Techniques

| | IR PiFM | Raman | FTIR | TOF-SIMS | XPS | TXRF | SEM/EDS | TEM | Auger |
|---|---|---|---|---|---|---|---|---|---|
| **Species Detected** | M.I. | M.I. | M.I. | M.I. | M.I. | E.I. | E.I. | E.I. | E.I. |
| **Imaging/Mapping** | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| **Lateral Resolution** | < 10 nm | > 0.5 μm | > 10 μm | > 0.2 μm | 10 μm – 2 mm | ~ 10 mm | 1 nm*<br>0.5μm EDS | 0.2 nm | > 10 nm |
| **Depth Probed** | 20 nm | > 500 nm | 1 μm | 1 nm | 10 nm | 10 nm | 1 μm | ~ 100 nm | 10 nm |

* Imaging    M.I. Molecular information    E.I. Elemental information

## Example Application of PiFM to ASD:

## PiFM study of SAM/ALD

# Info from Web on ALD $Al_2O_3$

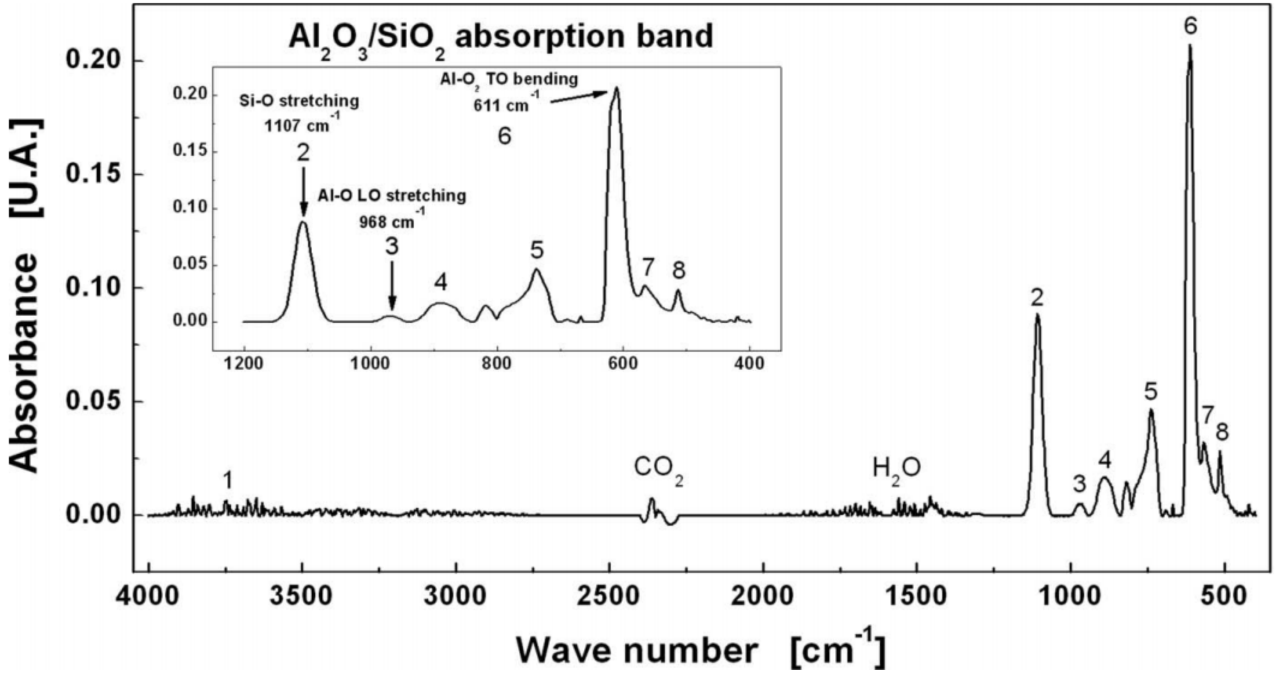



Table I. Peak designation, wave number of the peak's maximum absorbance, and associated vibrational modes of the corresponding chemical bonds for the as-deposited FTIR spectrum of $Al_2O_3$/ $SiO_X$ /Si.

| Number | Position [$cm^{-1}$] | Mode Type | Chemical Bond |
|---|---|---|---|
| 1 | 3716 | Stretching | AlO-H |
| 2 | 1107 | TO Stretching | Si-O |
| 3 | 968 | LO Stretching | Al-O |
| 4 | 889 | Condensed Tetrahedra | $Al\text{-}O_4$ |
| 5 | 739 | Condensed Tetrahedra Stretching | $Al\text{-}O_4$ |
| 6 | 611 | TO Bending | $Al\text{-}O_2$ |
| 7 | 567 | Condensed Octahedra Stretching | $Al\text{-}O_6$ |
| 8 | 513 | Condensed Octahedra Stretching | $Al\text{-}O_6$ |

*Journal of The Electrochemical Society*, **160** (10) B201-B206 (2013)
0013-4651/2013/160(10)/B201/6/$31.00 © The Electrochemical Society

**Chemical and Morphological Characteristics of ALD $Al_2O_3$ Thin-Film Surfaces after Immersion in pH Buffer Solutions**

**Joel Molina Reyes,[z] Berni M. Perez Ramos, Carlos Zuñiga Islas, Wilfrido Calleja Arriaga, Pedro Rosales Quintero, and Alfonso Torres Jacome**

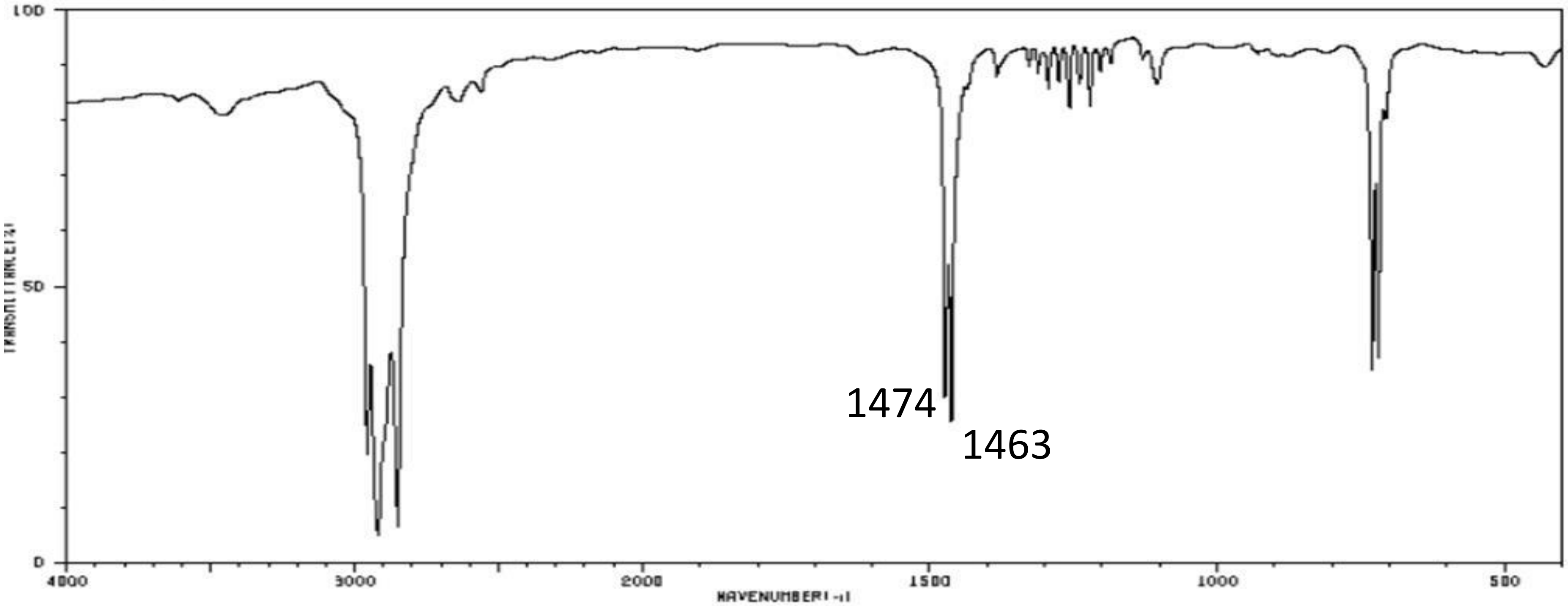
*National Institute of Astrophysics, Optics and Electronics, INAOE, Tonantzintla, Puebla 72000, México*

# Info from Web on SAM

| HIT-NO=4257 | SCORE= ( ) | SDBS-NO=10730 | IR-NIDA-03680 : LIQUID FILM |
|---|---|---|---|

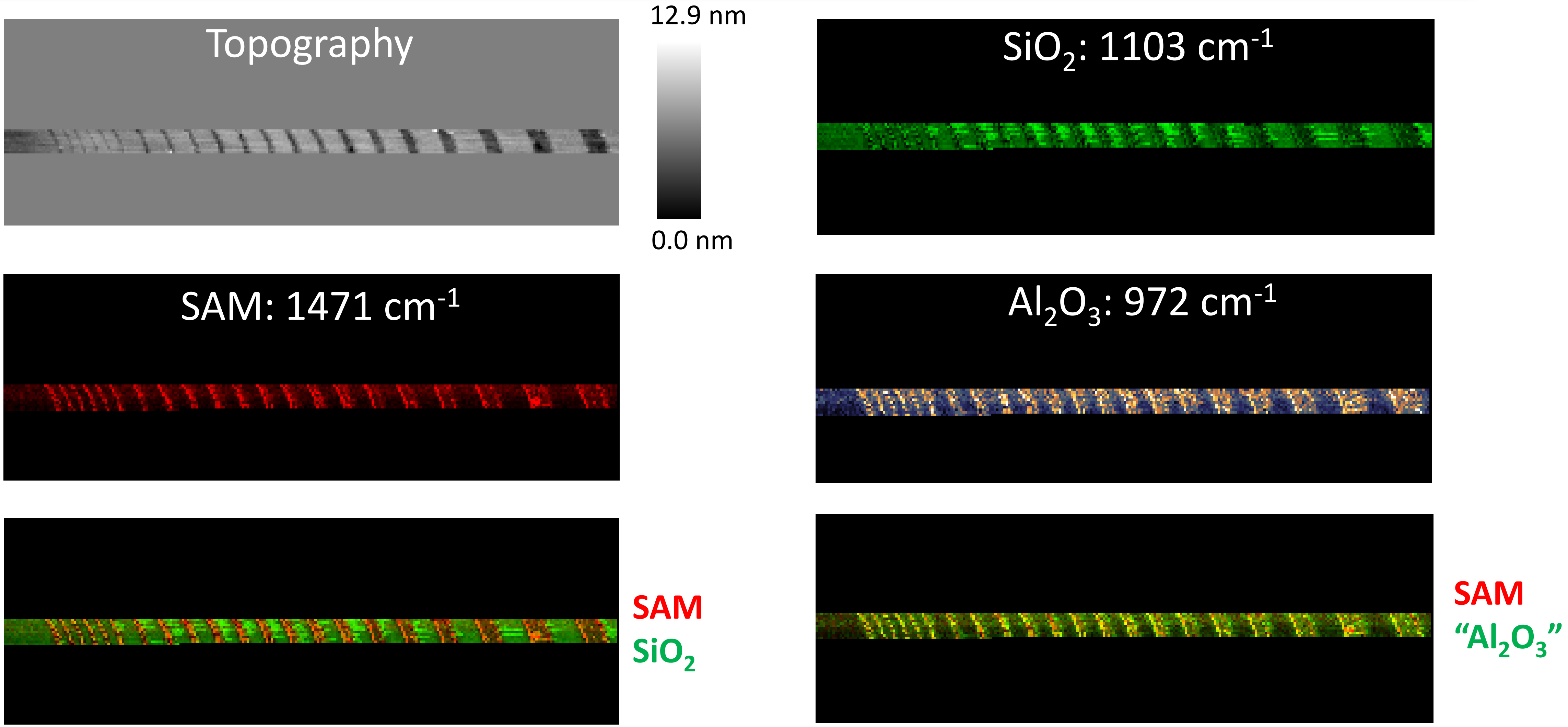
1-OCTADECANETHIOL

$C_{18}H_{38}S$

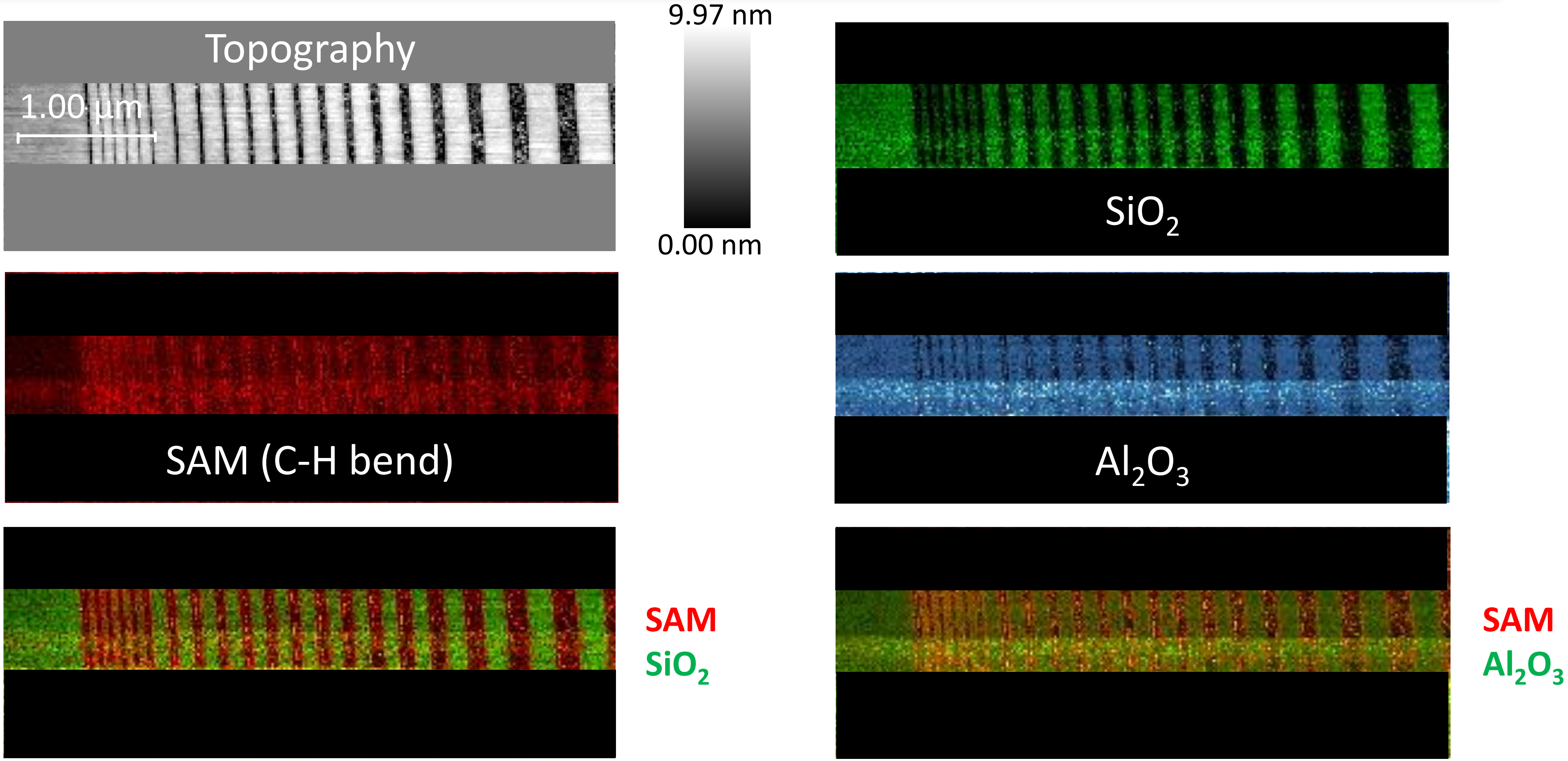



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 3611 | 81 | 2560 | 81 | 1276 | 84 | 720 | 36 |
| 3462 | 79 | 1474 | 28 | 1258 | 79 | 707 | 77 |
| 3452 | 79 | 1463 | 24 | 1240 | 84 | 431 | 86 |
| 2956 | 18 | 1384 | 84 | 1221 | 79 | | |
| 2918 | 4 | 1328 | 86 | 1203 | 86 | | |
| 2850 | 6 | 1312 | 84 | 1105 | 84 | | |
| 2639 | 79 | 1294 | 81 | 731 | 34 | | |

# PiFM Images on Sample 1



# PiFM Images on Sample 2



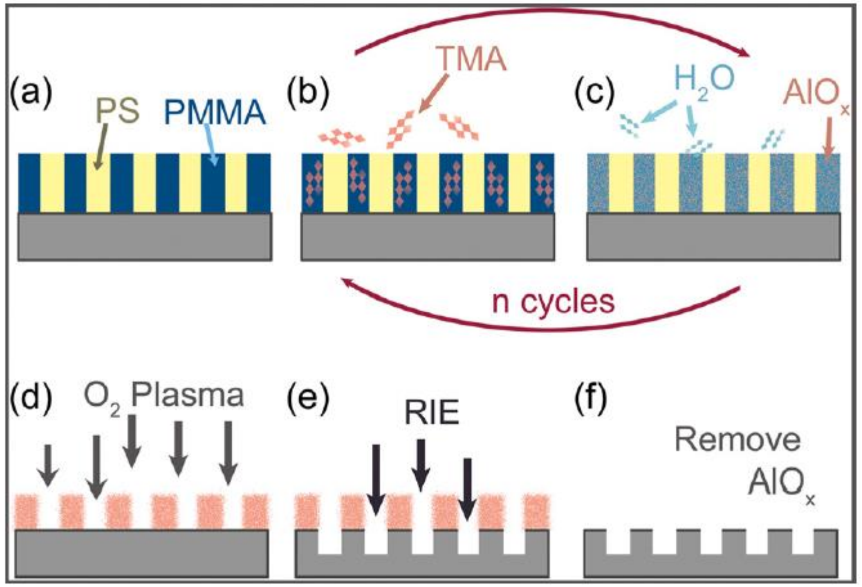
Example Application of PiFM to ASD:

PiFM study of Sequential Infiltration Synthesis (SIS) of $AlO_x$ in PS-b-PMMA Self-Assembled Fingerprint Patterns



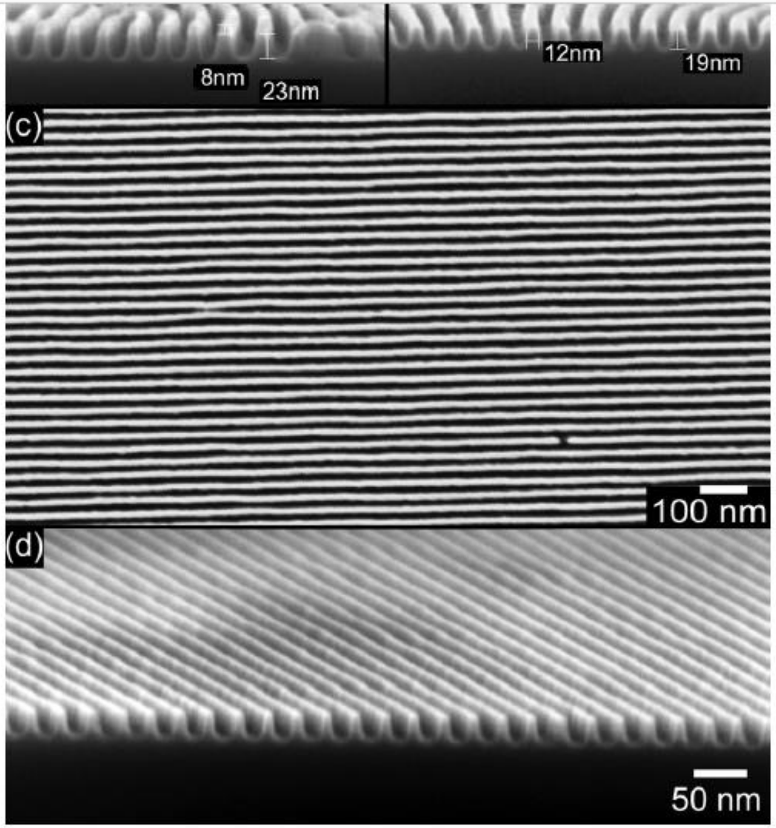
# Sequential Infiltration Synthesis (SIS)

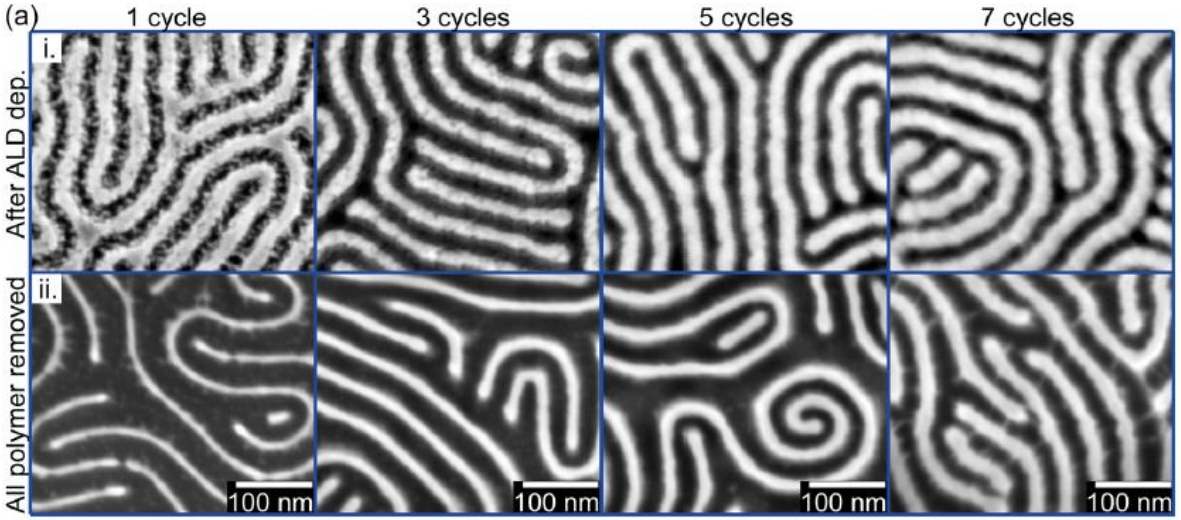



**SIS process invented by:**
Q. Peng, Y.-C. Tseng, S. B. Darling, and J. W. Elam, Adv. Mater. 22, 5129 (2010).

**These figures from:**
R. Ruiz, L. Wan, J. Lille, K. C. Patel, and E. Dobisz, "Image quality and pattern transfer in directed self assembly with block-selective atomic layer deposition," JVSTB 30, 06F202 (2012).

27 nm full pitch lines - pattern transfer to Si



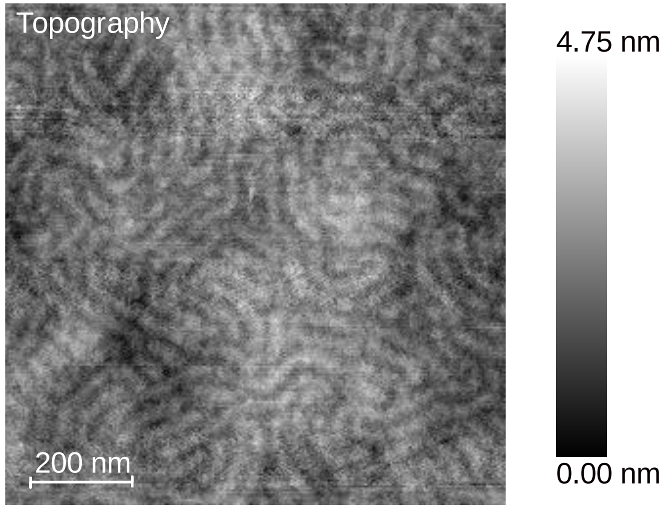




$AlO_x$ lines - 41 nm full pitch

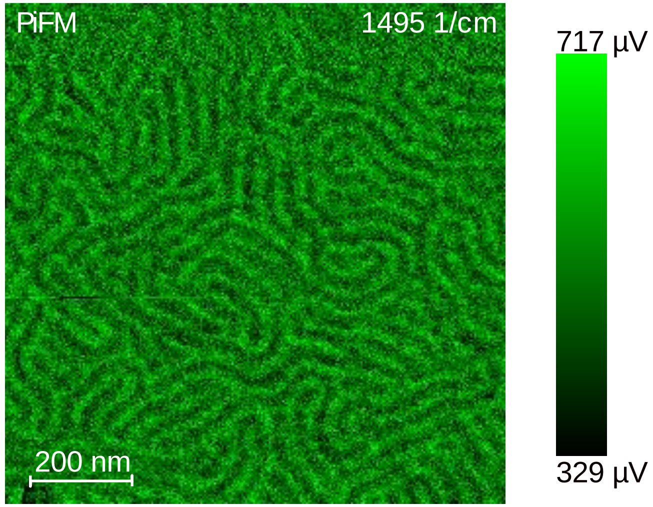
TMA (trimethyl aluminum ) reacts only with carbonyl groups in the PMMA. TMA → aluminum oxide by exposure to water. Use ALD tool run in static mode.

# Clean PS-b-PMMA (41 nm FP Lamellar) PiFM Images

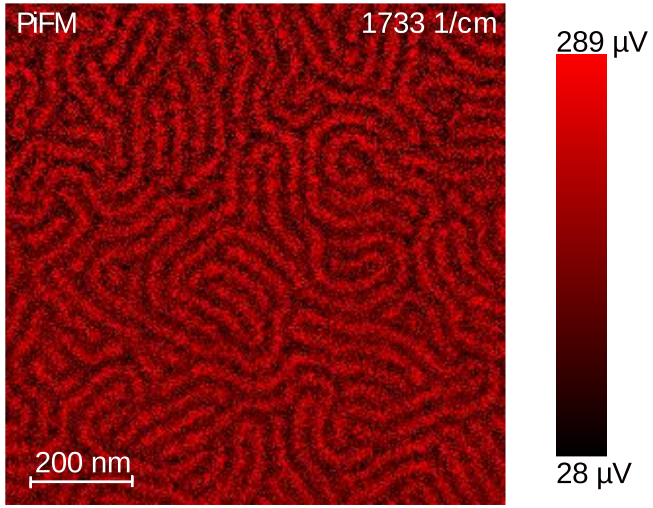
AFM Topography

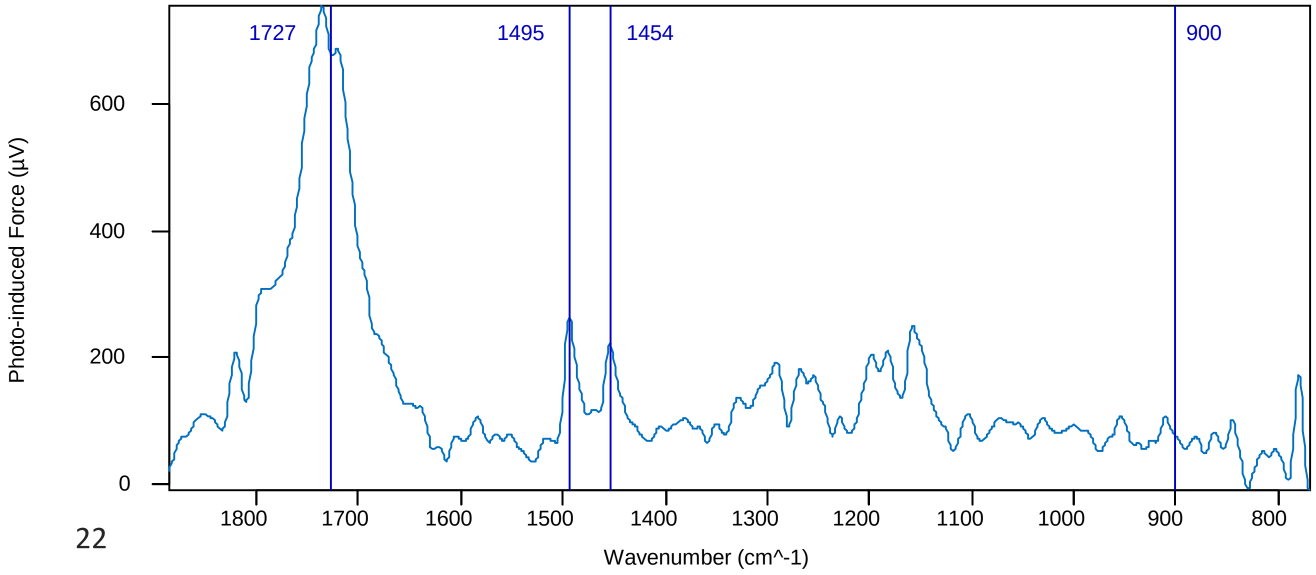



PS



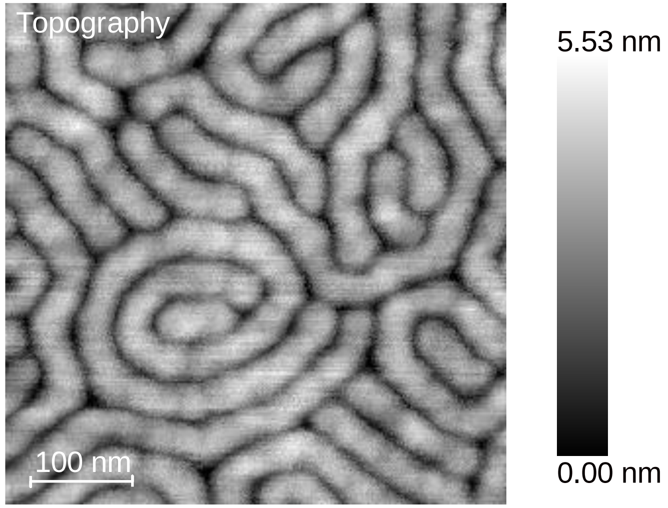

PMMA



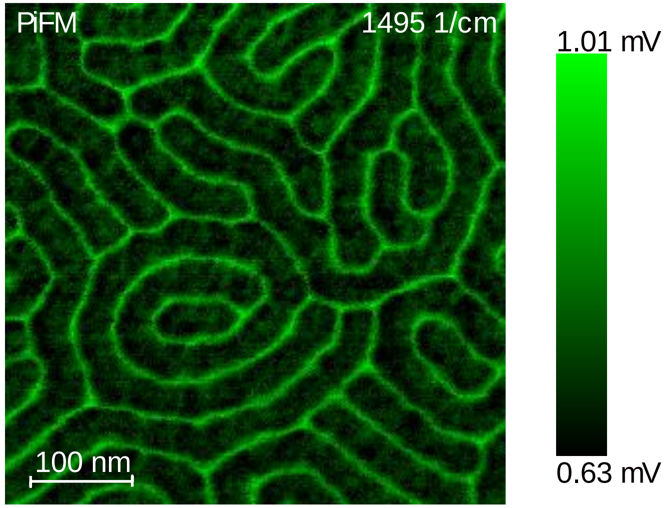



# SIS $AlO_x$ PS-b-PMMA (41 nm FP Lamellar) PiFM Images

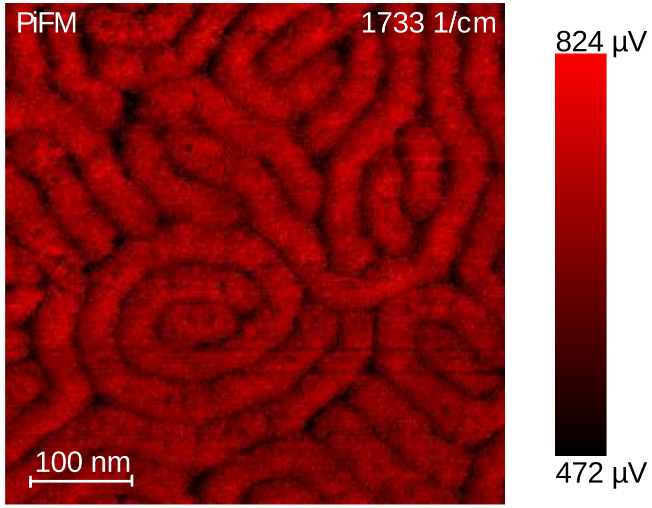
AFM Topography

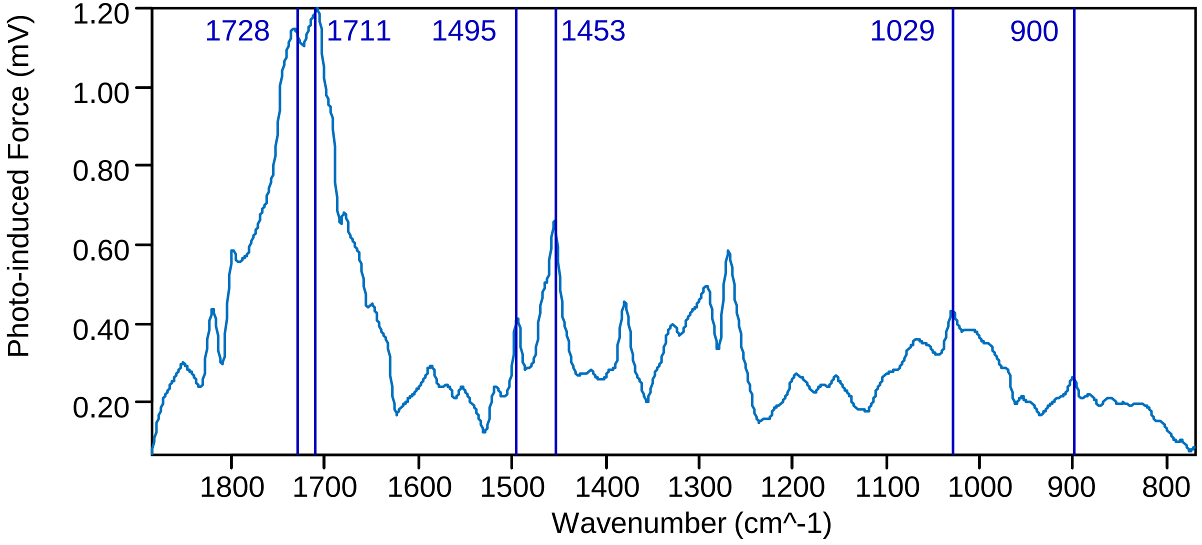



PS

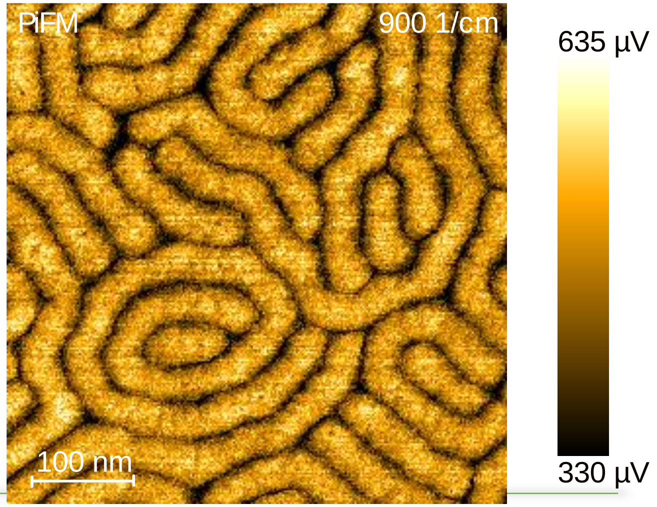



PMMA




AlOx



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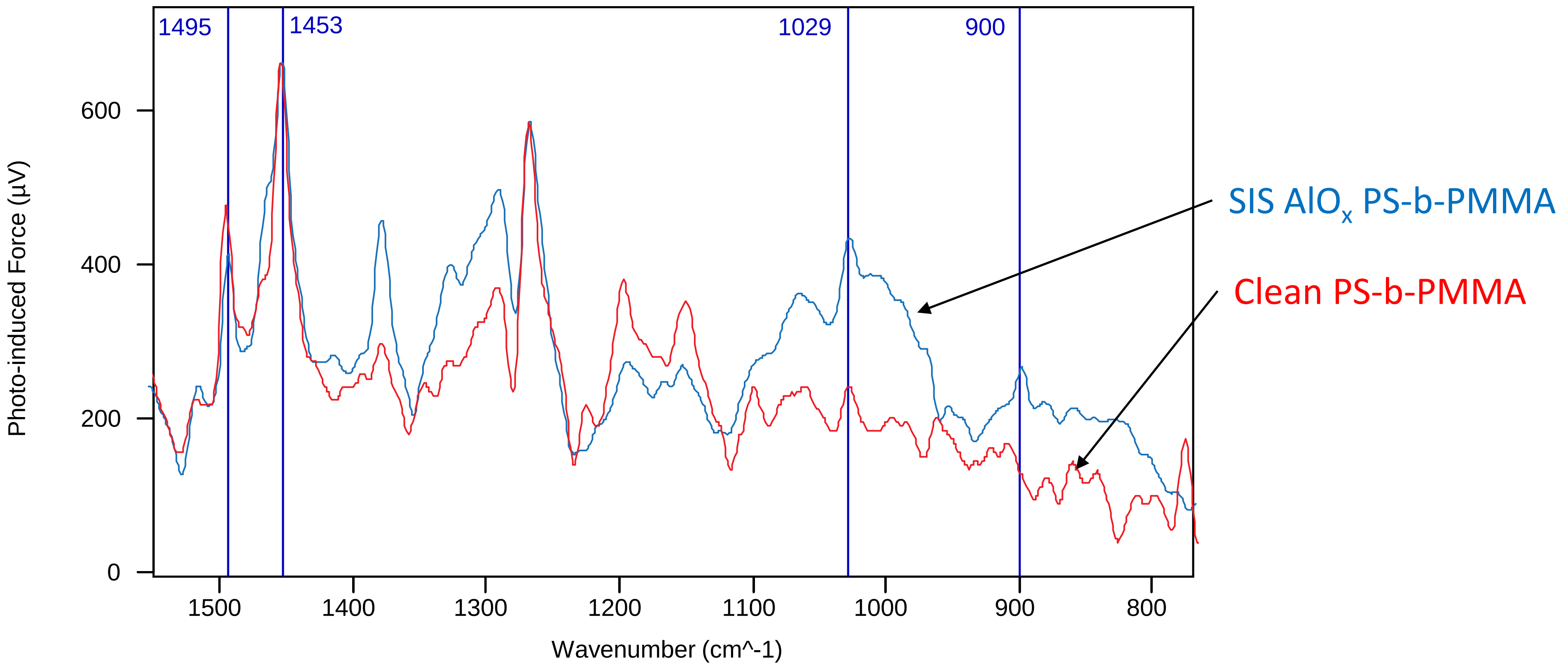
# SIS PS-b-PMMA and clean PS-b-PMMA PiFM spectra

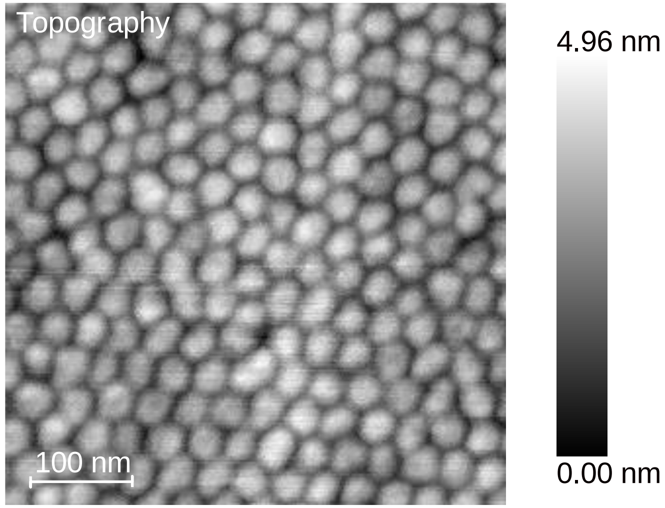



<u>SIS parameters for these samples:</u>

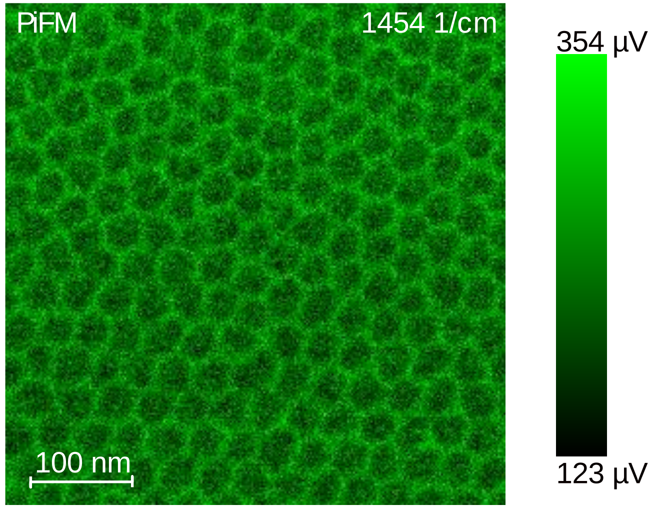
- 3 SIS cycles @ 90 C
- 5 min TMA
- $N_2$ purge
- 5 min $H_2O$

# SIS PS-b-PMMA (37 nm FP Hexagonal) PiFM Images

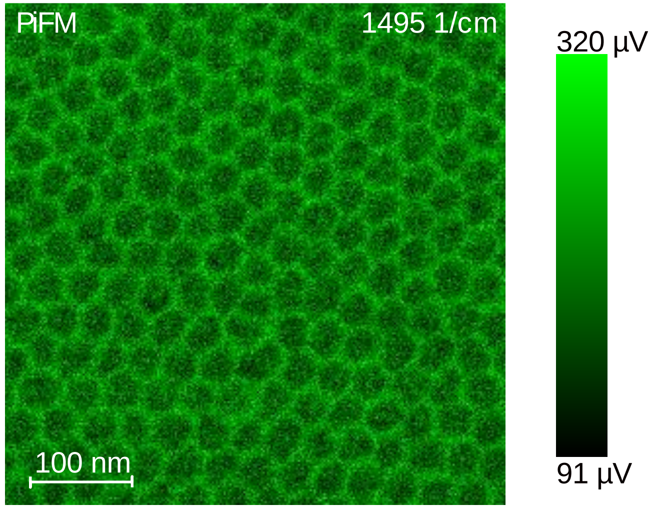
AFM Topography



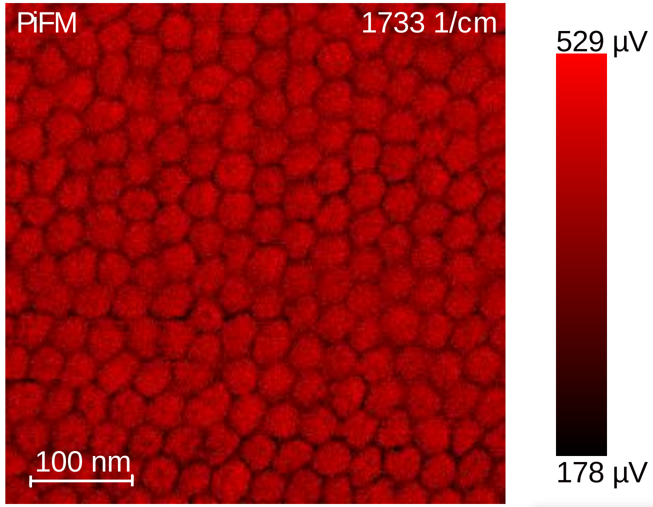

PS



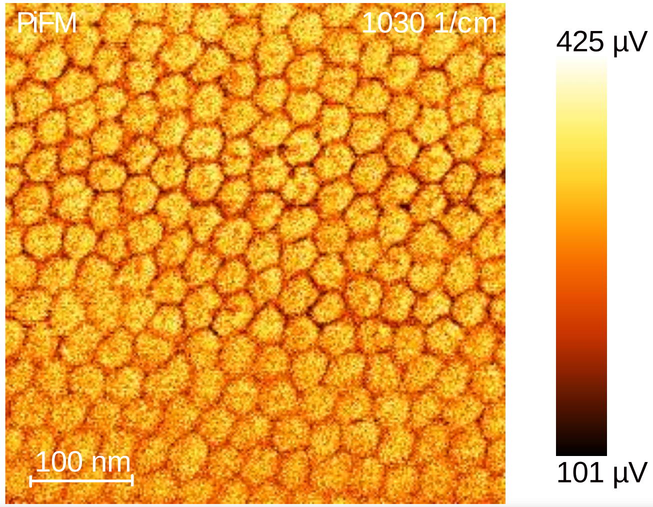

PS




PMMA

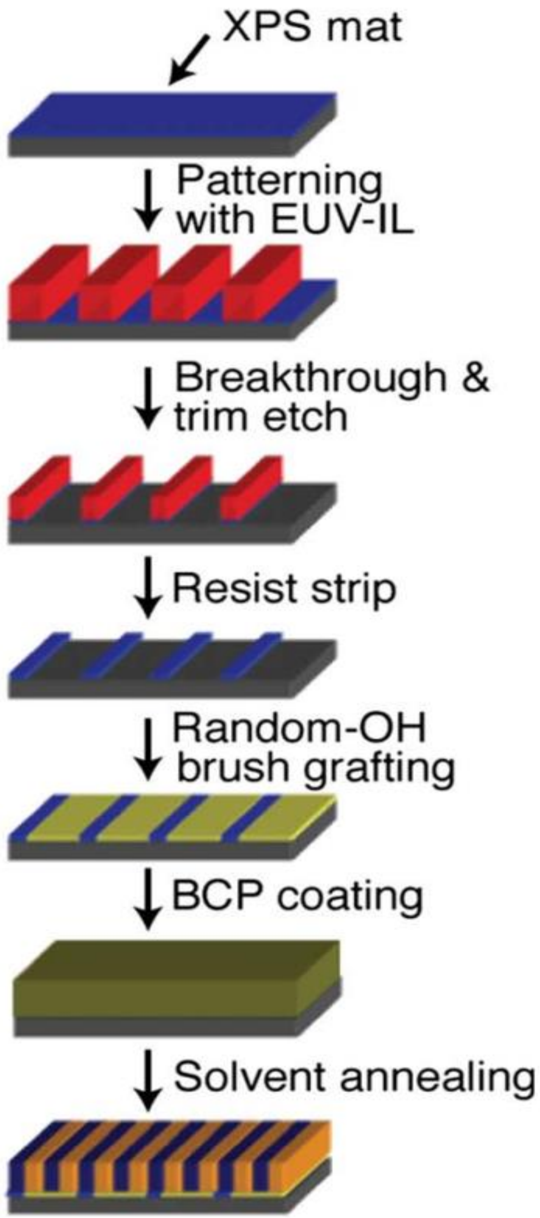



AlOx



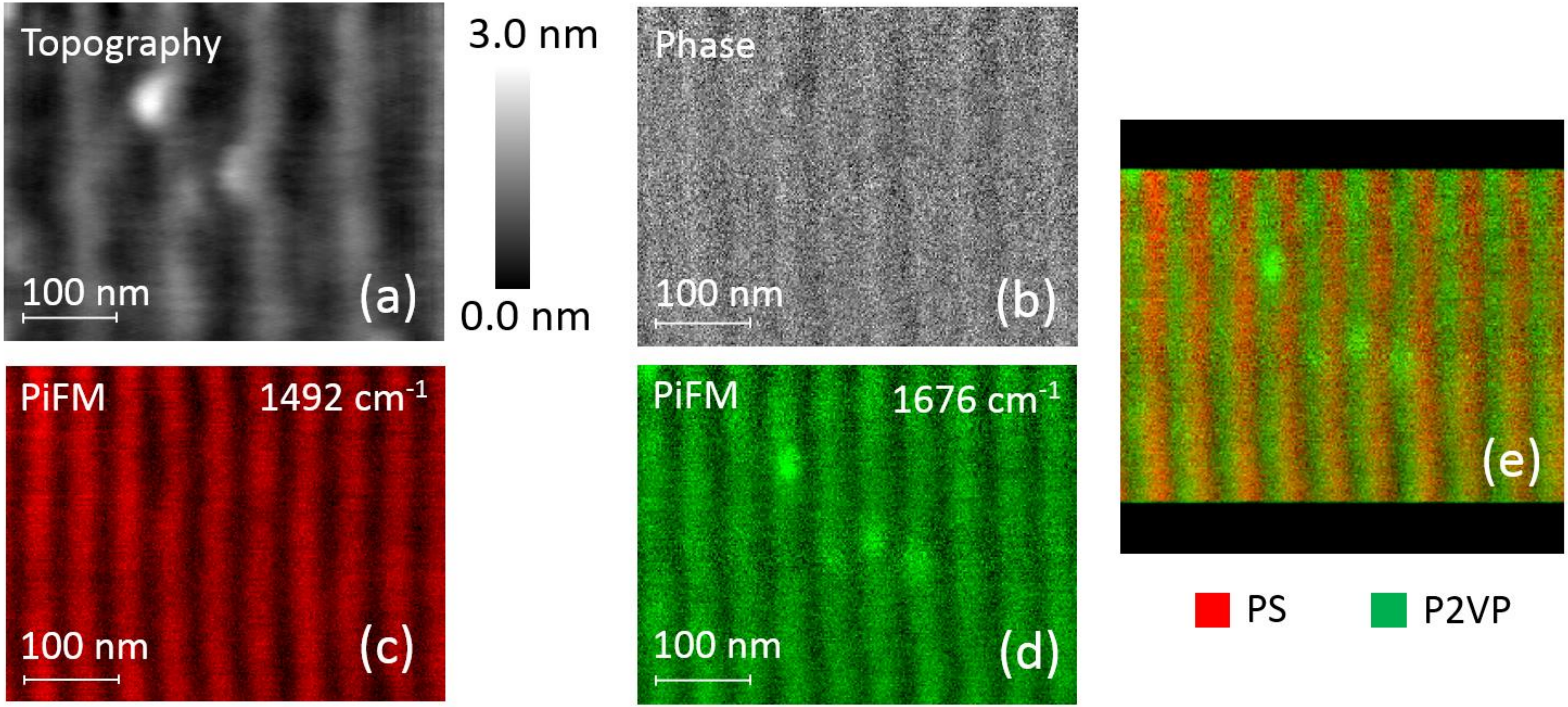
# Example Application of PiFM to Directed Self Assembly (DSA)

# Directed Self-Assembly (DSA) with PS-b-P2VP

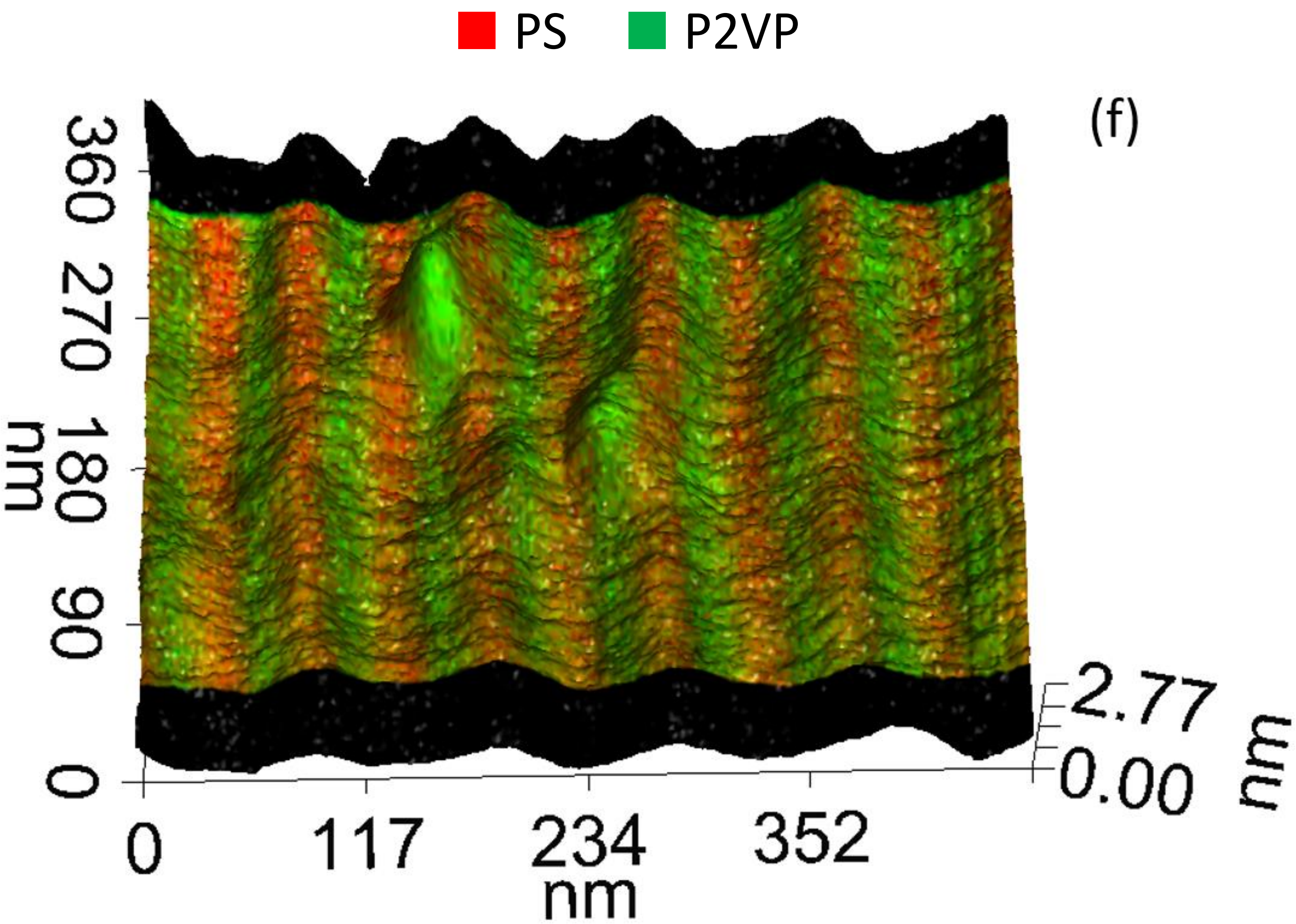


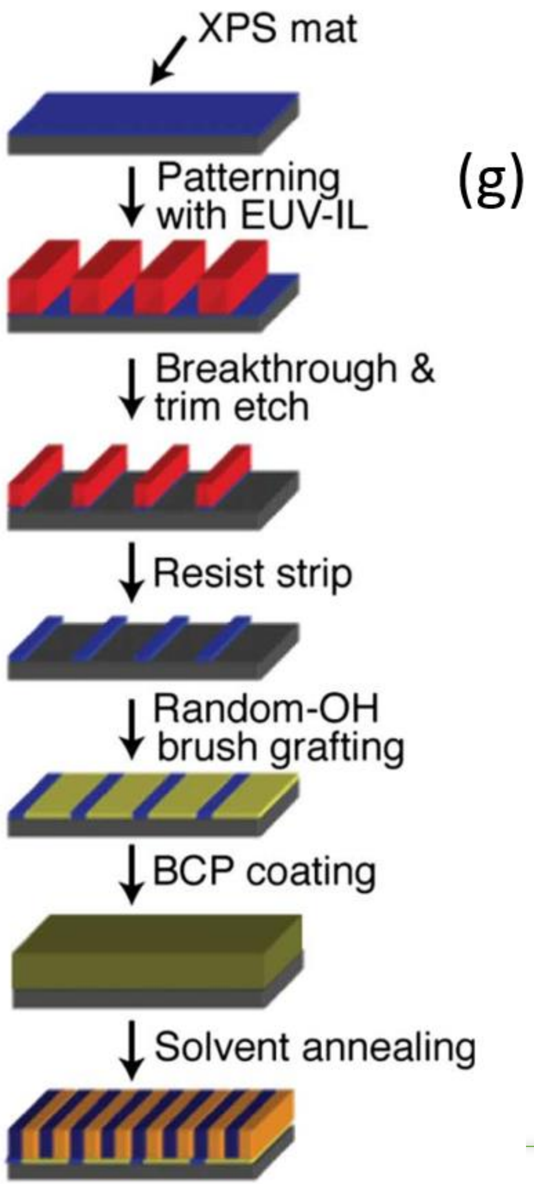

Multi-patterning is required for sub 20 nm patterns. One method utilizes DSA. Double patterning in DSA is shown schematically for PS-P2VP block copolymer.

# Directed Self-Assembly (DSA) with PS-b-P2VP



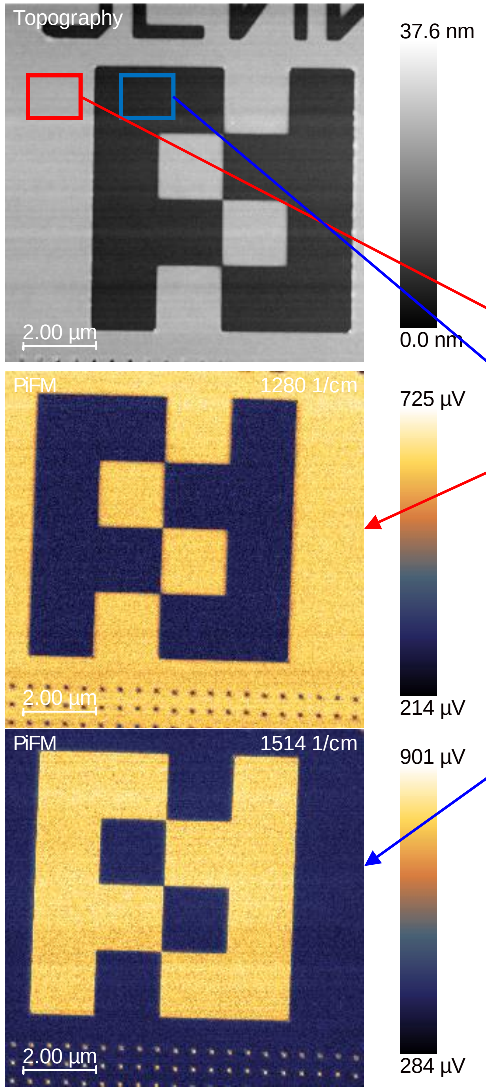
# Directed Self-Assembly (DSA) with PS-b-P2VP



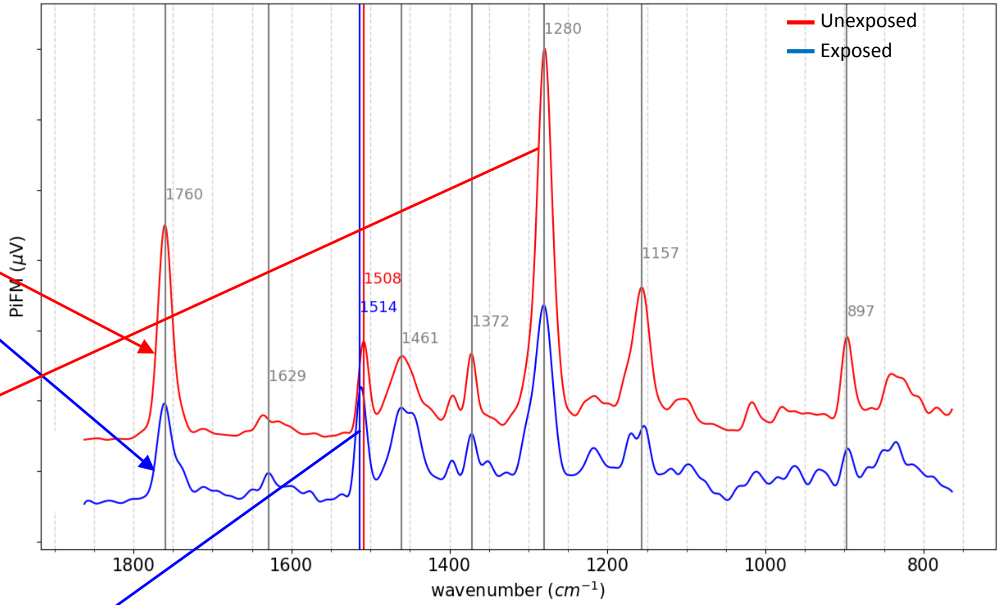



# Example Application of PiFM to EUV Lithography

# Imaging of Latent EUV Images in TBOC CA Resist

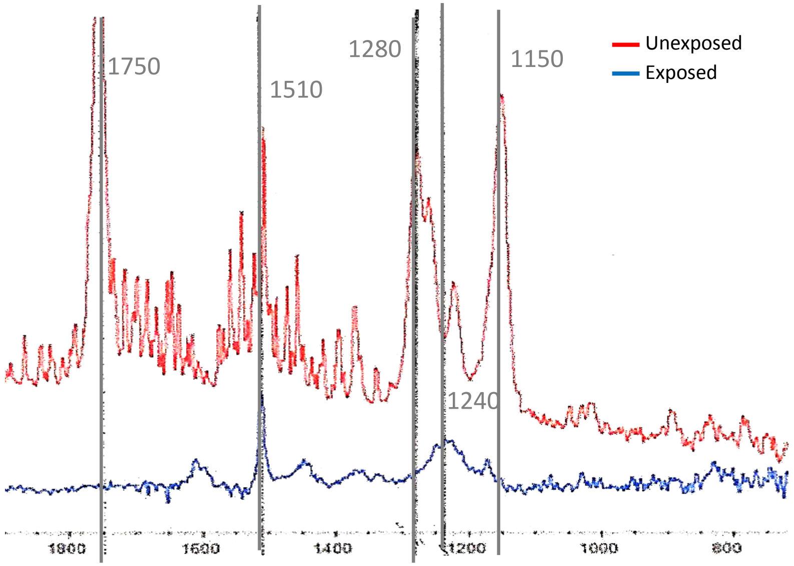



## PiFM spectra




*The averaged spectra taken in the red and blue regions highlighted on the topography image, which are the unexposed and exposed areas respectively.*

## FTIR spectra

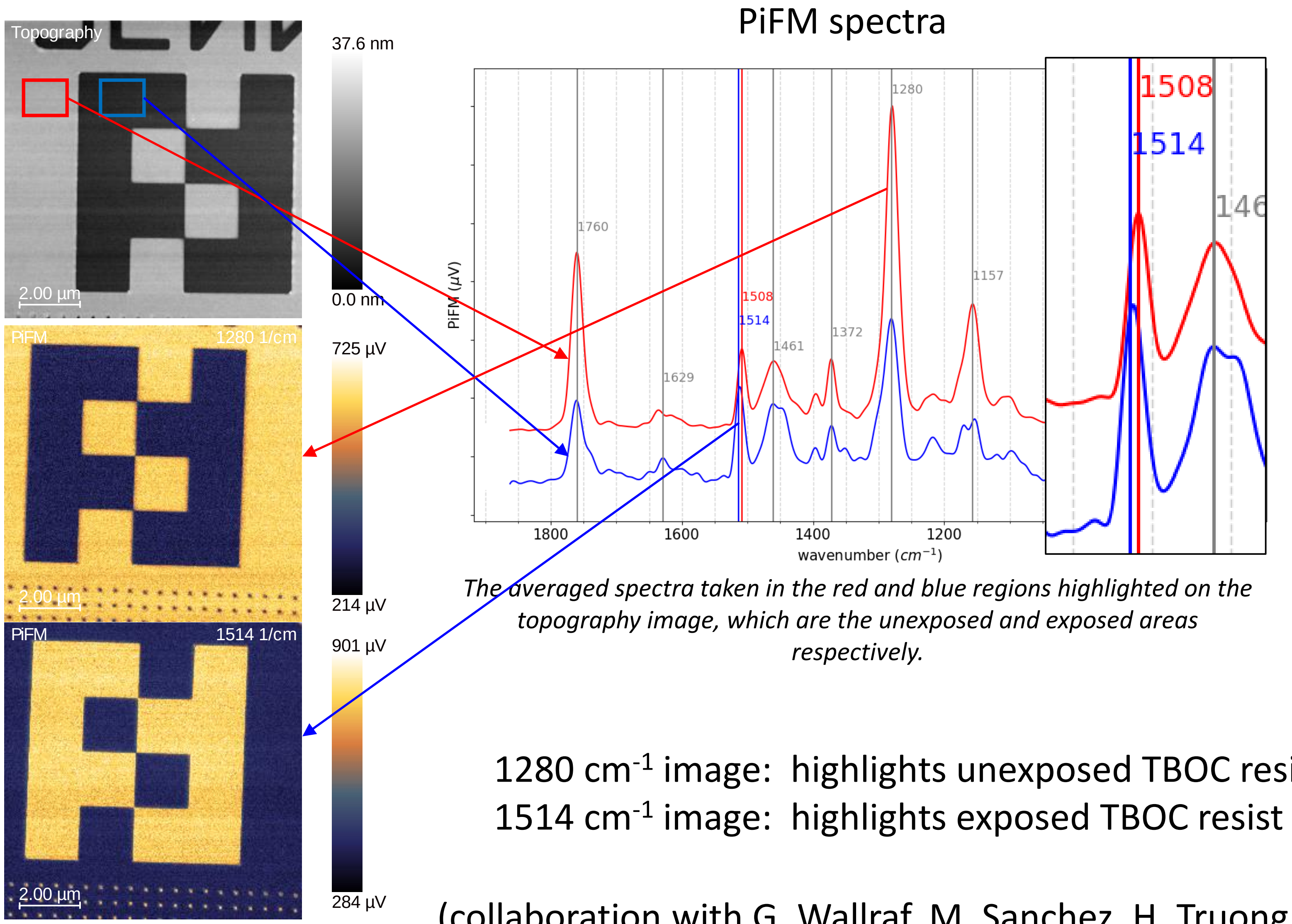



*Conventional FTIR spectra for the exposed and unexposed TBOC resist.*

- Exposed to 13.5 nm EUV at ALS, Berkeley
- 1280 $cm^{-1}$ image: highlights unexposed TBOC resist
- 1514 $cm^{-1}$ image: highlights exposed TBOC resist

(collaboration with G. Wallraf, M. Sanchez, H. Truong – IBM Almaden)

# Imaging of Latent EUV Images in TBOC CA Resist




*The averaged spectra taken in the red and blue regions highlighted on the topography image, which are the unexposed and exposed areas respectively.*

- PiFM can see chemical changes to molecular films
- Application to ASD:
- ✓ Study localized chemical modification / degradation of inhibitor films

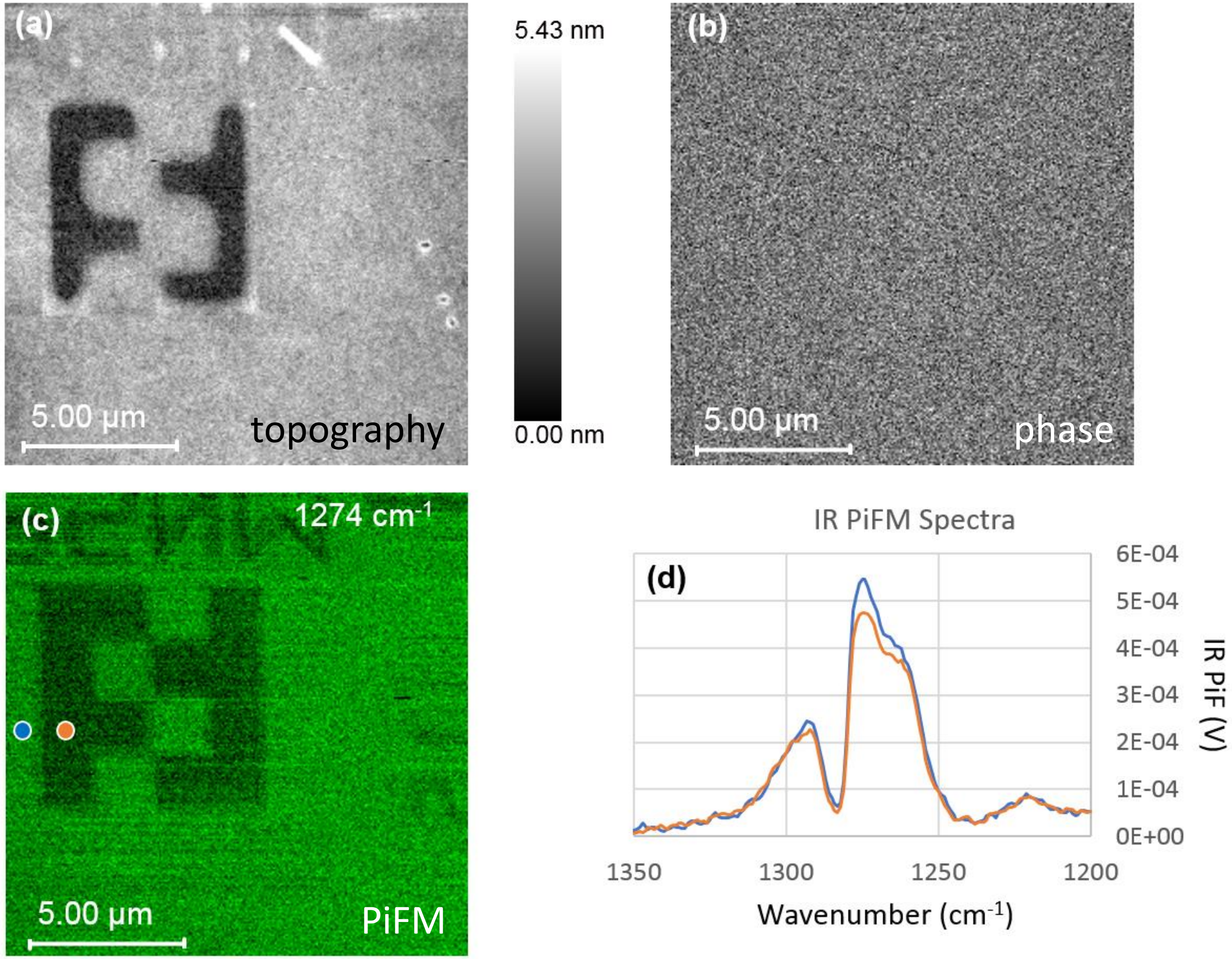
1280 $cm^{-1}$ image: highlights unexposed TBOC resist
1514 $cm^{-1}$ image: highlights exposed TBOC resist (peak shifts from 1508 to 1514 $cm^{-1}$)

(collaboration with G. Wallraf, M. Sanchez, H. Truong – IBM Almaden)



# Characterization of EUV Resist Exposure

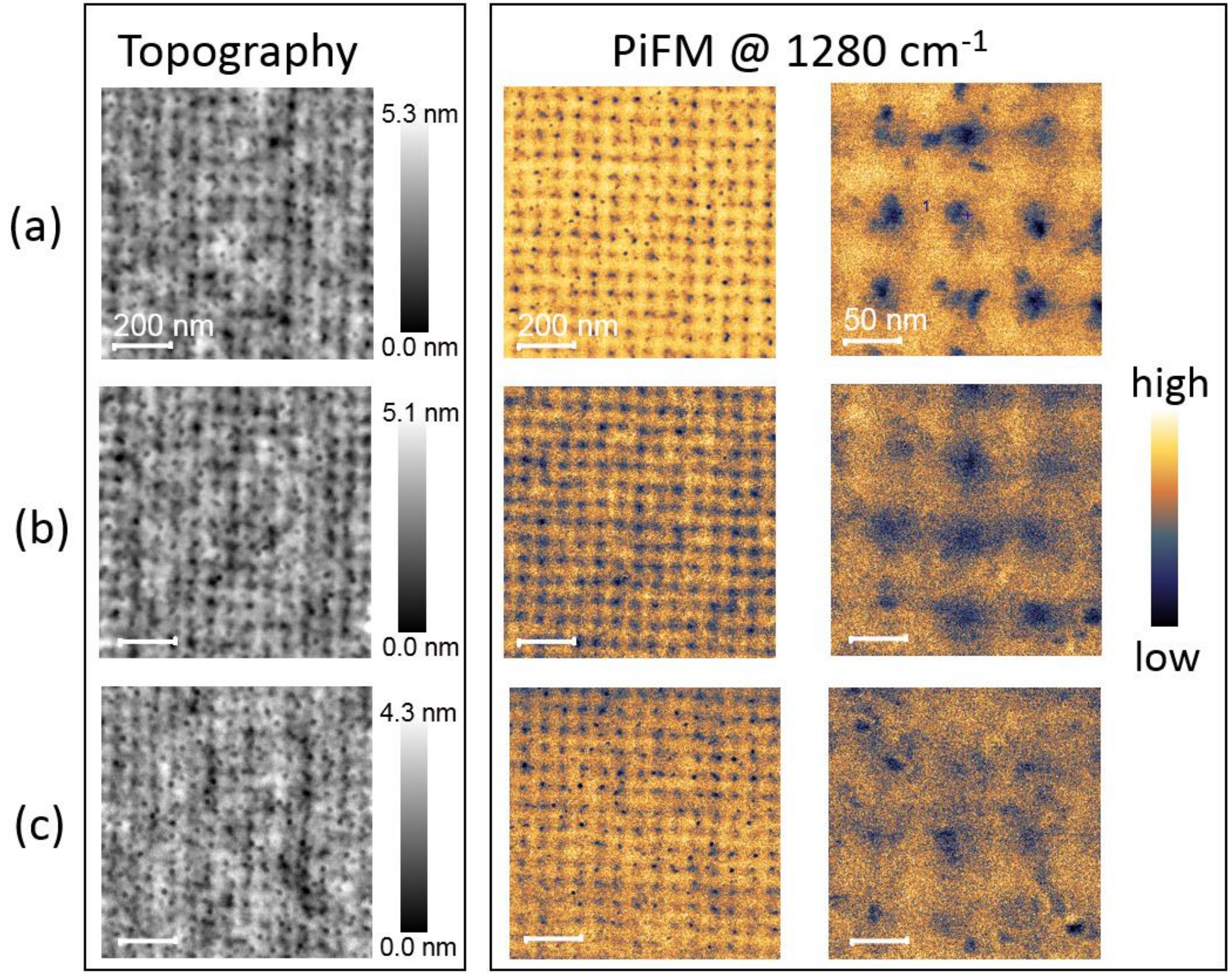



Chemically amplified photoresist (tBOC)

Exposed to EUV light ($\lambda$ = 13.5 nm) at ALS Lawrence Berkeley National Laboratory.

Exposure creates shrinkage, resulting in depression in topography (a).

# Characterization of EUV Resist Exposure




**Dose Level**

*90 mJ/cm²*

*78 mJ/cm²*

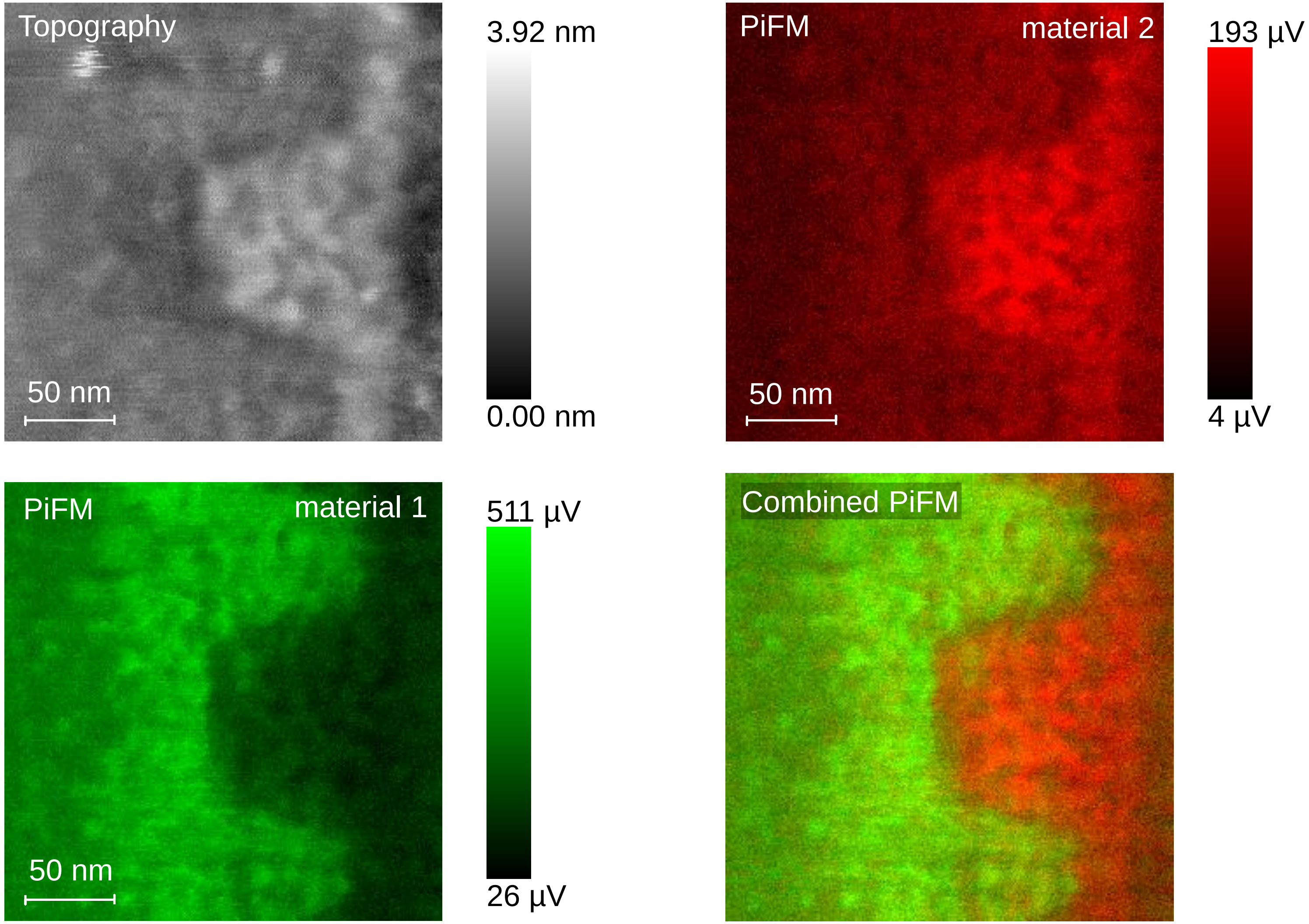
*60 mJ/cm²*

Topographical variations make it difficult to compare the effectiveness of dosage via AFM images.

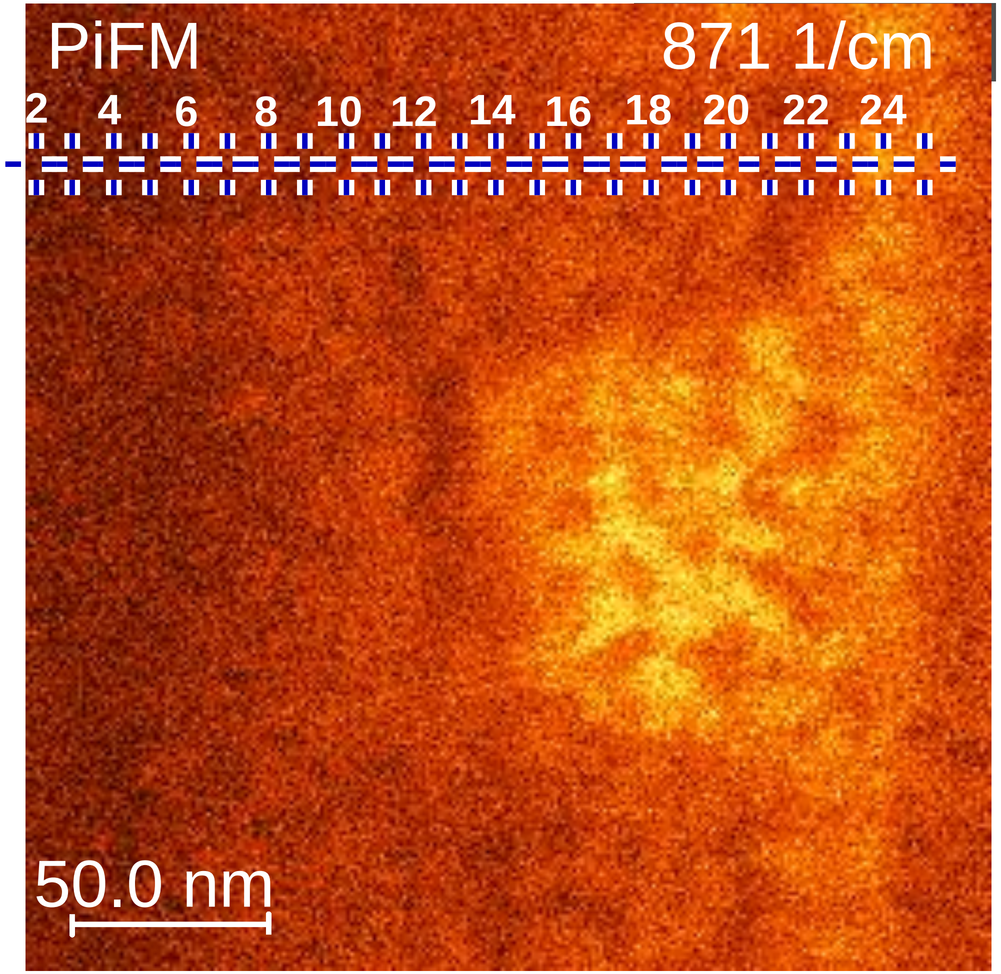
PiFM is immune from topographical variations and clearly show that 60 mJ/cm$^2$ is not sufficient dosage.

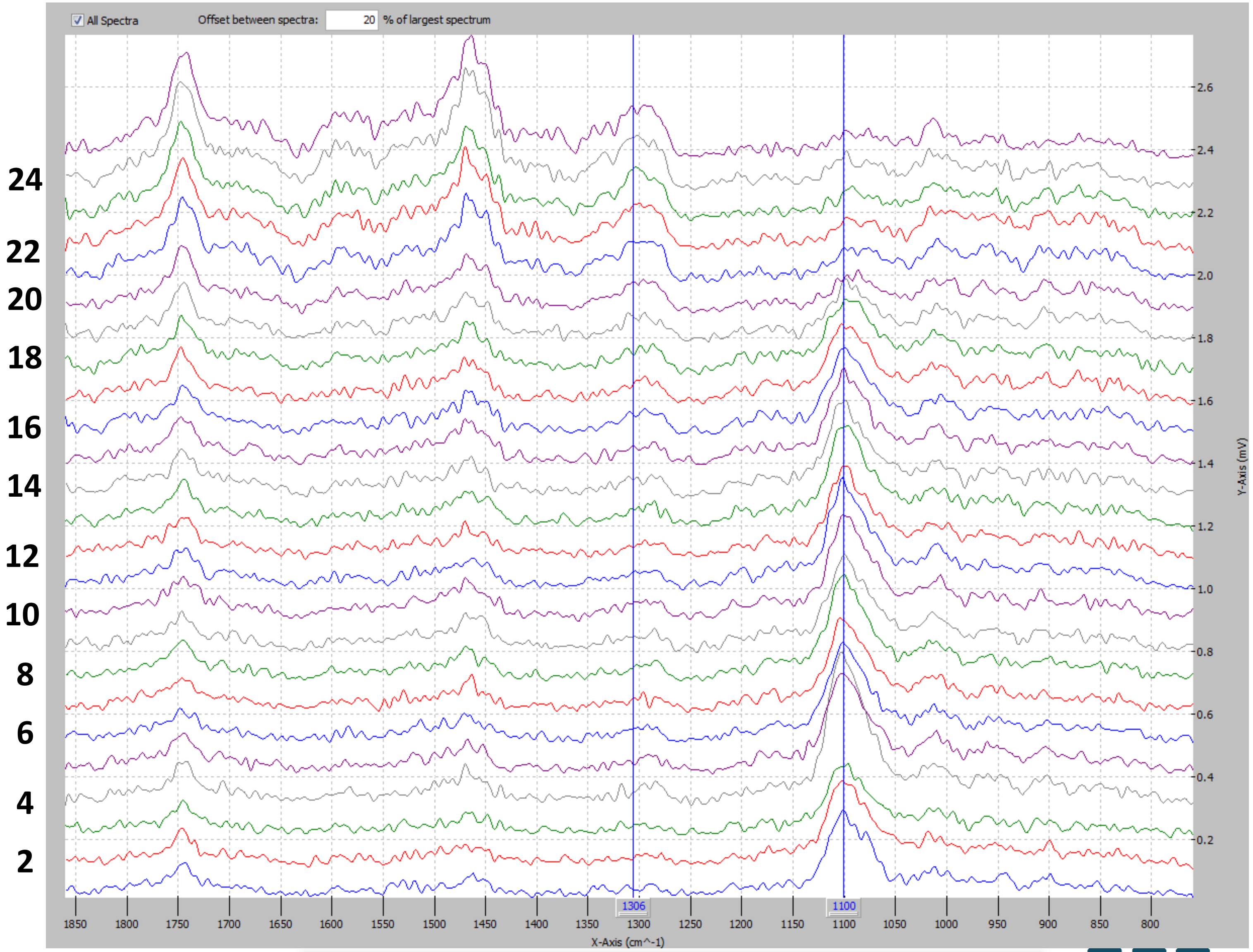
# Example Application of PiFM to Cross-section and Defect Analysis

# Cross-section of a Trench

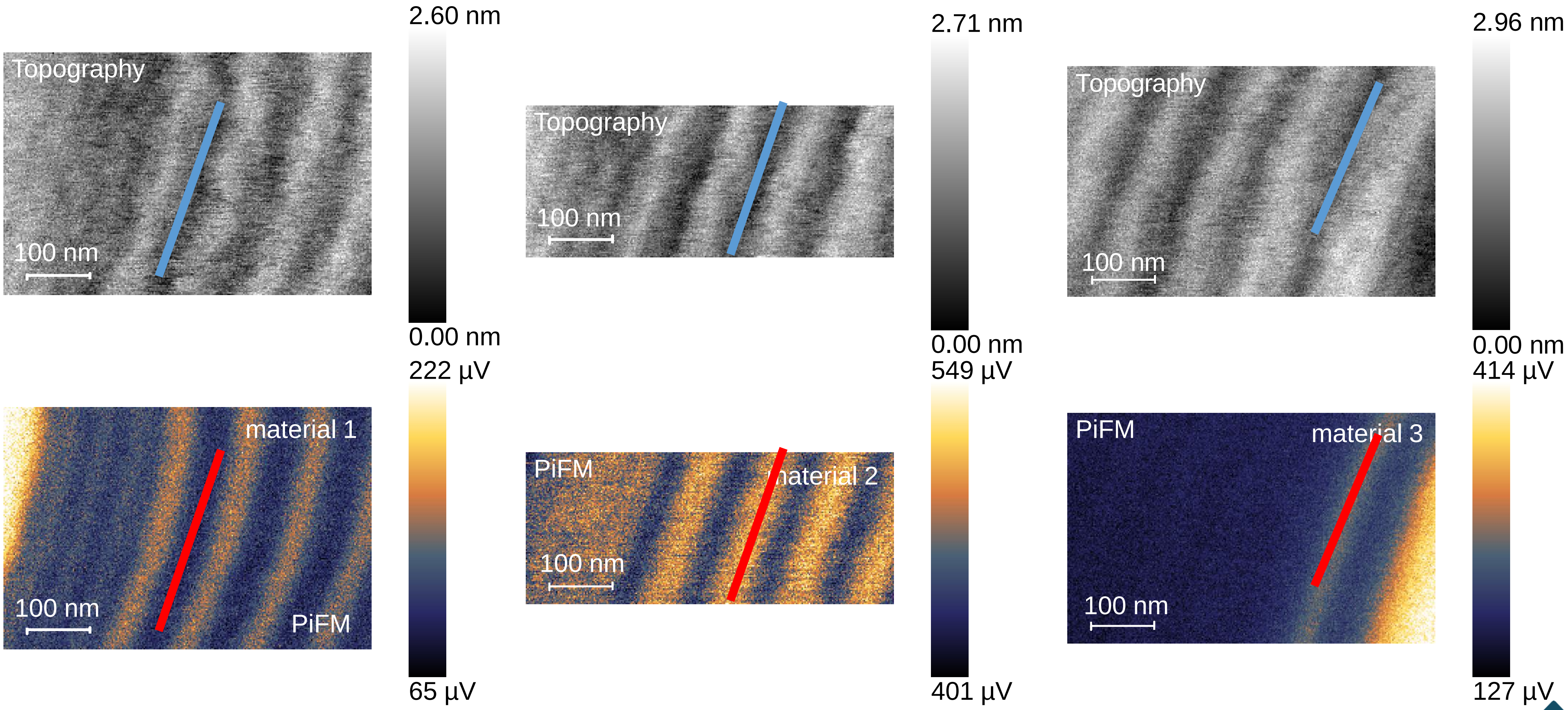


# PiFM Spectra with 10 nm Step Size (Trench)



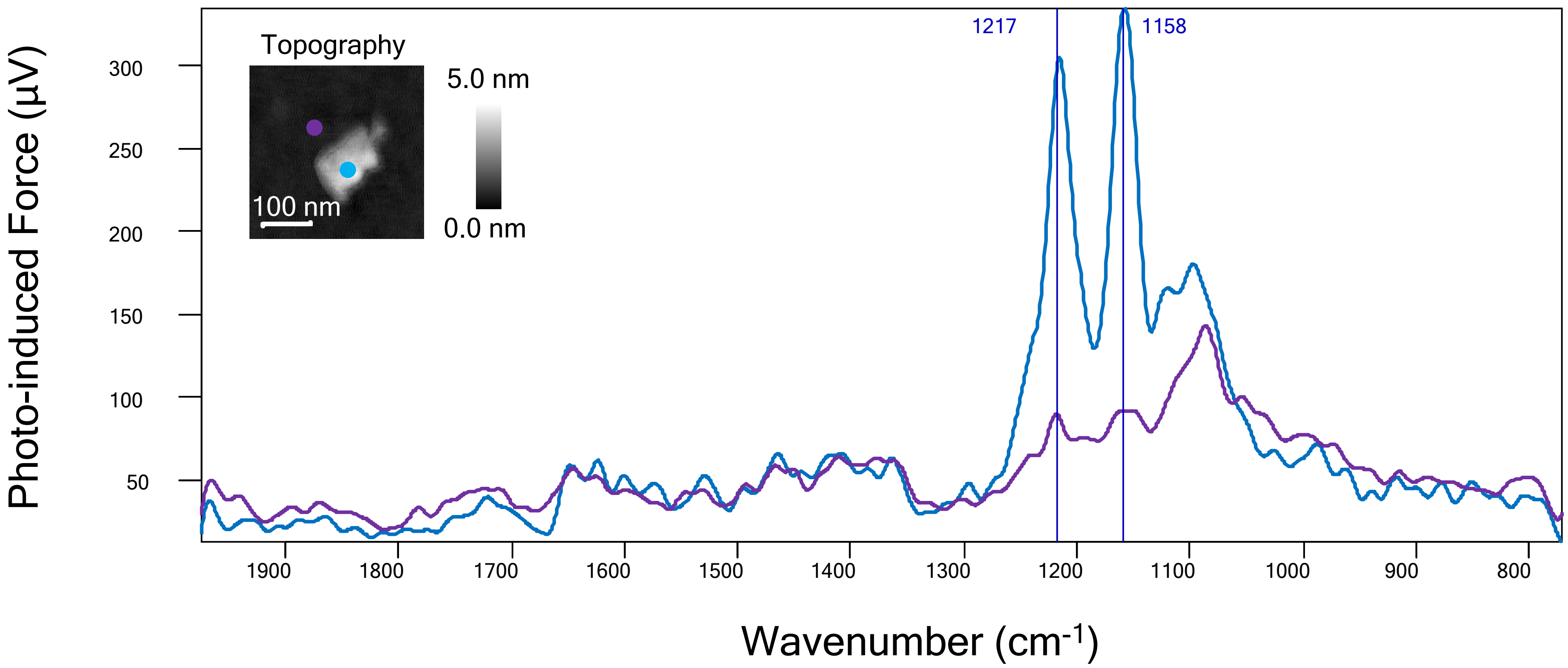



# Cross-section of Multilayer Stack



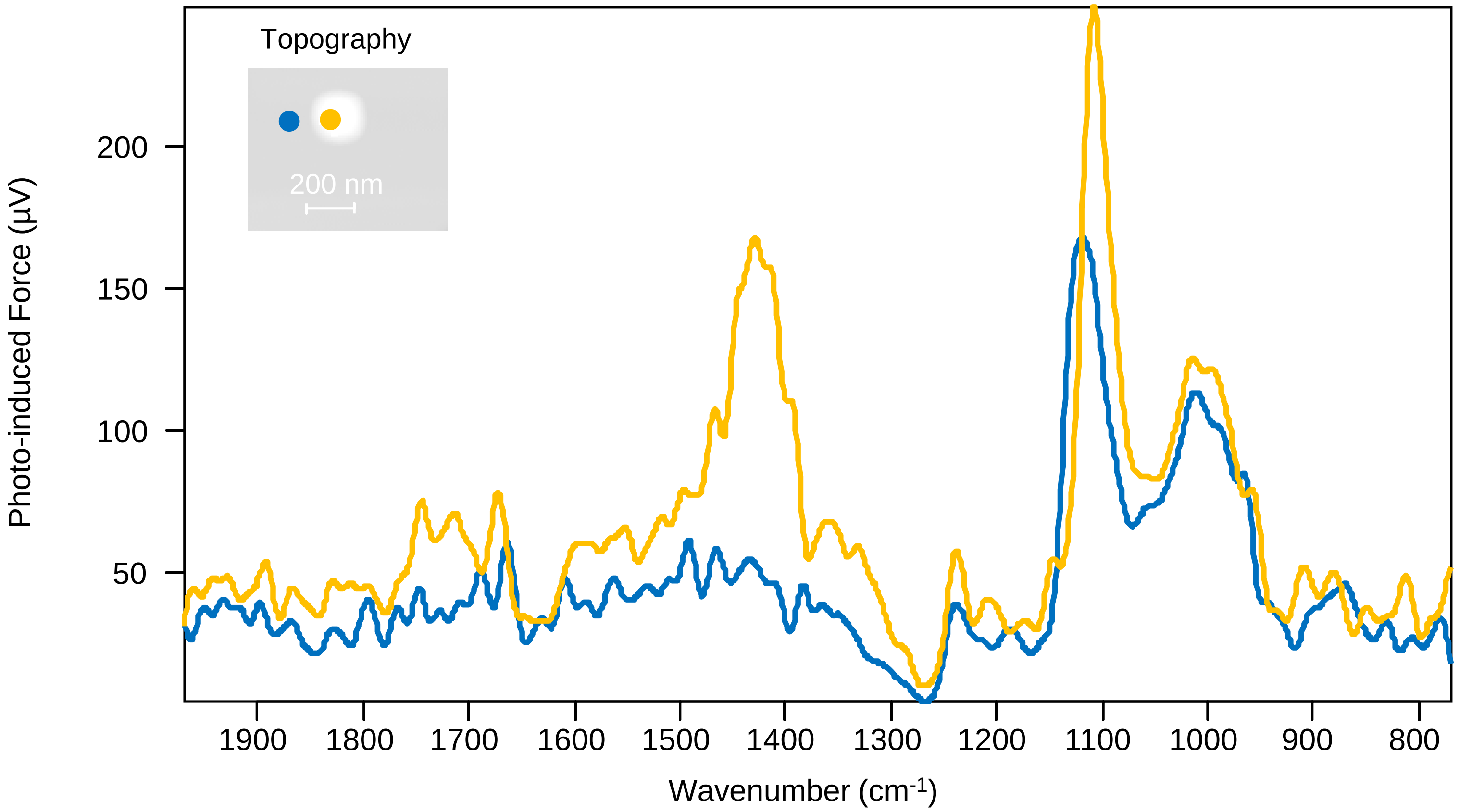
# Nanoscale Chemical Analysis of Defects (sample 1)

PiFM spectra from a defect particle ~ 100 nm x 150 nm in size and about 5 nm tall. On (blue) and off (purple) the defect.



# Nanoscale Chemical Analysis of Defects (sample 2)

PiFM spectra from a defect particle ~ 180 nm x 180 nm in size and about 40 nm tall. On (gold) and off (blue) the defect.



# Summary

- Photo-Induced Force Microscopy (PiFM) is a relatively new technique combining an AFM with local visible & IR spectroscopy
- PiFM is easy to use and can achieve <10 nm lateral resolution and can sense a monolayer of material
- PiFM images and spectra can be used to identify and study molecular materials at the nm scale
- IR PiFM characterizations on various novel patterning techniques were shared.
- Examples of analysis of cross-sectional samples and defects on substrates were shared.
- It is the first robust technique that provides nanoscale molecular information in a compact form-factor, nicely complementing the other elemental analysis tools.
- We welcome interesting samples to study together