



**molecular**  
V I S T A

# Infrared Photo-induced Force Microscopy (IR PiFM) Potential for EUV Metrology

EUV Supplier Showcase

August 16, 2021

Sung Park, Molecular Vista

[sung@molecularvista.com](mailto:sung@molecularvista.com), 408-915-2595 Ext. 104

# Current Status of Analytical Techniques

|                    | Raman               | FTIR               | TOF-SIMS            | XPS                     | TXRF    | SEM/EDS                        | TEM      | Auger   |
|--------------------|---------------------|--------------------|---------------------|-------------------------|---------|--------------------------------|----------|---------|
| Species Detected   | M.I.                | M.I.               | M.I.                | M.I.                    | E.I.    | E.I.                           | E.I.     | E.I.    |
| Chemical Mapping   | Yes                 | Yes                | Yes                 | Yes                     | Yes     | Yes                            | Yes      | Yes     |
| Lateral Resolution | > 0.5 $\mu\text{m}$ | > 10 $\mu\text{m}$ | > 0.2 $\mu\text{m}$ | 10 $\mu\text{m}$ – 2 mm | ~ 10 mm | 1 nm*<br>0.5 $\mu\text{m}$ EDS | 0.2 nm   | > 10 nm |
| Depth Probed       | > 500 nm            | 1 $\mu\text{m}$    | 1 nm                | 10 nm                   | 10 nm   | 1 $\mu\text{m}$                | ~ 100 nm | 10 nm   |

\* Imaging

M.I. Molecular information

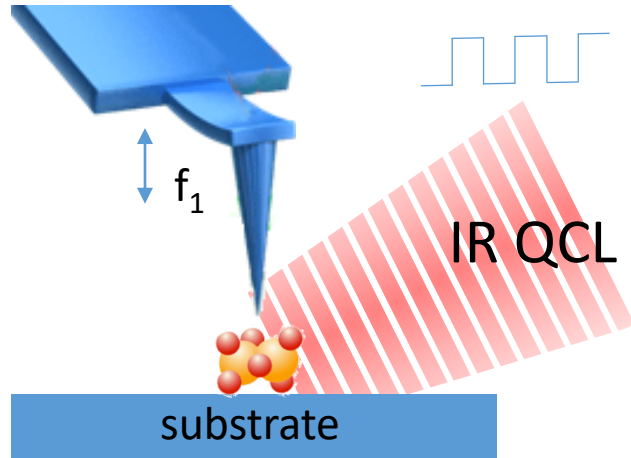
E.I. Elemental information

Elemental information cannot identify nanoscale organic defects and ultrathin residues, which are becoming more commonplace. Existing tools for molecular information do not have spatial resolution to analyze sub-200 nm particles.



# Infrared Photo-induced force microscope (IR PiFM)

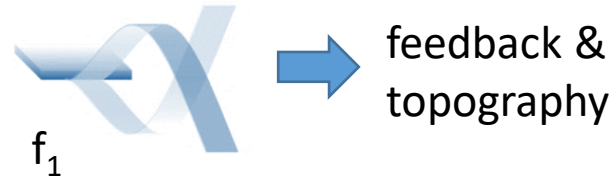
Dipole-dipole attractive force from nano-sized sample absorption region is detected via AFM cantilever.



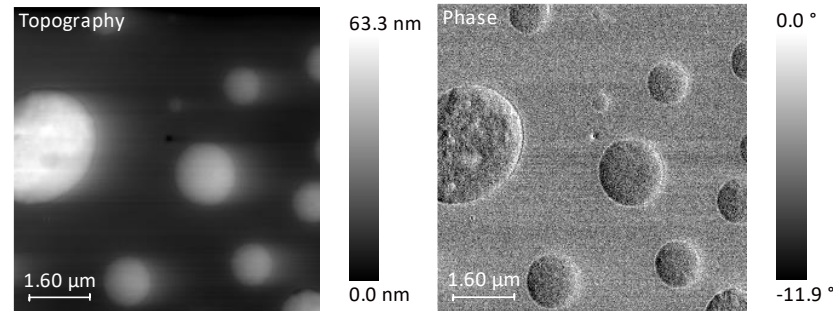
QCL (quantum cascade laser): tunable IR laser (770 – 1900  $\text{cm}^{-1}$ )

IR PiFM combines IR spectroscopy with AFM to acquire topography and both IR absorption (PiF-IR) spectra and chemical map images with sub-10 nm spatial resolution.

One vibrational resonance of the cantilever is used to perform standard modes of AFM.

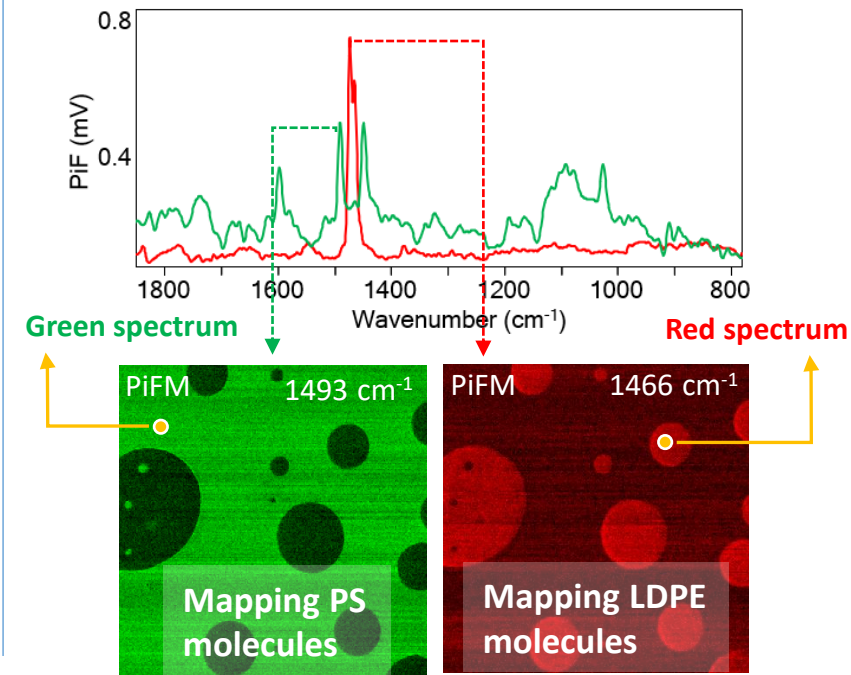
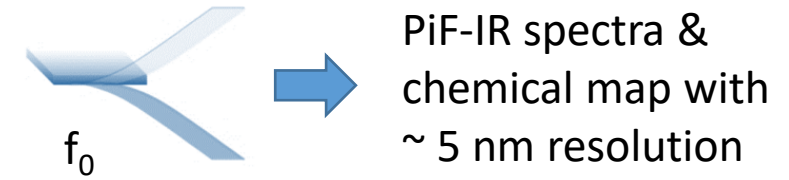


PS-LDPE Blend



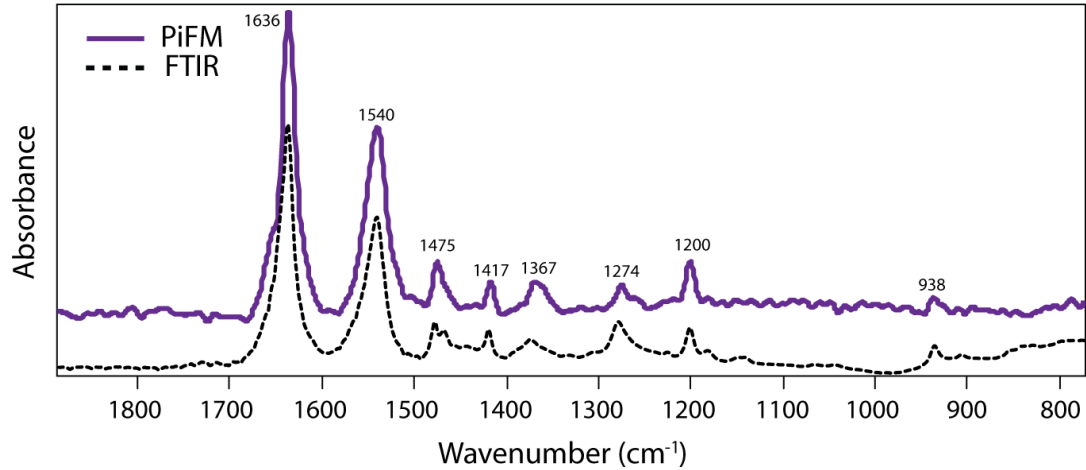
Standard AFM topography and phase images are acquired at  $f_1$ . As typical with AFM images, the molecular identity of features are unknown even though spatial resolution is excellent.

Concurrently, a second resonance of the cantilever is used to detect photo-induced force (PiF) of the sample.

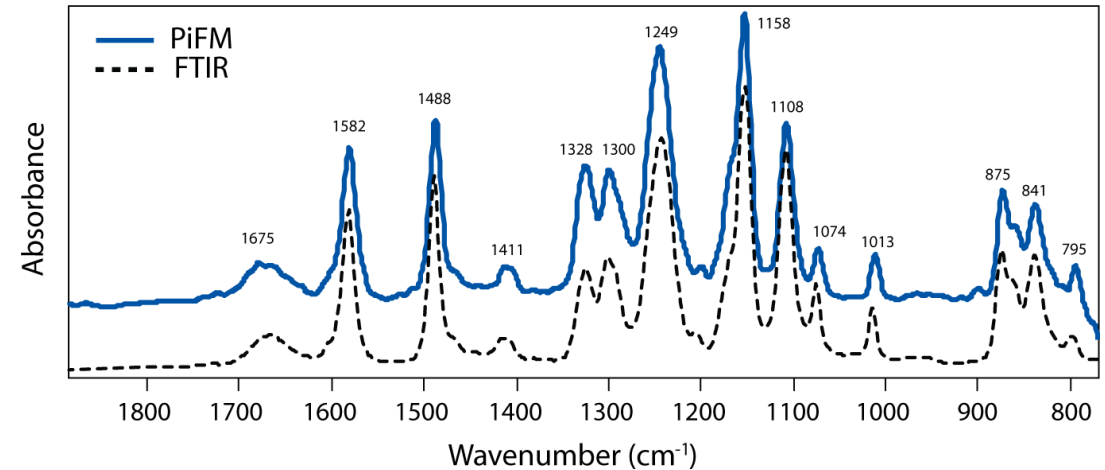


# Excellent Agreement between Nanoscale PiF-IR and FTIR Spectra

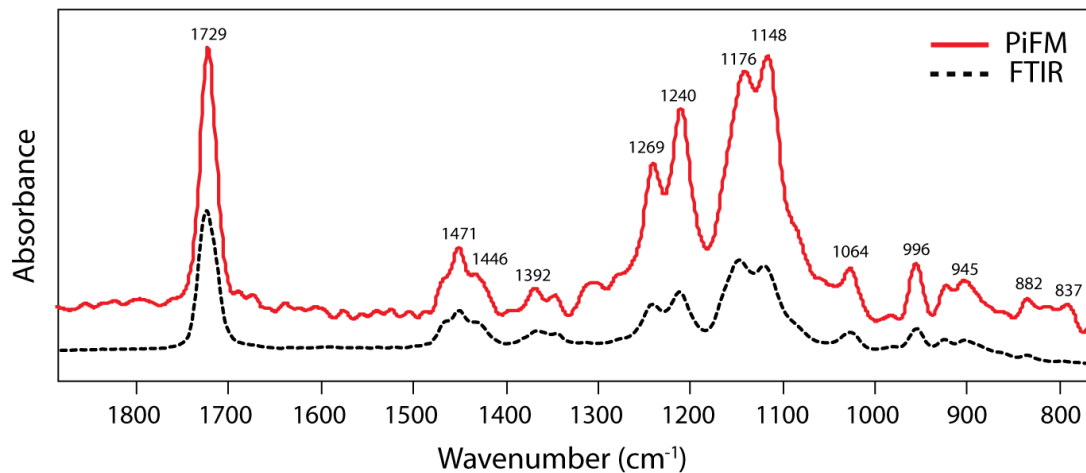
## PiFM and FTIR of Nylon



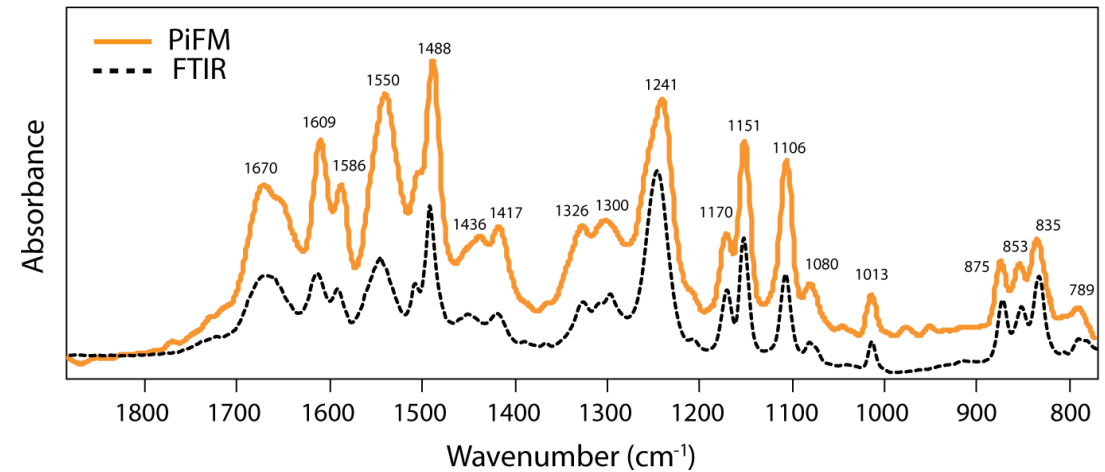
## PiFM and FTIR of PES (Polyethersulfone)



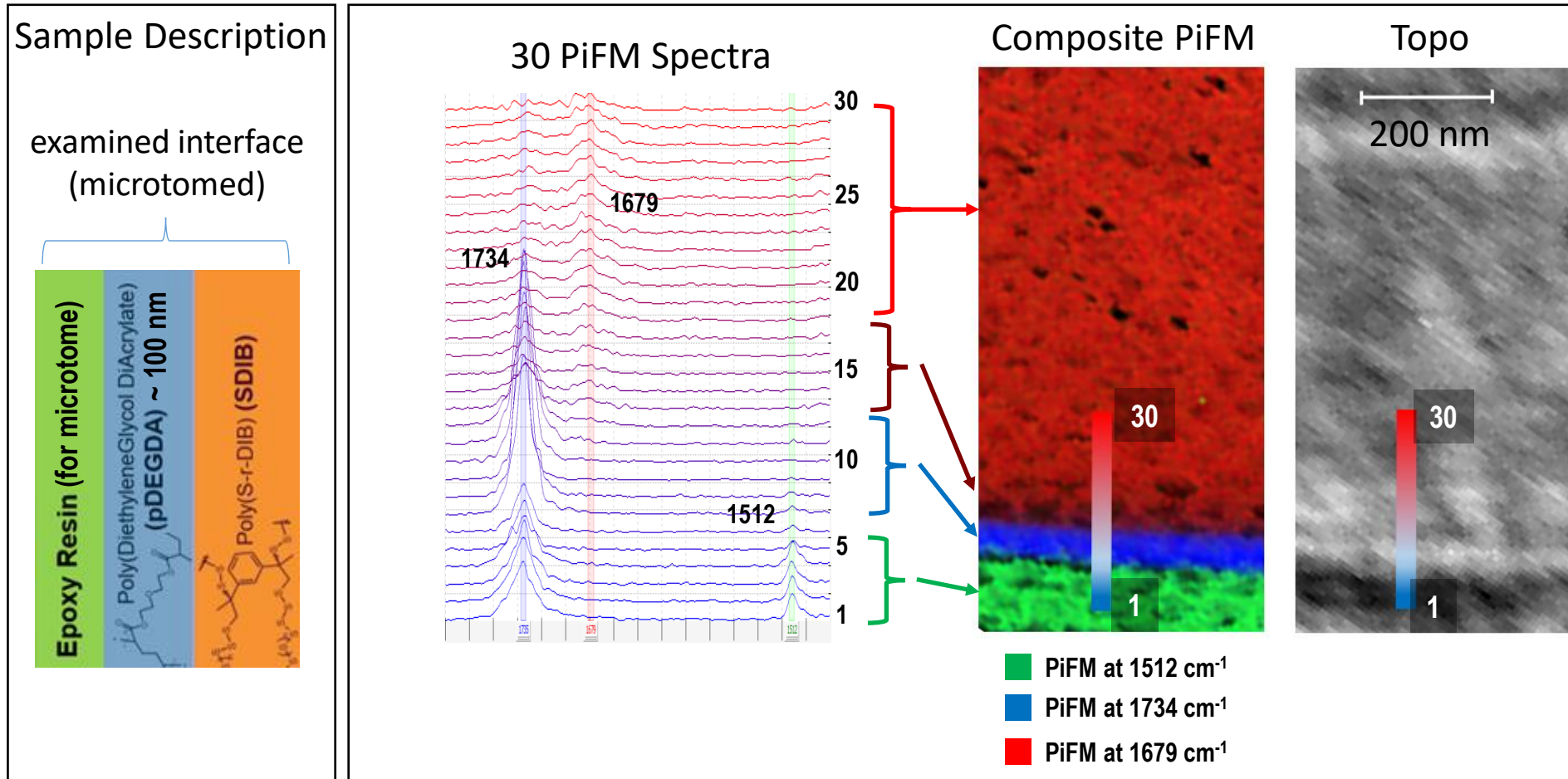
## PiFM and FTIR of PMMA - Poly(methyl methacrylate)



## PiFM and FTIR of Polyimide



# Chemical Analysis across Polymer Interfaces

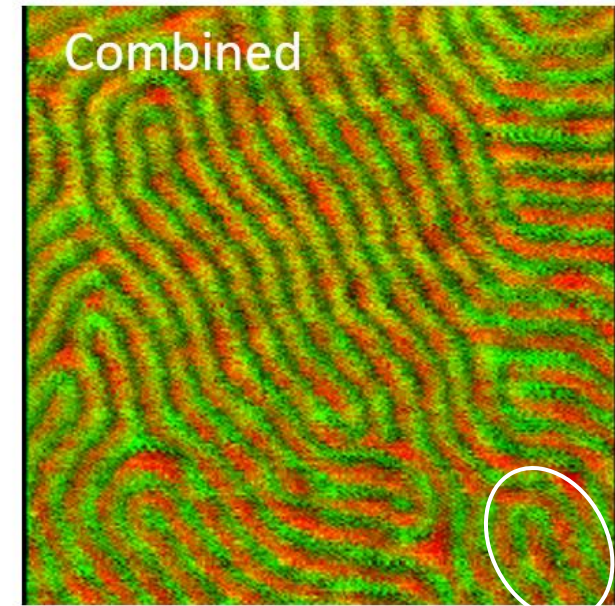
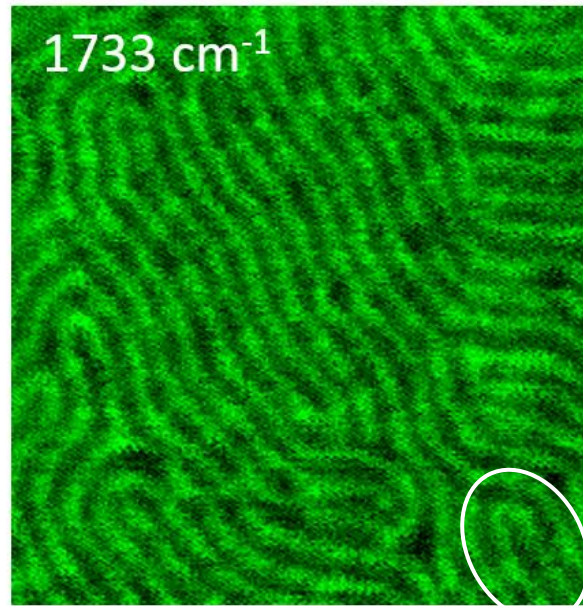
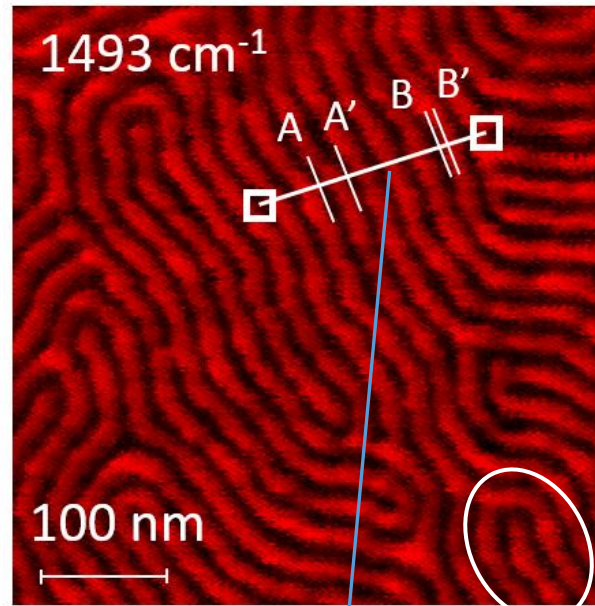


- Microtomed sample to analyze interface between two polymer layers
- 30 spectra across the interface with 10 nm spacing show gradual and sudden changes in peak strength with single steps
- ~ 50 nm mixing in the interface shown in spectra 13 to 18
- Demonstrates PiFM sensitivity and spatial resolution

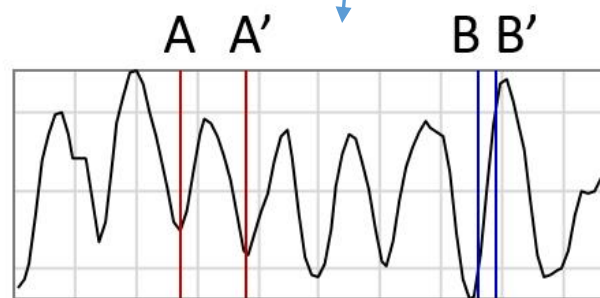


# Exceptional Spatial Resolution in Chemical Mapping

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



■ PMMA ■ PS



A-A': 21 nm  
B-B': 6.5 nm

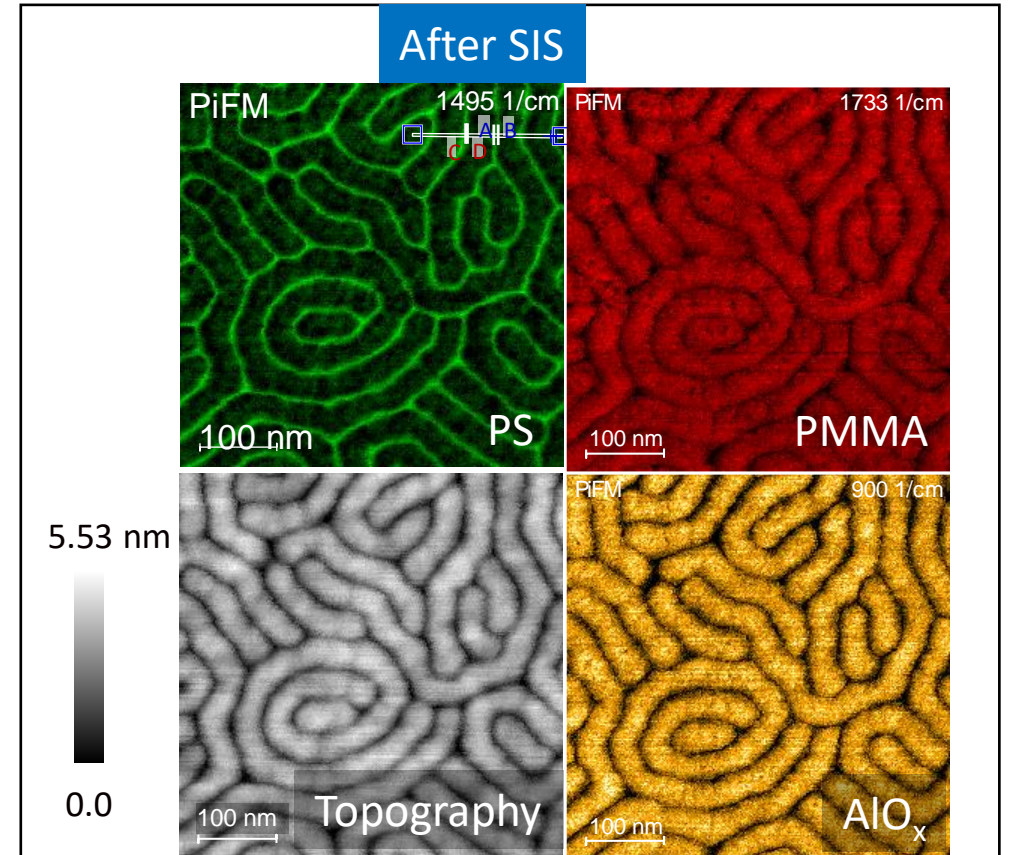
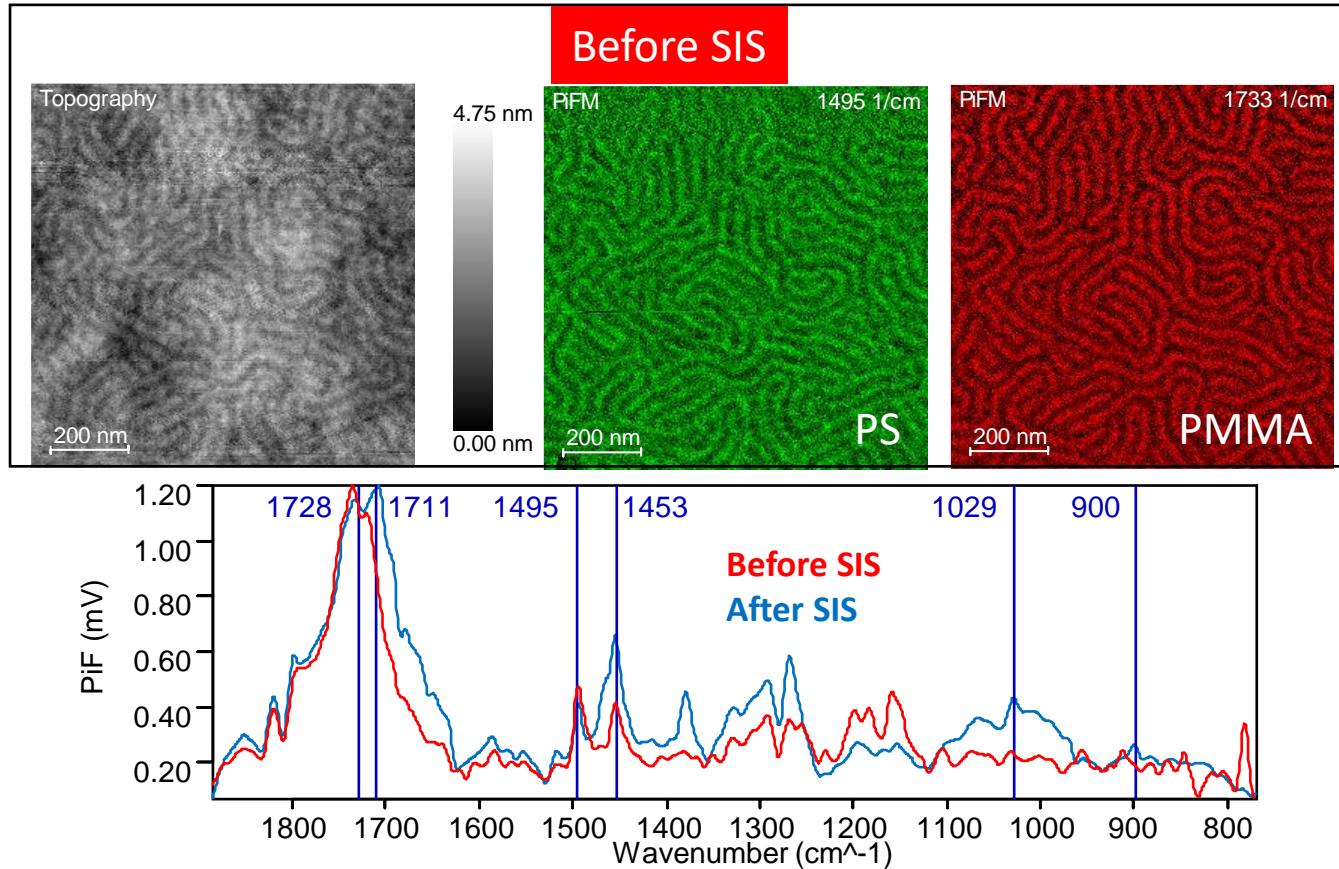
IR PiFM can monitor chemical homogeneity of photoresist with  $\sim 5$  nm spatial resolution

Cross-section of PiF signal for PS

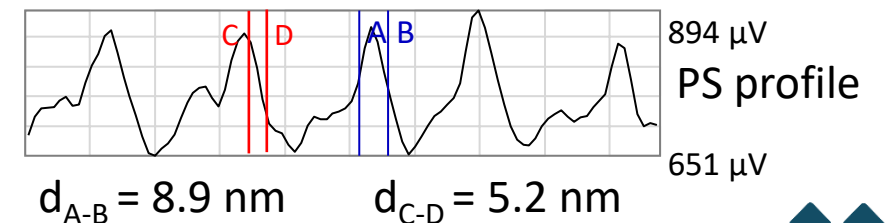




# SIS AlO<sub>x</sub> PS-b-PMMA (41 nm FP Lamellar) PiFM Images



Selective infiltration of trimethyl aluminum (TMA) into PMMA molecules and subsequent exposure to water vapor forms aluminum oxide only in the PMMA block of the PS-b-PMMA block copolymer. Before SIS, the width of PS and PMMA blocks are equal as seen above. After SIS, PS width is reduced to 8.9 nm from 21 nm (see PS profile plot). PiFM image @ 900 cm<sup>-1</sup> highlights the alumina molecules, which are located only in PMMA blocks as expected.





# Complements other Nanoscale 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.    |
| Chemical Mapping   | Yes          | Yes                 | Yes                | Yes                 | Yes                     | Yes     | Yes                            | Yes      | Yes     |
| Lateral Resolution | ~ 5 nm       | > 0.5 $\mu\text{m}$ | > 10 $\mu\text{m}$ | > 0.2 $\mu\text{m}$ | 10 $\mu\text{m}$ – 2 mm | ~ 10 mm | 1 nm*<br>0.5 $\mu\text{m}$ EDS | 0.2 nm   | > 10 nm |
| Depth Probed       | 20 nm & bulk | > 500 nm            | 1 $\mu\text{m}$    | 1 nm                | 10 nm                   | 10 nm   | 1 $\mu\text{m}$                | ~ 100 nm | 10 nm   |

\* Imaging

M.I. Molecular information

E.I. Elemental information

IR PiFM brings molecular analysis to the realm of true nanoscale, providing both IR absorption spectra and chemical mapping with ~ 5 nm spatial resolution and monolayer sensitivity.

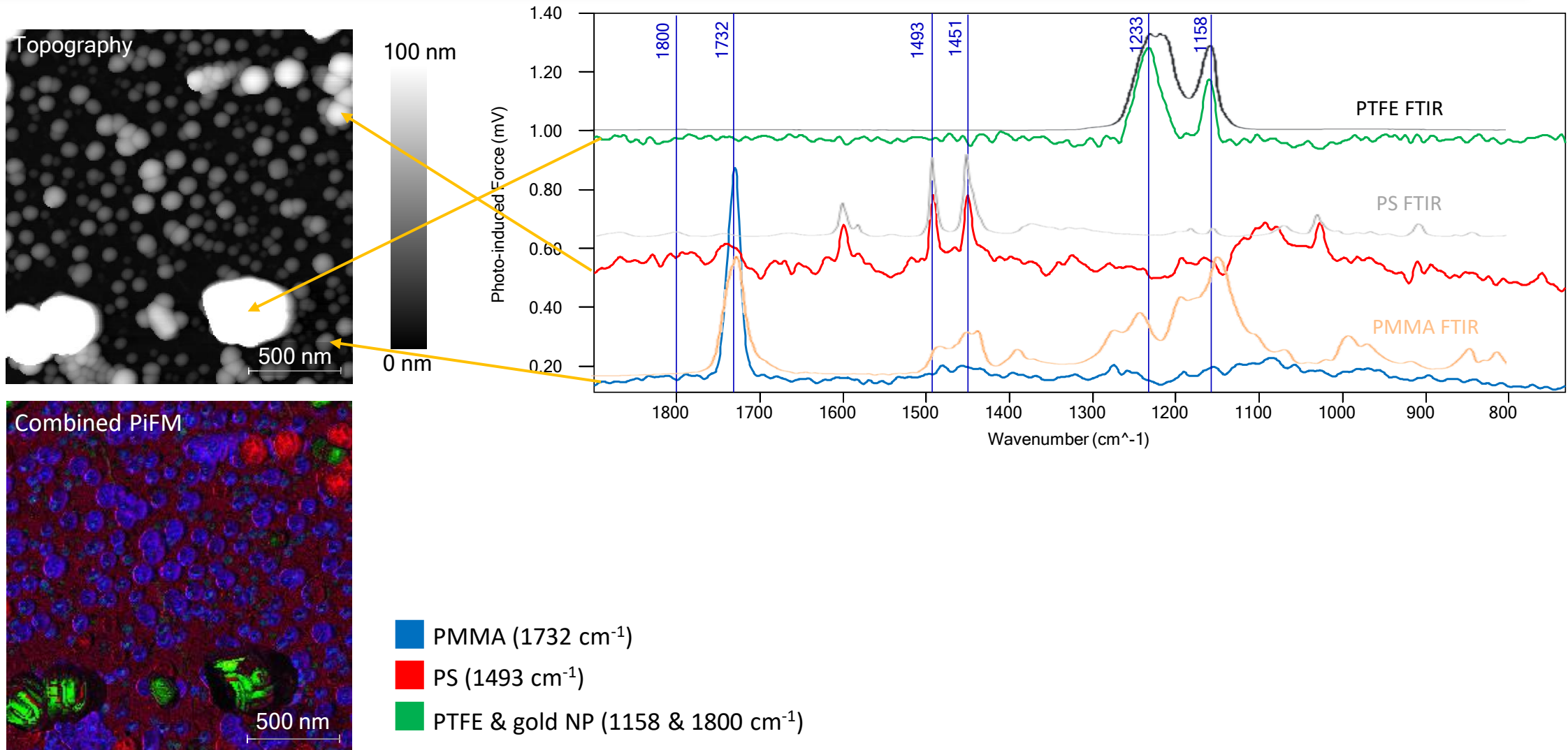


---

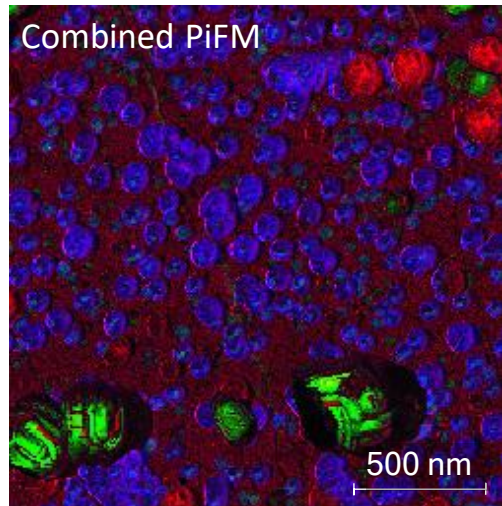
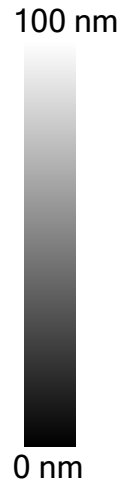
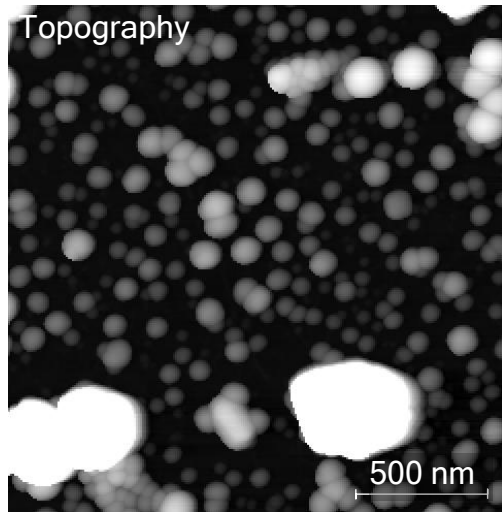
# Potential EUV Applications



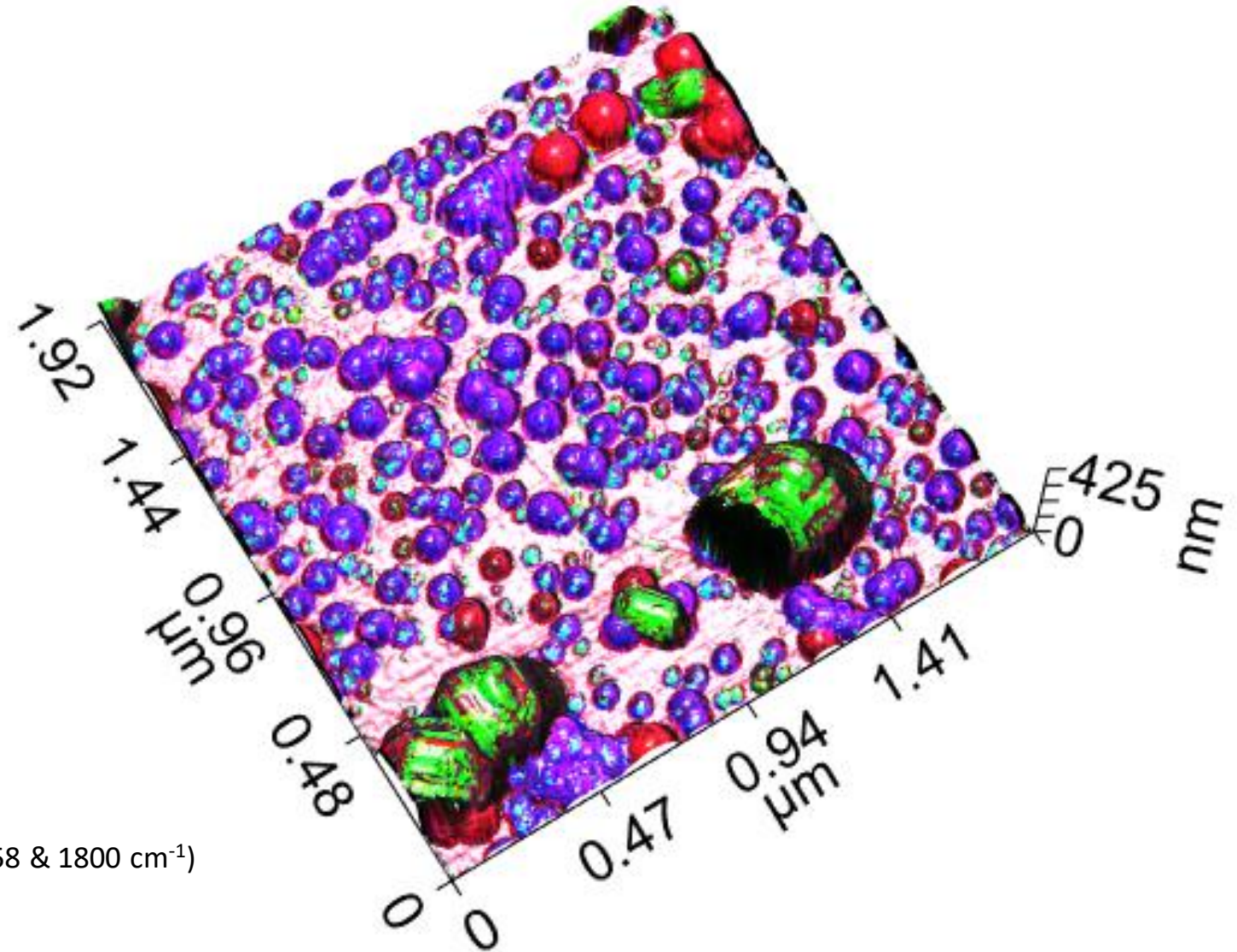
# Identification of Nanoparticles based on PiF-IR Spectra



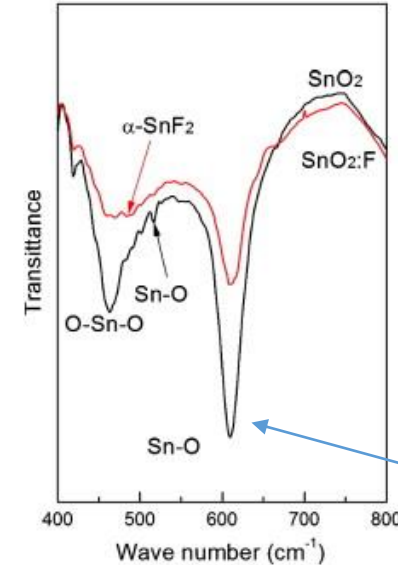
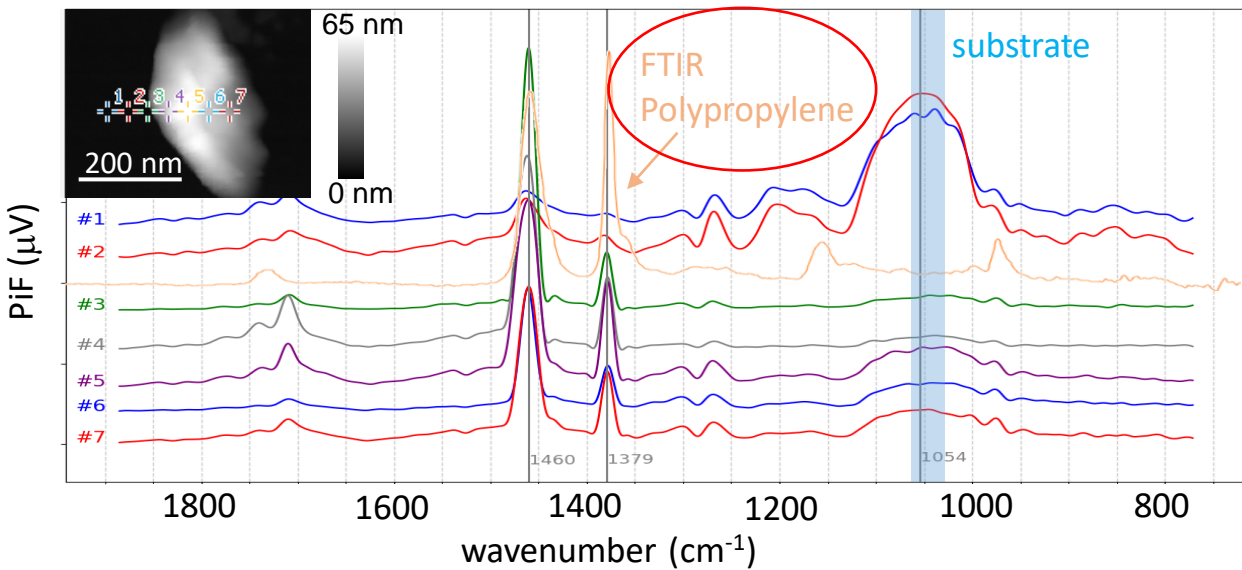
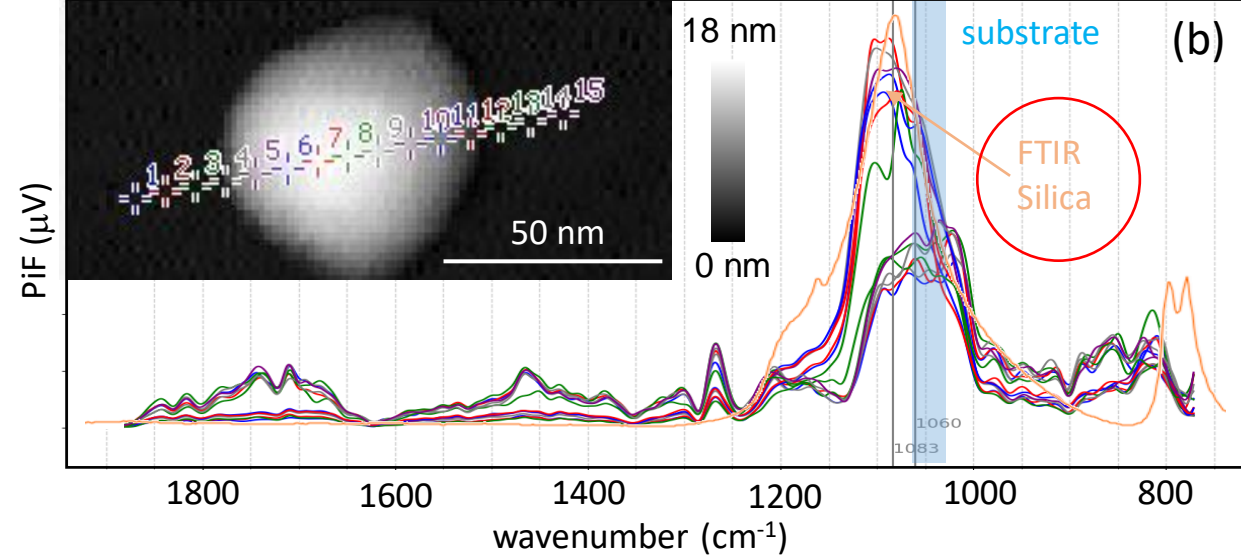
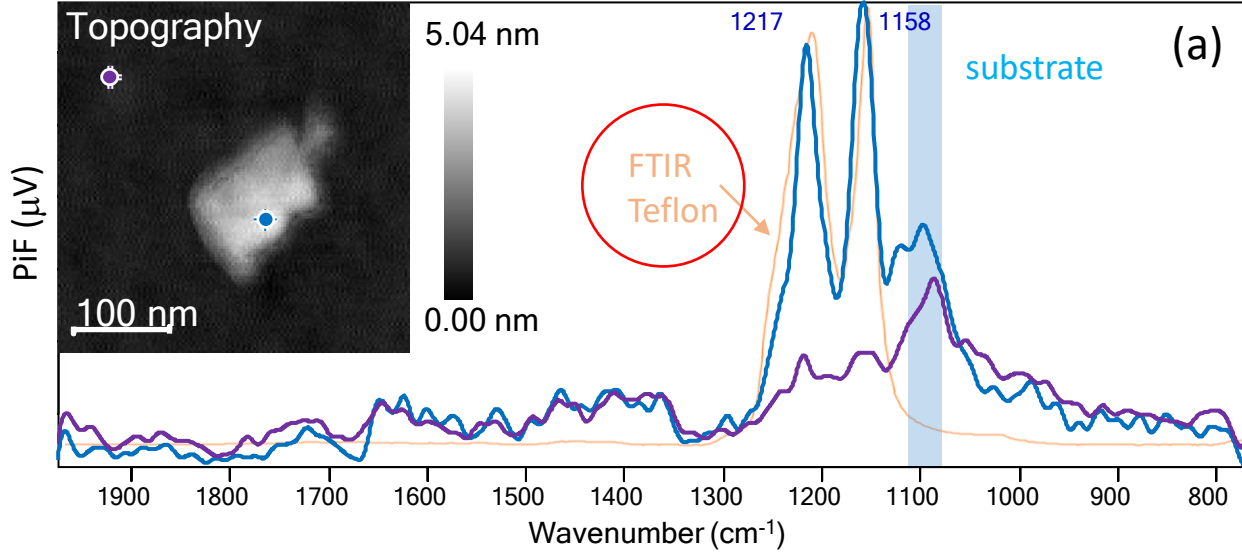
# Identification of Nanoparticles based on PiF-IR Spectra



- PMMA ( $1732\text{ cm}^{-1}$ )
- PS ( $1493\text{ cm}^{-1}$ )
- PTFE & gold NP ( $1158\text{ & }1800\text{ cm}^{-1}$ )



# Nanoscale Defect Identification via PiF-IR Spectra



The characterization of fluorine doped tin oxide films by Fourier Transformation Infrared spectrum

[Materials Letters](#)

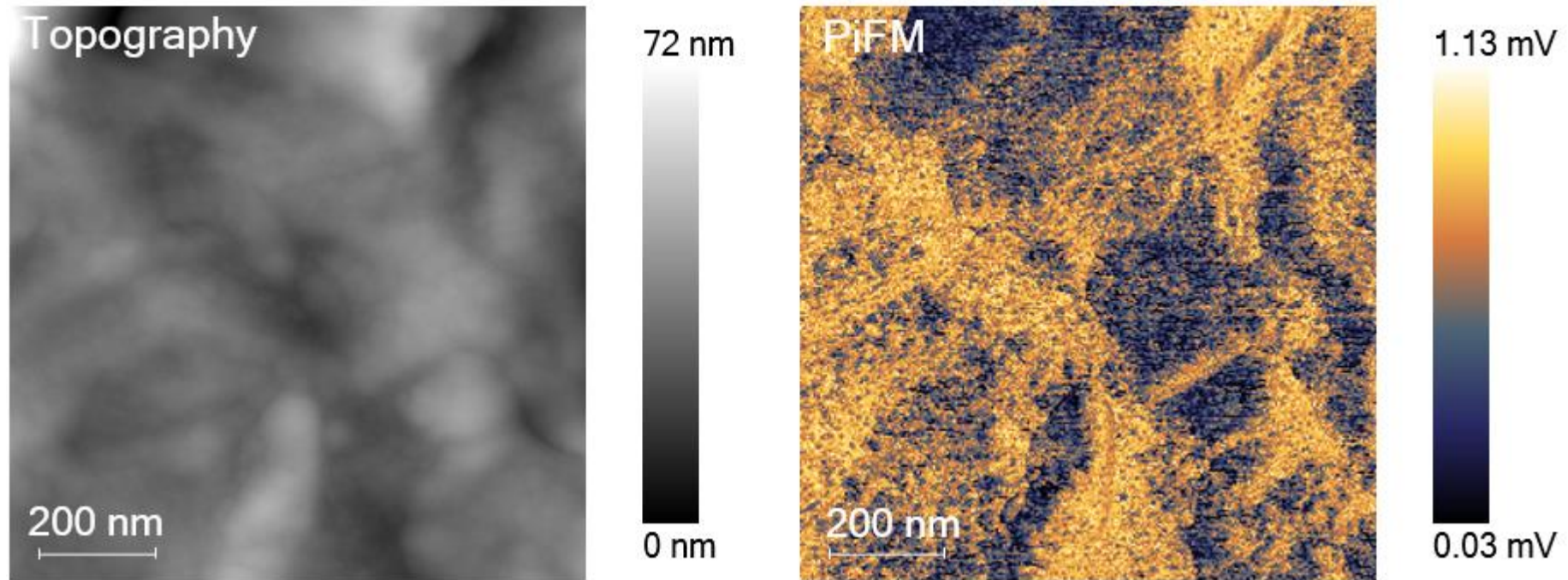
Volume 64, Issue 24, 31

December 2010, Pages 2707-2709

Sn-O band is accessible via a new laser.



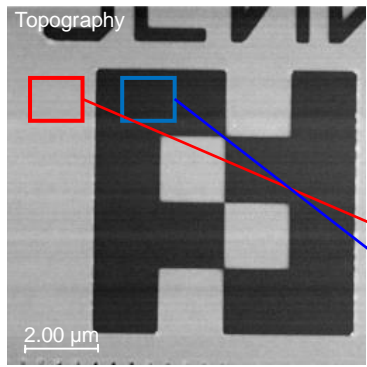
# Trace Residue Visualization & Identification



Monolayer of residue, which caused poor adhesion, identified via PiF-IR spectrum and mapped via IR PiFM.



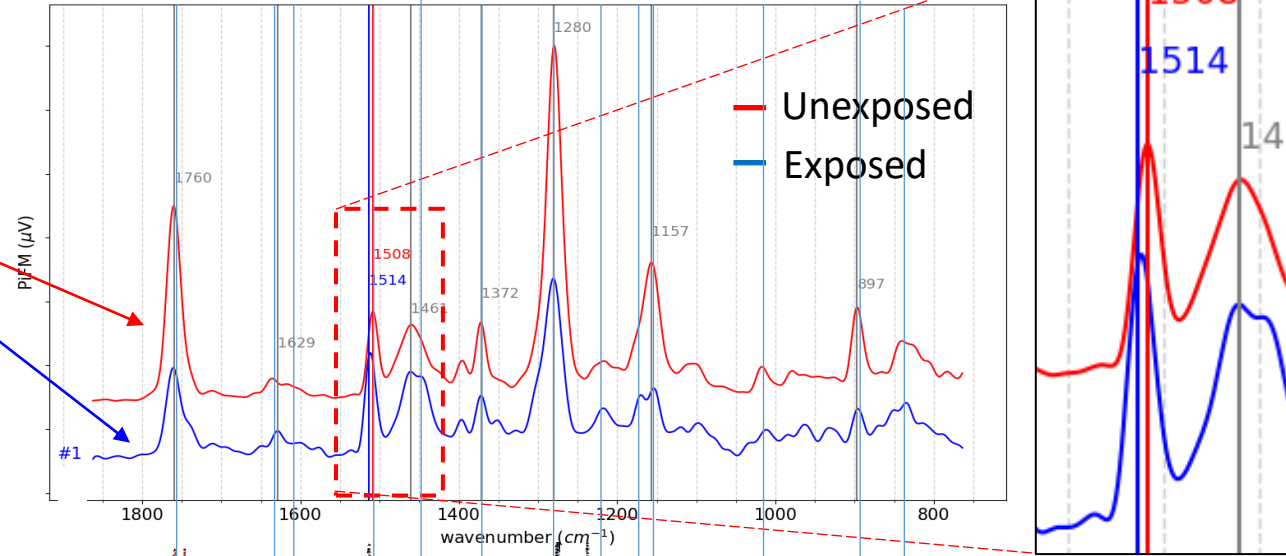
# Imaging of Latent EUV Images in TBOC CA Resist



37.6 nm  
0.0 nm

Exposure creates shrinkage, resulting in depression in topography.

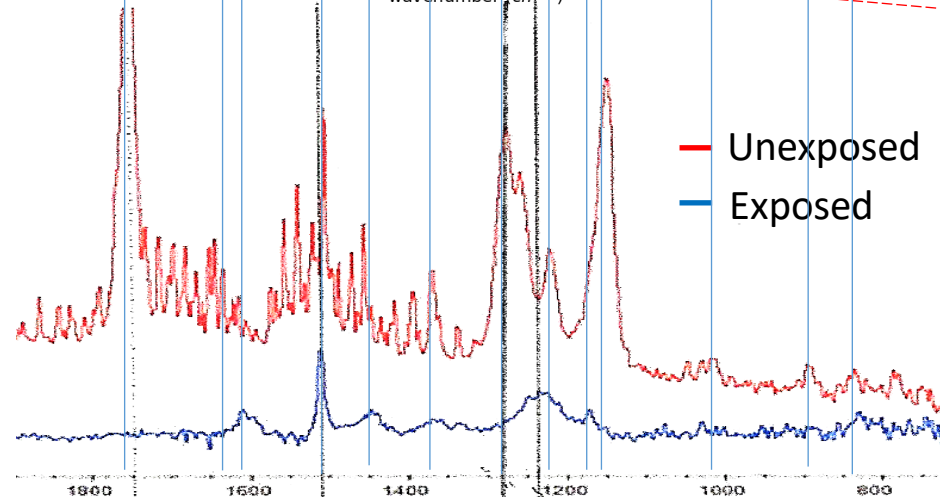
PiF-IR spectra



- Exposed to 13.5 nm EUV at ALS, Berkeley

PiFM can see chemical changes to molecular films

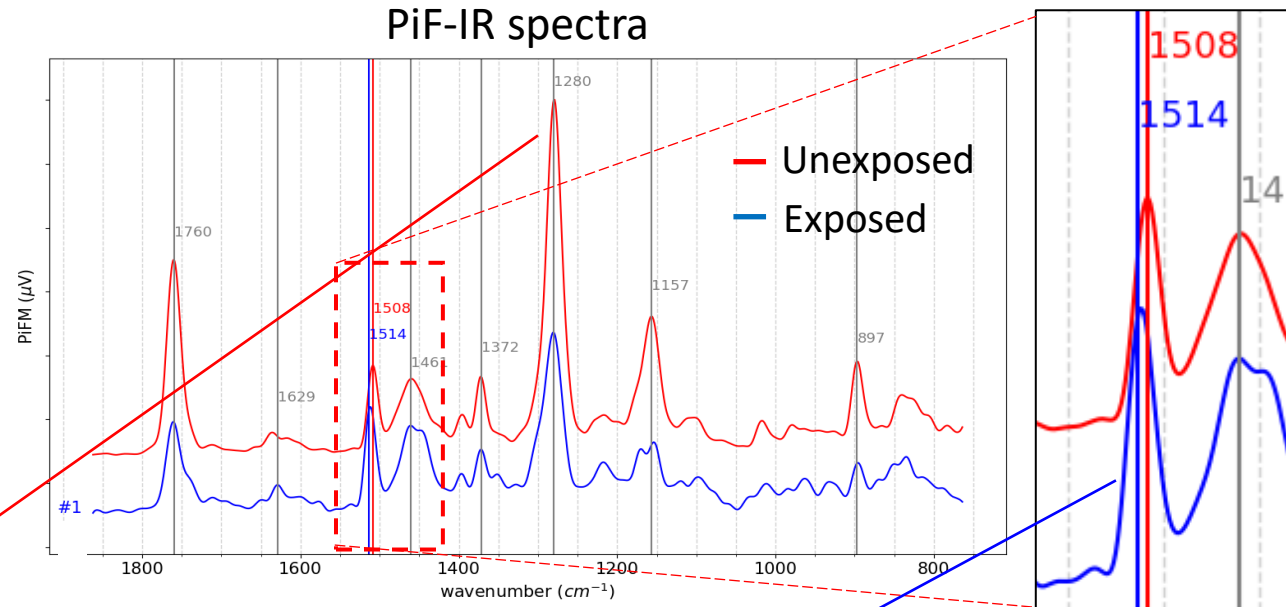
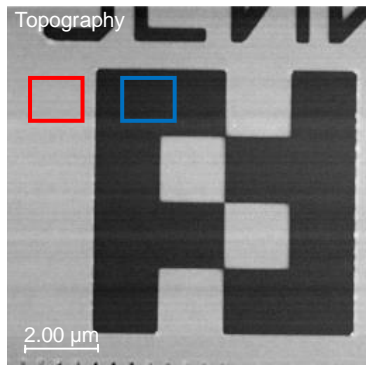
FTIR spectra



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



# Imaging of Latent EUV Images in TBOC CA Resist



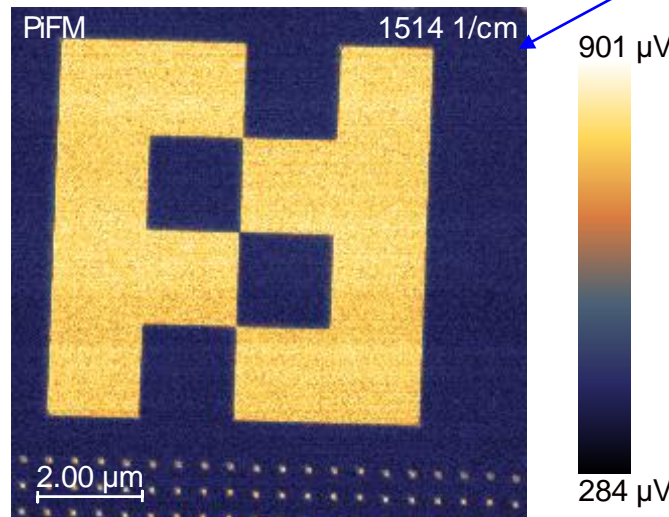
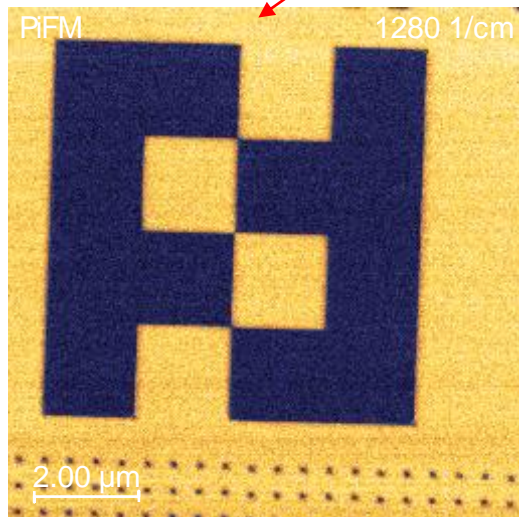
- Exposed to 13.5 nm EUV at ALS, Berkeley

PiFM can see chemical changes to molecular films

1280  $\text{cm}^{-1}$ : highlights unexposed TBOC resist

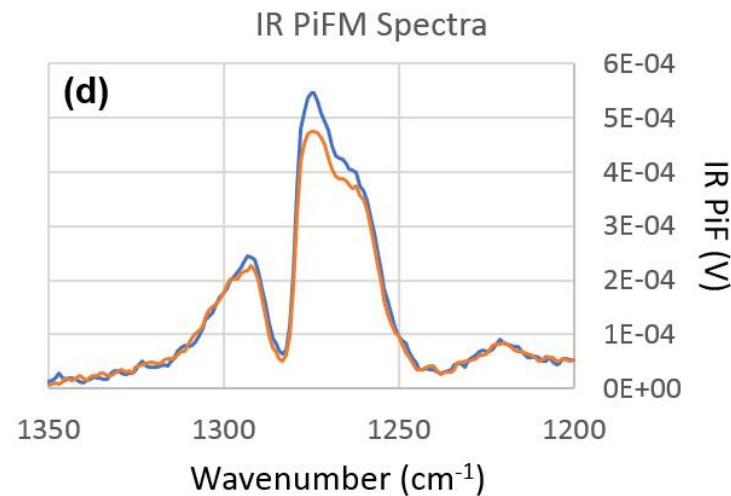
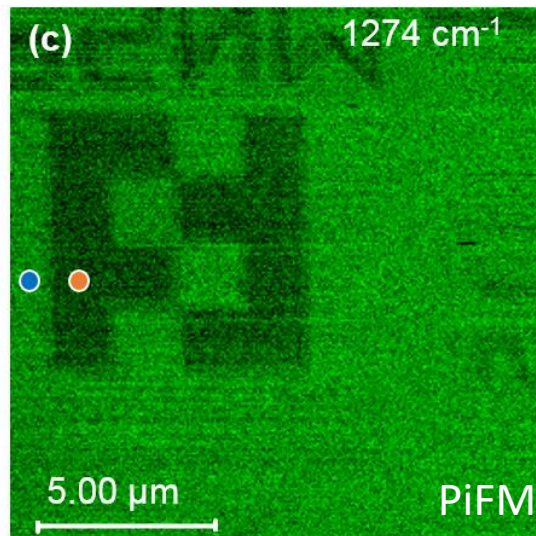
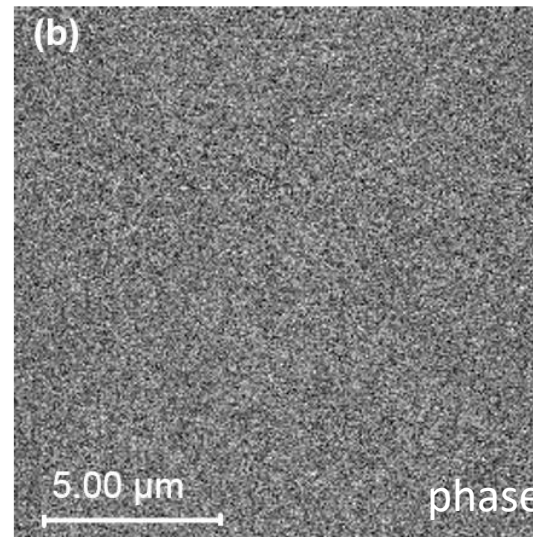
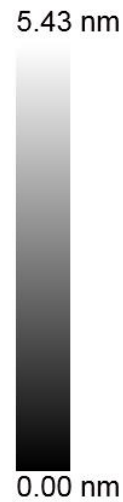
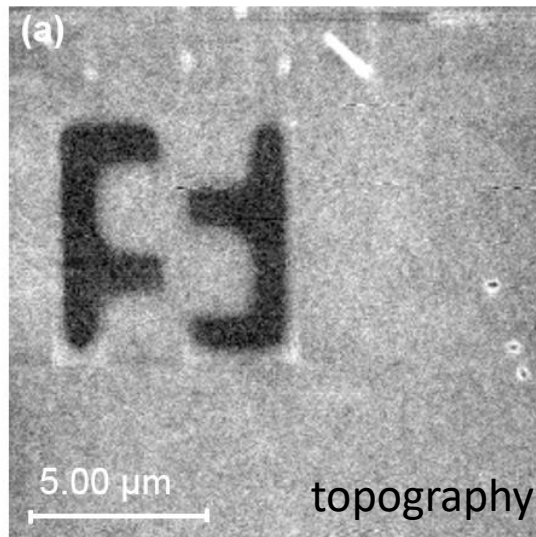
1514  $\text{cm}^{-1}$ : highlights exposed TBOC resist (peak shifts from 1508 to 1514  $\text{cm}^{-1}$ )

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





# Characterization of Low-dosage Exposure



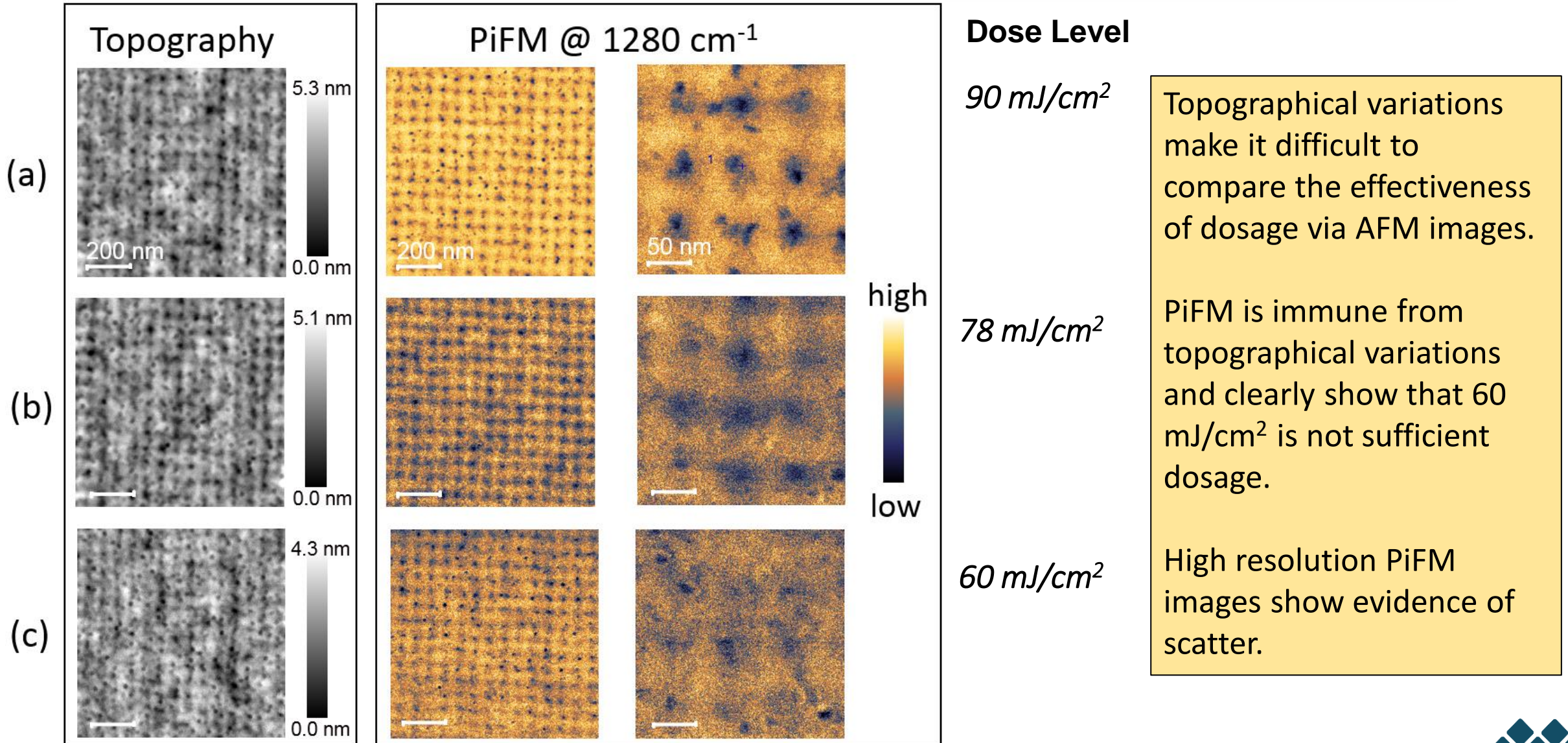
Chemically amplified photoresist (tBOC)  
Exposed to EUV light ( $\lambda = 13.5$  nm) at  
ALS Lawrence Berkeley National  
Laboratory.

Low dose exposure creates incomplete shrinkage, resulting in poor definition in (a). However, PiFM image at 1274 cm<sup>-1</sup> highlights exposed regions (dark regions) by monitoring the drop in the IR absorption at 1274 band.

Blue – Unexposed  
Orange – Exposed



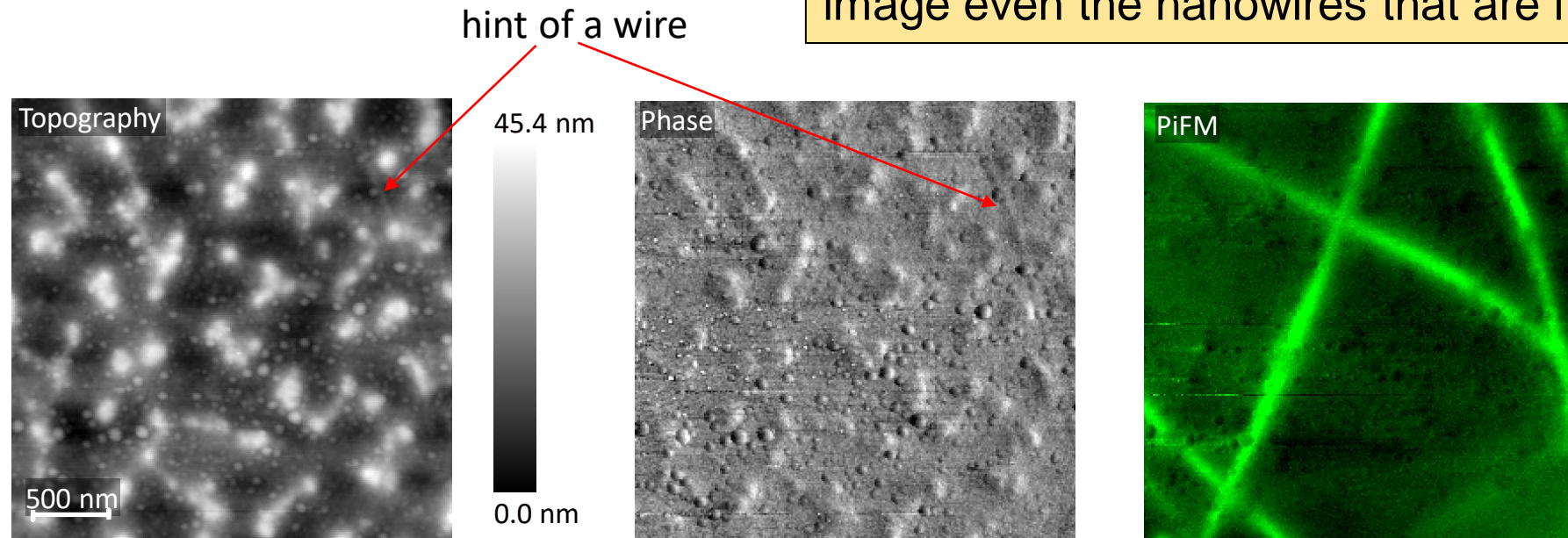
# Characterization of EUV Resist Exposure



# Imaging Buried Conductive Layer



Metallic structures underneath a dielectric layer can be imaged by IR PiFM as demonstrated here with silver nanowires that are buried under 100 nm thick protective coating. While the topography and phase images can only show a hint of a buried silver wire that happens to be near the surface, PiFM can image even the nanowires that are fully buried.



# Thank You

---

Email: [info@molecularvista.com](mailto:info@molecularvista.com)

Website: [www.molecularvista.com](http://www.molecularvista.com)

