COVALENT METROLOGY

Welcome

COVALENT METROLOGY

PHOTO-INDUCED FORCE MICROSCOPY (PIFM): AUGMENTING SURFACE ANALYSIS WITH AFM CHEMICAL MAPPING

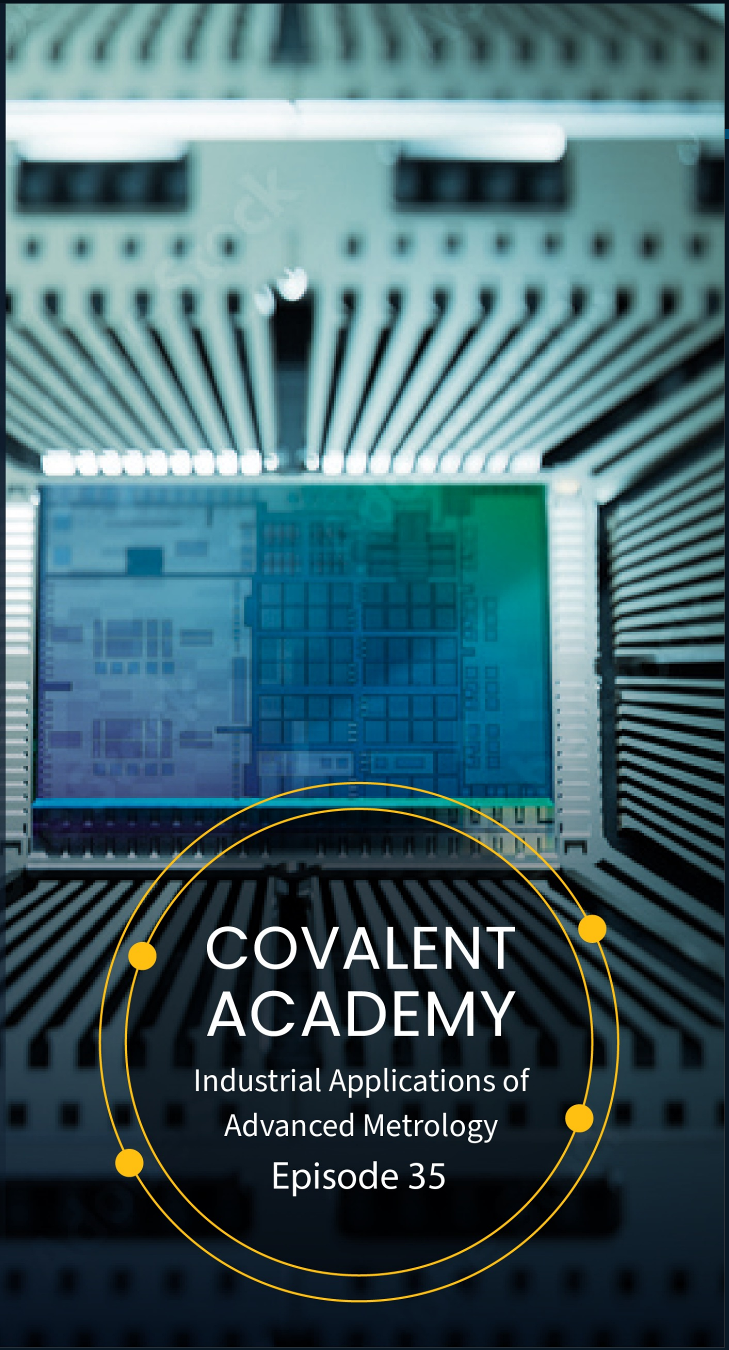
Sung Park, PhD
Cofounder and CEO,
Molecular Vista

Graceson Aufderheide
Applications Engineer,
Molecular Vista

July 27, 2023 | 11am PT

COVALENT METROLOGY

MOLECULAR VISTA



COVALENT METROLOGY

Silicon Valley-based analytical labs and platform delivering quality data and expert analysis for advanced materials and device innovation

Comprehensive Solutions Stack

- 70+ cutting-edge instruments, offering 100+ techniques
- Analytical Services
- Advanced Modeling
- Method Development
- Enterprise Metrology Solutions

Affordable and Fast

- Fast Turnaround Times
- Volume Savings
- Instant Access to Data and Reports in Secure Portal

Flexible Business Model

- Custom Consulting Solutions and Certified On-site Support
- Training and Certification on Instrumentation
- Co-op and Tool-Share Opportunities
- Laboratory Audits

Rich Network of Partnerships

- Partner to the World's Leading Instrument Manufacturers and Labs
- Expanding Instrumentation, Lab Connections, and Learning

Who We Are, Who We Serve

- 500+ Clients, 40 – 60 Added / Quarter
- 60+ Employees, 25% + hold PhDs
- Cutting-edge Analytical Capabilities
- Silicon Valley Lab based in Sunnyvale, CA

Covalent Analytical Services

COVALENT METROLOGY

PCBA, Semiconductor, and Electronic Device Metrology & Failure Analysis

- DPA / Mechanical Cross-section
- Dye & Pry Test
- EBIC / OBIC failure analysis
- Hot Spot Detection
- IR Imaging / Emission Microscopy
- NIR Imaging
- Root-Cause Failure Analysis

Electron Microscopy and Scanning Probe Microscopy

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM)
- Scanning Acoustic Microscopy (SAM)
- SEM (+ EDS)
- FIB-SEM (+ EDS)
- S/TEM (+ EDS / + EELS)
- Nano-indent / Nano-scratch

Optical Microscopy & Spectroscopy

- Chromatic Aberration
- Digital Optical Microscopy
- FTIR and ATR-FTIR
- Laser Scanning Confocal Microscopy
- Spectral Ellipsometry
- UV-Vis-NIR Spectroscopy
- White Light Interferometry

X-Ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micron-spot ED-XRF
- WDXRF
- Micro-computed X-ray Tomography (Micro-CT)
- 2D X-ray Inspection & X-ray Radiography

Elemental / Chemical Composition Analysis

- EPMA
- GD-OES
- GC-MS
- ICP-MS and LA-ICP-MS
- Raman Microscopy & Spectroscopy
- NMR (1D or 2D; solid / liquid)

Particle Analysis

- Dynamic Light Scattering (DLS)
- Laser Diffraction Particle Size Analysis (PSA)
- **Particle Zeta Potential**

Material Property Characterization

- DSC
- DMA & TMA
- Rheometry
- TGA
- **Solid Surface Zeta Potential**
- Porometry / Porosity
- Gas Adsorption
- Gas Pycnometry
- Foam Density
- Tap Density

Surface Spectroscopy Analysis

- Dynamic-SIMS
- ToF-SIMS (Static-SIMS)
- Ion Scattering Spectroscopy (ISS)
- Ultraviolet Photoelectron Spectroscopy (UPS)
- X-ray Photoelectron Spectroscopy (XPS)

Covalent Partners

Today's webinar is in partnership with

MOLECULAR VISTA

- Team of Experts behind:
  - **Photo-Induced Force Microscopy (PiFM)**
  - **Photo-Induced Force IR Spectroscopy (PiFIR)**
- Techniques **enable mapping and analyzing the chemistry of smaller volumes than ever before**.
- Collaboration with Covalent brings these solutions to new applications and supports advanced device & materials research.

Other Covalent Partners

Rigaku

JEOL Solutions for Innovation

HORIBA Scientific

ThermoFisher SCIENTIFIC

TELEDYNE CETAC TECHNOLOGIES Everywhereyoulook™

Anton Paar

TA Instruments

KEYENCE

J.A. Woollam

Asylum Research an Oxford Instruments company

Digital Surf

PVA TePla

Toray Research Center, Inc.

Introducing

COVALENT METROLOGY

Dr. Sung Park

Co-founder and CEO, Molecular Vista

MOLECULAR VISTA

- Received a PhD in Applied Physics from Stanford University in 1986.
- After graduating, he worked for almost 2 decades **developing new scientific instrumentation** specializing in **advanced technologies for atomic force microscopy**.
- In **2012, he co-founded Molecular Vista** to empower analysts to **probe and understand matter at the molecular level through quantitative visualization**.

Infrared Photo-induced Force Microscopy

July 27, 2023

Sung Park
sung@molecularvista.com

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.	E.I.	E.I.	E.I.	E.I.
Chemical Mapping		Yes	Yes	Yes	Yes	Yes (Elemental)	Yes (Elemental)	Yes (Elemental)	Yes
Lateral Resolution		> 0.5 μm	> 10 μm	> 0.2 μm	10 μm – 2 mm	~ 1 mm	1 nm* 0.5μm EDS	0.2 nm* 1 ~ 20 nm EDS	~ 10 nm
Depth Probed		> 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

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.

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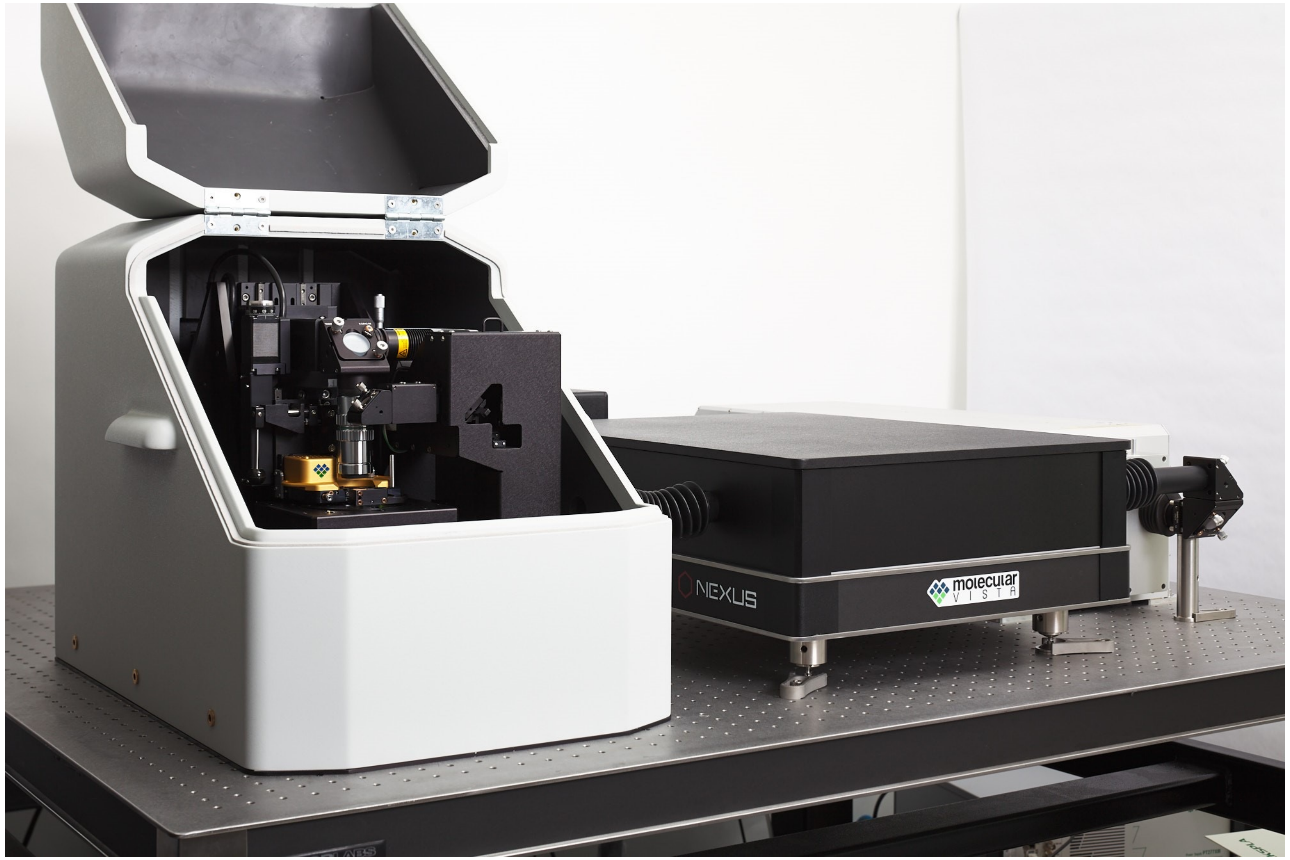
IR PiFM on Vista AFM Platform



Vista 75

- Sample Size: 4” diameter x 1” height
- Scan Range: 80 x 80 x 12 μm^3
- AFM + multiple laser sources
- IR PiFM + other optional near-field techniques
- If a sample can be analyzed via AFM, IR PiFM is possible
- Vista One and Vista 200 also available

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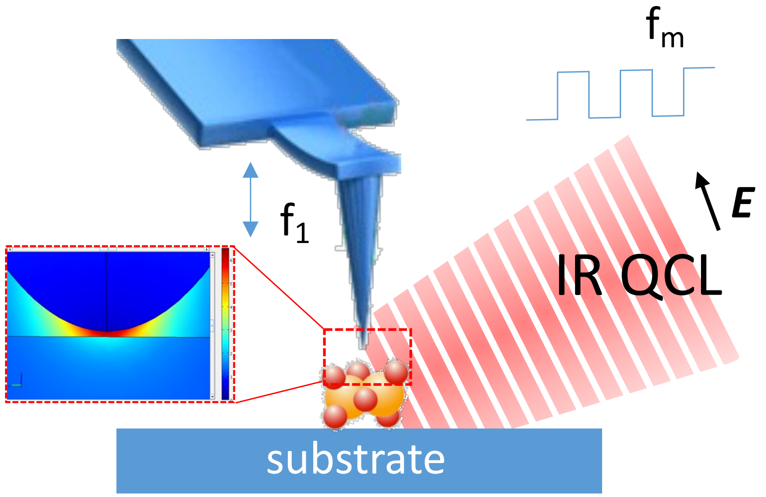
Infrared Photo-induced force microscope (IR PiFM)

(a)

Bi-modal Non-contact AFM



Broad tunable IR laser
(589 – 4400 cm^{-1})

Norway spruce fiber wall

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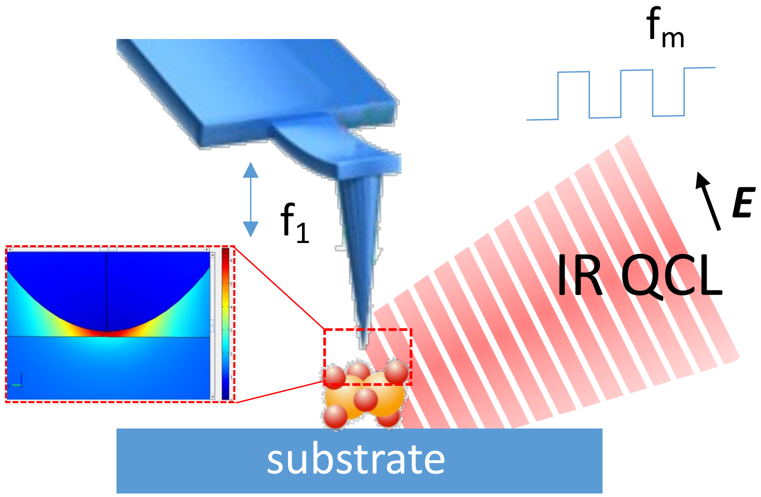
Infrared Photo-induced force microscope (IR PiFM)

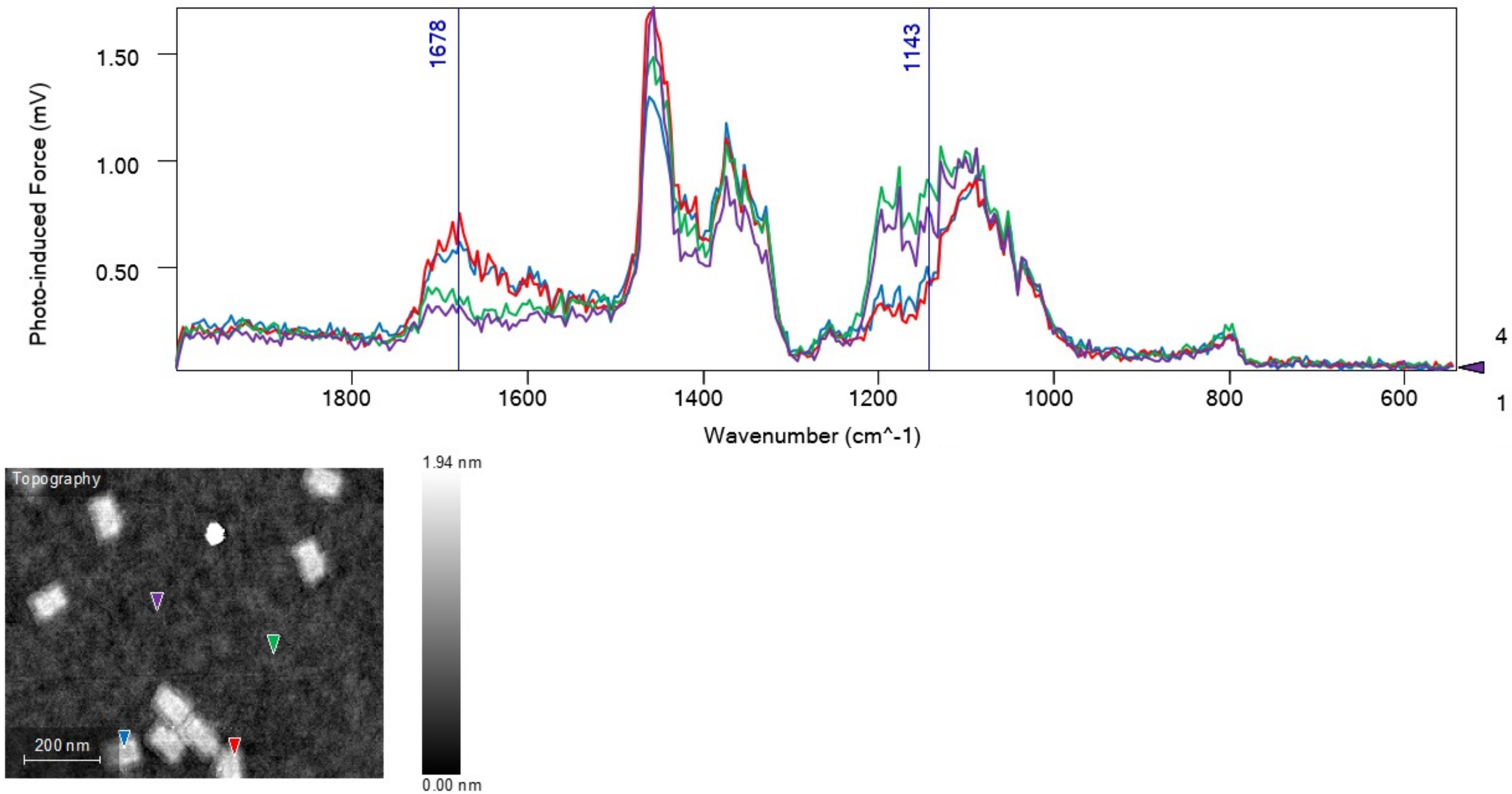
Monolayer Sensitivity

(a) Bi-modal Non-contact AFM



Broad tunable IR laser
(589 – 4400 cm^{-1})

(b) (DNA origami, ~ 1.1 nm thick) (substrate)



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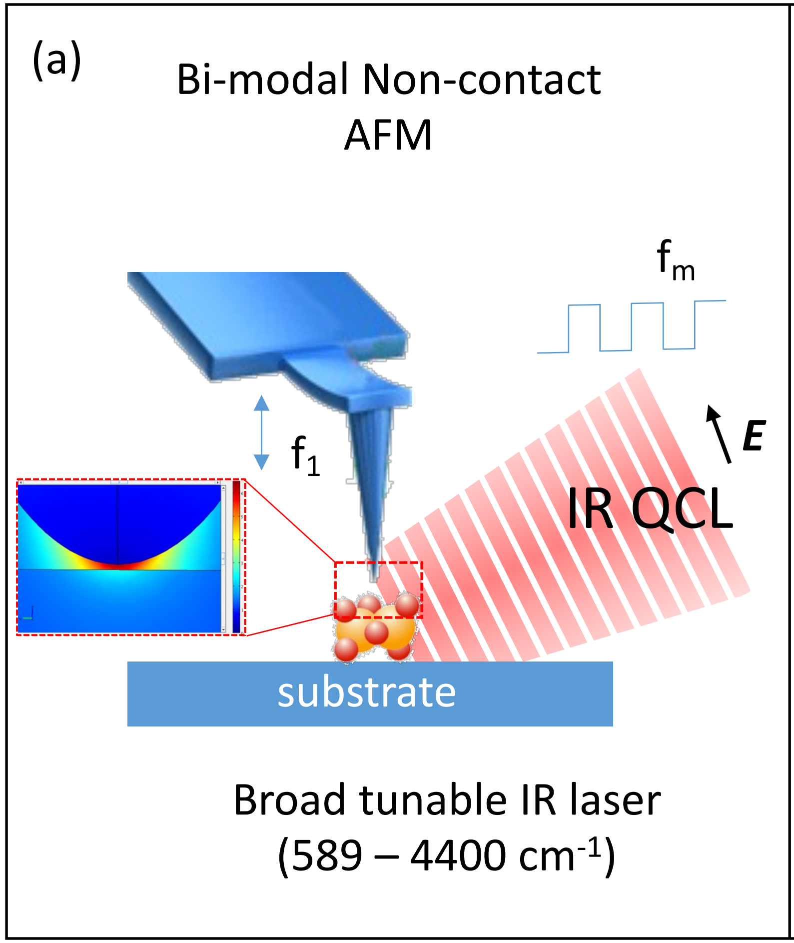
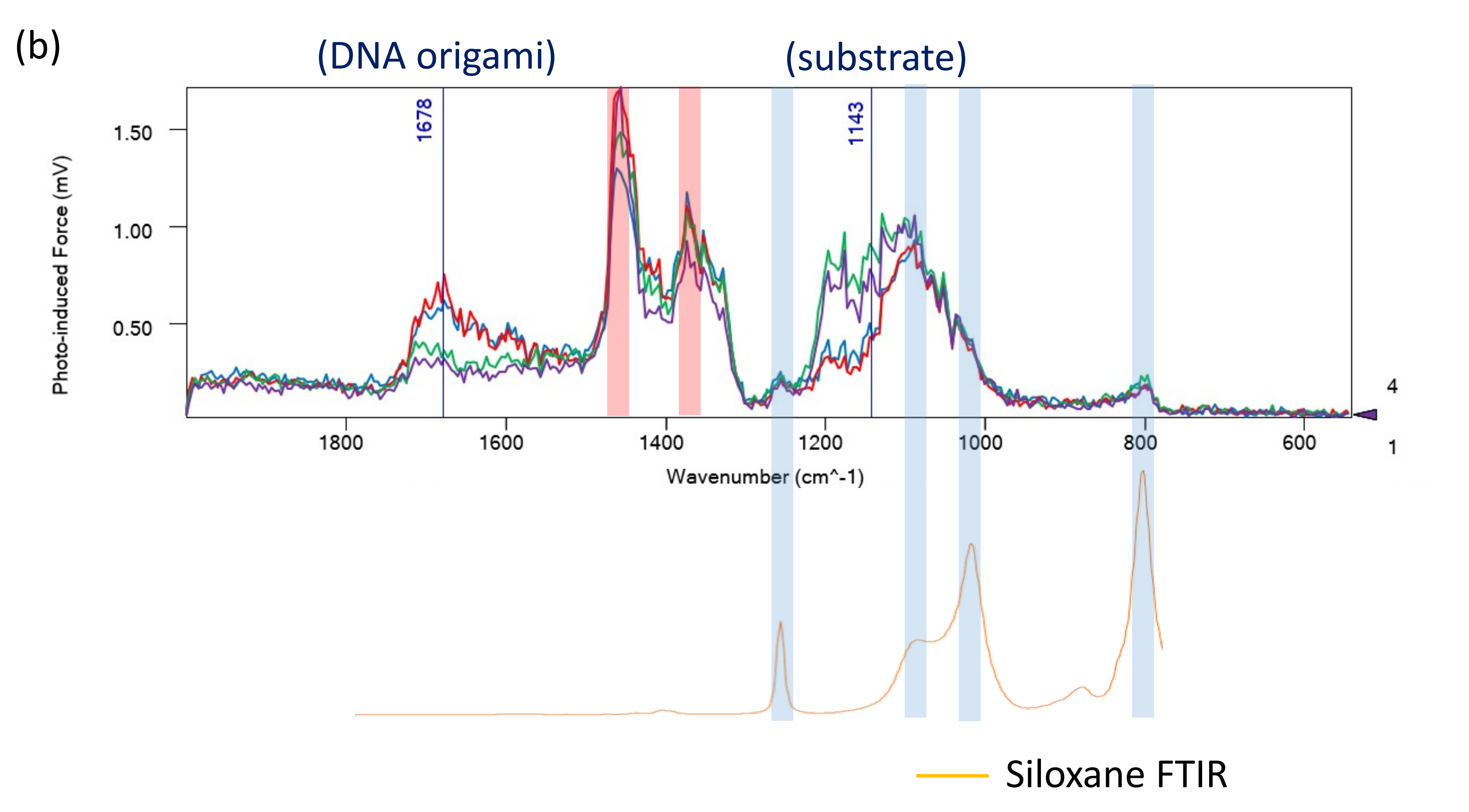
Infrared Photo-induced force microscope (IR PiFM)

Monolayer Sensitivity





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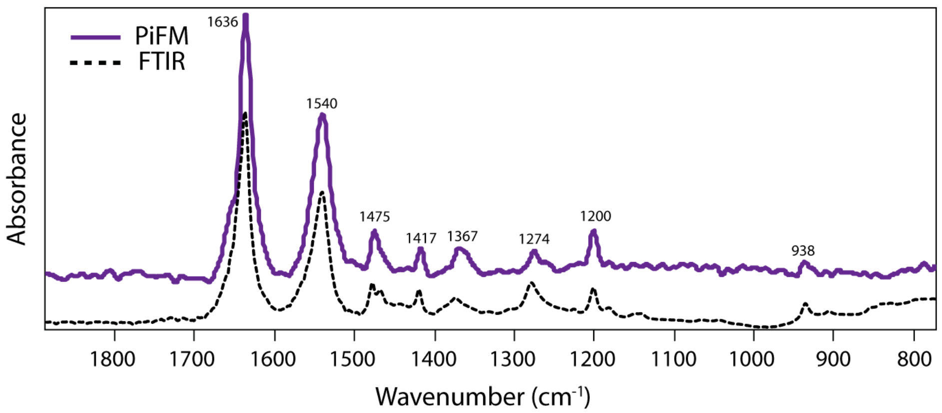
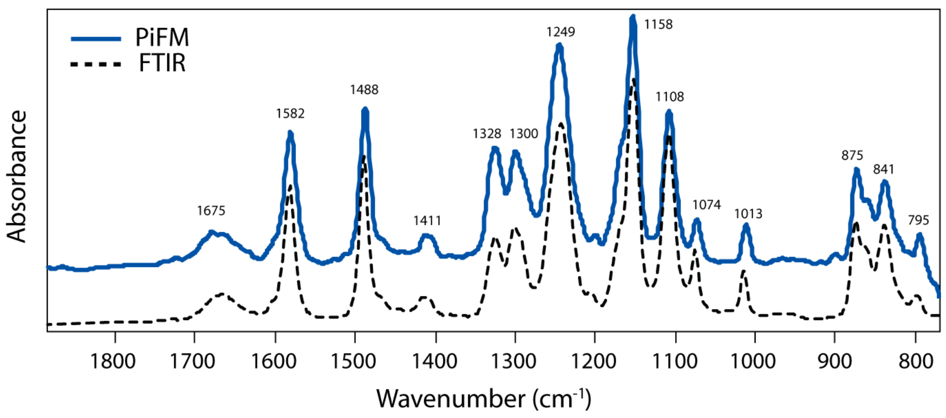
Excellent Agreement between Nanoscale PiF-IR and FTIR Spectra

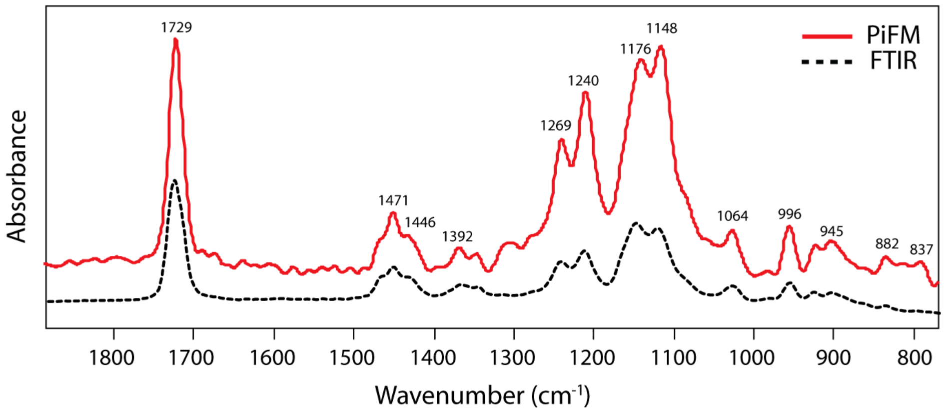
PiFM and FTIR of Nylon



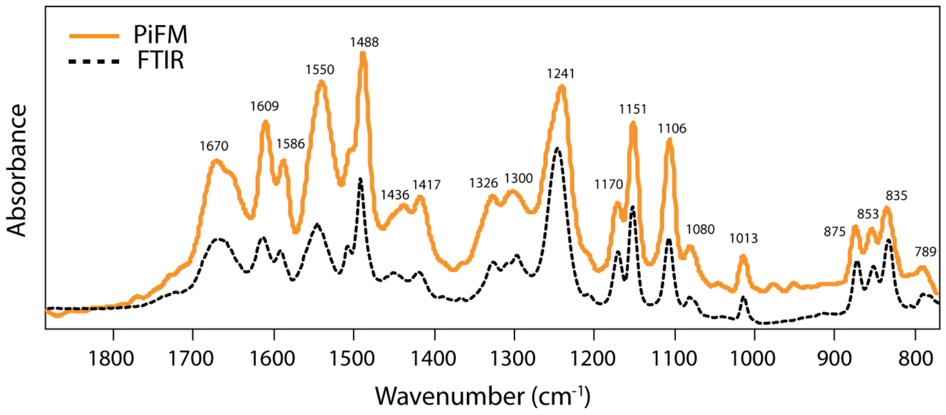
PiFM and FTIR of PES (Polyethersulfone)



PiFM and FTIR of PMMA - Poly(methyl methacrylate)



PiFM and FTIR of Polyimide



Excellent agreement between PiF-IR spectra (originating from ~ 5 nm region) and FTIR spectra (originating from ~ 10 μm region) on homogeneous samples.

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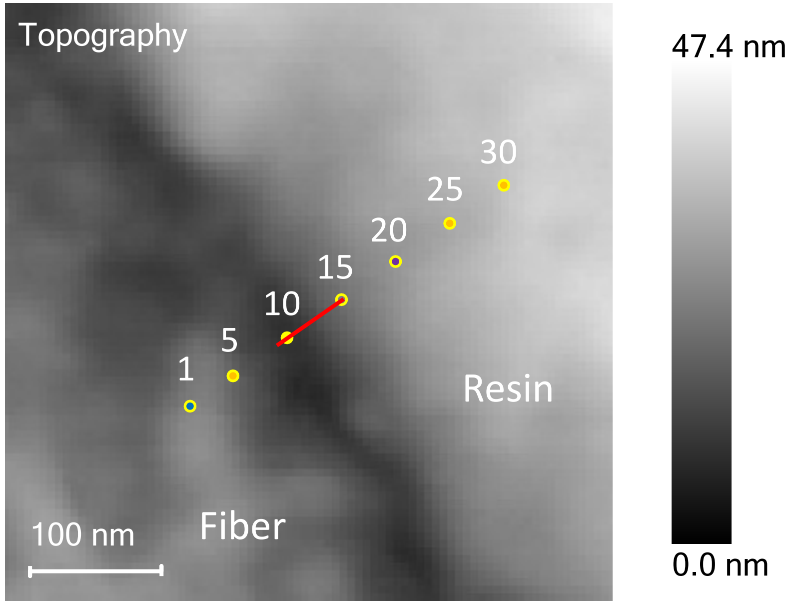
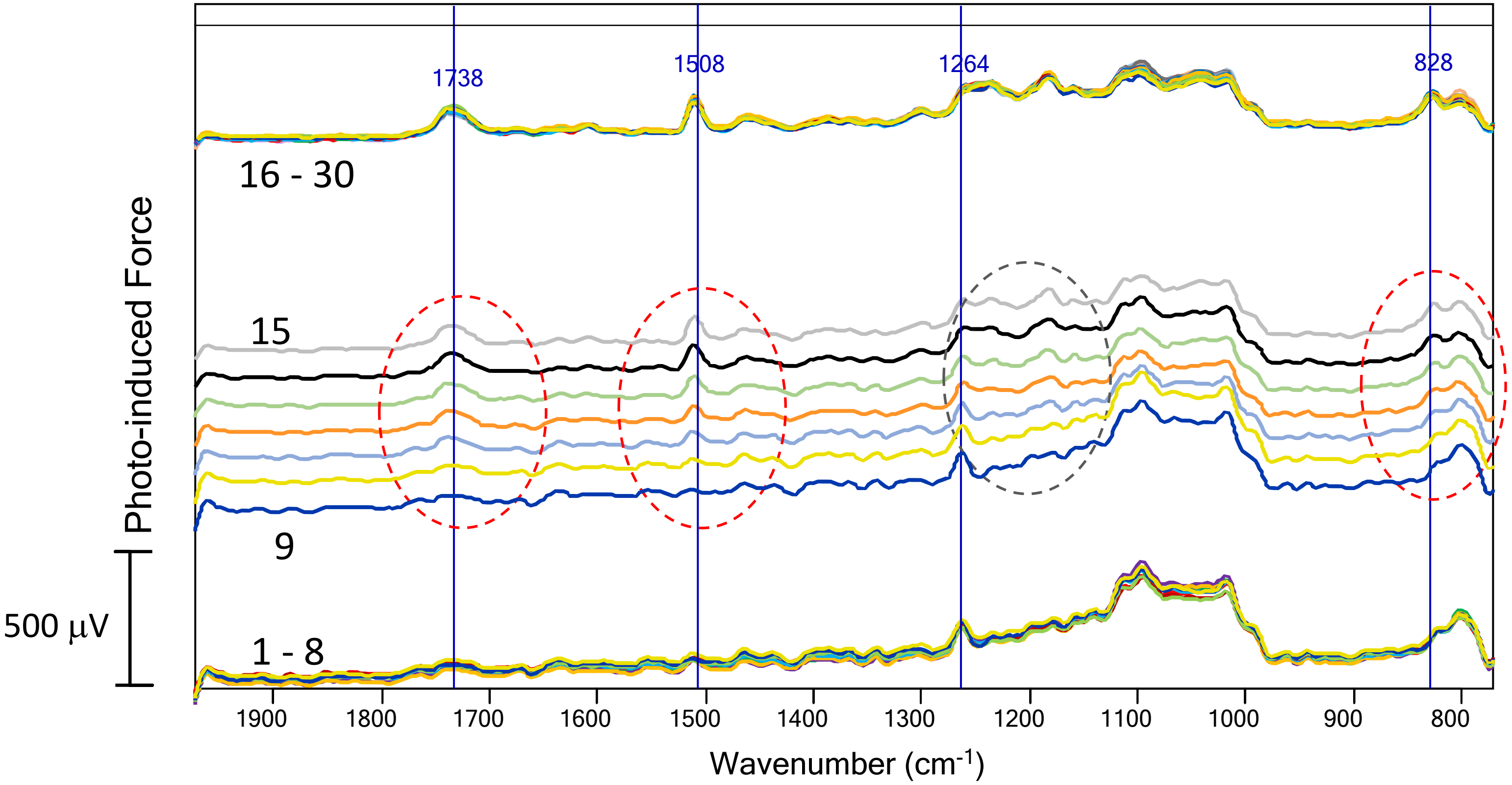
Excellent Repeatability

Carbon Fiber-Resin Interface



30 spectra with 10 nm spacing



The interface between a carbon fiber and resin are analyzed by preparing a cross-section of the composite fiber via microtome. 30 PiF-IR spectra are acquired across the interface with ~ 10 nm spacing. The first 8 spectra in the carbon fiber and the last 16 – 30 spectra are very repeatable, with all the spectral changes taking place over 9 – 15 spectra. The SNR is good enough to discern chemical changes for each 10 nm changes in spatial location.

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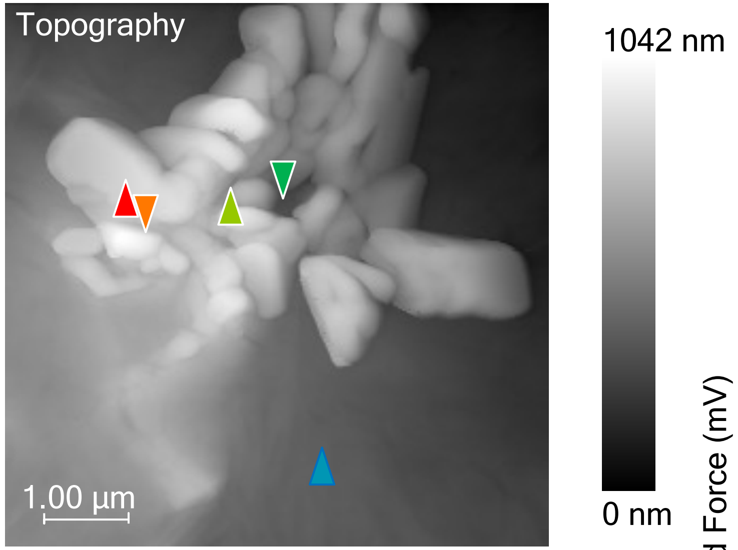
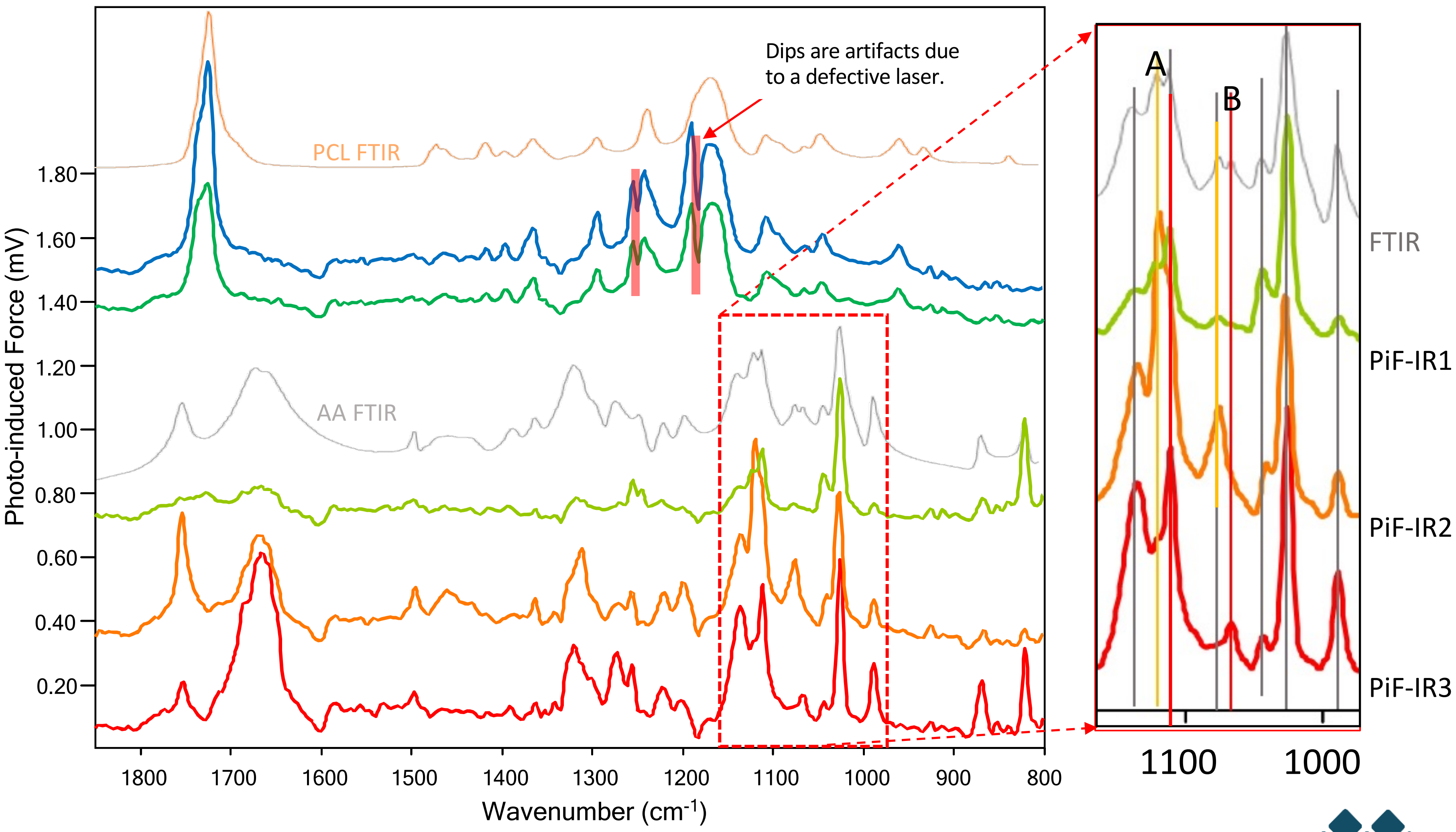
Discrimination of Molecular Orientation



The two spectra (blue and dark green) on homogeneous PCL match the PCL FTIR well. The three spectra acquired on the AA crystals show different peak strengths compared to the AA FTIR. PiF-IR is most sensitive to modes that are out of the sample plane. As such, PiF-IR spectra on different crystal orientations highlight different peaks compared to FTIR, which is an ensemble average of billions of PiF-IR spectra. Note that for the FTIR doublets A and B, the red and orange spectrum each showcase different singlets.

Poly(e-Caprolactone)/Ascorbic Acid (PCL/5AA) – AA Crystals



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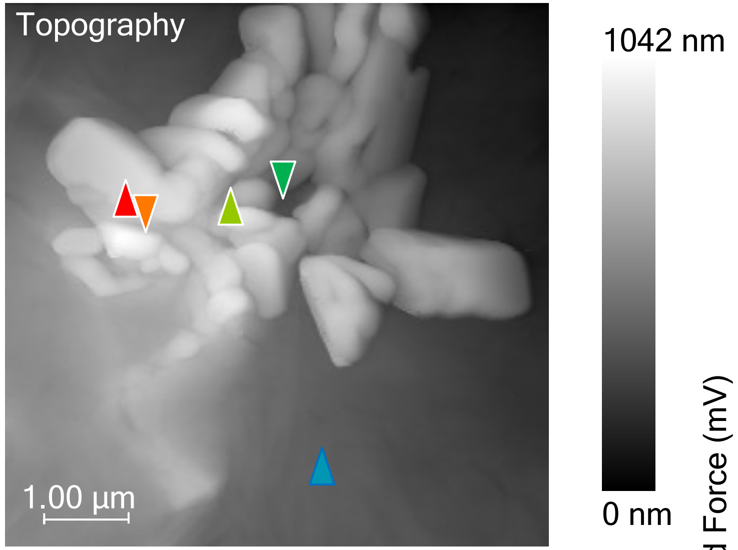
Discrimination of Molecular Orientation



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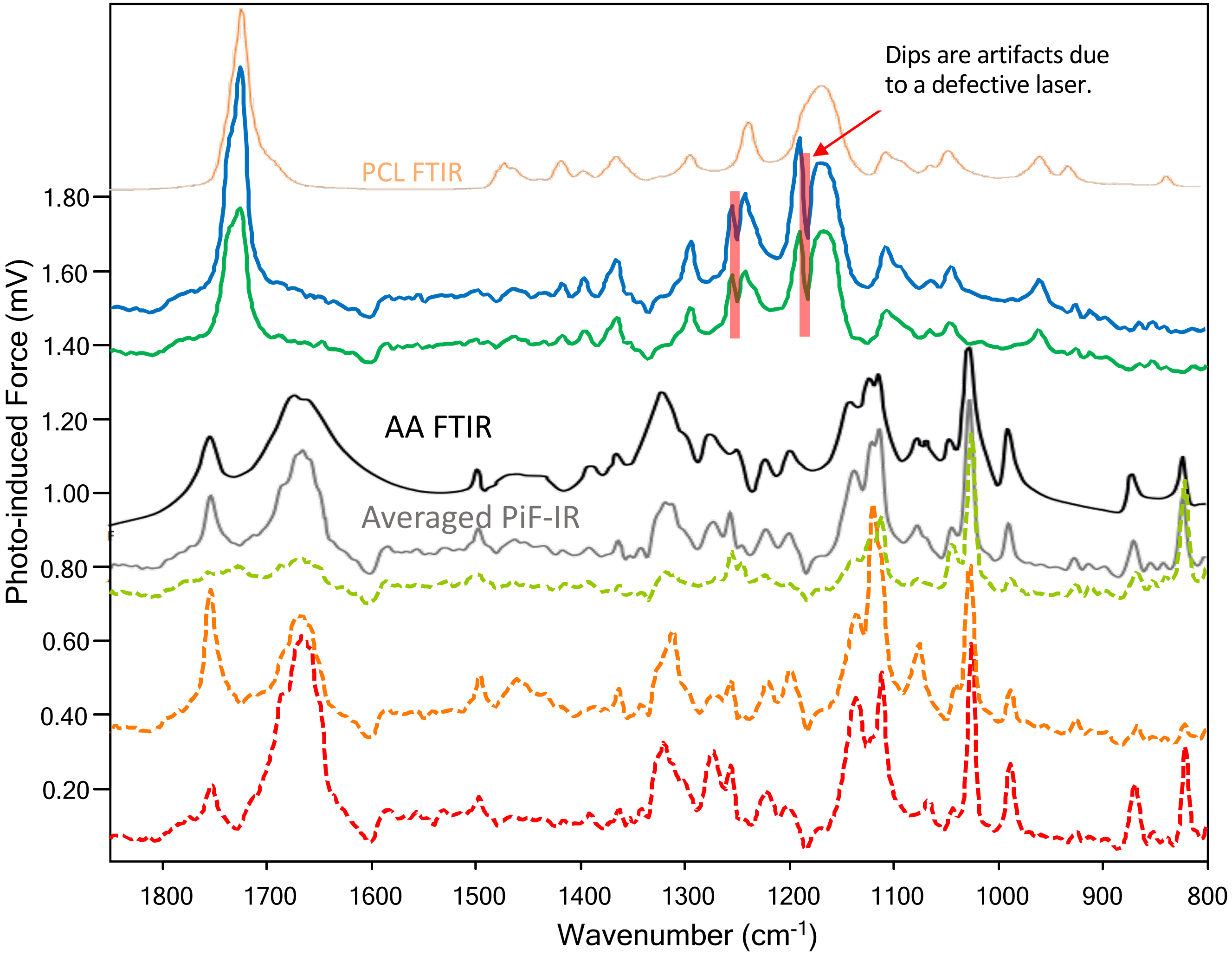
Ensemble averaged FTIR versus local PiF-IR spectra



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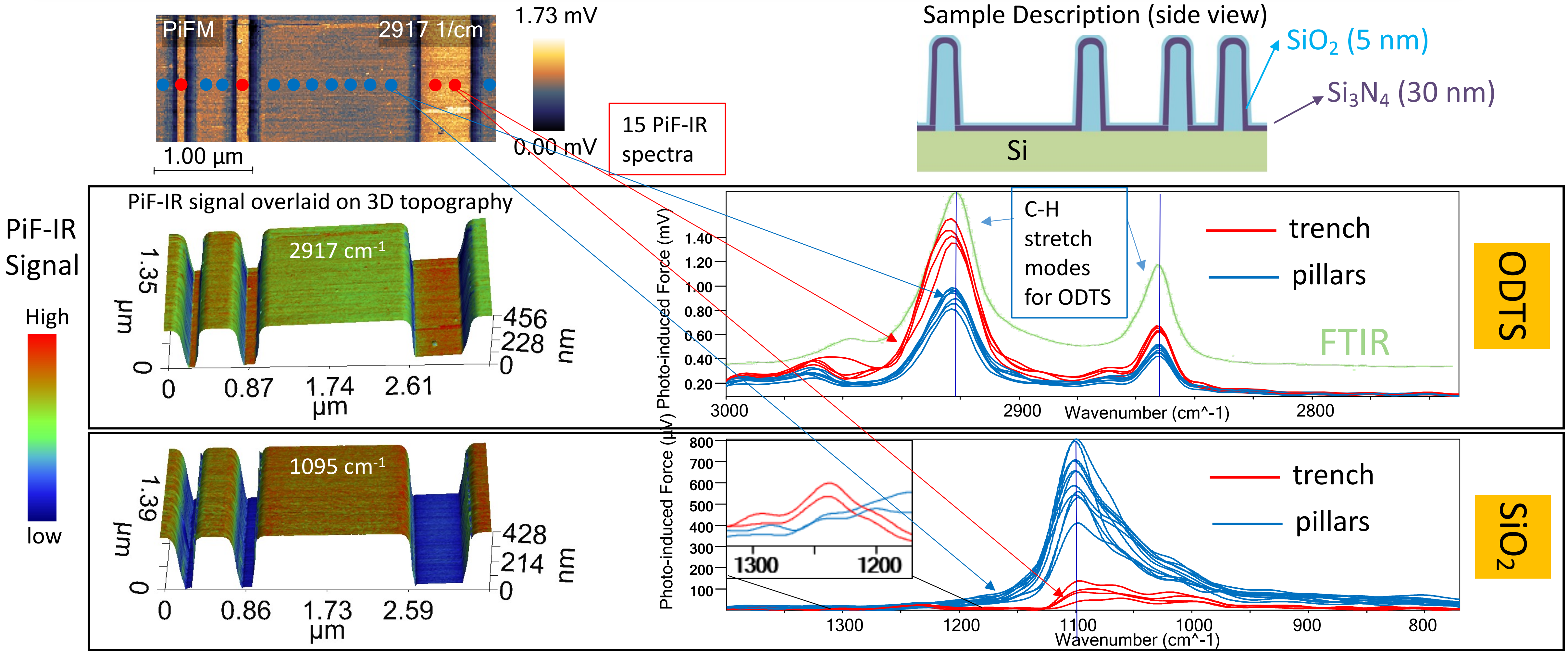
ODTS on SiO_2 (Organic & Inorganic Films)



Octadecyltrichlorosilane (ODTS) molecules are self-assembled on top of a 5nm-thick SiO_2. ODTS SAM layer is thin enough that PiF-IR spectra for the SiO_2 (bottom panel) can be acquired through the SAM layer. Note that the spectra for SiO_2 are different for the pillars (blue) and trenches (red), indicating different forms of SiO_2. As a results, higher packing density of ODTS (upper panel) is observed for the trenches.

Defects and Residue

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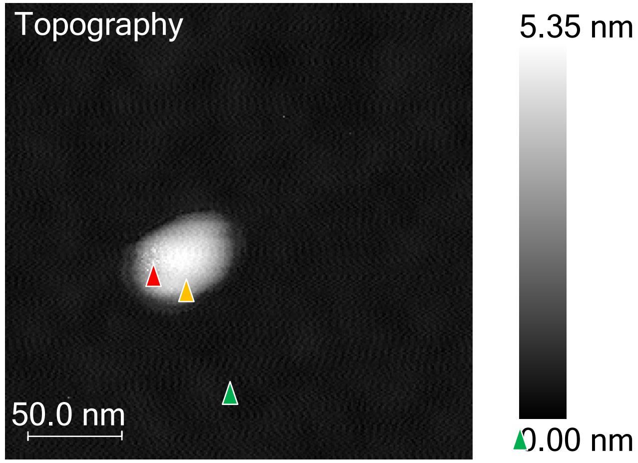
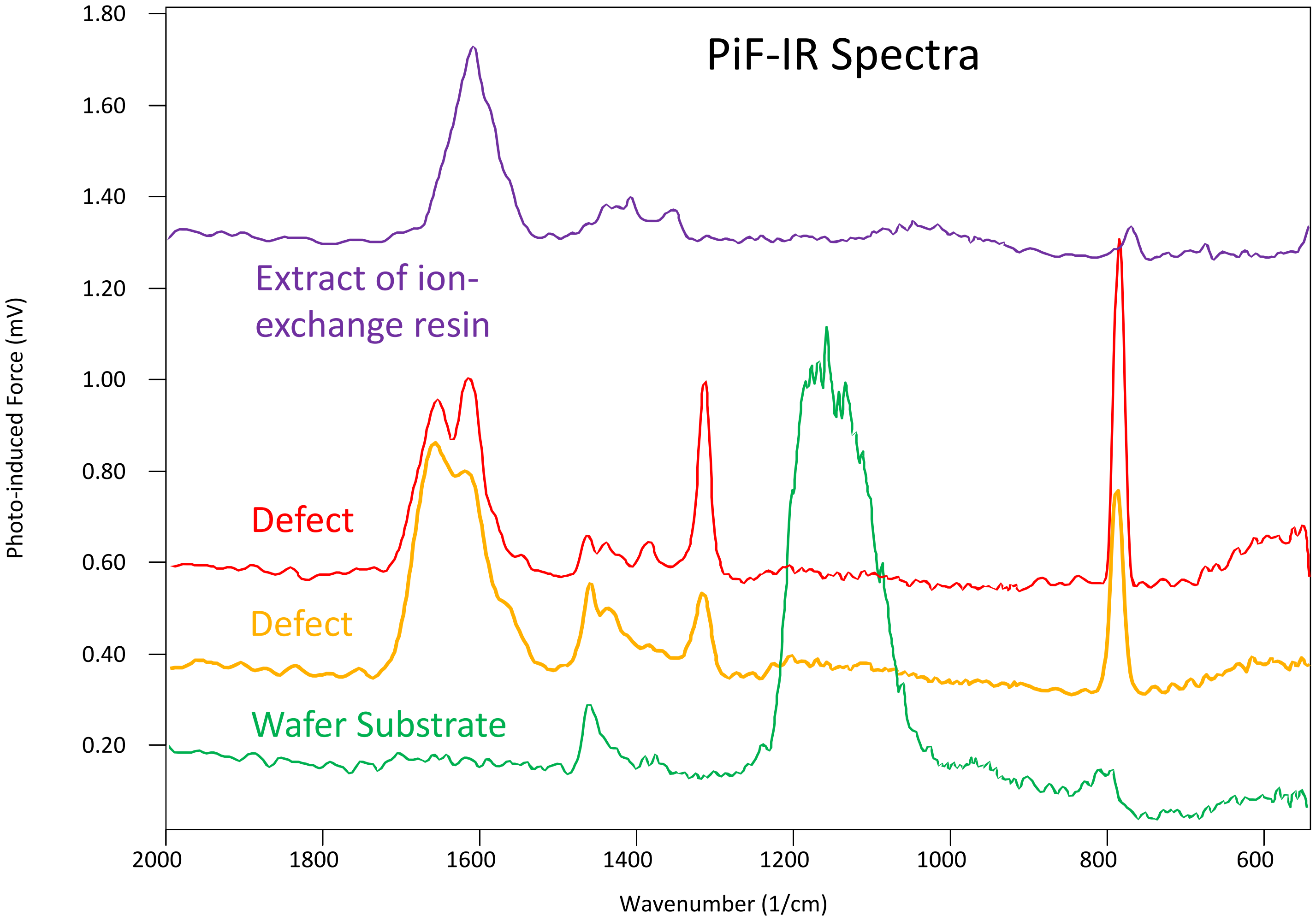
Defect/Residue on Wafer Processed by Ultrapure Water

Extract of ion-exchange resin drop-cast on glass

Defect on wafer





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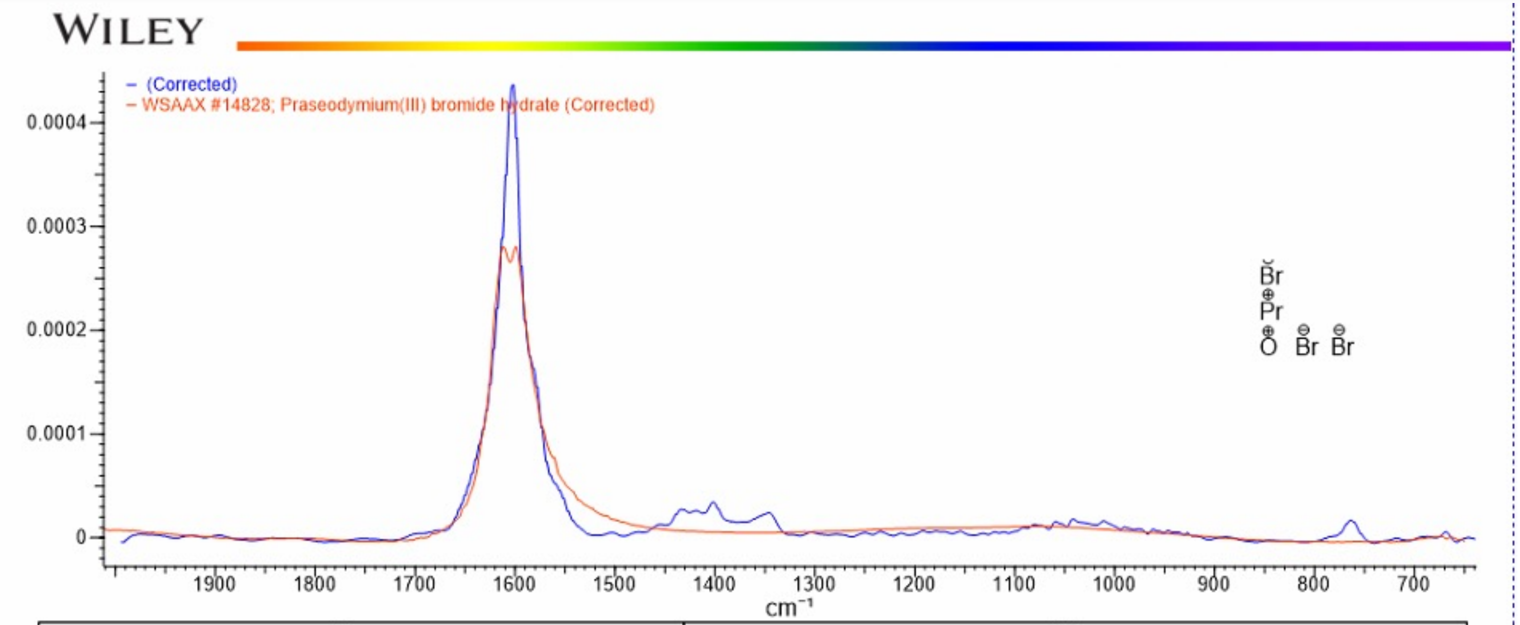
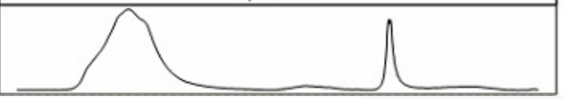
One Component Search - Resin



Name	Value
Name	Praseodymium(III) bromide hydrate
CAS Registry Number	225505-12-4
Catalog Number	575267
Comments	MW calculated on anhydrous base
Exact Mass	377.662662 u
Formula	$PrBr_3$*xH_2O
InChI	InChI=1S/3BrH.O.Pr/h3*1H;;/q;;;;+3/p-3
InChIKey	OLPNCVJBIOCRHH-UHFFFAOYSA-K
Molecular Weight	380.620 g/mol
Purity	>=99.99% trace metals basis
Source of Sample	Aldrich
SpectraBase Compound ID	2G1jnOvJyLb
Wiley ID	SIAL_ATR-IR_021740

HQI	Tag	rrectio	DB	ID	Name	Spectrum
86.03			WSAAX	14828	Praseodymium(III) bromide hydrate	

About Cobalt(II) Bromide Hydrate

Most metal bromide compounds are water soluble for uses in water treatment, chemical analysis and in ultra high purity for certain crystal growth applications.

American Elements
https://www.americanelements.com › cobalt-ii-bromide-h...

Cobalt(II) Bromide Hydrate | AMERICAN ELEMENTS ®

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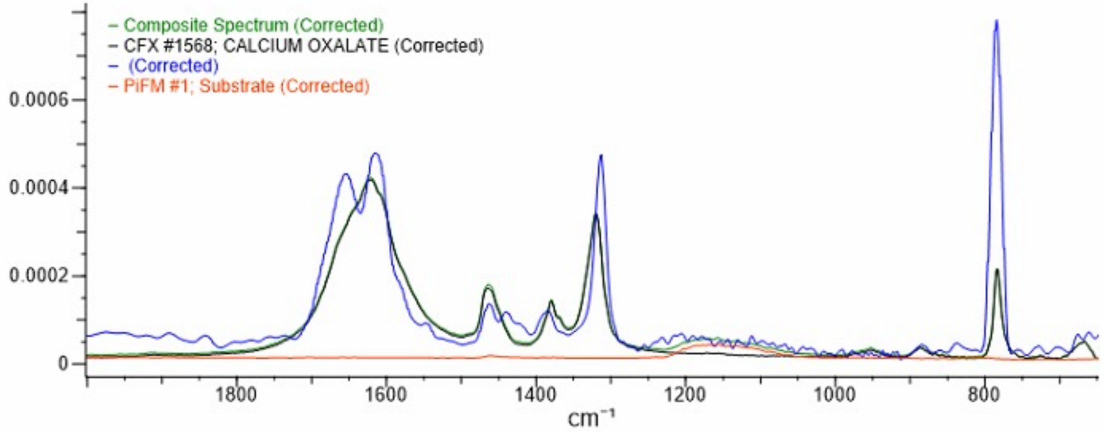
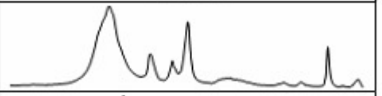
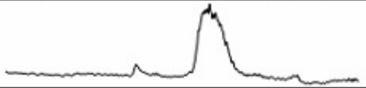
Two Components Search – Defect (red spectrum)

WILEY



Database/Hit List Structure

HQI	Ratio	Exclude	recti	DB	ID	Name	Chemical Structure	Spectrum
65.84	N.A.					Composite Spectrum		
	0.92			CFX	1568	CALCIUM OXALATE		
	0.08					PiFM #1; Substrate		

The result of the two components search for the defect 1 is same to the top result of the one component search.

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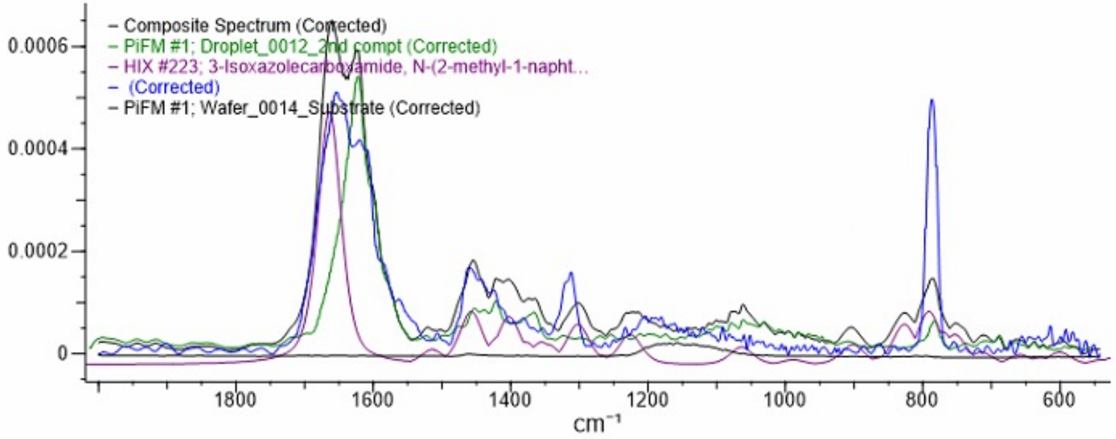
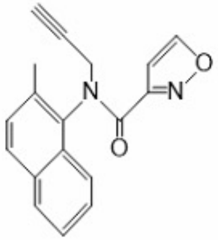
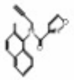
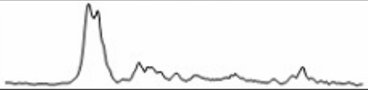
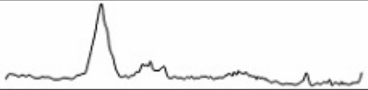
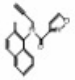
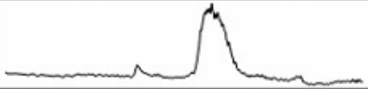
Three Components Search – Defect (gold spectrum)

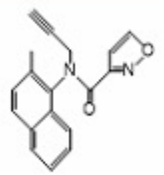
WILEY





HQI	Ratio	Exclude	recti	DB	ID	Name	Chemical Structure	Spectrum
76.55	N.A.					Composite Spectrum		
	0.49					PiFM #1; Droplet_0012_2nd compt		
	0.48			HIX	223	3-Isoxazolecarboxamide, N-(2-methyl-1-naphthalenyl)-N-2-propynyl-		
	0.03					PiFM #1; Wafer_0014_Substrate		

Structure/Properties



Substructs | Sel. Substructs | Original Data Files
All Properties | Attachments | Preferred Properties

Name	Value
Name	3-Isoxazolecarboxamide, N-(2-methyl-1-naphthalenyl)-N-2-propynyl-
CAS Registry Number	86314-77-4
Formula	$C_{18}H_{14}N_2O_2$

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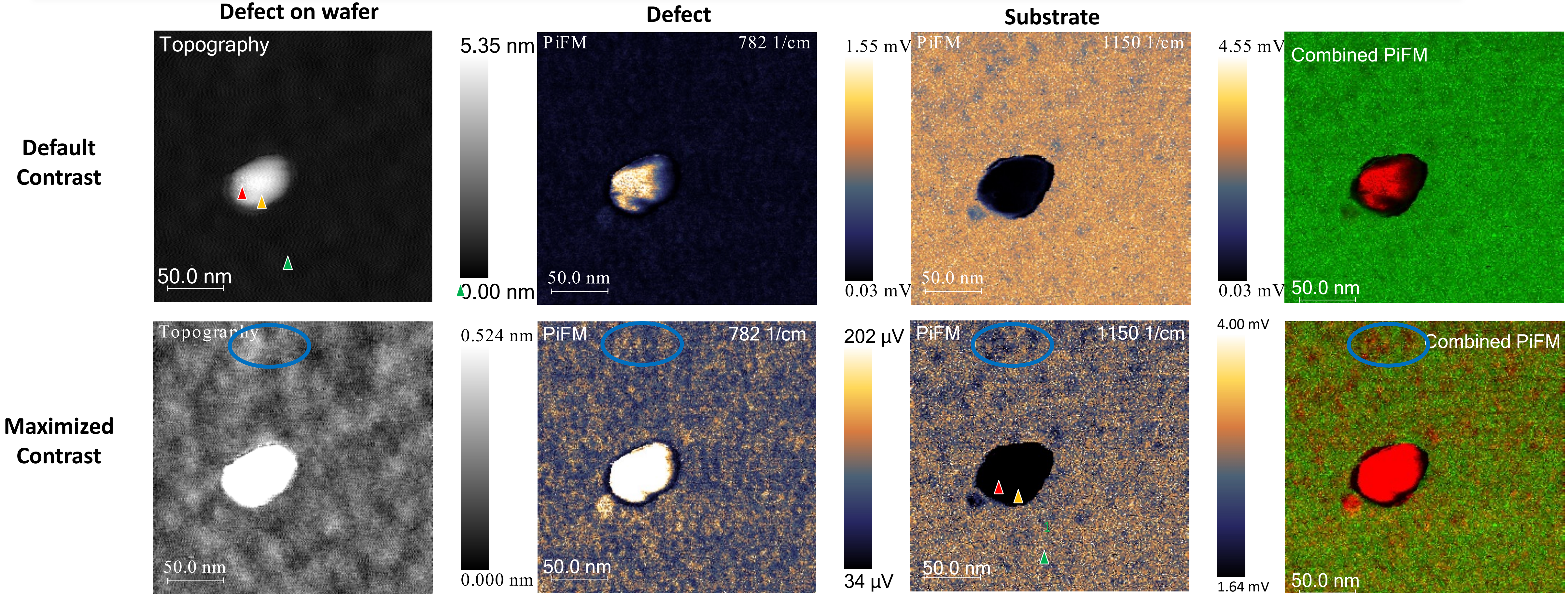
Analysis of Wafer Defect/Residue Processed by Ultrapure Water



The bottom row of images are the same as the top row but the contrast has been maximized to show the PiFM signal variation on the substrate. There are increases in signal at 782 cm^{-1} on the substrate where 1150 cm^{-1} decreases, and the topography height also increases slightly (blue circles). This suggests that there are also very thin layers of the defect on the substrate along with the larger defect. IR PiFM is surface sensitive, and any intervening residue between the substrate and the tip will reduce the signal strength of the substrate (in this case 1150 cm^{-1}).

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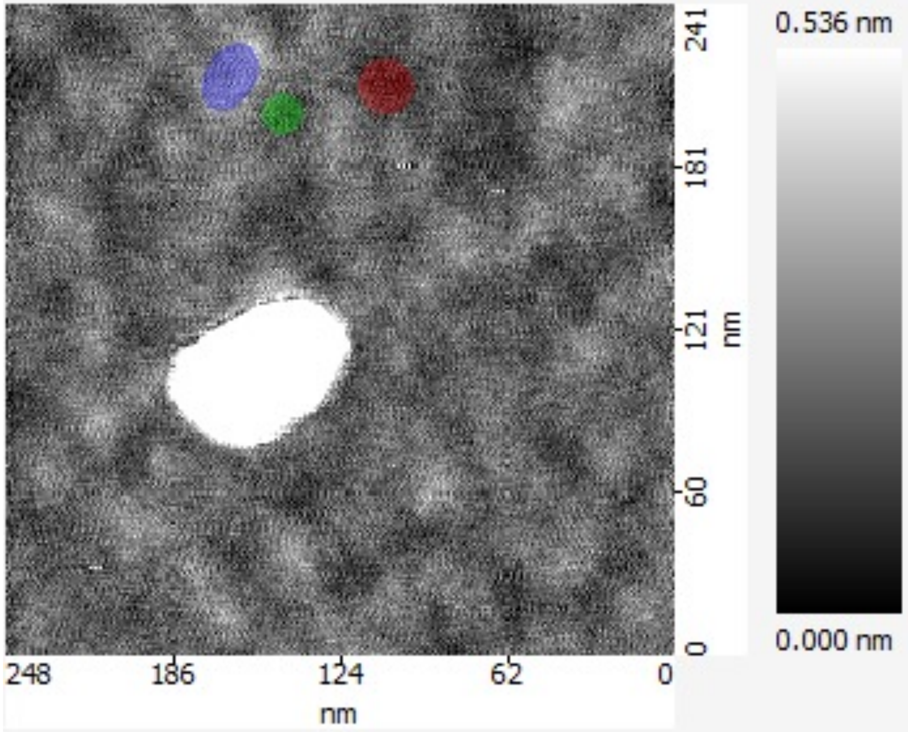
Analysis of Wafer Defect/Residue Processed by Ultrapure Water



	Blue	Red	Green
Avg (nm)	0.3371	0.1163	0.159
Min (nm)	0.1246	-0.09823	-0.04752
Max (nm)	0.5448	0.3054	0.3342
Median (nm)	0.3388	0.1185	0.1553
Ra (nm)	0.05337	0.05252	0.05484
Rms (nm)	0.06715	0.06598	0.06927
Skew	-0.131	-2.038e-4	0.108
Kurtosis	0.1085	0.004612	-0.03459
oj. Area (nm^2)	372.5	318.6	172.5

The average height of the residue seems to be about 0.2nm thick, which may indicate a monolayer.

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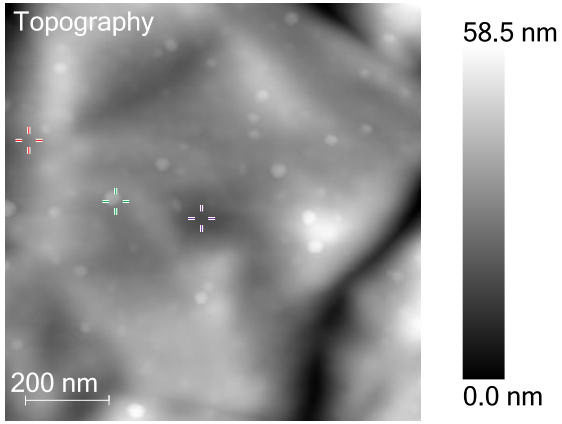
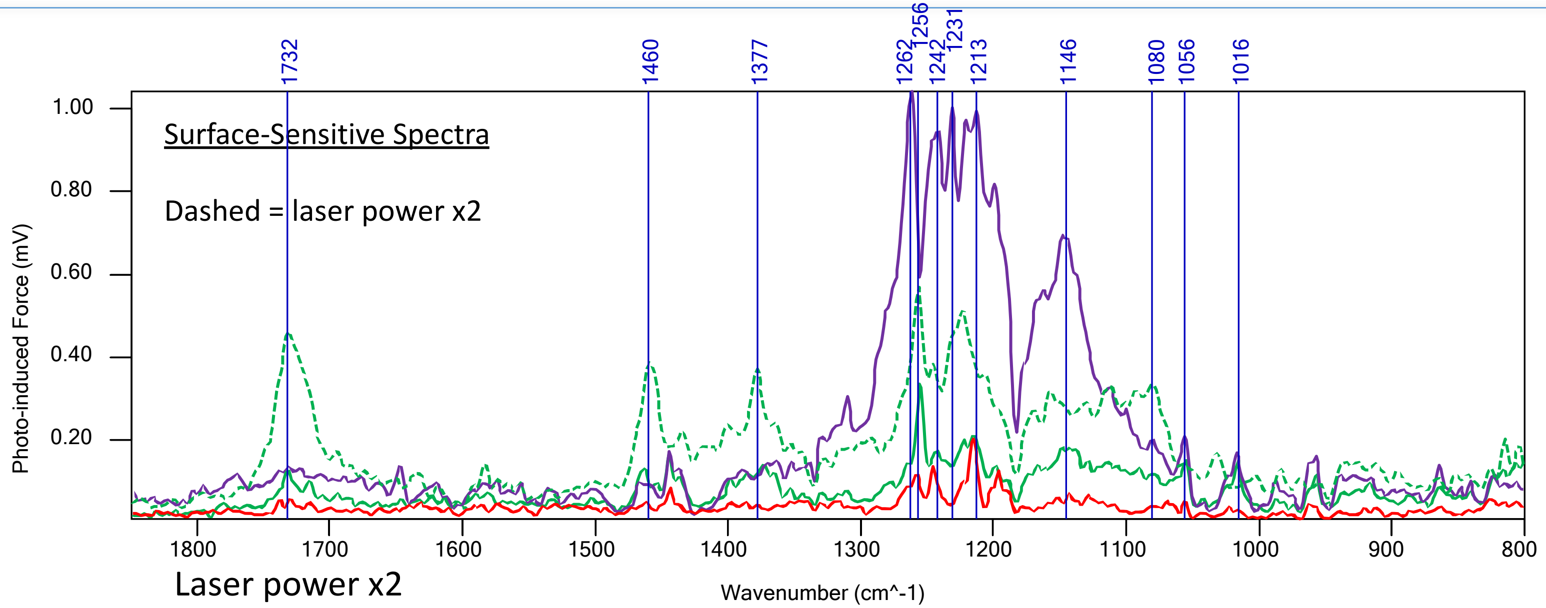
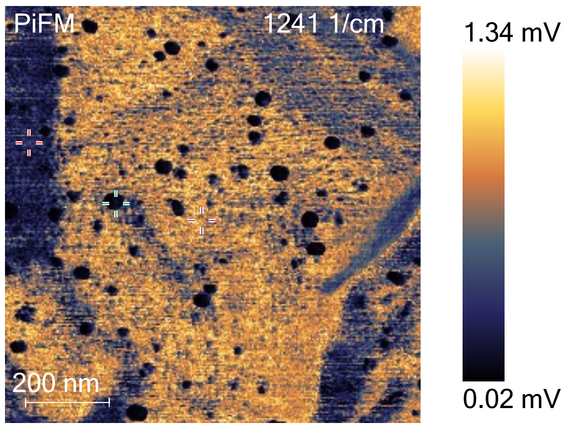
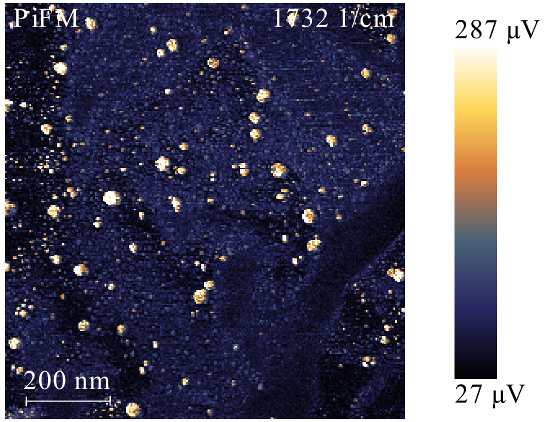
Failure of Contact Pad Analyzed: 1 µm^2
Topography, PiFM and Spectra

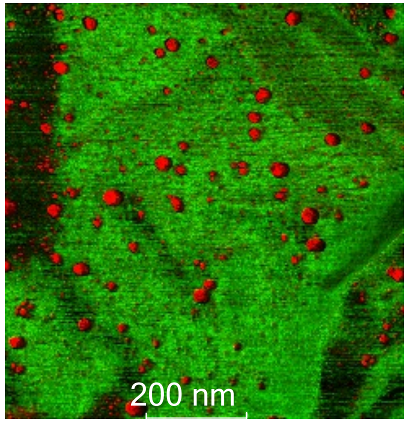




The purple surface-sensitive spectrum shows similar peaks to those on the edge, well defined peaks at 1262, 1242, 1231, 1213 within the broad peak centered around 1230 cm^{-1}. However, the center shows additional contaminants, these are small particles found on the sample surface, with peaks around 1732, 1460, 1377, 1256 and 1225 cm^{-1}.







C-F compound (1241 cm^{-1})

2nd contaminant (1732 cm^{-1})

ALD Films

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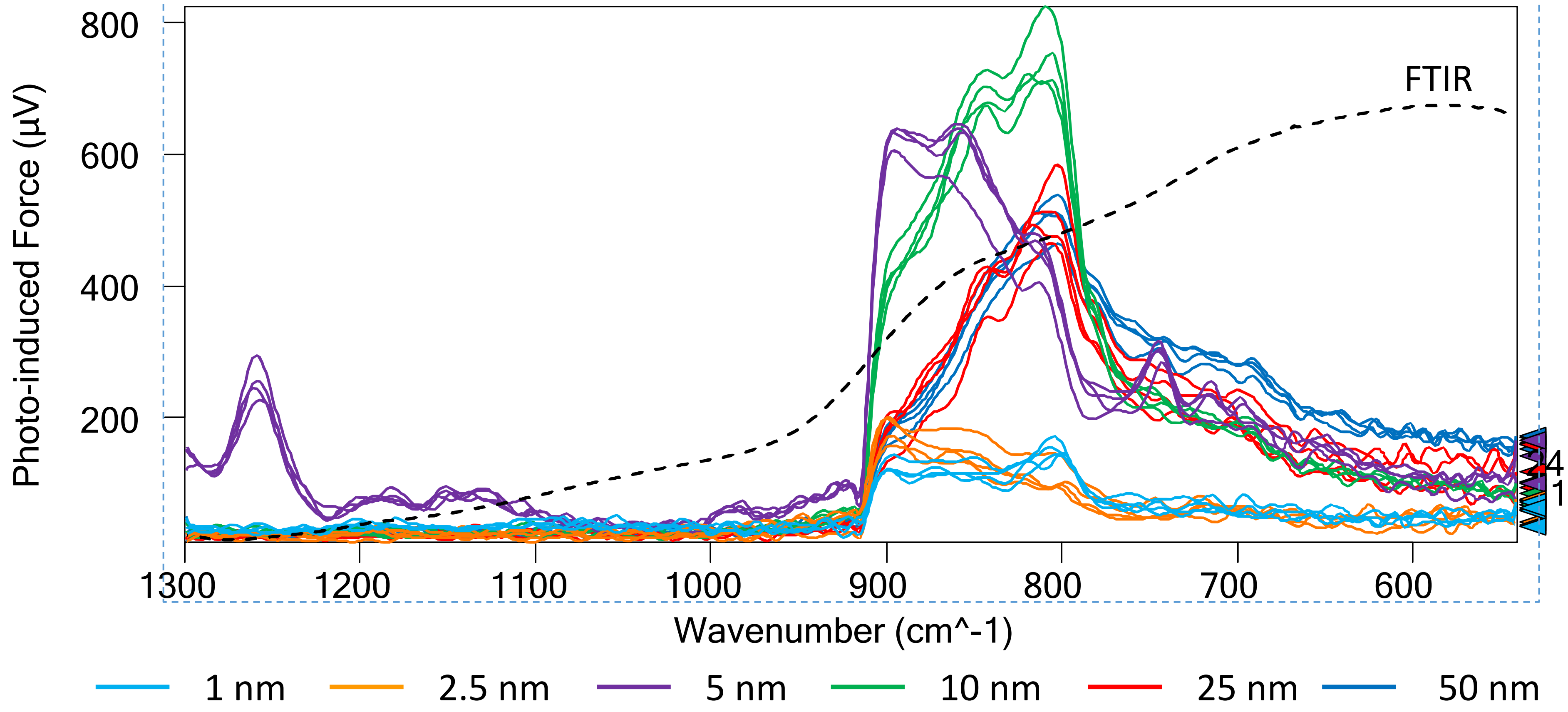
PiF-IR Analysis of ALD Grown Al_2O_3



Four spectra (1 µm spacing) are acquired from each sample; they are reasonably repeatable indicating that each sample is homogeneous. Compared to the broad FTIR spectrum, PiF-IR spectra display sharper features that vary with thickness.

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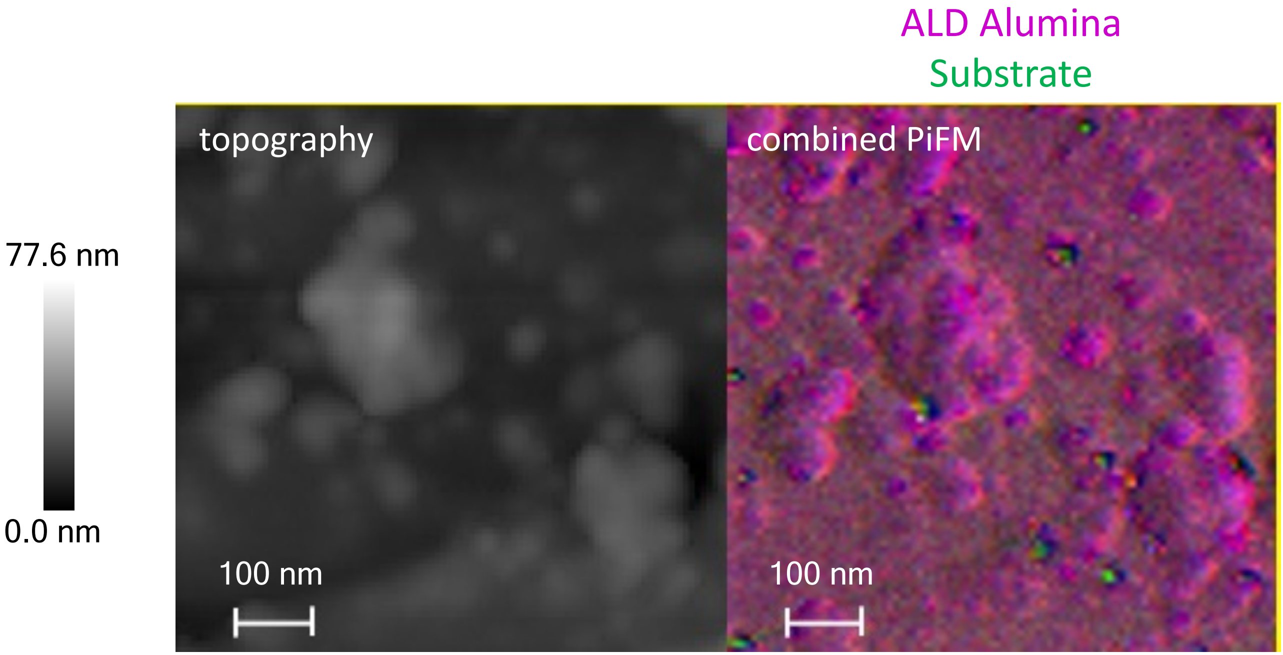
PiFM Image of ALD Grown Al_2O_3



Alumina is grown on top of a substrate material via ALD and examined via IR PiFM. Topography is show on the left. A combined PiFM image consisting of one PiFM image for alumina (purple) and another one for the substrate (green) clearly shows multiple pinholes (~ 10 nm in size) in the alumina layer.

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Surface Contaminations and Monolayers

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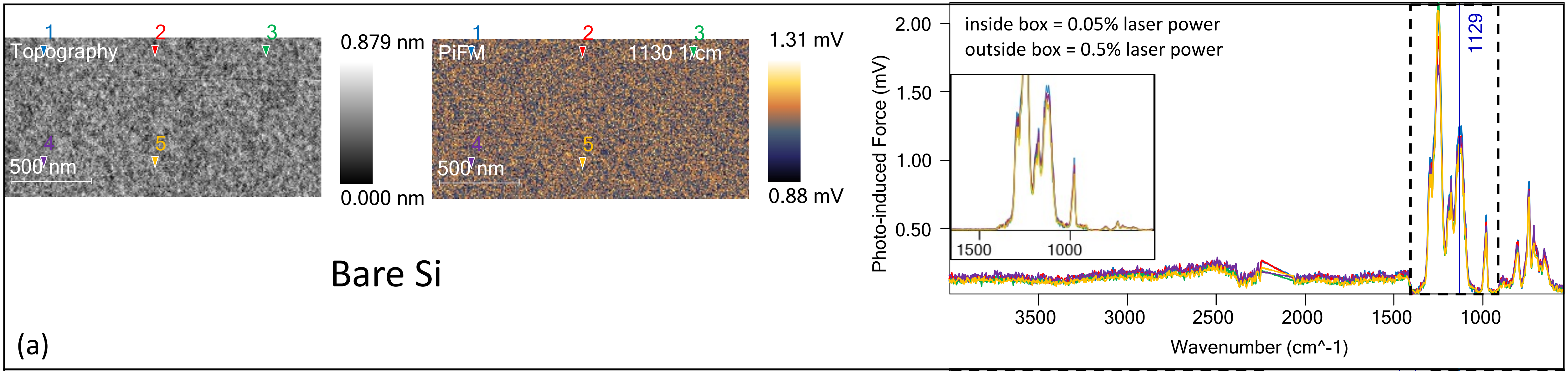
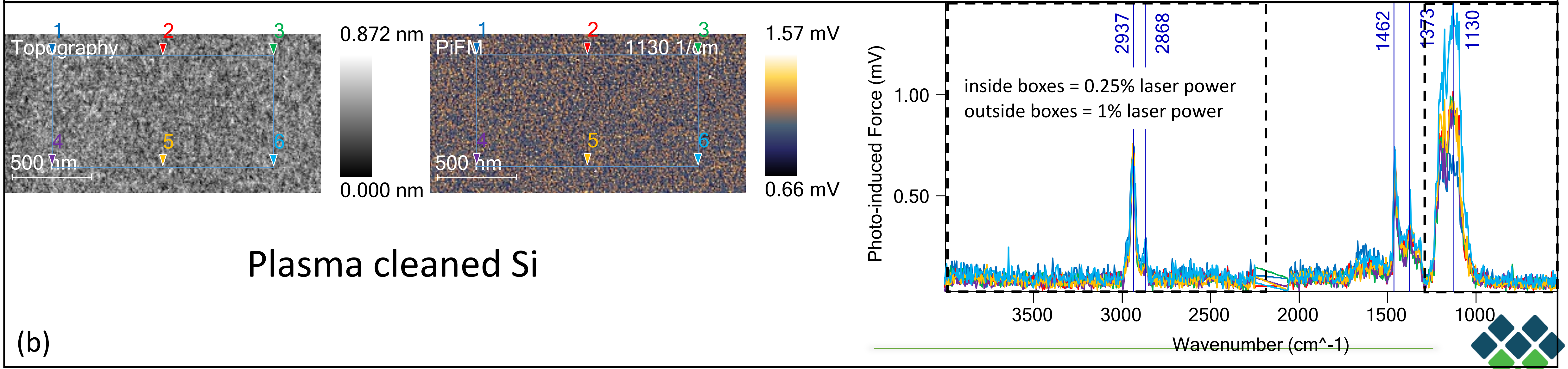
Organic Contaminants on Substrates





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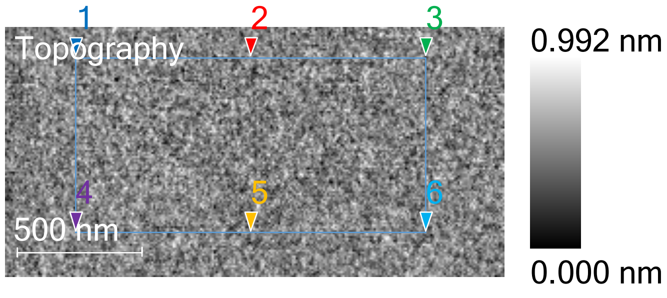
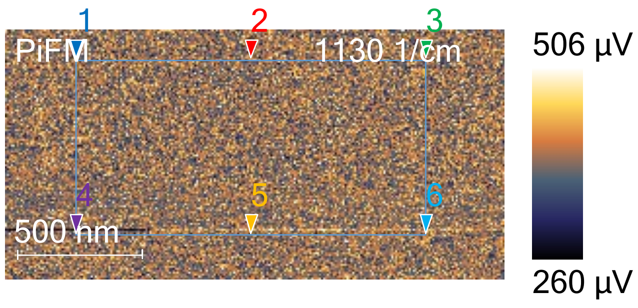
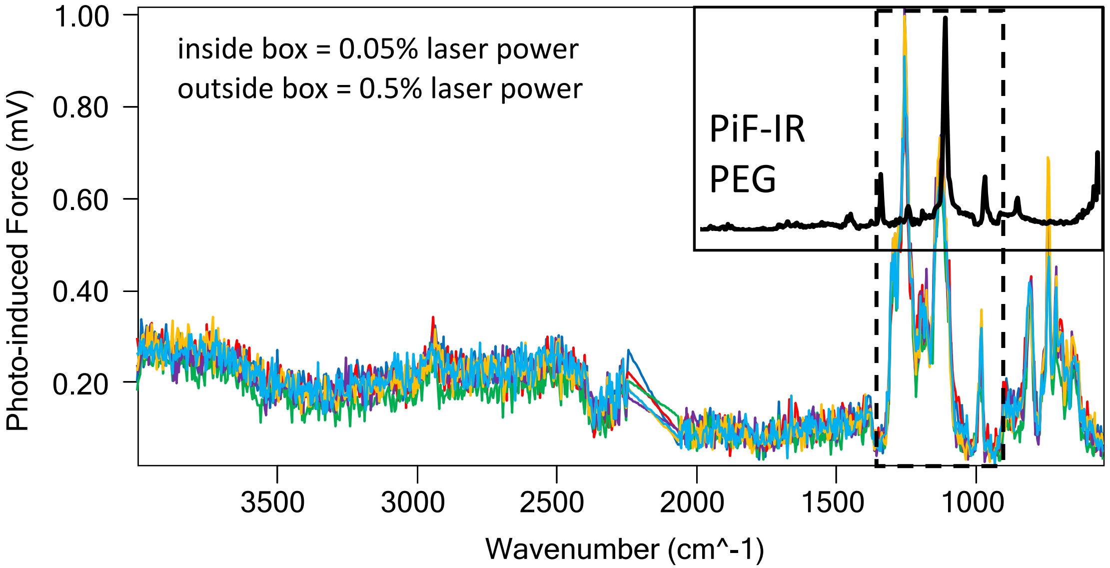
Unsuccessful monolayer of PEG on Si





PEG on Si



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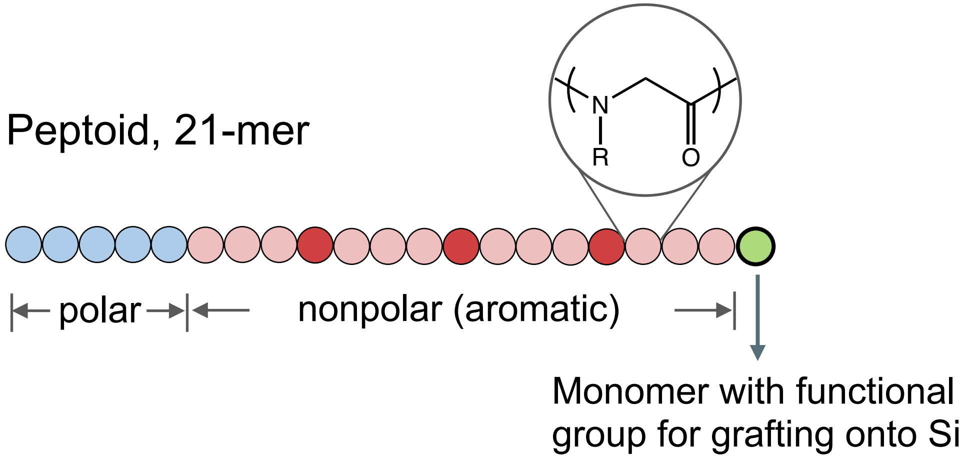
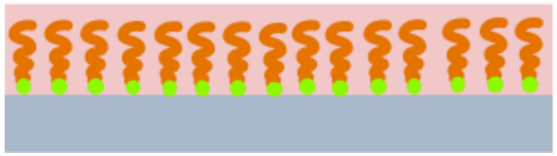
Monolayer of peptoid film





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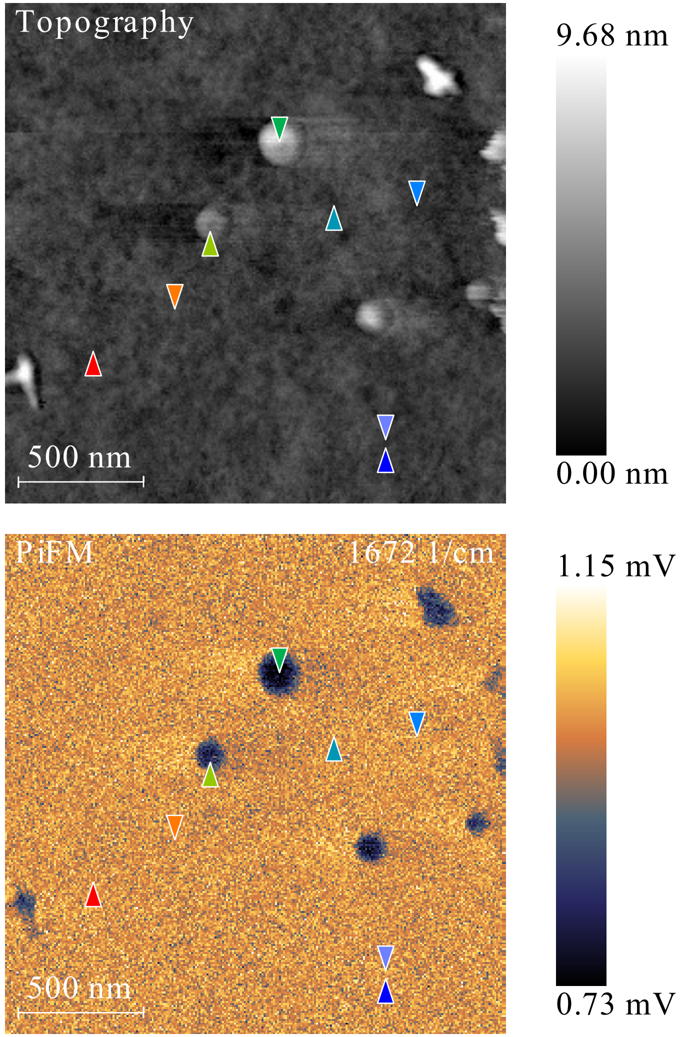
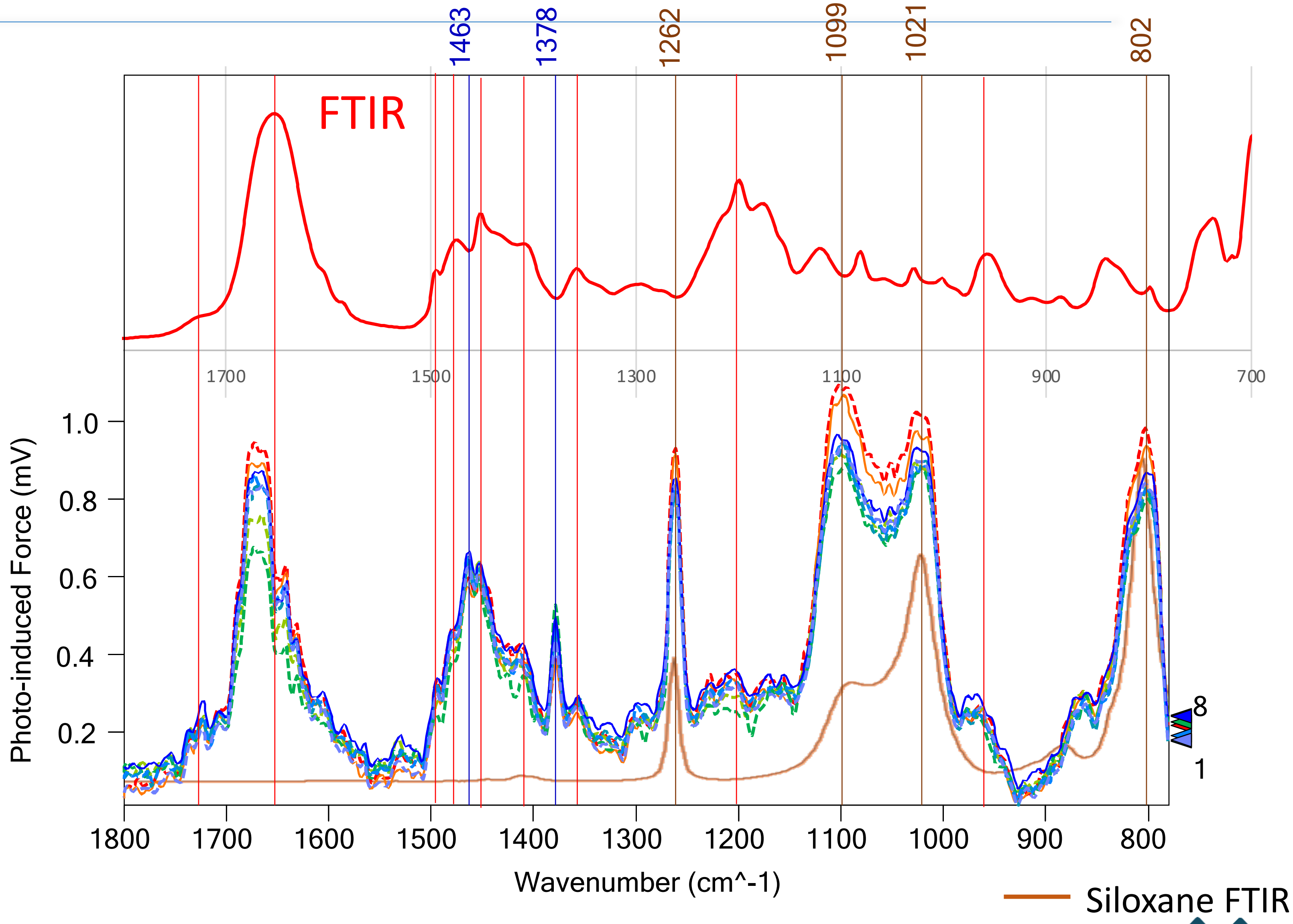
30 nm thick peptoid film





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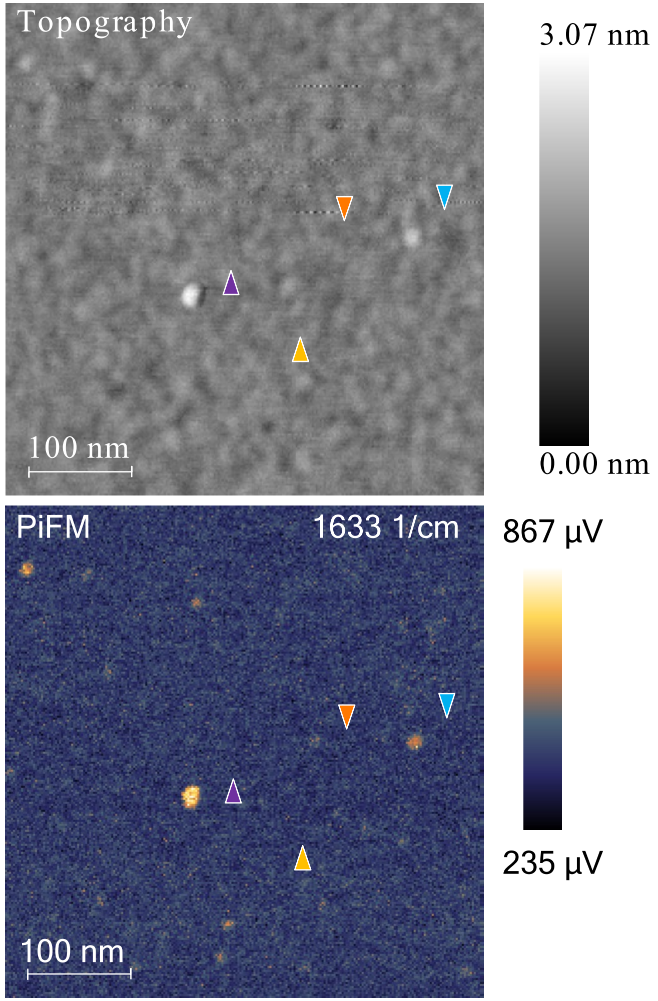
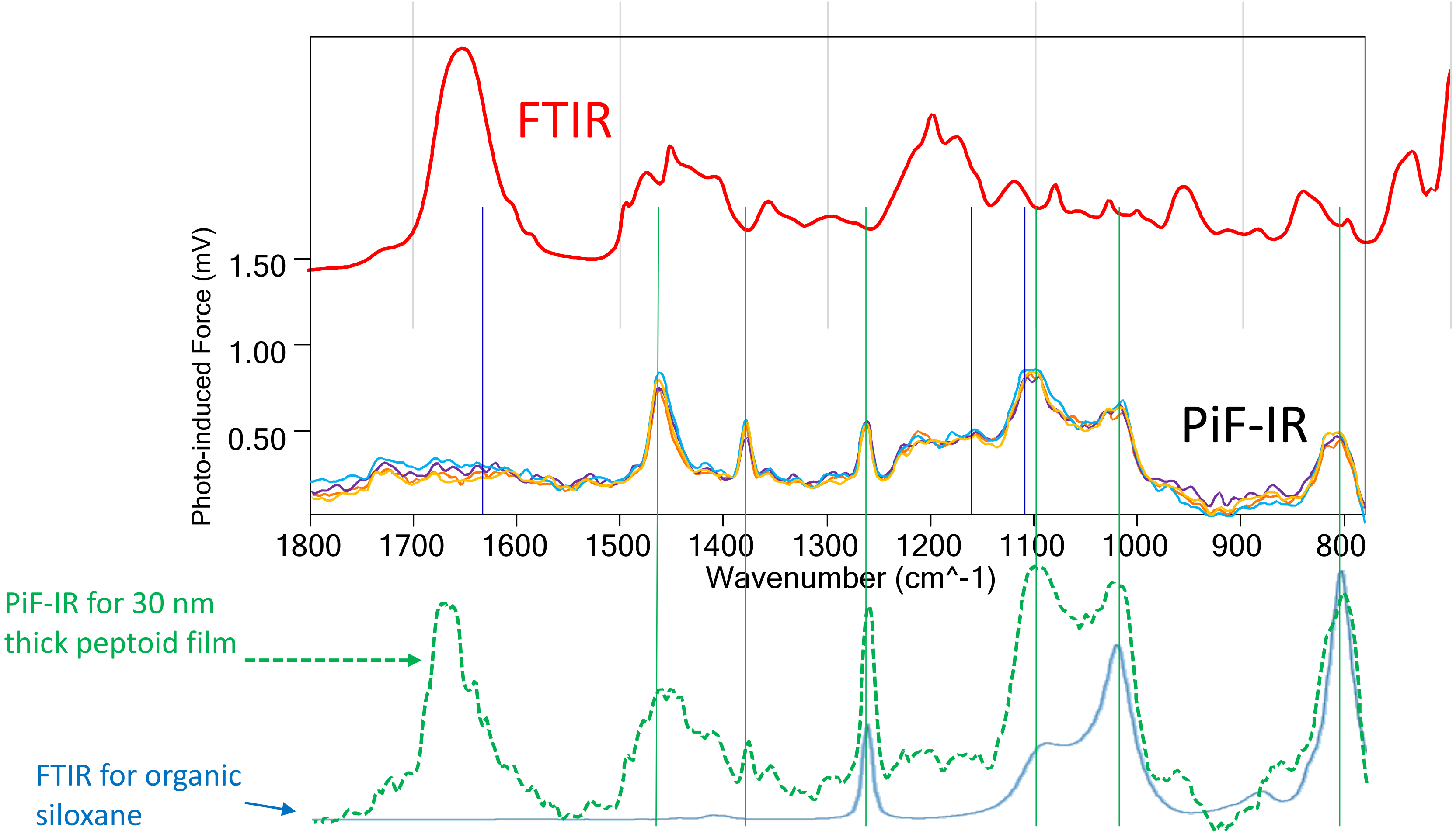
“Monolayer” of peptoid molecules





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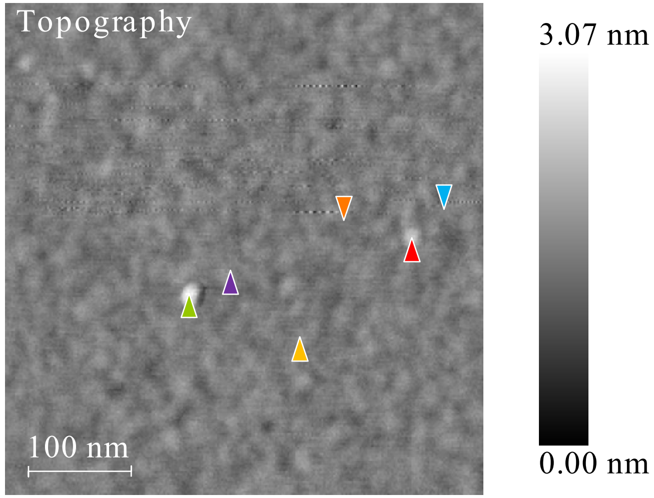
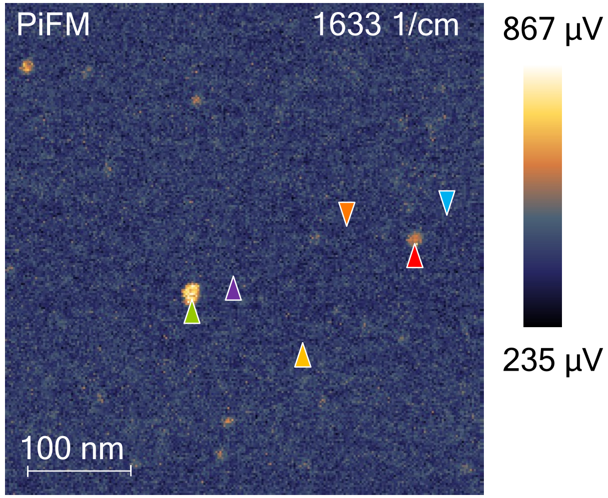
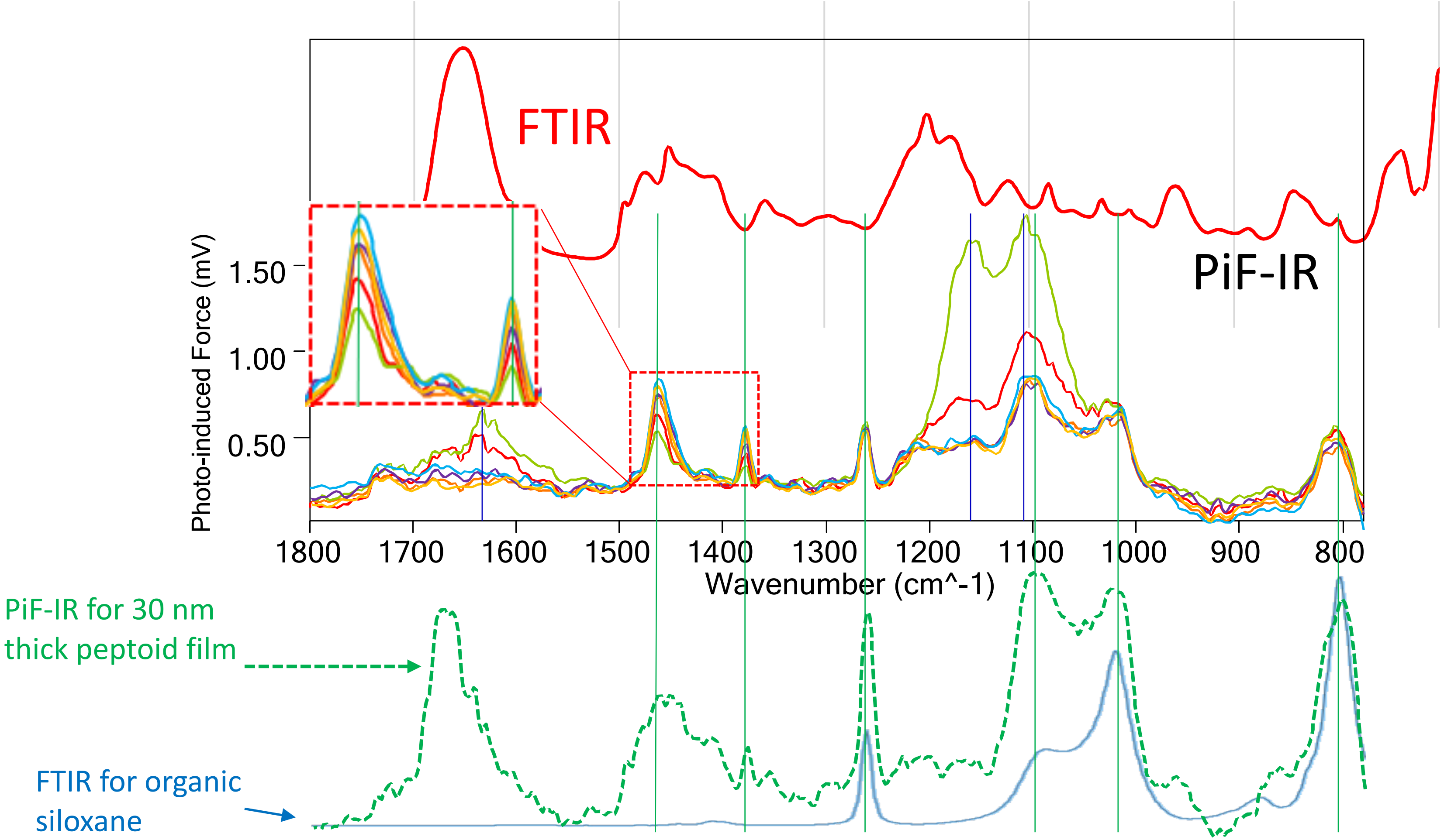
Only fragments of peptoid molecules







Height: 1.8 nm x Width: 16 nm

Height: 1.2 nm x Width: 16 nm

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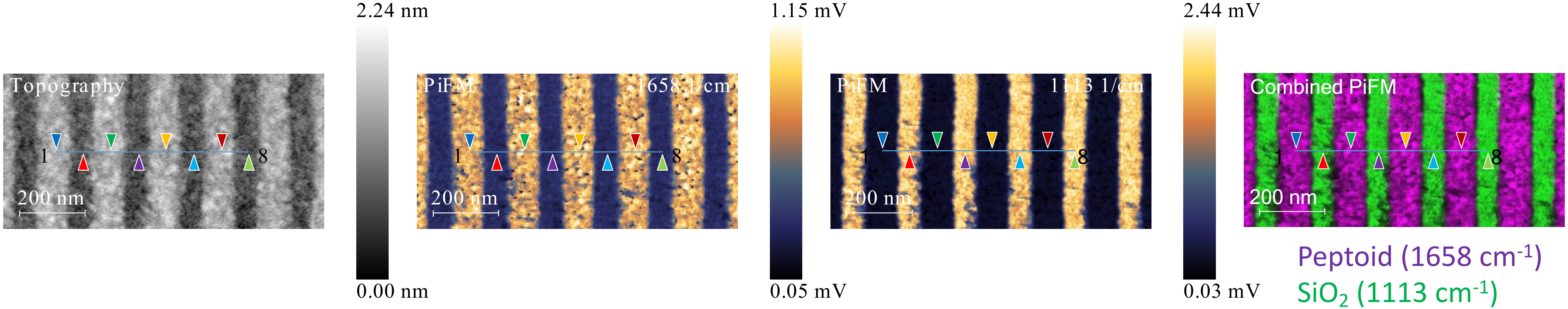
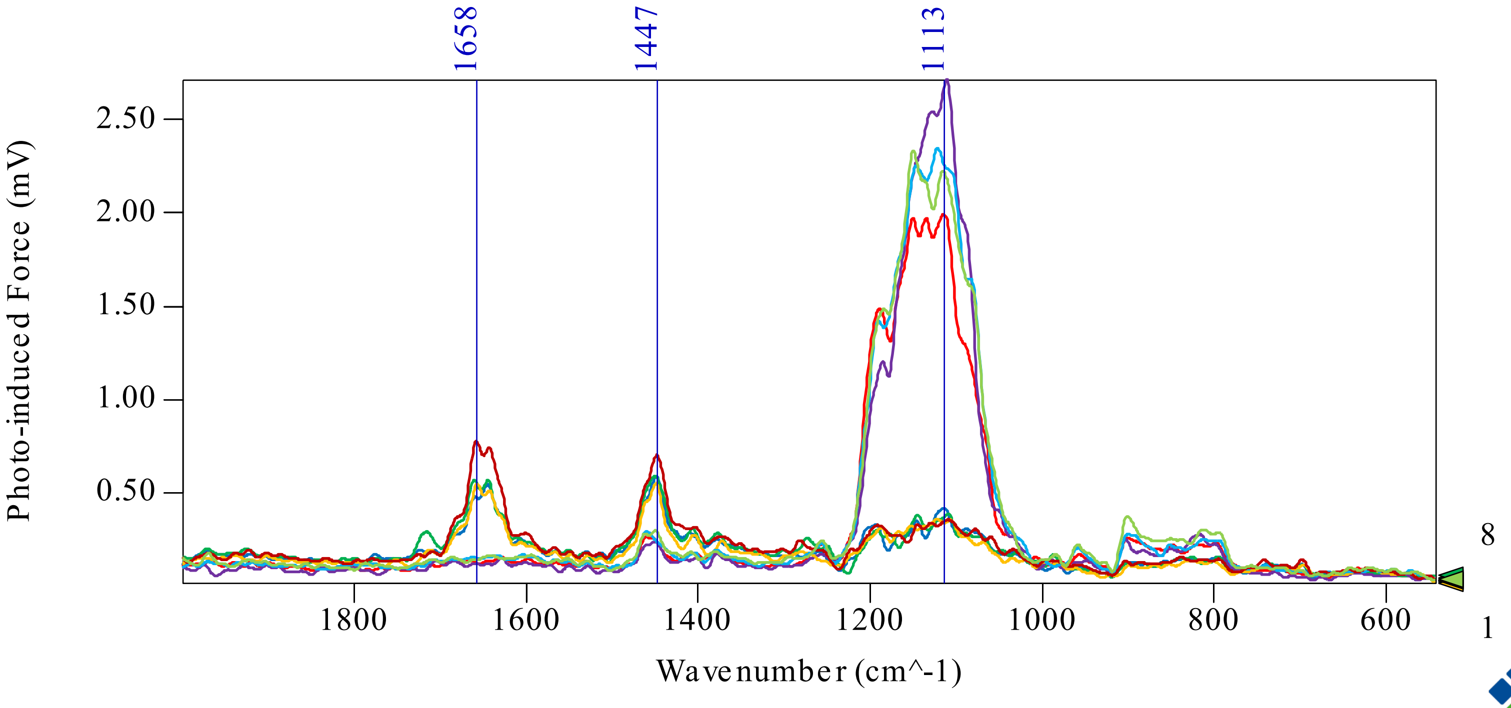
Monolayer of peptoid film patterned via e-beam lithography



Peptoid (1658 cm^{-1})

SiO_2 (1113 cm^{-1})

- All spectra on taller lines have peaks around 1658 and 1447 cm^{-1}
- The spectra on the substrate show strong peak around 1113 cm^{-1}
- Images clearly highlight peptoid lines (1658 cm^{-1}) and substrate (1113 cm^{-1})



Chemical Metrology of EUV Resist

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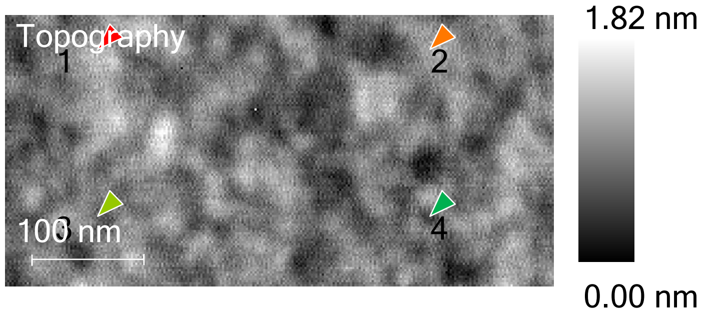
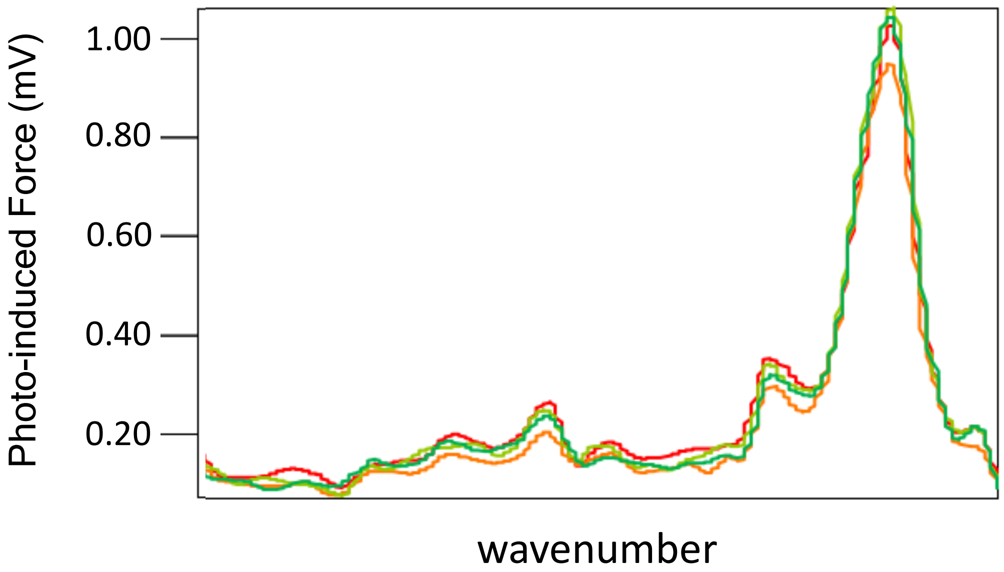
Multiple PiF-IR Spectra (Repeatability & Variability)





The repeatability of the four PiF-IR spectra at different locations is decent and indicates that the chemical composition of the metal oxide EUV resist is reasonably homogeneous. The values of the wavenumbers are hidden per manufacturer's request.

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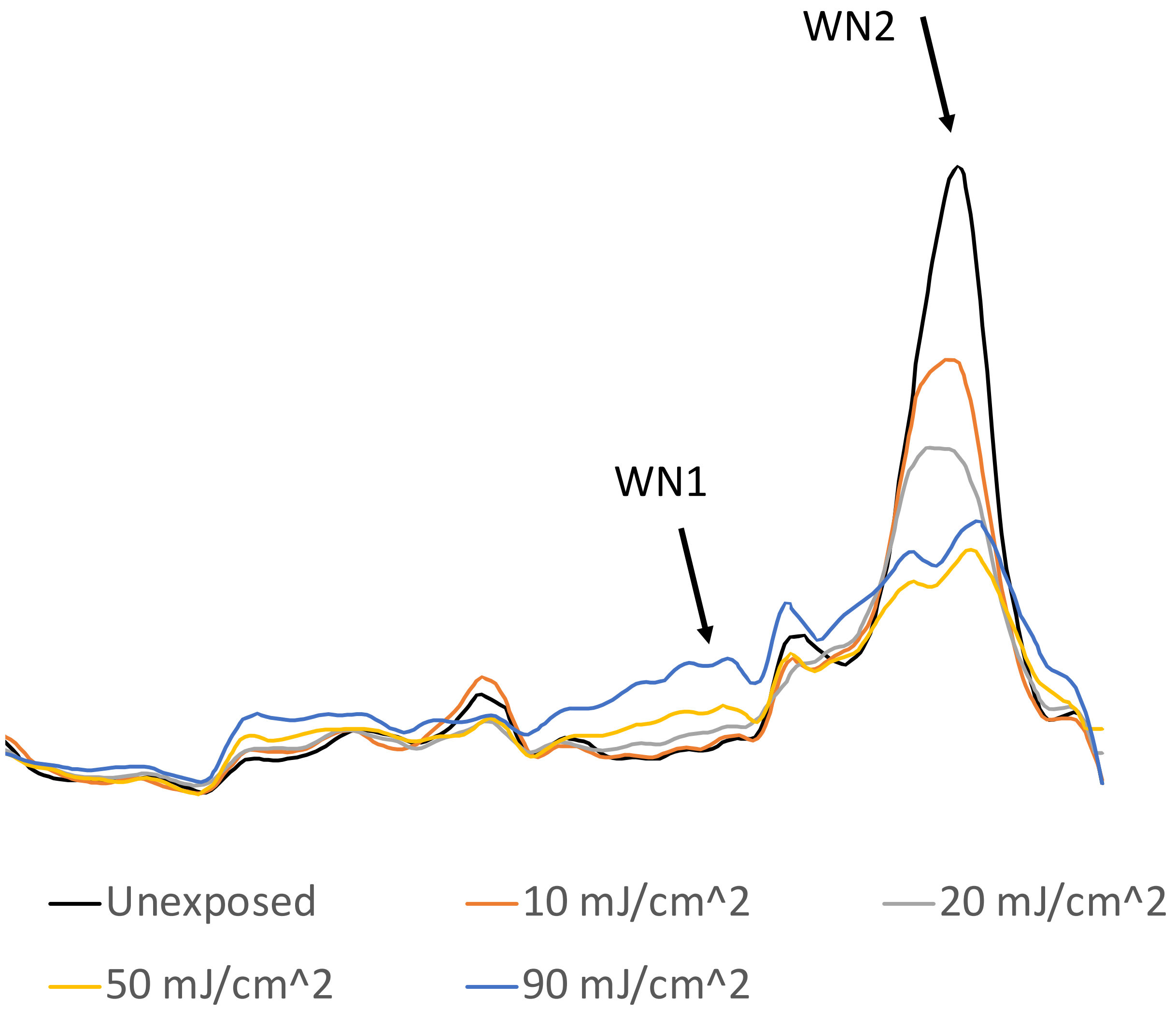
Comparison of Averaged PiF-IR Spectra with Exposure



EUV resists exposed at four dose values are analyzed via PiF-IR spectra. Four spectra are acquired at each dose as in the reference resist (unexposed) and averaged for comparison.

A reduction in PiF signal @WN2 is observed with exposure while an increase in PiF signal at WN1 is observed with exposure.

PiFM images are acquired at these two wavenumbers and presented in the next slide.

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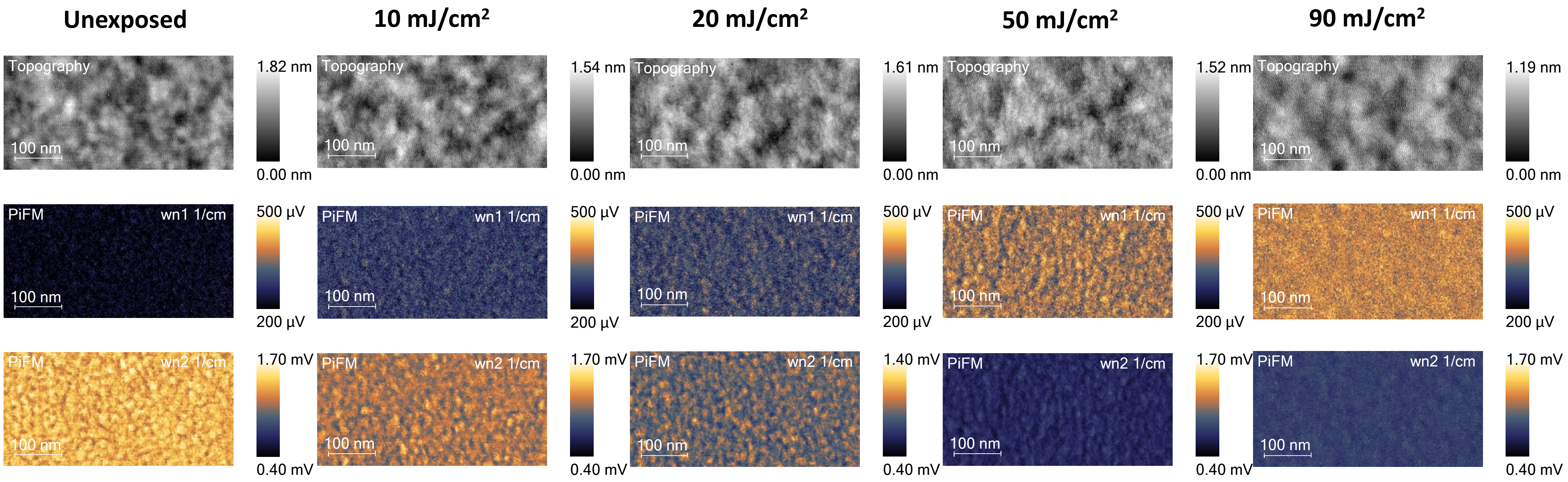
PiFM Images of Metal Oxide EUV Resist @ Different Exposure



Similar trends are observed in the PiFM images at the two wavenumbers. The intensity at wn2 decreases with dose while the intensity at wn1 increases with dose. For each wavenumber, the same tip with the same laser intensity is used; the display scale is the same as well.

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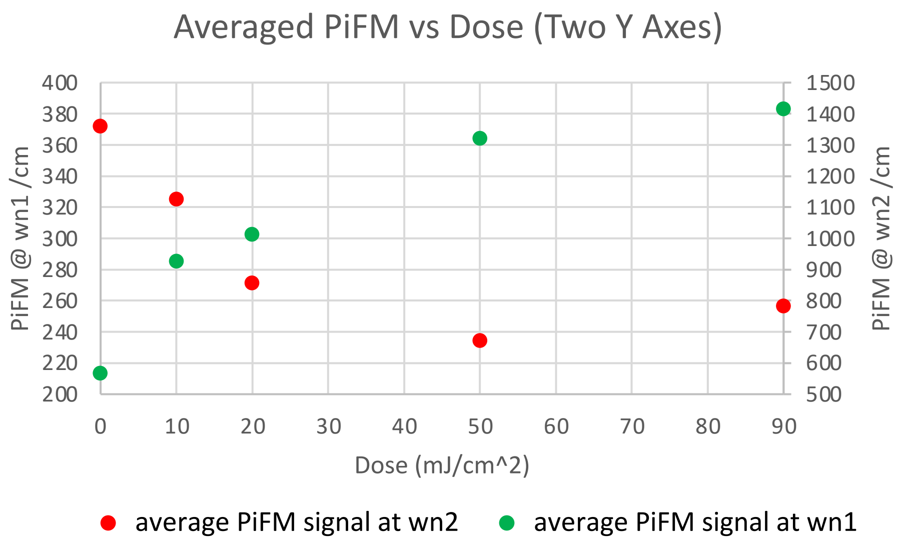
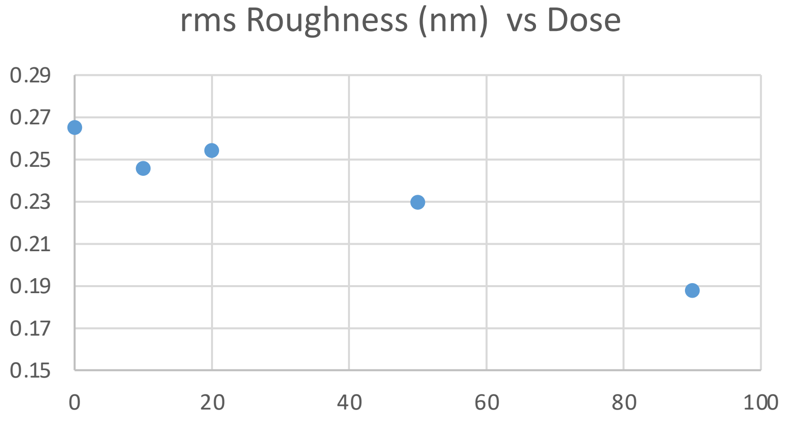
PiFM Signal @ wn1 and wn2 cm^{-1} vs Dose

Clear trends are observed at two wavenumbers. The area average of PiF intensity at wn2 decreases with dose while the area average of PiF intensity at wn1 increases with dose. The signal at wn2 suggest that the chemical change upon exposure seems to stall somewhere between 30 and 50 mJ/cm^2.



Somewhat similar trend is observed for the rms roughness if one outlier datum is ignored.



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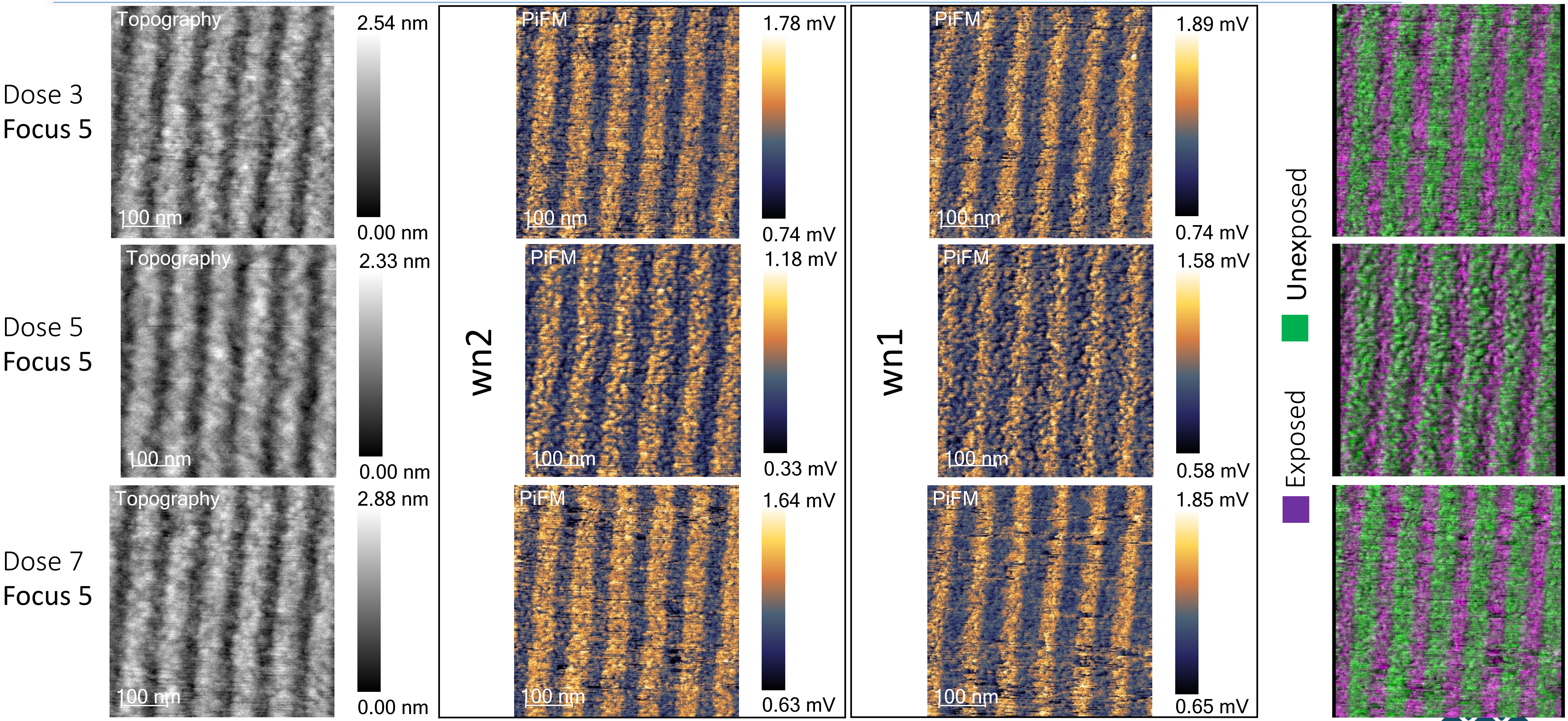
Preliminary Results on Patterned MO EUV Resist @ Different Doses



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Summary

- IR PiFM measures sample's nanoscale infrared absorption via mechanical force detection.
- It achieves sub-5 nm spatial resolution, single-molecule-level sensitivity, orientation discrimination, and ease-of-use.
- It works equally well with both organic and inorganic materials even at nominal thickness of ~ 1 nm.
- For defect analysis, it complements other existing nanoscale analytical tools, which can only provide elemental information.
- Examples of analyzing surface functionalization/contamination, ultrathin ALD films, and latent chemical images of EUV resists have been shared.
- For accurate identification of defects, it is important that the IR spectra database includes the spectra for all material the sample may be exposed to in its processing steps.

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Thank you.

Samples

- Norway spruce – Tapani Vuorinen, Aalto University, Finland
- Peptoid – Beihang Yu, Lawrence Berkeley Lab, USA
- PCL/AA – Phuong Nguyen-Tri, Université du Québec à Trois-Rivières, Canada
- ODTS on SiO_2 – Stacey Bent, Stanford University, USA
- Various Substrates – Jeff Chinn, IST, USA
- Metal oxide EUV Resist – Patrick Naulleau, Lawrence Berkeley Lab, USA

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Some Quick Housekeeping...

COVALENT METROLOGY

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**10% discount for jobs quoted at $1,500 - $2,999; jobs over $3,000 qualify for the 15% discount*

Schedule a **Free Discovery Consult Appointment** to discuss your needs with a Covalent expert

Calendly Link in the Chat

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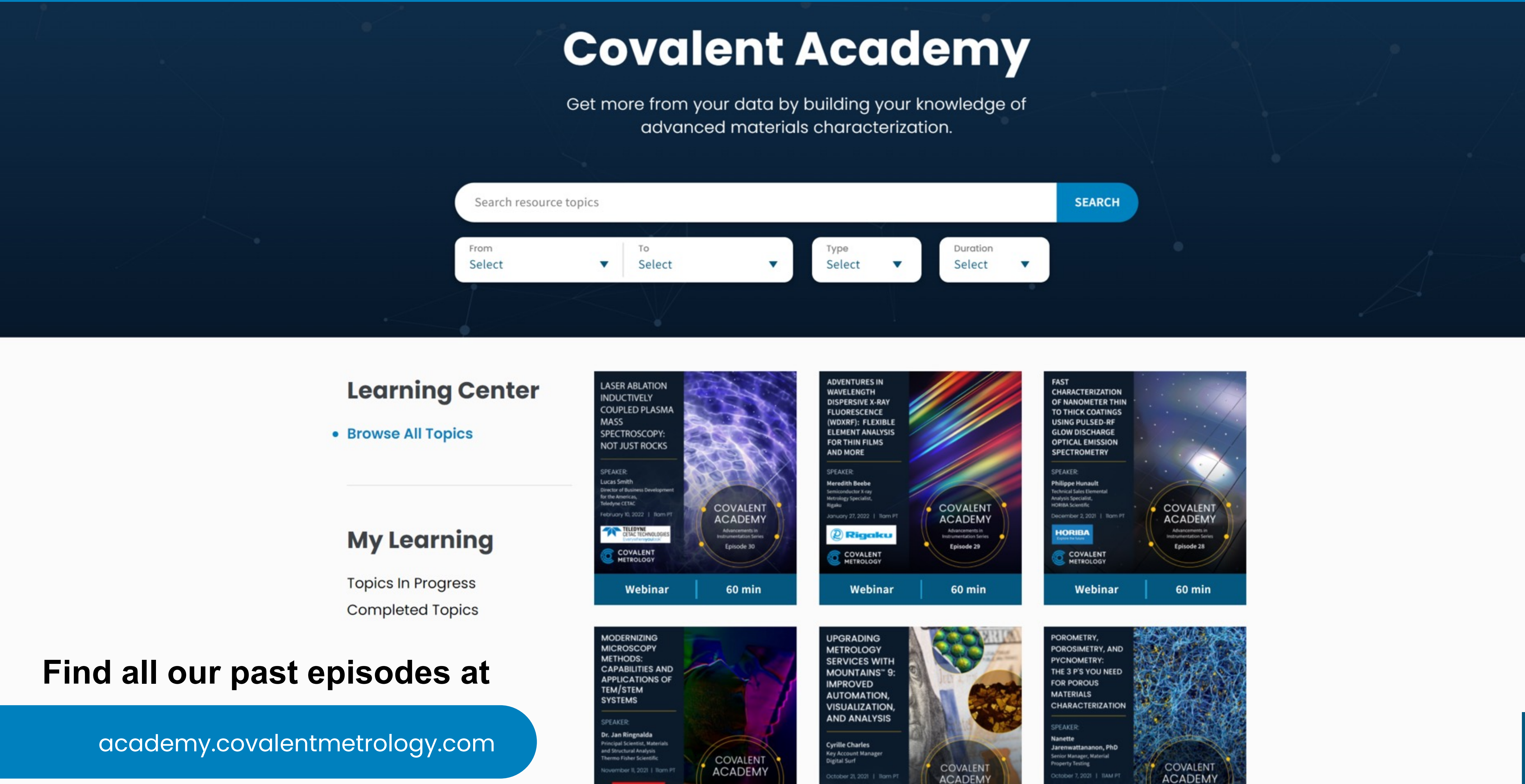

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Q & A Session

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Thank You