inpria®

JSR A JSR Company

FRACTILIA

MOx resist formulation, chemistry, and processing impacts on the power spectral density of line-edge roughness

Amrit Narasimhan[a], Chris A. Mack[b], Peter De Schepper[c], Kai Jiang[a], Michael Kocsis[a], Jason Stowers[a], Kazuki Kasahara[d]
[a]Inpria Corporation, 1100 NE Circle Blvd, Corvallis, OR, USA 97330,
[b]Fractilia, LLC, Austin, TX, USA,
[c]Inpria Corporation, Kapeldreef 75, Heverlee, Belgium B-3001,
[d]JSR Micro, Inc., 1280 N. Mathilda Ave, Sunnyvale, CA 94089, USA

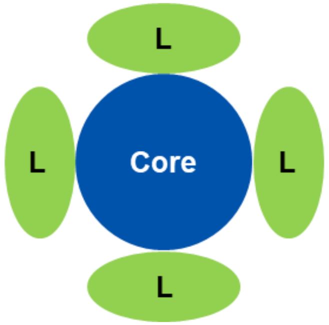
SPIE. ADVANCED LITHOGRAPHY+ PATTERNING

Outline

- A Brief Introduction to MOR & PSD Analysis
- Methodology
- Solvent-Ligand Co-optimization
- Effect of Stack, Etch, & Resist Thickness
- MOR Process Advancements: ESPERT^{TM}
- Comparison of P32 and P24 exposures
- Summary

MOx Resist Imaging Chemistry

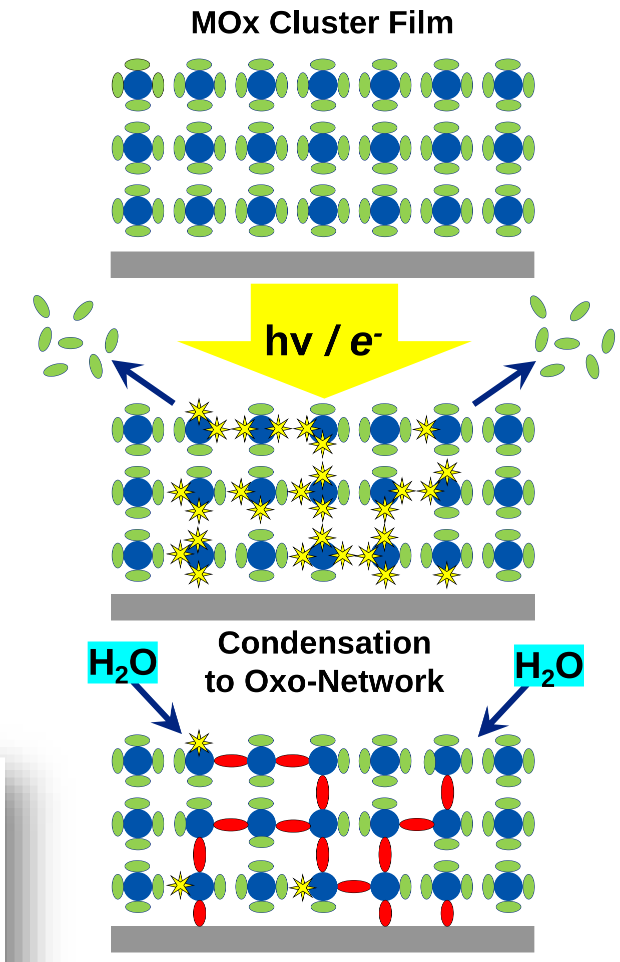
Building Blocks: Reactive molecular metal-oxo-core passivated with radiation sensitive ligands

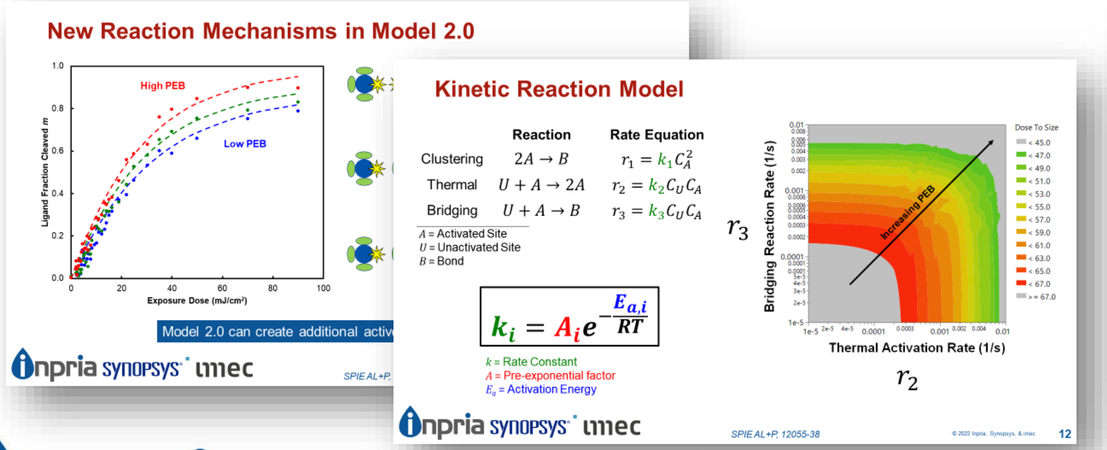


Radiolysis: Ligands cleave on exposure, deprotecting electrophilic metal centers to form active sites

Hydrolysis: H_2O/OH nucleophiles attack active sites

Condensation: Hydroxylated active sites condense to form oxo-network





New Reaction Mechanisms in Model 2.0

Model 2.0 can create additional activ

SPIE AL+P,

Kinetic Reaction Model

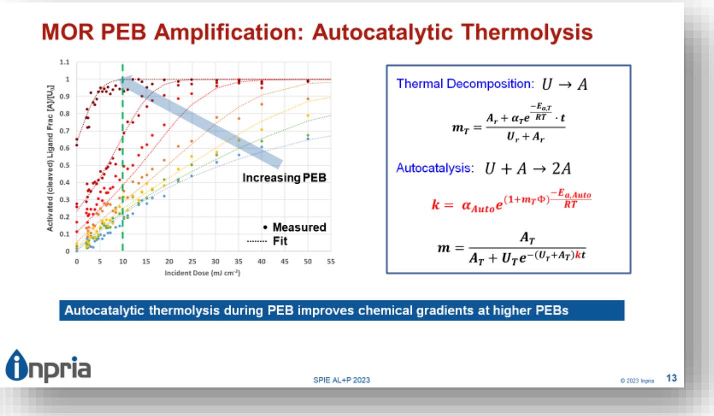
	Reaction	Rate Equation
Clustering	$2A \rightarrow B$	$r_1 = k_1 C_A^2$
Thermal	$U + A \rightarrow 2A$	$r_2 = k_2 C_U C_A$
Bridging	$U + A \rightarrow B$	$r_3 = k_3 C_U C_A$

A = Activated Site
U = Unactivated Site
B = Bond

$$\boxed{k_i = A_i e^{-\frac{E_{a,i}}{RT}}}$$

k = Rate Constant
A = Pre-exponential factor
E_a = Activation Energy

SPIE AL+P, 12055-38 © 2022 Inpria, Synopsys, & imec 12



MOR PEB Amplification: Autocatalytic Thermolysis

Thermal Decomposition: $U \rightarrow A$

$$m_T = \frac{A_r + \alpha_T e^{\frac{-E_{a,T}}{RT}} \cdot t}{U_r + A_r}$$

Autocatalysis: $U + A \rightarrow 2A$

$$k = \alpha_{Auto} e^{(1+m_T\Phi)\frac{-E_{a,Auto}}{RT}}$$

$$m = \frac{A_T}{A_T + U_T e^{-(U_T+A_T)kt}}$$

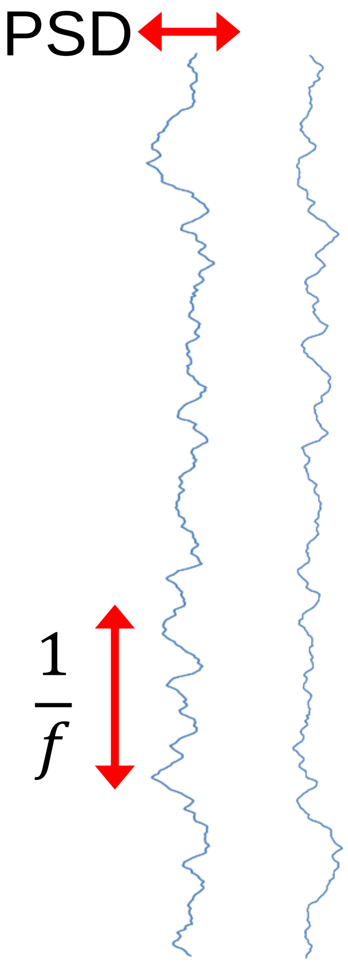
Autocatalytic thermolysis during PEB improves chemical gradients at higher PEBs

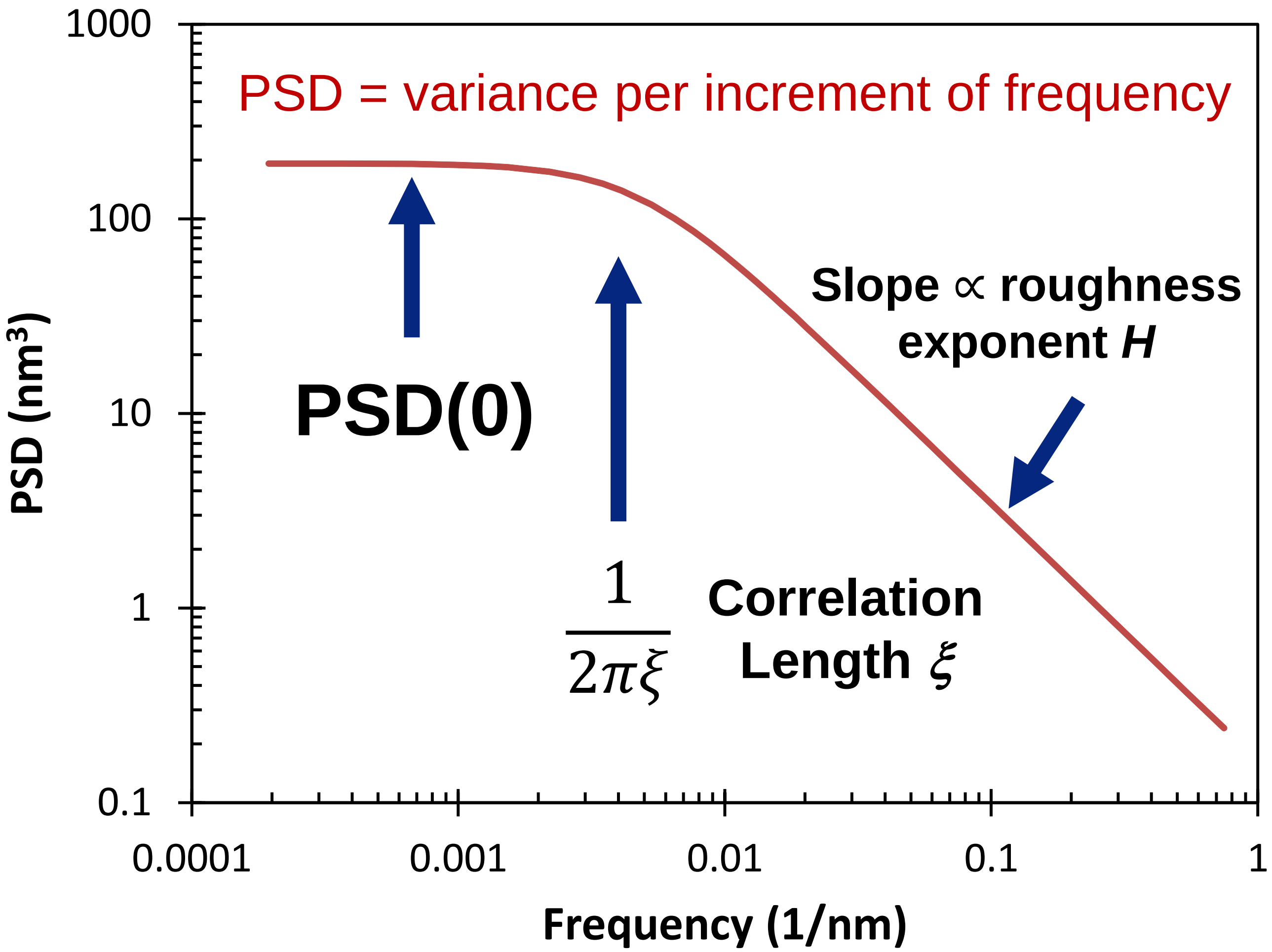
SPIE AL+P 2023 © 2023 Inpria 13

Key
- ● core
- ⬭ ligand
- ✳ activated site
- ⬭ oxo-bond

Hinsberg – SPIE 2017
Needham – SPIE 2022
Meyers – SPIE 2023

The Importance of PSD Analysis

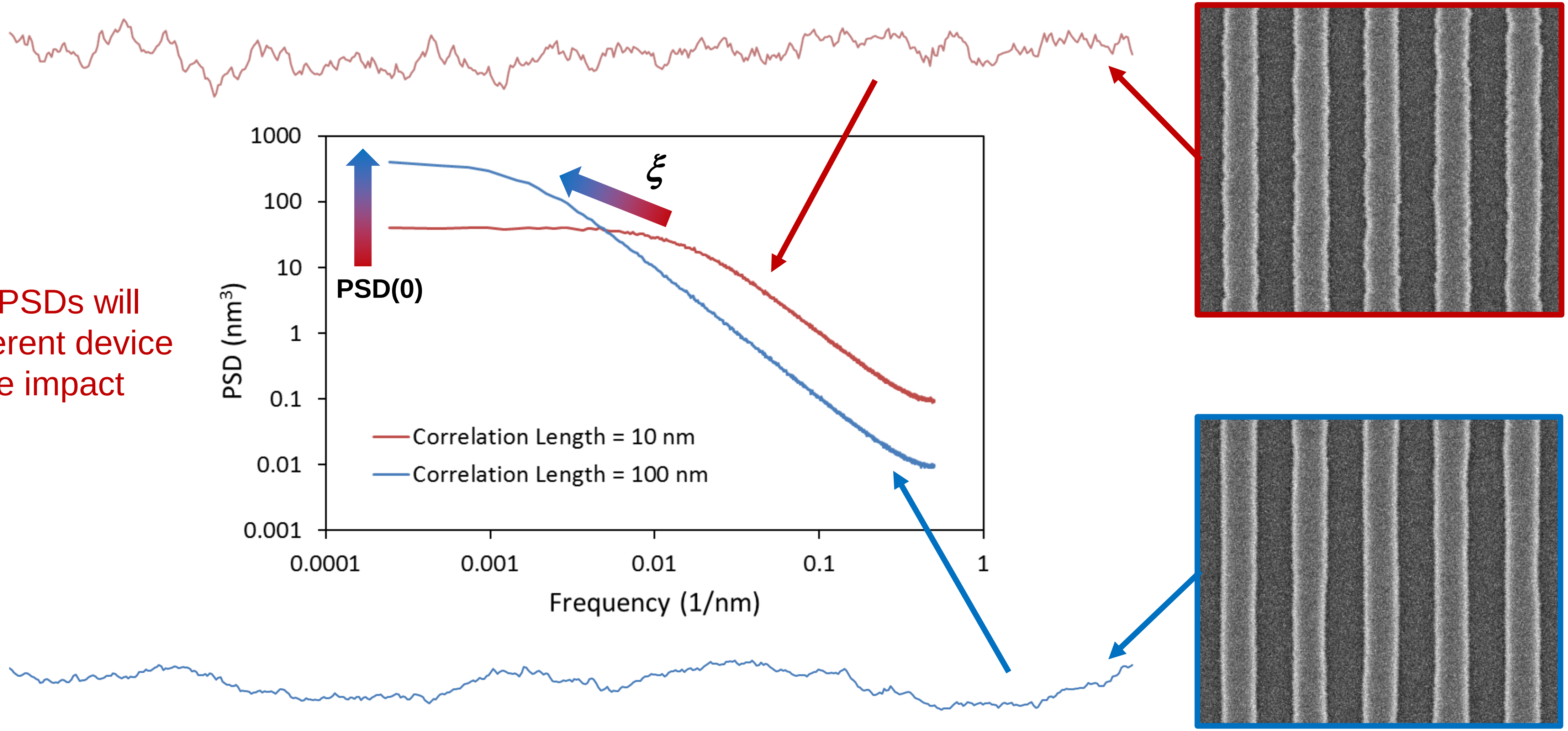




The Importance of PSD Analysis

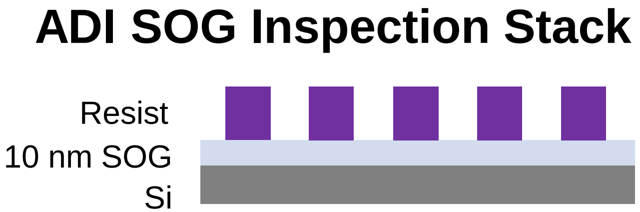
These line edges have the same LER

These PSDs will have different device feature impact

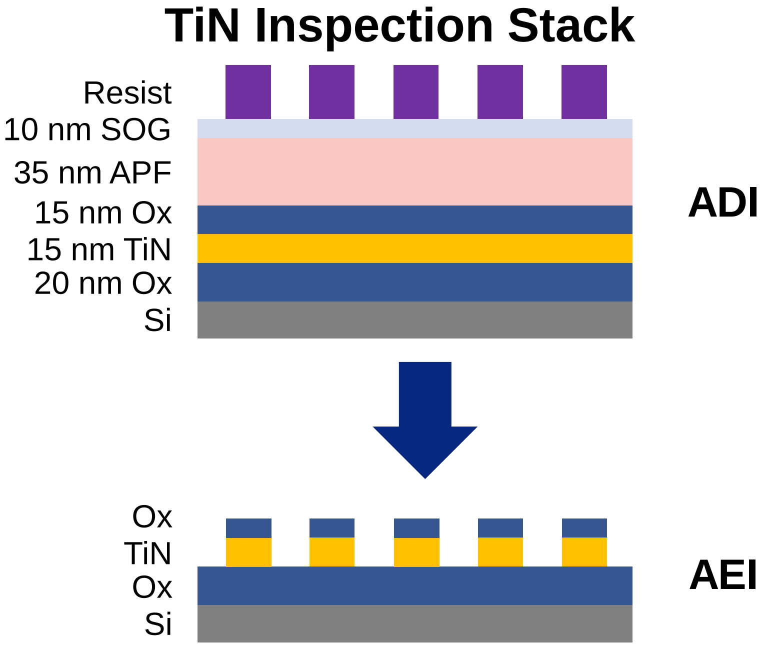


Methods

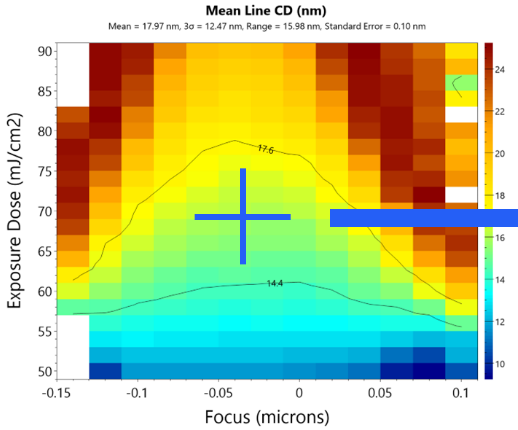
- NXE3400 at IMEC
- L/S Reticles
  - P32: IMEC EUVLINES33
  - P24: IMEC TAPES3
- Exposure Information
  - On SOG: Dose meanders at pre-determined best-focus
  - On TiN stack: FEMs
- MetroLER™ Data Pipeline



ADI SOG Inspection Stack

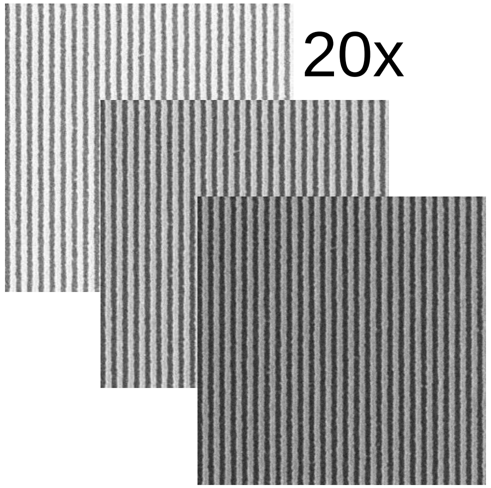


TiN Inspection Stack



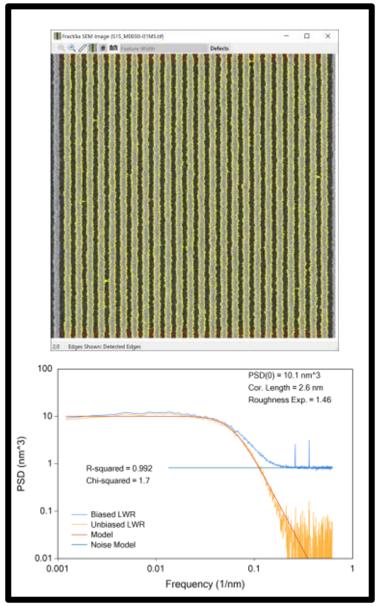
Mean Line CD (nm)

Mean = 17.97 nm, 3σ = 12.47 nm, Range = 15.98 nm, Standard Error = 0.10 nm

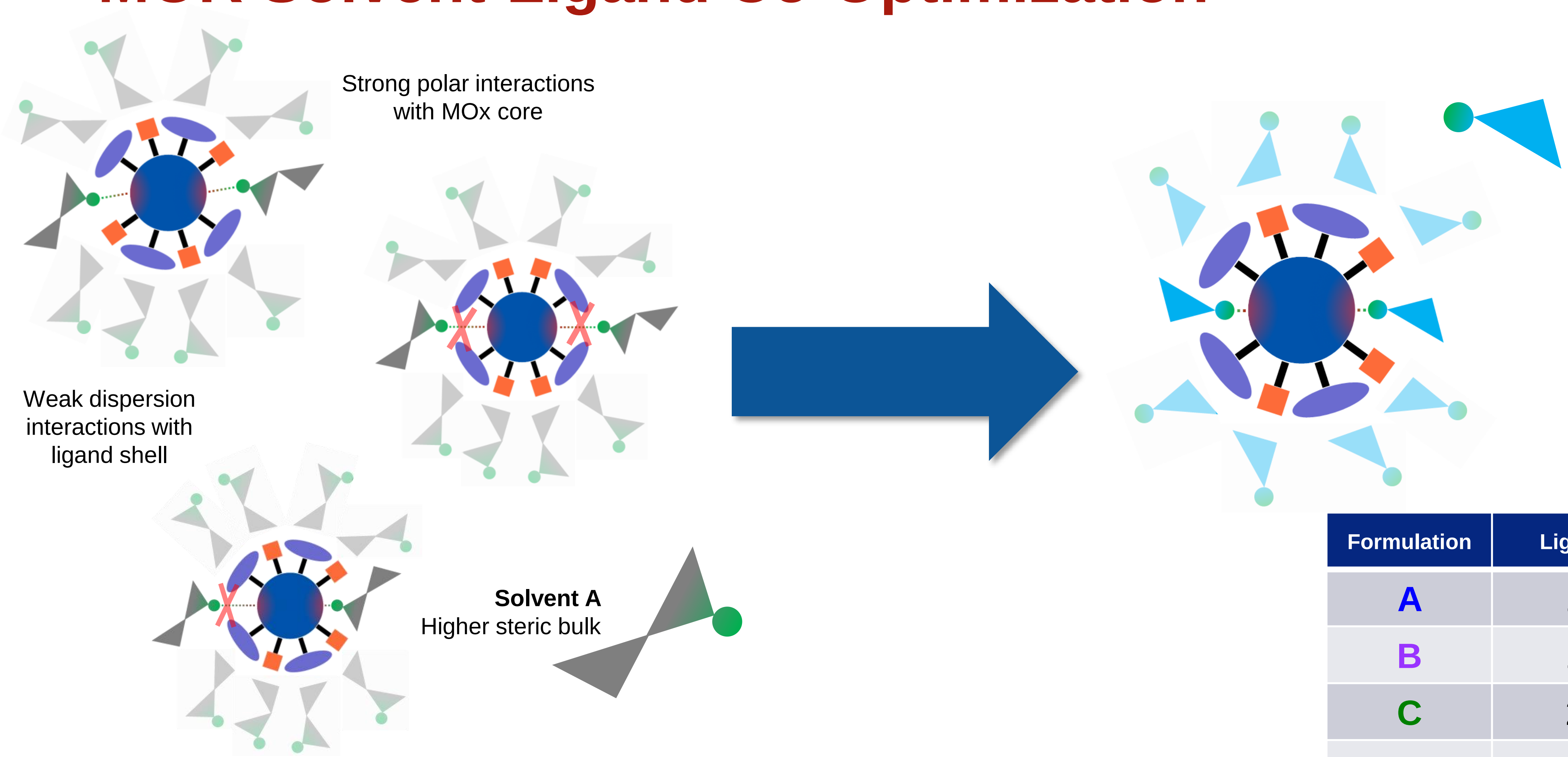


20x

MetroLER™



MOR Solvent-Ligand Co-Optimization



Strong polar interactions with MOx core

Weak dispersion interactions with ligand shell

Solvent A
Higher steric bulk

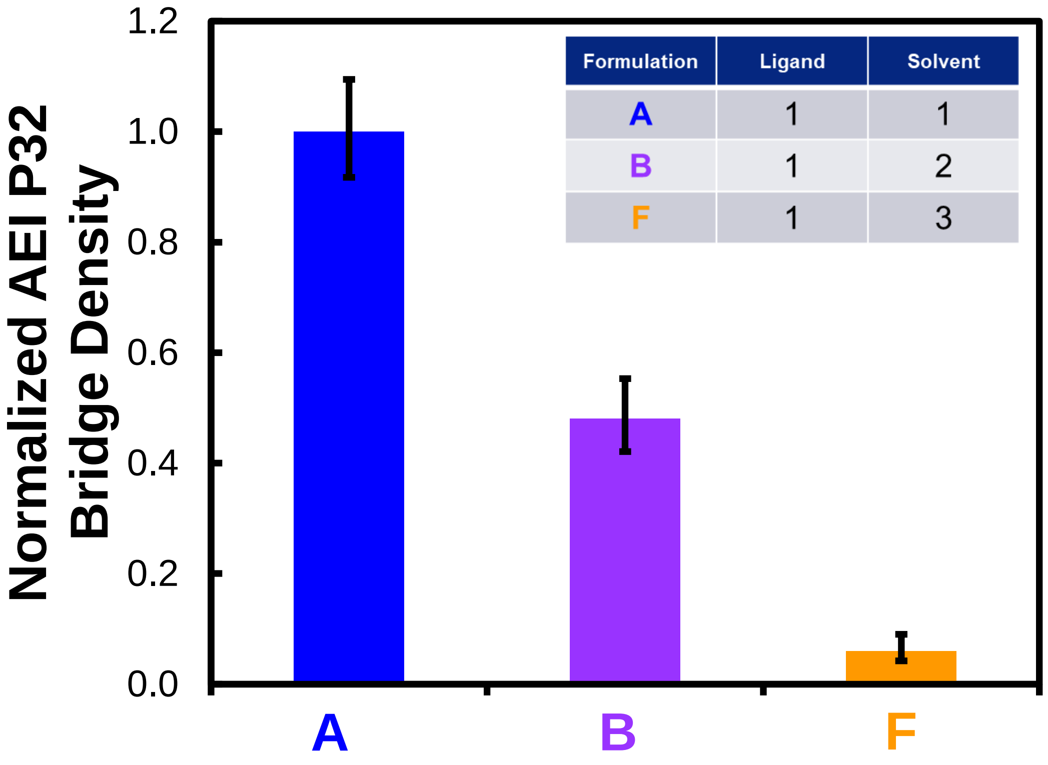
Solvent B
Lower steric bulk

Formulation	Ligand	Solvent
A	1	1
B	1	2
C	2	1
D	2	2
E	3	1
F	1	3

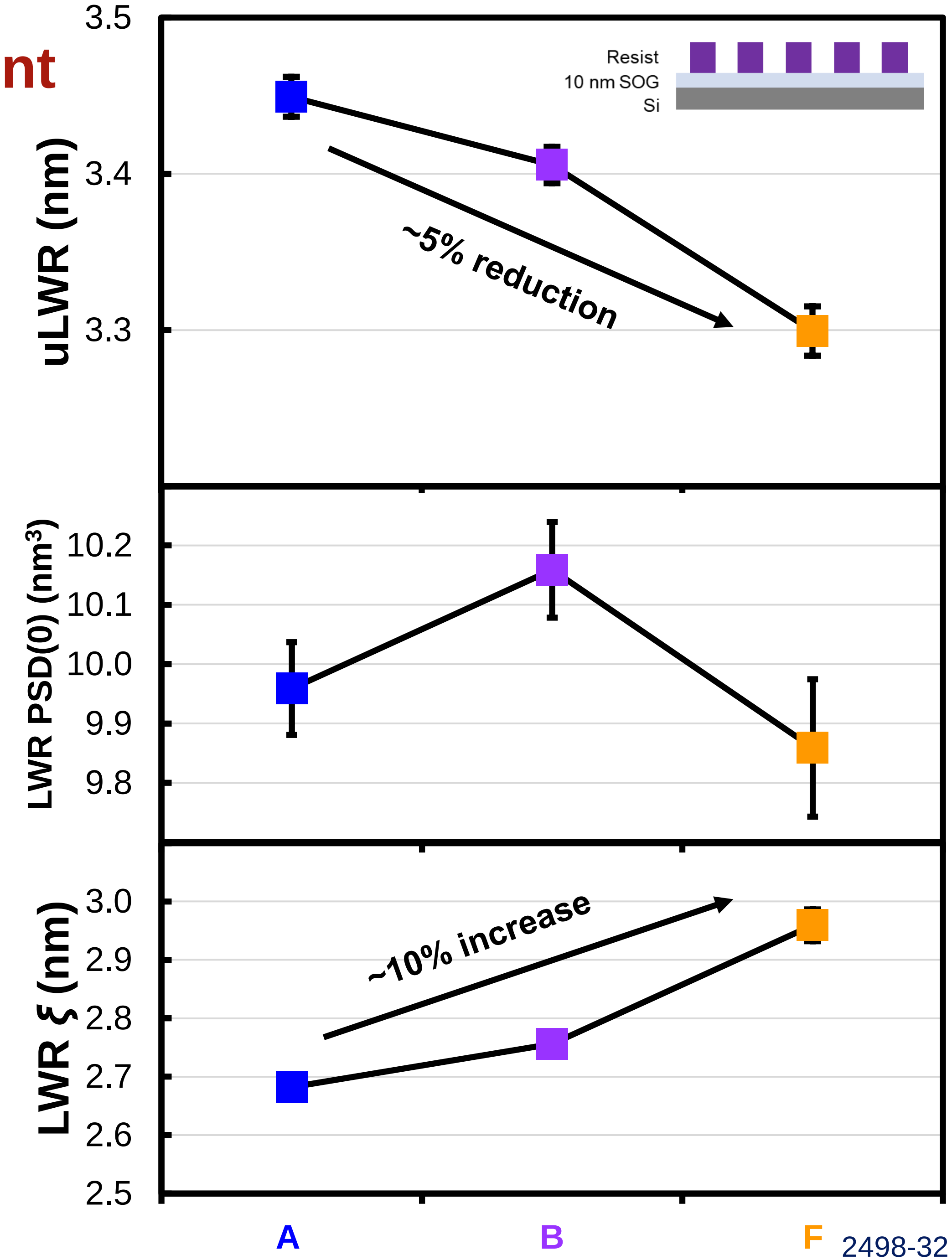
Narrowing the distribution of solvent-cluster interactions reduces material stochastics

MOR Solvent Change can Drive Improvement

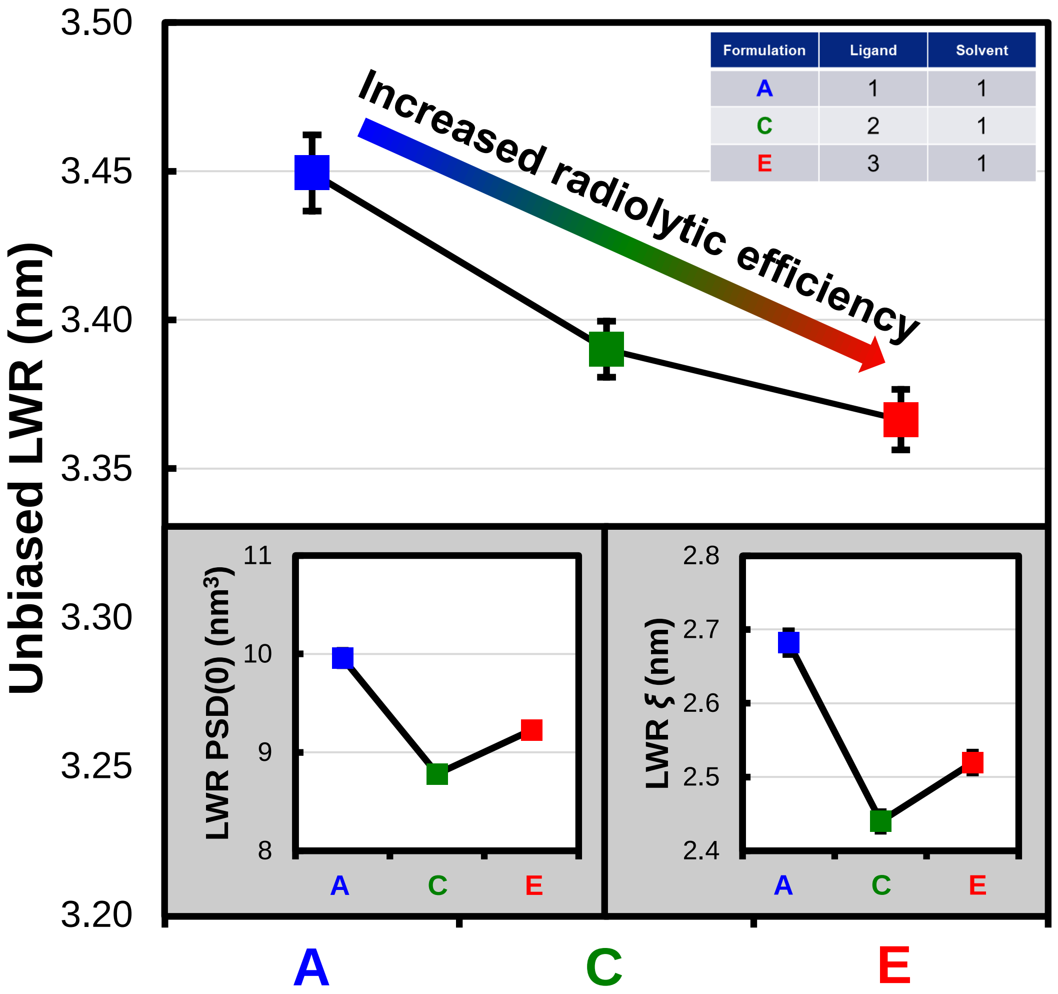
- Formulation changes over the past year have yielded a significant reduction in AEI defectivity
- These formulation changes are associated with a 5% reduction in uLWR and a 10% increase in Correlation Length, with no significant difference in PSD(0)



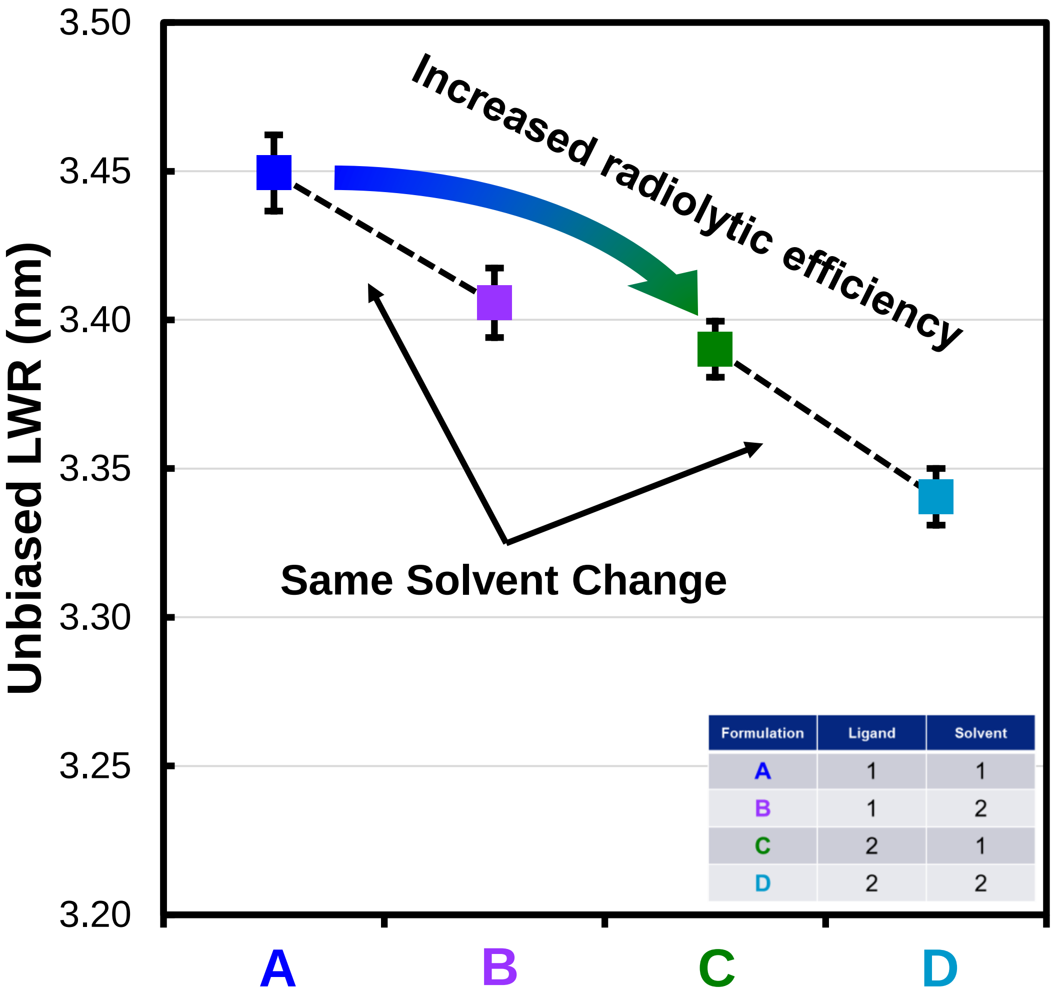
Formulation	Ligand	Solvent
A	1	1
B	1	2
F	1	3



More Efficient Ligands Reduce uLWR



Formulation	Ligand	Solvent
A	1	1
C	2	1
E	3	1

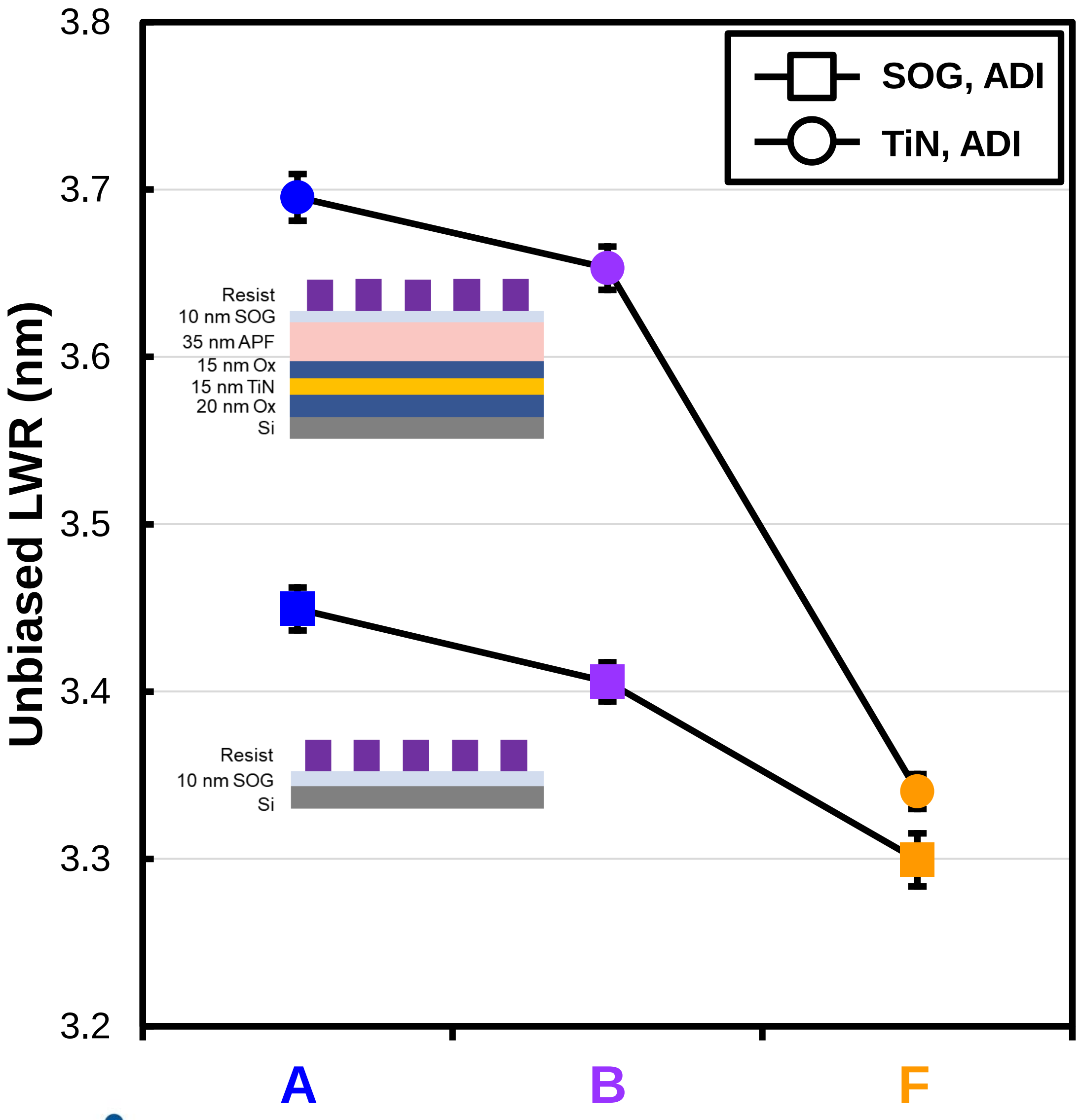


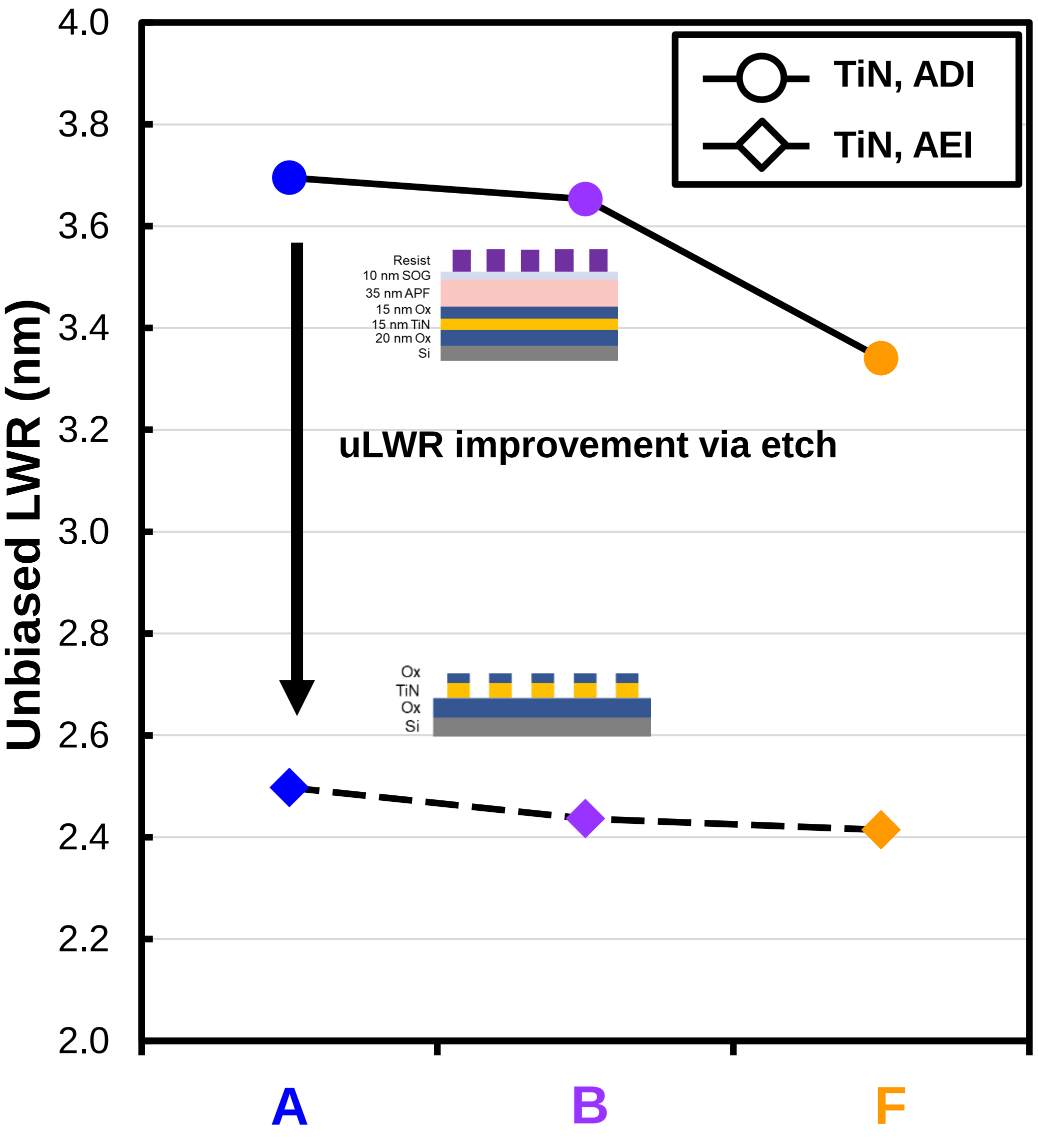
Formulation	Ligand	Solvent
A	1	1
B	1	2
C	2	1
D	2	2

Resist improvements made via solvent and ligand changes can be additive

How does uLWR change with Stack & Etch?

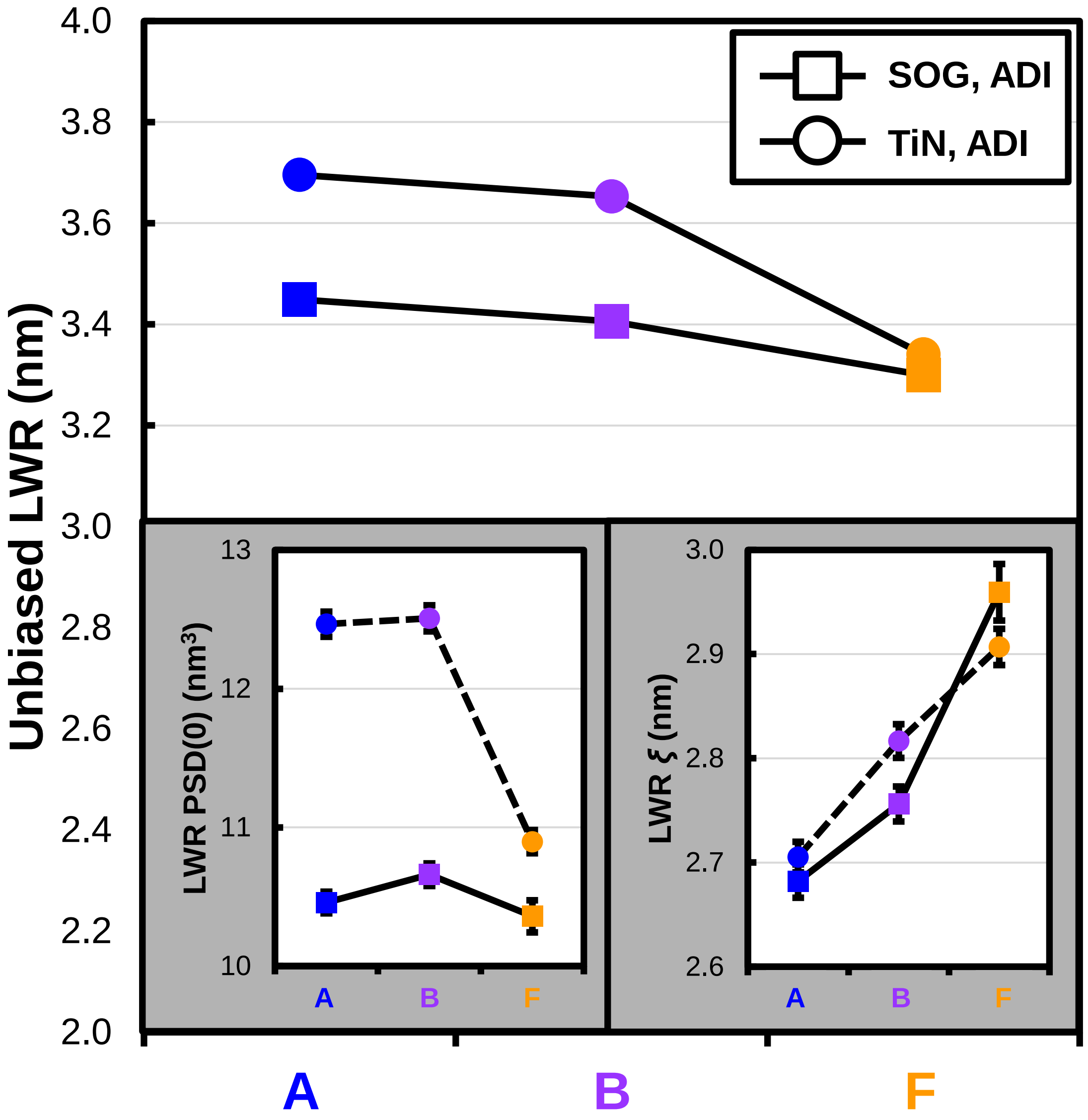
Formulation	Ligand	Solvent
A	1	1
B	1	2
F	1	3

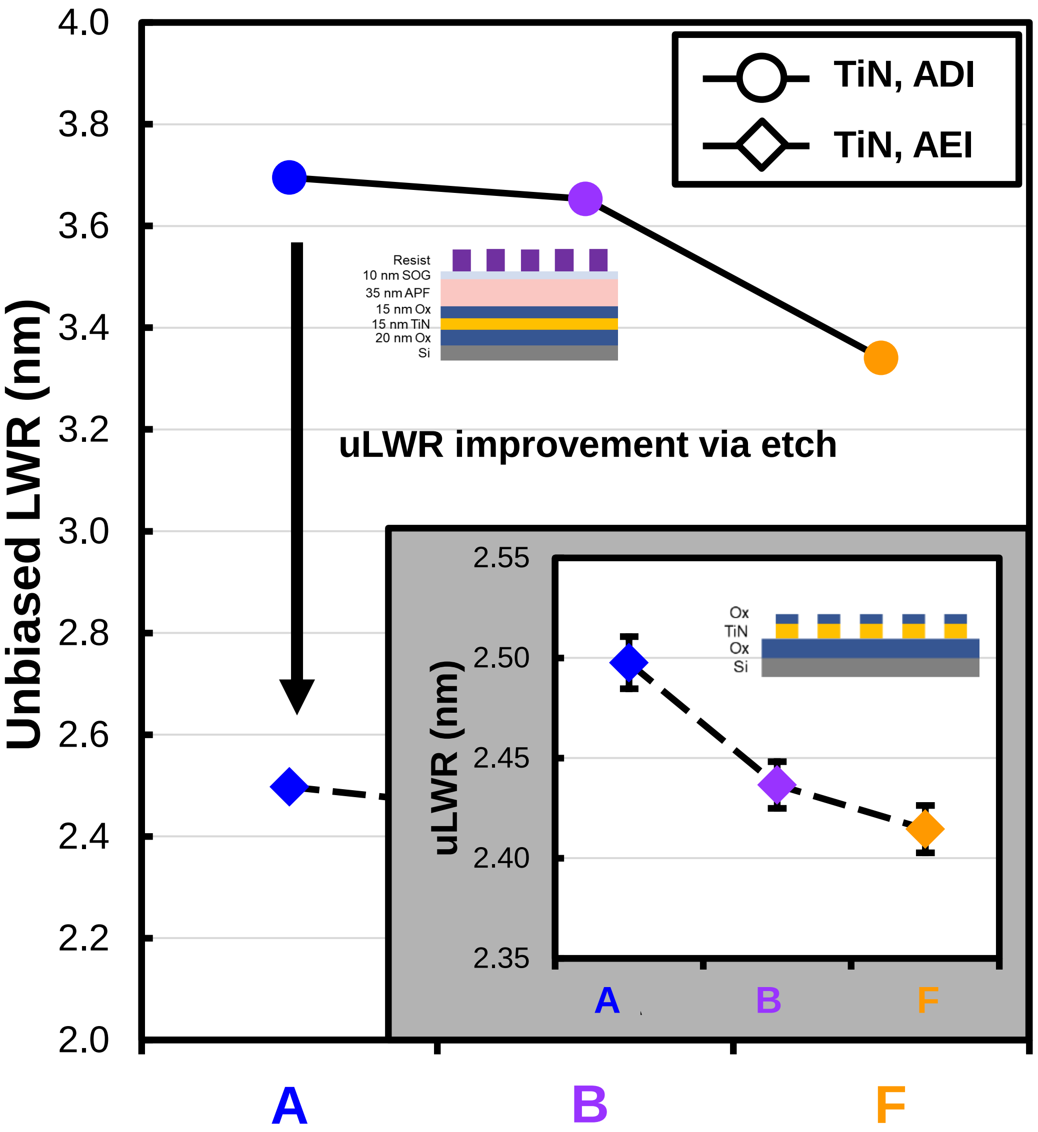




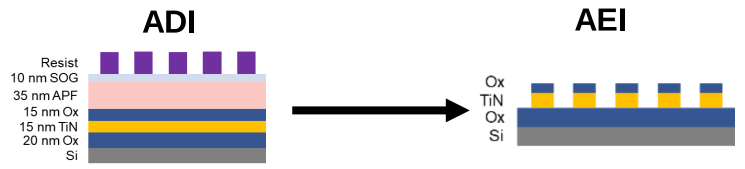
How does uLWR change with Stack & Etch?

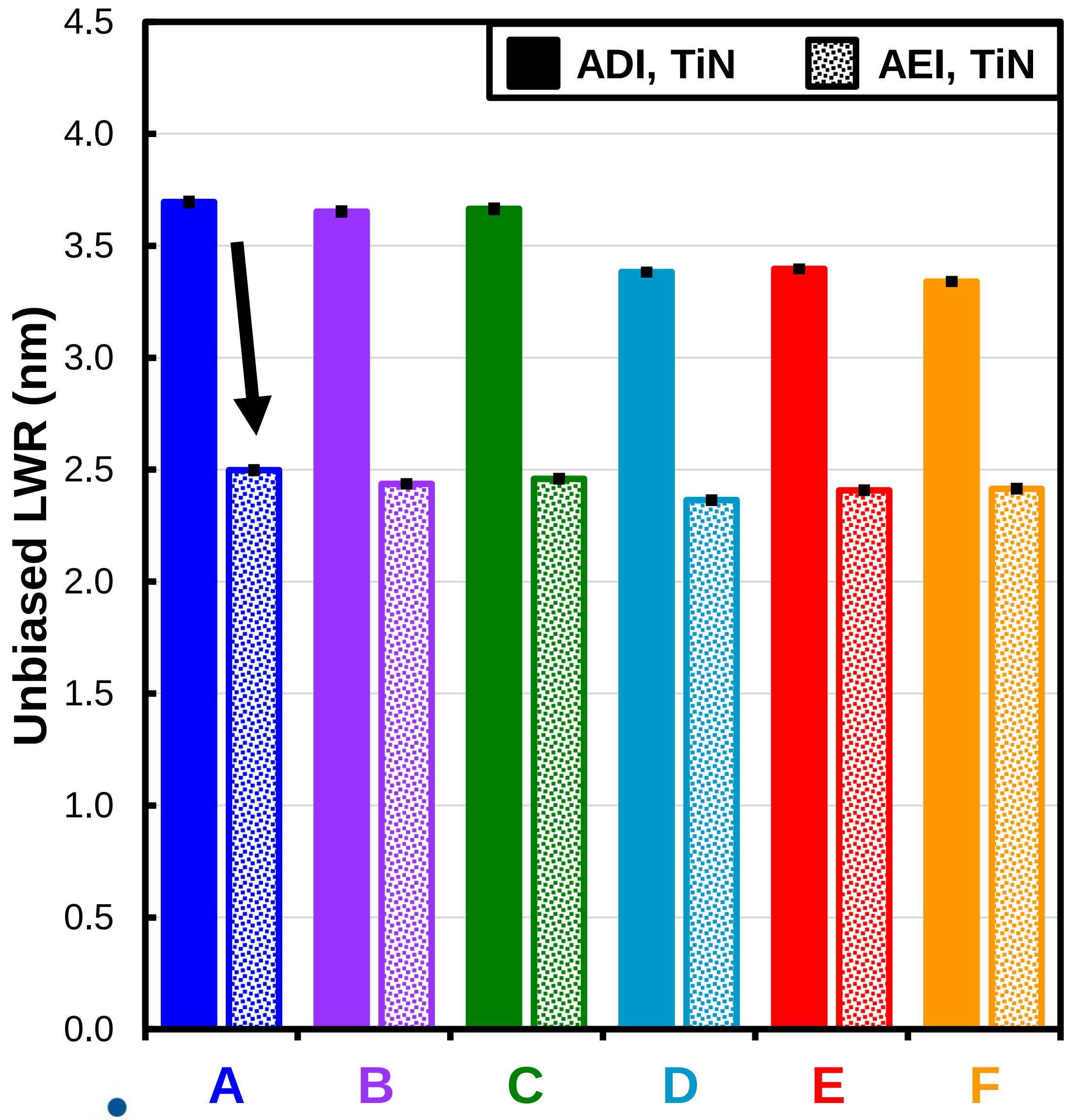
Formulation	Ligand	Solvent
A	1	1
B	1	2
F	1	3

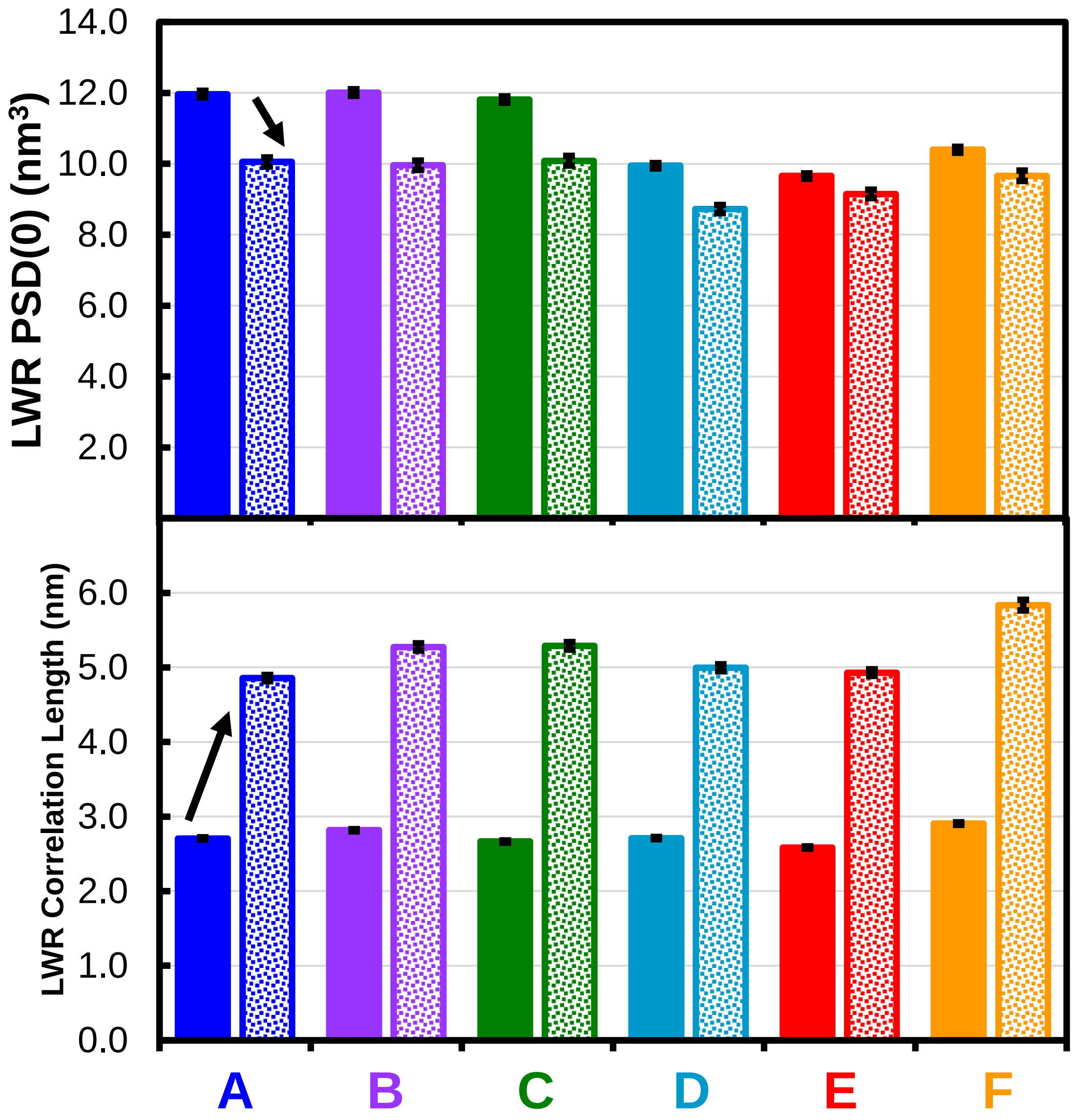




Etch Smooths by Increasing ξ



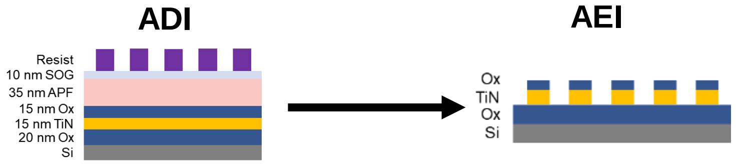


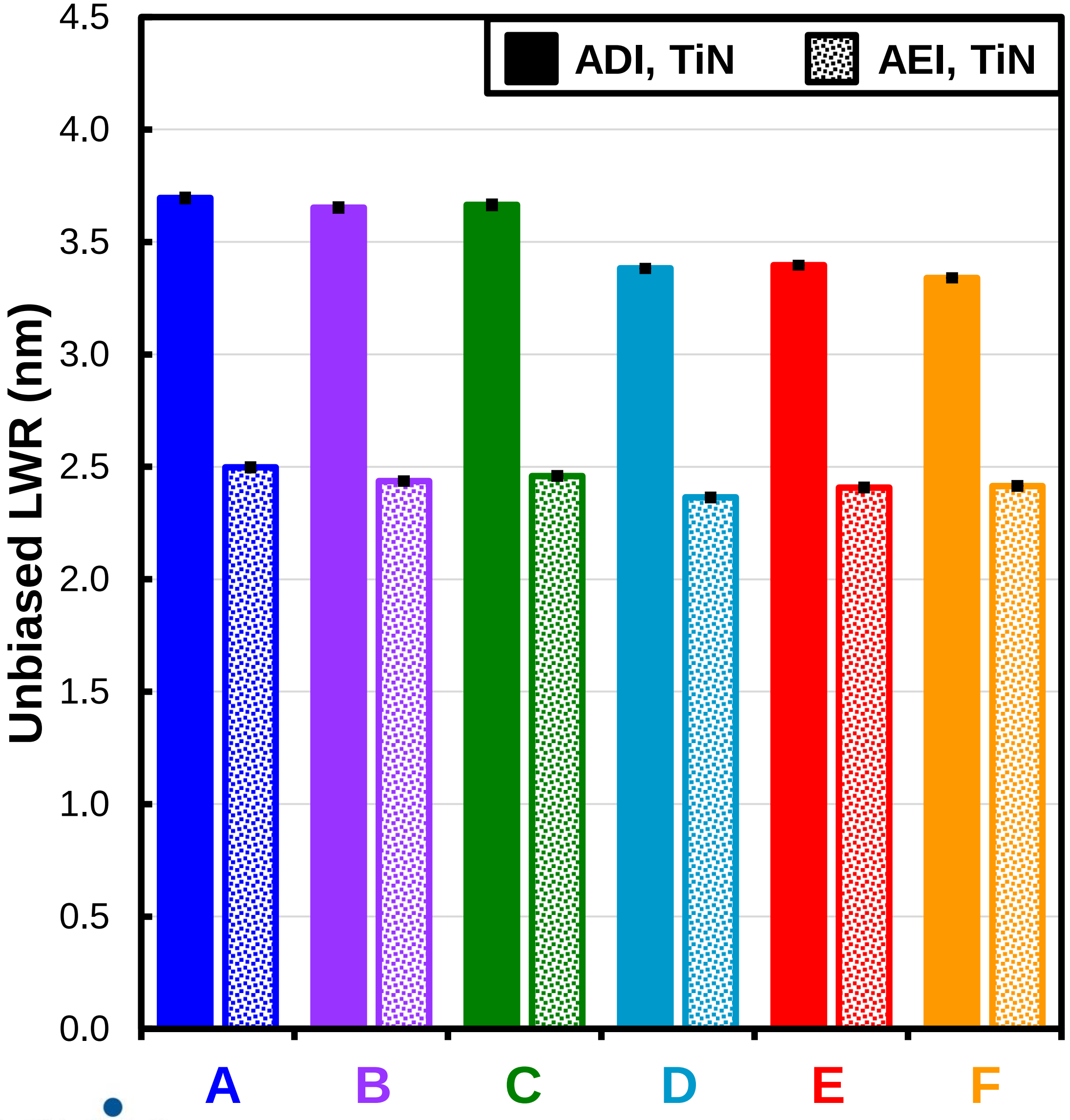


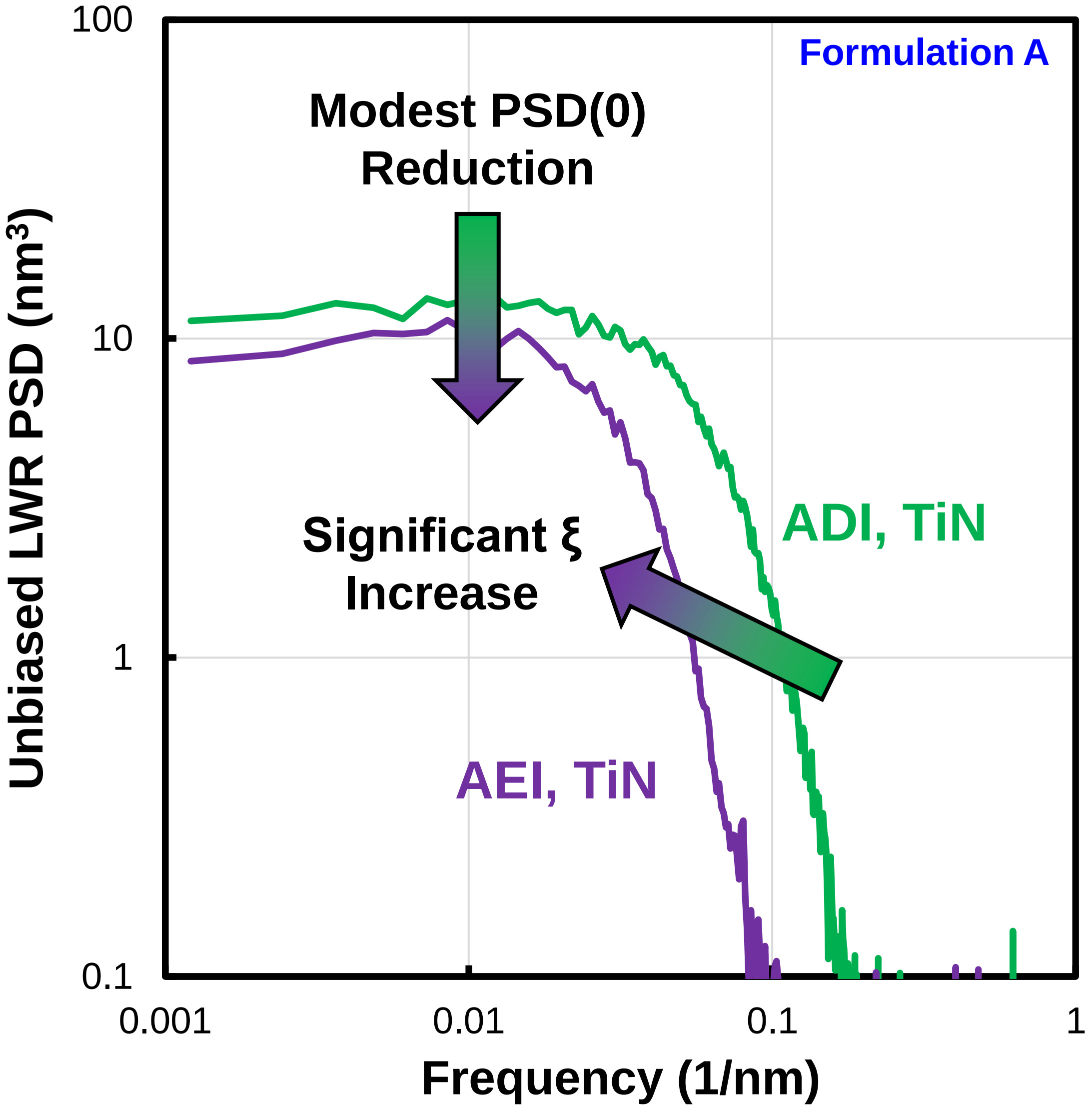
inpria FRACTILIA

SPIE. ADVANCED LITHOGRAPHY+ PATTERNING

Etch Smooths by Increasing ξ





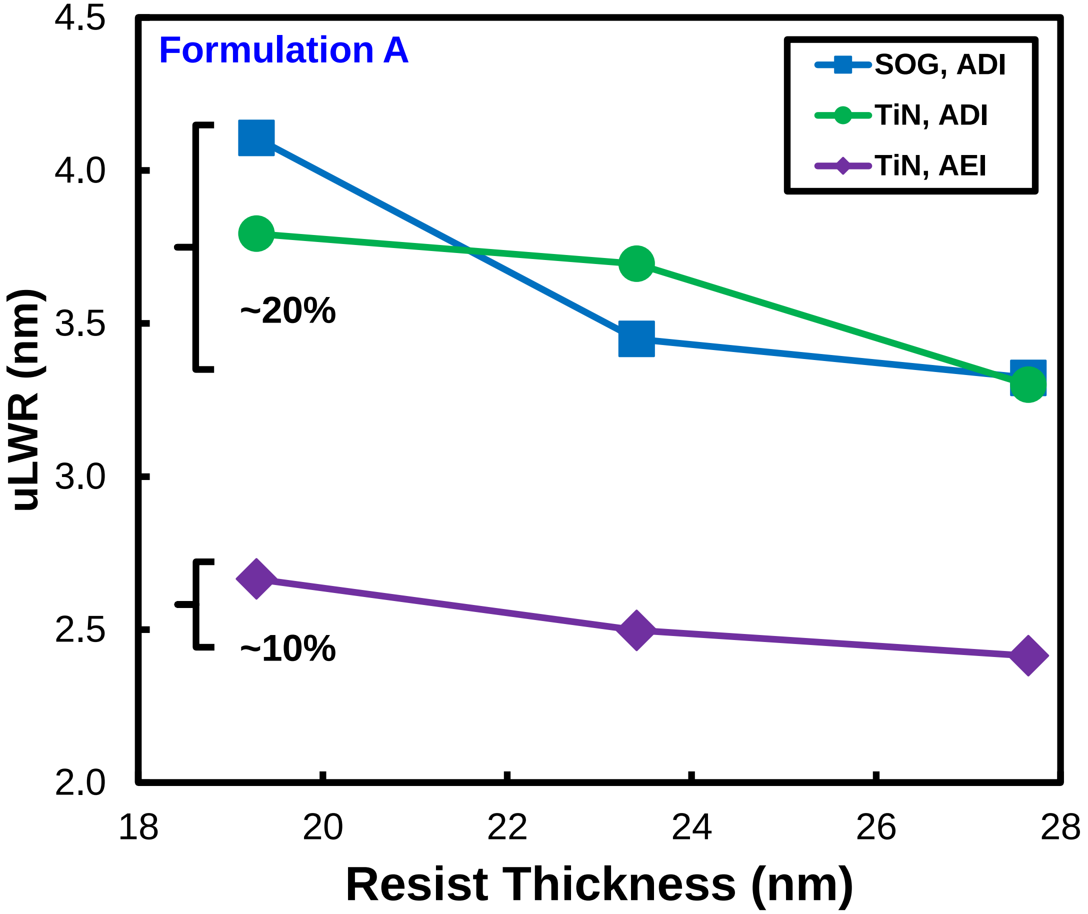


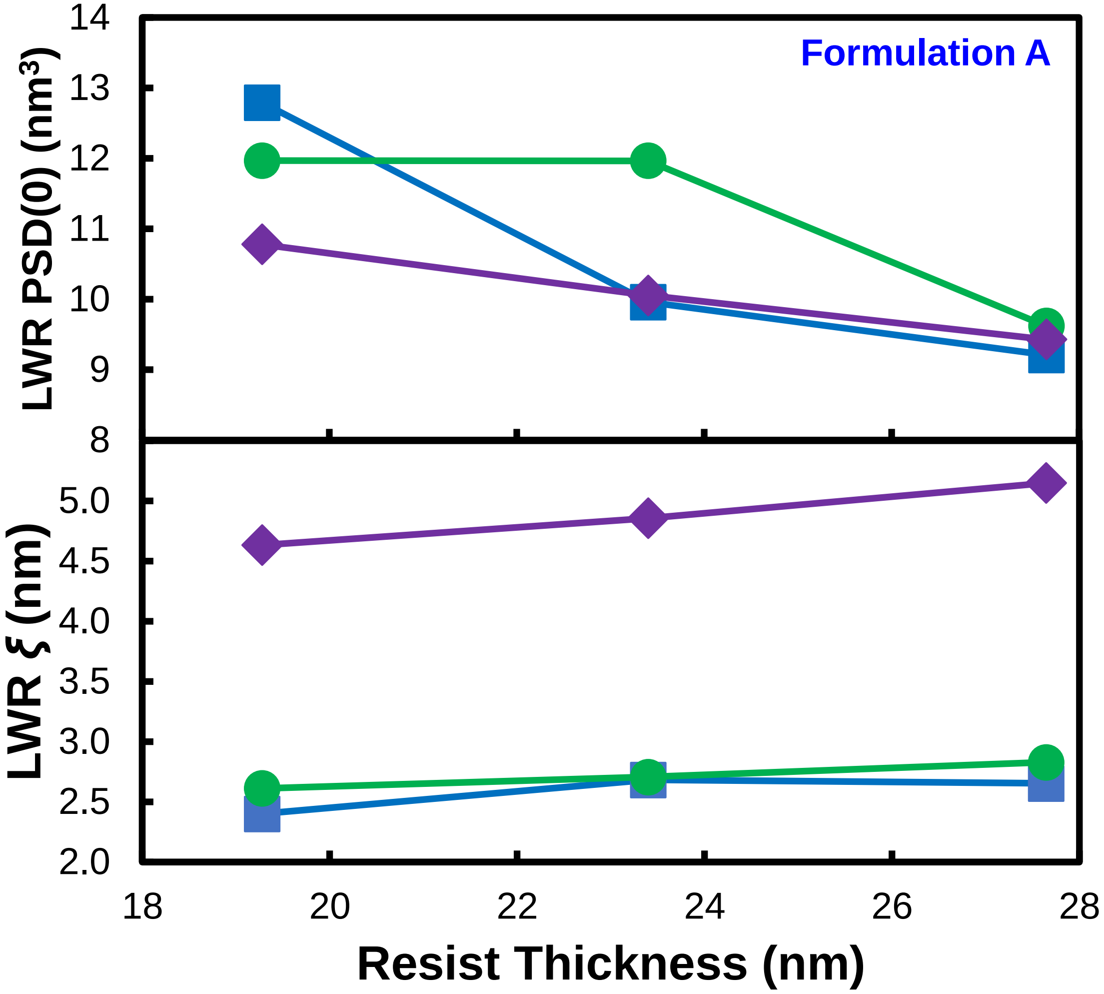
Formulation A

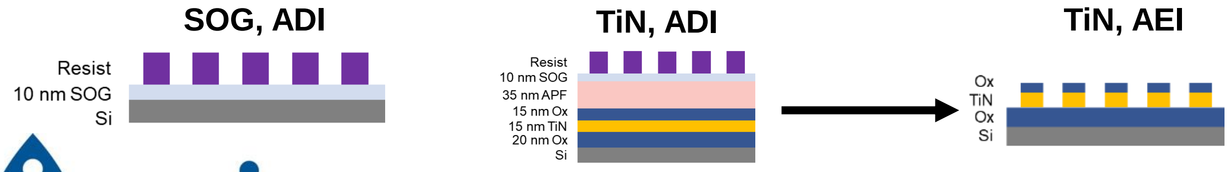
Modest PSD(0) Reduction

Significant ξ Increase

uLWR vs. Resist Thickness

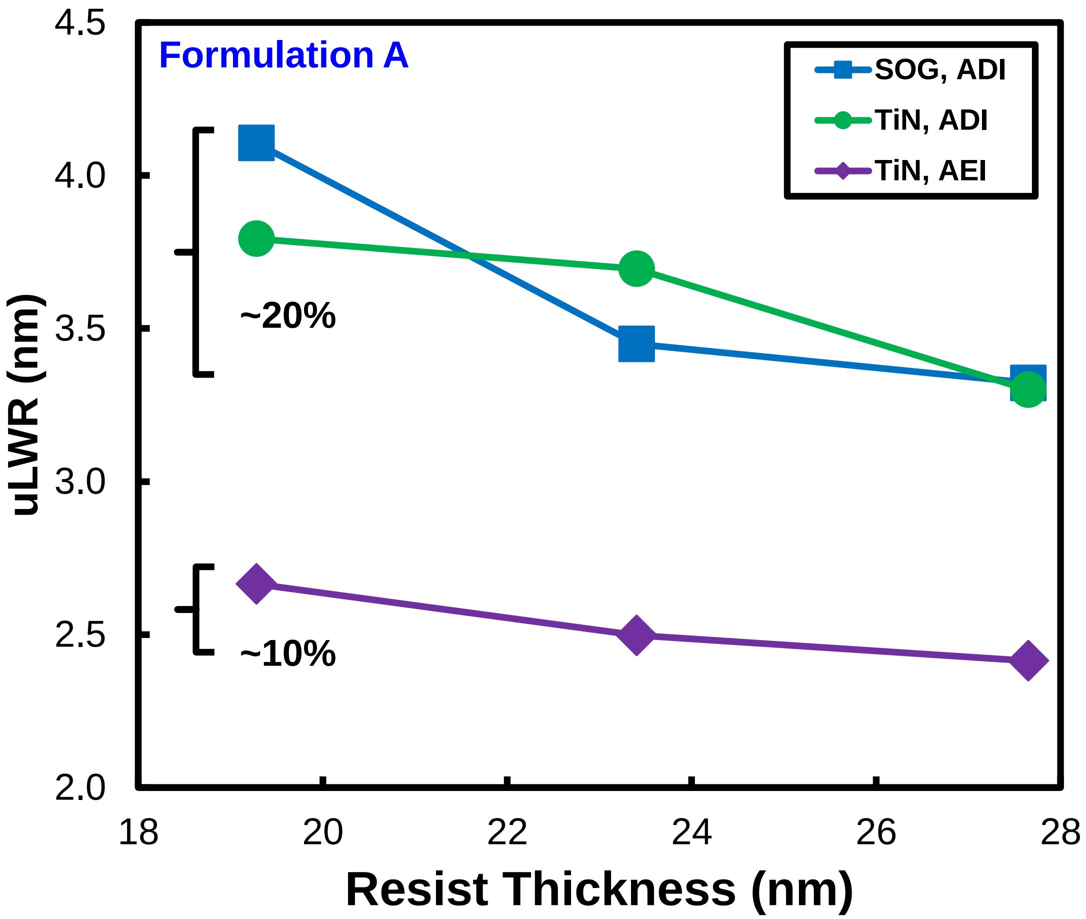


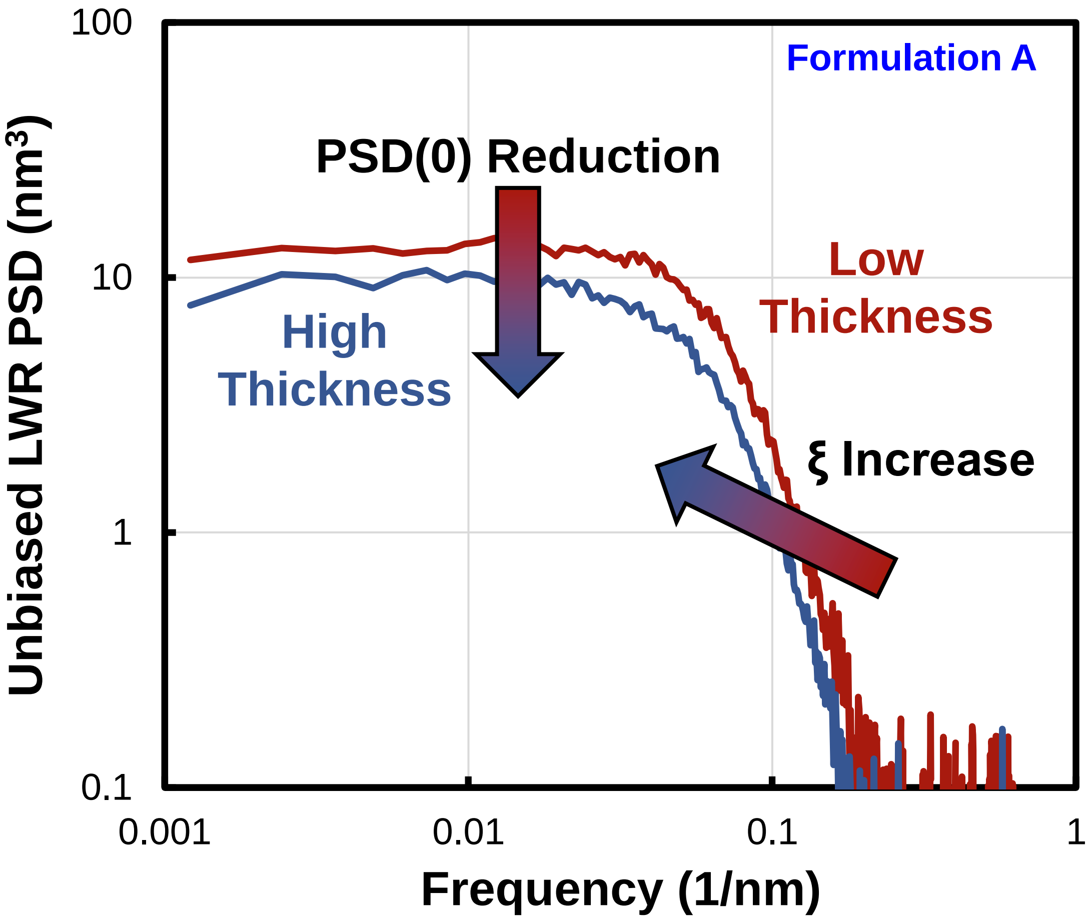


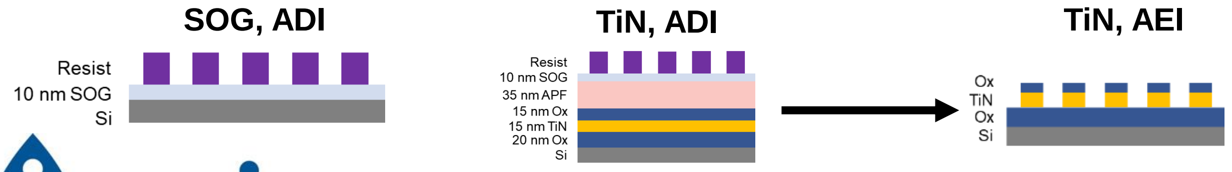


uLWR reduction via increased resist thickness are driven by a reduction in PSD(0) and an increase in ξ

uLWR vs. Resist Thickness

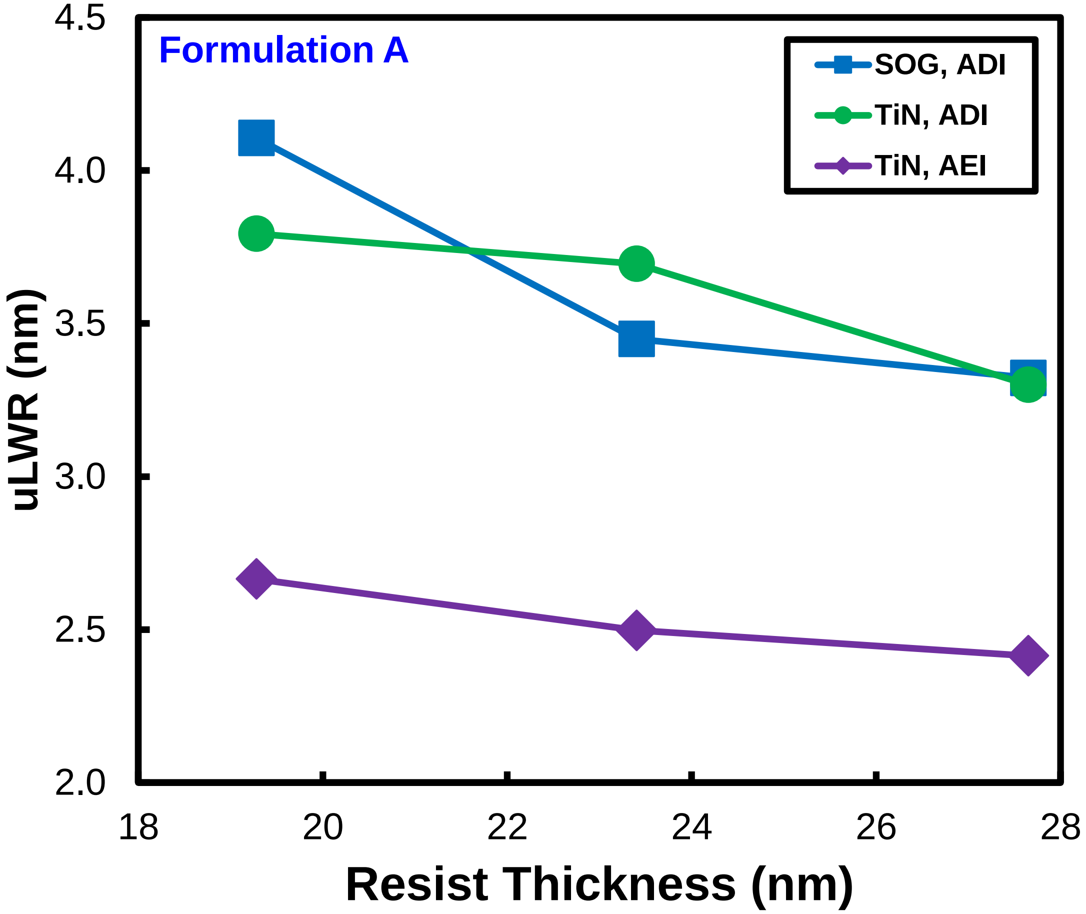


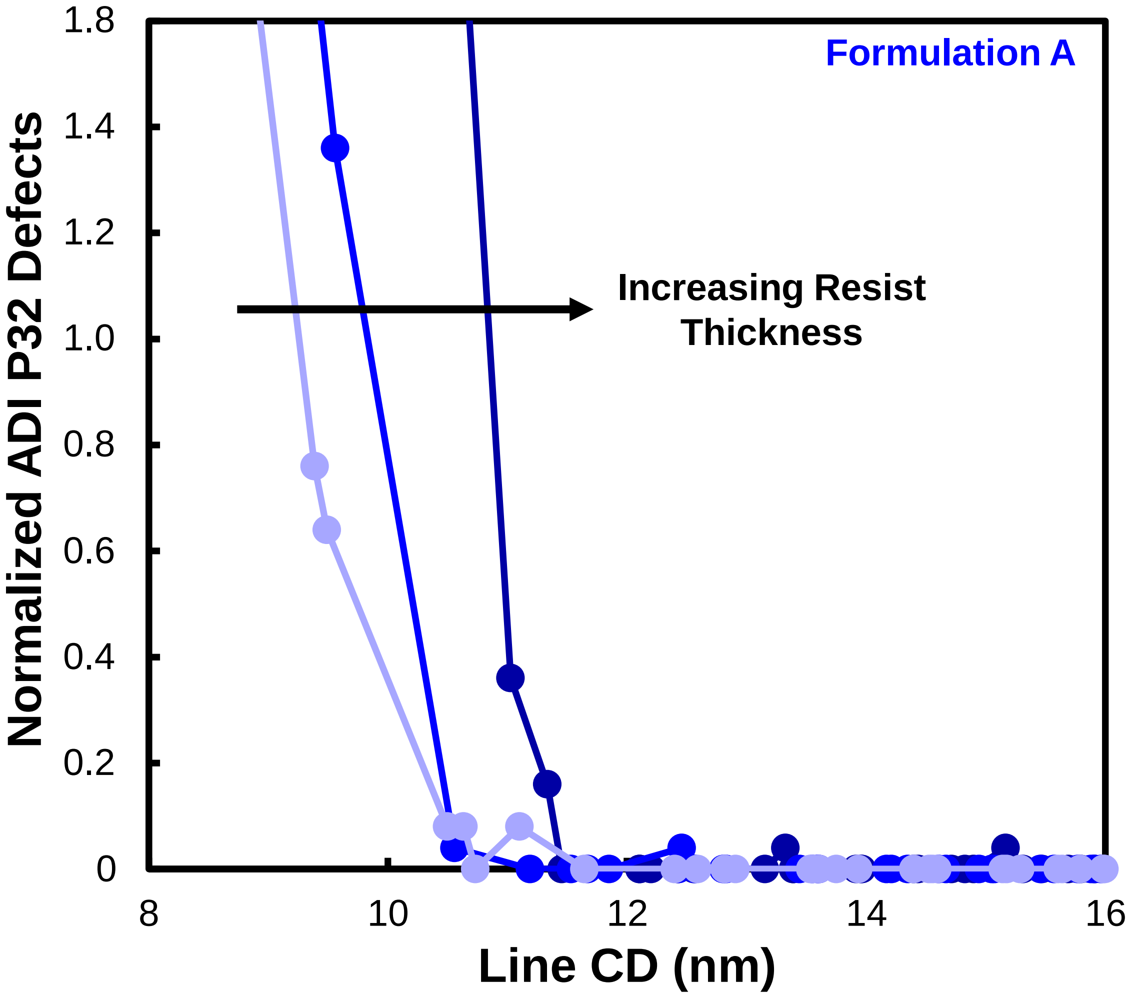




uLWR reduction via increased resist thickness are driven by a reduction in PSD(0) and an increase in ξ

Resist Thickness: uLWR & Defectivity Trade-off

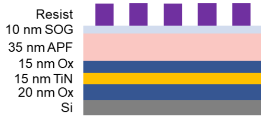




Increasing Resist Thickness

SOG, ADI

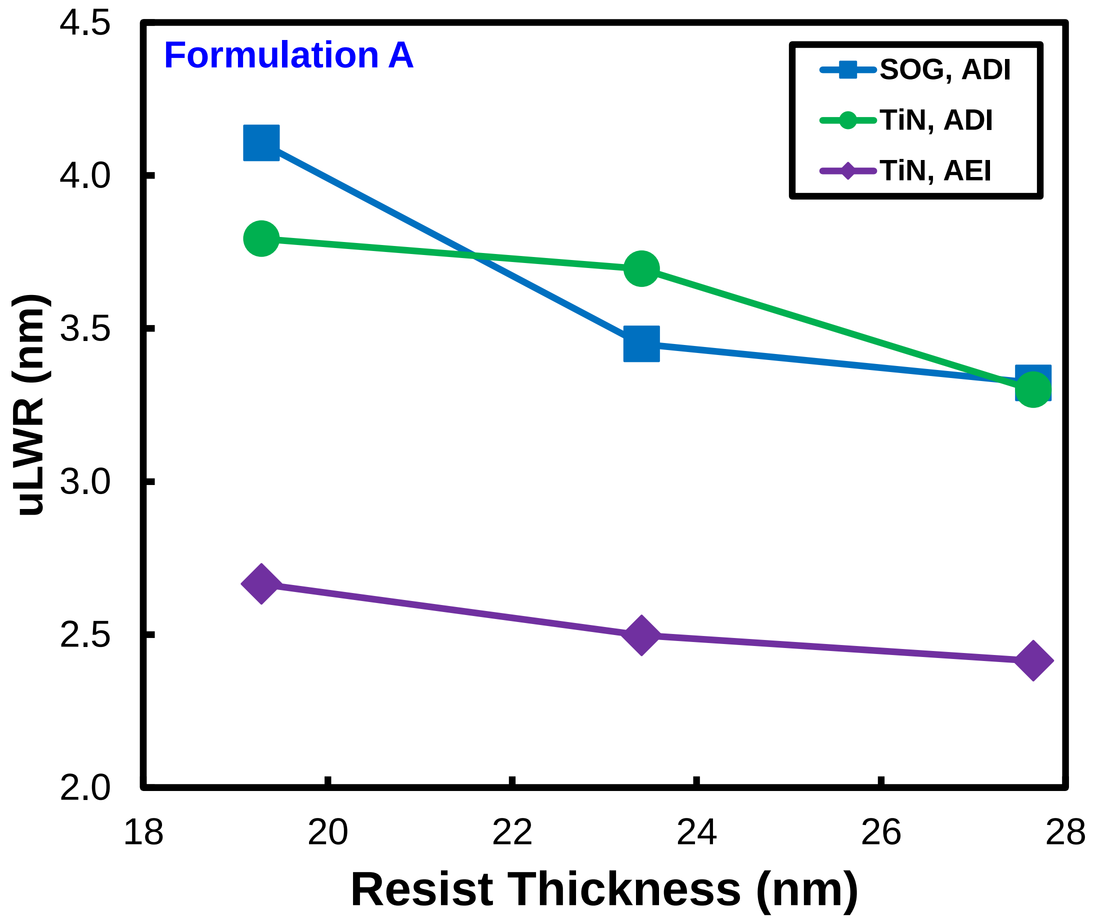
TiN, ADI

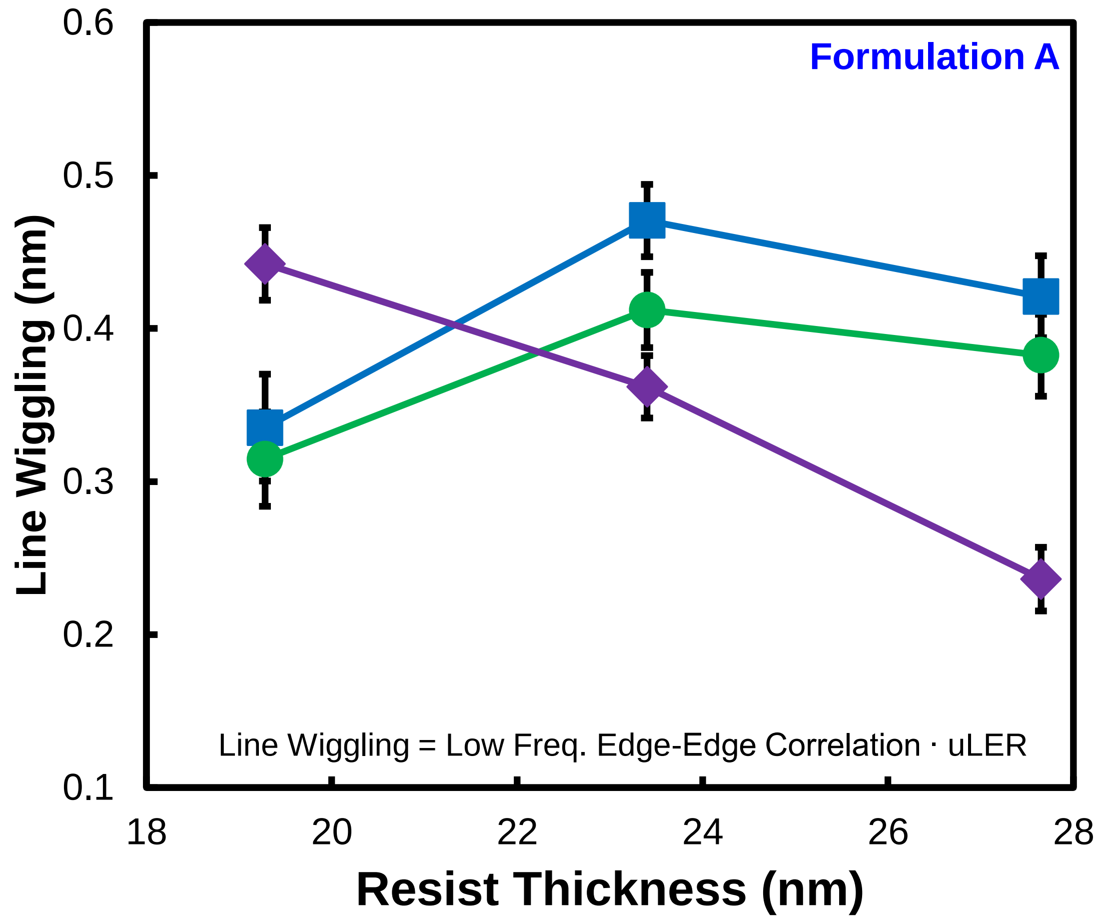


TiN, AEI

uLWR improvements via increased resist thickness trade-off against line-breaks/pattern collapse

Line Wiggling vs. Resist Thickness





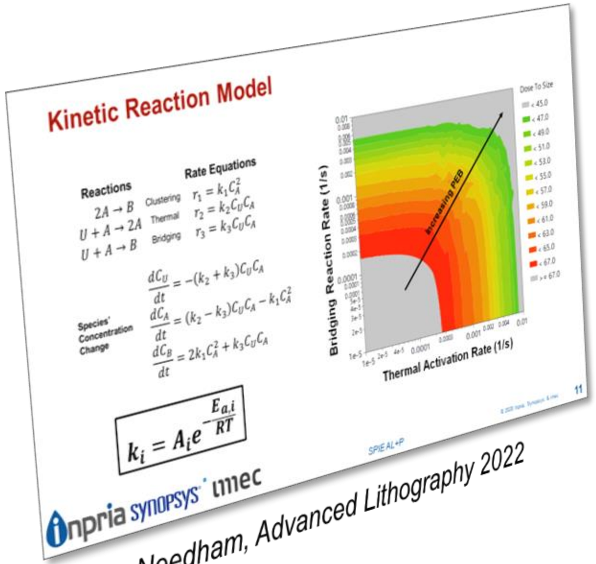
Line Wiggling = Low Freq. Edge-Edge Correlation · uLER

SOG, ADI

TiN, ADI **TiN, AEI**

We observe uLWR reduction at all steps, but the trend in Line Wiggling is reversed from ADI to AEI

MOR Process Chemistry: ESPERT^{TM}



Kinetic Reaction Model

Reactions		Rate Equations
$2A \rightarrow B$	Clustering	$r_1 = k_1 C_A^2$
$U + A \rightarrow 2A$	Thermal	$r_2 = k_2 C_U C_A$
$U + A \rightarrow B$	Bridging	$r_3 = k_3 C_U C_A$

Species' Concentration Change

$$\frac{dC_U}{dt} = -(k_2 + k_3) C_U C_A$$

$$\frac{dC_A}{dt} = (k_2 - k_3) C_U C_A - k_1 C_A^2$$

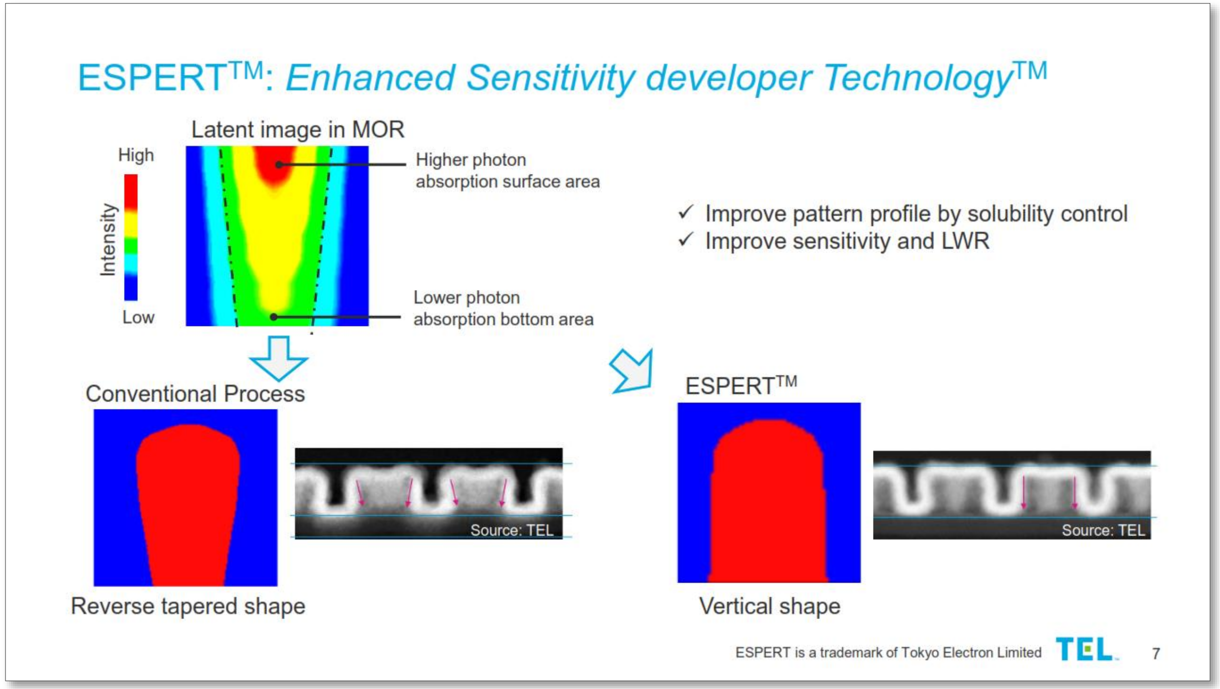
$$\frac{dC_B}{dt} = 2k_1 C_A^2 + k_3 C_U C_A$$

$$\boxed{k_i = A_i e^{-\frac{E_{a,i}}{RT}}}$$

SPIE AL+P

11

Needham, Advanced Lithography 2022



ESPERT^{TM}: *Enhanced Sensitivity developer Technology*^{TM}

- ✓ Improve pattern profile by solubility control
- ✓ Improve sensitivity and LWR

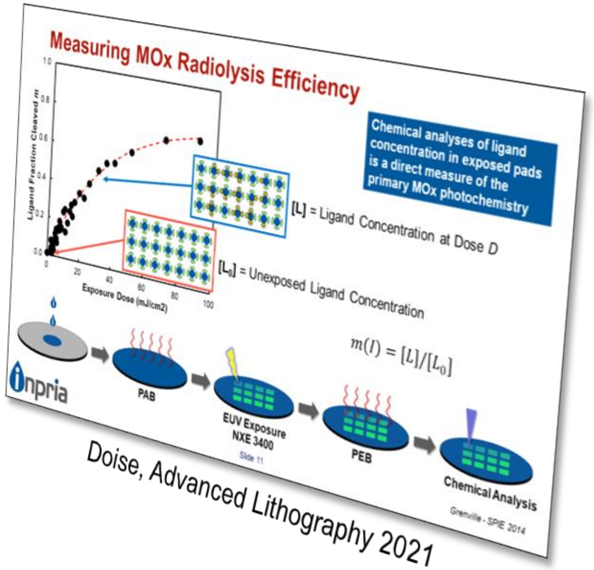
Reverse tapered shape

Vertical shape

ESPERT is a trademark of Tokyo Electron Limited

7

Dinh, Advanced development methods for high-NA EUV lithography - 12498-4



Measuring MOx Radiolysis Efficiency

Chemical analyses of ligand concentration in exposed pads is a direct measure of the primary MOx photochemistry

[L] = Ligand Concentration at Dose *D*

[L₀] = Unexposed Ligand Concentration

$$m(I) = [L]/[L_0]$$

Slide 11

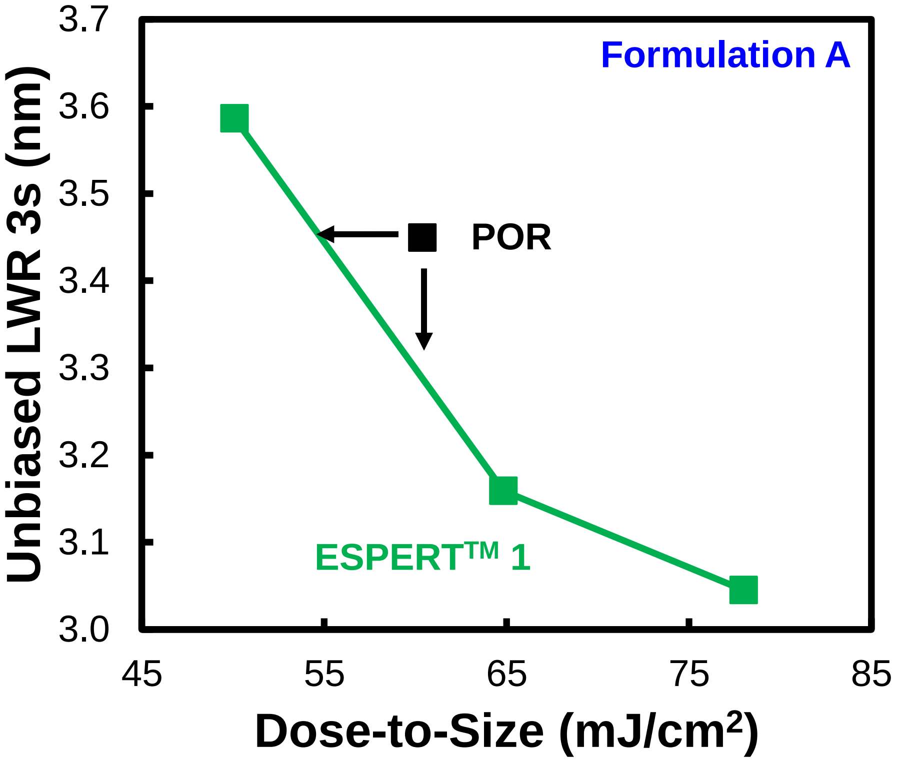
Grenville - SPIE 2014

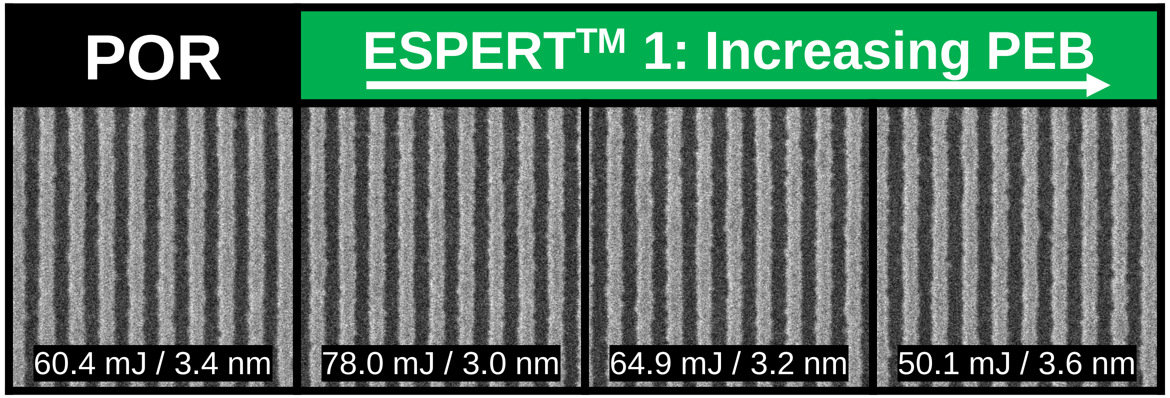
Doise, Advanced Lithography 2021

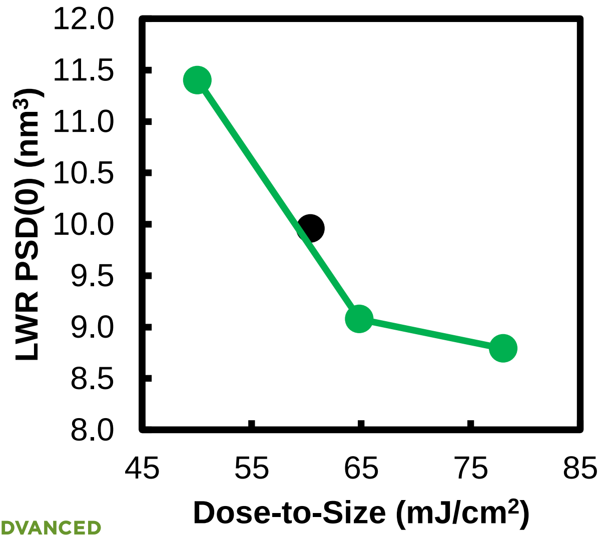
MOR chemistry enables industry process innovations that boost performance and further reduce CoO for advanced nodes

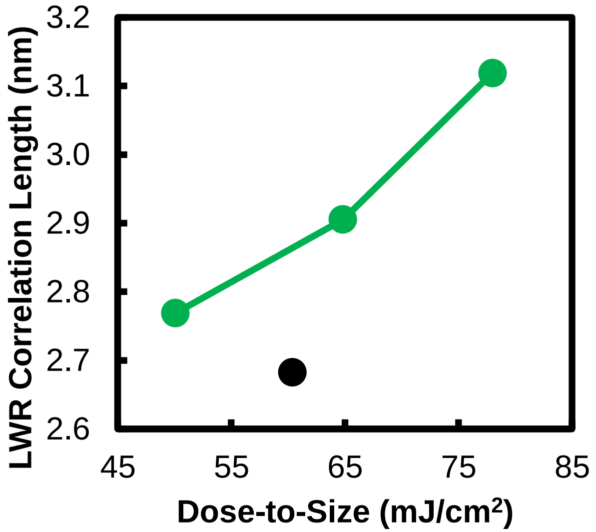
ESPERT^{TM} 1: RLS Improvement

- ESPERT^{TM} 1 apodization yields a different RLS trade-off than the POR wafer process
- The RLS improvement is driven by an increase in Correlation Length
- ESPERT^{TM} 1 allows for RLS improvement without in-bottle resist modification, preserving material stochastics





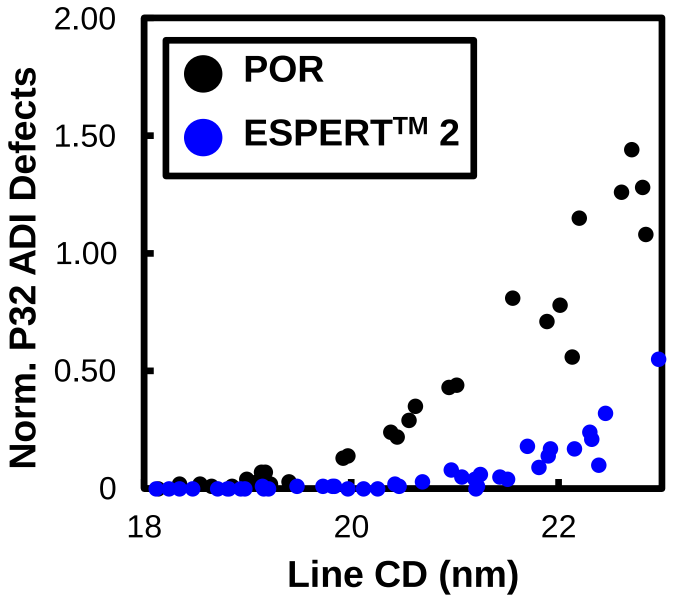


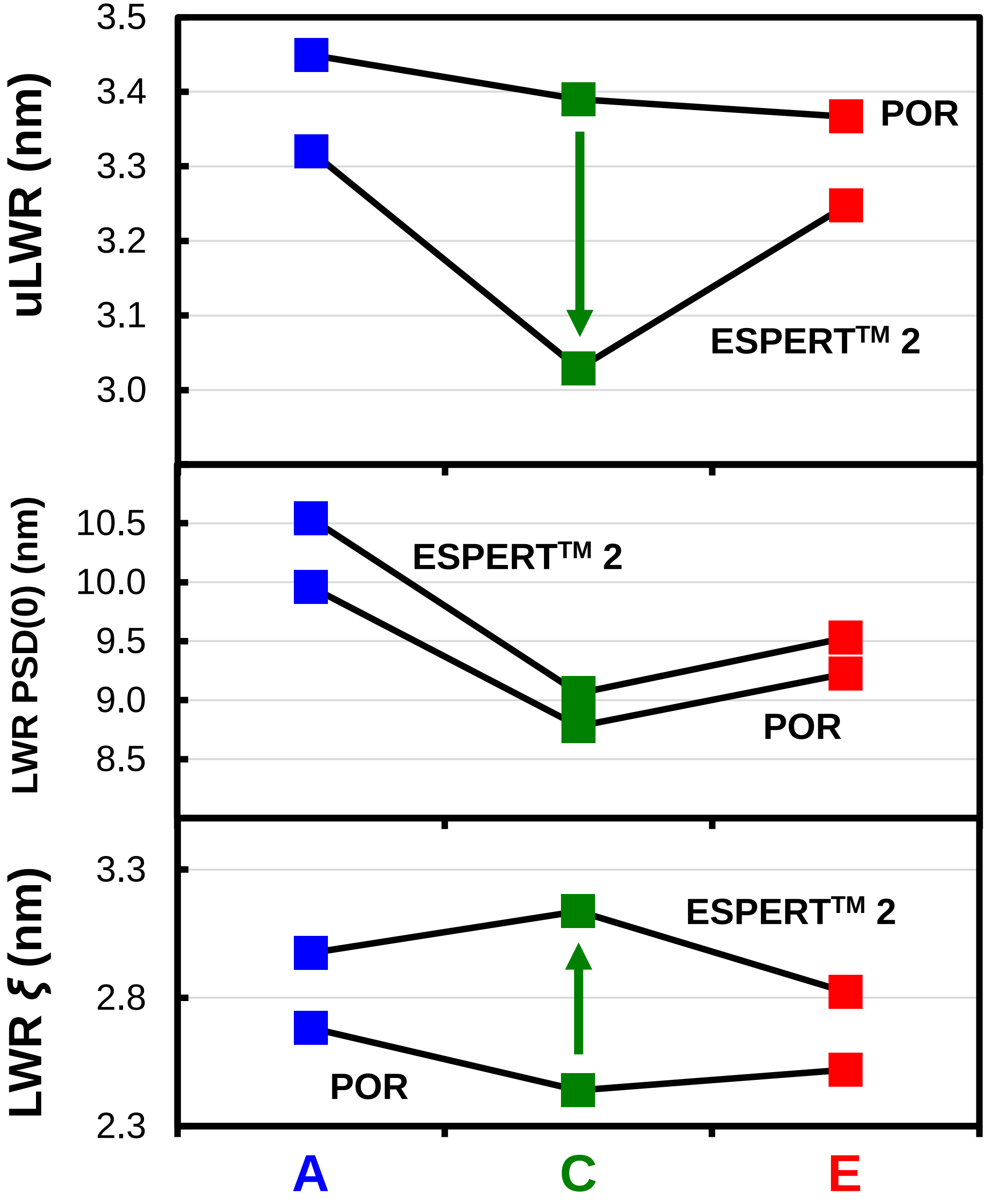


ESPERT™ 2: Ligand Variation

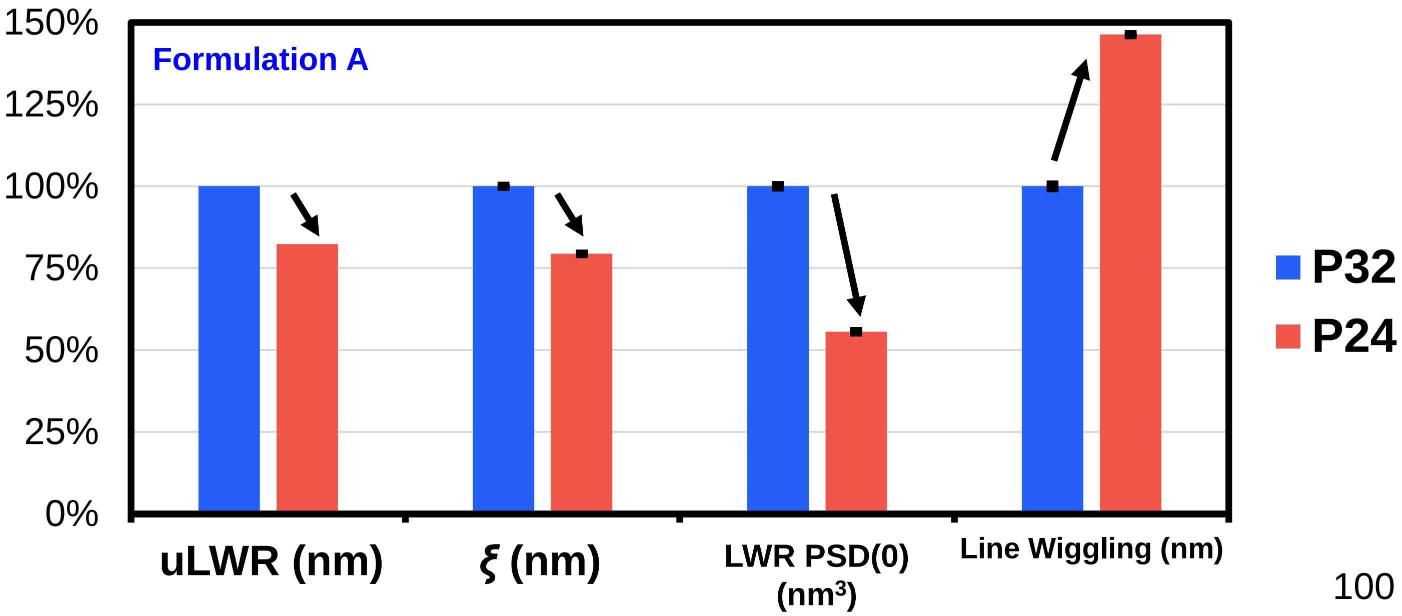
- With the POR develop process, there is a clear relationship between resist radiolytic efficiency and uLWR, but that is not the case with ESPERT™ 2
- ESPERT™ 2 reduces bridging defects and widens the defect-free window
- Different process knobs with ESPERT™ 2 require different process tuning

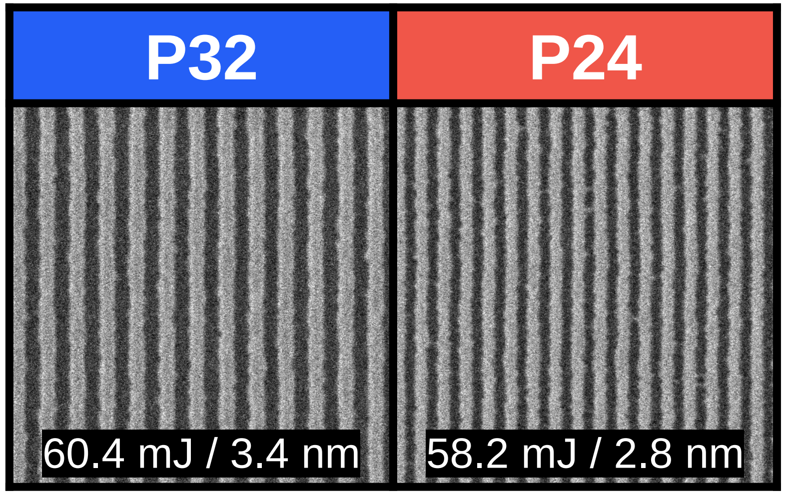
Formulation	Ligand	Solvent
A	1	1
C	2	1
E	3	1



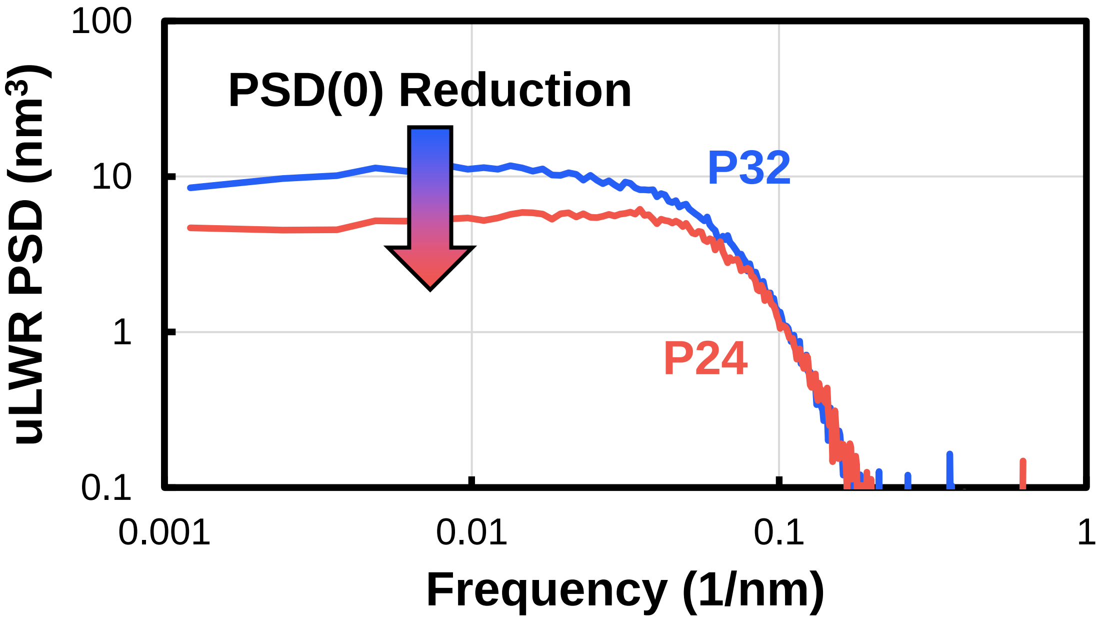


P32 vs. P24 – POR Process





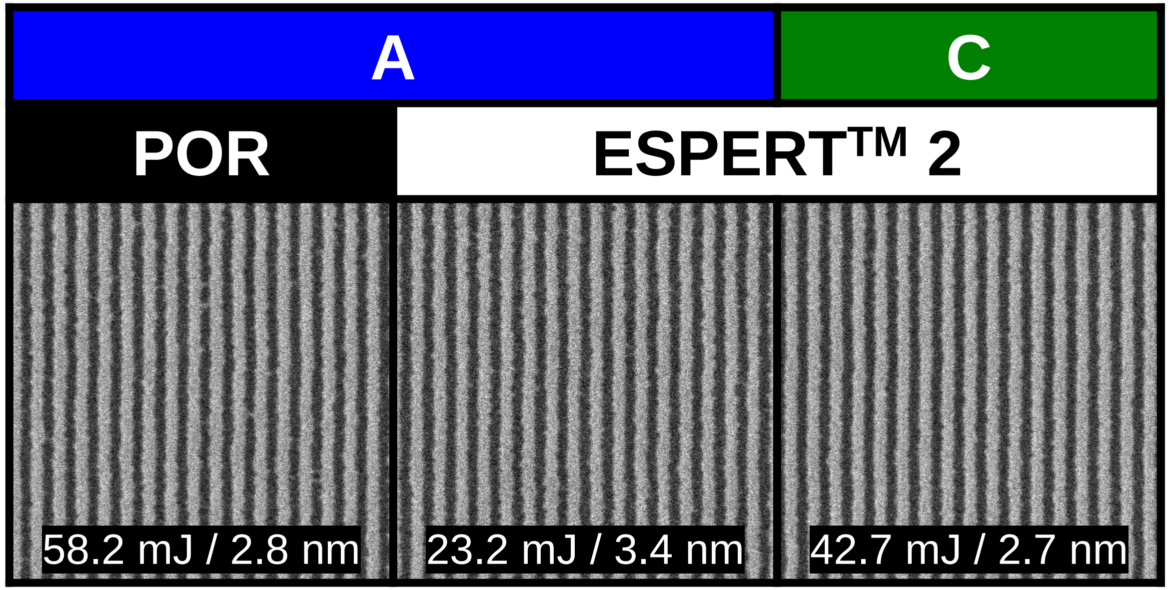
- Reduction in uLWR, ξ, PSD(0) at P24
- However, we also see an increase in Line Wiggling at P24,
  - same film thickness (~22 nm) for both exposures

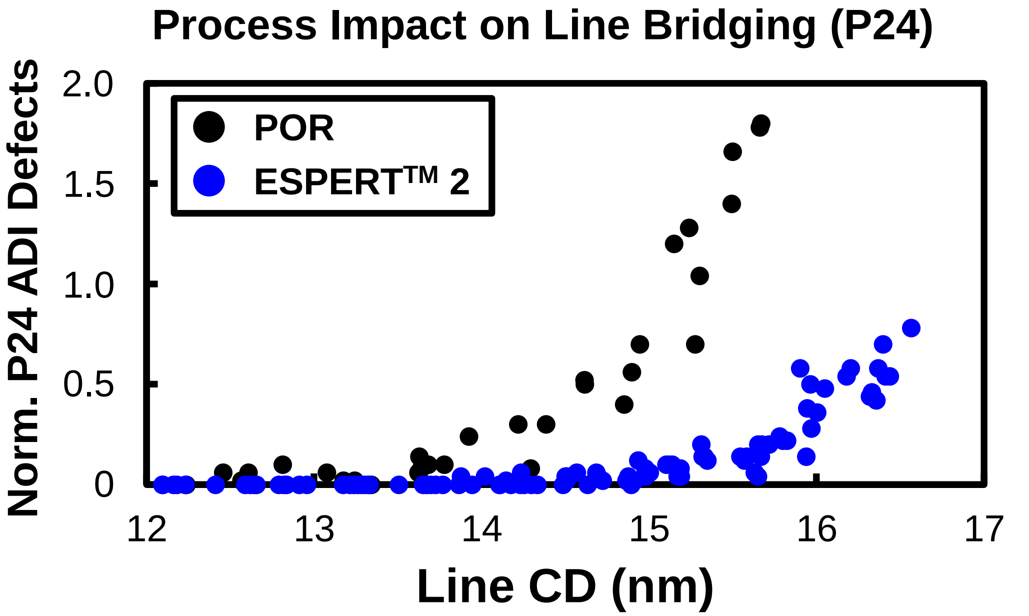


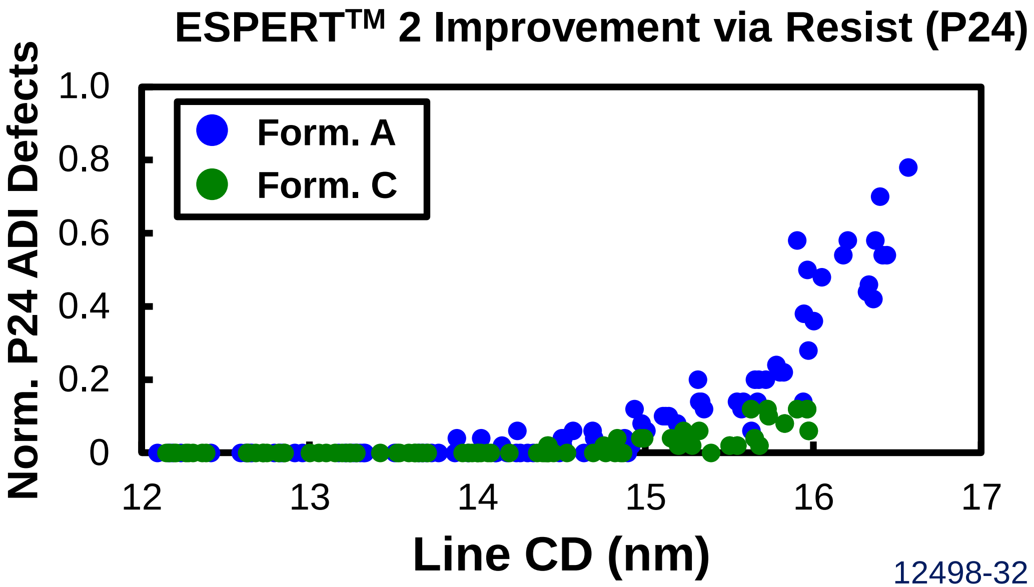
ESPERT™ 2: P24 Optimization

Formulation	Ligand	Solvent
A	1	1
C	2	1

- ESPERT™ 2 yields a defectivity reduction and an improvement in the ADI defect window
- The benefits of Resist C and ESPERT™ 2 from P32 also hold at P24

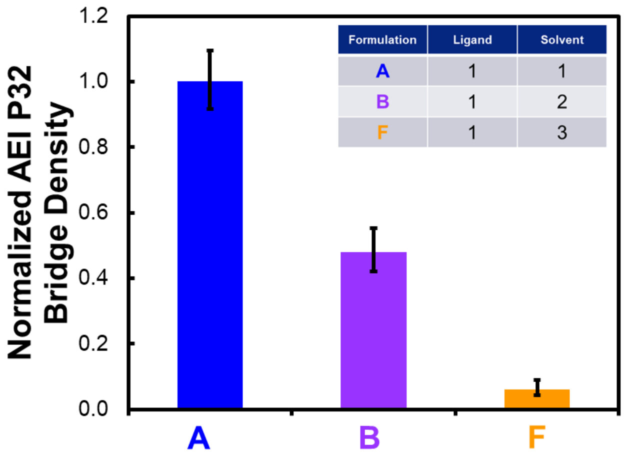




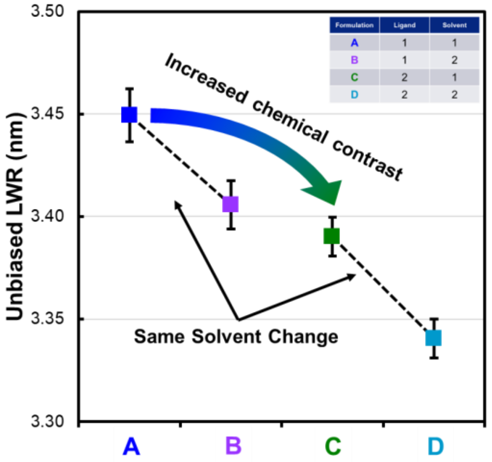


Summary

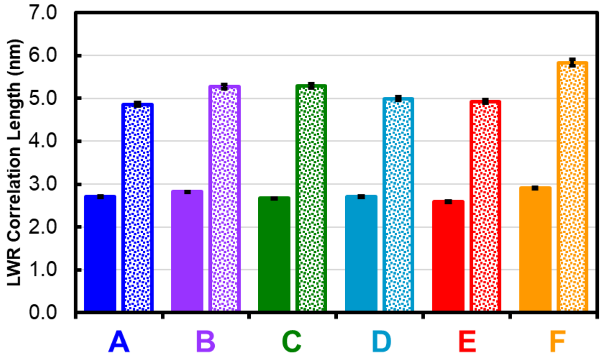
- Inpria has made resist improvements via solvent-ligand co-optimization
- Inpria MOR attain low AEI uLWR via etch smoothing of high frequency noise due to increased correlation length
- Resist-thickness driven uLWR improvements persist at AEI
- ESPERT™ 1
  - improves chemical image contrast at the line edge
  - lower uLWR at lower Dose-to-Size
- ESPERT™ 2
  - new process knobs for DtS and uLWR
  - new ligand-process co-optimization will be needed for defectivity improvements
- The Inpria POR process is capable of printing P24 LS at 0.33 NA. Process optimization will make additional improvements

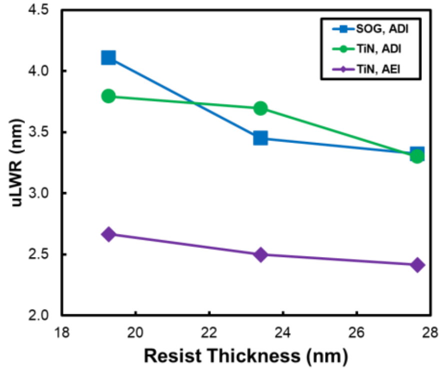


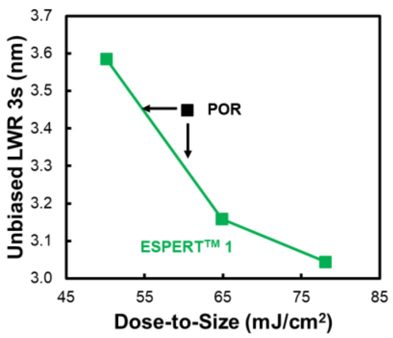
Formulation	Ligand	Solvent
A	1	1
B	1	2
F	1	3

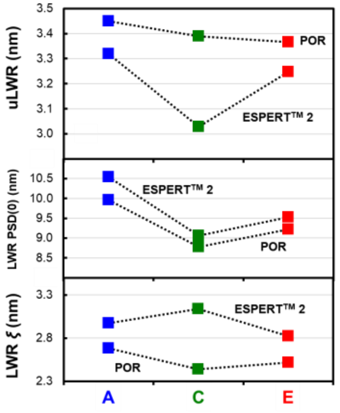


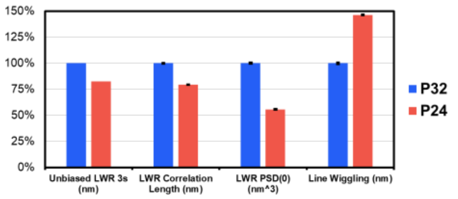
Formulation	Ligand	Solvent
A	1	1
B	1	2
C	2	1
D	2	2

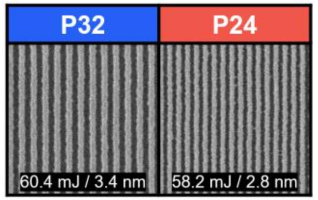












Acknowledgements

Thank you to the teams at:

imec

Tokyo Electron Ltd.

… And to all our partners & collaborators inpria®

JSR A JSR Company

FRACTILIA

Thank You