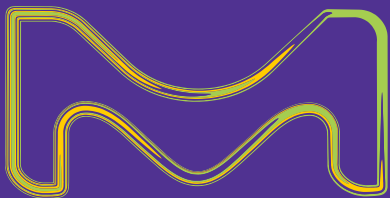


# Aqueous Materials for Advanced Lithography

Strategic Materials Conference Taiwan 2019

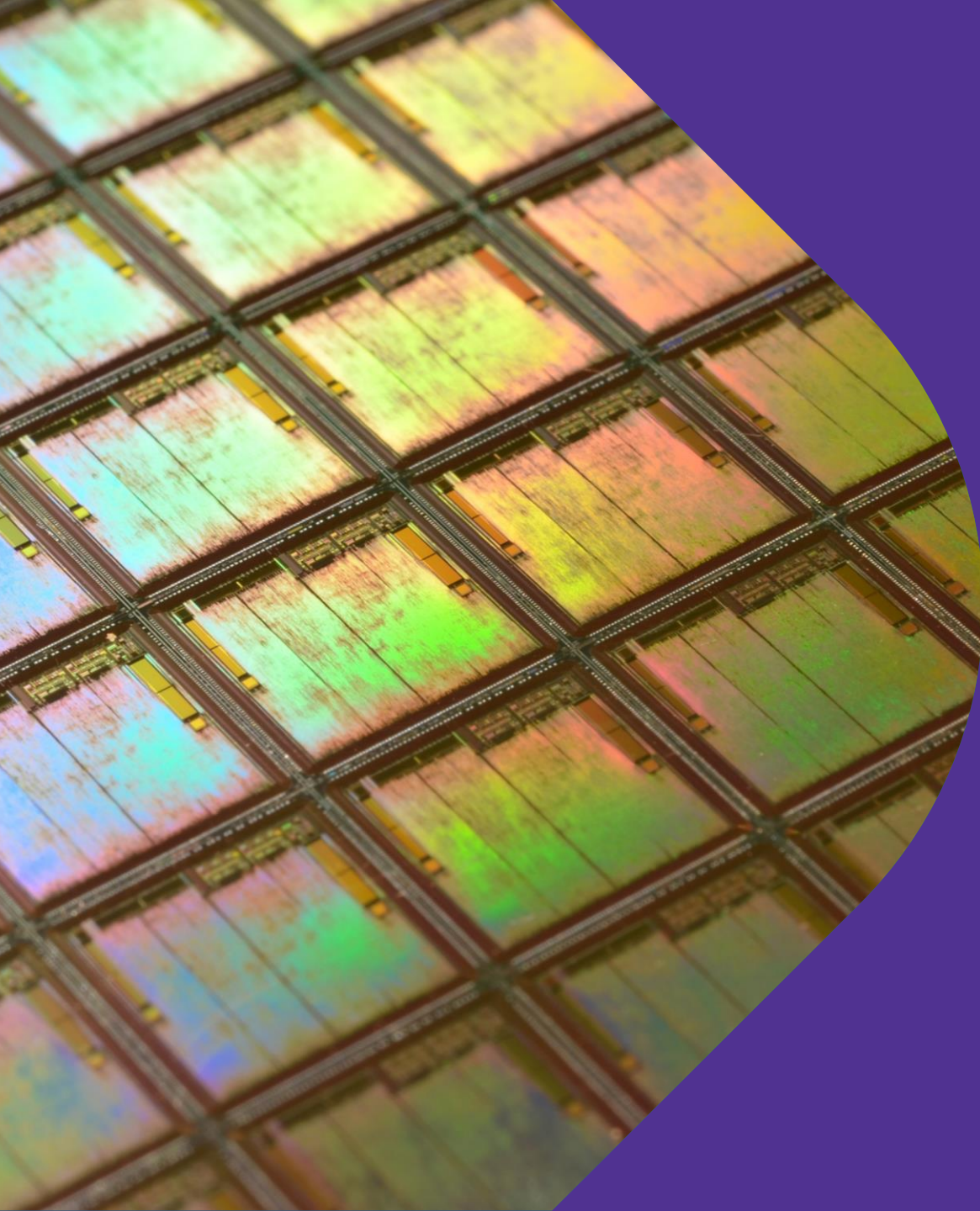
Yi Cao  
Taipei, 9/19/2019



MERCK

# Agenda

- 01 Overview and product roadmap
- 02 Rinse materials
- 03 Chemical shrink materials
- 04 Summary



# 01 overview and product roadmap



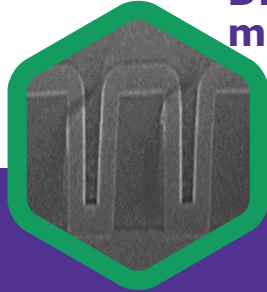
# Merck Performance Materials – Semiconductor Solutions

## Our solutions enable electronic industry

**Patterning materials**



**Dielectric materials**



**Deposition materials**



**we enable**

- smaller structures to continue Moore's law
- higher memory capacity, faster processing speed and less power consumption
- improved yields and lower processing costs

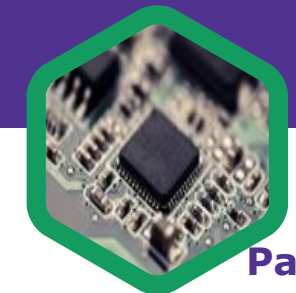
**Process materials**



**CMP materials**



**Packaging materials**



**Mobile Devices**



**Servers for Big Data**

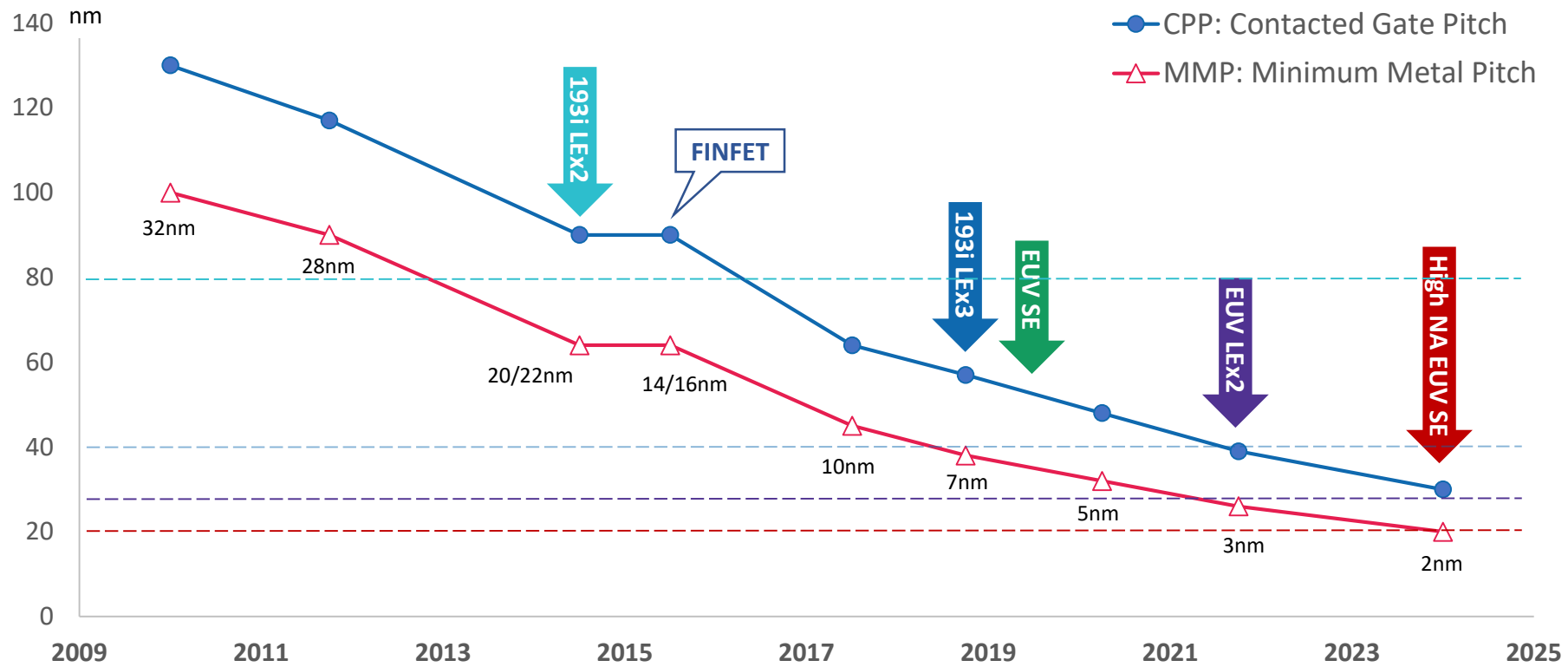


**Wearables and other IoT devices**



Further expanded portfolio with the on-going Versum acquisition

# Lithography roadMap

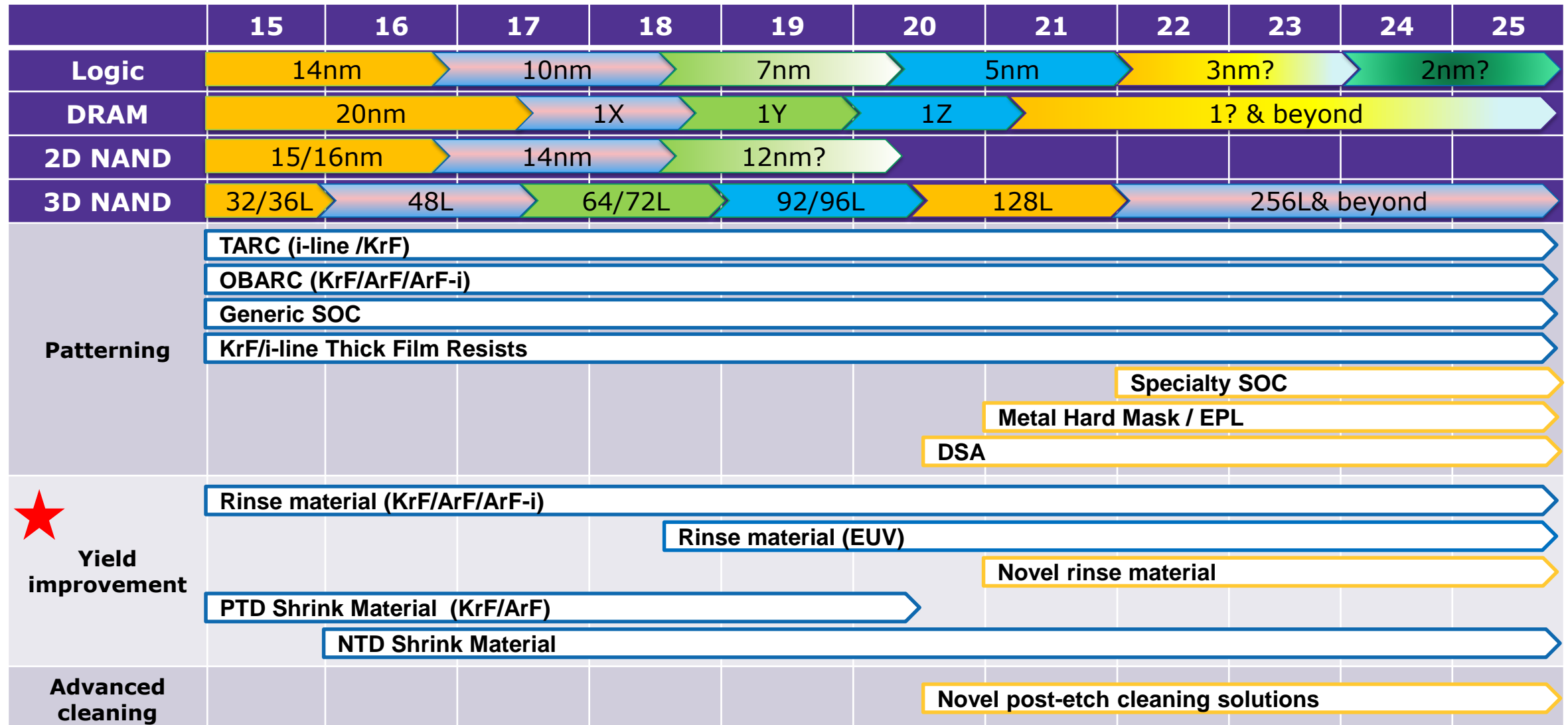


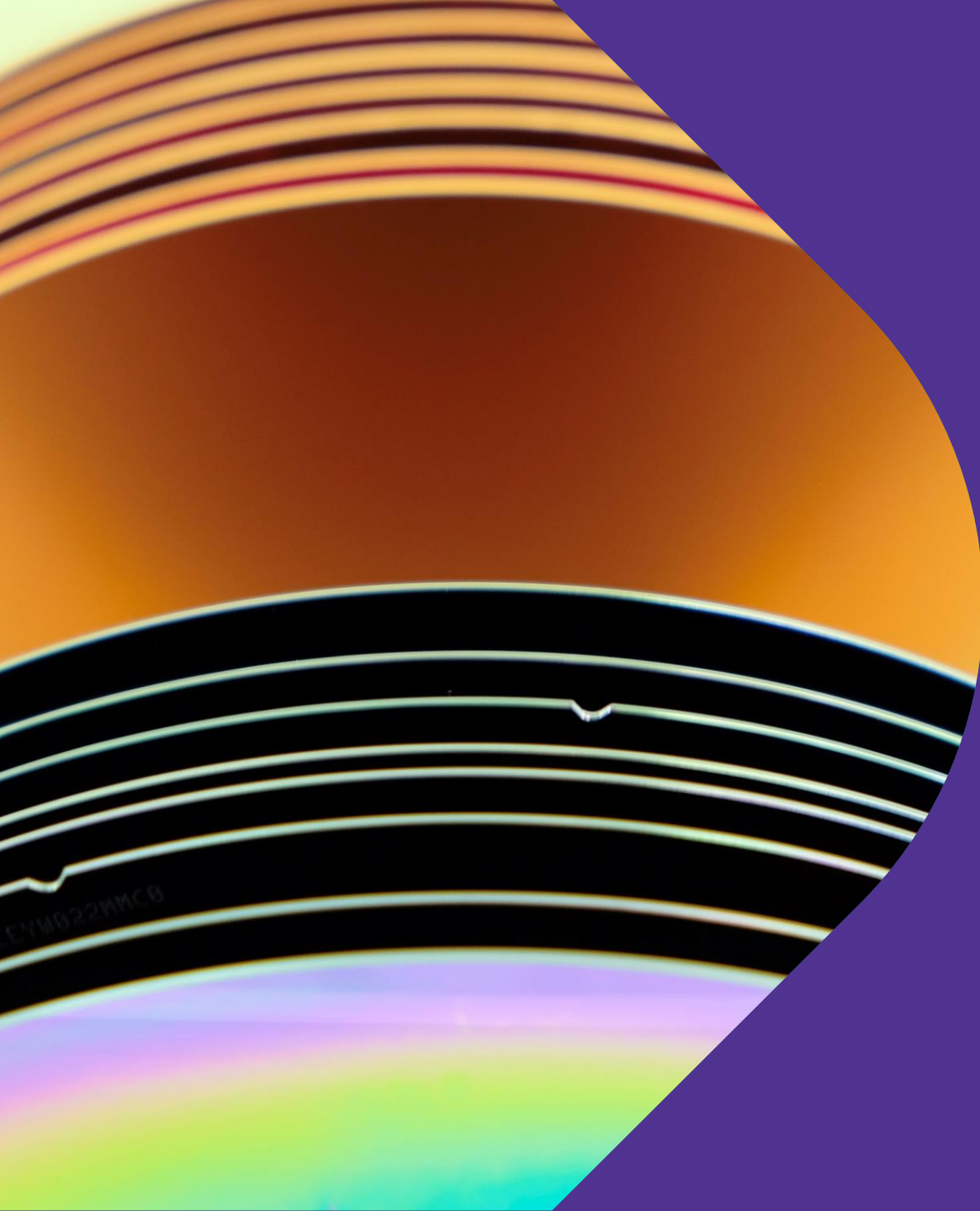
- ✓ EUV process makes economic sense when replacing 3 masks.
- ✓ Double SAQP for pillar patterning may render EUV process of cost advantages.

# Lithography & cleaning materials roadmap

Commercial product

Development stage





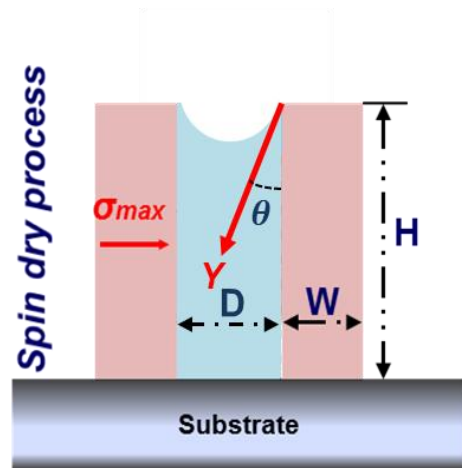
## 02 Rinse Materials

# Rinse materials

## Concept

### Pattern collapse:

- Capillary effect (rinse surface tension)
- Resist deformation (Young's modulus)

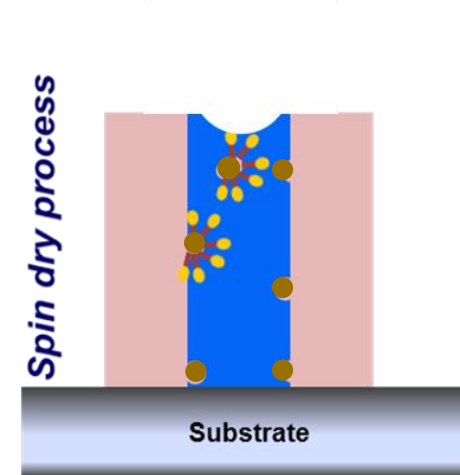
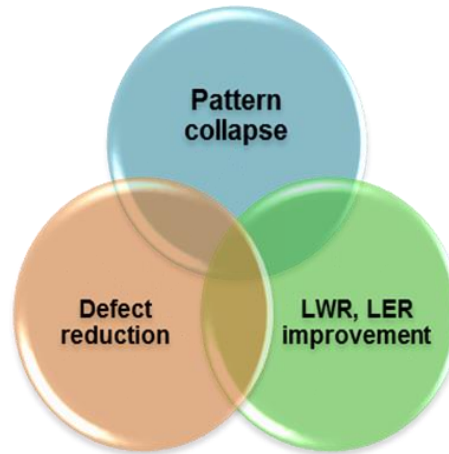


$$\sigma_{max} = 6\gamma A^2 \cdot \cos \theta / D$$

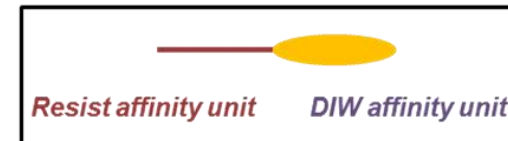
- $\sigma$  : Stress to resist  
 $\gamma$  : Surface tension of rinse  
 $A$  : Aspect ratio =  $H/W$   
 $\theta$  : Contact angle  
 $D$  : Space width

### Defect reduction & LWR, LER improvement:

- Resist & DIW affinity part of FIRM chemical
- Clean resist scum & leveling pattern surface



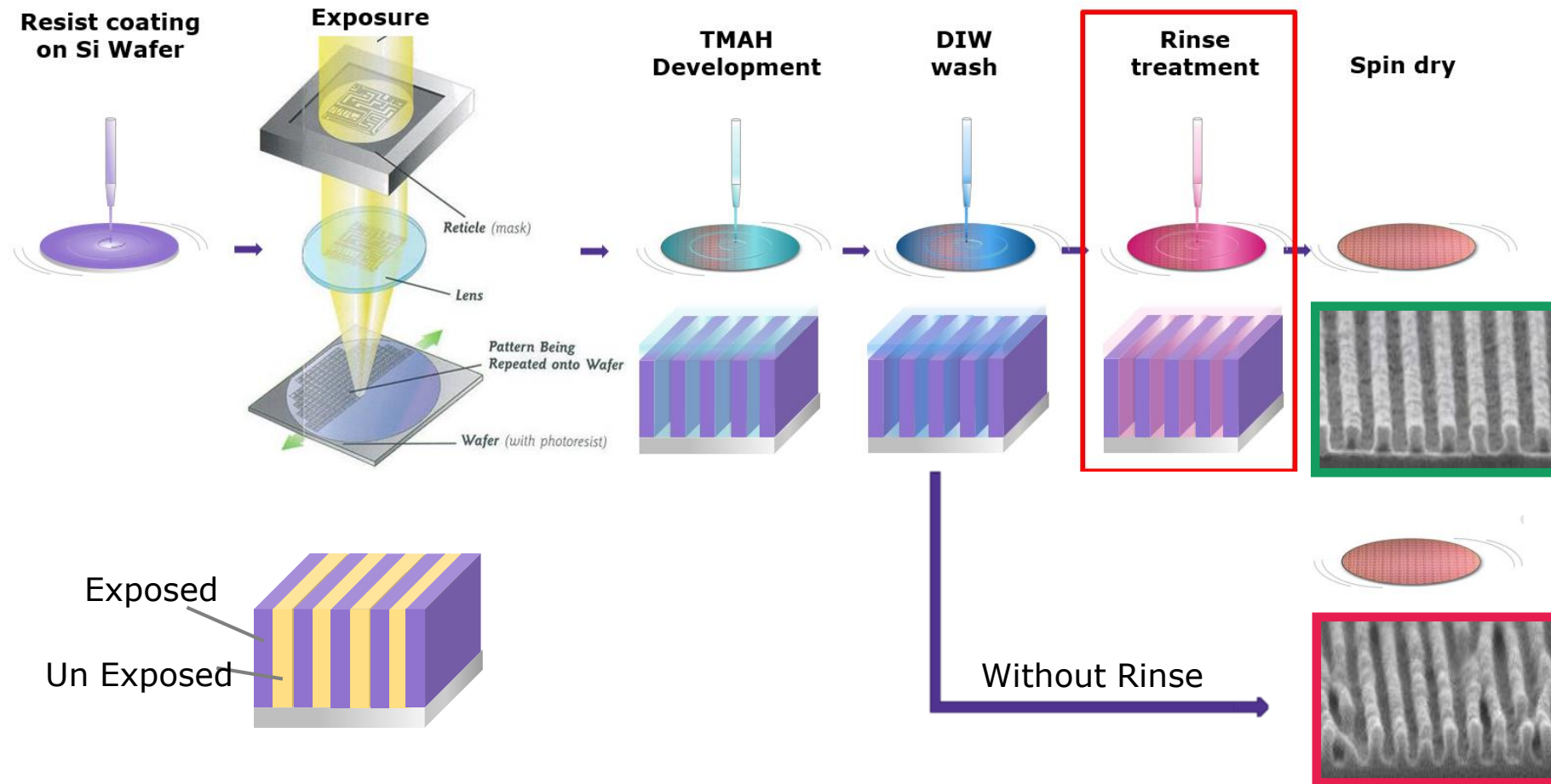
**FIRM chemistry**





# Rinse materials

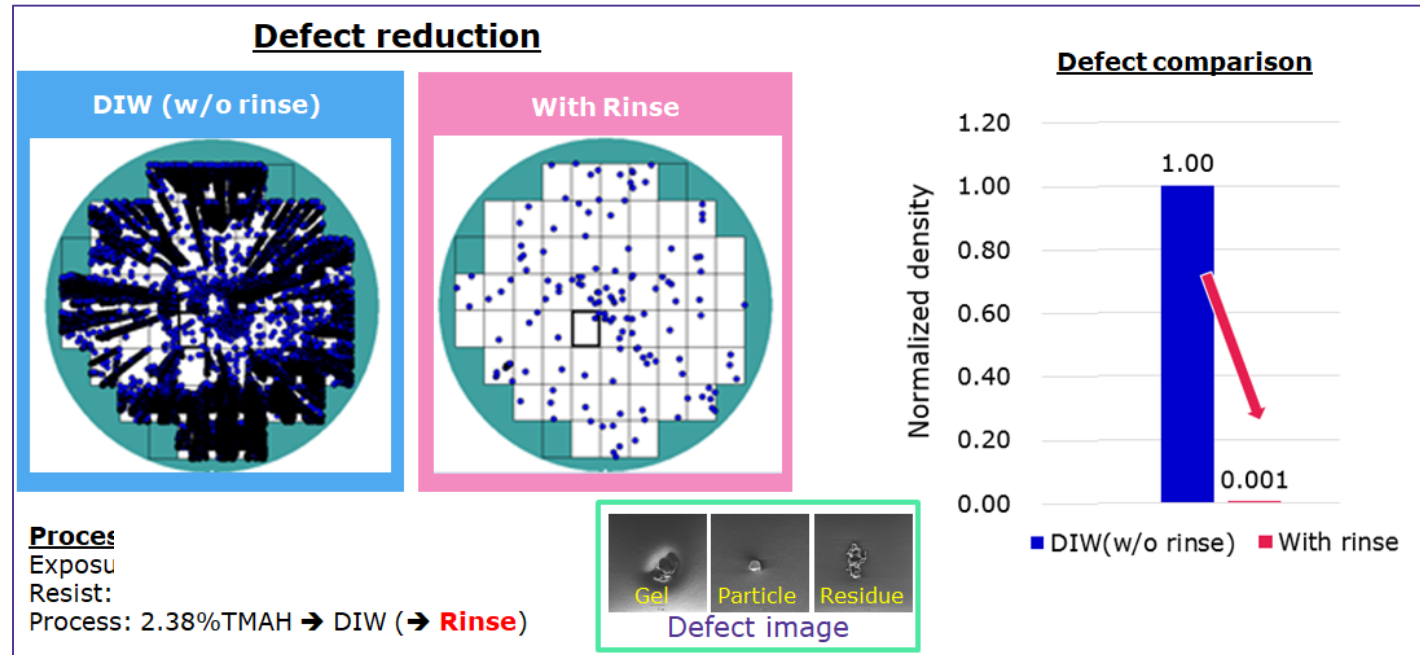
## The process and benefits



**Fully integrated in resist development**

# Rinse materials

## The process and benefits

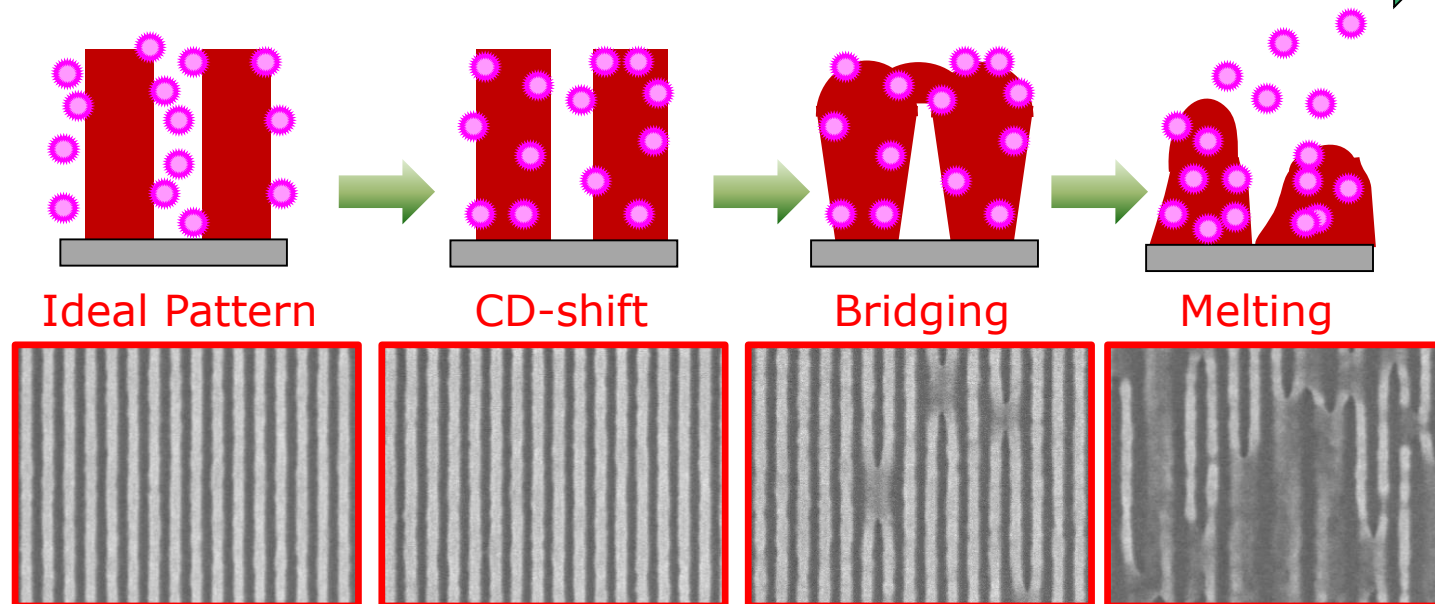


## Key Benefits

- ✓ Straightforward process
- ✓ Pattern collapse mitigation
- ✓ Defect reduction

# Rinse materials

## Material design



### Considerations

- Resist chemistry
- Loading of surfactants
- Bulkiness of surfactants
- Melting control
- Functionality

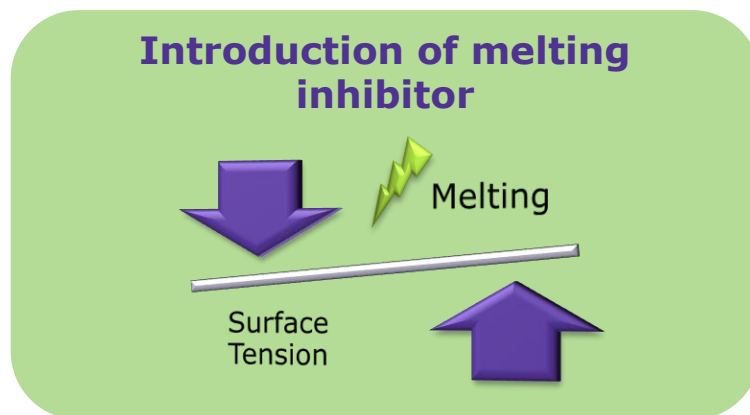
\*The affinity is defined by solubility parameter.

**Surfactant penetration is one of the key factors for resist compatibility**

# Rinse materials – ArF

## Commercial products

Product Name	SPC-116A	SPC-124A	SPC-402
*Surface tension (mN/m)	33.3	37.5	33.4
Chemical	Nonionic	Nonionic	Nonionic + Additive
Application	ArF-d	KrF & ArF-d (ArF-i)	ArF-i



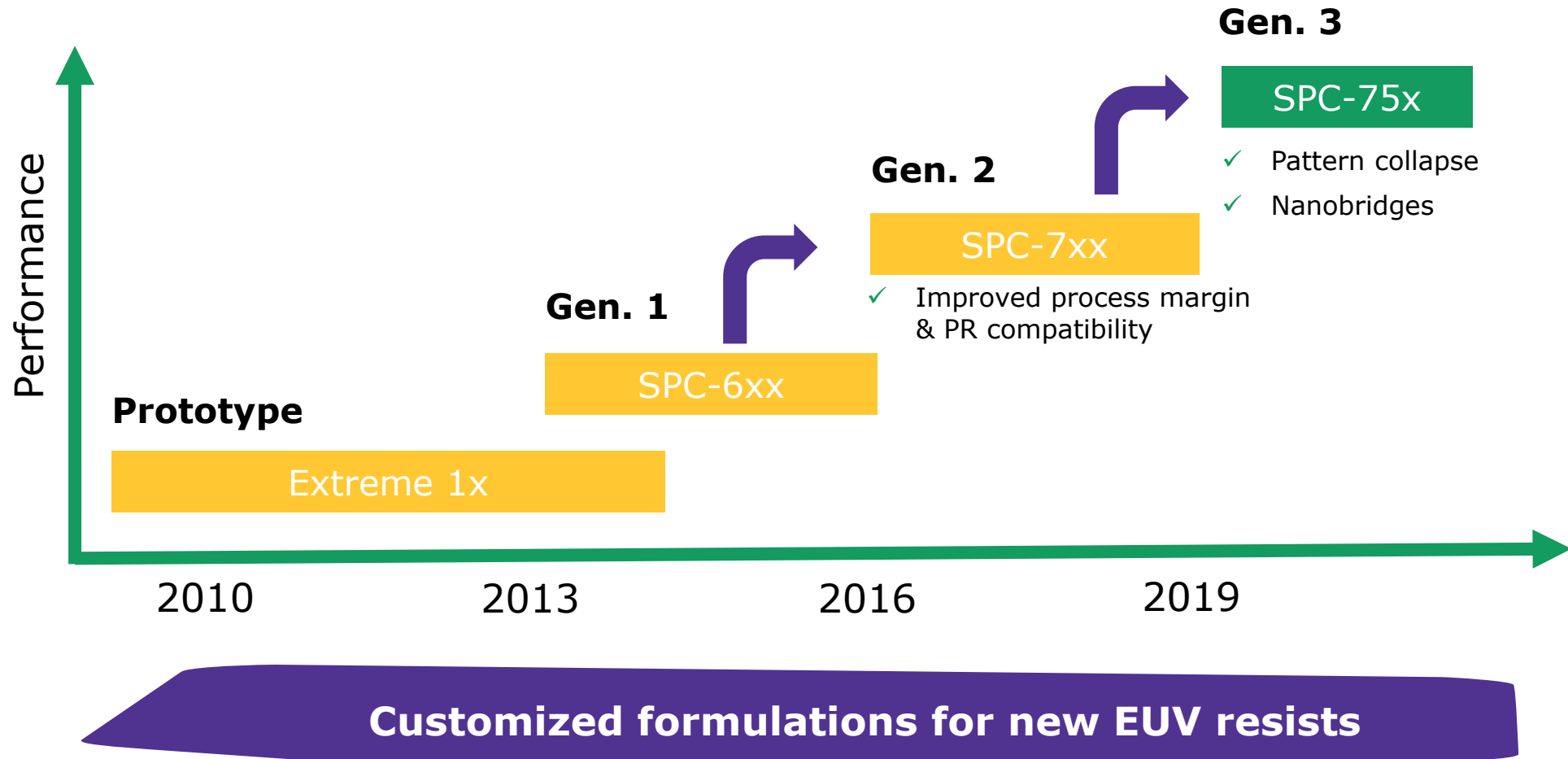
- Broadly adopted in the industry.
- Proven resist compatibility.

	W/O FIRM	SPC-124A	SPC-402
ArF-i ADI	32.8nm	35.3nm	31.2nm
FIRM dispense for 10s			
HB 130C60s	31.9nm	melting	30.3nm



# Rinse materials

## EUV Rinse – development roadmap

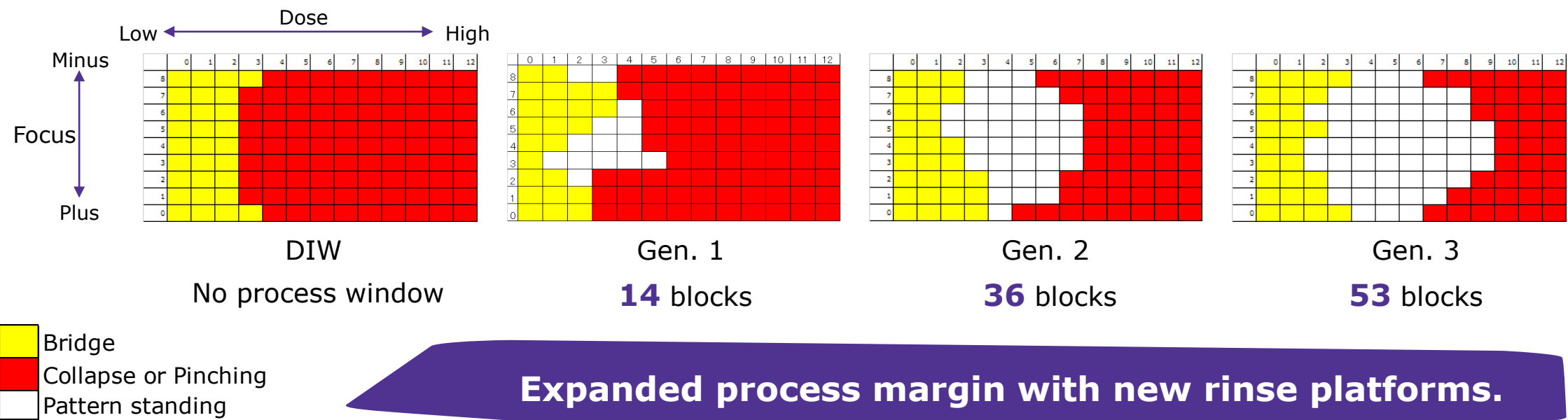


# Rinse materials

## Lithographic performance on EUV Resist B

**Process conditions**  
Exposure tool: NXE3300 (0.33NA, Dipole)  
EUV Resist B/ 45nm thick (**16nm L/S**)  
Dose: 41 mJ/cm<sup>2</sup> center / 1.5mJ/cm<sup>2</sup> step  
Focus: 0.02um center / 0.02um step

	DIW	Gen. 2	Gen. 3
Minimum CD (nm) (Pattern collapse margin)	N/A	15.5	14.5



# Rinse materials

## Lithographic performance on EUV Resist C

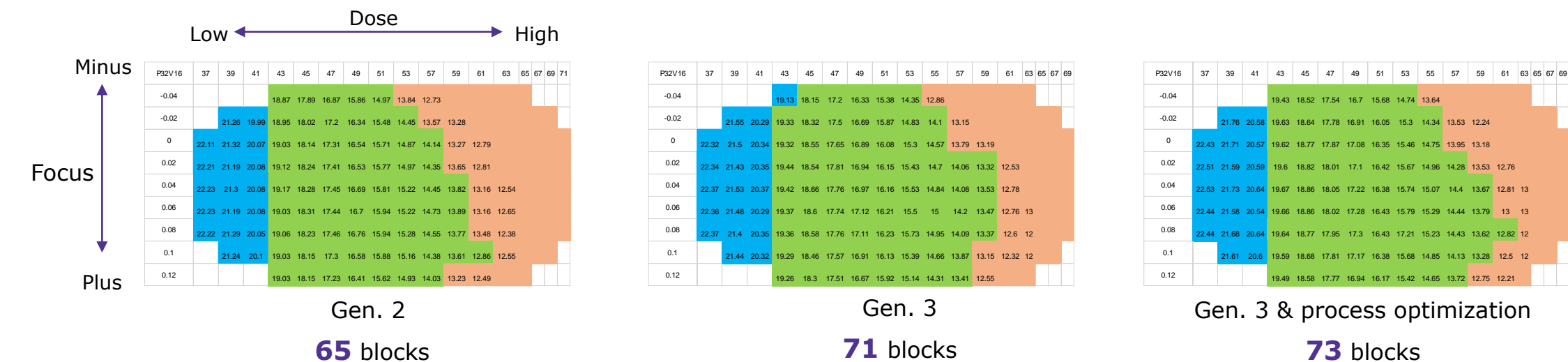
### Process conditions

Exposure tool: NXE3300 (0.33NA, Dipole)

EUV Resist C / 35nm thick (**16/nm hp**)

Dose: 53 mJ/cm<sup>2</sup> center / 2.0mJ/cm<sup>2</sup> step

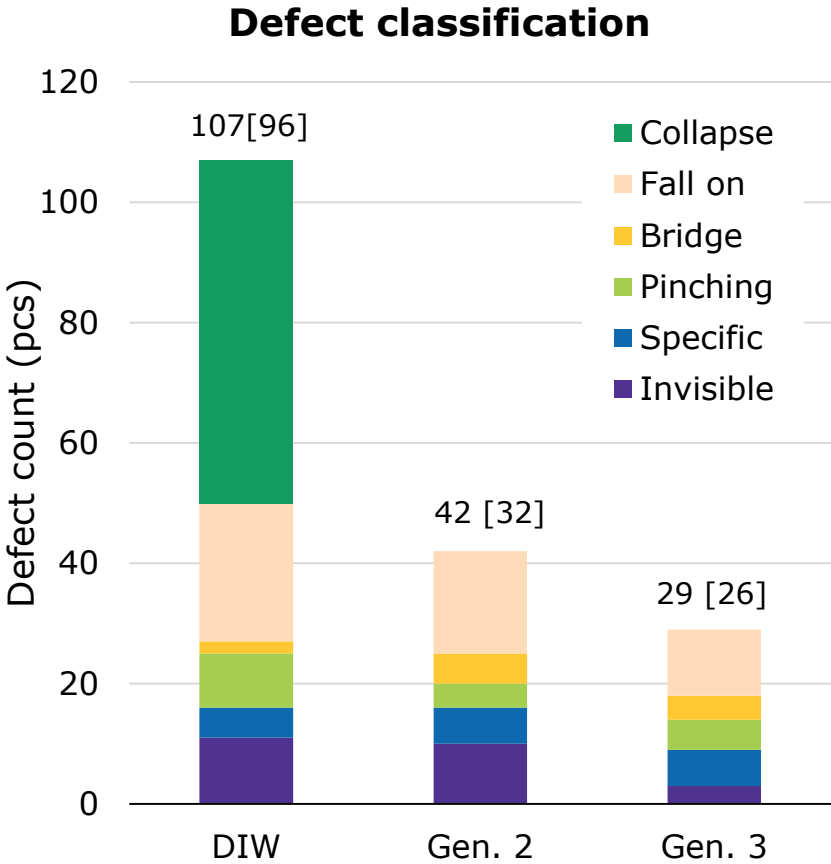
Focus: 0.04um center / 0.02um step



Process window is improved by both material design and process optimization.

# Rinse materials

## EUV rinse – defectivity



\*[]: Defect count excluding invisible

**Process conditions**

Exposure tool: NXE3300 (0.33NA, Dipole)

EUV resist / 35nm thick (**18nm L/S**)

Dose / Focus: 40.5 mJ/cm<sup>2</sup> / -0.05um

Inspection area (Exposed area): 161.2cm<sup>2</sup>

	DIW	Gen. 2	Gen. 3
Defect map			
Defect Density (pcs/cm2)	0.66	0.26	0.18

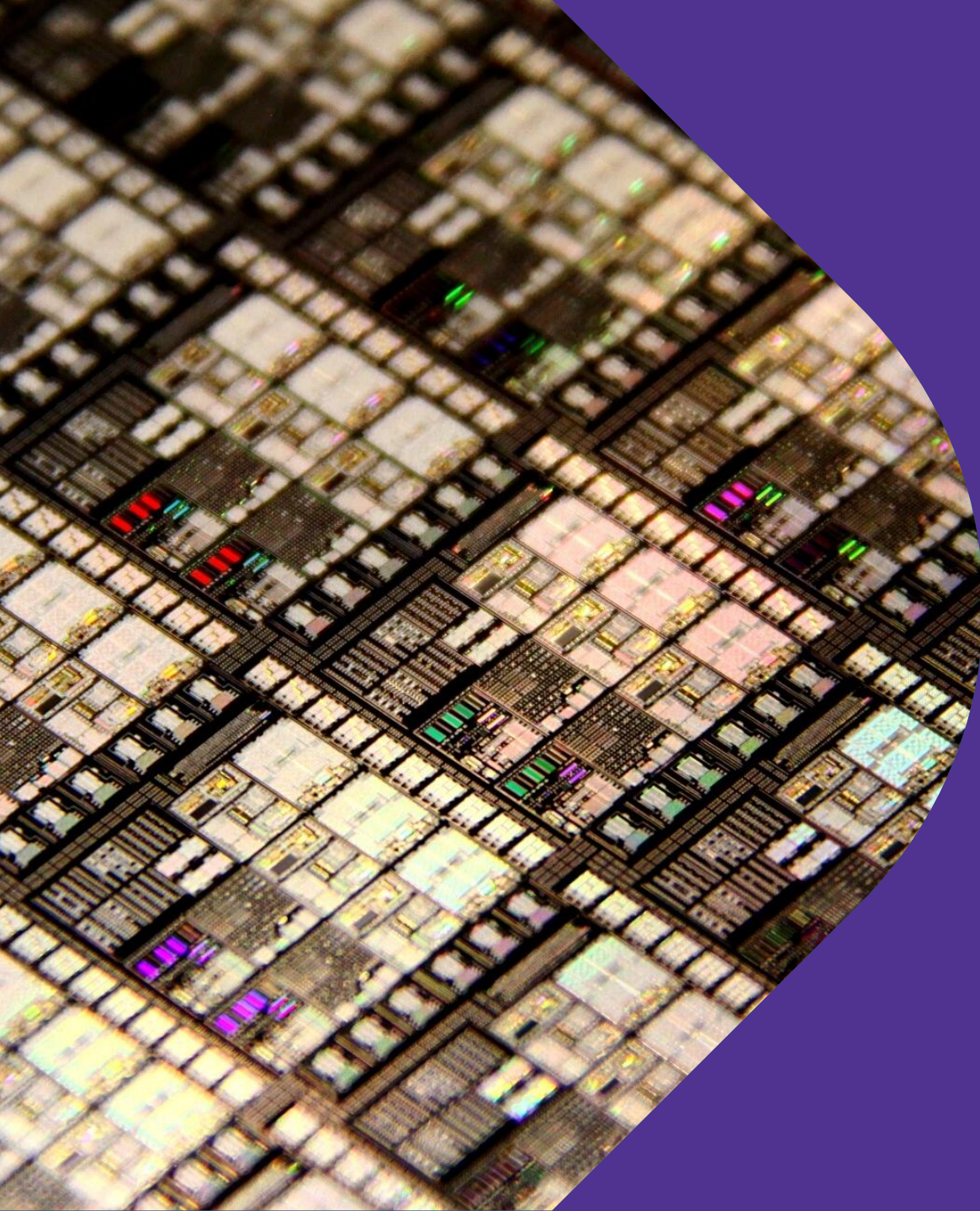
	Collapse	Fall on	Bridge	Pinching	Specific
Defect type					

- ✓ Pattern collapse dominates in regular process.
- ✓ Rinse process is effective in eliminating defects.
- ✓ Pinching defects are reduced with rinse process.



# SUMMARY

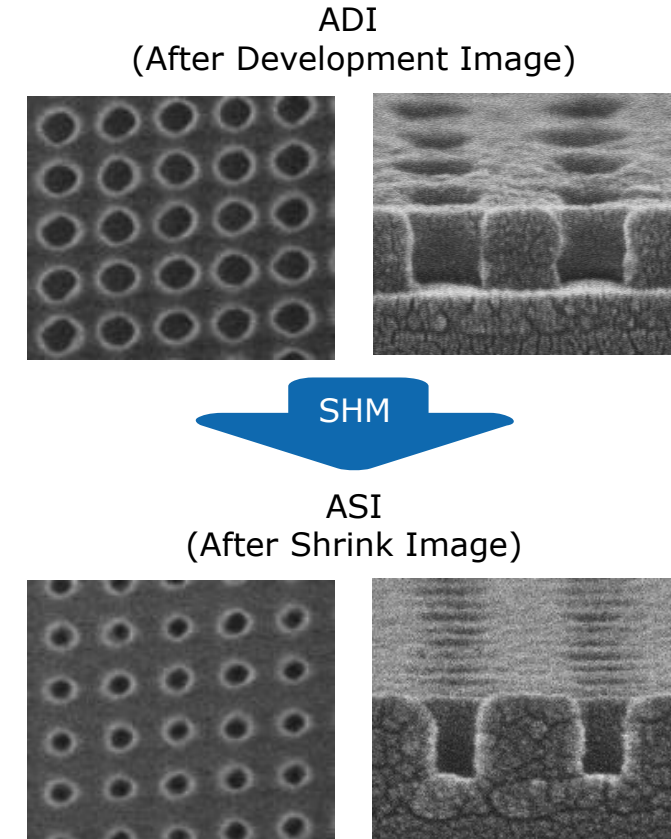
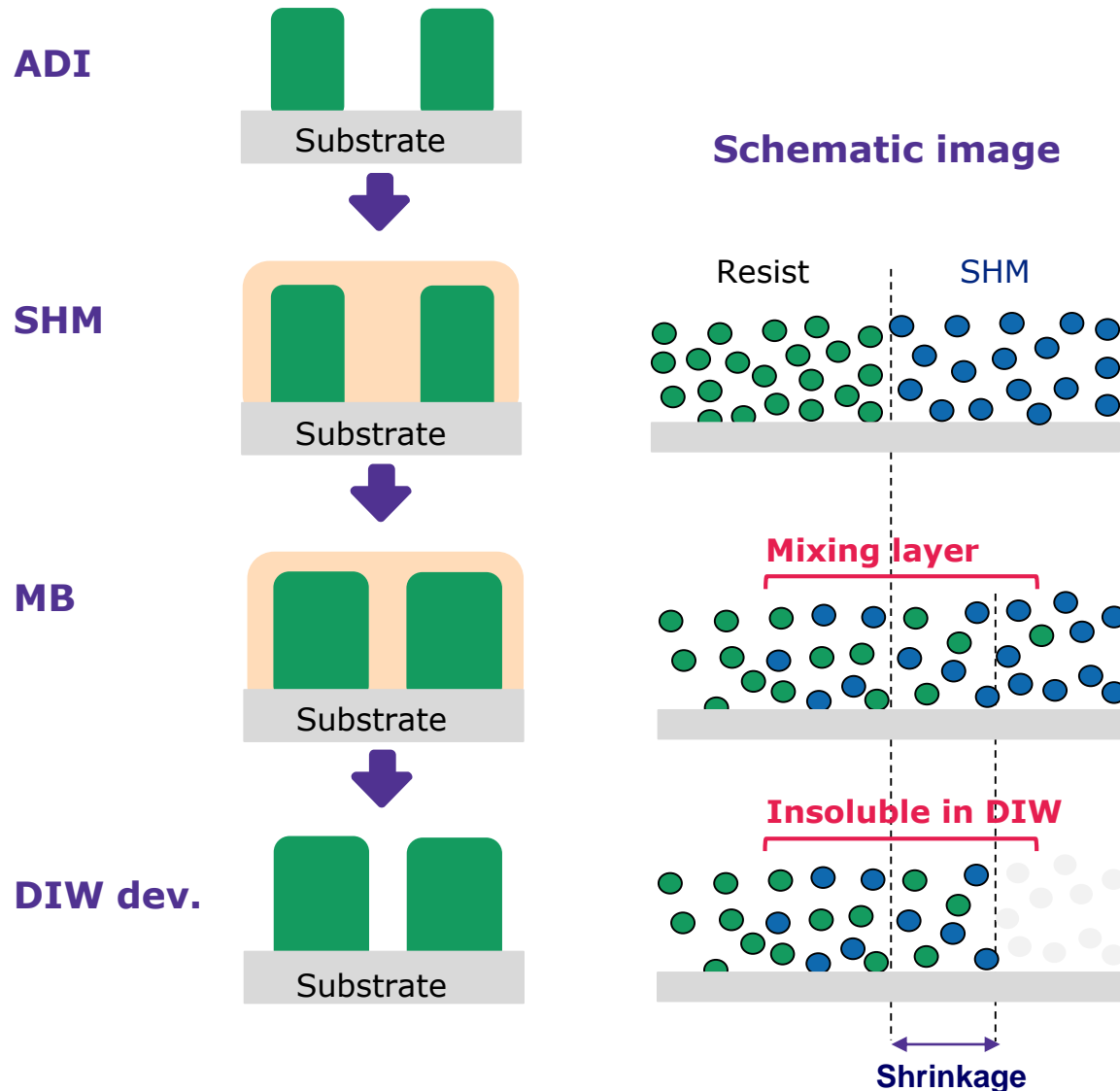
- **Rinse materials** offer benefits of pattern collapse mitigation and defect improvement, therefore, superior process margins for yield improvement.
- Merck offers rinse materials for both ArF and EUV lithography processes.
- Rinse process has been implemented in volume production of the first generation of EUV lithography.
- 16nm half pitch is resolved with rinse process with sufficient pattern collapse margin.
- Defectivity is significantly improved with EUV rinse.
- Collaborating with TEL, Merck offers not only innovative materials but also expertise in process optimization.



# 03 chemical shrink materials

# Shrink materials

## The process & mechanism



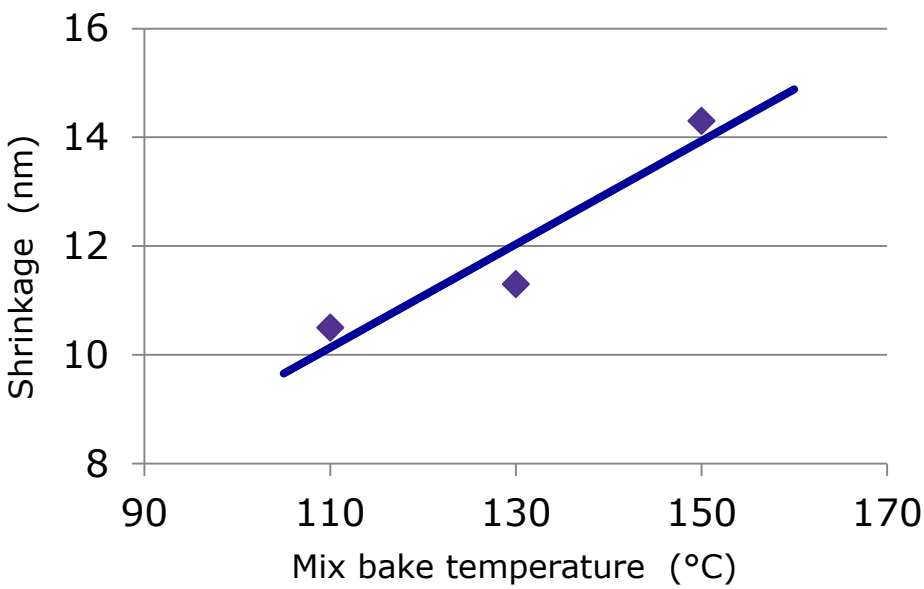
- Constant shrinkage through pitch
- Whole track compatible process
- In-process tunable shrinkage
- Reduced **C**ost **o**f **O**wnership

# Shrink materials

## Shrinkage controllability

### Shrink Process

Film thickness: 100nm  
Mixing Bake: 110, 130, 150°C/ 60sec  
Development: DI-Water



	ADI
Top Image	
CD (nm)	65.5

	110°C/60s	130°C/60s	150°C/60s
Top Image			
CD (nm)	<u>55.0</u>	<u>54.2</u>	<u>51.2</u>
Shrinkage (nm)	10.5	<b>11.3</b>	<b>14.3</b>

Shrink amount is tunable with mixing bake temperature.

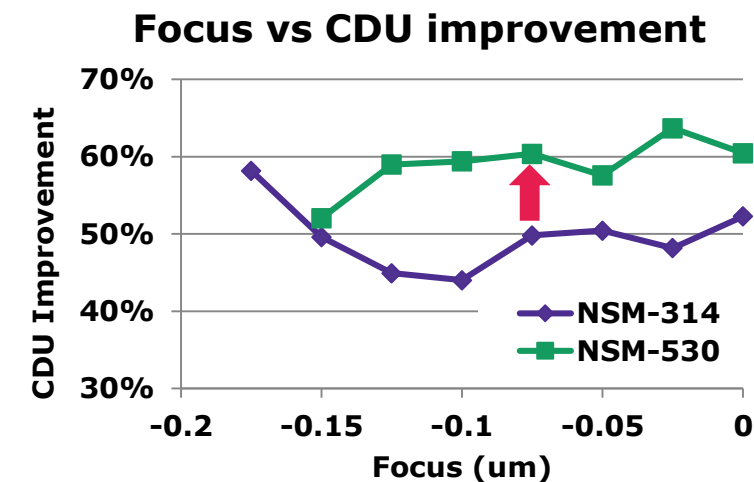
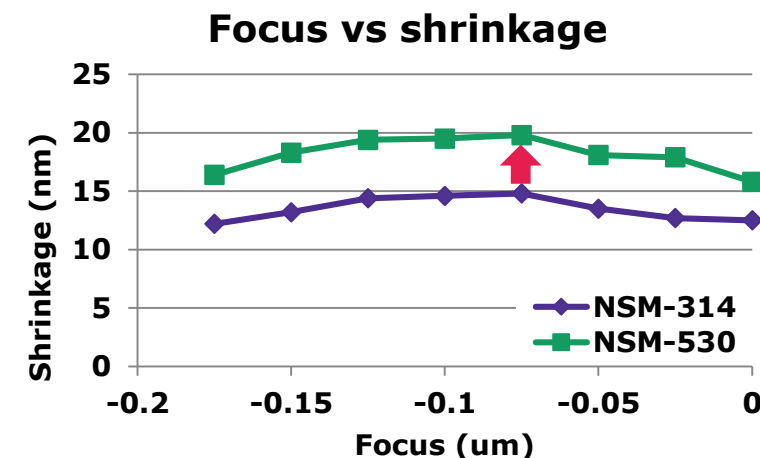


# Shrink materials

## Local CD uniformity

Grid hole: 110nm pitch

Focus	-0.175 $\mu\text{m}$	-0.150 $\mu\text{m}$	-0.125 $\mu\text{m}$	-0.100 $\mu\text{m}$	-0.075 $\mu\text{m}$	-0.050 $\mu\text{m}$	-0.025 $\mu\text{m}$	0.000 $\mu\text{m}$
Control (ADI)								
StDev CD	2.51	2.46	2.56	2.34	2.65	2.38	2.45	2.2
	46.24	48.61	50.35	50.55	50.69	48.56	47.98	46.01
NSM-314 Shrink-D								
StDev CD	1.05	1.24	1.41	1.31	1.33	1.18	1.27	1.05
	34.02	35.46	35.97	35.94	35.91	35.08	35.27	33.56
Shrinkage	12.2 nm	13.2 nm	14.4 nm	14.6 nm	14.8 nm	13.5 nm	12.7 nm	12.5 nm
NSM-530 Shrink-D								
StDev CD	1.32	1.18	1.05	0.95	1.05	1.01	0.89	0.87
	29.88	30.28	30.96	31.06	30.93	30.51	30.13	30.23
Shrinkage	16.4 nm	18.3 nm	19.4 nm	19.5 nm	19.8 nm	18.1 nm	17.9 nm	15.8 nm



**Local CD Uniformity is improved by >50%.**

# Shrink materials

## Proximity effects

### Test Conditions

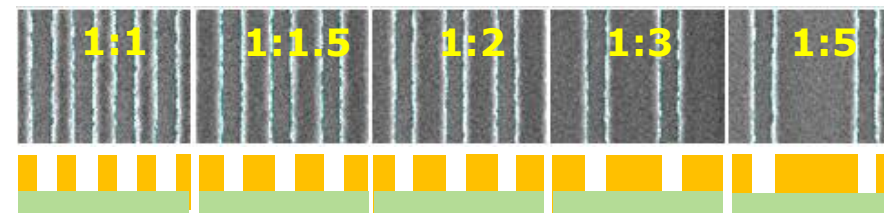
NTD resist

Shrink Materials: NSM-314, 530

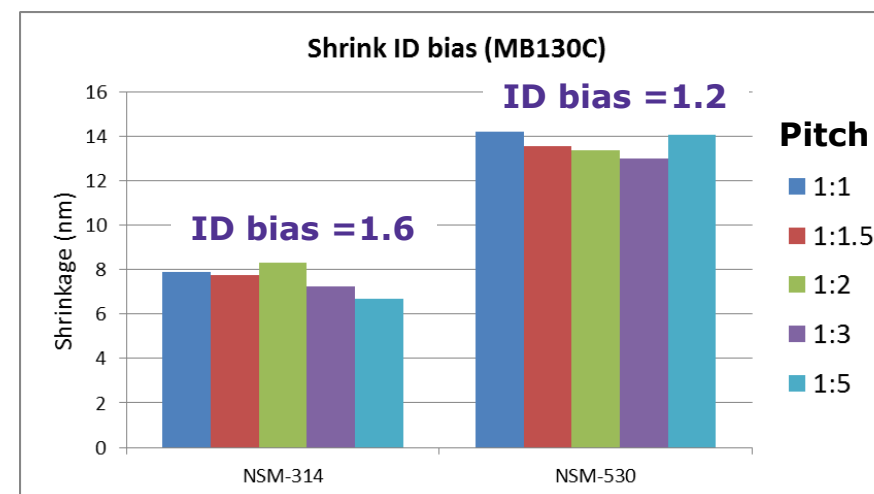
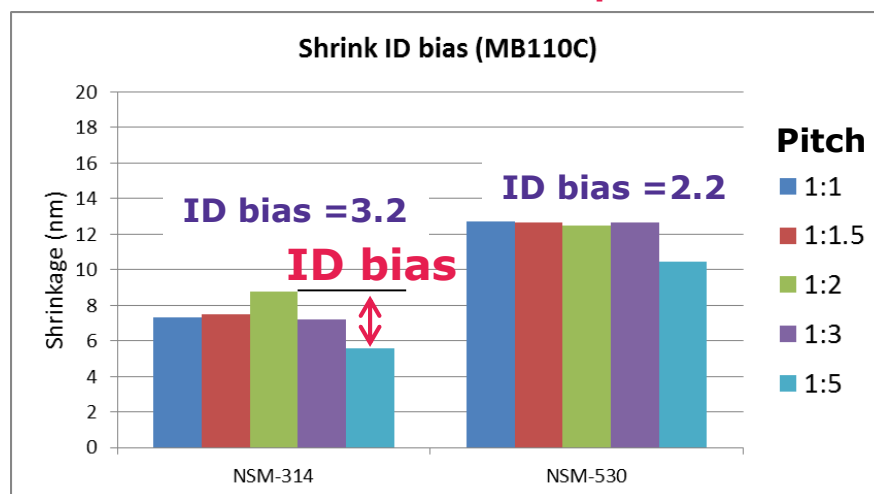
Mixing Bake: 110, 130°C / 60sec

Development: DI-Water

### Resist Pattern Pitch



**\*ID bias = Isolated and dense pattern bias**



**Significantly higher shrinkage and lower iso-dense bias are achieved with NSM-530.**

# Shrink materials

## Resist compatibility

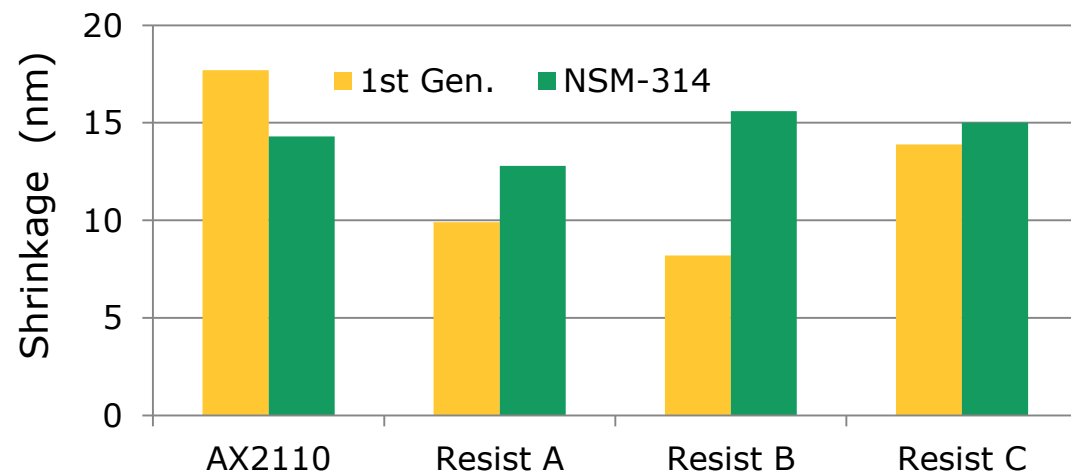
### Test conditions

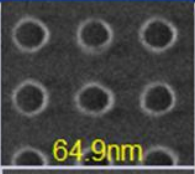
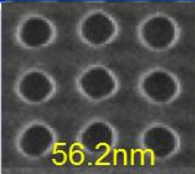
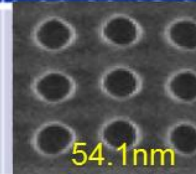
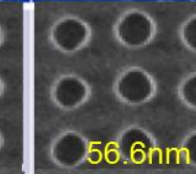
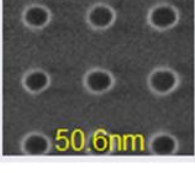
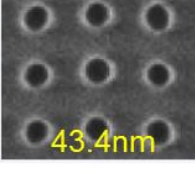
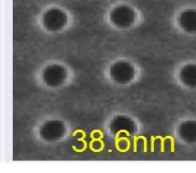
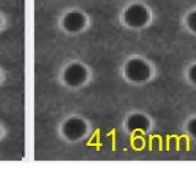
NTD resists from multiple suppliers

Shrink: 1<sup>st</sup> Gen shrink material and NSM-314

Mixing Bake: 150°C/60sec

Development: DIW



	AZ AX2110	Resist A	Resist B	Resist C
ADI				
NSM-314				

**Good compatibility with various resists.**



## 04 summary



# SUMMARY

- Merck is specialized in **aqueous materials** to enhance photoresist performance.
- **Rinse process** has been proven effective in mitigating pattern collapse, improving process margin, and depressing defectivity in multiple generations of lithography.
- **Chemical shrink** is a viable technology assisting pattern scaling with:
  - ✓ Cost-effective process enhancing resolution
  - ✓ Improvement of DOF & local CD uniformity with shrinkage tunable by process
  - ✓ Reduced proximity effects

