IRRESISTIBLE MATERIALS

Multi-Trigger Resist

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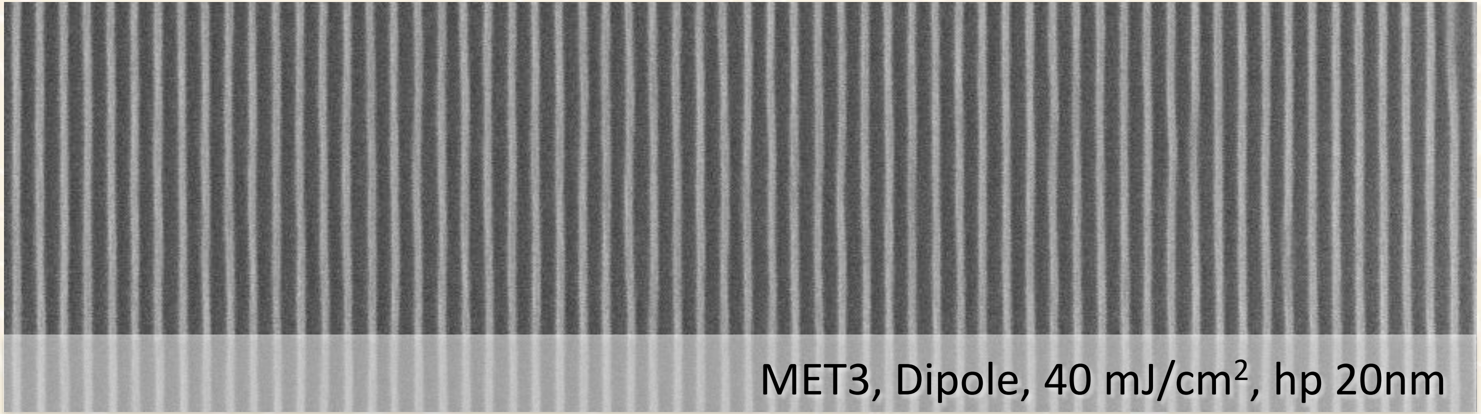


UNIVERSITY OF BIRMINGHAM

nano-c nanostructured carbon

imec

Objectives

In order to enable N5/N3 and beyond, we must address both materials and photon stochastics. Our strategy is shown below:

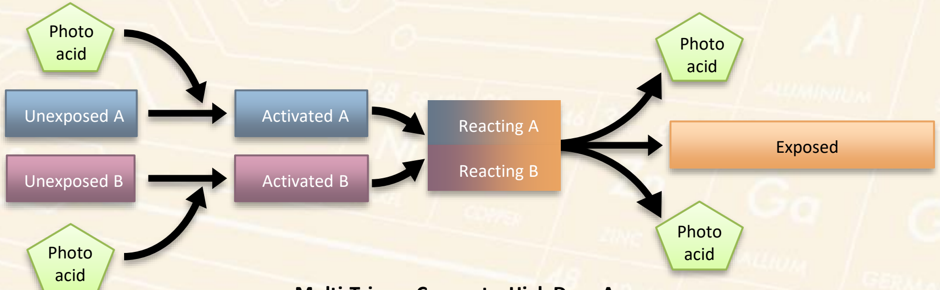
Materials Stochastics

We are addressing material stochastics through reduction in the number of resist components, as the multi-trigger effect should allow the elimination of quencher.

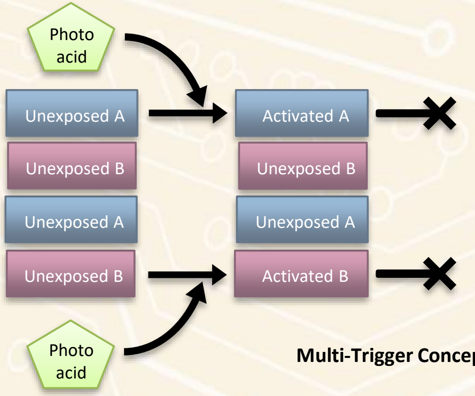
Photon Stochastics

We are addressing photon stochastics via the increase of opacity, and via the introduction of the multi-trigger effect, which suppresses the photon shot noise/increases edge contrast via an inherent dose dependent quenching.

Multi Trigger Mk 1



Multi-Trigger Concept – High Dose Area



The activated molecules are next to unexposed molecules – photoacids quenched and reaction stops (unless one of the intervening molecules is subsequently activated

Multi-Trigger Concept – Low Dose Area

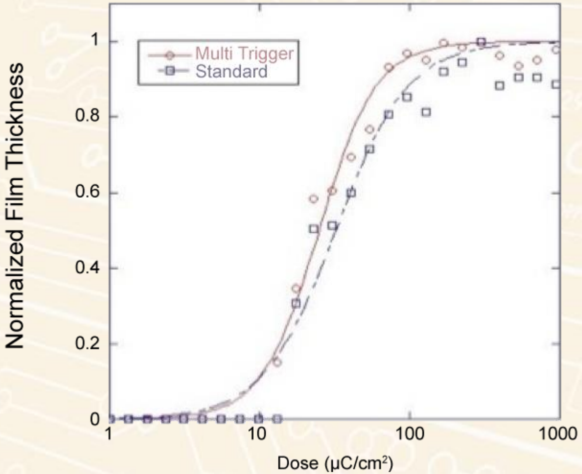
MULTI-TRIGGER MECHANISM

1. Photons produce Initiators (e.g. PAG acid)
2. Initiators activate resist molecules
   - 3a. If two activated molecules are adjacent they react (resist exposure)
     AND
     Both initiators are released
   - 3b. If an activated molecule is not close to a second activated molecule the initiator remains bound and there is no exposure event.

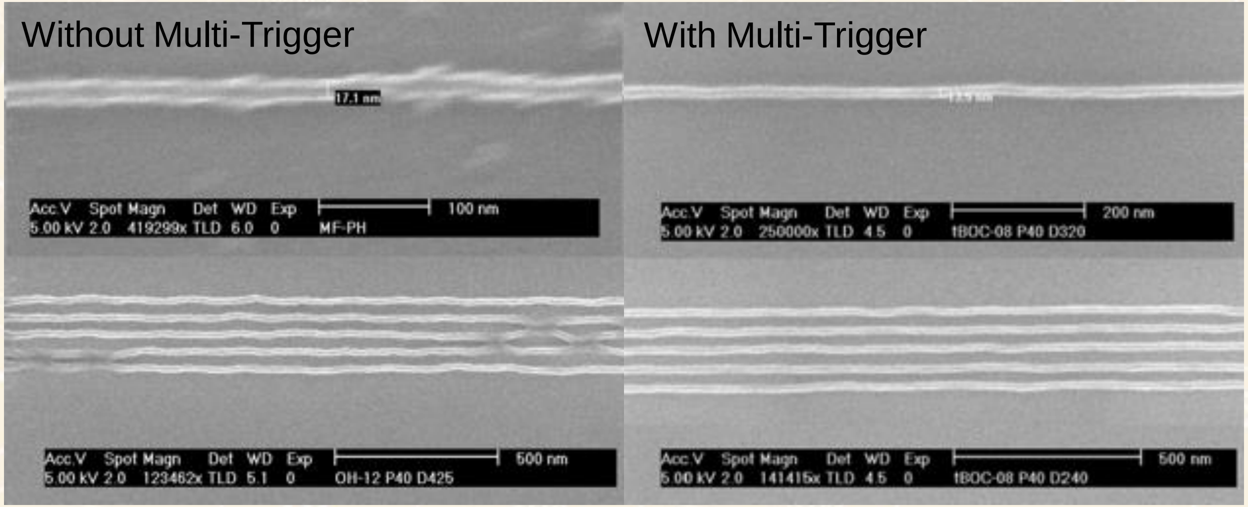
Self limiting reaction - **Gives better edge definition**

The strength of the quenching effect can be varied by modifying the ratio of the two components

Evidence for a Multi-Trigger Effect



	Standard	Multi-Trigger
Sensitivity (μC/cm2)	32	25
Contrast	1.0	1.3



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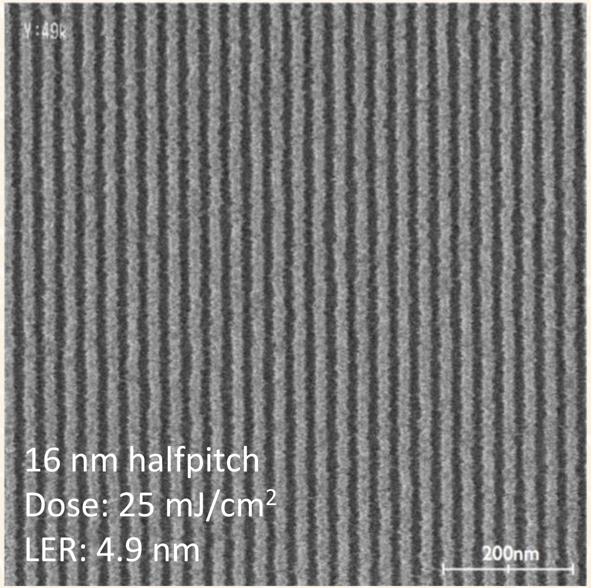
Demonstration of the Multi-Trigger Quenching Effect

The self-quenching concept has been demonstrated in NXE3300 at imec

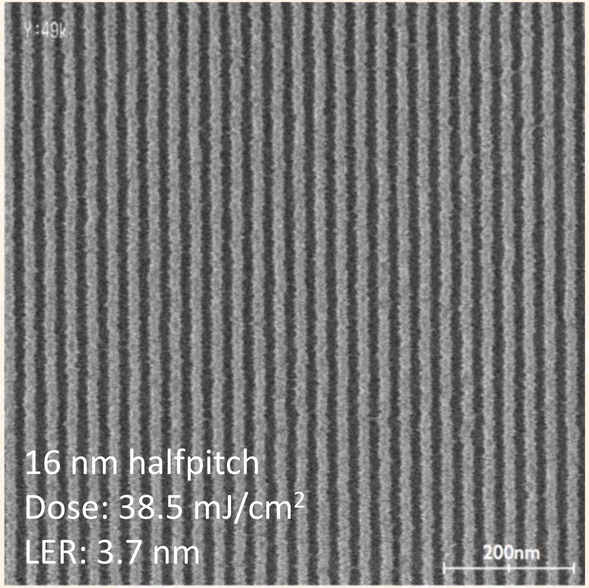
MTR2200

Formulated for weak MTR effect



MTR2204

Formulated for strong MTR effect

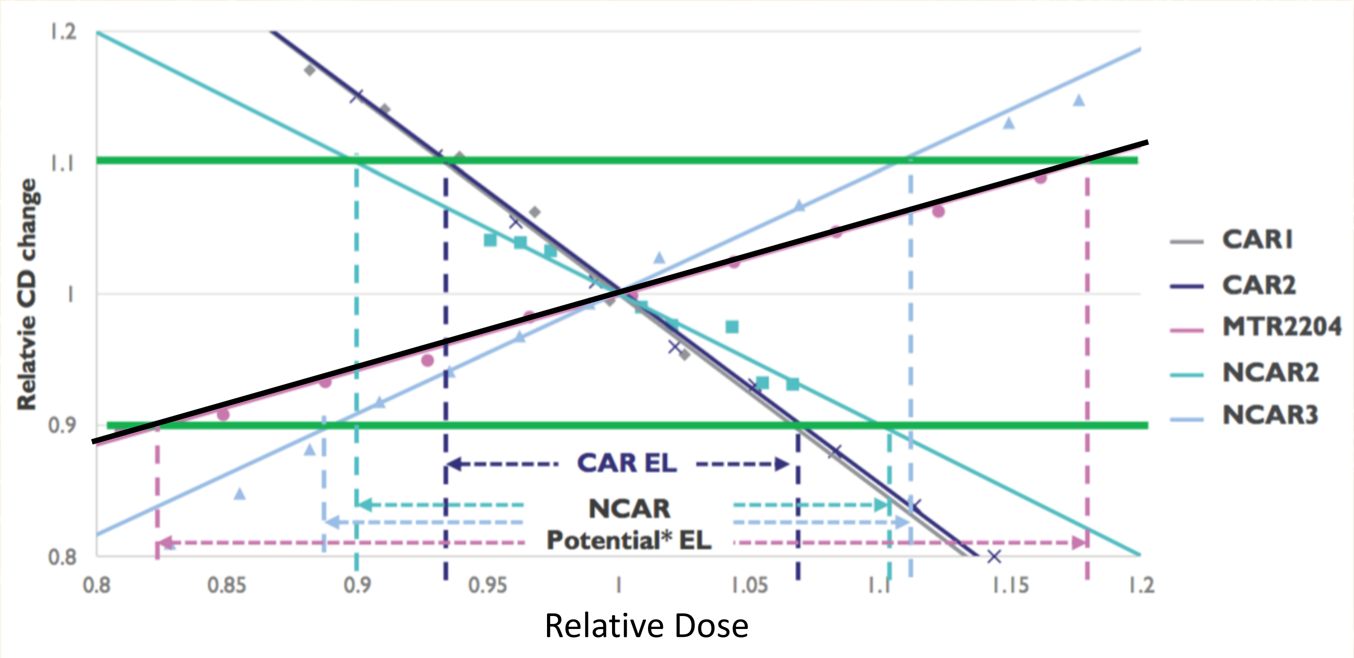


25nm FT

The MTR system is ultimately designed to enable the whole film to act as a dose dependent quenching system – eliminating quencher stochastics

imec results
Unbiased LER values

Evidence for a Multi-Trigger Effect



MEEF values of 1.0 – 1.1 reported

Proposed Multi Trigger Mechanism

Molecule A

Molecule A has a protected crosslinkable functional group

- Can not crosslink when protected
- If protonated will deprotect (and regenerate proton) in presence of a nucleophile

Molecule B

Molecule B has proton activated crosslinking functional group

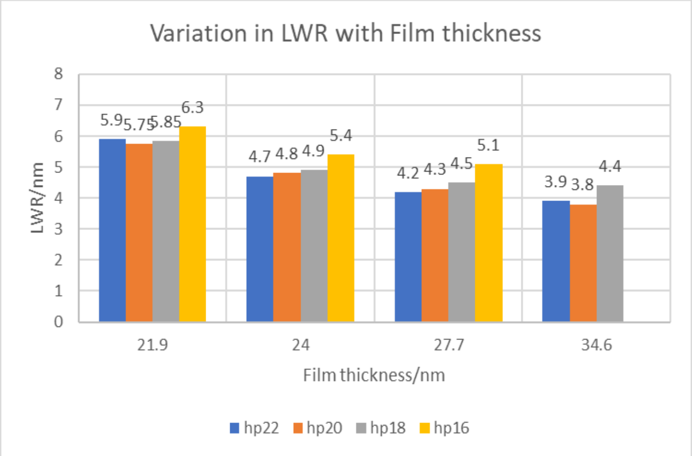
- Can self-crosslink, or crosslink with deprotected molecule A (regenerating two protons in second case)
- Electrophilic. Becomes nucleophilic if protonated.

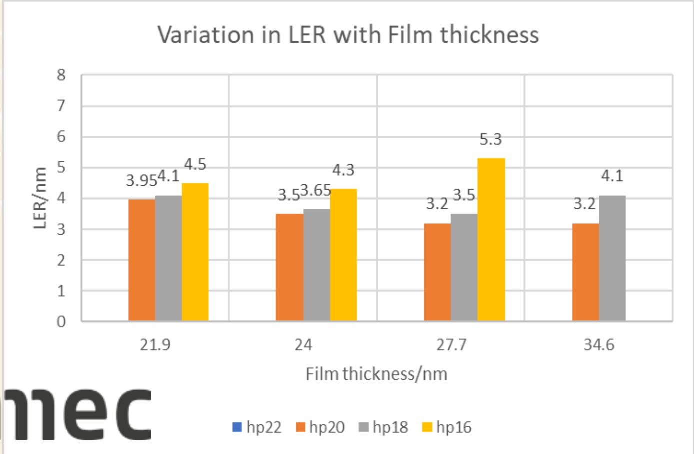
Unexposed B

Molecule B will self crosslink to any adjacent molecule B. However the crosslinking will stall if a molecule A is adjacent – unless molecule A is protonated. By varying the ratio of A to B the MTR effect can be modulated.

Recent MTR 2204 Results

MTR2204: film thickness roughness dependence





Best LWR:

- 34nm film thickness for all HP

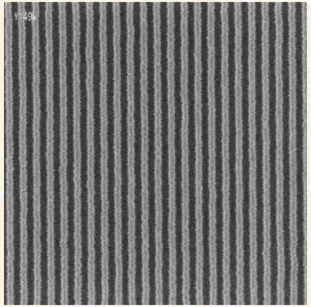
But:

- at 34nm FT, pattern collapse occurs for 16nm HP and 18nm HP.

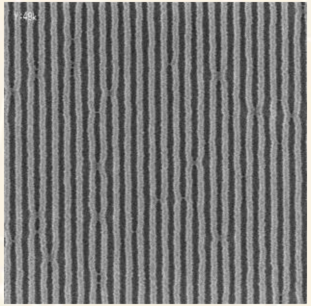
Best LER using:

- 24nm FT for 16nm HP
- 28nm FT for 18nm HP
- 34nm FT for 20nm HP

34nm FT



20nm hp



18nm hp, pattern collapse

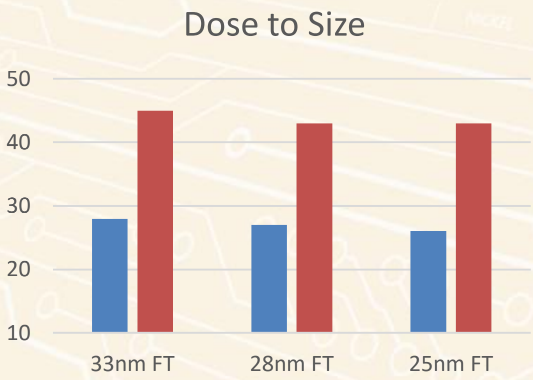
Demonstration of the Multi-Trigger Quenching Effect

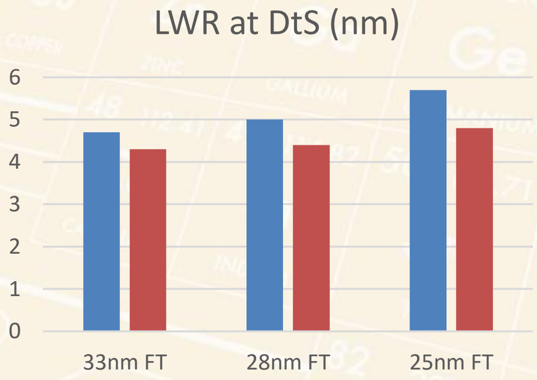
MTR2200
Formulated for weak MTR effect

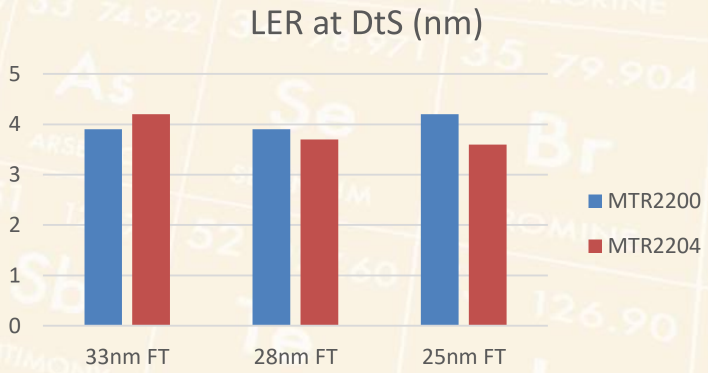
MTR2204
Formulated for strong MTR effect

Pitch 36nm

No PEB







Better LWR for MTR2204 for all FT
Benefit of MTR2204 for LWR and LER more pronounced at thinner film thickness
Benefit of MTR2204 for LWR and LER most obvious at pitch 32nm

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Biased LWR and LER values

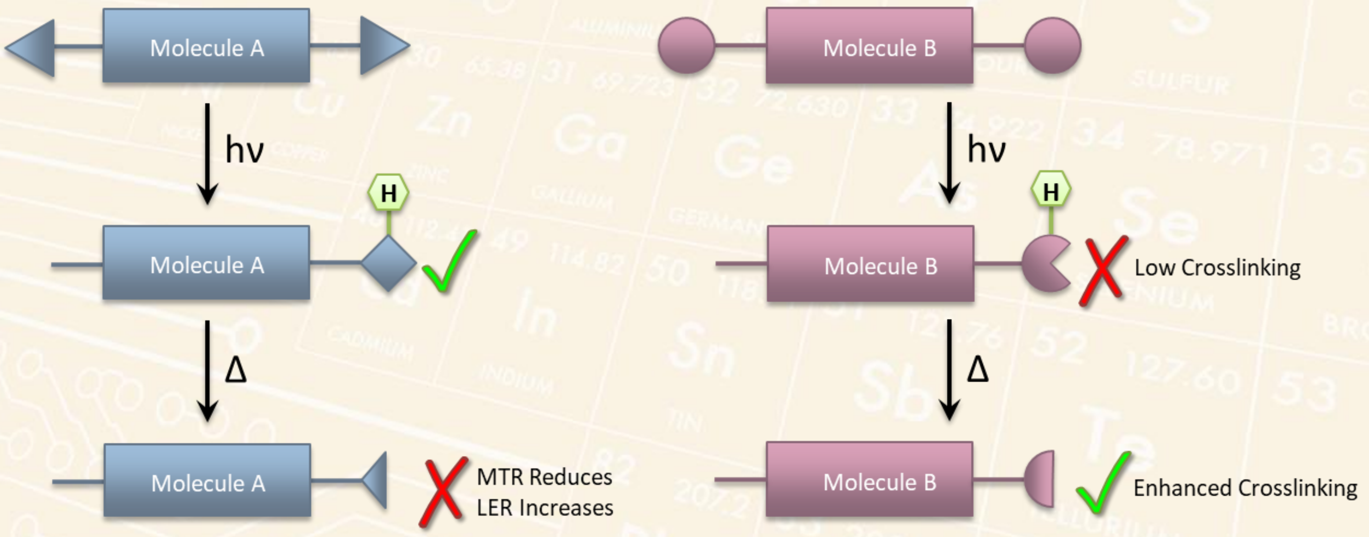
Near Term Materials Developments Status

The current IM resist is a multi-component material that is designed to address poor aerial images, and photon stochastics via the multi-trigger mechanism.

Current work is addressing the following:

1) Enhance thermal stability of the activated state
2) Ancillary Process Optimisation (*not discussed here*)
3) Increase Opacity

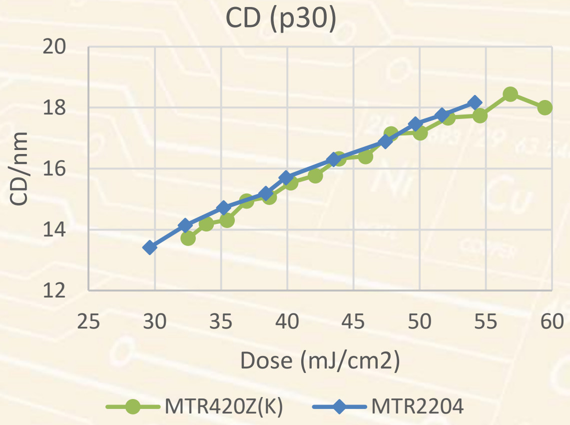
1) Enhance Thermal stability of the activated state

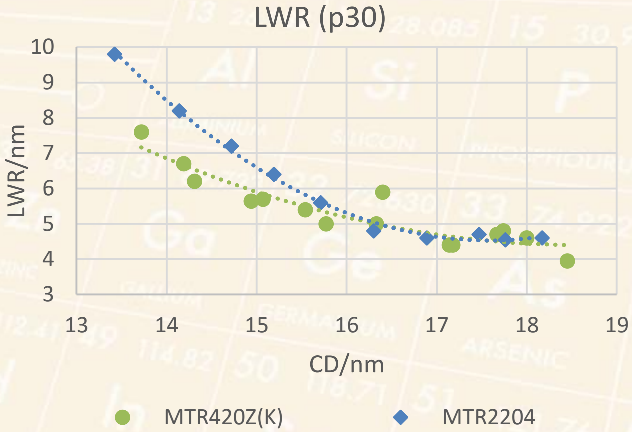


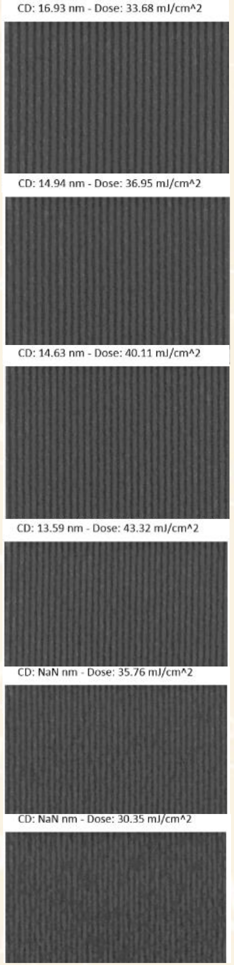
Influence of a post exposure bake on the MTR resist matrix

- By introducing higher energy leaving groups onto molecule A, we believe that we can enhance crosslinking without increasing the LER

MTR4 Higher Thermal Stability Variant







P32
LWR 4.90nm

P30
LWR 5.64nm

P28
LWR 5.40nm

P26
LWR 5.55nm

P24

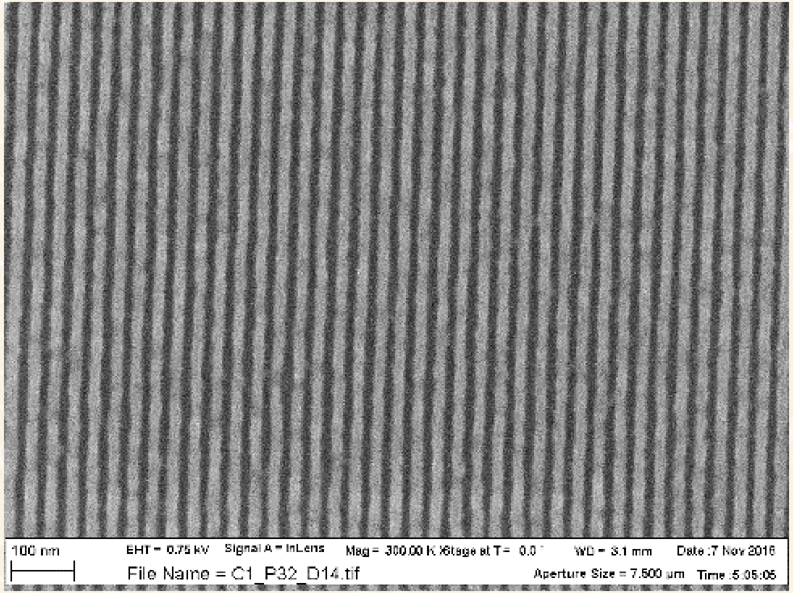
P22

- MTR420Z(K) has same dose and better LWR than MTR2204
- MTR4 with 90C PEB
  - PEB has no impact on dose
  - LWR gets worse by 19% on average
  - Impact on LWR slightly less than standard thermal stability variant (~ 23%)

Exposures undertaken by ASML PAUL SCHERRER INSTITUT PSI

MTR4 Higher Thermal Stability Variant

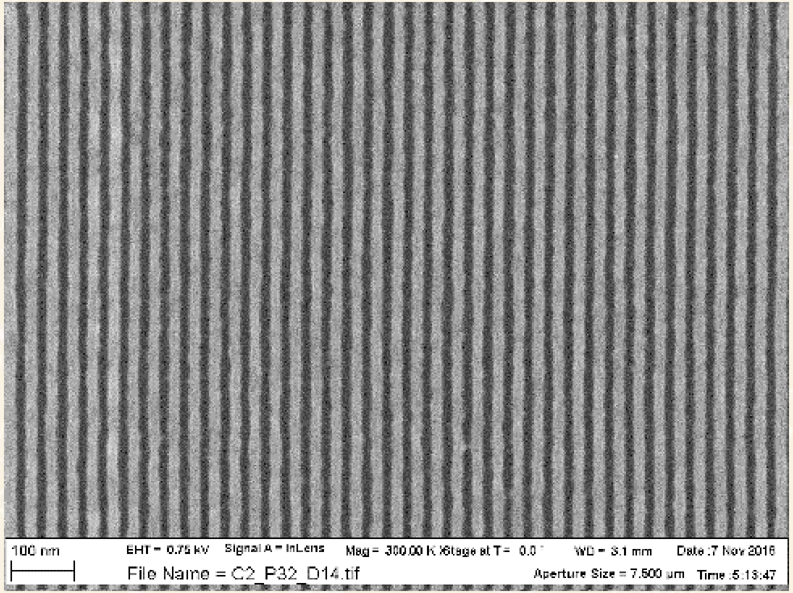
P32



MTR2xxx

49.3mJ/cm^2, CD 16.6nm, LER 3.29nm

P32



MTR4xxx

49.3mJ/cm^2, CD 16.8nm, LER 2.62nm

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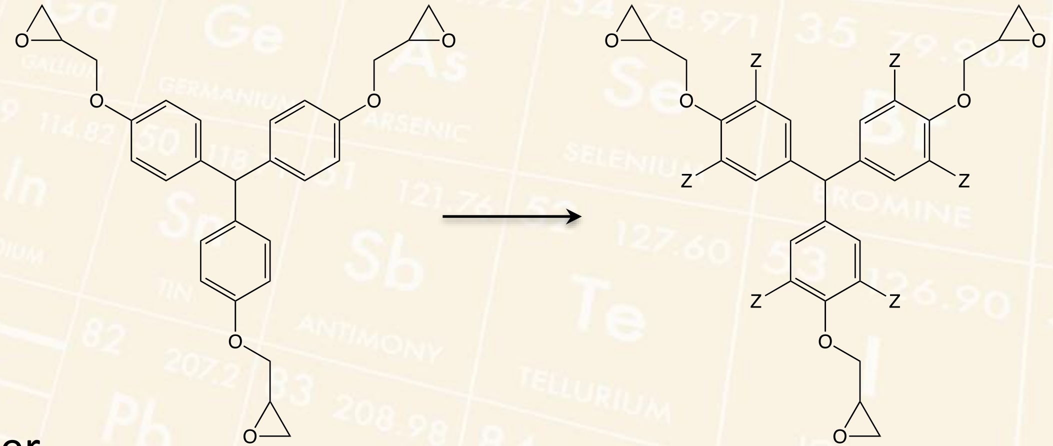
3) Increase Opacity

Increasing the opacity of the resist will reduce the photon stochastics

Strategy is to incorporate non-metal high-Z elements in to the resist:

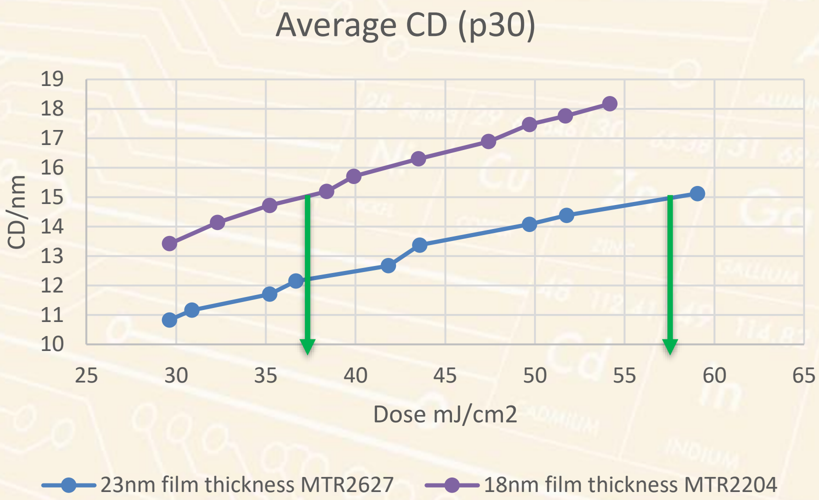


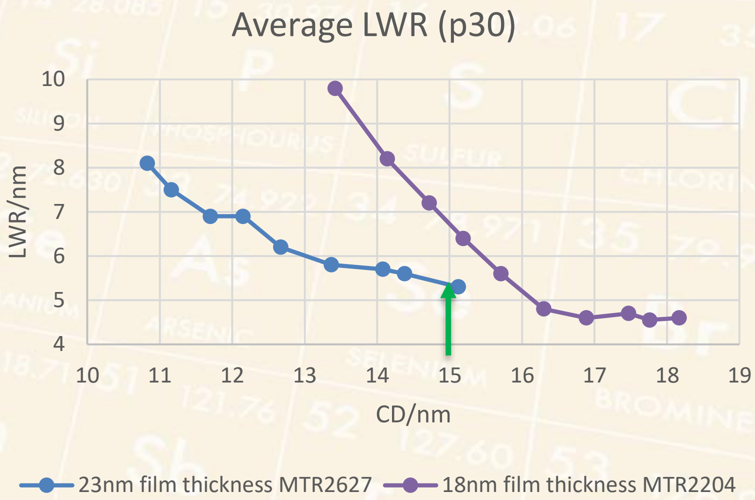
Will also increase the T_g of the crosslinker

Formulation does not include nucleophilic quencher

Exposures undertaken by ASML PAUL SCHERRER INSTITUT PSI

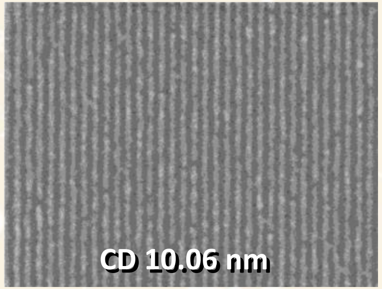
Increase Opacity Resist mk I – Compare to MTR2204





- MTR2627 patterns better at thicker FT without pattern collapse
- Dose is higher than MTR2204
  - 57mJ/cm^2 v 37mJ/cm^2
- LWR at 15nm is lower
  - 5.4nm compared to 6.6nm
- Can see patterns at sub 11nm which is not possible with MTR2204

p24



Increased Opacity Resist mk I – Comparison to MTR2204

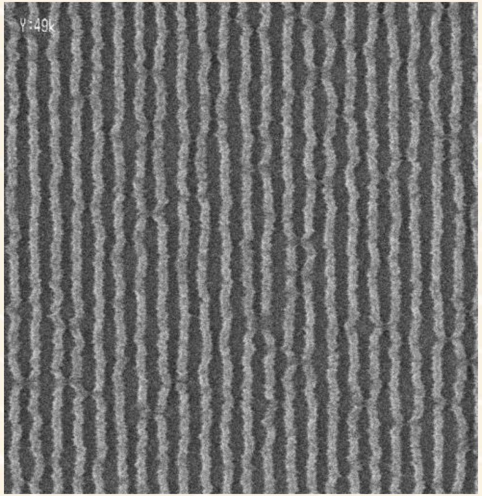
- Used 40nm pitch (20nm hp) and look when underdosed – narrow lines
- Wiggle free line aspect ratio of 2.5 is a significant increase (25%)

Pitch 40nm

No PEB

33-34nm film thickness

MTR2204

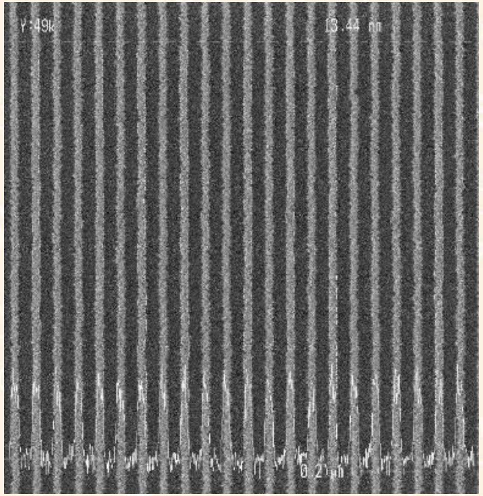


~16.5nm width
29.5mJ/cm^2

Improvement →

Less wiggling
Better resolution

MTR262Z(D)



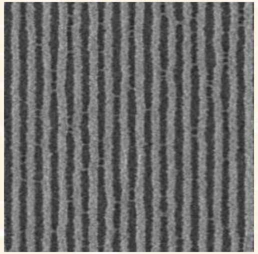
13.4nm width
33mJ/cm^2

Rectangular scans

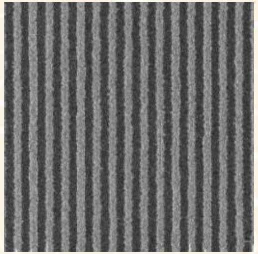
NXE3300 data

High opacity resist mk I: 33nm film thickness

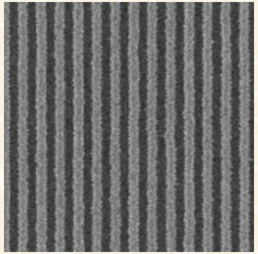
hp16nm
37.5mJ/cm²
CD 15.92nm
LWR 6.22nm

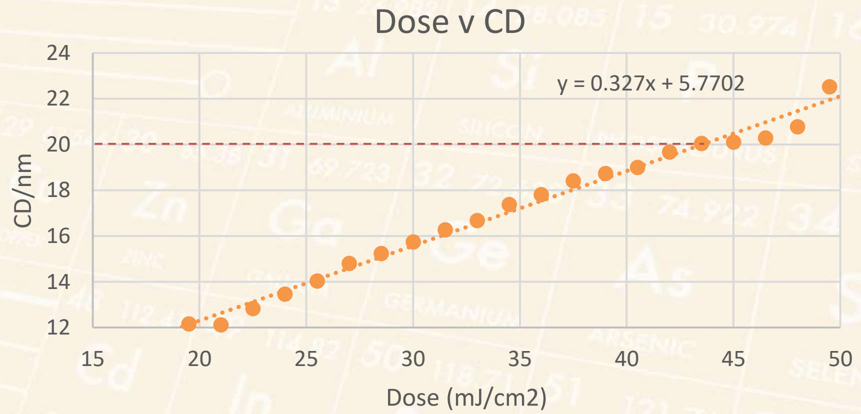


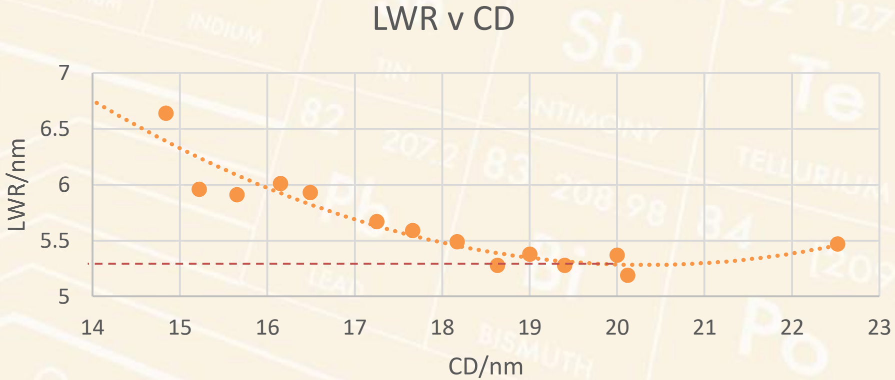
hp18nm
37.5mJ/cm²
CD 17.83nm
LWR 5.63nm



hp20nm
34.5mJ/cm²
CD 15.93nm
LWR 5.57nm







Pitch 40nm

No PEB

33nm film thickness

Dose to size 44mJ/cm²

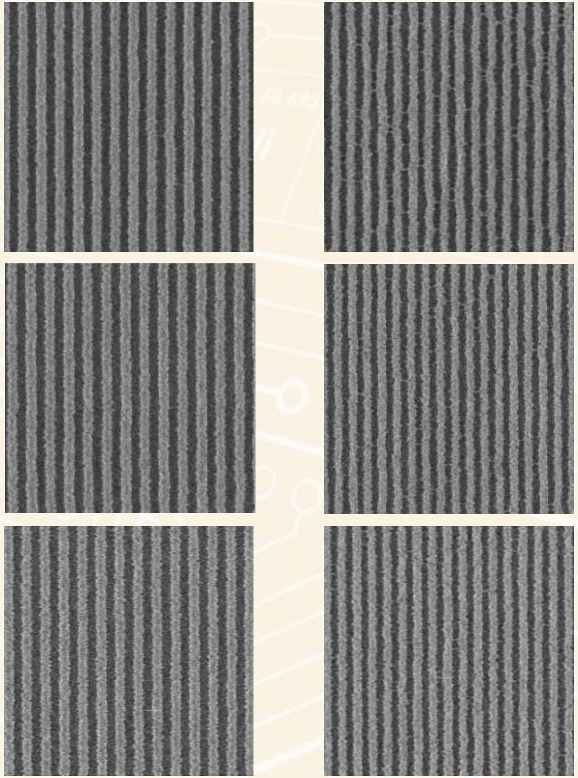
LWR at DtS 5.3nm

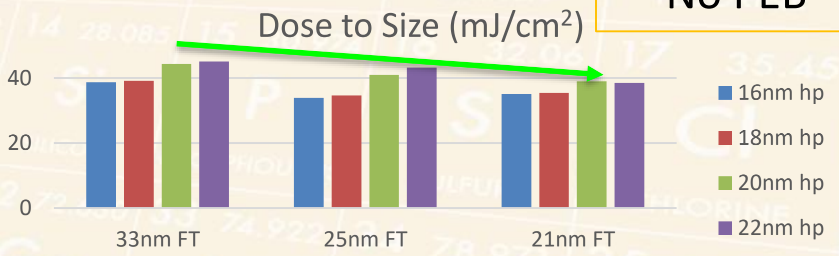
Rectangular scans, biased LWR

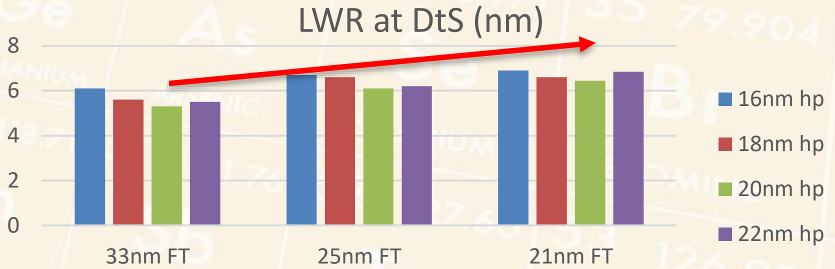
High opacity resist mk I varying film thickness

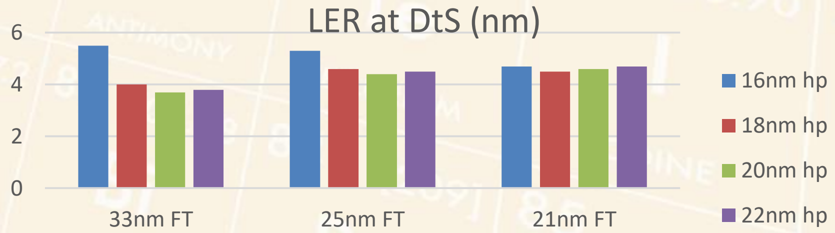
No PEB

	Pitch 40nm	Pitch 32nm
33nm FT		
25nm FT		
21nm FT		





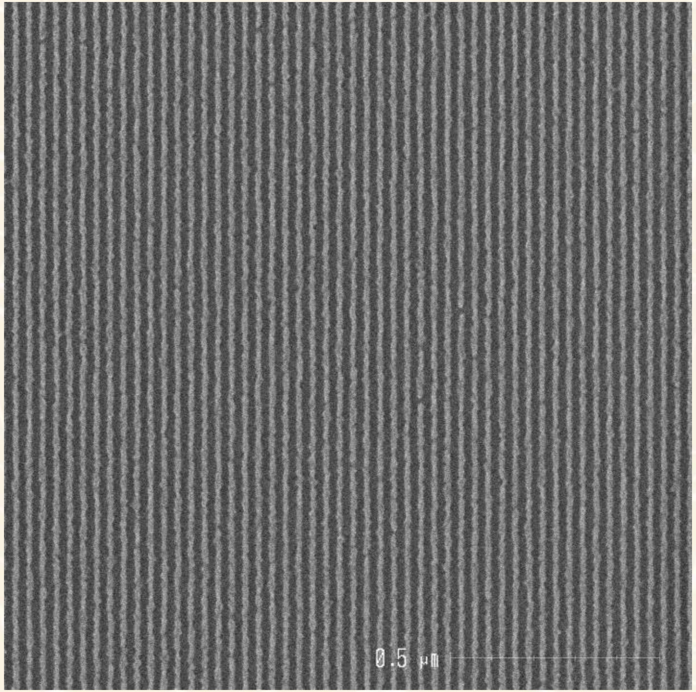




Best LWR at 33nm FT for all pitches
Bridging at p32 improved with lower FT
LER is best at FT 21nm for p32 only

Rectangular scans, biased LWR, images at DtS

Underdosed region: 21nm FT, no PEB



Hp16nm
Dose 22.5mJ/cm^2

MetroLER™ (by Fractilia) results (100 images)

CD = **12.96nm (3.0nm under hp)**
Unbiased LWR = 5.42nm
Unbiased LER = 4.12nm

50.5 breaks/mm
0.5 bridges / mm

High Opacity Resist mk I

Square scan [CD SEM CD = 12.17nm, biased LWR 6.89nm, biased LER 4.71nm]

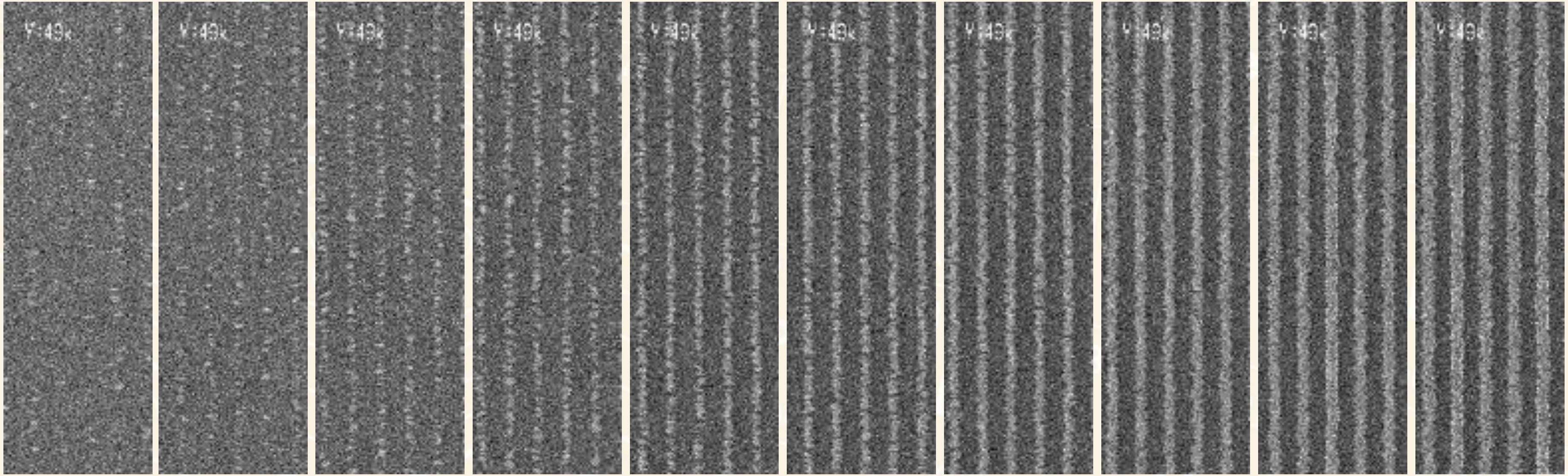
High opacity resist mk I: using a 90C PEB

Patterns appear with straight lines even at sub-10 mJ/cm^2 doses
Resist patterning is very fast: dose to size is 15.6mJ/cm^2

Pitch 40nm

21nm FT

4 mJ/cm^2 | 5 mJ/cm^2 | 6 mJ/cm^2 | 7 mJ/cm^2 | 8 mJ/cm^2 | 9 mJ/cm^2 | 10 mJ/cm^2 | 11 mJ/cm^2 | 12 mJ/cm^2 | 13 mJ/cm^2



Rectangular scans

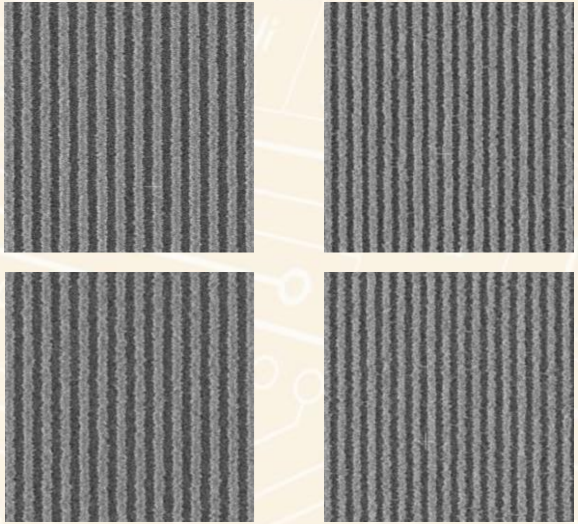
High opacity resist mk I: with and without PEB

21nm FT

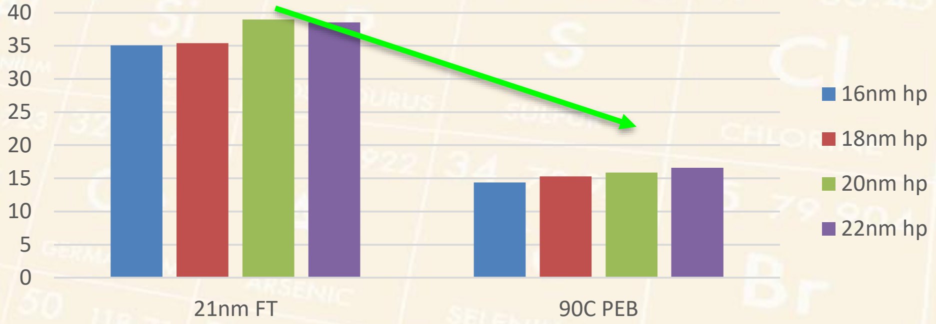
Pitch 40nm | Pitch 32nm

No PEB

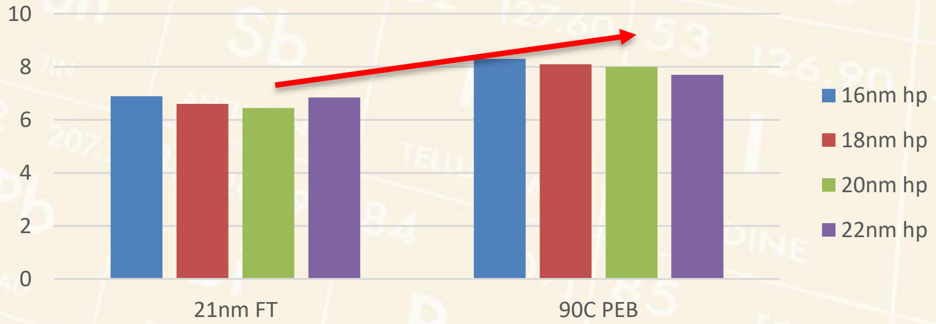
90C PEB



Dose to Size (mJ/cm2)



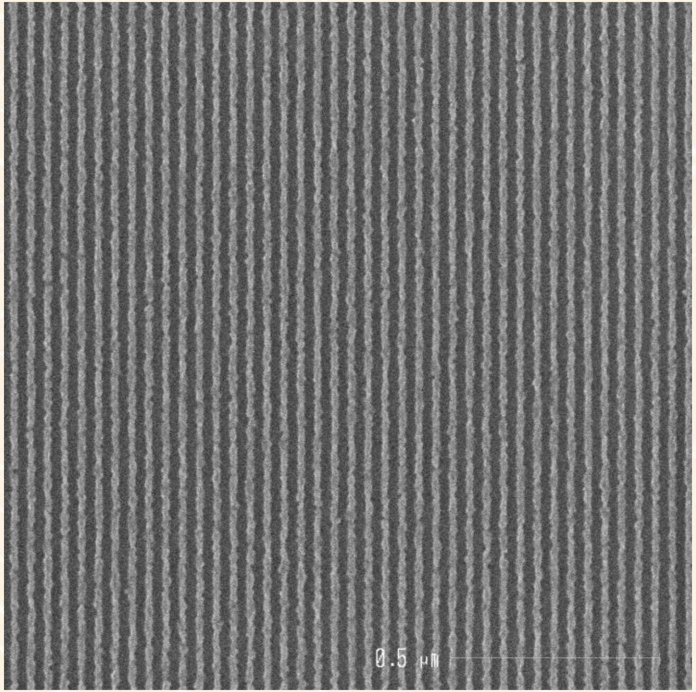
LWR at DtS (nm)



Dose reduced by average of 58% with PEB
LWR increases with 90C PEB though

Rectangular scans, biased LWR, images at DtS

Underdosed region: 21nm FT, 90C PEB



Hp20nm
Dose 13.0mJ/cm^2

MetroLER™ (by Fractilia) results (100 images)

CD = **16.85nm (3.1nm under hp)**
Unbiased LWR = 7.05nm
Unbiased LER = 4.98nm

9.12 breaks/mm
0.00 bridges / mm

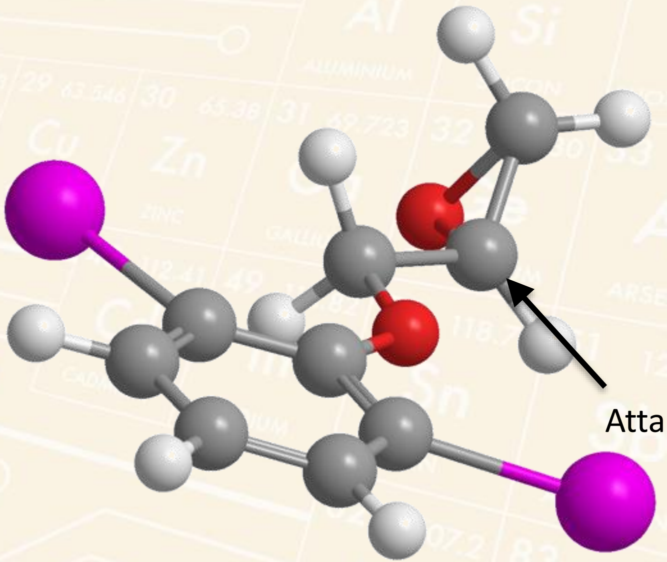
High Opacity Resist mk1

Square scan [CD SEM CD = 15.87nm, biased LWR 9.92nm, biased LER 6.70nm]

High opacity resist

- We would like to improve LWR for dense lines
- A number of routes currently being explored
  - Introducing nucleophilic quencher in similar manner to MTR2204
  - Increasing MTR ratio
  - Modifying high opacity crosslinker

Possible steric hindrance of reaction



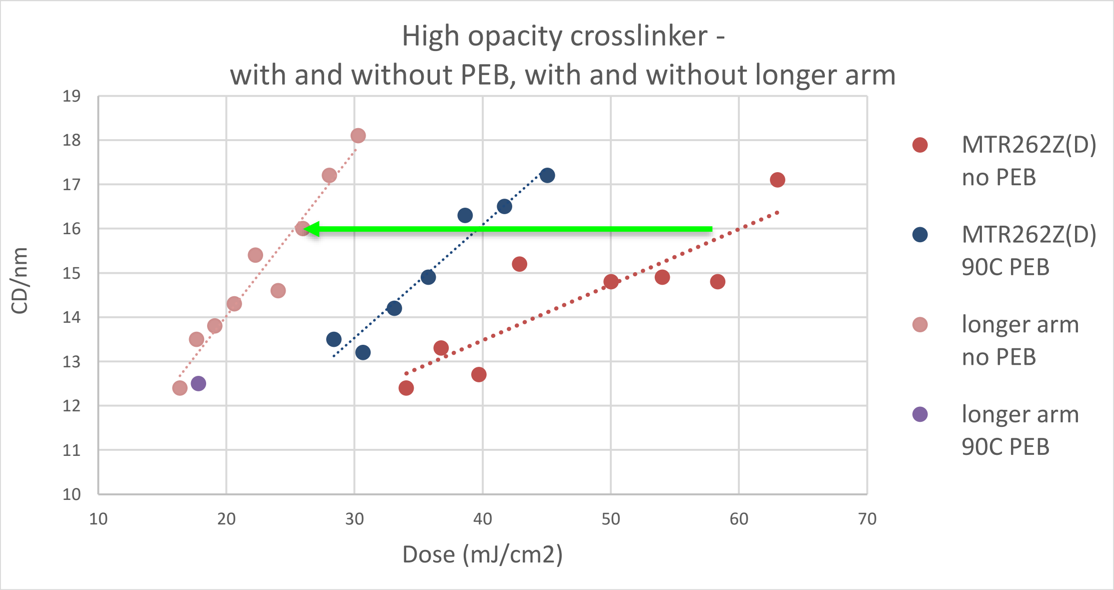
Attack here is hindered by the high-Z

High-Z Crosslinker mk I vs High-Z Crosslinker mk II

To improve sensitivity we synthesised a mkII high-Z crosslinker which incorporated longer arms to reduce steric hindrance

Pitch 32nm

PSI exposures



Longer arm crosslinker has much lower dose to size than mk1

Exposures undertaken by

High-Z crosslinker mk II

Pitch 30nm

mkI: MTR2627

62mJ/cm²
CD 14.2nm LWR 4.19nm
Dose to size 69mJ/cm²

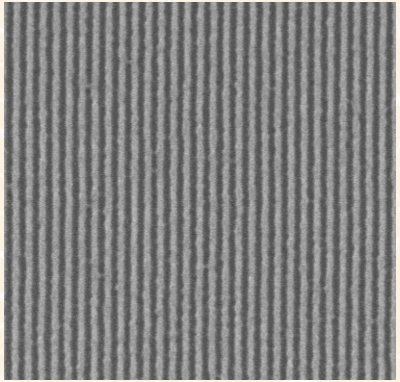
No PEB

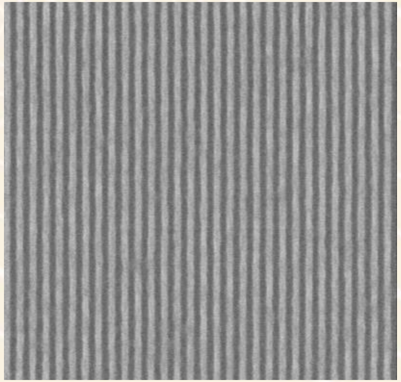
40% dose-to-size reduction

No change in LWR

PEB

37mJ/cm²
CD 14.1nm LWR 4.28nm
Dose to size 40mJ/cm²





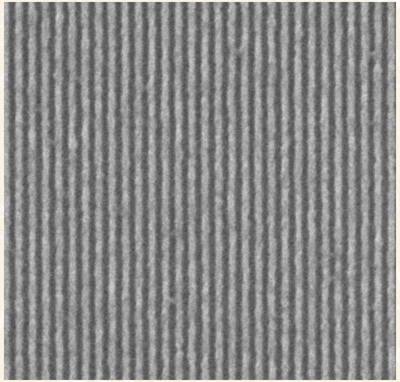
65% dose-to-size reduction

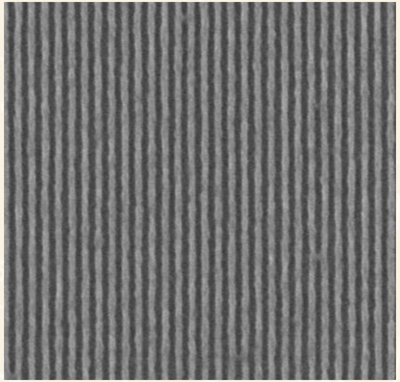
36% LWR increase

55% dose-to-size reduction

No change in LWR at DtS

mkII: MTR2827





19mJ/cm²
CD 14.1nm LWR 5.68nm
Dose to size 24mJ/cm²

No PEB

25% dose-to-size reduction

23% reduction in LWR

PEB

16mJ/cm²
CD 13.8nm LWR 4.36nm
Dose to size 18mJ/cm²

Exposures undertaken by ASML PAUL SCHERRER INSTITUT PSI

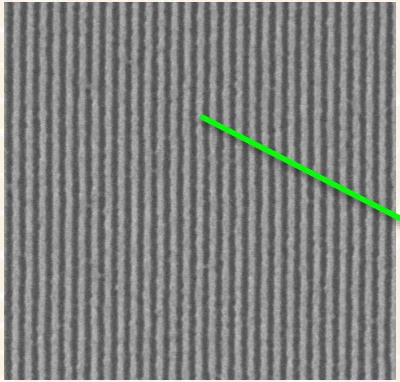
High-Z crosslinker mk II

Pitch 30nm

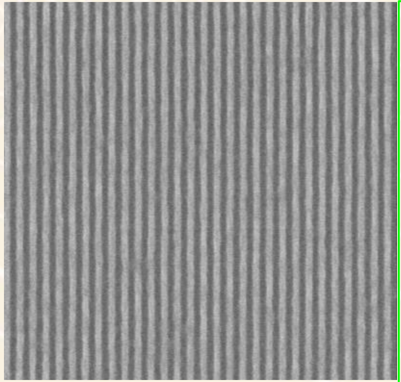
mkI: MTR2627

62mJ/cm²
CD 14.2nm LWR 4.19nm
Dose to size 69mJ/cm²

No PEB



PEB

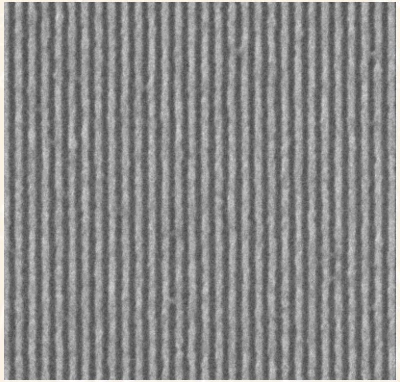


37mJ/cm²
CD 14.1nm LWR 4.28nm
Dose to size 40mJ/cm²

74% dose-to-size reduction

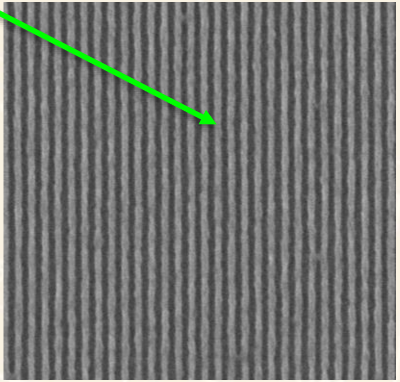
No change in LWR at DtS (4.3nm average p28, p30, p32)

mkII: MTR2827



19mJ/cm²
CD 14.1nm LWR 5.68nm
Dose to size 24mJ/cm²

No PEB



PEB

16mJ/cm²
CD 13.8nm LWR 4.36nm
Dose to size 18mJ/cm²

High-Z crosslinker mk II NXE3300 first result

Pitch 32nm

No PEB

24nm film thickness

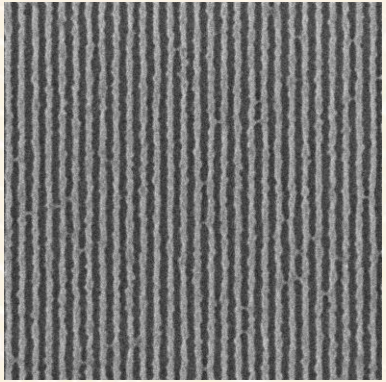
mkI: MTR262C

mkII: MTR282C

46mJ/cm^2
CD 14.2nm LWR 6.86nm
Dose to size 54mJ/cm^2

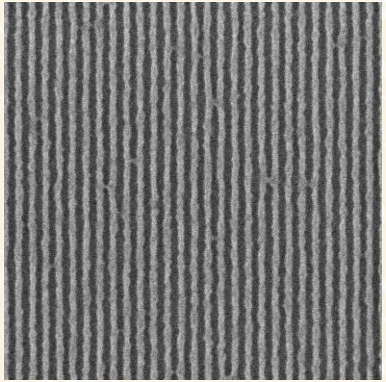
No PEB

30% dose-to-size reduction



57% dose-to-size reduction

18% LWR reduction



20.5mJ/cm^2
CD 14.4nm LWR 5.52nm
Dose to size 23mJ/cm^2

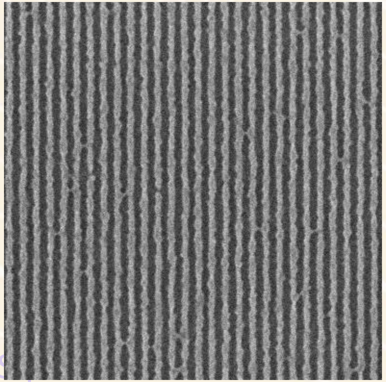
No PEB

11% dose-to-size reduction

No change in LWR on average

No change in LWR on average

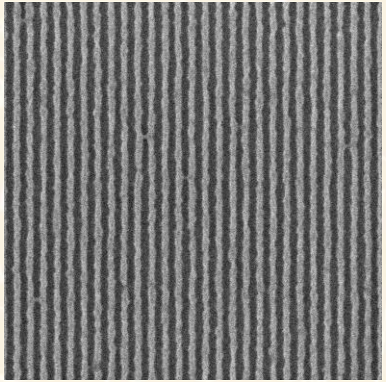
60C PEB



34mJ/cm^2
CD 14.2nm LWR 6.92nm
Dose to size 40mJ/cm^2

45% dose-to-size reduction

19% LWR reduction



60C PEB

18mJ/cm^2
CD 14.2nm LWR 6.01nm
Dose to size 21mJ/cm^2

(Post coat delay of 5 days)

Expanding Multi Trigger Tunability

We have talked about having molecule A and molecule B with different functional groups to control the behaviour.

Molecule A

Molecule B

In practice it is the functionality that is important rather than the molecule and we can add multiple functionalities in to a single molecule. For instance by introducing unprotected phenols on molecule B we can tune performance.

Unexposed B

Functionality A

Functionality B

Functionality C

Exposures undertaken by

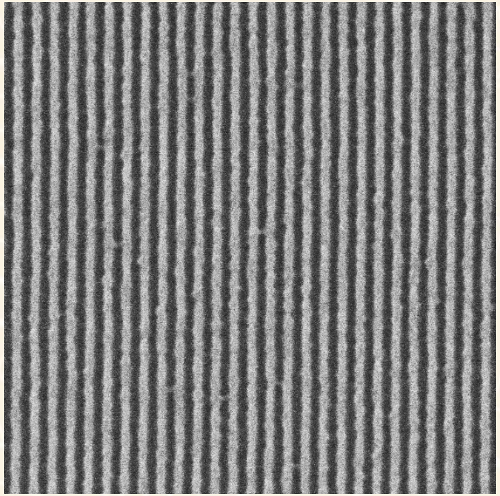
Modification of high opacity mk I crosslinker

Pitch 30nm

No PEB

20nm FT

MTR2627

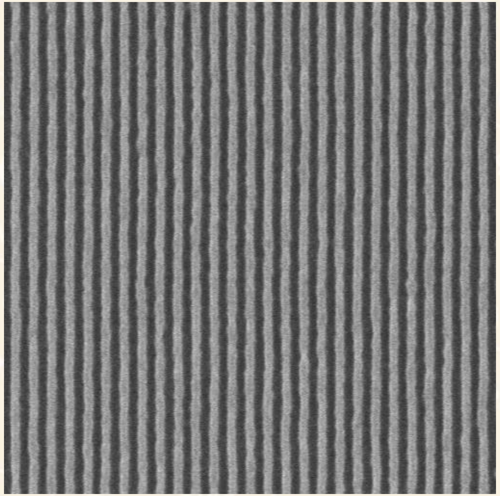


$62 mJ/cm^2$, CD 14.2nm
LWR 4.19nm, LER 3.34nm
Dose to size $69 mJ/cm^2$

47% dose-to-size reduction

33% LWR reduction

Crosslinker with unprotected phenols



$34 mJ/cm^2$, CD 14.7nm
LWR 2.72nm, LER 2.45nm
Dose to size $36 mJ/cm^2$

- An alternate method of changing MTR ratio by using protected and unprotected phenols
  - Small amount of residual phenol functionality in the standard crosslinker, which will alter the kinetics of the crosslinking reaction
- Intend to start a new synthesis study introducing phenols into high opacity crosslinker in different ratios to combine this functionality in 1 molecule

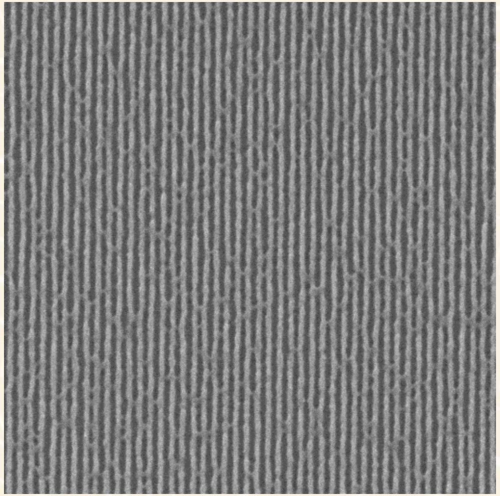
SEMS square scan

Exposures undertaken by ASML PAUL SCHERRER INSTITUT PSI

Modification of high opacity mk I crosslinker

Pitch 24nm
No PEB
20nm FT

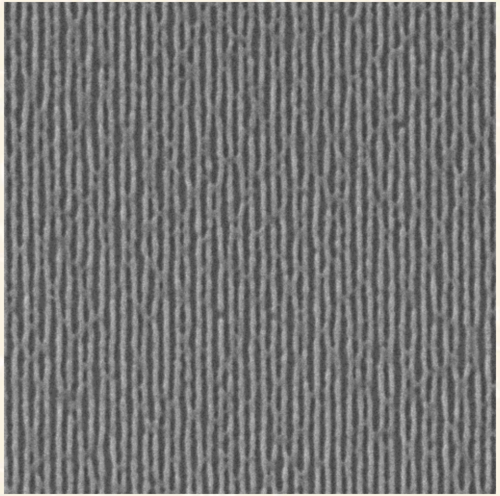
MTR2627



48mJ/cm^2, CD 11.1nm
LWR 4.88nm, LER 4.54nm
Dose to size 55mJ/cm^2

47% dose-to-size reduction

Crosslinker with unprotected phenols



24mJ/cm^2, CD 11.2nm
LWR 5.97nm, LER 5.94nm
Dose to size 29mJ/cm^2

- Lines are defined but there is bridging and pattern collapse
- We will try process variations (e.g. reducing film thickness) to improve this

SEMS square scan

Progress on metals levels

- We have continued to see good progress on trace metal reduction improvements for resist month-on-month.
- Results for high opacity formulation tested on NXE3300:
  - Less than 50ppb total
  - no metal greater than 10ppb

- The most recent results on the in house synthesised molecule (prior to formulation) indicate that all metals other than chromium (1.4ppb) are below detection limits

			Detection Limits ppb	Detected ppb
1.	Aluminum	(Al)	0.5	1.2
2.	Barium	(Ba)	0.1	0.55
3.	Beryllium	(Be)	0.5	<0.5
4.	Bismuth	(Bi)	0.5	<0.5
5.	Cadmium	(Cd)	0.1	<0.1
6.	Calcium	(Ca)	0.5	3.5
7.	Chromium	(Cr)	0.1	0.15
8.	Cobalt	(Co)	0.1	<0.1
9.	Copper	(Cu)	0.5	<0.5
10.	Gallium	(Ga)	0.1	<0.1
11.	Iron	(Fe)	0.5	9.9
12.	Lead	(Pb)	0.1	0.31
13.	Lithium	(Li)	0.1	<0.1
14.	Magnesium	(Mg)	0.1	1.9
15.	Manganese	(Mn)	0.1	0.29
16.	Molybdenum	(Mo)	0.1	0.18
17.	Nickel	(Ni)	0.5	2.6
18.	Potassium	(K)	0.5	0.50
19.	Sodium	(Na)	0.5	2.9
20.	Strontium	(Sr)	0.1	<0.1
21.	Thallium	(Tl)	0.5	<0.5
22.	Tin	(Sn)	0.1	1.4
23.	Titanium	(Ti)	0.2	<0.2
24.	Zinc	(Zn)	0.5	6.5
25.	Zirconium	(Zr)	0.1	<0.1
Note: All elements were analyzed by ICP-MS/ICP-AES.				
		total		31.9

IRRESISTIBLE MATERIALS

Summary

- IM are developing new resist material for EUV lithography
- Multi-Trigger chemistry enhances chemical gradient without quenchers
- Small formulation changes can change resist performance significantly
- Film thickness impacts dose, LER, LWR and pattern collapse
- Improved thermal stability leads to increased cross-linking which lowers LWR, top loss, collapse
- Adding non metallic high-Z element to crosslinker to improves resolution and LWR and enables higher aspect ratio
    - Investigating whether due to chemistry or material changes
- Introducing new element of MTR tuning by using unprotected phenols
    - Can modulate speed of resist

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Screen

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SCREEN

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Summit

Innovate UK

EPSRC Engineering and Physical Sciences Research Council

nffa.eu nanoscience foundries & fine analysis

Thank you
Any Questions?

IRRESISTIBLE MATERIALS

MET3, Dipole, 40 mJ/cm^2, hp 20nm