Further Investigation of the Multi-Trigger Resist System

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MET3, Dipole, 40 mJ/cm², hp 20nm
Outline

• Introduction of MTR Mechanism
• Experimental Investigation of Mechanism
• High Opacity Results
In a traditional CAR system, the photoacid reacts with a resist molecule and is immediately regenerated. Initiators are lost to base quenchers, or catalytic inefficiencies, or reactions stop due to lack of energy (end of PEB), but otherwise the reaction will continue indefinitely.
RLS Control – Base Quencher in CAR
Multi Trigger

**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**
Evidence for a Multi-Trigger Effect

<table>
<thead>
<tr>
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<th>Standard</th>
<th>Multi-Trigger</th>
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<tbody>
<tr>
<td>Sensitivity (µC/cm²)</td>
<td>32</td>
<td>25</td>
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<tr>
<td>Contrast</td>
<td>1.0</td>
<td>1.3</td>
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</table>
Evidence for a Multi-Trigger Effect

MEEF values of 1.0 – 1.1 reported
Proposed Multi Trigger Mechanism

Molecule A has a BOC protected crosslinkable functional group
• Can not crosslink when protected
• If protonated will deprotect (and regenerate proton) in presence of a nucleophile

Molecule B has proton activated crosslinking functional group
• Can self-crosslink, or crosslink with deprotected molecule A (regenerating proton in second case)
• Electrophilic. Becomes nucleophilic if protonated.

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.
Outgassing Measurements

Two samples examined at SUNY Polytechnic CORE Programme

- **MTR2224**: Quencherless MTR formulation
- **MTR2Z(4)24**: As above but with dummy Molecule B

(Labelled MTR and Dummy in the following slides)

The experiment exposes the samples to EUV and measures small molecule outgassing as a proxy for reactions. Focused on benzene (PAG activation), CO$_2$ and isobutylene (BOC deprotection)

Measurements undertaken by: Steven Grzeskowiak, Robert L. Brainard, and Greg Denbeaux
Expose sample to EUV light and monitor signal through time using Pfeiffer PrismaPlus mass spectrometer.
Benzene (78 amu)

Scan Number

Intensity (AU)

MTR
MTR (Heated)

Dose ≈ 5 mJ/cm²

Benzene (78 amu)

Scan Number

Intensity (AU)

Dummy
Dummy (Heated)

Dose ≈ 5 mJ/cm²

Dose ≈ 5 mJ/cm²
Isobutylene (41 amu)

Scan Number vs. Intensity (AU)

Isobutylene (41 amu)

MTR (Heated)

MTR

Dose ≈ 5 mJ/cm²

Intensity (AU)

-1.0E-09

0.0E+00

1.0E-09

2.0E-09

3.0E-09

4.0E-09

5.0E-09

6.0E-09

0

10

20

30

40

50

60

Scan Number

Dose ≈ 5 mJ/cm²

Dummy (Heated)

Dummy

Intensity (AU)

-1.0E-09

0.0E+00

1.0E-09

2.0E-09

3.0E-09

4.0E-09

5.0E-09

6.0E-09

0

10

20

30

40

50

60

Scan Number
$\text{CO}_2$ (44 amu)

Scan Number vs. Intensity (AU)

- MTR
- MTR (Heated)

Dose $\approx 5 \text{ mJ/cm}^2$

Scan Number

$\text{CO}_2$ (44 amu)

Scan Number vs. Intensity (AU)

- Dummy
- Dummy (Heated)

Dose $\approx 5 \text{ mJ/cm}^2$
BOC Deprotection


Investigation of BOC Removal

• In the literature there are thousands of examples of acid assisted BOC deprotection
• Where protonation at room temperature leads to carbon dioxide and isobutylene production
Investigation of BOC Removal

• Our mechanism shows a waiting step between protonation and deprotection
• Therefore we should be able to show that the BOC protected component of our resist (xMT) is stable at room temperature to TFA

• Set up a series of $^1$H NMR spectroscopy experiments investigating how stable the Boc group is
• xMT is dissolved in chloroform and excess TFA charged, Evaporated *in vacuo* at room temperature, 30 °C and 40 °C
Investigation of BOC Removal

xMT No TFA:

$^1$H NMR spectrum of xMT is not very resolved
Theorised due to the constrained nature of the xMT
Investigation of BOC Removal

xMT + TFA (25 equivalents)

$^1$H NMR spectrum of xMT becomes more resolved
Critically BOC remains

xMT

CHCl$_3$ aromatic proton

BOC

4.00

12.98
Investigation of BOC Removal

xMT + TFA (25 equivalents) evaporated in vacuo at RT

CHCl₃ aromatic protons + TFA
Investigation of BOC Removal

xMT + TFA (25 equivalents) evaporated at 30 °C

xMT aromatic protons + some BOC removal
Investigation of BOC Removal

$\text{CHCl}_3 + \text{TFA}$

$xMT + \text{TFA (25 equivalents) evaporated at 40 °C}$

See large decrease in BOC, showing deprotection

aromatic protons
Investigation of BOC Removal

• An experiment devised to prove that vacuum is needed at 40 °C

• xMT is dissolved in deuterated chloroform and excess TFA charged, Held at 40 °C before running $^1$H NMR spectrum
Investigation of BOC Removal

xMT + TFA (25 equivalents) held at 40 °C

No BOC deprotection

CHCl₃ aromatic protons
Investigation of BOC Removal

- Found that for xMT a strong acid is not enough by itself to cause BOC deprotection
- Evaporation causes further concentration as well as driving forward any equilibrium to CO$_2$ and isobutylene
- Furthermore the reaction happens at 40 °C

- Further experiment to see if a nucleophile could facilitate BOC deprotection. Methanol was used as the nucleophile because it is similar in nature to the protonated crosslinker.
- NMR study where excess TFA and excess methanol were added to xMT and evaporated *in vacuo* at various temperatures
The Impact of MeOH

Excess TFA, Excess MeOH, R.T

Excess TFA, Excess MeOH, 40 °C

Excess TFA, Excess MeOH, Dried in vacuo, R.T

Excess TFA, Excess MeOH, Dried in vacuo, 30 °C

Excess TFA, Excess MeOH, Dried in vacuo, 40 °C
Initial results indicate methanol improves the BOC deprotection, with in general more BOC deprotection happening at lower temperatures.
Increasing the Opacity

To improve sensitivity to the resist we synthesised a crosslinker which incorporates a non-metal high-Z element.
Comparing normal crosslinker and high opacity crosslinker

Data collected at BMET

MTR2204
P48
Dose: 40mJ/cm²
CD: 24.3nm
LWR: 4.50nm
LER: 3.38nm

MTR2627
P48
Dose: 60mJ/cm²
CD 25.1nm
LWR 2.5nm
LER 1.9nm

MTR262Z(D)
P48
Dose: 70mJ/cm²
CD 24.3nm
LWR 2.8nm
LER 1.9nm

High Opacity Variants
Data collected at PSI – pitch 28nm and 26nm

MTR2204
P28
Dose: 39mJ/cm²
CD 14.7nm
LWR: 5.90nm

MTR262Z(4)
P28
Dose: 62mJ/cm²
CD 13.1nm
LWR 5.07nm

MTR2204
P26
Dose: 43mJ/cm²
CD 13.2nm
LWR 6.55nm

MTR262Z(4)
P26
Dose: 49mJ/cm²
CD 10.7nm
LWR 6.41nm

Underdosed but still lower LWR
Increase Opacity – PSI data, compare to MTR2204

- MTR2627 works better at thicker FT without pattern collapse
- Dose is higher than MTR2204 (57mJ/cm² v 37mJ/cm²)
- LWR at 15nm is much lower (5.4nm compared to 6.6nm)
- LWR below 15nm at p30 also significantly lower
- Sub 11nm lines possible at p26 and p24

Exposures undertaken by
Increase Opacity – PEB sweep with MTR4 and MTR2

- Significant decrease in dose to size after 70°C
- Dose required to achieve 16nm lines at p32 using a 90°C PEB is 60% of the dose when using no PEB.
- The LER is slowly decreasing with increasing temperature
- not a sudden change in LER at 80°C or 90°C in common with the dose change
Possible steric hindrance of reaction

Attack here is hindered by the high-Z
High-Z Crosslinker mk I vs High-Z Crosslinker mk II

In an attempt to improve sensitivity to the resist 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
LER of longer arm version is slightly lower
High-Z crosslinker mk II

Effect of PEB on dose is less than standard high opacity crosslinker
Results indicate LER is better with 90C PEB
High-Z crosslinker mk II

High opacity crosslinker mk I
No PEB, p32
Dose 39.7mJ/cm²
CD 12.7nm LER 4.61nm

High opacity crosslinker mk I
No PEB, p32
Dose 50.0mJ/cm²
CD 14.8nm LER 4.75nm

High opacity crosslinker mk I
No PEB, p28
Dose to mask 490mJ/cm²
CD 12.7nm LER 5.07nm

High opacity crosslinker mk I
90C PEB, p28
Dose to mask 390mJ/cm²
CD 12.1nm LER 4.34nm
Final thoughts

• We have demonstrated in solution and at room temperature xMT is stable in acid conditions
• BOC deprotection happens when warmed to 40 °C with excess TFA
• Nucleophile (methanol) seems to promote BOC deprotection
• Original high-Z crosslinker showed excellent LER, but suffered from worse sensitivity
• By synthesising a less sterically hindered version we showed improved sensitivity
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