Molecular Resists for Next Generation Lithography: A Rich Diversity of Possibilities

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Materials Patterning:
A Diverse Challenge & Enabling Technology

Size Scale (m)

- $10^3$
- $10^2$
- $10$
- $10^{-1}$
- $10^{-2}$
- $10^{-3}$
- $10^{-4}$
- $10^{-5}$
- $10^{-6}$
- $10^{-7}$
- $10^{-8}$
- $10^{-9}$
- $10^{-10}$

Casting
Extrusion
Molding
Milling
Micromachining
Self-Assembly
Nanolithography
Synthetic Chemistry
Co-deposition
Bonding
Adhesives
Welding
Mechanical Fastening
Photolithography: High Volume Champ

- Thin Film
- Photoresist
- UV Light
- Chrome Mask
- Exposed Regions
- Positive Tone
- Negative Tone
- Post Develop
- Post Etch

$$R = k_1 \frac{\lambda}{NA}$$

$$DOF = \frac{\lambda}{NA^2}$$
Chemically Amplified Resists (CARs): The Modern Workhorse Material

Step 1. Acid Generation

\[
\text{Phenyl-S-SO}_3\text{CF}_3 + \text{Polymer Resin} \xrightarrow{\text{hv}} \text{H}^+\text{SO}_3\text{CF}_3 + \text{PAG decomposition by-product}
\]

Photoacid generator polymer resin, > 95 wt% (PAG), < 5 wt%

Step 2. Acid-Catalytic Deprotection

Acid-catalytic reaction
Switch polymer polarity

(1) Expose
(2) Bake (PEB)
(3) Develop
There exists a now well-known trade-off in resolution, LER, and sensitivity for chemically amplified resist materials.

RLS limitation is intrinsic to CARs → must reduce constant.

Modern CAR design at minimal constant - performance still does not meet the requirements.

Resolution$^3 \times $LER$^2 \times $Sensitivity \approx constant
Challenges with Chemical Amplification

Image Blur

Line Edge Roughness (LER)

Traditional CAR photoacid diffusivity: > 10 nm

Traditional CAR 3σLER: > 5 nm
Material Designs to Solve RLS

- **Base Quencher** – shown to reduce LER and improve resolution, but at cost of sensitivity
- **Molecular Resists** – reduce pixel size to improve LER

- **Polymer-bound PAGs**
  - reduce photoacid diffusion length to improve resolution
  - has shown LER improvements
  - sensitivity penalty reduced by increased PAG loading
  - several years into development – only recently began 22 nm patterning – LER still greater than desired

- UNCC-GT-Intel program
The Road to Molecular Resists

Advantages vs. Polymers

1. Reduced pixel size
2. Synthetic control
   • monodisperse
   • stereo- and regio-chemical control
3. Development
   • no microscopic heterogeneous deprotection
   • reduced swelling
   • high molecular chemical contrast

Current Molecular Resists

• Based on blending PAG and base into molecular glass matrix
• 50 nm resolution or better
• LER (3$\sigma$) of 6 nm or less

Da Yang, et. al., J. Materials Chemistry 2006

Polymer (50 repeat units) 5~10 nm

Monomer

Rough line edge

Completely soluble Completely insoluble
Molecular Resists: An Unfulfilled Promise?

- Most all blended molecular resists have LER (3σ) of 5 nm or more
- Inhomogenities have significant effect on LER
- Inhomogenities due to physically blended additives, polydisperse molecular weights – e.g. varying levels of protecting group
- Resolution in molecular resists also limited to due to diffusion of typically small blended acids

- Some Possible Solutions:
  - Single Molecule Resists
  - Negative Tone MRs

![Graph showing increasing homogeneity and decreasing LER](image)

Opportunities with Molecular Resists

- Single Component vs. Multi-Component

- Positive Tone vs. Negative Tone
Opportunities with Molecular Resists

- Aqueous Development vs. Solvent Development
- Chemically Amplified vs. Non-Amplified (Inhibited)
Opportunities with Molecular Resists

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- Positive Tone vs. Negative Tone
Single Molecule CARs

- A molecular resist that contains PAG functionality and acid labile protecting groups on a base soluble, etch resistant molecular glass core.

Advantages:
1. Molecularly homogeneous resist film
2. Highest PAG loading possible with no PAG segregation
3. Binding photoacid to molecular glass allows control of acid diffusion
   - resolution and LER improved
   - loss of photospeed offset by high PAG loading.
TAS-tBoc-SbF$_6$ EUV Results

- EUV exposures done on PSI tool in Switzerland
- 50 nm 1:1 lines resolved with low LER of 4.9 nm
- 30 nm 1:1 lines open only at very high dose
- Failure not due to acid blur, but due to pattern collapse/diffusion limitations

LER (3$\sigma$) = 4.9 nm
Single Molecule Bound Sulfonic Acids

- Design covalently binds sulfonic acid moiety directly to larger molecular glass core to control photoacid diffusion - improving both resolution and LER
- Next generation evolution of molecular resists and polymer-bound PAG resists
- Resist design space greatly increased compared to TAS allowing for systematic variation of each component
- Multi-functional cores allow selective attachment of acid and PAG, maintaining high homogeneity in a complex molecule
- Acid can be selectively attached to core or designed directly on the core
- Non-ionic PAGs now available to improve solubility issues with TAS
NBB : NDI-BHMOBS-Boc

- NBB first example of non-ionic bound sulfonic acid molecule resist
- Sulfonic acid is directly part of molecular glass core
- Norbornene dicarboximide PAG
- Superior solubility in casting solvent as compared to TAS compounds
- Has good adhesion and forms excellent films
- Zero dark loss over 30 sec. development in 0.261N TMAH
NDI-BHMOBS-tBoc E-beam Litho

- NDI-BHMOBS-tBoc shows poor sensitivity under 100 keV e-beam ~ 3x of TAS
- Excellent image quality and resolution, down to at least 40 nm 1:3 lines/space
- No appreciable acid blur, even at 90°C PEB, above Tg
- Excellent LER ($3\sigma$) = 4.8 nm
- Suffers from pattern collapse starting at 60 nm 1:1 lines (aspect ratio > 2) using current developer and rinse protocols

\[ \gamma = 5.8 \]
Opportunities with Molecular Resists

- Single Component vs. Multi-Component

- Positive Tone vs. Negative Tone
Chemical Amplification & Acid Diffusion: A Necessary Curse?

1. Acid Generation

\[ \text{Photoacid generator polymer resin, } > 95 \text{ wt\% (PAG), } < 5 \text{ wt\%} \]

2. Acid-Catalytic Deprotection

Acid-catalytic reaction

Switch polymer polarity

Step 1. Acid Generation

Step 2. Acid-Catalytic Deprotection

(1) Expose

(2) Bake (PEB)

(3) Develop
Advantages of Cationic Polymerization

- Most high resolution CARs are based on photoacid catalyzed deprotection of protecting groups
- CARs based on cationic polymerization have been used for many years for micropatterning – SU-8

- Potential advantages of cationic polymerization CARs
  - superior mechanical strength – high MW cross-linked film
  - superior environmental stability – highly stable cationic chain propagation controls conversion
  - intrinsic diffusion control – active cation directly attached to exponentially growing chain/network
  - no outgassing – zero mass loss process
Still More Problems: Resist Pattern Collapse

- Photoresist
- Exposure
- PEB
- Exposed Regions
- Development
- Rinse
- Dry
- Thin film
- Silicon substrate

Resist line bending or breakage
Resist adhesion failure

θ

F

200 nm
500 nm
Synthesis of Resists

- Molecular resist core made by acid-catalyzed condensation of phenol with a ketone or aldehyde

- Core functionalized by reaction with epichlorohydrin in the presence of base

- Final product purified by recrystallization or column chromatography
Comparison of Epoxide MR E-beam

- Resolution increases as functionality decreases
- Maximum aspect ratio increases as functionality increases

2-Ep  3-Ep  4-Ep

75 μC/cm² (100keV)
75 μC/cm² (100keV)
75 μC/cm² (100keV)
t = 50 nm
LER = 2.8 nm
t = 110 nm
LER = 2.3 nm
t = 70 nm
LER = 2.3 nm

50 μC/cm²
t = 50 nm
LER = 2.3 nm

50 μC/cm²
t = 50 nm
LER = 2.3 nm

25 nm 1:1
25 nm 1:1
25 nm 1:1

100 nm
100 nm
100 nm

50 nm 1:1
50 nm 1:1
50 nm 1:1

60 nm
60 nm
60 nm

35 nm 1:1
35 nm 1:1
35 nm 1:1
SU-8 E-beam Litho

- SU-8 is a well-known CA epoxide resist
- SU-8 shown in literature to produce isolated lines down to sub-30 nm
- SU-8 2000 used after dilution in PGMEA to form thin films, 60 C PEB
- 70 nm 1:1 begins to show bridging and line “wobble”
SU-8 vs. Epoxide Molecular Resist

- SU-8 shows inferior resolution and LER to 4-Ep
- Swelling appears to be main failure for SU-8
- Differences likely due to extent of cross-linking in molecular resist 4-Ep compared to oligomeric SU-8
Further Improvements: Quenchers?

- Even up to very high base loadings (1:1 PAG:base), the base has little effect on the cross-linking
Base Quencher Ineffective in Epoxide Resists

- In standard CARs, the photoacid is regenerated after each reaction. The base acts to quench the acid and reduce catalytic chain length.

- In cationic polymerization CARS, the photoacid reacts only once. The active cation is the species that gets regenerated after each reaction. Base has less effect on the active cation.
Nucleophilic Quenchers

- What will act to quench a cationic polymerization?

A strong nucleophile such as a triflate anion.

\[
\text{NH}_4^+ \text{SO}_{\text{CF}_3} \quad \text{Added to 4-Ep}
\]

\[
\text{DUV Contrast PEB 60}^\circ\text{C}
\]

Graph showing the relationship between dose and NRT for different conditions.
Photo-Decomposable Nucleophile (PDN)

- Addition of strong nucleophile shows significant effect in quenching
- Only needs to terminate polymerization outside the exposed region
- What type of chemical can achieve this??

TPS-Tf added to 4-Ep formulation
- Triflic acid acts like chain transfer agent – regenerating the initial photoacid
Photo-Decomposable Quencher – TPS-Tf

- Behavior looks like reduced PAG loading at low dose, but can obtain the same performance as no additive
- Has benefits of nucleophilic quencher with less drawbacks
- Contrast improved ($\gamma_0 = 0.49$, $\gamma_{1:4} = 1.14$, $\gamma_{1:2} = 1.13$)

![Chemical structures of TPS-SbF$_6$ and TPS-Tf]

DUV Contrast PEB 60°C

DUV Contrast PEB 90°C
4Ep EUV at PSI PEB 60°C with TPS-SbF$_6$/TPS-Tf

- Modified resist formulation, 1:2 TPS-Tf:TPS-SbF$_6$
- Dose-to-size = 15 mJ/cm$^2$ (Dose-to-Mask = 45 mJ/cm$^2$ July 08)
- LER (3σ) = 4.0 nm for 50 nm lines
- LER (3σ) = 4.5 nm for 25 nm lines
Opportunities with Molecular Resists

- Aqueous Development vs. Solvent Development

- Chemically Amplified vs. Non-Amplified (Inhibited)
TMAH Developed Epoxides

- These systems have excellent performance under both e-beam and EUV, but they are developed in organic solvents.
- The industry standard for development is aqueous base solutions of 0.26N TMAH.
- This concept is extendable to aqueous base development with the design of new resist molecules and blends.
Base Developed Epoxides – Blended Resists

- Shows similar behavior in solvent and base
- $\gamma = 4.2$ in AZ300
- Can be reasonably imaged with no PEB – due to additional etherification mechanism
- High resolution imaging currently underway
Opportunities with Molecular Resists

- Aqueous Development vs. Solvent Development
- Chemically Amplified vs. Non-Amplified (Inhibited)
Non-Amplified Resists

• Positive Tone
  – DNQ/Novalac – DNQ inhibits dissolution of novalac, undergoes Wolff rearrangement to become dissolution promoter – requires water during exposure to operate in positive tone mode
  – PMMA – chain scission – reduction in MW leads to solubility difference – electronics/absorbance of chain can be altered to improve photosensitivity, but still limited

• Negative Tone
  – HSQ/Acetyl or Chlorobenzyl Calixarenes – photoinduced radical generation which induces cross-linking – high resolution, but relatively large number of cross-links required to render insoluble – low sensitivity
Non-Amplified Resists

- These designs have minimal ways to improve sensitivity.
- The dissolution inhibitor (DI) resists can be potentially be made very sensitive (but not with DNQ).
- DIs using photosensitive protecting groups were investigated in early 1980s (pre-CARs).
- Huge amount of literature on photosensitive protecting groups in total synthesis – most non-ionic PAG chromophores can be applied as photosensitive protecting groups.
- Molecular resists provide precise control of functionality needed for high resolution non-amplified resists.
- Molecular resist dissolution behavior means that very high amounts of DI are required to render the film insoluble.
Predictive Modeling Is Possible in MRs

- We have greatly improved the understanding of the dissolution behavior of molecular resists.
- The previous work has only been done for pure components, but an actual resist consists of a mixture of soluble and insoluble species.
- A study has been carried out to understand this effect on the dissolution of actual molecular resists.

\[
\log(DR) = \log\left(\frac{D}{1 + \exp(-\log(D))}\right) + OH_{\text{req}}
\]

\[
y = -0.66x + 4.82 \\
R^2 = 0.85
\]
1st Gen Non-Amplified MRs

Ex. 1

Ex. 2

- Desire to investigate ultimate tradeoffs in non-amplified vs. CA resists
- No high sensitivity positive tone non-CA resists reported for high resolution imaging
- DNQ cannot be used because Wolff rearrangement requires in-situ water – DNQ in vacuum leads to cross-linking
- Designs based on dissolution inhibition by compounds with photosensitive functional groups
- Should provide some learning on future single component systems
NBnHPF

- Synthesized by Williamson etherification, purified by simple column
- Can be imaged as single component system or imaged as blended system (with BHPF)

Single Component | Blended System
---|---
100% | 25-50%

50-75%
NMR of NBnHPF

Materials can be isolated as clean pure compounds!
NBnHPF/C4MR Blends

- 55 nm thick film
- Processed with **No PEB**
- Cleanly dissolves in 0.26N TMAH – no apparent delamination on HMDS primed surfaces
- Sensitivity adjustable by formulation - 0, 10, 20, 25% C4MR in NBnHPF – down to 1 mJ/cm2 at 248 nm exposures
- 20% C4MR has sensitivity of 10 mJ/cm2 with contrast of 8.26 under DUV
- Might be faster under EUV due to potentially improved photoreaction rate constant of NBn PPG (photoactive protecting group).
Summary

• Molecular resists offer a rich class of materials for next generation resists
  – Ability to synthesize and isolate pure, single species an inherent advantage
• Predictive materials design modeling tools have been developed
  – Predict Tg, solubility, dissolution rate,…
• Outstanding results have been demonstrated in early negative tone materials
  – Low LER, very high sensitivity, very high resolution
• A new method for “diffusion control” has been developed and demonstrated in negative tone MRs using PDNs
• Single component MRs have been demonstrated
• Highly sensitive non-amplified MRs have been developed
• Learning how far platforms can be pushed…

4-Ep
PSI
25 nm 1:1
15 mJ/cm²
LWR: 5-6 nm
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