Effect of PAG Location on Resists for Next Generation Lithographies

Ober Research Group
Cornell University
Materials Science & Engineering
Ithaca, NY 14853
Development Trends in Microlithography

Architectures

Contact Printer
Cyclized Rubber
DNQ - Novolak
HS Copolymers
Hydrocarbon Polymers

Year
75 85 95 05
Resolution (µm)
10
1.0
0.1

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Positive Chemically Amplified Photoresist Chemistry

Aqueous Base Dissolution

\[(\text{CH}_3)_4\text{N}^+\text{OH}^-\]

\[\text{hv} \rightarrow \text{H}^+\]

PAG

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Photoacid Generators - PAGs

\[
\text{RSO}_3^{-} + \text{RSO}_3^{-} \rightarrow \text{RSO}_3^{-} + \text{RSO}_3^{-} + \text{HI} + \text{H}^+ \quad \text{h}^+ \quad \text{Homolysis}
\]

- Radical Abstraction / Protonation
- Dissociation

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Rutherford Backscattering

- Depth resolution ~ 200 A
- RBS spectrum contains information about target’s:
  - mass
  - concentration
  - depth profile
- Most photoacid generators (PAGs) have a self-label such as Sb, I, etc.
Diffusion of PAG and Photogenerated Acid

- Exposed SbPAG - experimental
- Exposed SbPAG - simulated
- Unexposed SbPAG - experimental
- Unexposed SbPAG - simulated

Photogenerated acid (2)

PAG (1)

120°C/60s

$\text{SbF}_6^-$

Chemical structures:

1. $\text{SbF}_6^-$
2. $\text{PAG}$

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Photoacid Generator (PAG) Distribution

Uneven distribution of PAG

Si wafer

T-topping

Closure

Footing
Effect of Block Copolymers As Additives

THPMA-b-IBMA with and without IBMA-b-MMA additive

PAG concentration (a.u.)

Normalized film thickness

with bcp
without bcp

THPMA-b-IBMA with
MMA-b-IBMA

 wafer
air

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Block Copolymers as Additives

IBM zero thinning resist

MMA-tBMA-MAA

with 2 wt% MMA-b-IBMA

5800 A thick films; PAB -140C/60s PEB - 140C/60s; Dev. - 0.05 TMAH
Effect of Block Copolymer Additives - SIMS Measurements

Photoacid generator

\[ \text{CF}_3(\text{CF}_2)_3\text{SO}_3^- \]

(5 wt%)

Block copolymer additive

2 wt%
Polymers for Chemically Amplified Photoresists

\[
pK_a = 9-10
\]

\[
pK_a = 9-10 / pK_a = 4-5
\]

\[
pK_a = 4-5
\]

\[
pK_a = 4-5 / \text{Anhydride}
\]

Collaboration with G. Barclay, Shipley
Labeling of Photoacid Generators for RBS

Self Labeled

No Label

Heavy Atoms: Sb (51), As (75), Br (79), I (127)
Light Atoms: C (12), N (14), O (16), F (18), S (32)
Design of Labeled PAGs for RBS Study

Iodonium Polar PAGs

I-1

I-2

I-3

I-4

Non Polar Sulfonate Esters

Br-1

Br-2

Br-3

Br-4

I - Labeled
Collaboration with G. Barclay, Shipley

Br - Labeled

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Design of Non-Polar Sulfonate Ester PAGs

- Thermally Stable in Phenolic and Methacrylate Matrices
- Photogenerates acid via “Blocked” Photo-Fries

Collaboration with G. Barclay, Shipley
Model Photoresist Matrices

248 nm

Hydrophilic

70/30

Hydrophobic

193 nm

Collaboration with G. Barclay, Shipley
Distribution of Polar Ionic PAGs in Poly(4-Hydroxystyrene)

The distribution of Iodonium PAGs is uniform through the depth of the PHS film independent of counter ion.

Collaboration with G. Barclay, Shipley
Distribution of Polar Ionic PAGs in 193 nm Acrylic Matrices

Degree of segregation is dependent upon length of fluoronated counter ion

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RBS Spectra of N-Oxy Sulfonate in PHS

Heavy Atoms: Sb (51), As (75), Br (79), I (127)
Light Atoms: C (12), N (14), O (16), F (18), S (32)

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RBS Spectra of Iodonium Triflate in PHS

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Distribution of Non-Polar PAGs in PHS Copolymers

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Distribution of Non-Polar PAGs in Model 193 Matrices

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Distribution of Non-Polar PAGs in Model 193 Matrices

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Comparison of PAG Distribution Different Resist Matrices

PAG concentration, atomic %

Normalized film thickness

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Dissolution Behavior

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Dissolution Behavior of Matrix Containing Model PAG

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