Molecular Glass Photoresists for EUV Lithography

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Introduction

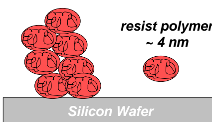
EUV lithography, in which high-energy photons with a wavelength of 13.4 nm (100 eV) are used to pattern resists, is one of the leading candidates for next generation lithography. This technique is expected to produce feature sizes in the sub-50 nm regime due to the extremely short wavelength employed. At sub-50 nm feature size, conventional chemically amplified resists have performance issues such as line edge roughness (LER), molecular size and uniformity and acid diffusion control that combine to hinder optimal resist performance and resolution. The ultimate resolution of a photoresist is largely determined by the size of an individual molecule which is presently about 5 ~10 nm for a polymeric photoresist depending on its molecular weight as well as three-dimensional structure. To date, little work has been carried out on low molecular-weight amorphous resist materials, which may provide breakthroughs in nano-patterning.

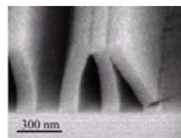
Research Goal

Creation and lithographic evaluation of low molecular-weight organic resist materials (which we refer to as "molecular glasses") that readily form stable amorphous glasses above room temperature as well as establishing guidelines for the design of amorphous molecular materials.

Limitations of Polymeric Photoresists

- Resolution
  - High molecular weight
  - Molecular weight distribution
- Swelling
- Residual stress
  - Adhesion (collapse)
  - Distortion
- Line width roughness (LWR)
  - Aerial image quality and processing condition
  - Phase compatibility
  - Acid diffusion
  - Molecular weight and molecular weight distribution
  - Compositional heterogeneity in the line edge regions
  - Statistical nature during the dissolution of polymers

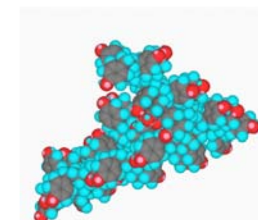




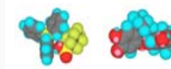
http://www.xraylith.wisc.edu

Molecular Glass Photoresists

- Molecular glass resists – low molecular weight amorphous organic photoresists
  - Small and homogeneous molecular size of ~1 nm
  - Many of same features as polymer
  - Better phase compatibility
  - High resolution, low LWR
  - Broad range of compositions possible
  - More uniform distribution of resist additives
- Greatest focus of effort in past 12 months
- Shown to be patternable
- Demonstrated low LER, high resolution via e-beam (60 nm) and EUV (35 nm)

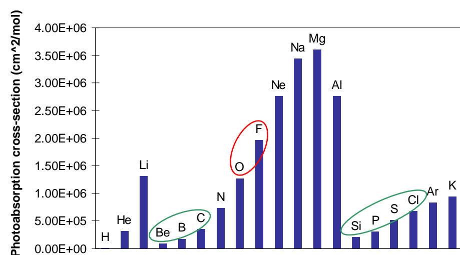


Molecular size ~ 4 nm
Poly(hydroxy styrene), DPn = 50



Molecular size ≤ 1 nm
Molecular glass resist components

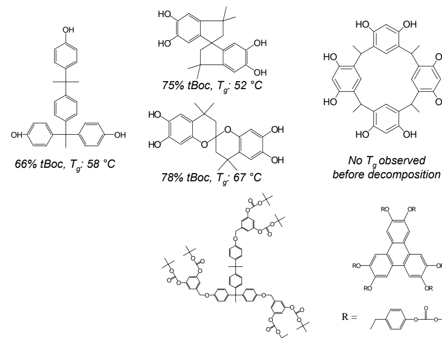
Absorbance at EUV Wavelength



- Resist absorption at 13.5 nm depends only on chemical composition and density of the material

Cornell Molecular Glass Design

- High T_g
  - Rigid molecular structure, e.g. star shape molecule, fused aromatic rings, biphenyl or spiro type connections
  - Strong attractive forces
  - H-bonding
- Amorphous
  - Low tendency toward crystallization
  - Unsymmetrical structure
- Etch resistance
  - High C/H ratio
- EUV
  - Less oxygen

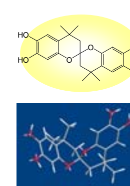


Increase T_g by introducing rigid core materials or rigid side chain linkages

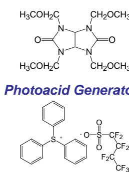
Negative-tone Molecular Glass Resist

Components

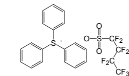
Monomer



Powderlink™ Crosslinker



Photoacid Generator

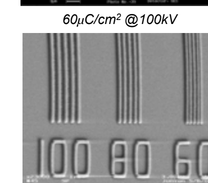


Processing Conditions

15 wt% Powderlink™
5 wt% TPS Nonaflate
PAB: 115ºC, 60s
PEB: 115ºC, 60s
Development: 0.026N TMAH, 10s

E-beam Images

$60 \mu C/cm^2$ @100kV



Dose range 60 – 240 $\mu C/cm^2$ @100kV
60 nm pattern image at $180 \mu C/cm^2$ @100kV

Positive-tone Molecular Glass Resist

Resist

EUV Images

Processing Conditions

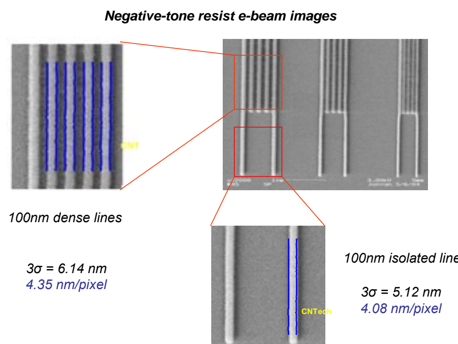
5 wt% TPS Nonaflate
0.14 wt% TOA
PAB: 115ºC, 60s
PEB: 115ºC, 60s
Development: 0.026N TMAH, 30s

10.0mJ/cm² bright field resist shows good iso-dense bias

Images obtained at Lawrence Berkeley National Laboratories by EUV microexposure tool

Line Edge Roughness - Preliminary Results

Negative-tone resist e-beam images



100nm dense lines

3σ = 6.14 nm
4.35 nm/pixel

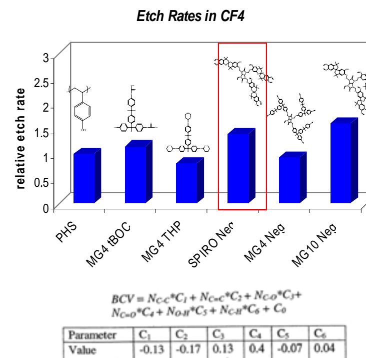
100nm isolated line

3σ = 5.12 nm
4.08 nm/pixel

Calculation program by Professor Francesco Cerrina research group at University of Wisconsin-Madison

Nitride Etch Resistance

Etch Rates in CF4



$$BCV = N_{C-C}*C_1 + N_{C=C}*C_2 + N_{C-O}*C_3 + N_{C=O}*C_4 + N_{O-H}*C_5 + N_{C-H}*C_6 + C_0$$

Parameter	C_1	C_2	C_3	C_4	C_5	C_6
Value	-0.13	-0.17	0.13	0.4	-0.07	0.04

Yu, T.; Ching, P.; Ober, C. K. Proceedings of SPIE **2001**, 4345, 945-948

Summary and Outlook

- 60 nm pattern obtained with negative-tone resist by e-beam
- 35 nm pattern obtained with positive-tone resist by EUV
- Molecular glass resist shows good iso-dense bias, etch resistance and LER data
- Current research focusing on high T_g molecular glass resists and LWR studies
- Future work - molecular glass resists for EUV and 193 nm lithography

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