EUV Resist Materials Based on Molecular Glass Resist and Non-PFOS Photoacid Generators

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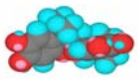
EUV Photoresists and Photoacid Generators



- EUV lithography requires novel resists and non-PFOS photoacid generators to fulfill its full potential
- Specific requirements: Low EUV absorbance, high resolution (<50 nm features) low line edge roughness (LER)
- Also required are high sensitivity PAG's (2-5 mJ/cm^2) that meet stringent environmental concerns (replacement of PFOS)

Our group designs and evaluates next generation photoresists and photoacid generators for EUV lithography

Molecular Glass Resists

Introduction

Conventional photoresists are polymeric **(large, polydisperse systems)**

Objective

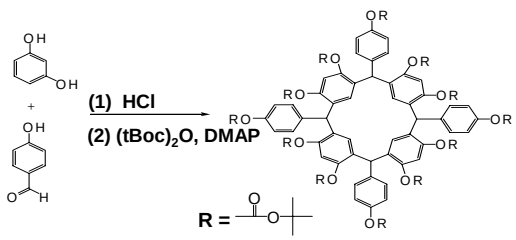
Design and evaluation of next generation resists (small amorphous molecules, monodisperse systems) **for the production of sub 50 nm images using modern lithographic techniques.**

Polymeric Resists — *High LER*

Molecular Glass Resists — *Low LER*

Design and Synthesis

Cores with high thermal and etch properties. Calix[4]resorcinarene with acid labile groups



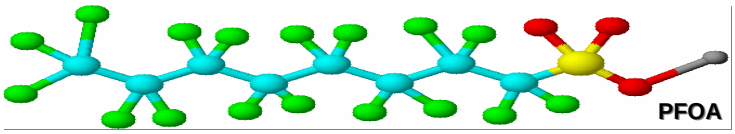
Properties

Amorphous small molecules with high T_g (120 °C)

Non-PFOS Photoacid Generators

Introduction

Perfluorooctanesulfonate (PFOS) PAGs are critical components in chemically amplified resist



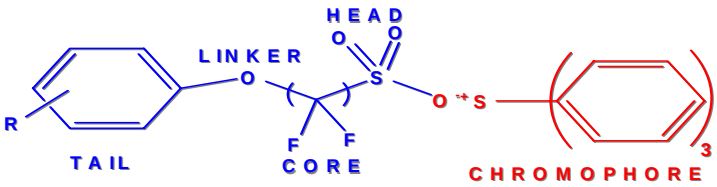
Strengths -Strong acid, miscibility, stability, optical properties, larger size
Issues - Fluorous self assembly, acid diffusion, absorption, potential organic pollutant (POP)

Objective

Develop Non-PFOS PAGs to address both performance and safety concern

PAG Design and Synthesis

PAGs with Functionalized Fluororganic Sulfonate



Properties

High thermal stability (T_d = 233 °C), soluble in standard litho solvents, lower (theoretical) absorption and limited outgassing at EUV

Results and Discussion

- Mild efficient synthetic methods were developed to synthesize both molecular glass and non-FPOS PAGs
- Fundamental resist properties including their solubility, amorphous nature, thermal properties and their film forming qualities were investigated
- Physico-chemical and photochemical properties of non-PFOS PAGs such as solubility, thermal properties, absorption characteristics, outgassing at EUV and formulation stability were evaluated
- Photoresist formulation containing 70 % *t*BOC protected Calix[4]resorcinare with non-PFOS PAG was evaluated at EUV and the resist performance is listed below:

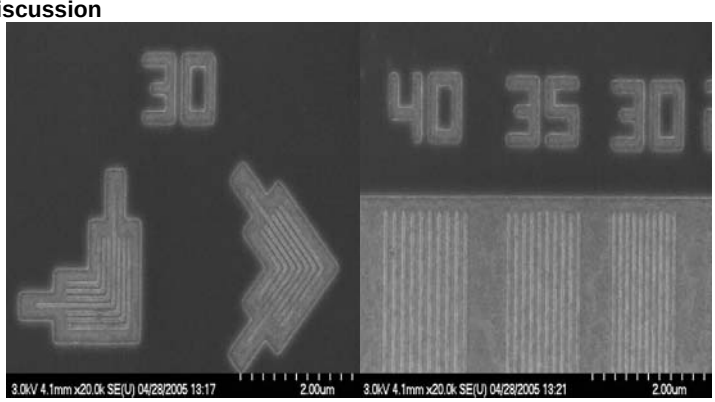
  Energy to Size (E_s) – 21mJ/cm^2

  Resolution (dense) – 30 nm

  LER (100 nm) – 4.6 nm

  Exposure Latitude – 18 %

- Estimation of P_{OW} and BCF of non-PFOS PAG anions indicates no or low bioaccumulation



SEM Images obtained after EUV exposure of 70 % tBOC protected Calix[4]resorcinarene with non-PFOS PAG (100 nm film, 5 % non-PFOS PAG, PAB 125 °C, PEB 80 °C, developed in 0.026N TMAH)

Conclusions

- EUV transparent novel molecular glass resist with high thermal and etch quality as well as ability to form defect-free film was developed
- Novel PAGs with reduced fluorine content along with good physico-chemical and environmentally benign properties were developed
- Resist composition with molecular glass resist and non-PFOS PAG shows superior EUV performance

Cornell University

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