PRESCREENING OF RESISTS FOR EUVL FROM N7 DOWN TO N3 NODES (and beyond?) BY EBL AND HIM

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**Brief Outline of the Presentation**

- INFRASTRUCTURE and GLOBAL COLLABORATIONS
- Semiconductor Technology Advancement
- Next Generation Lithography Roadmap for HVM
- Resists Technology Challenges
- Designed & Developed Resist Formulations for NGL: EBL, HIM => EUV
- High Resolution Various L/S Patterning on Designed & Developed Resists Formulations
- Summary/recommendations
Resist Development and Formulation: Production facility at Advanced Materials Research Center (AMRC) & Materials Synthesis and scaleup facility @ IIT Mandi, India

- Facility for photosensitive compound production
- High Resolution Mass Spectrometer (HRMS)
- Quality control: Moisture titrator
- GPC Instrument
- 500 MHz NMR
- Single Crystal X-Ray Diffractometer
- Quality control: Viscosity tuning
- Yellow room for resist formulation
- Bulk scale production of polymers and allied chemicals
Center for Design & Fabrication of Electronic Devices (C4DFED), IIT Mandi, India

He⁺ Ion Beam Lithography (HIBL)  Electron Beam Lithography (EBL)

Reactive Ion Etching (RIE)  Fe-SEM  Ellipsometry
Sirius will allow us to follow the photodynamics processes under EUV irradiation with:

- Much higher intensity and resolution;
- Decrease experimental and data processing time;
- Carry out imaging experiments with high resolution;
- Use of several spectroscopic techniques in situ;
- Real time experiments
International collaborations: joint skills of polymer and materials synthesis and characterization, ebl and HIM patterning, etch, devices (IIT Mandi), and EUV photodynamic studies at LNLS/UFRGS Brazil. {EUVL Exposure & Patterning: CXRO LBNL/other tools/steppers pending}


EUV photodynamic studies at LNLS/UFRGS Brazil contd.


Mechanistic Insights of Sn-Based Non-Chemically-Amplified Resists under EUV Irradiation
Guilherme K. Belmonte, Suelen W. Cendron, Pulikanti Guruprasad Reddy, Cleverson A. S. Moura, Mohamad Ghulam Moinuddin, Jerome Peter, Satinder K. Sharma, Gabriela Lando, Marcelo Puiatti, Kenneth E. Gonsalves and Daniel E. Weibel,
Looking for Future ~ N7 down to N3 Node and Beyond

- Double Exposure (~193nm Immersion) lithography (DEL)
- Electron Beam projection Lithography (EBL) (Throughput typically 50x lower than optical lithography)
- Ion Beam projection Lithography (IBL) (Ions scatter much less than electron (higher resolution and throughput))
- NIL & DSA related lithography (Large area concerns)

✓ Extreme Ultraviolet Lithography (EUVL)  
(λ ~13.5 nm for higher resolution, no need RET, 15 to 50% cost reduction compared to multi-patterning schemes)

Since EUV sources are still scarce, thus the access for resists developer to run the experiments essential to develop materials, is limited
One of the key metrics for EUV resist is the sensitivity towards EUV radiation.
However, it is observed that the exposure energy within the resist film that is mainly responsible for the resists chemistry.
This applies to both high KeV electrons, He$^+$ ion and EUV photons.

\[ \lambda_{\text{De Broglie}} = \frac{1.23}{\sqrt{V}} \text{ nm} \]

Surface suffers from large interaction volume at the surface in case of e-beam (spot size 0.8 nm) and generated SE with \(~50\)eV

Beam is well collimated beyond the SE depth. Recoil contribution is negligible (spot size 0.35 nm)

A 92eV (13.5 nm) photon is absorbed, creates photoelectron with K.E. (~80 eV) that loses energy and liberates SE’s (10 to 60 eV) in resist that leads to further chemistry


We are developing organic, inorganic, hybrid resists containing elements having high EUV absorption capacity
EUV λ ~13.5 nm interaction with the resist.

The photon energy of EUV (13.5 nm, 92.5 eV) is much higher than ionization potential of resist materials (~10 eV). Reaction mechanisms change from photochemistry to radiation chemistry. (A review paper: Kozawa and Tagawa, 2010)

Acid diffusion is key problem in conventional resists.

Patterning-collapse, blurriness, and overlay issues.

Resolution (R), line edge and width roughness & sensitivity (RLS).

Photon absorbance in EUVL is 14X less than established ArF Lithography

So, There is a need to design a totally new chemistry for EUV photo-resist materials to support less than 16 nm technology


Dramatic enhancement of resist sensitivity is very difficult due to RLS trade-off

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Design principles for sub 7 nm node for EUV resists
Alessandro Vaglio Pret et al in “Modeling & simulation of low energy electron scattering in organic and inorganic photoresists”
Proc SPIE XXXIV 1014609 (27 March 2017)*

*Alternative materials with higher electronic absorption/atomic density are likely to help lithographic performance for future nodes by reducing electron blur and increasing absorption. However, adequate exposure dose, high aerial image quality and good chemistry have to follow:

• At 7 nm node, state of the art organic CARs and metal oxide materials have comparable lithographic performance and are ready for fab at appropriate exposure doses.

• At 5 nm technology node the organic materials start showing failure mechanism that cannot be attributed only to photon shot noise, while higher absorption and lower blur of metal oxide materials allow a better control of the printing features.

• At 3 nm technology node CARs fail printing while metal oxide materials are advantageous due to higher resolution and higher absorption.

*Based on modified version of electron scattering model in PROLITH

• Minimize shrinkage of nano patterns pre and post exposure processing => zero to marginal

• Convergent and divergent materials design and chemistries have been developed by us for preparing various resist formulations from hybrid/inorganic CARs to non-CARs as well as MOCs/MOFs, organometallics, organic-inorganic hybrids and activated monolayers in an attempt to meet the stringent requirements for EUVL, the all encompassing RLS. Initial prescreening by ebl and HIM.

• NOTE: Nanolevel molecular architecture essential for above to occur. #Intelligent materials design and synthesis. (Data Analytics/AI) #Excitation selectivity in model tin-oxo resist: a computational chemistry perspective, Jonathan H. Ma et al SPIE Advanced Lithography vol 11323EUVLXI 11321F (2020)
Synthesis of organic/inorganic and hybrids

NMR, IR, GPC, TGA, DSC, and XPS
Thin Film Formation

Pre-Bake
Spin coat (thickness <40 nm)
Sub 20 nm L/S patterns
Post Bake
Development

HRSEM Imaging
AFM Measurement
Developed Resist Technology

- Ni-Core MOC
- Cu-Core MOC
- PAS resist
- He+ & EBL Active RESIST
- MAPDST-triphenyl tin copolymer
- MAPDST-Dibutyl tin copolymer

Advanced sub-15 nm patterning

- Poly(TPMA)
- TPM-FEMA hybrid copolymer
- Sn based CAR
- Ni doped ZnO MOC
Evolution of Resists Technology Formulations

**Chemical Structures of HR Resists for NGL Node**

**Sub-22 nm**
- Non-ionic homo- and co-polymer
- High Mw
- High sensitivity
- For Sub-22 nm patterning

**Sub-18 nm**
- Polyarylenesulfonium salt based PR
- Organic-organometallic hybrid PR
- Moderate sensitivity
- Sub-15 nm

**Sub-15 nm**
- Polymer-nanoparticle hybrid PR
- Enhanced sensitivity
- Enhanced LWR

**Sub-10 nm**
- Metal-organic materials as smart PR
- Enhanced sensitivity
- Low Mw provides sub-7 nm patterns
<table>
<thead>
<tr>
<th>Resist: Negative tone</th>
<th>Resist</th>
<th>Sensitivity (µC/cm²)</th>
<th>Contrast</th>
<th>Resolution (nm)</th>
<th>n-CAR</th>
<th>Industrially optimized</th>
<th>LER/LWR (nm)</th>
<th>Shelf life (days)</th>
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<tbody>
<tr>
<td>HSQ</td>
<td>300-5000</td>
<td>2.2</td>
<td>&lt;10</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>3</td>
<td>Low @ RT (3 Months)</td>
</tr>
<tr>
<td>NEB-31</td>
<td>100</td>
<td>-</td>
<td>~40</td>
<td>Yes</td>
<td>Yes</td>
<td>-</td>
<td></td>
<td>Low (Salt)</td>
</tr>
<tr>
<td>MAPDST-Dibutyl tin polymer</td>
<td>430</td>
<td>2.27</td>
<td>~10</td>
<td>Yes</td>
<td>No</td>
<td>0.88 ± 0.02 / 1.22 ± 0.04</td>
<td>Test after 6 Month @ RT</td>
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<tr>
<td>MAPDST-Ag</td>
<td>172</td>
<td>2.77</td>
<td>&lt;18</td>
<td>Yes</td>
<td>No</td>
<td>1.56 ± 0.04 / 2.44 ± 0.04</td>
<td>To be tested</td>
<td></td>
</tr>
<tr>
<td>Ag-NPR-Terpolymer</td>
<td>50</td>
<td>1.45</td>
<td>&lt;18</td>
<td>Yes</td>
<td>No</td>
<td>2.64 ± 0.30 / 2.40 ± 0.26</td>
<td>To be tested</td>
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<tr>
<td>PAS</td>
<td>130-180</td>
<td>2.17</td>
<td>~20</td>
<td>Yes</td>
<td>No</td>
<td>1.83 ± 0.10 / 2.60 ± 0.10</td>
<td>To be tested</td>
<td></td>
</tr>
<tr>
<td>Poly(TPMA)</td>
<td>153</td>
<td>1.98</td>
<td>~50</td>
<td>Yes</td>
<td>No</td>
<td>-</td>
<td>Tested after 8 month</td>
<td></td>
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<tr>
<td>Ni Doped Zinc Oxide MOC</td>
<td>1400</td>
<td>&lt;10</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td>2.30 ± 0.34 / 2.93 ± 0.19</td>
<td>To be tested</td>
<td></td>
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<tr>
<td>Copper Oxide MOC</td>
<td>1400</td>
<td>~10</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td>2.08 ± 0.26 / 2.53 ± 0.15</td>
<td>To be tested</td>
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<tr>
<td>Nickel-mTA MOC</td>
<td>~20</td>
<td>1.78</td>
<td>&lt;10</td>
<td>Yes</td>
<td>No</td>
<td>1.81 ± 0.06 / 2.90 ± 0.06</td>
<td>To be tested</td>
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<tr>
<td>Nickel-DMA MOC</td>
<td>~35</td>
<td>&lt;10</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td>2.16 ± 0.04 / 3.03 ± 0.06</td>
<td>To be tested</td>
<td></td>
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Nickel based Metal Core Organic Cluster (Ni-MOC) Formulation for NGL Applications

- **Resist-A**
  Ni-mTA, MOC was synthesized by the reaction of nickel acetylacetonate, m-toluic acid & triethylamine at 65°C for 24h

- **Resist B**
  Ni-DMA, MOC was synthesized by the reaction of nickel acetylacetonate, 3,3 dimethyl acrylic acid & triethylamine at 65°C for 24h
Figure: The resist pattern of Ni-MOC by He$^+$ BL: (a) 18 nm (L/S), (b) 12 nm (L/3S), (c) 10 nm L/4S, and (d) 9 nm (L/4S) at ~22 μC/cm$^2$.

Rudra Kumar, Manvendra Chauhan, Mohamad G. Moinuddin et al., "Development of Nickel-Based Negative Tone Metal Oxide Cluster Resists for Sub-10 nm Electron Beam and Helium Ion Beam Lithography", ACS Applied Materials & Interfaces 12(17), 19616, (2020); doi:10.1021/acsami.9b21414
He\(^+\)BL HR Resists Patterns for NGL Node

Resist B: Nickel-DMA Higher Resolution Patterns at Dose = 35 μC/cm\(^2\)

Figure: The resist pattern of Ni-DMA by He\(^+\) BL: (a) 15 nm (L/S), (b) 14 nm (L/S), (c) 12 nm (L/S), (d) 10 nm (L/2S), and (e) 8 nm (L/2S) at ~ 35 μC/cm\(^2\)

All New Nickel Based Metal Core Organic Cluster (MCOC) Resist for N7+ Node Patterning:
Satinder K. Sharma, Rudra Kumar, Manvendra Chauhan, Mohamad Ghulam Moinuddin, Jerome Peter, Subrata Ghosh, Chullikkattil P. Pradeep, and Kenneth E. Gonsalves

*Proc.SPIE 11326 Advances in Patterning Materials and Processes XXXVII  1132604 (26 March 2020)*
Nickel doped Zinc Metal Organic Cluster (Zn-MOC) for e-beam lithography applications

- Zn-MOC was synthesized by the reaction of zinc acetate, m-toluic acid, and triethylamine at 65°C for 24h
- 10 wt% Nickel Doped Zn-MOC was developed with 2 wt% iodonium PAG
- Pattern was developed in acetonitrile for 30 sec

Substrate: 2” inch p-type silicon
Resist: Zn-MOC in ethyl lactate solution
Spinning conditions: 3000 RPM for 45 sec
Pre-exposure bake: 90°C for 60 Sec
Post exposure bake: 50°C for 60 Sec
e-beam Dose: 1400 µc/cm²

FESEM images of EBL exposed Ni doped ZnO-MOC

Figure. FESEM images of EBL exposed Ni doped ZnO-MOC resist: (a) 7 nm; (b) 10 nm; (c) 12 nm patterns
Copper Metal Organic Cluster (Cu-MOC) e-Beam Lithography Patterns for NGL

- Copper MOC was synthesized by the reaction of copper acetate, m-toluic acid, and triethylamine at 65°C; 24h
- Pattern was developed in acetonitrile for 30 sec

Substrate: 2” inch p-type silicon
Resist: Cu-MOC in ethyl lactate solution
Spinning conditions: 3000 RPM for 45 sec

Pre-exposure bake: 90 °C for 60 Sec
Post exposure bake: 50 °C for 60 Sec
e-beam Dose: 1400 µC/cm²

MOC platforms have a relatively simple material composition, CuOx clusters surrounded by organic ligands, & different activation mechanism compared to CARs.

Upon EUV exposure the CuOx clusters (MOC) and forms the resist pattern, whereas unexposed areas are soluble.
Polyarylene Sulfonium Salt – Universal Photo-Resist

- Polyarylene sulfonium salts were synthesized through free radical polymerization process.
- Molecular weight ~ 5,675 g/mol⁻¹; Poly Dispersity Index = 1.3
- Polyarylene sulfonium salts were successfully explored as a new organic n-CAR for higher to lower node lithographic applications.
- PAS acts as a dual tone resist. Both positive and negative tone features can be patterned while changing the developer.

Lithography Parameters

- Substrate: 4” inch p-type silicon
- Resist formulations: 2 wt% PAS in Acetonitrile
- Spinning parameters: 4500 RPM for 60 S
- Film Thickness: ~ 33 nm
- Pre exposure bake: 100ºC for 60 S
- Post exposure bake: 50 ºC for 60 S
- EUVL exposure: 37.7 mJ cm⁻²
- Developer: 0.05N TMAH/35 sec/DIW/30 S

Synthesis

Ref: ACS Appl. Mater. Interfaces., 2017, 9, 17–21

Figure: PAS thin films; a) Optical image; b) AFM image.
Polyarylene Sulfonium Salt based Resists – EUVL HR Patterning at LBNL Berkeley, USA

Ref: ACS Appl. Mater. Interfaces., 2017, 9, 17-21
1. Synthesis of EUV radiation sensitive ligands that introduce sufficient photochemical and mechanical stress to dissociate complex on exposure, based on concepts successfully developed in our lab. Photodynamic studies at Sirius LNLS Campinas Brazil. Significantly lower dose anticipated

2. Hybrid surface functionalized MOC or MOF with PAGs

3. Hybrid MOC or MOF/Inorganic or hybrid CARS and n-CARS.

4. Activated monolayers of discrete inorganics
Acknowledgments

Team Members from IIT Mandi

Dr Satinder K. Sharma EE IIT Mandi

Dr. Subrata Ghosh SBS IIT Mandi

Postdoctoral Research Fellows

Dr. Jerome Peter (Organometallic hybrid Resist Synthesis, Alumni)
Dr. Rudra Kumar (MOC Resist Synthesis)
Dr. Lalit Khillare (Organic Materials)
Dr. Gangadhar Purohit
Dr. Ravikiran Nagarjuna

Doctoral Research Fellows

Mr. Mohd. Ghulam Moinuddin
Mr Manvendra Chauhan (Lithography)
Dr. Guruprasad Reddy (Resist Synthesis, Alumni)

Advanced Material Research Centre (AMRC), IIT Mandi

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MAPDST-Dibutyl Tin Hybrid Copolymer for Higher Resolution Patterning Applications

MAPDST-Dibutyl tin copolymer

- MAPDST-Dibutyl tin copolymer was synthesized through free radical polymerization process.
- Molecular weight ~ 8221 g/mol; Poly Dispersity Index = 1.51
- Calculated x and y composition from NMR analysis is 3.8 : 96.2
- High optical density tin metal (10-12) incorporated in the resist structure.
- Sn-C bond undergo structural changes towards light.
- Resolution got improved 20 nm to 12 nm nodes compared to the poly-MAPDST

Lithography Parameters

Substrate: 2” inch p-type silicon
Resist: 3 wt% of MAPDST-Dibutyl tin copolymer in Acetonitrile solution

Spinning conditions: 4500 RPM; 1500 acceleration for 60 sec
Pre-exposure bake: 70 ºC for 60 Sec
Post exposure bake: 70 ºC for 60 Sec
Developers: 0.026N TMAH/80 sec; DI/60 sec

- Calculated thin film thickness 40-45 nm.
- Calculated RMS roughness = 0.3-0.7 nm with scale bar ±3nm

Helium ion (He\textsuperscript{+}) exposed Nano patterns at 50 \( \mu \text{C/cm}^2 \)

High Resolution He\textsuperscript{+} Resists Patterns for NGL Node

Sensitivity, Contrast

Resolution < 15nm

LWR/LER
Comparison of Photo-Exposed with e-beam Exposed MAPDST-co-ADSM

EUV exposed MAPDST-co-ADSM

EBL exposed for MAPDST-co-ADSM

Photo-Chemical

Sn

Photo-absorbance

Sn
Insights into the EUV Photo Fragmentation Mechanism

- The incorporation of a high EUV absorber centre (Sn) covalent linked in the MAPDST-co-ADSM resist exhibited improved sensitivity and lithography resolution down to sub-15 nm.
- The labile triflate moiety was partially lost under EUV irradiation but resisted the EUV absorbed energy up to 10 min of continuous irradiation.
- Dissociation of Sn-C and Sn-O with final formation of SnO₂ was observed.
- Changes in intensity and shape of the typical carbonyl untreated features indicated that new C=O functionalities were formed after irradiation and oxidation.

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