Advancement Towards Sub-15 nm Resists Patterning for High Volume Manufacturing of Semiconductor Industry

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Contribution and Funding
Brief Outline of the Presentation ......

- Semiconductor Technology Advancement
- Next Generation Lithography Roadmap for HVM
- Resists Technology Challenges
- Various Designed & Developed Resists Formulations for NGL; EBL, HIBL, EUV
- High Resolution Various L/S Patterning on Designed & Developed Resists Formulations
- Summary
Semiconductor Technology Advancement & Next Generation Lithography Roadmap (HVM)

Looking for Future ~ 10nm Node or 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)*

No consensus exists about the winner for HVM. Most likely will be EUVL !!!

Since EUV sources are still being under development phase, thus the limited access for resists developer to run the experiments, needed to develop materials ....... ???
One of the key metrics for EUV resist is the sensitivity towards EUV radiation. However, it is absorbed 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.

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

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

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

**ELENA’19**

**EUV (\(\lambda = 13.5 \text{ nm}\))**

**He+ ion (0.35 nm)**

**e-beam (0.8 nm)**

**EUV (\(\lambda = 13.5 \text{ nm}\))**


We are developing organic, inorganic, hybrid & , containing elements having high EUV absorption capacity resists for
EUV Photo Resists Technology Challenges

- 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. Ref: Garner, C Michael, "Lithography for enabling advances in integrated circuits and devices." Phil. Trans. R. Soc. A (2012) 370, 4015.

High Sensitivity (so allowing weak sources); High resolution (for small feature sizes); Low LER (line edge roughness); Post exposure instability; Minimal out-gassing (contaminate optics)

How to Improve RLS Trade-off for EUVL

Organic Resists

Inorganic Resists

Hybrid Resists (Blending)

Organo-Metallic Resists

- Organic Resists
- Inorganic Resists
- Hybrid Resists (Blending)
- Organo-Metallic Resists

Recently, organometallics have emerged as promising NGL resists applications.
IIT Mandi Developed Indigenous Resists Technology

Advanced sub-15 nm patterning

- Poly(TPMA)
- Ni-Core MOC
- Cu-Core MOC
- PAS resist
- He+ & EBL Active RESIST
- MAPDST-triphenyl tin copolymer
- EUVL
- Sn based CAR
- ZnO MOC
- MAPDST-Dibutyl tin copolymer

IIT Mandi Design & Developed Resists for NGL
Evolution of Resists Technology Formulations at IIT Mandi (H.P), India

**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
Polyarylene Sulfonium Salt – Universal Photo-Resist

❖ Polyarylene sulfonium salts were synthesized through free radical polymerization process.

❖ Molecular weight ~ 5,675 g/mol\(^{-1}\); Poly Disparity Index = 1.3

❖ Polyarylene sulfonium salts were successfully explored as a new organic n-CAR for higher to lower node lithographic applications.

❖ PAS act as a dual tone resist. Both the 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

![Synthesis Diagram](image)

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

**Figure:** PAS thin films; a) Optical image; b) AFM image.

\(R_z = \sim 0.349 \text{ nm}\)
Polyarylene Sulfonium Salt based Resists – EUVL HR Patterning at LBNL Berkeley, USA

Line Patterns

Complex Patterns

Ref: *ACS Appl. Mater. Interfaces*, 2017, 9, 17–21
MAPDST-triphenyl tin copolymer

- MAPDST-Triphenyl tin copolymer was synthesized through free radical polymerization process.
- Molecular weight 6933 g/mol; Poly Disparity Index = 2.0
- Calculated x and y composition from NMR analysis is 97.3: 2.7
- Resolution got improved 20 nm to 15 nm nodes compared to the poly-MAPDST
- Calculated thin film thickness ~ 45 nm
- 30 & 20 nm patterns @ 450 uC/cm² and 18 & 15 nm @ 700 uC/cm²
- e-beam exposure dose used 200-700 uC/cm²
- Due to incorporation of tin monomer poly-MAPDST resolution got improved from 20 nm to 15 nm nodes.
High-resolution XPS spectra for the S 2p region of the pristine and irradiated films at 103.5 eV.

The loss of SOx like $\text{SO}_4$, $\text{SO}_3$, $\text{S}=\text{O}$ are functional groups with the increase of irradiation time (decomposition of the triflate moeity).
HR-XPS spectrum of untreated film shows mainly a low oxidized Tin (Ph4-Sn-O/Ph3-Sn-O) [Ref]

- A new signal appearing at higher binding energy can be correlated with SnO/SnO₂ oxidation states of Tin.

- Overlapping of the XPS signals corresponding to O-Sn and O-C

- Results finally are confirming that the Tin linked to the polymer backbone and 3 aromatic rings is oxidizing when irradiated at 103.5 eV

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MAPDST-Dibutyl Tin Hybrid Copolymer for Higher Resolution Patterning Applications

MAPDST-Dibutyl tin copolymer was synthesized through free radical polymerization process.
- Molecular weight ~ 8221 g/mol; Poly Disparity 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\(^+\)) exposed Nano patterns at 50 \(\mu\text{C/cm}^2\)

Sensitivity, Contrast

Resolution < 15nm

Trade-off

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

Photo-absorbance

Sn

Changed Polarity

Untreated

15s

30s

120s

300s

174 172 170 168 166 164 162 160

174 172 170 168 166 164 162 160

Sn 3d

Sn 3d

Sn 3d

Sn 3d

498 496 494 492 490 488 486 484 482

500 498 496 494 492 490 488 486 484 482

UNEXPOSED Sn

EXPOSED Sn

Relative Intensity (a.u)

Binding Energy (eV)

Relative Intensity (a.u)

Binding Energy (eV)
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 de typical carbonyl untreated features indicated that new C=O functionalities were formed after irradiation and oxidation
Resist Synthesis

- Stable silver nano-particles were synthesized by a phase-transfer reaction of silver ions with 1-dodecanethiol as a capping agent.
- Silver nano-particles were blended with MAPDST at room temperature and under a nitrogen atmosphere.
- The synthesis was executed with a 24 weight % of silver nano-particles and 76 weight % of MAPDST in acetonitrile solution.

Lithography parameters

- Resist solution: 1.5 wt % of MAPDST-Ag resist was dissolved in 1 ml of Ethyl lactate solution
- Spinning parameters: 5000 RPM / 1500 acceleration for 40 sec.
- Prebake temperature: 70 °C for 60 sec
- Post bake temperature : 55 °C for 60 sec
- Developer : 0.22N Tetra Methyle Amonium hydroxide for 60 sec/DI water rinsing at 60 sec
- Various high resolution L/S and complex patterns at ~ 300uC/cm² doses
Various L/S & Complex EBL Patterns on MAPDST-Ag Copolymer Hybrid Resist

L/10S
L/5S
L/4S
L/2S
L/S

100 nm pitch
50 nm pitch
CD 18nm

NRT Analysis for NP Hybrid Copolymer Resist

Sensitivity Curve for MAPDST-Ag

\( \gamma = 2.77 \)

\( E_0 = 172 \ \mu\text{C/cm}^2 \)
NP based Hybrid Copolymer Resist High Resolution HIBL Line Patterns Down to ~ 11 nm for NGL

L/S patterns

- The neat organic thin films are significantly limited for HR patterns. Thus the inclusion of metals NP in resist is an reasonable approach to improve the resist sensitivity by increasing the irradiation absorbance compared to traditional organic resist.

- Due to metal content into the film, a thinner film thickness (as low as 20 nm) can be applied for the collapse free nano-patterning with high etch resistance.

- MCR are to keep a high-performing switching solubility mechanism, to maintain patterning fidelity & to mitigate shot noise with a better trade-off between sensitivity and LER compared to CARs.
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 dissolved.

Figure. Synthesis process of Cu-MOC

Figure. Single Crystal XRD of Cu-MOC

Figure. Single line exposure patterned Cu-MOC: 14 nm at the dose 1400 µC/cm²
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℃ 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℃ for 60 Sec
Post exposure bake: 50℃ for 60 Sec
e-beam Dose: 1400 µC/cm²

**Figure.** FESEM images of EBL exposed Ni doped ZnO-MOC resist (dose 1400 µC/cm²)
Nickel Metal Organic Cluster (Ni-MOC) Formulation for NGL Applications

- Nickel MOC was synthesized by the reaction of nickel acetylacetonate, m-toluic acid, & triethylamine at 65°C for 24h
- Pattern was developed in MIBK:IPA = 1:3 for 50 sec

Substrate: 2” inch p-type silicon
Resist: Ni- 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

Figure. ~11 nm at the dose 410 μC/cm²
He$^+$-Ion Beam Exposure on Ni-MOC (Dose: $\mu$C/cm$^2$) Resist for NGL Application

(a) 12 nm L/2S  \hspace{1cm} (b) 13 nm L/2S  \hspace{1cm} (c) 14 nm L/2S  \hspace{1cm} (d) 15 nm L/2S

(e) 12 nm L/3S  \hspace{1cm} (f) 10 nm L/4S  \hspace{1cm} (g) 9 nm L/4S  \hspace{1cm} (h) 18 nm L/S

Figure. Pattern analysis of: (a-d) L/2S features at variable doses 20 $\mu$C/cm$^2$, 30 $\mu$C/cm$^2$, 40 $\mu$C/cm$^2$ and 50 $\mu$C/cm$^2$, respectively. (e-g) L/3S and L/4S features at doses 20 $\mu$C/cm$^2$, respectively. (h) L/S features at 40 $\mu$C/cm$^2$. 
Sensitivity Analysis of NiO-MOC resist (Ni-mTA)

* More information related to NiO-MOC will be presented in Poster.

Nickel-DMA Cluster (Ni-DMA) Formulation for NGL Technology Node

- Nickel-DMA was synthesized by the reaction of nickel acetylacetonate, 3,3 dimethyl acrylic acid, and triethylamine at 65°C for 24h
- Pattern was developed in MIBK:IPA = 1:3 for 50 sec

Substrate: 2" inch p-type silicon
Resist: Ni-DMA 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

Figure. Contrast curve comparison between EBL and HIBL

\[ E_{\text{HIBL}} = 22.89 \, \mu\text{C/cm}^2 \]
\[ \gamma_{\text{HIBL}} = 1.789 \]
\[ E_{\text{EBL}} = 328 \, \mu\text{C/cm}^2 \]
\[ \gamma_{\text{EBL}} = 2.504 \]
He⁺ (HIBL) HR Resist Patterns on Ni-MOC at Various L/S for NGL Node

- **15nm**
  - L/3S
  - L/2S
  - L/S

- **12nm**
  - L/3S
  - L/2S
  - L/S

- **10nm**
  - L/4S
  - L/3S
  - L/2S

- **8nm**
  - L/4S
  - L/2S

He⁺ Dose ~35 µC/cm²
### Summary of IIT Mandi Developed Resists for Global Photoresists Market

<table>
<thead>
<tr>
<th>Resist</th>
<th>Industrially Adopted Photoresists</th>
<th>HSQ</th>
<th>NEB-31</th>
<th>MAPDST-Dibutyl tin polymer</th>
<th>MAPDST-Ag</th>
<th>Ag-NPR-Terpolymer</th>
<th>PAS</th>
<th>Poly(TPMA)</th>
<th>Ni Doped Zinc Oxide MOC</th>
<th>Copper Oxide MOC</th>
<th>Nickel-mTA MOC</th>
<th>Nickel-DMA MOC</th>
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<td>1.83 ± 0.10 / 2.60 ± 0.10</td>
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**Indigenous Resist by IIT Mandi**

- HSQ: High Sensitivity Qualitative Resist
- NEB-31: Novel Eco-friendly Resist
- MAPDST-Dibutyl tin polymer
- MAPDST-Ag
- Ag-NPR-Terpolymer
- PAS
- Poly(TPMA)
- Ni Doped Zinc Oxide MOC
- Copper Oxide MOC
- Nickel-mTA MOC
- Nickel-DMA MOC

**Industrially Adopted Photoresists**

- HSQ: High Sensitivity Qualitative Resist
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- MAPDST-Dibutyl tin polymer
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- PAS
- Poly(TPMA)
- Ni Doped Zinc Oxide MOC
- Copper Oxide MOC
- Nickel-mTA MOC
- Nickel-DMA MOC
We successfully synthesize various radiation sensitive photoresists including PAS, MAPDST-ADSM, MAPDST blend Ag, CuO-MOC, Nickel doped ZnO-MOC, Ni based organic Cluster, at the facility available in IIT Mandi, India

➢ 20 nm line features of the PAS resist was achieved at the EUV dose 37.7 mJ cm$^{-2}$.

➢ 12, 15, 20, 30 nm with various L/S were achieved by using MAPDST-triphenyl tin hybrid resists (~100 to 1200 µC/cm$^2$)

➢ 15 nm features with L/S feature were achieved by using MAPDST-butyl tin hybrid resists at He$^+$ dose of 50 µC/cm$^2$

➢ ~2nm Ag nano particle were blended inside the MAPDST polymer to increase the sensitivity for higher throughput

➢ NiO-MOC resist generates 9 nm Line Patterned at the He$^+$-ion dose ~20 µC/cm$^2$

➢ CuO-MOC and Nickel doped ZnO-MOC resists generate minimum 14 nm and 7 nm Line Patterns, respectively

➢ Ni based MOC resist generates 12 nm Line space Pattern at the He+ (HBL) at dose ~35 µC/cm$^2$
Resist Development and Formulation: Production facility at Advanced Materials Research Center (AMRC) & Resist Group facility @ IIT Mandi

- High Resolution Mass Spectrometer (HRMS)
- Facility for photosensitive compound production
- Bulk scale production of polymers and allied chemicals
- Quality control: Moisture titrator
- Resist for sharp wall patterning
- Quality control: Viscosity tuning
- Yellow room for resist formulation
- Single Crystal X-Ray Diffractometer
- 500 MHz NMR
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Dr. Pradeep Parameswaran (Inorganic), IIT Mandi

Postdoctoral Research Fellows
Dr. Jerome Peter (Organic Resist Synthesis)
Dr. Rudra Kumar (MOF Resist Synthesis)

Doctoral Research Fellows
Mr. Mohd. Ghulam Moinuddin (Lithography)
Mr. Guruprasad Reddy (Resist Synthesis)

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