Nanoparticle EUV Photoresist Studies

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1. Zr nanoparticle photoresist studies

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3. Summary
Small molecular size and good etch resistance are advantages with nanoparticle photoresist (NP).

**NP design**

- **Inorganic Cores**
  - Small molecular size metal oxide
  - Good etch resistance

- **Organic Ligands**
  - Multiple carboxylic acid choices
  - Dispersion in organic solvents

**Process flow**

- Si wafer → NP coating → NP film → Soft bake → EUV Exposure → Development with organic solvent → Exposed area remains → Negative tone

- Mask

**Litho performance**

- Exposed by NXE3300
- Resolution: 27nmLS
- Litho workshop 2016

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Outgas measurement with e-beam/EUV exposure

Expose samples with electrons or EUV and measure the outgassed species. Measure outgassed species with a mass spectrometer to determine reaction in the film during exposure.

Can we detect these components?

 ✓ Outgas measurement test with e-beam/EUV exposure has been carried out.

Collaboration with Prof. Robert Brainard and Prof. Greg Denbeaux
**Preliminary result from outgas test**

Background was Subtracte(d) (The outgassing from the virgin silicon wafer was used as the background signal).

**CO₂ Mass Spectrum (Electron Ionization)**

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

**MS condition:**
- Extrel MAX300 Quadrupole Mass Spectrometer
- Multiplier Voltage: 1380 V
- Ionization Energy: 70 eV

**Collaboration with**
Prof. Robert Brainard
and Prof. Greg Denbeaux

- Zr type NP with mechaacrylic acid ligand showed CO₂ outgas during 80eV exp.
- Ligand dissociation mechanism seems to be occured.

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Film analysis with EUV exposure / IR

Sample: Zr type NP with methacrylic acid ligand
Dose: 50mJ/cm², 100mJ/cm²

EUV exposure at LBNL
Wafer analysis at Cornell

IR spectra (powder)

Asymmetric COO-

C-O stretching

Symmetric COO-

Zr-O

IR Intensity after exp. (divided by Zr-O peak)

Symmetric COO-

Asymmetric COO-

C-O stretching

✓ IR analysis of film also indicates ligand dissociation mechanism.

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Ligand dissociation mechanism seems to be main mechanism but need further study.
EUV performance of Zr type NP

- Scum improvement was achieved by PAG, ligand and process optimization.
- Below 20nm resolution is not achieved so far due to scum issue.

Resolution data =>

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New metal cores - Motivation -

Motivation of new metal core studies

![Graph showing EUV Photoabsorption (cm²/gm) vs. Atomic Number with points for H, C, O, Ti, Zn, In, Zr, and Hf.](image)

Atomic Data and Nuclear Data Tables, 54, 181-342 (1993)

Preliminary KrF microscale patterning

- Zr type NP: 150mJ/cm²
- Hf type NP: 150mJ/cm²
- Ti type NP: 150mJ/cm²
- Zn type NP: 150mJ/cm²
- In type NP: 150mJ/cm²

✓ Microscale patterning was achieved with Zr, Hf, Ti, Zn and In NP using ABM contact aligner.

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New metal cores - KrF and e-beam patterning -

KrF nanoscale patterning

Ti type NP

SEM image

150mJ/cm², 500nmLS

Zn type NP

SEM image

150mJ/cm², 500nmLS

In type NP

SEM image

150mJ/cm², 500nmLS

E-beam patterning with new metal core NP

Zr type NP

45nmLS

New metal core

45nmLS

30nmLS

25nmLS

20nmLS

✓ Nanoscale patterning was also achieved using Ti, Zn and In type NPs.

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New metal cores - EUV patterning at LBNL B-MET -

- 22nm line and space
- 21nm line and space
- 20nm line and space
- 19nm line and space
- 18nm line and space

✓ New metal core showed 18nm line and space resolution with EUV exposure.

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New metal cores - EUV patterning at PSI -

- 29.06 mJ/cm$^2$ for 25nm line and space
- 78.37 mJ/cm$^2$ for 18nm line
- 82.35 mJ/cm$^2$ for 16nm line

✓ 16nm line and space pattern with no scum was achieved at PSI.

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NP litho performance progress

- 27nm LS at IMEC
- 26nm Line at B-MET
- 27nm LS at IMEC
- 18nm LS at B-MET
- 16nm LS at PSI

~2015  SPIE2016  ~2016  SPIE2017

Recent results will be updated

Excellent progress was achieved by new metal core application.

2/27(Mon) SESSION2 [10143-4] 2:40PM~
Title: Nanoparticle photoresist studies for EUV lithography
Presenter: Prof. Chris Ober

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Summary

- Ligand dissociation seems to be main patterning mechanism from outgas and IR tests.
- 16nmLS without scum was achieved by new metal core application.
- Nanoparticle photoresists have a great deal of room for EUV litho performance improvement.
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