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Chemically-Amplified Negative-Tone Molecular Resist using Polarity Change Reaction for EUVL

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OUTLINE

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- INTRODUCTION – Motivation
- CHALLENGE for LER Reduction
- DESIGN of CA Negative-Tone Molecular Resist using Polarity Change Reaction
- EB Lithographic Performance
- EUV Lithographic Performance
- MODIFICATION of Resist Compound
- SUMMARY

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Motivation :

hp 90 nm : Polymer Resists are used for mass production

Large LER due to the Resists

→ Elicitation of Transistor Performance Fluctuation

hp 32 nm : EUVL is the most promising lithography platform

Issues: Limits of CA Resists

Simultaneously meeting 3 major specifications is difficult

Sensitivity (Dose : 2-5 mJ/ cm^2)

LWR (LER) (< 1.5 nm)

Resolution (< 30 nm)

Approach to LER Reduction

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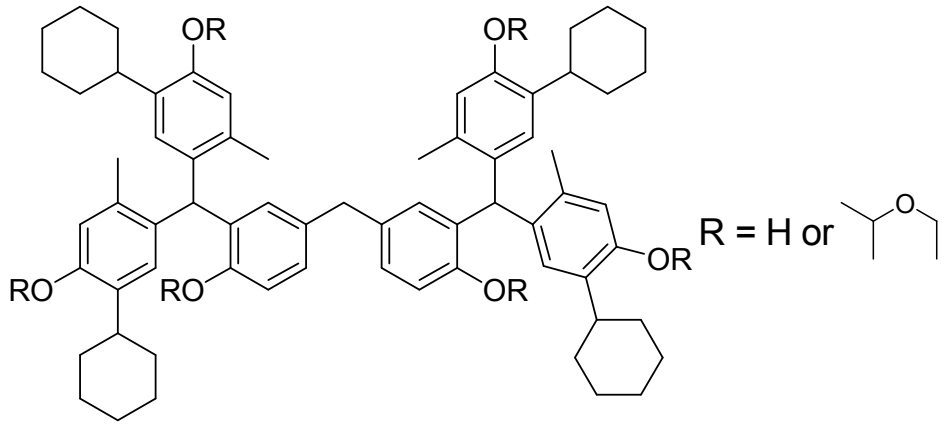
LER is the most critical issue of EUV resists

Molecular Resist

LER Origins of conventional resists

1. **Large molecular size**
2. **Large molecular weight distribution**
3. **Acid diffusion**
4. **Nonuniformity of resist components**



3M6C-MBSA-EE ■ **Positive, CA**

T. Hirayama, et al., Jpn. J. Appl. Phys. 44, 7B (2005) 5484.

Material Design of Negative-Tone Molecular Resist

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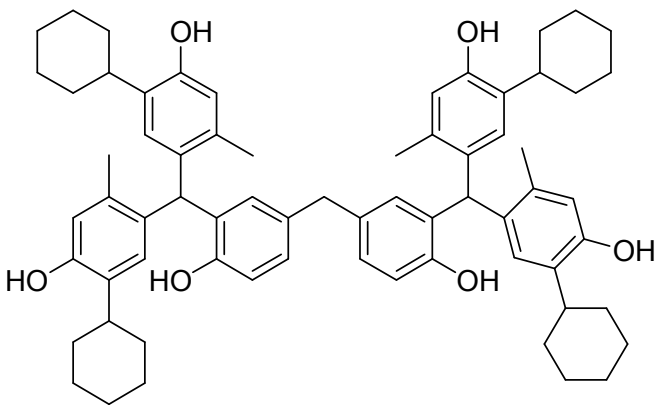
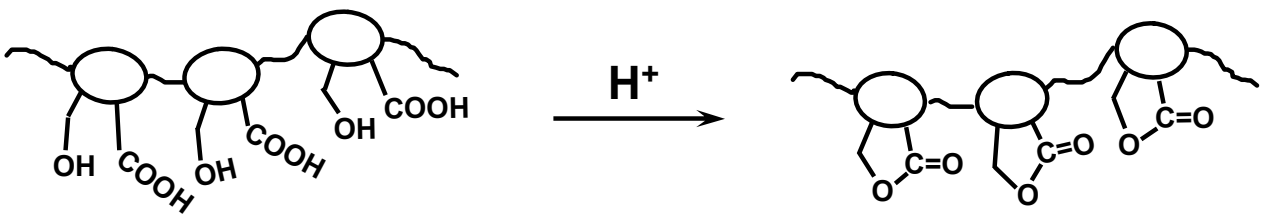
- Low Molecular Weight/ Small Molecular Weight Distribution
  → Apply polyphenols used in positive molecular resist
- Non-Crosslinking Mechanism
  → Polarity Change Reaction（Intramolecular Esterification）
- Fundamental study by EB ⟺ EUV evaluation



polyphenol: 3M6C-MBSA



Intramolecular Esterification (Lactonization)

T. Hattori, et al., Chem. Mater., 10 (1998) 1789.

Synthesis

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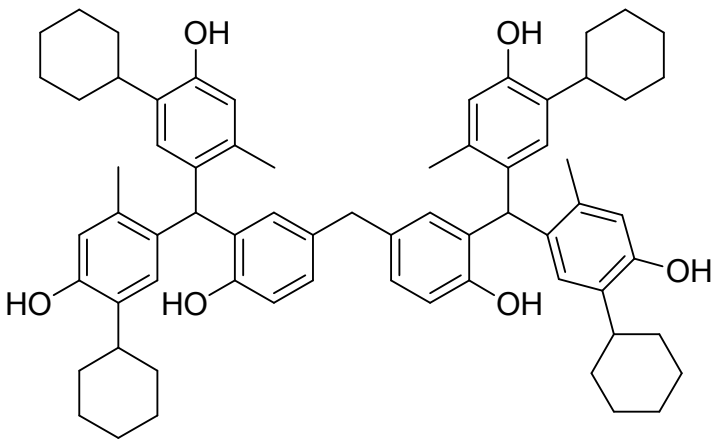
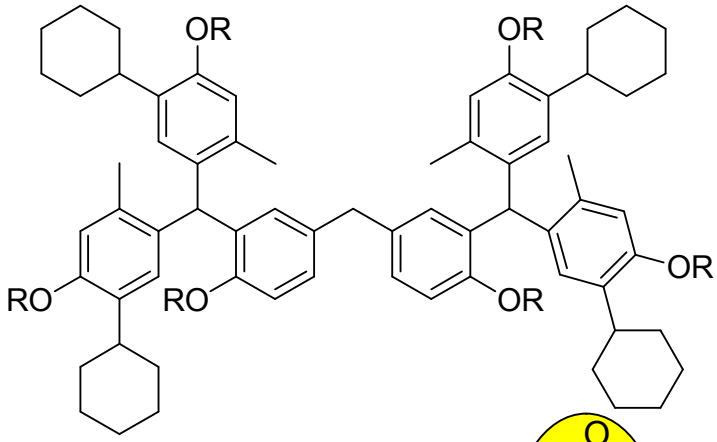
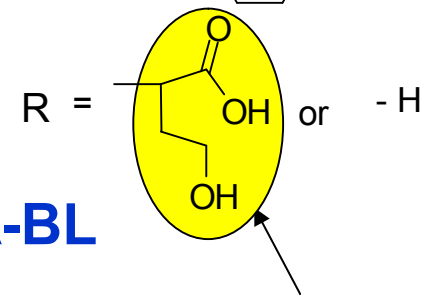


3M6C-MBSA

- amorphous film
- alkaline soluble
- etching durability
- diameter : ca. 2 nm

2 steps





3M6C-MBSA-BL

γ-hydroxycarboxyl group

- no organic elimination group in acid-catalyzed reaction
- good thermal property

Composition Analysis

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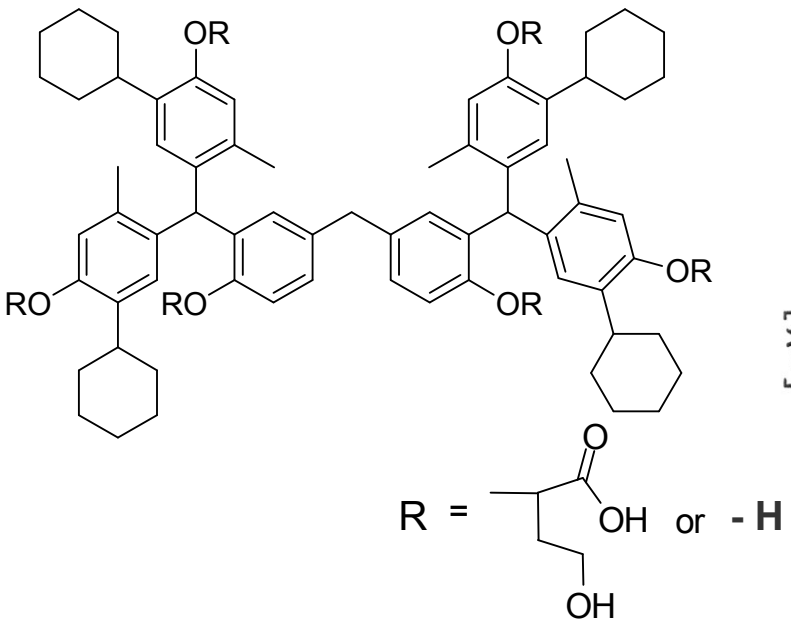

3M6C-MBSA-BL

protection ratio of phenolic –OH : 1.1 (average)

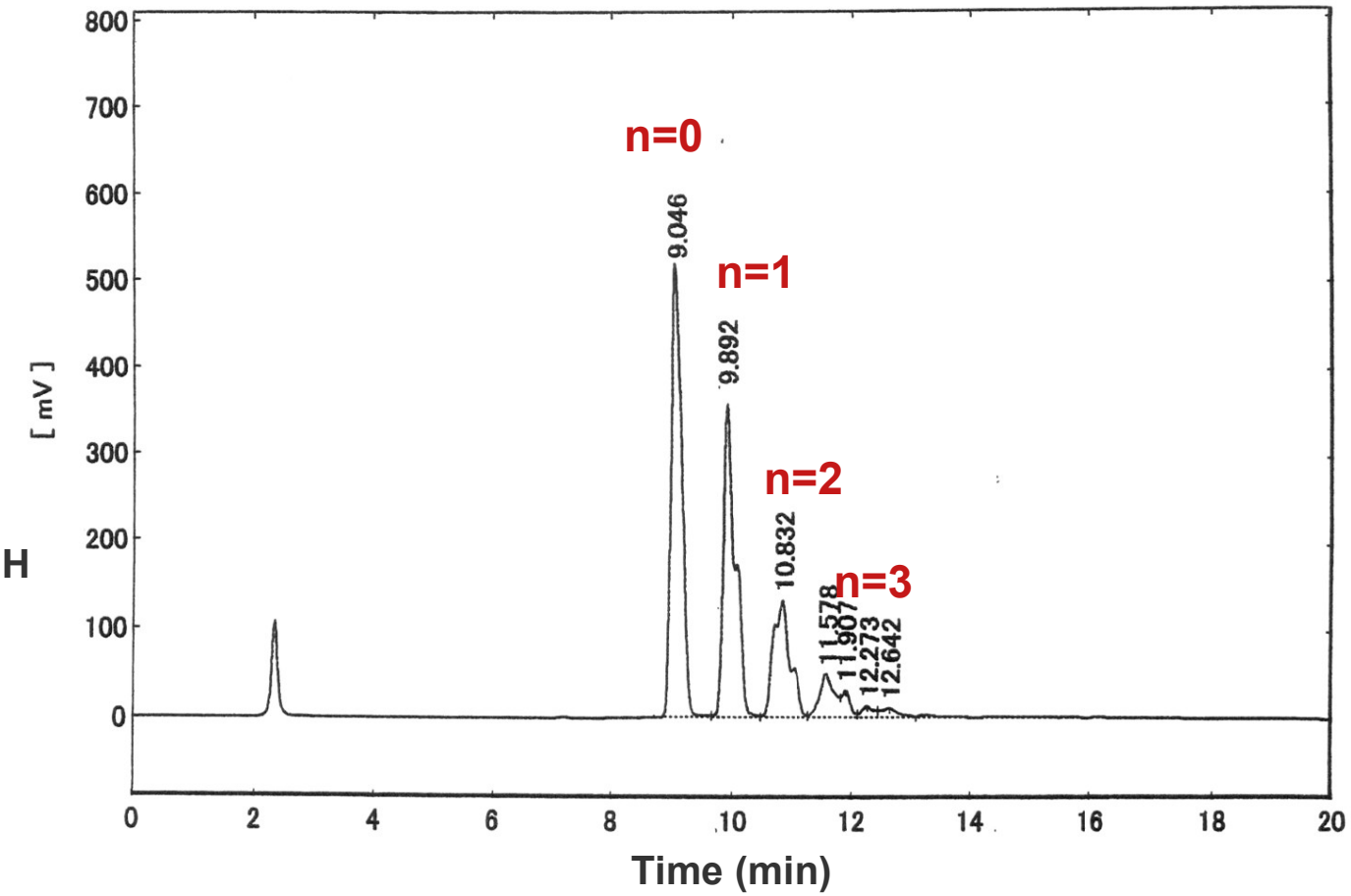

Fig. HPLC chromatogram (lactone form)

n : protected number of 3M6C-MBSA-BL

EB Lithographic Property
- Resist Formulation

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Table 1 Formulation of the resists evaluated

Sample	-BL Functionalized polyphenol base compound (X)	Composition (X/ PAG/ Quencher, in wt ratio)
Resist A	3M6C-MBSA-BL	100/10/ 0
Resist B	3M6C-MBSA-BL	100/15/ 0
Resist C	3M6C-MBSA-BL	100/30/ 0
Resist D	3M6C-MBSA-BL	100/10/ 0.003
Resist E	3M6C-MBSA-BL	100/12/ 0.0036

EB Lithographic Property
- PAG Concentration

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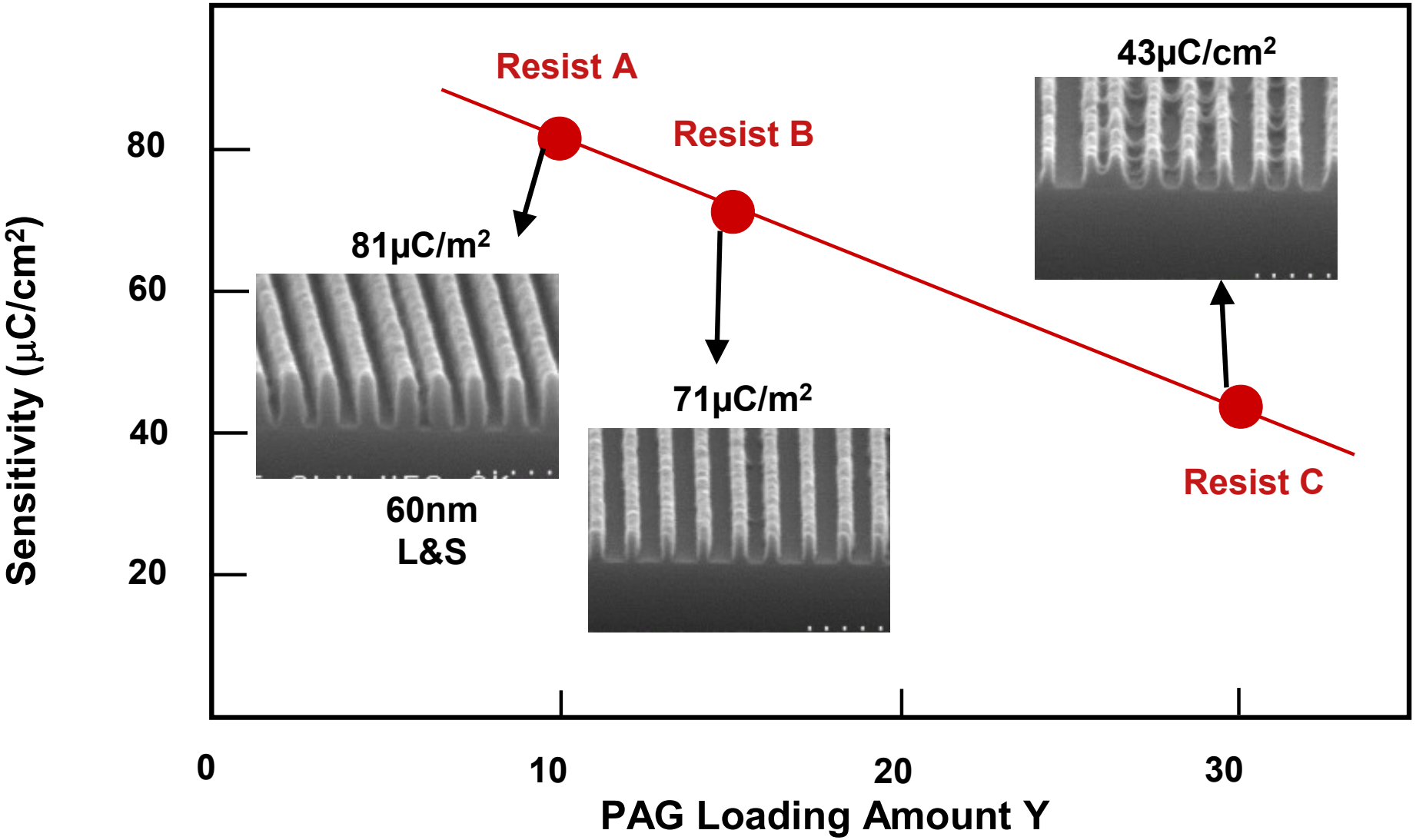
3M6C-MBSA-BL/ PAG = 100/ Y



K.Kojima, et al., Proc. SPIE, 6153 (2006) 164

EB Lithographic Property
- Optimization for Resolution

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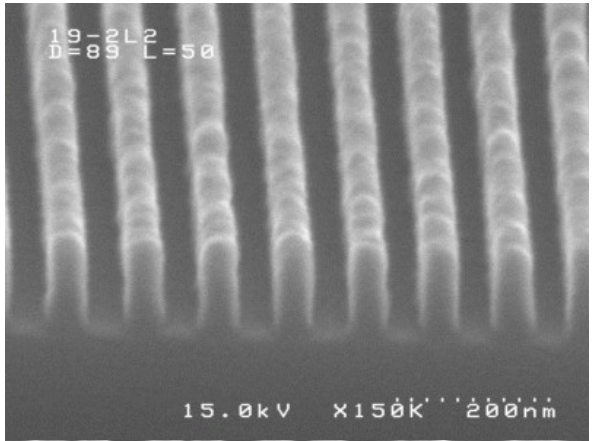
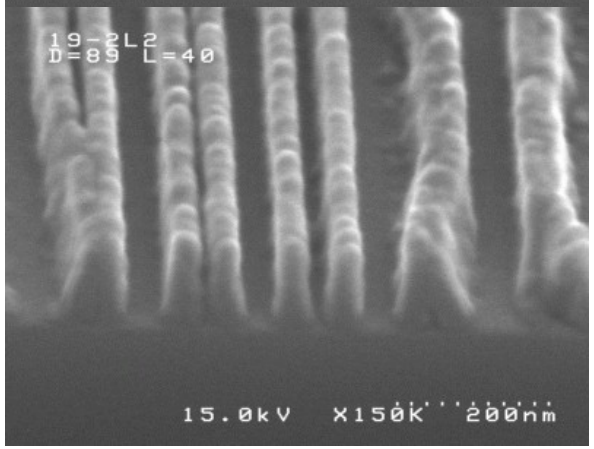
Resist D : thickness = 151 nm

Resist E : thickness = 131 nm

50nm

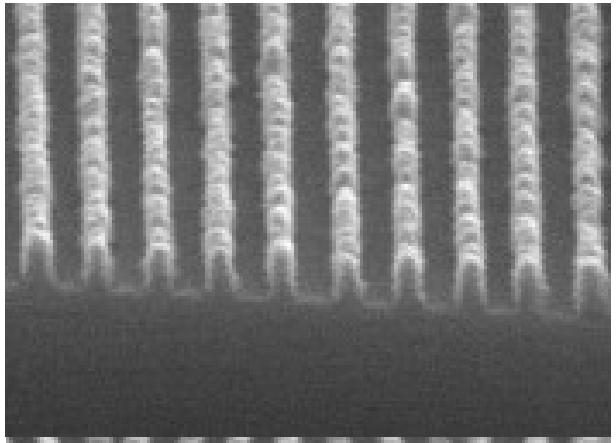


40nm

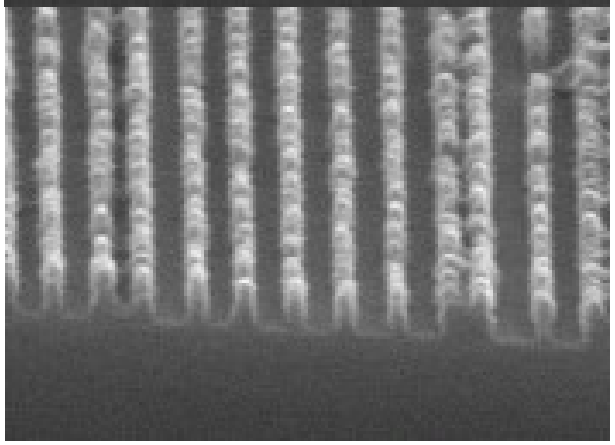


89μC/cm^2

50nm



40nm



72μC/cm^2

LER of Resist E

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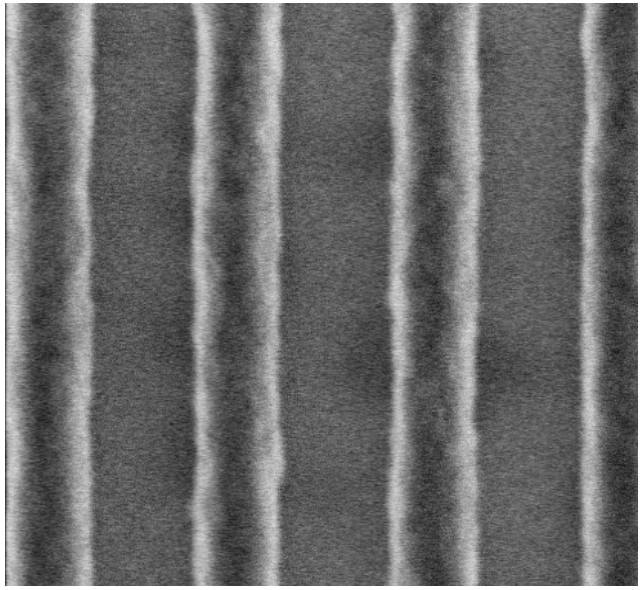

Fig. 100 nm L&S pattern of Resist E (X 200k SEM image)

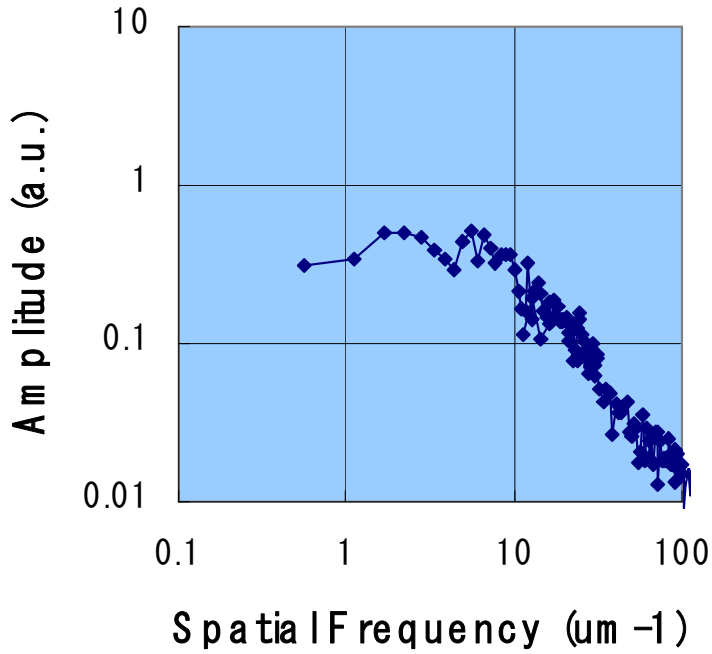

Fig. Fourier Amplitude Spectrum

LER (*L*=620 nm) = 4.5 nm

LER (*L*=1800 nm) = 6.2 nm

K.Kojima, et al., Proc. SPIE, 6153 (2006) 164

EUV Lithographic Performance (1)

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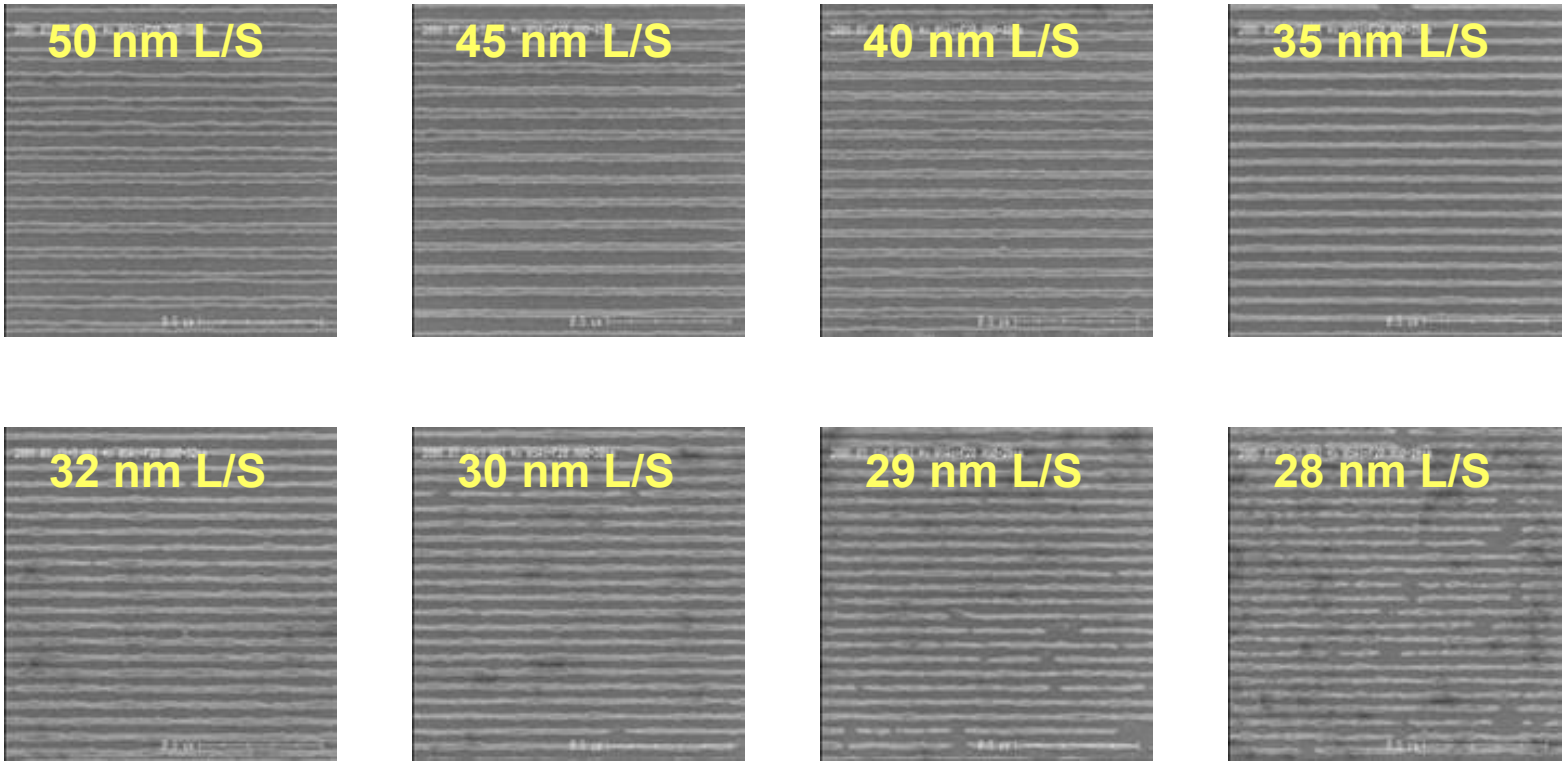
Resist Sample: Resist E

ASET High-NA Small-Field Exposure Tool *(HiNA3), NA=0.3, σ=0.0

Sensitivity: 45 mJ/cm^2



** H. Oizumi, et al., Proc. SPIE Vol. 5751, p. 102 (2005).*
H. Oizumi, et al., Proc. SPIE Vol. 6151, p. 765 (2006).

Modification of Resist Compound

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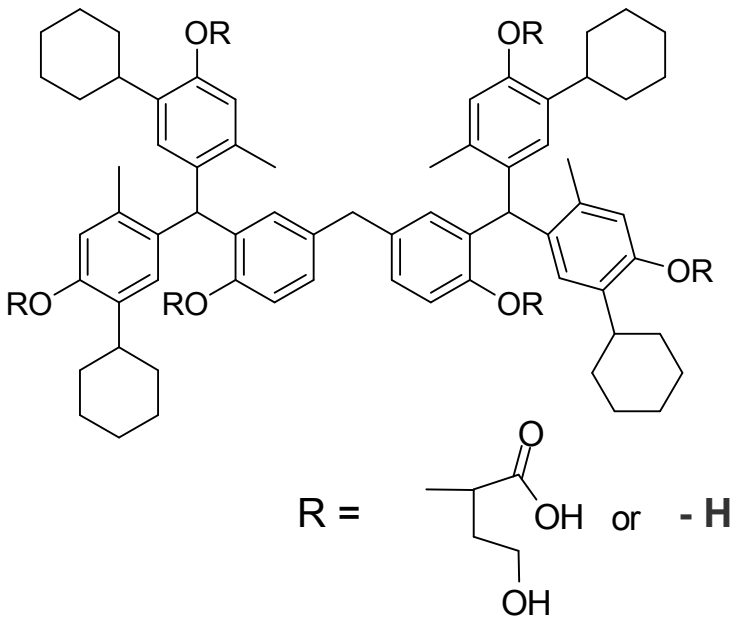

3M6C-MBSA-BL1

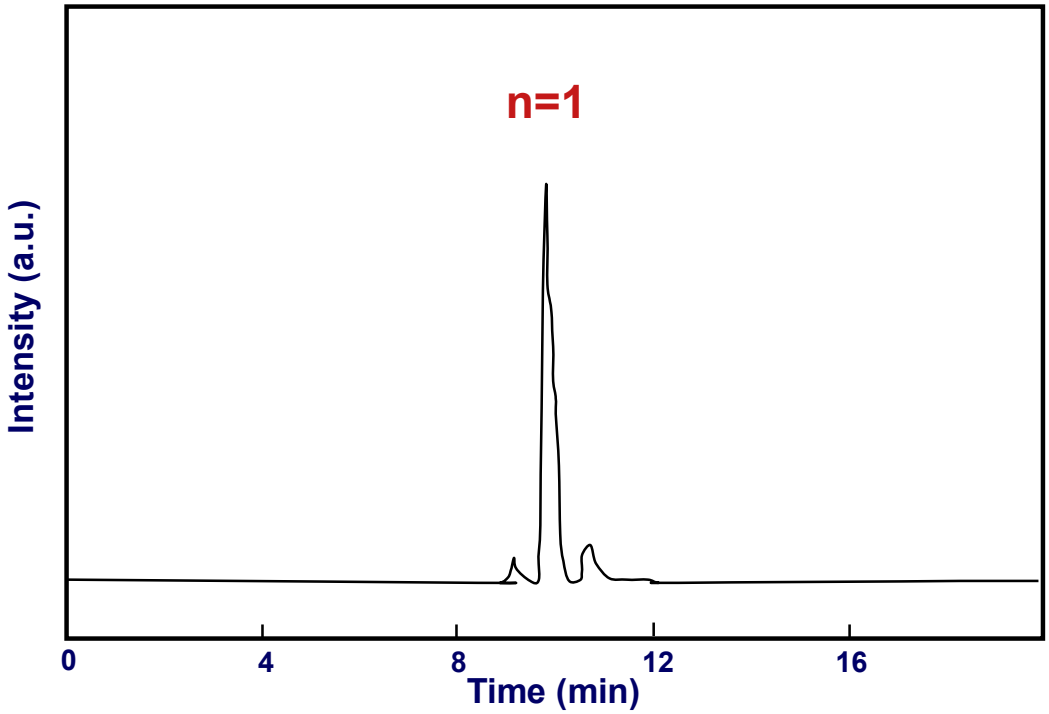

Fig. HPLC chromatogram (lactone form)

n : protected number of 3M6C-MBSA-BL

One functional group in a molecule

EB Lithographic Performance of 3M6C-MBSA-BL1

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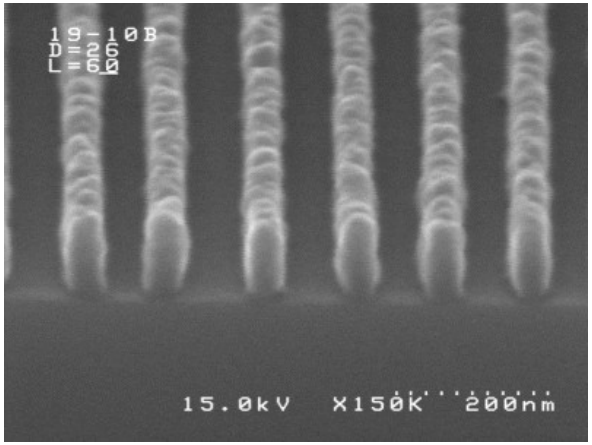
Table Formulation of Resists using 3M6C-MBSA-BL1

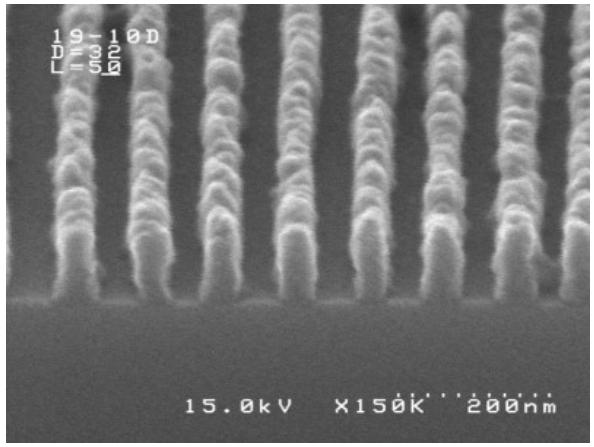
Sample	Formulation (BL-1/ PAG/ Q, in wt.ratio)	Dev. (%)	Sensitivity (uC/cm^2)	Resolution (nm)	Thickness (nm)
Resist G	100/ 12/ 0.036	2.38	26	60	146
Resist H	100/ 15/ 0.3	2.38	32	50	145

Resist G



60 nm L/S @26 uC/cm^2

Resist H



50 nm L/S @32 uC/cm^2

EUV Lithographic Performance (2)

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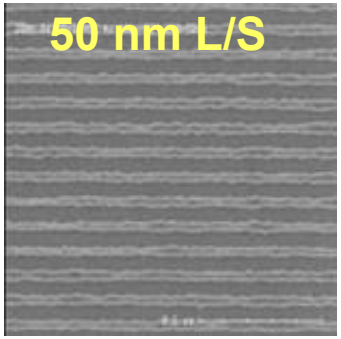
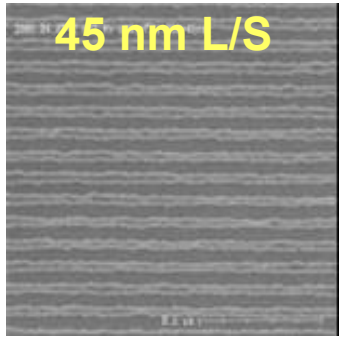
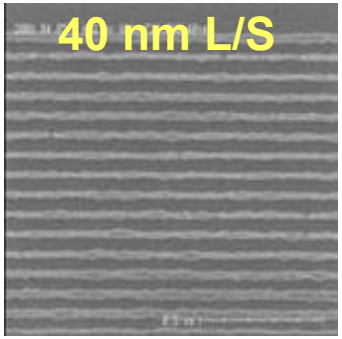
Resist Sample: Resist G

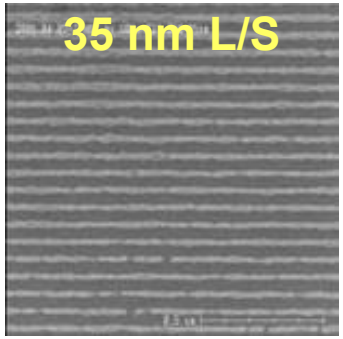
ASET High-NA Small-Field Exposure Tool *(HiNA3), NA=0.3, σ=0.0

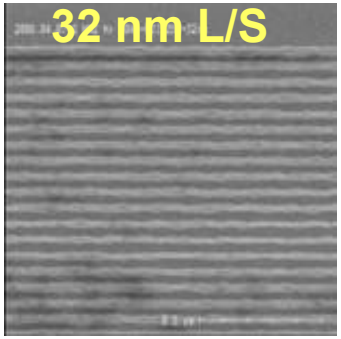
Sensitivity: 35 mJ/cm^2, Thickness: 61 nm

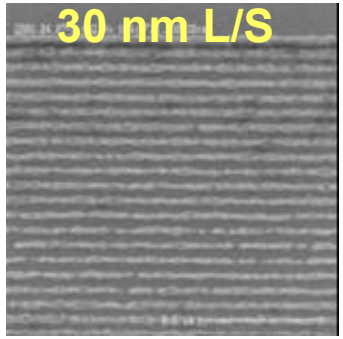


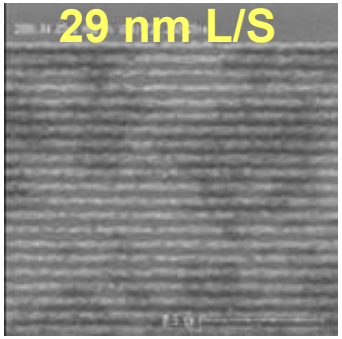


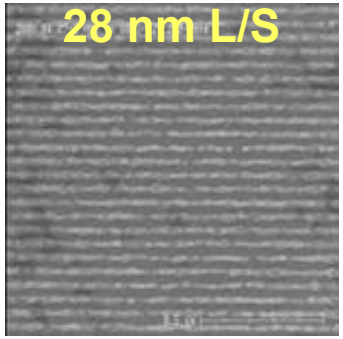












Summary

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1. By means of introducing polarity change chemistry to a polyphenol, a base compound for negative-tone molecular resist of 3M6C-MBSA-BL was successfully synthesized.
2. 40-nm L&S by EB and 28-nm resolution by EUV was achieved with the 3M6C-MBSA-BL based resist.
3. A modified resist comound 3M6C-MBSA-BL1 with one functional group in a molecule was obtained.
4. 50-nm L/S was obtained at an improved dose of 32 uC/cm^2.

Future Works

1. LER measurement by EUV
2. Optimization of resist composition

Acknowledgement

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