Development of Novel positive-tone Resists for EUVL

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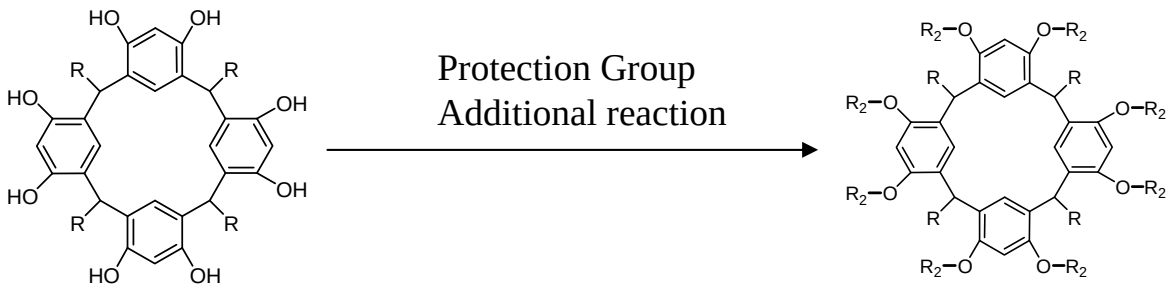
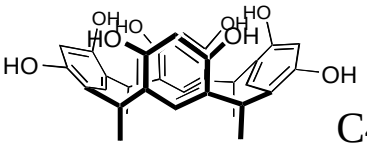
Concept for EUV resist

- **Cyclic Low Molecular Resists (CLM-Resists)**
  - Small molecular size. (about 2nm)
  - Higher Tg resist : The followed process is required with getting high temperature.
  - Many reactive groups such as hydroxyl groups.

- **Previous Work**
  - We had developed tetramethylcalix[4]-resorcinarene (C4-RA) and other CLM-resists.
  - CLM-resists is good performance for EUV resist.
  - The technical information is available on the *J.Photopolym.Sci.Technol.,16(2003)685* and *Proc.of SPIE, Vol.6923, 692346, (2008)*





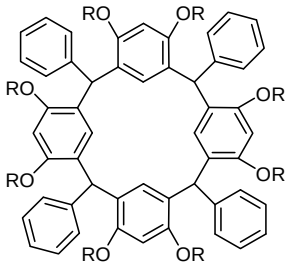
C4-RA

※R2：
Protection Group (PG) or H

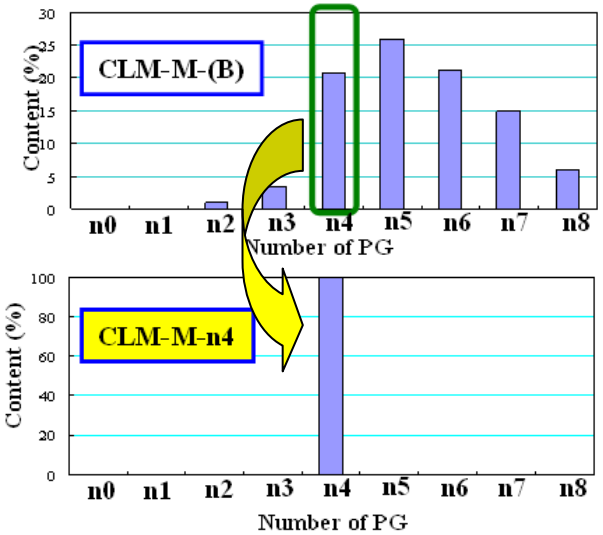
- Inhomogeneity of PG distribution issue
  - Mixture of compounds with different Protection Group (PG) number.
  - Ununiform substituted position of PG.

Concept for EUV resist -Effect of PG distribution: *Proc.of SPIE,Vol.7273,72732R-1,(2008)*

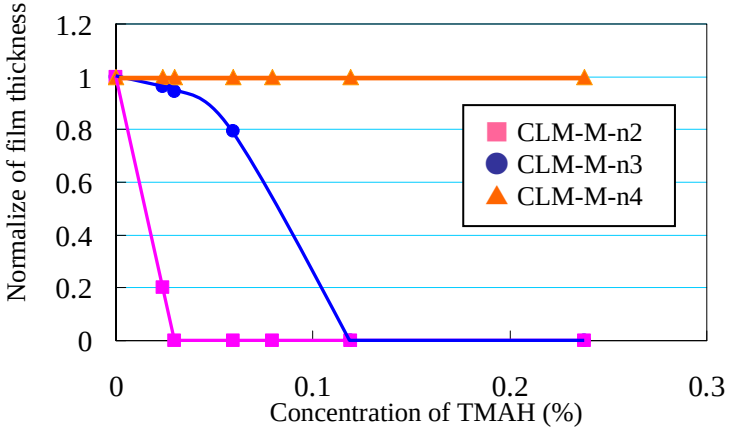
- We obtained 'CLM-M-n (from n1 to n8)' with monodisperse number of PG by chromatographic separation and evaluated its lithographic performance.



CLM-M



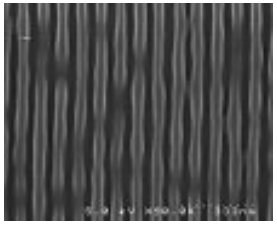
Alkaline developer solubility



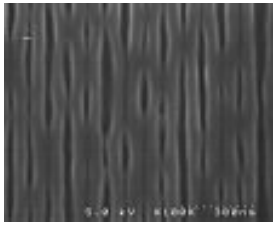
Proc.of SPIE, Vol.6923, 692346, (2008)

EB Evaluation

CLM-M

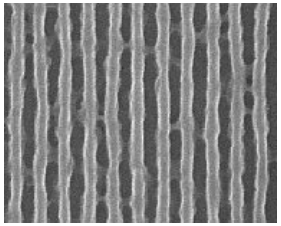


45nm L/S

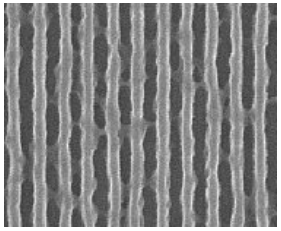


40nm L/S

CLM-M-n4



30nm L/S



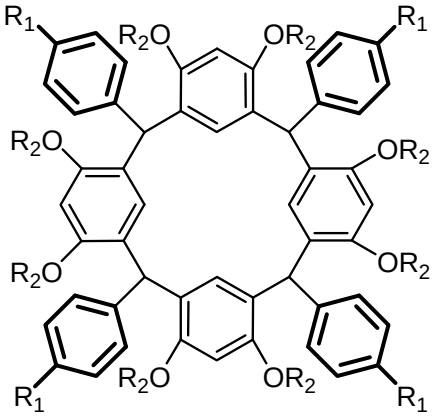
25nm L/S

EB exposure conditions
EB tool:50kV point beam
SEM:FE-SEM
F.T.=65nm／HMDS

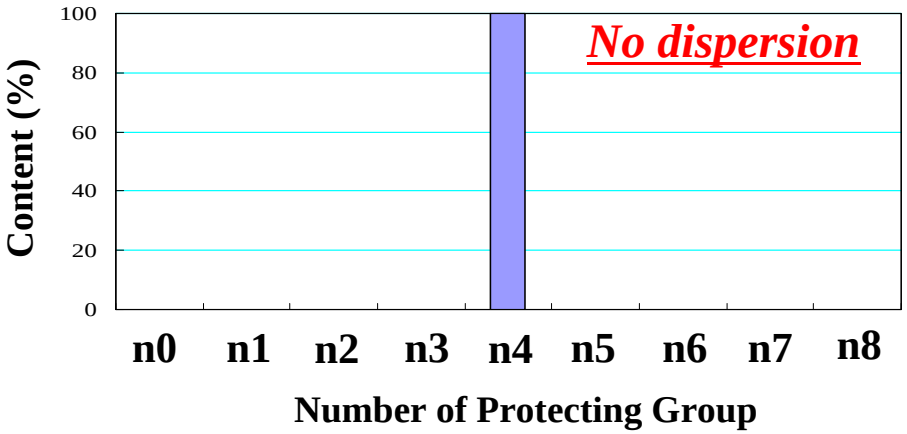
- **These results suggest that dissolution behavior at the exposed areas of CLM-M-n4 is more uniform than CLM-M, due to the no distribution of PG number.**

Synthesized optimally-controlled PG

- **We have developed new resist for which the substituted position and number of PG have no dispersion.**
- **These resists can be given by practical synthetic method.**
- **Also, these resists have adequate solubility of coating solvent (For example PGMEA ,PGME) and high thermal stability.**

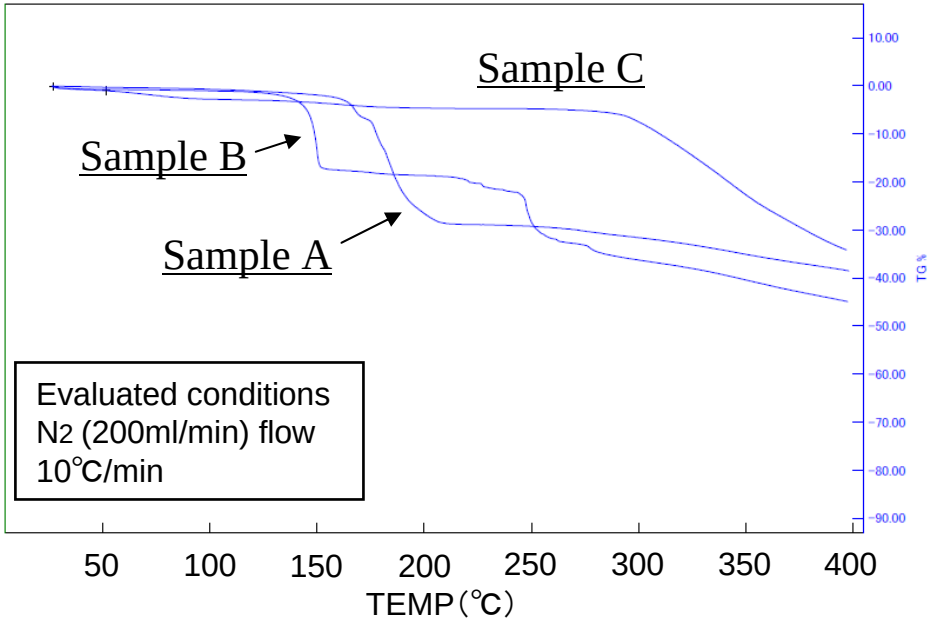


R1 : Protecting Group
R2 : Substituted Group or H

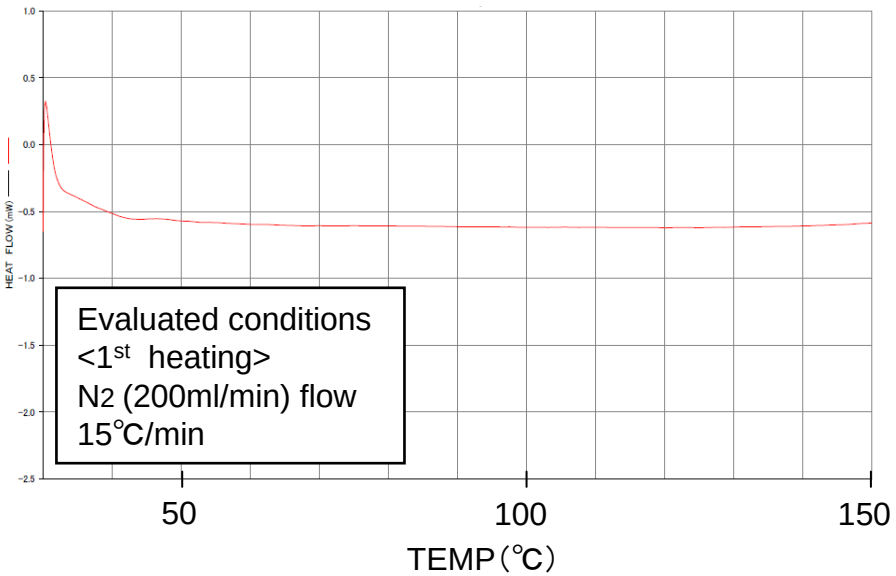


- **We prepared 3 type resists (Protecting Group is different : Adamantane-based types and other Cycloalkyl type) and evaluated these resists by EB and EUV lithography.**

Thermal Properties



TG thermograms of Resist A-C



DSC thermogram of Sample B

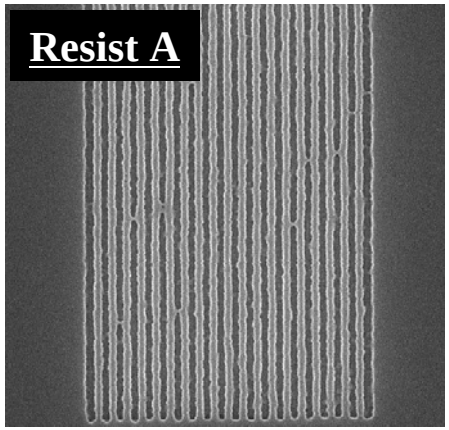
Td5 of Resist A-C

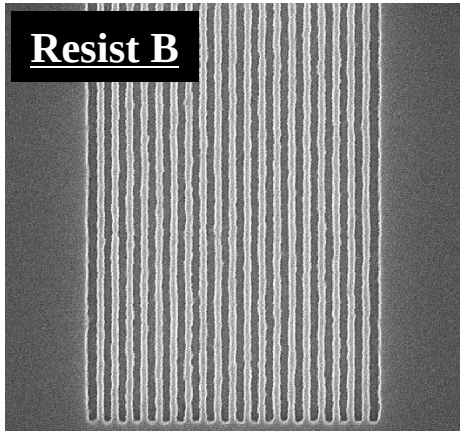
Resist A	168 ℃
Resist B	146 ℃
Resist C	269 ℃

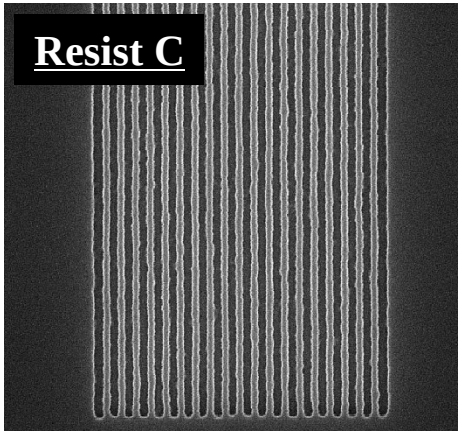
- **High decomposition temperature and No Tg（sample A-C）.**
- **These resists have a good thermal stability.**

EB Lithography

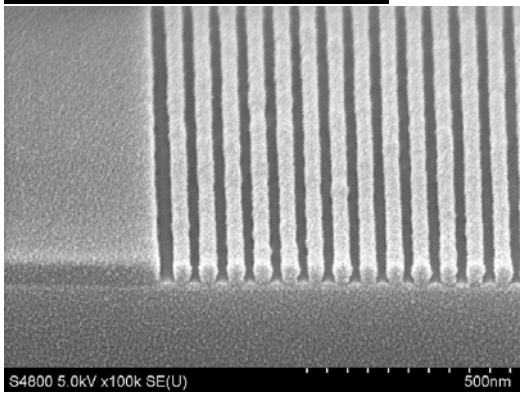
- **L/S of Resists @30nm** ※EB tool (50kV) resolution Limit is 30nm L/S



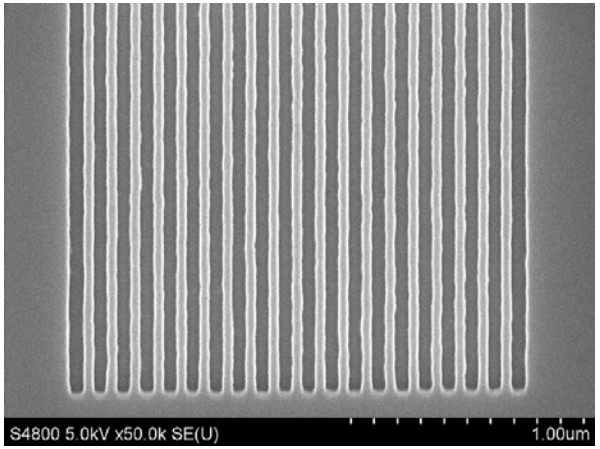




Cross section of Resist B

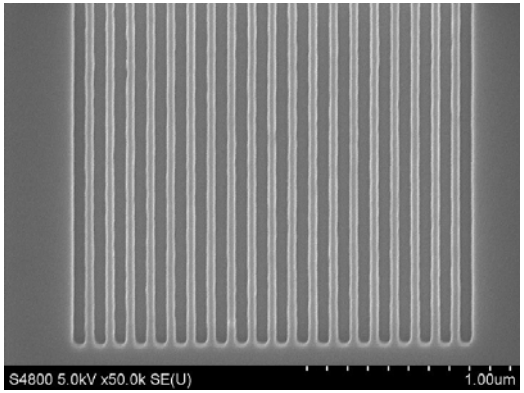


- **Pattern Roughness of Resist B @ 50nm L/S** (Measurement:1500nm in long direction in the period of 10nm)



Resist B
LWR：5.5
LER ：3.9

28 μ /cm2



＜Reference＞
ZEP520A
（Non-Chemical Amplified Resist）
LWR：5.4
LER ：3.7

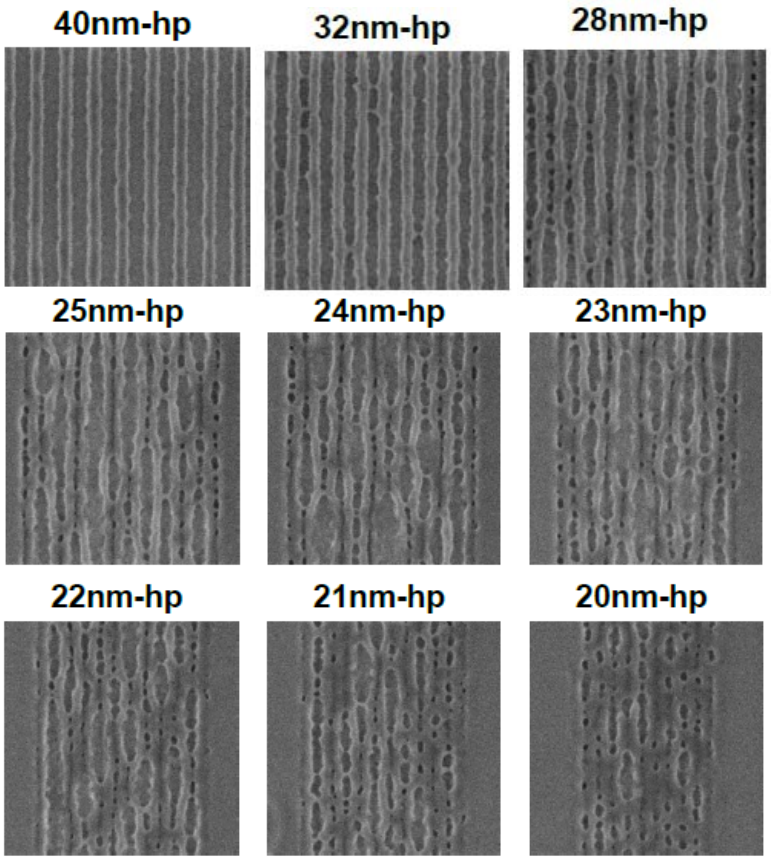
108 μ /cm2

- **Good resolution & Roughness is achieved by the effect of optimally-controlled PG of the resist.**

EUV Lithography

- **EUV lithographic evaluation was performed using small field exposure tool (SFET) at Selete.**

- **<u>EUV Lithography of Resist A</u>**
  - It was found that resist A have potential for 22nm hp resolution performance.



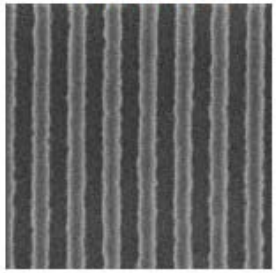
Process conditions
Film Thickness:59nm
Exposure tool:SFET
Dev.:TMAH 0.26N 30sec

EUV Lithography

Pattern Roughness of Resist A

- Resist A showed good LWR-4.9nm at 45 nm L/S.

45nm-hp



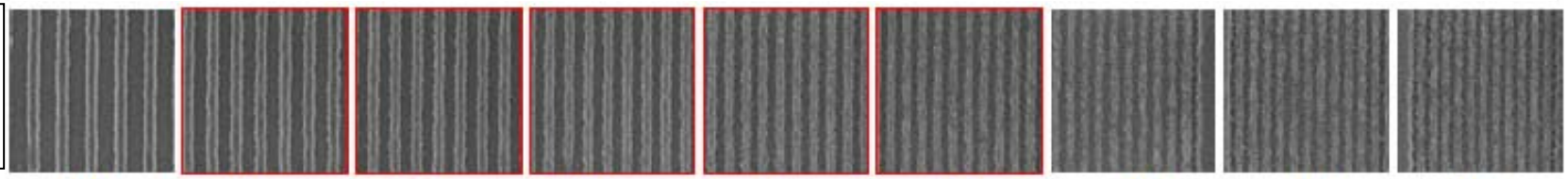
Film Thickness:58nm
Exposure tool: SFET

Dose:13.0J/cm2
LWR:4.9nm

EUV Lithography of Resist B

- To improve pattern roughness performance, we need to optimize the process condition , PAG and quencher.

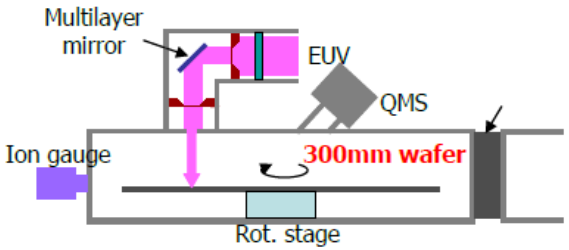
FT:58nm
Under-layer
Exposure Tool:
SFET



	60nm-hp	50nm-hp	45nm-hp	40nm-hp	35nm-hp	32nm-hp	30nm-hp	28nm-hp	26nm-hp
Dose	12.5	12.5	13	13.5	14	14.5	15	15	15
CD	51.3nm	48.8nm	44.3nm	40.2nm	36.9nm				
LWR	5.7nm	7.6nm	7.2nm	8.1nm	8.8nm				

Evaluation of Resist Outgassing

- **Outgassing evaluation was performed using "Pressure rise method".**

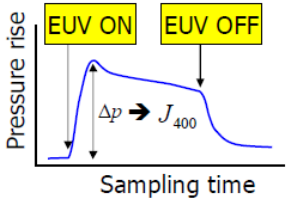


EUV Source	: EQ-10MR (Energetiq)
Power on Wafer	: 0.03mW/cm^2
Exposure area	: 1.43 cm^2
Base pressure	**: 8x10^{-7} Pa**

Resist outgassing 'RATE' [molecules·cm^{-2}·s^{-1}]

Maximum rate during exposure
→ indicator for exposure tool management

$$J_{400} = \frac{\Delta p S_e}{RTA} N_A \frac{400}{I}$$ (400mW·cm^{-2} assumed)



D_p : pressure rise
S_e : eff. pumping speed
R : Gas constant
T : temperature
A : area of exposure
NA : avogadro's no.
I : EUV intensity

subscript
i : time
D : established dose

Resist Outgassing (molecules/cm-2/s-1)

Resist A	3.4E+16
Resist B	3.8E+15
Resist C	2.6E+15

Resist matrix:P:Q=84:13:3 (wt%)
PAG:TPS-nf
Quencher : alkyl amine

- **The outgassing of these Resists is the same or less than that of conventional polymer resist.**

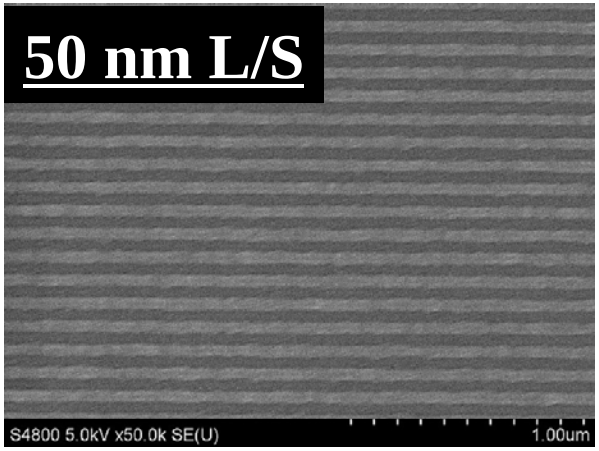
Summary

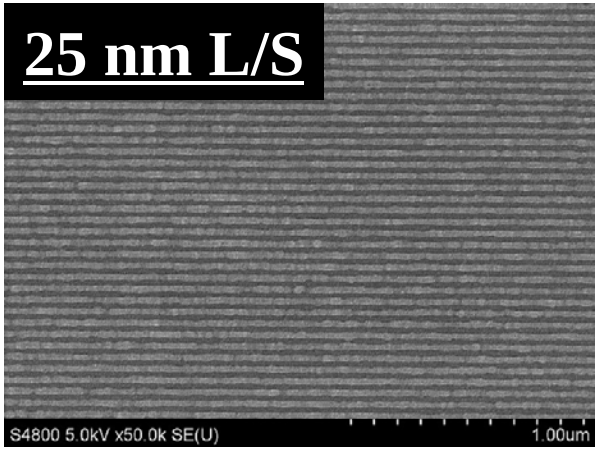
- We designed and synthesized a new Positive-tone Resist, for which there is no variation in the position and number of PG.
- These resist achieved a resolution of sub-30nm hp patterns with high sensitivity and good LWR.
- To improve these resists performance, we need to optimize the process condition , PAG and quencher.
- New development materials are under evaluation.

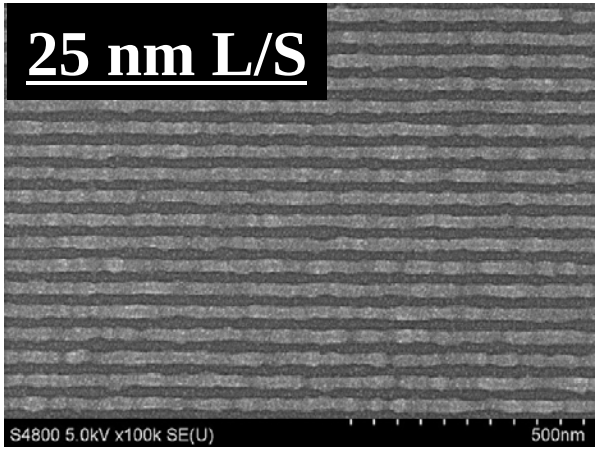
Thank You For Your Kind Attention !

Appendix 1（EUV exposure result of Resist A at PSI）

➢ **Top view**

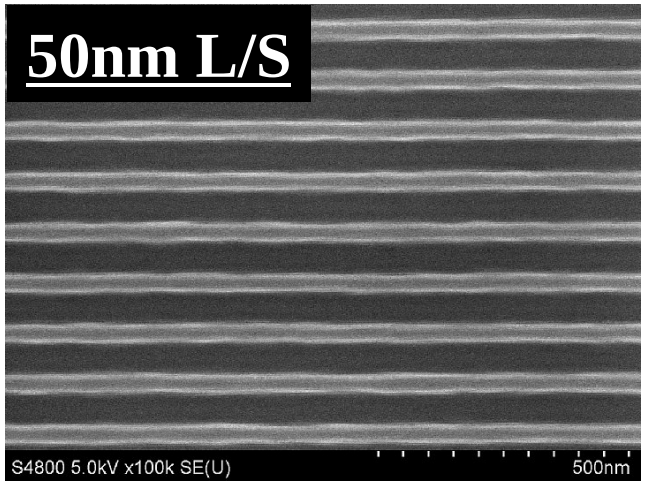


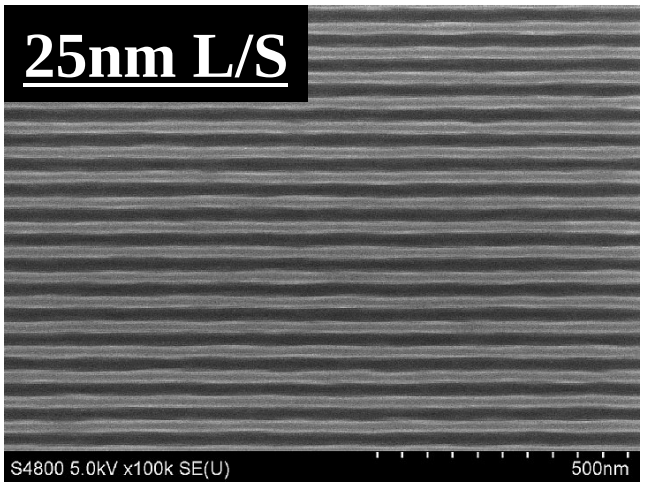
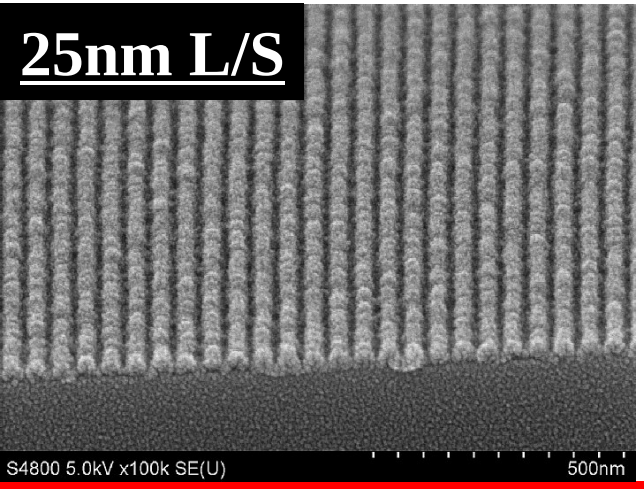
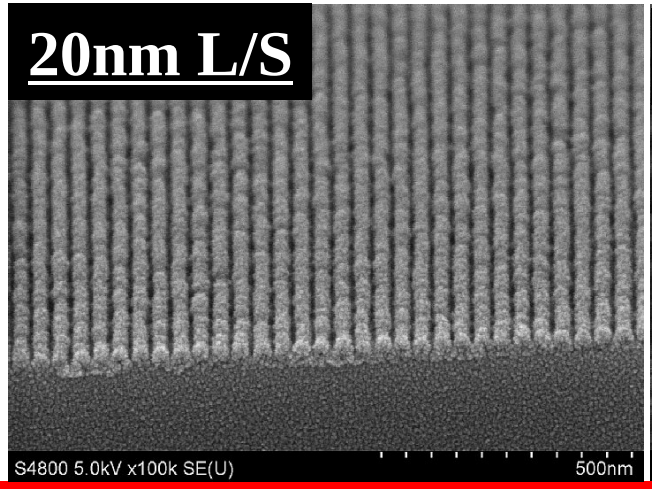
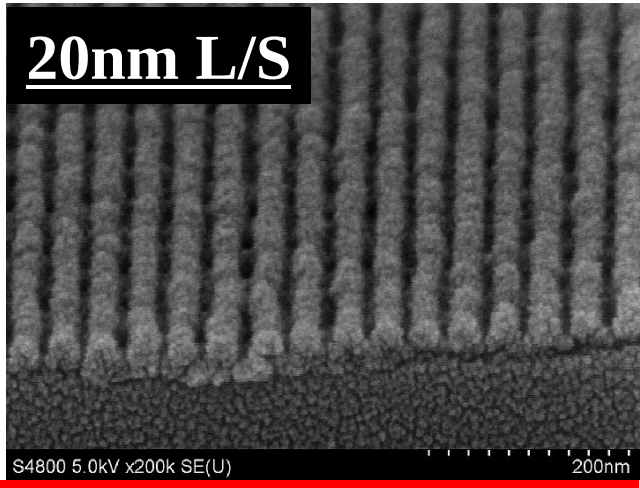




Appendix 2（EUV exposure result of Resist C at PSI）

- **Top view**





- **Cross Section**