Molecular Resist Materials for Extreme Ultraviolet Lithography

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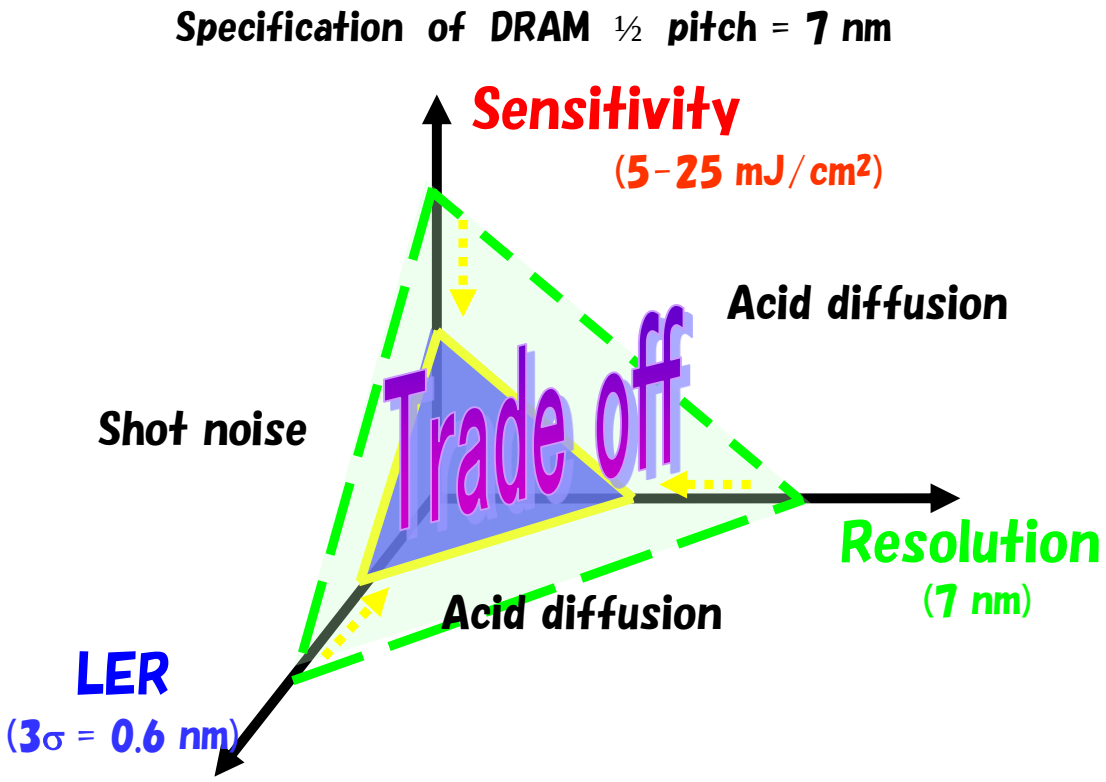
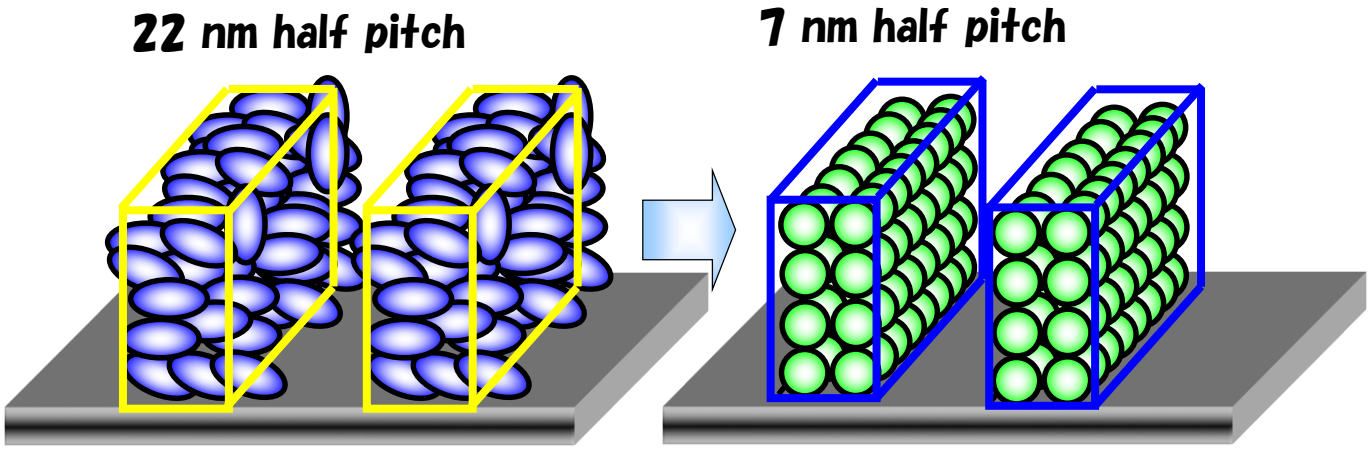
Main problem of EUV resist

Lithography roadmap

Year of production	2015	2017	2019	2021	2019	2023	2028
DRAM ½ pitch	32 nm	25 nm	20 nm	18 nm	16 nm	13 nm	7 nm
Exposure source	ArF (193 nm)						EUV



Advantage of Molecular resist



The origins of LER

- Molecular size
- Molecular dispersion

Advantage

- Very small molecular size
  High resolution

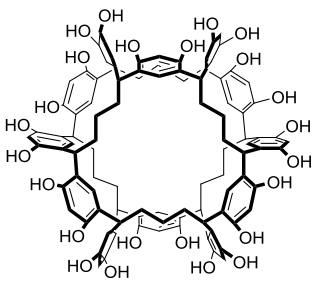
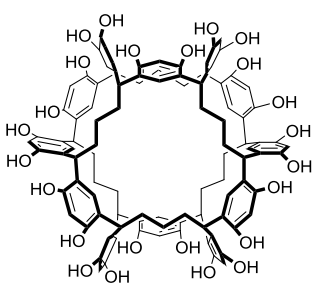
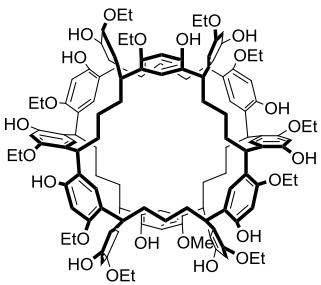
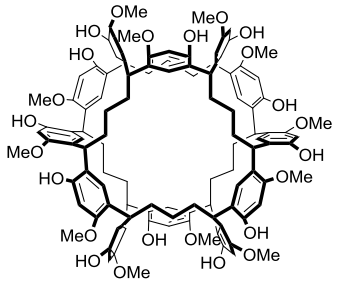
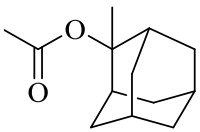
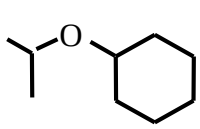
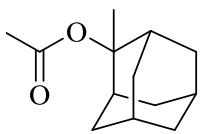
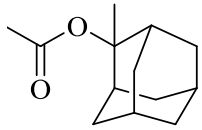
Molecular resist

- Small molecular size
- Uniform size
- Developable in TMAH
- Thermal stability
- Etching durability

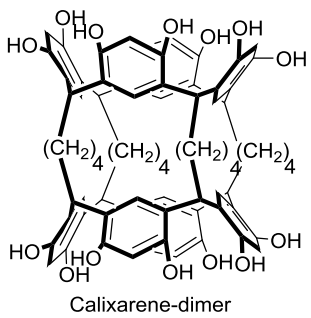
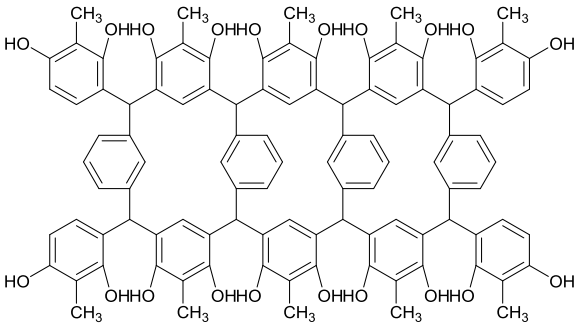
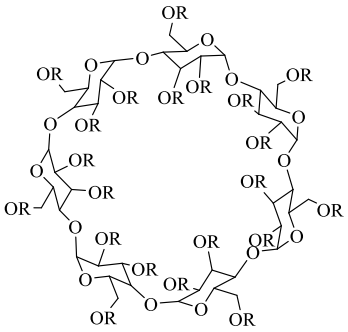
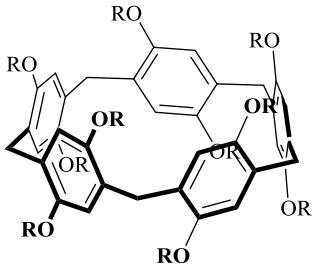
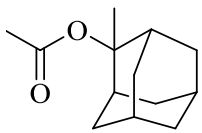
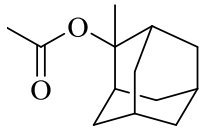
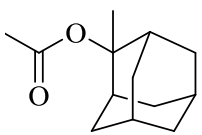
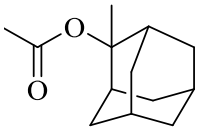
The Objective of this work

We evaluated the lithographic performance of molecular resist materials based on cyclic oligomers using EUV and EB exposure system. Also, we examined the etch durability of synthesized molecular resist materials.

Molecular resist

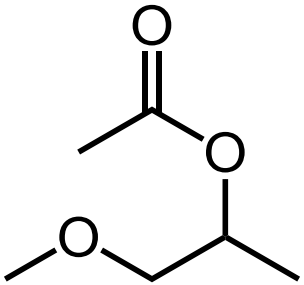
Sample Name	Resist 1	Resist 2	Resist 3	Resist 4
Core Structure	 Noria	 Noria	 Noria-OEt	 Noria-OMe
Protecting group				
Protecting ratio (%)	40	23	49	44
Casting Solvent	PGMEA	PGME	PGMEA	PGMEA

Molecular resists

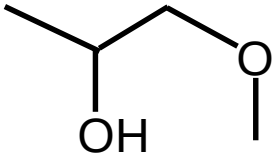
Sample Name	Resist 5	Resist 6	Resist 7	Resist 8
Core Structure	 Calixarene-dimer	 Tripleringed[14]arene	 B-Cyclodextrin	 Pillar[5]arene
Protecting group				
Protecting ratio (%)	37	30	64	35
Casting Solvent	PGMEA	PGMEA	Dyglyme	PGMEA

Samples

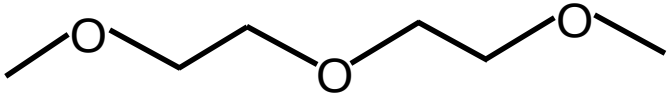
Solvent



Propyrene glycol methyl ether acetate
(PGMEA)

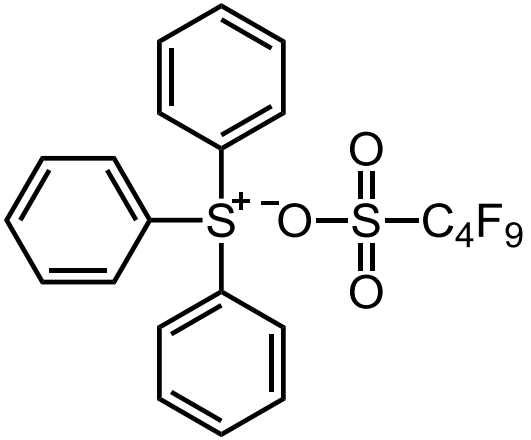


Propyrene glycol methyl ether
(PGME)



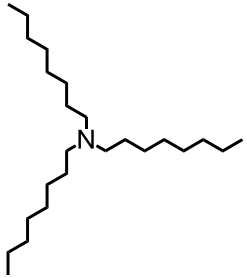
Dyglyme

Acid generator



Triphenylsulfonium nonaflate
(TPS-nf)

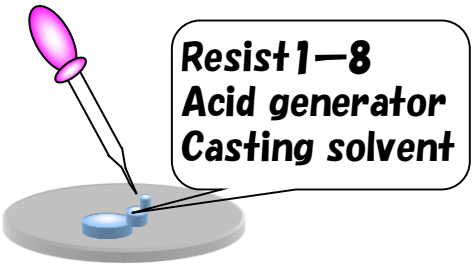
Amine



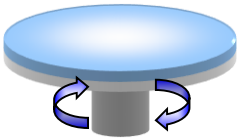
Trioctylamine

The weight ratio of the acid generator to molecular resists was 10 wt%.

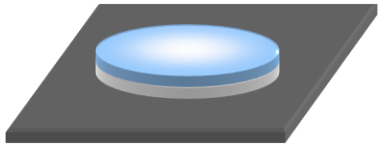
Experimental procedure



1. Application



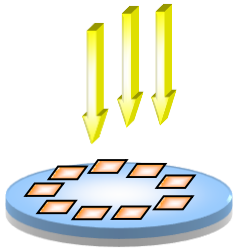
2. Spin coating
(condition: 3000rpm 30s)



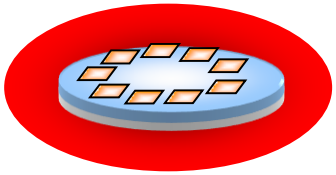
3. Prebake
(condition: 110℃ 90s)

EUV

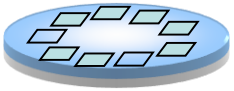
EUV



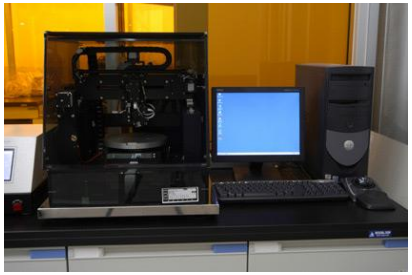
4. Exposure



5. Post-exposure bake (PEB)
(condition: 110℃ 60s)

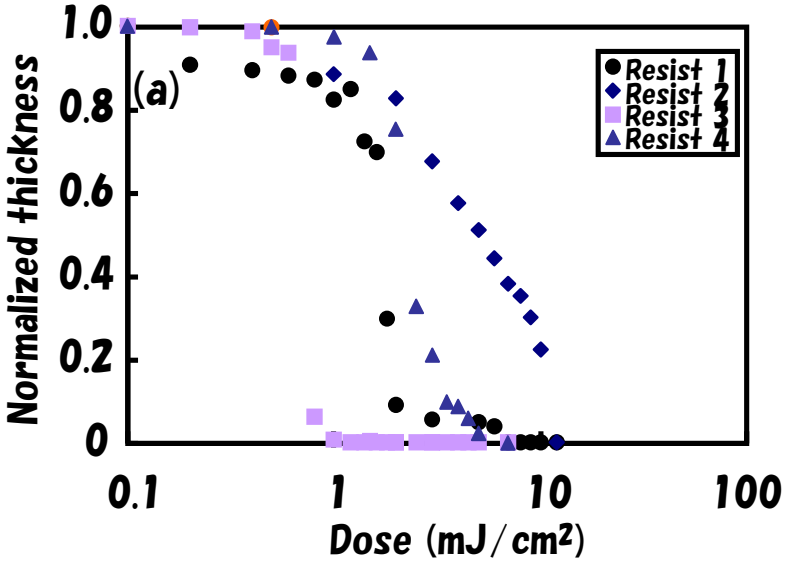


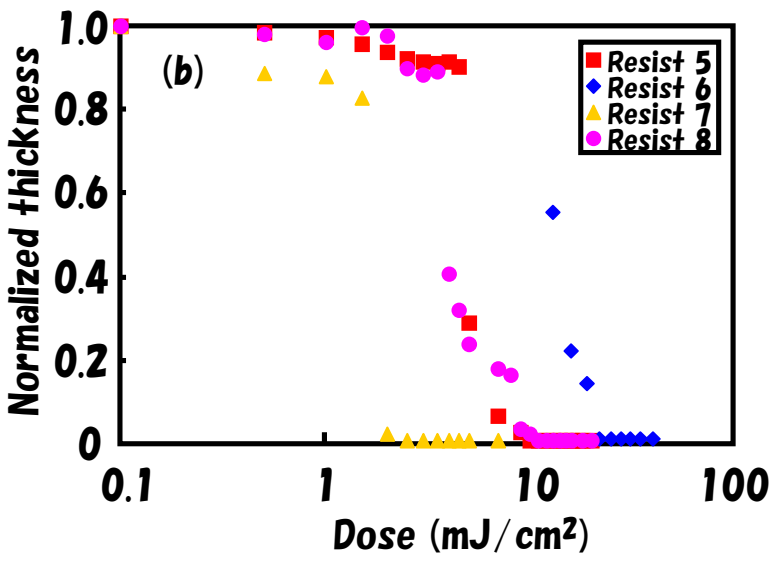
6. Development
& Rinse



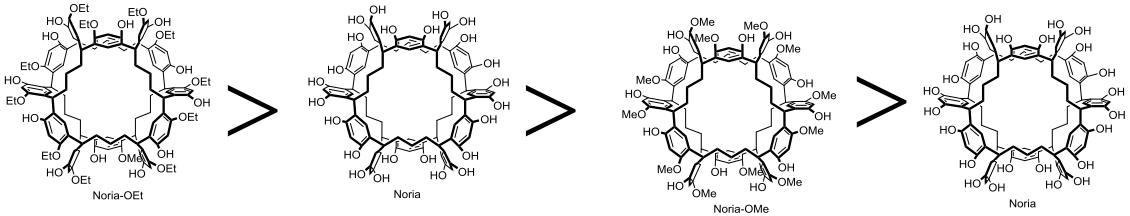
7. Measurement

Sensitivity curve of noria derivatives

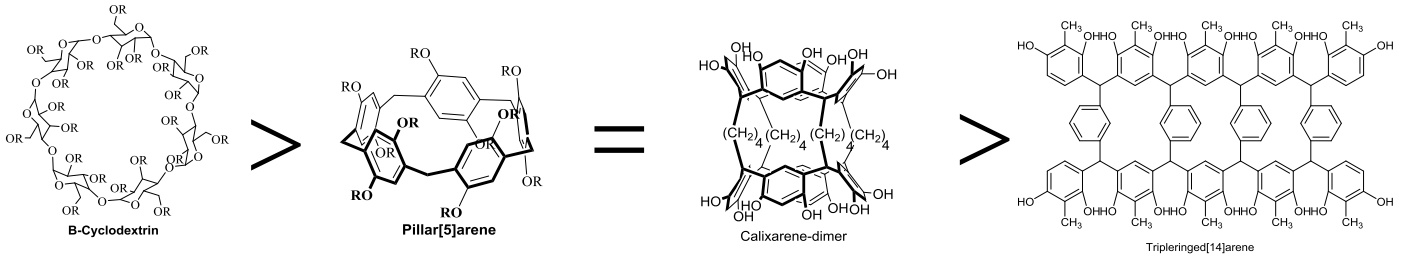




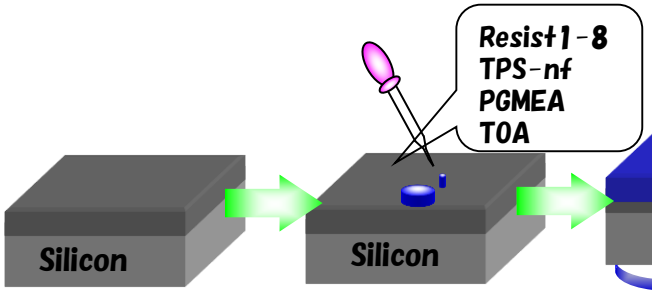
Resist 3 > Resist 1 > Resist 4 > Resist 2



Resist 7 > Resist 8 = Resist 5 > Resist 6



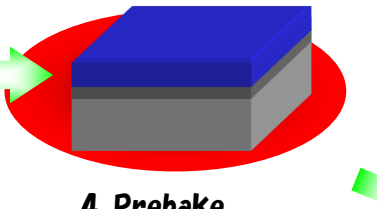
Experimental procedure



1. HMDS process

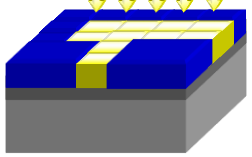
2. Application

3. Spin coating
(condition: 3000 rpm 30 s)

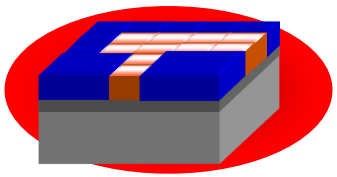


4. Prebake
(condition: 110 ℃ 90 s)

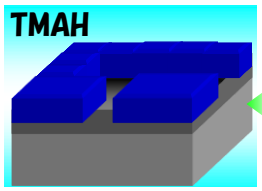
ELS-7700
electron beam (75kV)



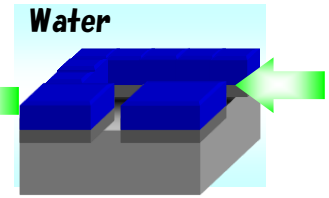
5. Exposure



6. Post exposure bake (PEB)



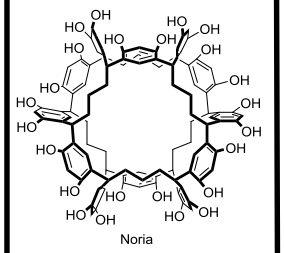
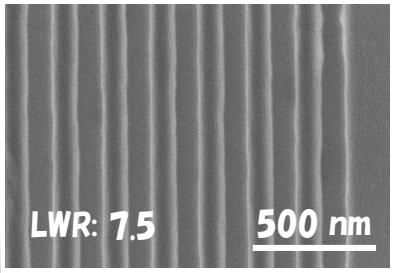
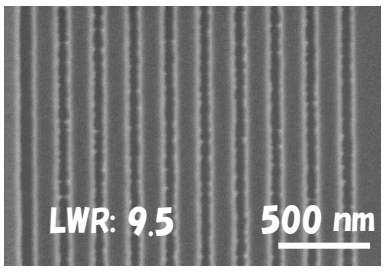
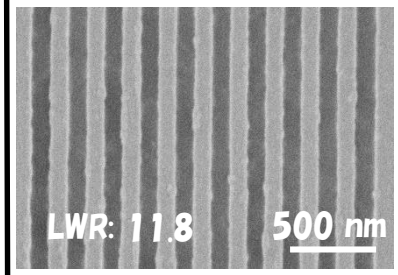
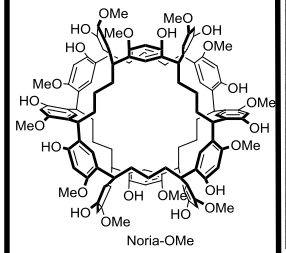
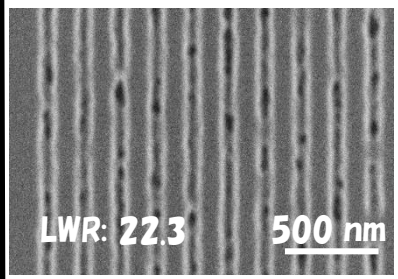
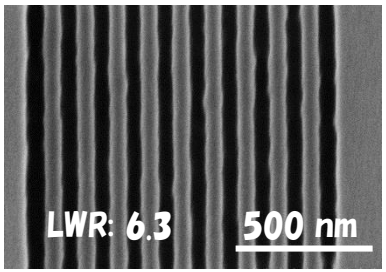
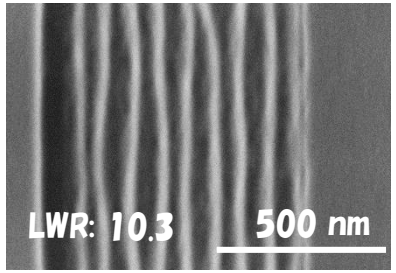
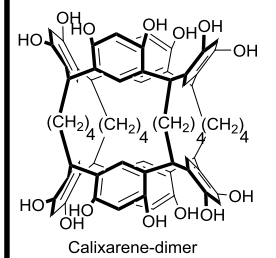
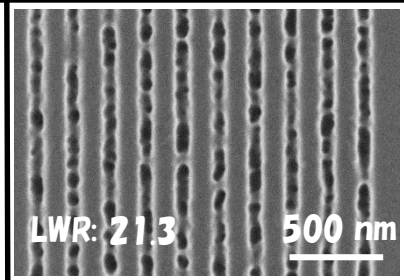
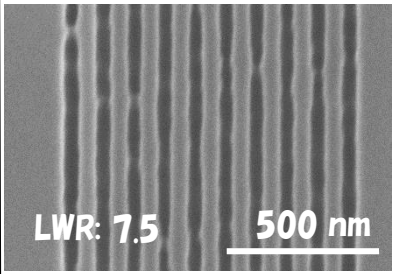
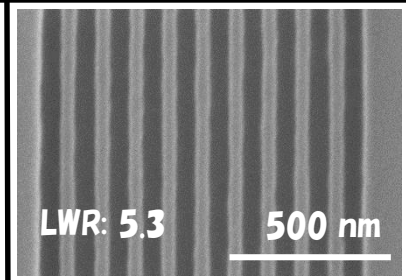
7. Development



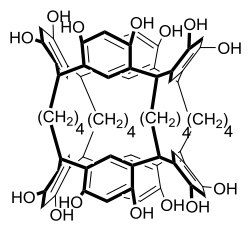
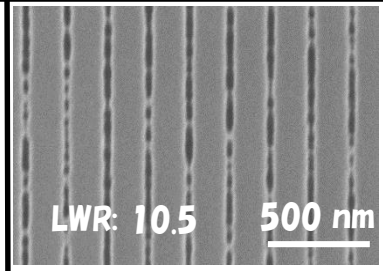
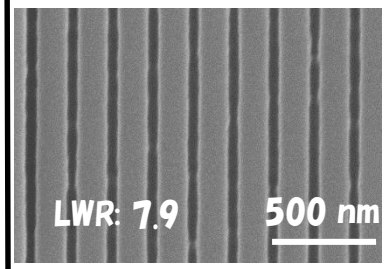
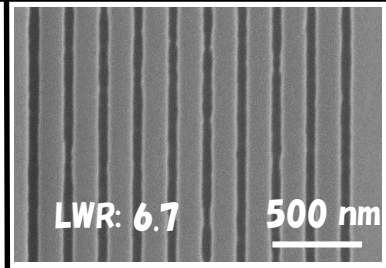
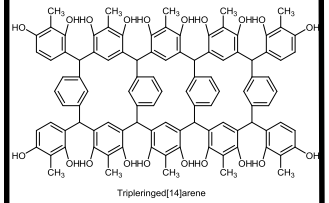
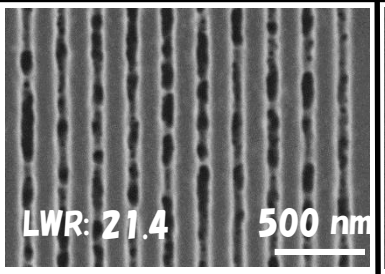
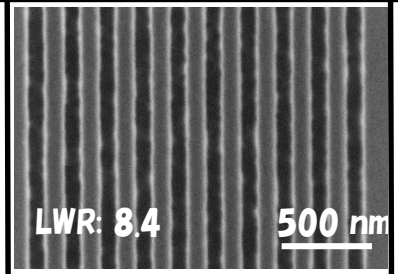
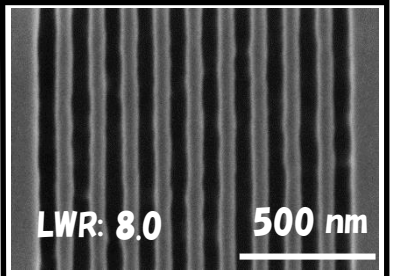
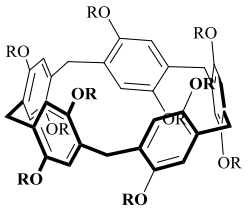
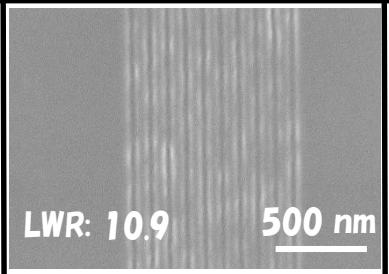
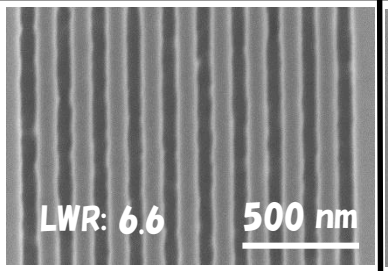
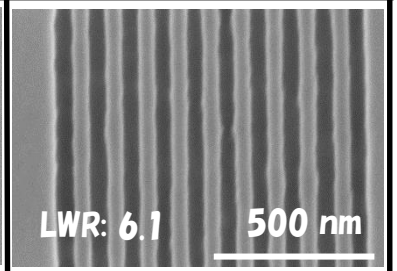
8. Rinse

9. SEM observation
(LWR measurement)

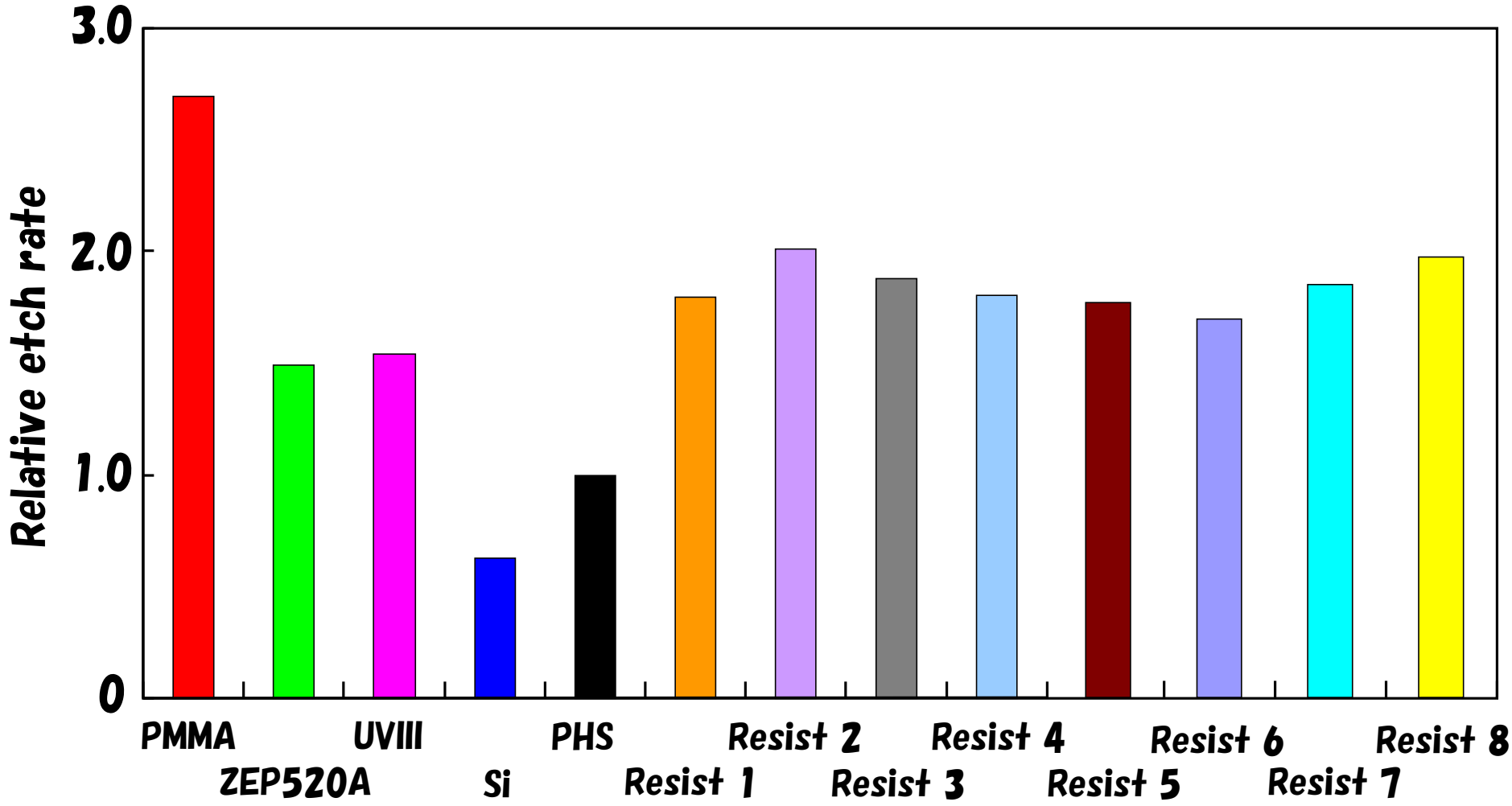
SEM micrographs of noria derivatives

	Exposure dose 40 μC/cm²	Exposure dose 100 μC/cm²	Exposure dose 200 μC/cm²
 Noria Resist 1	 LWR: 7.5 500 nm Line 80 nm, Pitch 200 nm	 LWR: 9.5 500 nm Line 40 nm, Pitch 200 nm	 LWR: 11.8 500 nm Line 100 nm, Pitch 200 nm
 Noria-OMe Resist 4	 LWR: 22.3 500 nm Line 50 nm, Pitch 200 nm	 LWR: 6.3 500 nm Line 50 nm, Pitch 120 nm	 LWR: 10.3 500 nm Line 30 nm, Pitch 80 nm
 Calixarene-dimer Resist 5	 LWR: 21.3 500 nm Line 50 nm, Pitch 200 nm	 LWR: 7.5 500 nm Line 40 nm, Pitch 100 nm	 LWR: 5.3 500 nm Line 50 nm, Pitch 100 nm

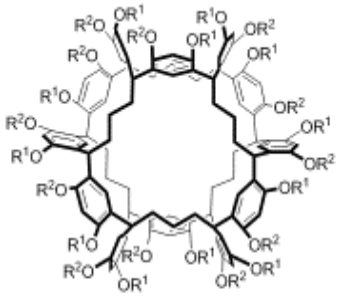
SEM micrographs of noria derivatives

	Exposure dose 200 μC/cm²	Exposure dose 300 μC/cm²	Exposure dose 500 μC/cm²
 Calixarene-dimer Resist 5	 LWR: 10.5 500 nm Line 20 nm, Pitch 200 nm	 LWR: 7.9 500 nm Line 45 nm, Pitch 200 nm	 LWR: 6.7 500 nm Line 50 nm, Pitch 200 nm
 Tripleringed[14]arene Resist 6	 LWR: 21.4 500 nm Line 60 nm, Pitch 200 nm	 LWR: 8.4 500 nm Line 60 nm, Pitch 120 nm	 LWR: 8.0 500 nm Line 80 nm, Pitch 200 nm
 Pillar[5]arene Resist 8	 LWR: 10.9 500 nm Line 20 nm, Pitch 100 nm	 LWR: 6.6 500 nm Line 55 nm, Pitch 150 nm	 LWR: 6.1 500 nm Line 40 nm, Pitch 100 nm

Etching durability



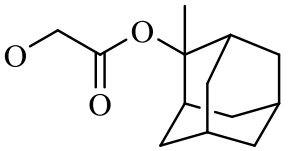
Molecular resists



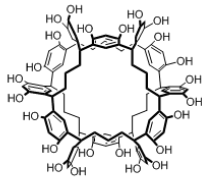
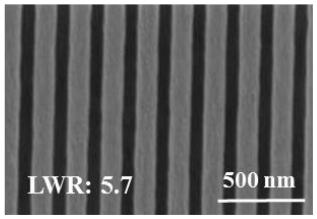
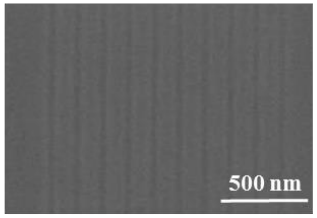
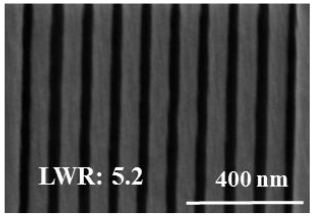
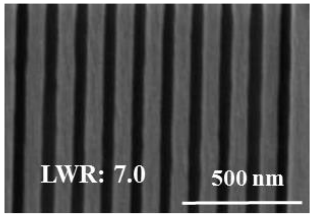
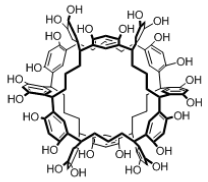
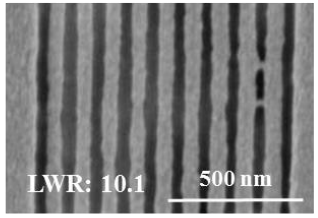
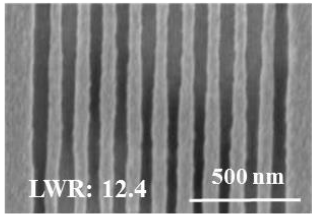
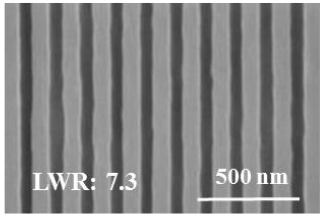
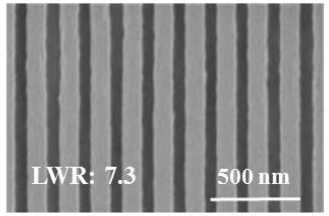
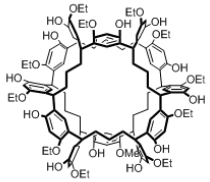
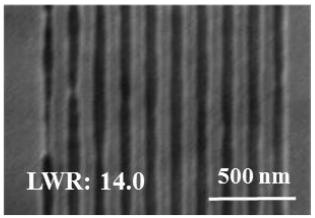
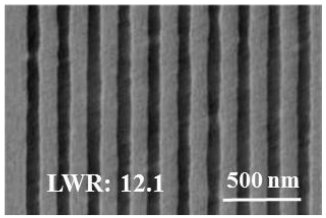
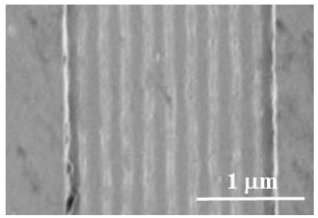
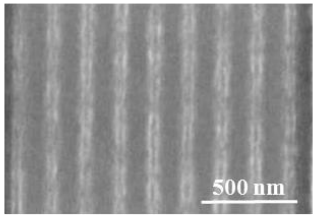
Noria-AD_{PD} OR^1 = OH : OR^2 = OH
PD = 27 and 45
(Resist 1 and 2)

Noria(OEt)-AD_{PD} OR^1 = OH : OR^2 = OEt
PD = 12 (Resist 3)

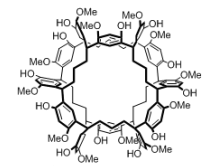
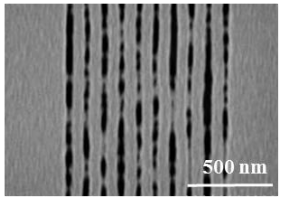
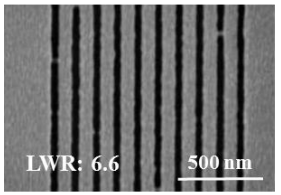
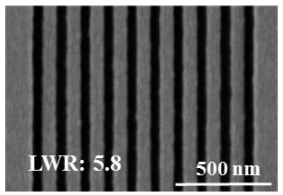
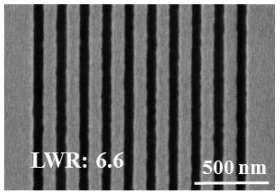
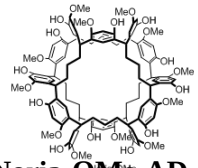
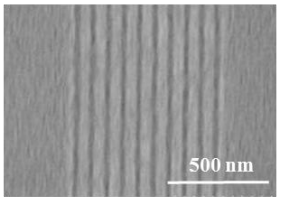
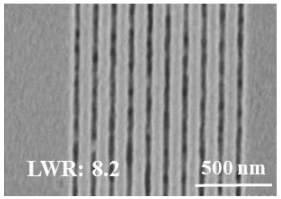
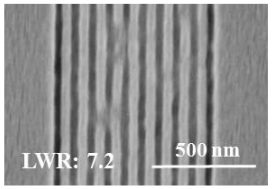
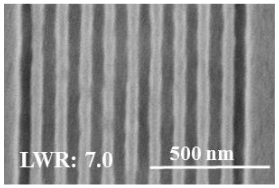
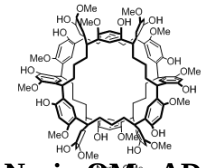
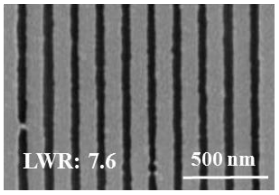
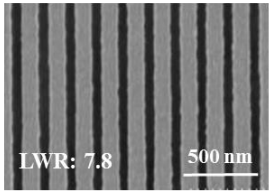
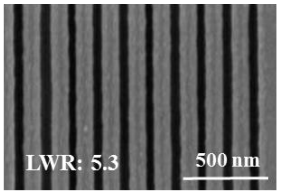
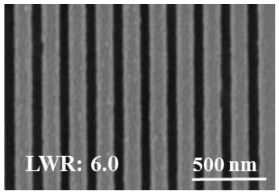
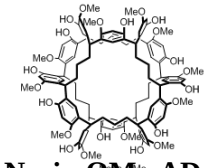
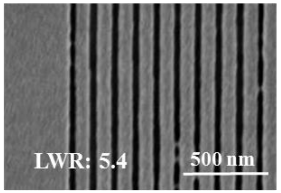
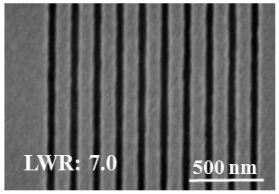
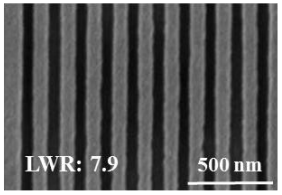
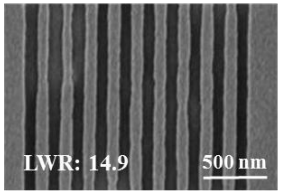
Noria(OMe)-AD_{PD} OR^1 = OH : OR^2 = OMe
PD = 18, 45, 55, and 75
(Resist 4-7)

Resist materials	Noria derivatives		
		OR^1	OR^2
Resist **1**	Noria-AD_{27}	OH or 	OH
Resist **2**	Noria-AD_{45}		OH
Resist **3**	Noria-OEt-AD_{13}		OEt
Resist **4**	Noria-OMe-AD_{18}		OMe
Resist **5**	Noria-OMe-AD_{45}		OMe
Resist **6**	Noria-OMe-AD_{55}		OMe
Resist **7**	Noria-OMe-AD_{75}		OMe

SEM micrographs of noria derivatives

	40 μC/cm²		80 μC/cm²	
Resist 1  Noria-AD$_{27}$	 Line 75 nm pitch 200 nm	 Line 25 nm pitch 150 nm	 Line 30 nm pitch 100 nm	 Line 50 nm pitch 120 nm
Resist 2  Noria-AD$_{45}$	 Line 40 nm pitch 100 nm	 Line 50 nm pitch 120 nm	 Line 60 nm pitch 150 nm	 Line 65 nm pitch 180 nm
Resist 3  Noria-OEt-AD$_{13}$	 Line 60 nm pitch 150 nm	 Line 80 nm pitch 200 nm	 Line 100 nm pitch 200 nm	 Line 130 nm pitch 200 nm

SEM micrographs of noria derivatives

	40 μC/cm²		80 μC/cm²	
Resist 4  Noria-OMe-AD$_{18}$	 Line 30 nm pitch 100 nm	 Line 30 nm pitch 120 nm	 Line 50 nm pitch 120 nm	 Line 60 nm pitch 150 nm
Resist 5  Noria-OMe-AD$_{45}$	 Line 20 nm pitch 80 nm	 Line 30 nm pitch 120 nm	 Line 30 nm pitch 80 nm	 Line 50 nm pitch 100 nm
Resist 6  Noria-OMe-AD$_{55}$	 Line 40 nm pitch 150 nm	 Line 60 nm pitch 180 nm	 Line 45 nm pitch 150 nm	 Line 55 nm pitch 180 nm
Resist 7  Noria-OMe-AD$_{75}$	 Line 30 nm pitch 120 nm	 Line 45 nm pitch 150 nm	 Line 65 nm pitch 150 nm	 Line 90 nm pitch 180 nm

Conclusion

- We developed positive-tone chemically amplified molecular resist materilas based on cyclic oligomers such as noria, calixarene-dimer, cyclodextrin, and pillar[5]arene, and investigated their lithographic performances using EUV and EB.
- We make clear that a small change in modification of noria resists can cause a significant change of sensitivity. Especially, it is useful for the improvement of resist sensitivities to use protecting groups such as 2-acetyloxy-2-methyladamantyl ester (AD) groups and ethoxy groups.
- The hole size of molecular structure is more important factor for sensitivity in EUV and EB resists.
- The etching rate of noria derivatives is similar to that of conventional resist materials such as PHS, ZEP520A and UVIII.
- The cyclic oligomers have the potential to offer exceptional resolution as future positive tone EUV and EB resist materials.