High-silicon negative tone resist and underlayer development for high NA EUV lithography

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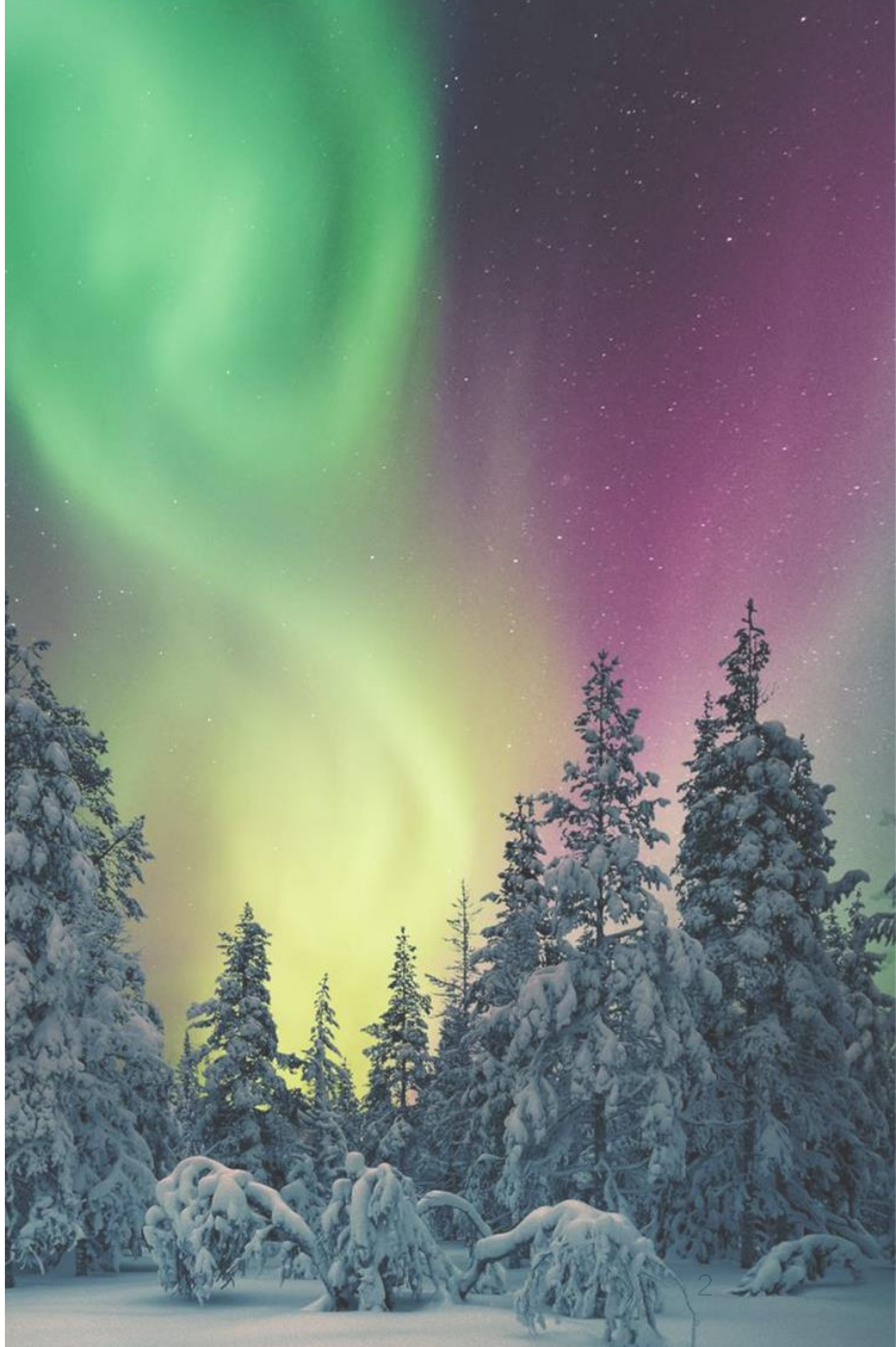
IWAPS 2022

Who we are

We are an innovative materials company with strong R&D capabilities and a portfolio of unique patents. We are one of the only European suppliers of EUV lithography materials. Pibond’s materials have been adopted in the latest semiconductor devices globally.

Our Experienced global management team includes industry veterans from some of the largest Semiconductor chip and device companies.

We have an audited supplier track record to the semiconductor industry from our 3000 square meter PPT *(parts per trillion)* Clean Room production facility in Finland.



State of the art facility

We enable, simplify, and increase the quality and performance of logic, memory, sensor and other semiconductor devices.

With over 112 patents with 85 issued and 27 pending, we continue to invest in R&D and grow our knowledge in the field.

RESPONSIBLE CARE®
OUR COMMITMENT TO SUSTAINABILITY

MANAGEMENT SYSTEM CERTIFICATION
DNV·GL
ISO 9001 = ISO 14001

PiBond

3,000 m2 of space

State of the art automation

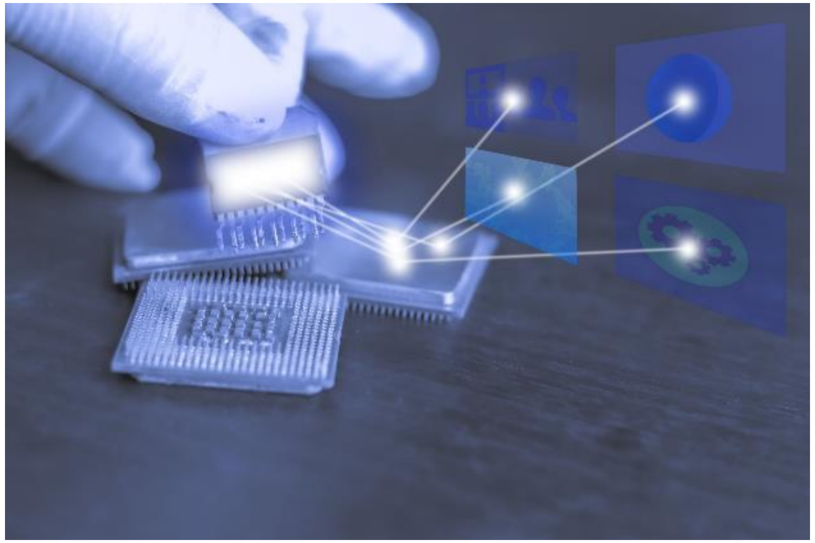
Extensive in-house semiconductor process testing capabilities

Class 10/100 Clean room production

Fully audited production track record

> 200 tons/year capacity of high value materials

PiBond is a leading innovator of Advanced Materials



PRESENT

Semiconductor Dielectrics for State-of-the-Art Applications

Optical Coatings for Image Sensors

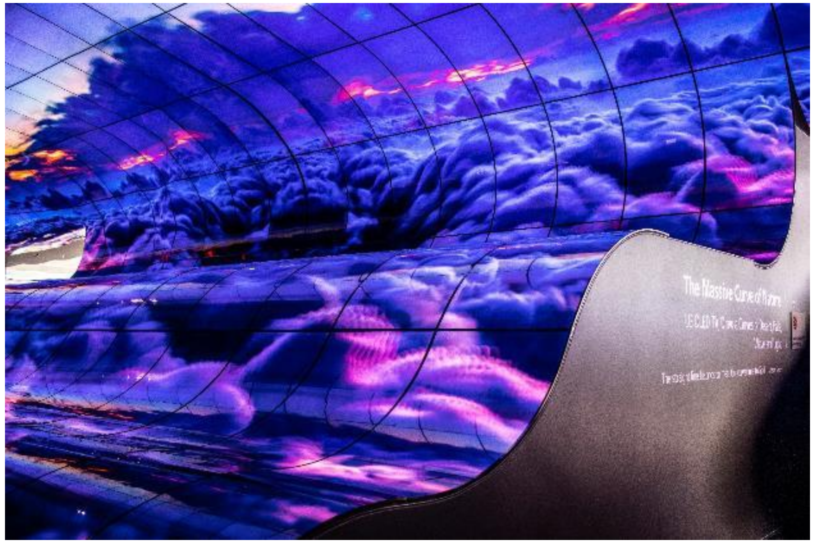
Enabling Layers for Sub-5nm microelectronics

FUTURE

Future Data Transfer Through Photonics

Semiconductor-level Precision and Reliability to Photonic Applications

Devices and components enabled by novel processes

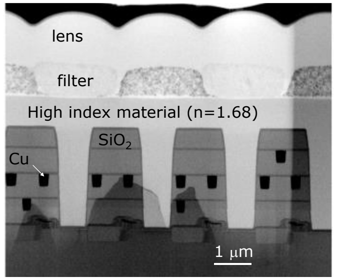


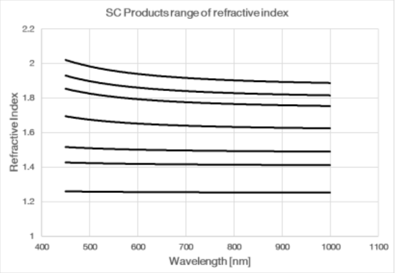
PiBond

Material technology platforms

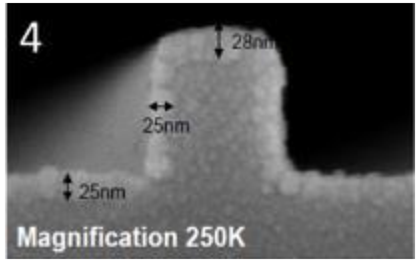
DIELECTRICS

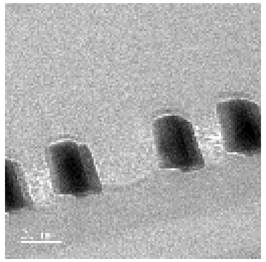
- Traditional spin-on dielectrics
- Optical dielectric, industry leading range of refractive indexes





- Novel conformal and low k dielectrics for sub 5nm metallization processes

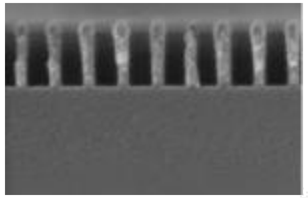




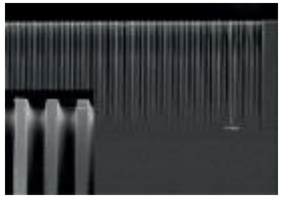
- CVD replacement

PATTERNING MATERIALS

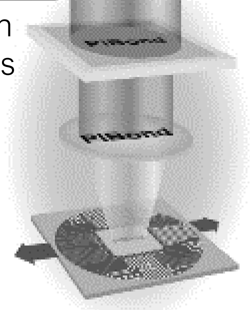
- Traditional and advanced litho underlayers: organic underlayer, silicon middle layer



Industry proven stacks & results

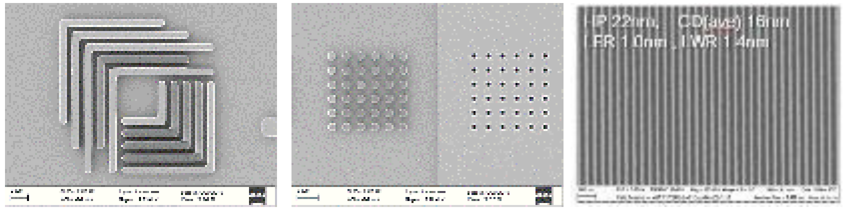


Designed chemistry & etch selectivity



- Auxiliary materials and removers
- Novel silicon-based photoresists

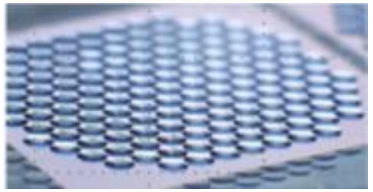
i-line – KrF – ArF – EUV



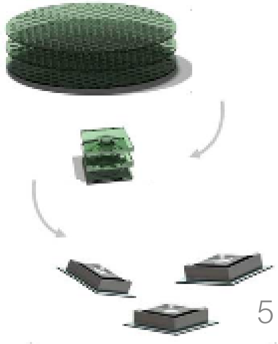
CLEAR SILICON RESINS

- High quality, high refractive index silicone materials

- Bonding adhesives for complex optics & ICs



- NIL patterned lenses and resists
- Wafer level optics and silicon photonics

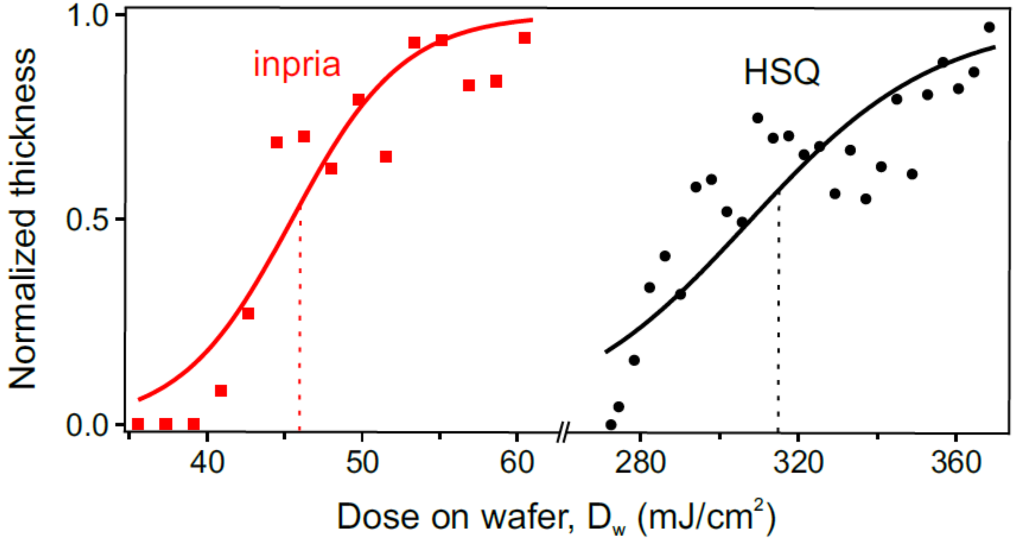


Content

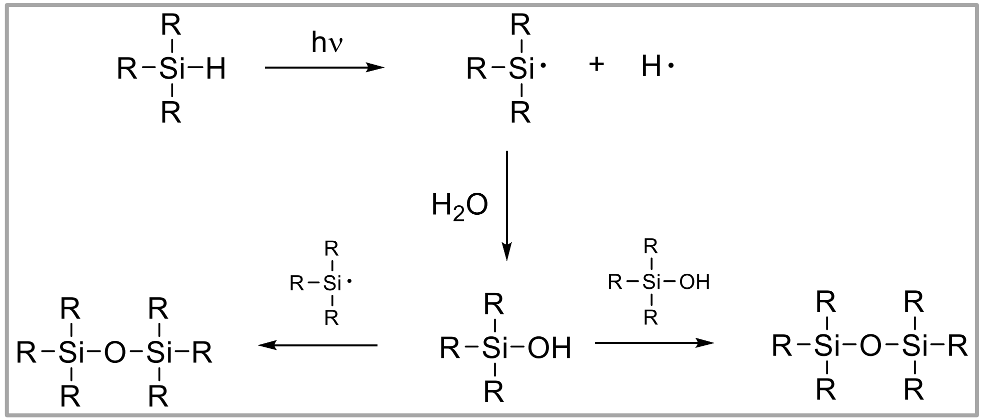
1. HSQ-based resist and possible patterning mechanisms
2. Lithography performances of developed polyhydrogen silsesquioxane-based resist @ PiBond
3. Chemical modifications of resin microstructure to improve lithographic performances
4. Our siloxane resist characteristics

HSQ and patterning

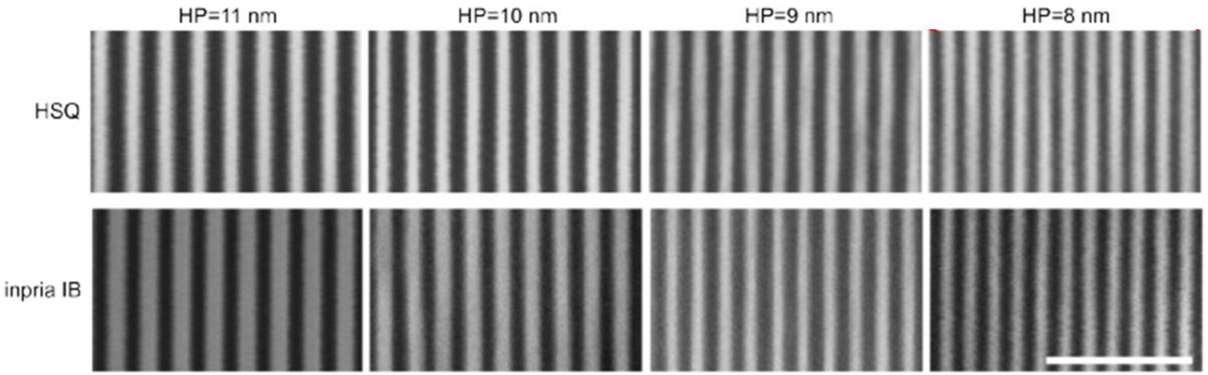
- HSQ used as e-beam resist for a long time
- HSQ also has been demonstrated to pattern sub-10nm features
- Main challenge: sensitivity



Solubility switch mechanism



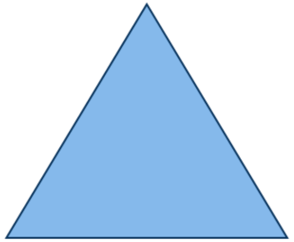
Namatsu, H., Yamaguchi, T., Nagase, M., Yamazaki, K., Kurihara, K. Microelectr. Eng. 1998, 41/42, 331-334



Mojarad, N., Hojeij, M., Wang, L., Gobrecht, J., Ekinci Y. Nanoscale, 2015, 7, 4031-4037
Päivänranta, B., Langner,A., Kirk, E., David, C., Ekinci, Y. Nanotechnology, 2011, 22, 375302

Silicon based resists

Material Design Strategy



Resolution
HP nm

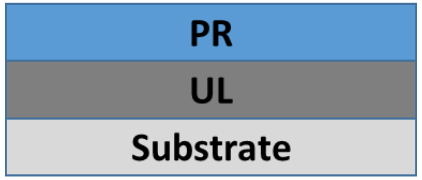
LWR
3σ nm
and stochastic
variation

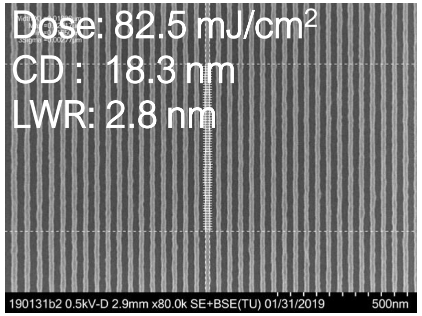
Sensitivity
dose mJ/cm²

High Si-content

High etch resistance

Low LWR

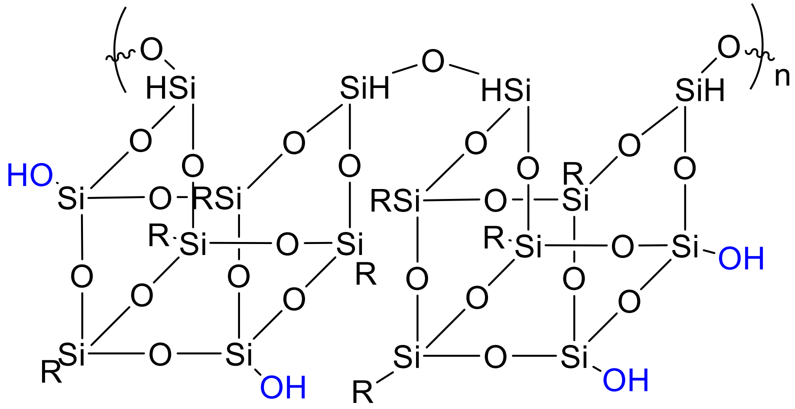




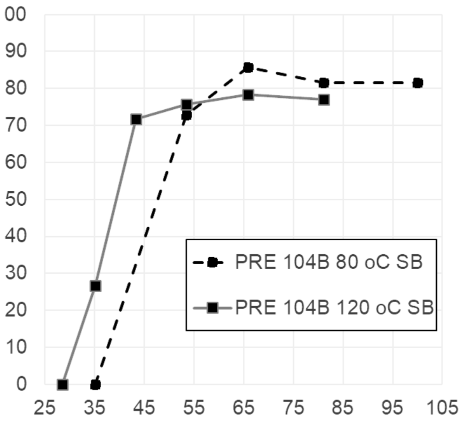
Dose: 82.5 mJ/cm²
CD : 18.3 nm
LWR: 2.8 nm

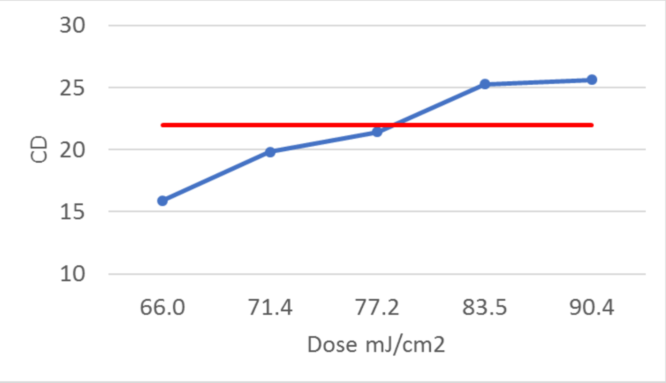
Simple processing

Process step	Parameter
Pre Bake	80°C -120°C, 1min
EUV exposure	40-95mJ/cm^2
Post exposure bake	NA
Development	TMAH 2.38%, 1-4min



Material	Bake	Thickness	Exposure dose	γ value
PRE 104B	80 °C	38.0 nm	65.8 mJ/cm2	3.7
PRE 104B	120 °C	37.6 nm	43.4 mJ/cm2	5.5





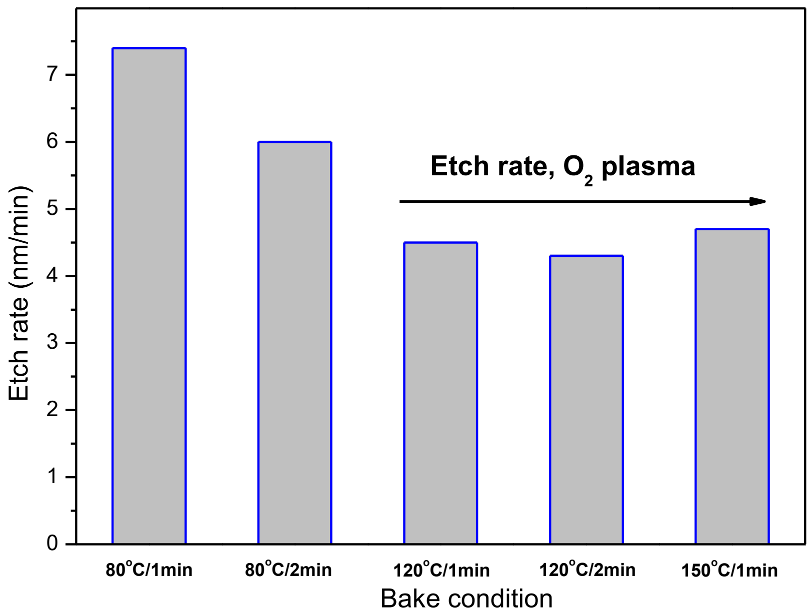
- Negative tone resist compatible with industry standard TMAH development
- Decent process window
- Dose requirement for film retention can be adjusted by process
- Good post coating delay: at least 24 h after 120 ^{o}C baking

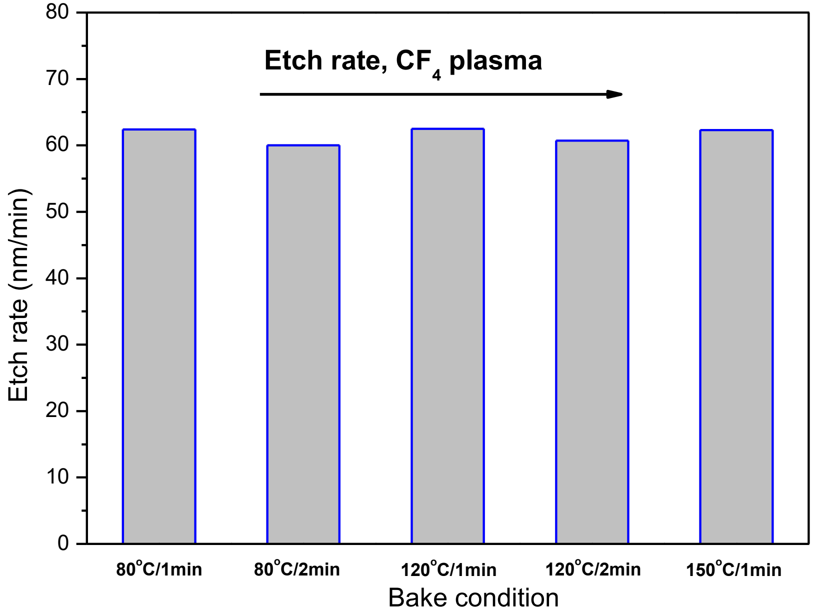
Simplified process

PRE 104B	Soft bake	Etch rate [nm/min]	selectivity PRE 104 : UL*
CF_4	80 °C/1min	62	1:0.4
	150 °C/1min	62	1:0.4
O_2	80 °C/1min	**7.3**	**1:45**
	150 °C/1min	**4.7**	**1:70**

*PiBond underlayer used as reference. Etch rate +300nm/min

- **Very high selectivity** to UL in O_2 plasma
  - Outperforms industry Si-HM's
- Increased bake increases O_2 etch resistance
- Enables bi-layer stack



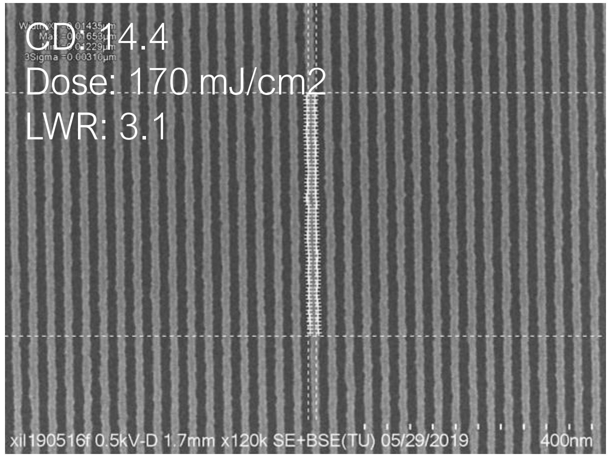


RIE recipe *		
Parameter	O_2	CF_4
RF TOP [W]	250	200
Pressure [mTorr]	50	30

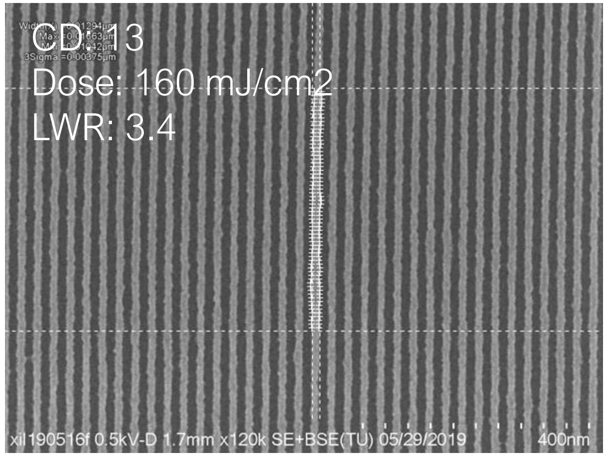
*Oxford RIE plasma lab 80

Polyhydrogen silsesquioxane resist in EUV lithography

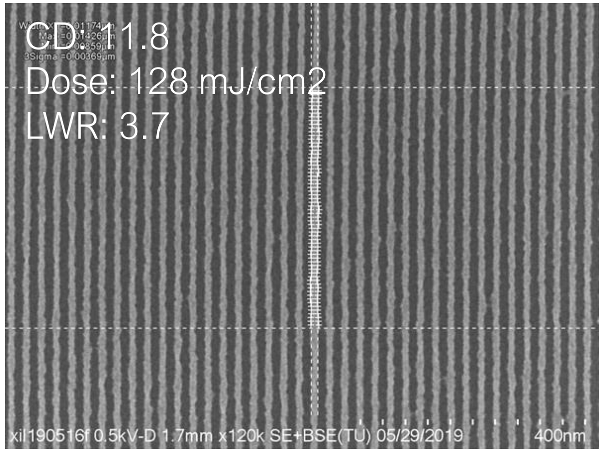
16nm HP


CD: 14.4
Dose: 170 mJ/cm2
LWR: 3.1

15nm HP


CD: 13
Dose: 160 mJ/cm2
LWR: 3.4

14nm HP


CD: 11.8
Dose: 128 mJ/cm2
LWR: 3.7

- High resolution can be obtained
  - Slight deviation from mask size, decent LWR
- Selected results, and parameters affecting the outcome discussed in this presentation

Process Conditions:
Substrate/Underlayer: Si
Spin: 1500rpm
Bake: 80C/1min
Exposure: PSI XIL-II, 22nm hp 1:1 pattern
Development: 5% TMAH/3min

Main challenge

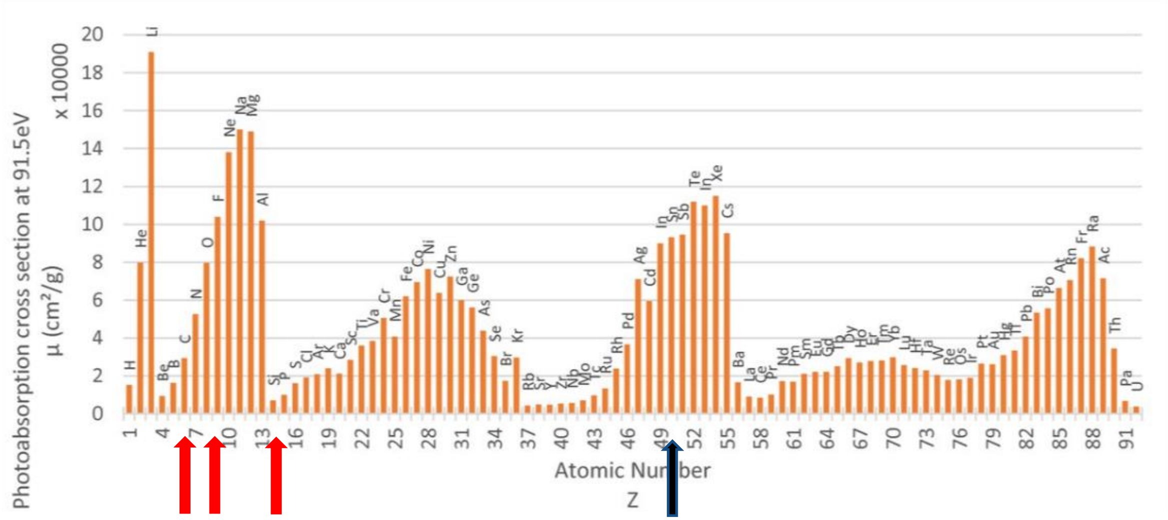
✓Sensitivity: low

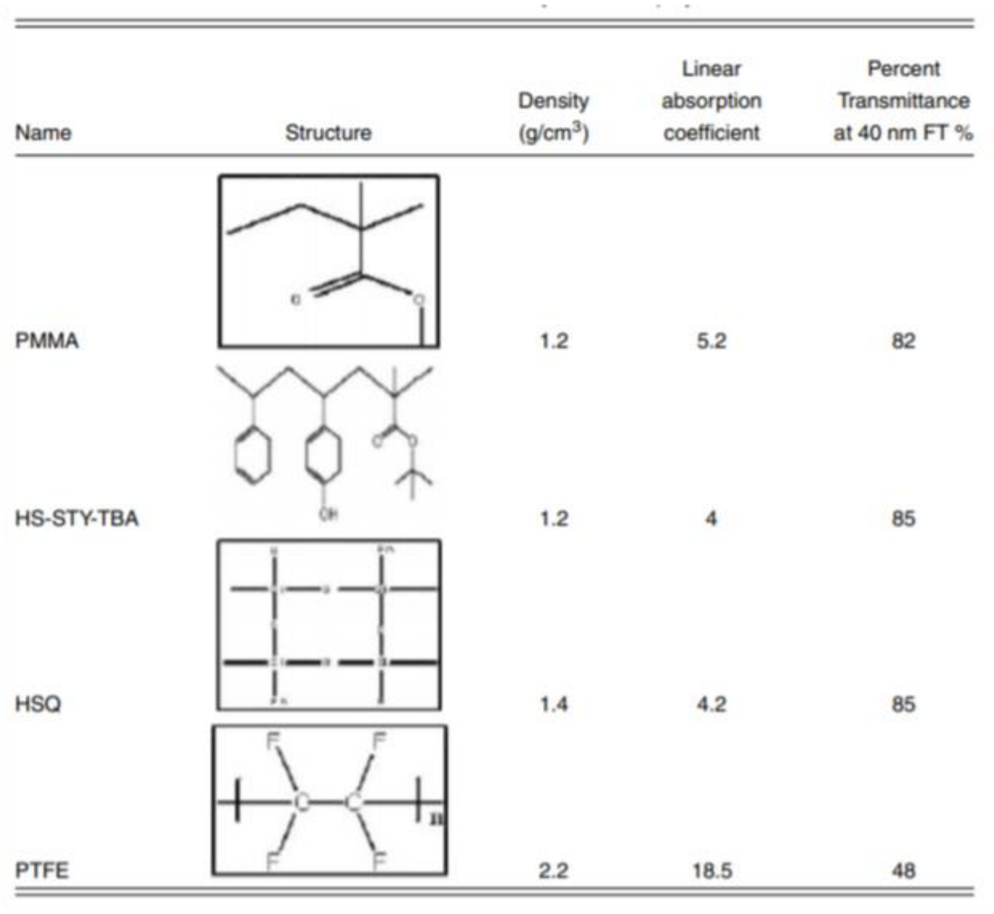
✓Solubility switch mechanism: can be modified or combined.

✓How to alter/improve the resist: chemistry modification

EUV reaction mechanisms - absorption

- Absorption:
  - HSQ resin structure close to $HSiO_{3/2}$
    → theoretical absorptivity close to CAR
    → similar analogy should suggest Sn-based resist materials to absorb significantly more than CAR





Name	Structure	Density (g/cm³)	Linear absorption coefficient	Percent Transmittance at 40 nm FT %
PMMA		1.2	5.2	82
HS-STY-TBA		1.2	4	85
HSQ		1.4	4.2	85
PTFE		2.2	18.5	48

Thackeray J. J. Micro/Nanolith. MEMS MOEMS, 10(3), 033009 (2011).

EUV reaction mechanisms - absorption

1

$$2HSiO_{3/2} \rightarrow H_2 + {=}OSi{-}SiO{=}$$

2

$$2HSiO_{3/2} \rightarrow H_2SiO + SiO_2 \qquad (1)$$

$$H_2SiO + HSiO_{3/2} \rightarrow H_3SiO_{1/2} + SiO_2 \qquad (2)$$

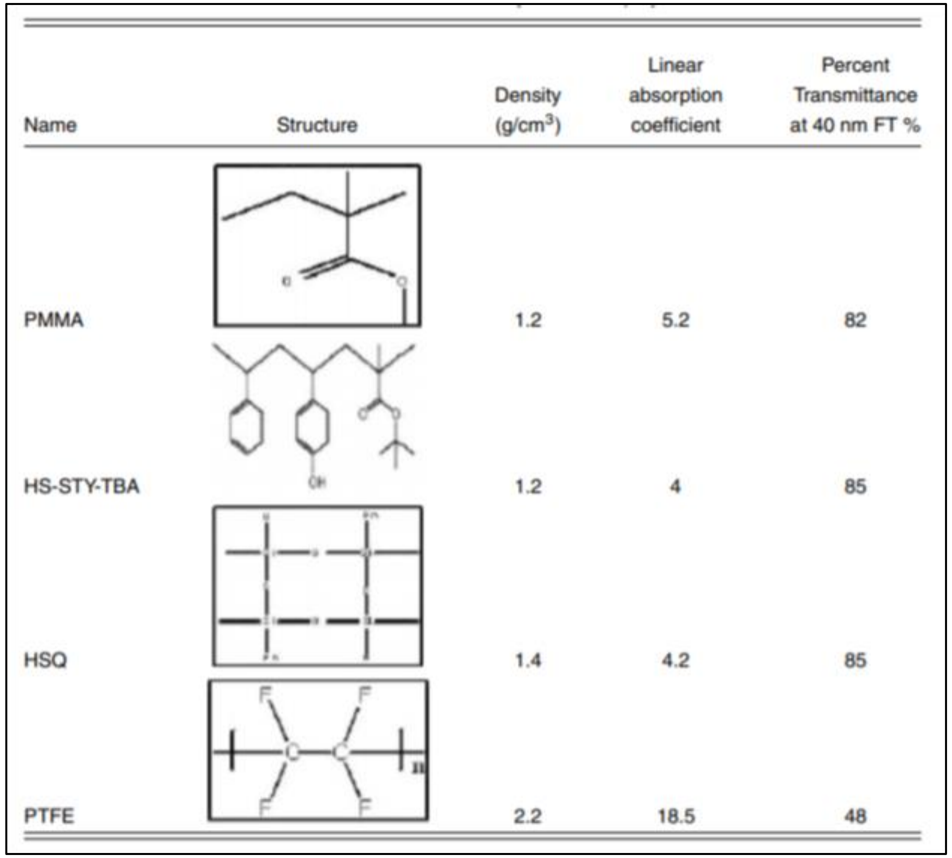
$$3H_2SiO + 6HSiO_{3/2} \rightarrow (H_8Si_4O_4) + SiH_4 + 4SiO_2 \qquad (3)$$

3

$$2HSiO_{3/2} \rightarrow H_2SiO_{2/2} + SiO_{4/2}$$

$$2H_2SiO \rightarrow 2H_2 + {=}OSi{-}SiO{=}$$

$$2H_2SiO \rightarrow SiH_4 + SiO_{4/2}.$$



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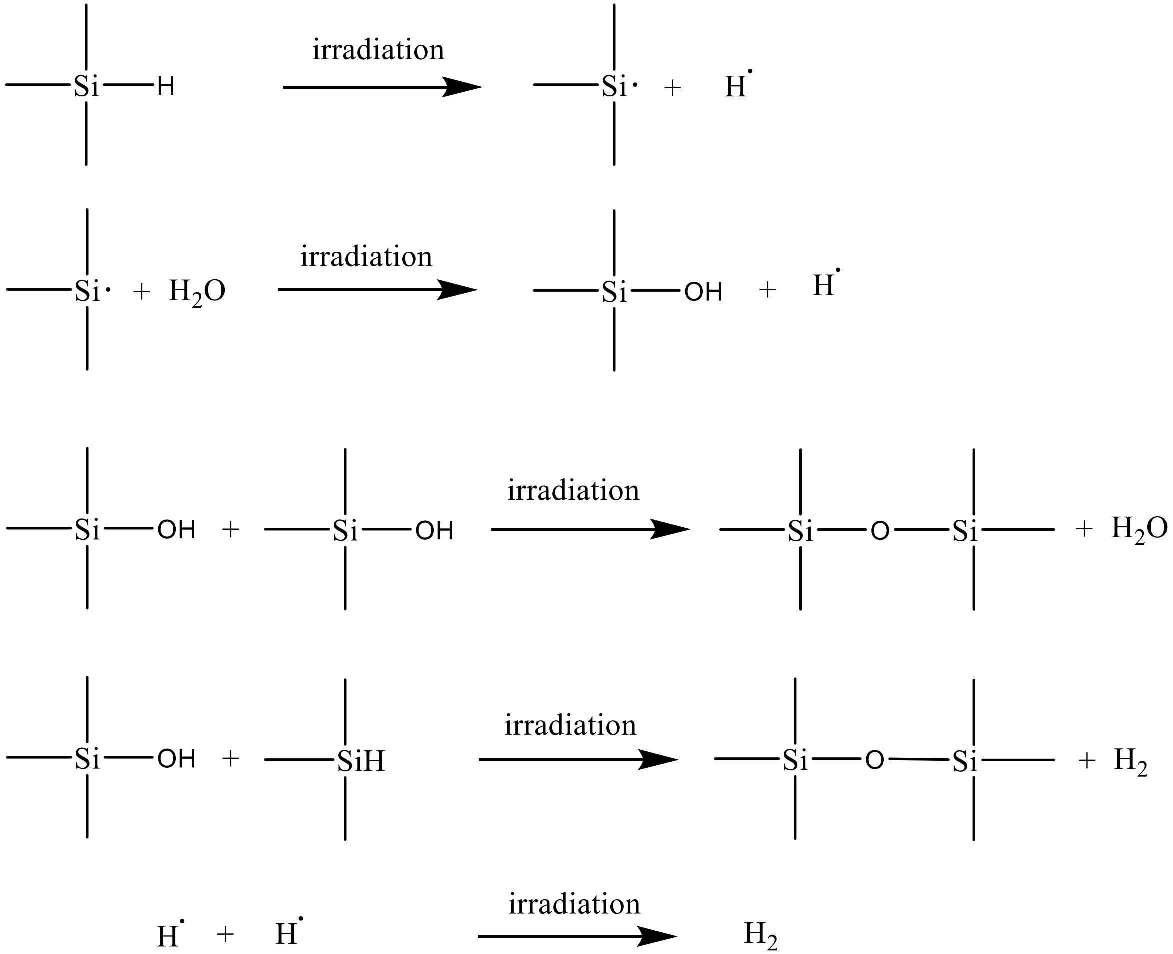
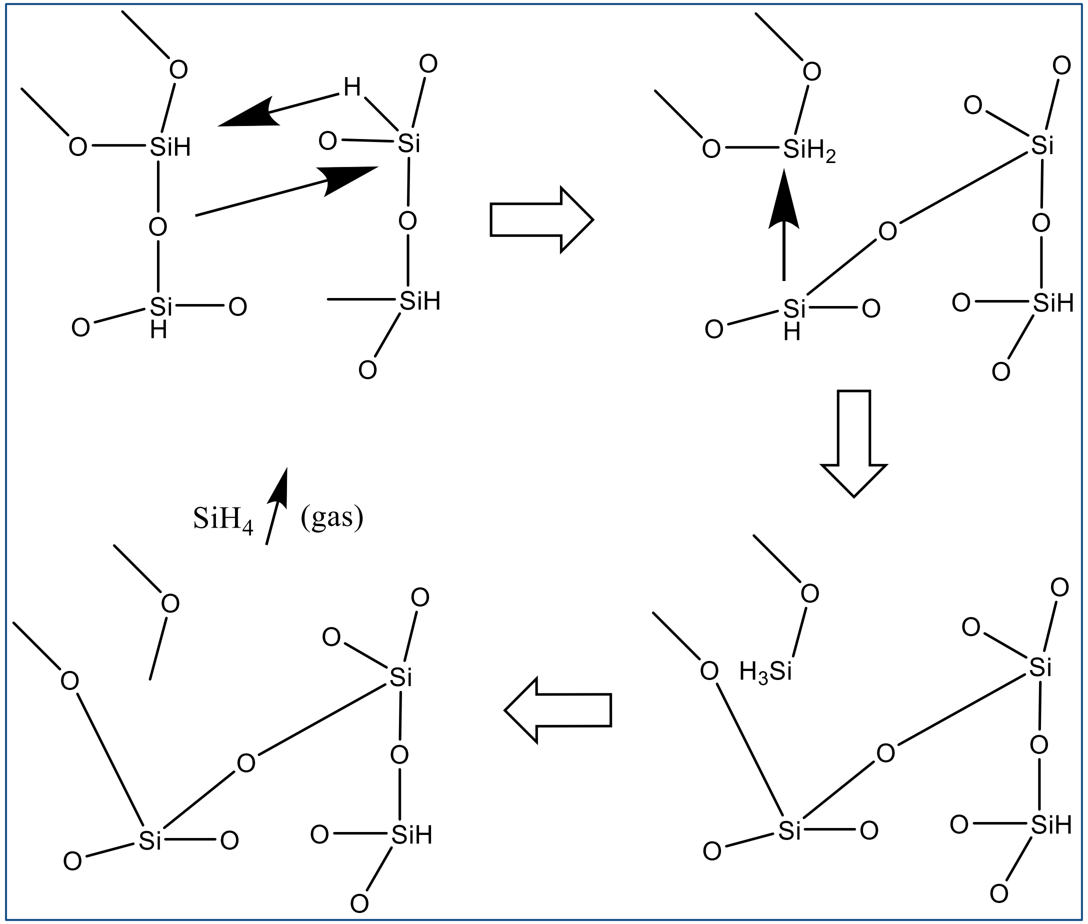
1. Namatsu, H., Yamaguchi, T., Nagase, M., Yamazaki, K., Kurihara, K. Microelectr. Eng. 1998, 41/42, 331-334
2. Volksen W, Miller RD, Dubois G. Low dielectric constant materials. Chem Rev 2009; 110:56e110.
3. Olynick, D. L., Cord, B., Schipotinin, A., Ogletree, D. F., & Schuck, P. J. (2010). *J Vac Sci & Tech B 28(3), 581–587.*

Mechanism 1_Condensation

Not likely to take place in a vacuum, the presence of water molecules is extremely rare

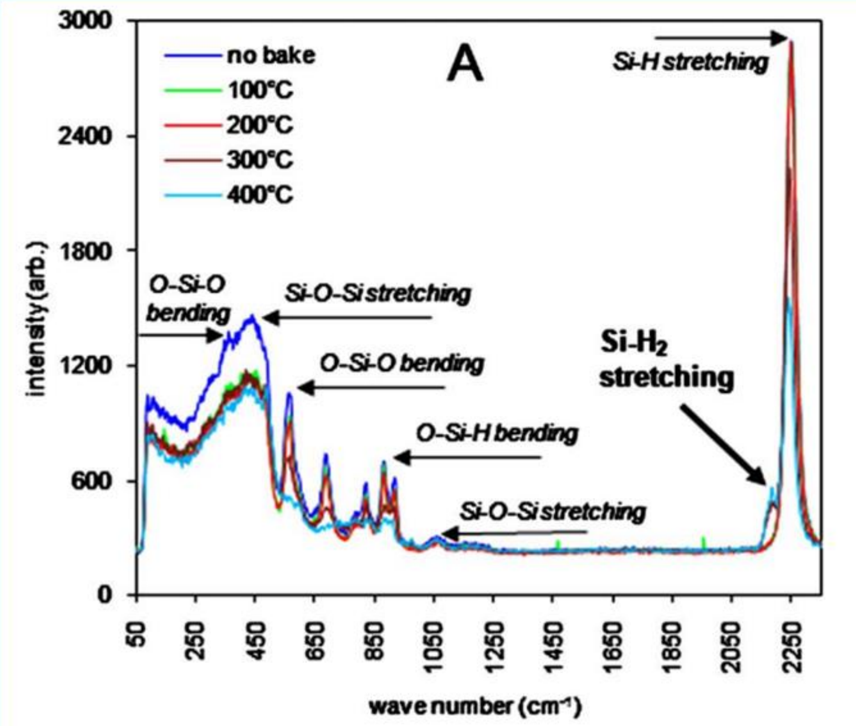


Mechanism 2_Bond redistribution



Ashish et al, "Extreme Ultraviolet-Printability and Mechanistic Studies of Engineered Hydrogen Silsesquioxane Photoresist Systems," *ACS Appl. Polym. Mater.* 3, 4, 1964–1972 (2021)

HSQ_mechanism 2_crosslinking *via* bond redistribution



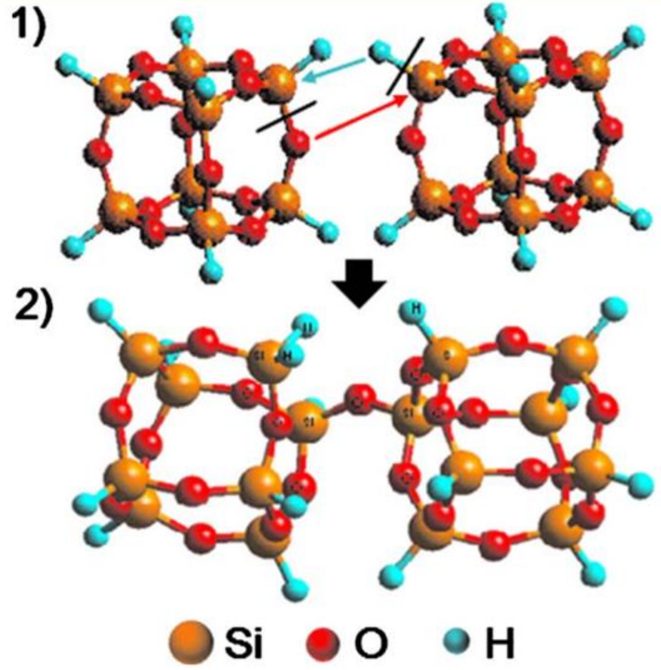
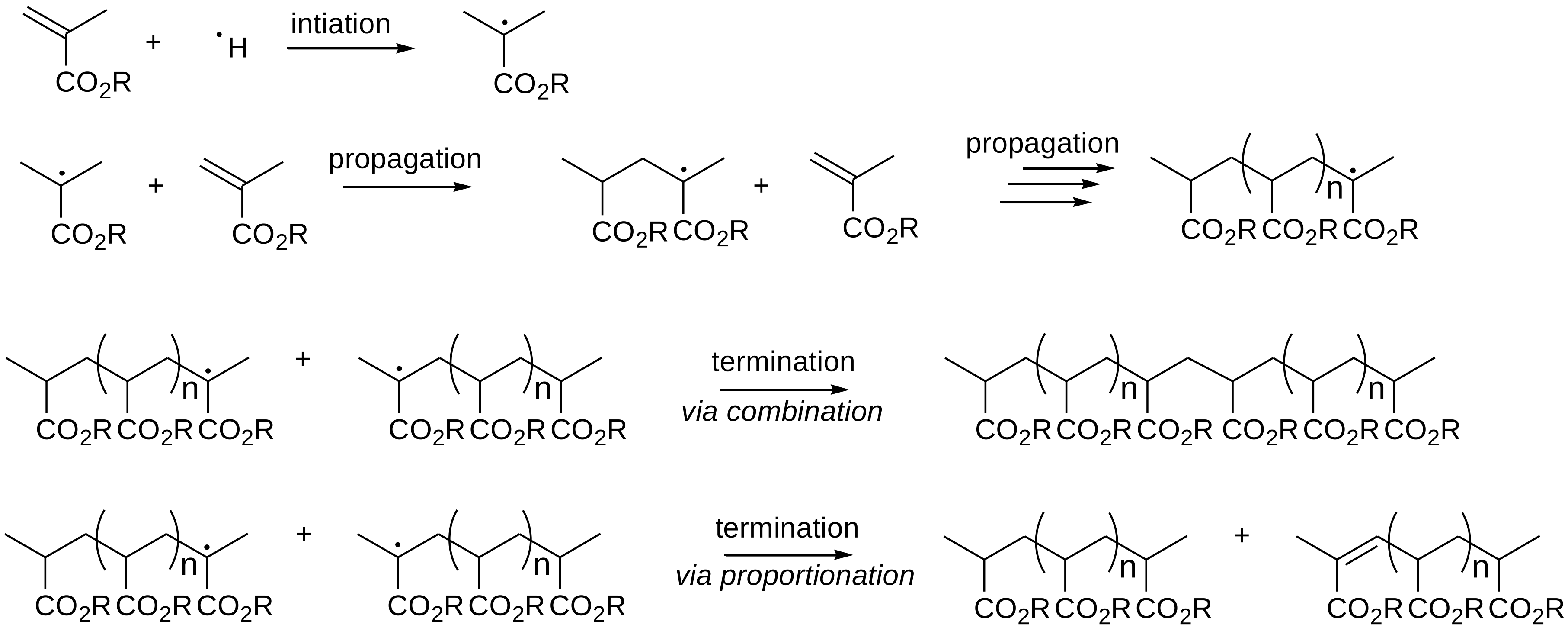


FIG. 3. (Color online) Schematic illustration of the redistribution reaction that may be partially responsible for cross-linking in HSQ. A Si—H and Si—O bond are broken on adjacent HSQ cages (1). The resulting oxygen radical bonds to the site formerly occupied by the hydrogen atom on the adjacent cage, while the now-free hydrogen atom bonds to the Si atom at the site formerly occupied by the oxygen atom, resulting in two slightly altered HSQ cages connected by an oxygen atom (2). Note that this reaction does not depend on the presence of any external reactant, such as water, in order to occur.

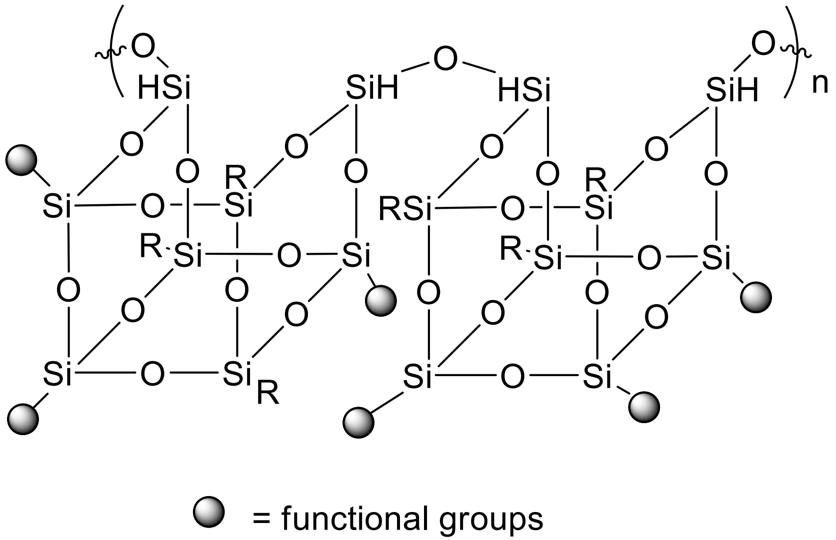
D. L. Olynick et al, Journal of Vacuum Science & Technology B 28, 581 (2010)

Mechanism 3_Patterning mechanism



Improved material design at PiBond

- Specific organic functional groups used to modify polyhydrogensilsesquioxane resin performance:
  - Increase resin reactivity
  - Increase resin EUV absorption
  - Add functions to impart in altered dissolution to developer



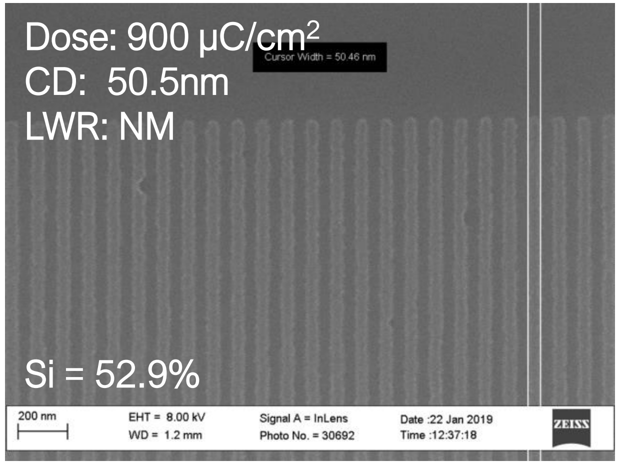
A : group to increase resin reactivity

B : group to enhance absorption

C : group to alter resin solubility to developer

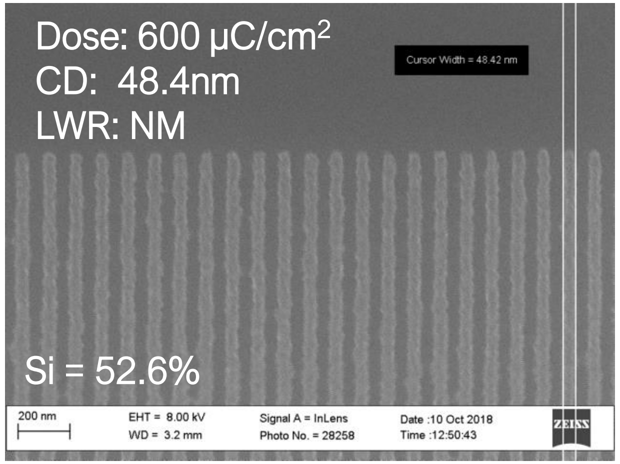
A : group to increase resin reactivity

Reference



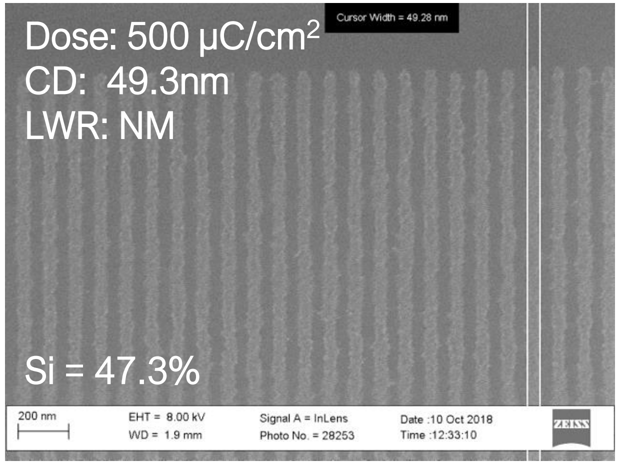
Dose: 900 μC/cm^2
CD: 50.5nm
LWR: NM
Si = 52.9%

2.5% functional A
33% more sensitive

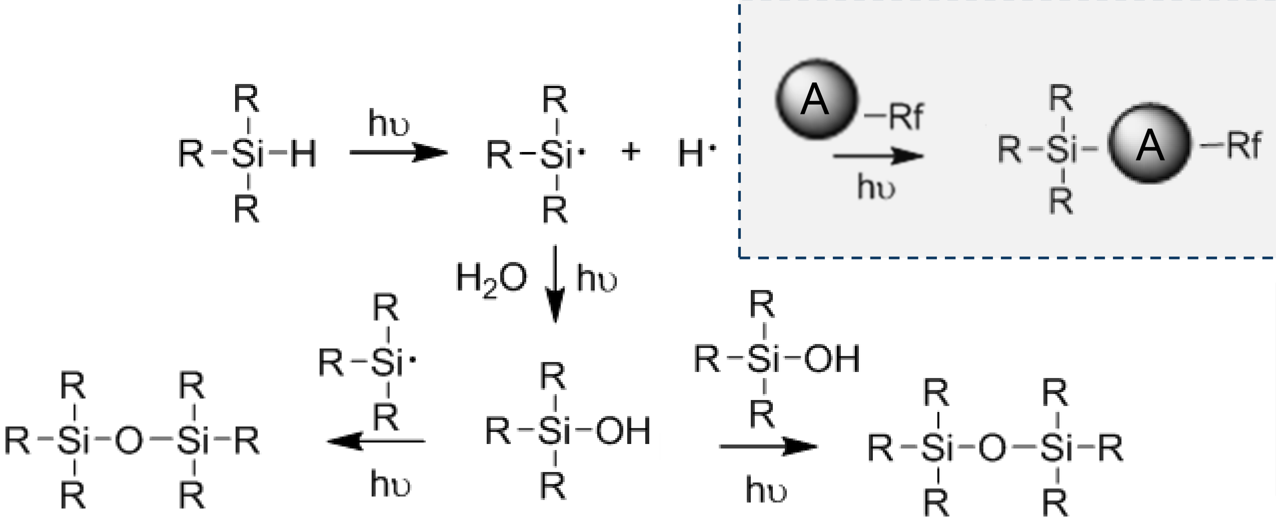


Dose: 600 μC/cm^2
CD: 48.4nm
LWR: NM
Si = 52.6%

5% functional A
42% more sensitive



Dose: 500 μC/cm^2
CD: 49.3nm
LWR: NM
Si = 47.3%

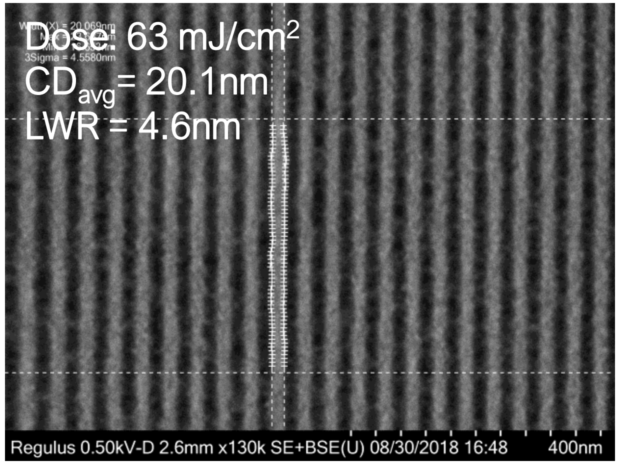


⇦ Alternative reaction path

Process Conditions:
Substrate/Underlayer: Si
Thickness: 20nm@1500rpm
Bake: 80C/1min
Exposure: Vistec EBL, 50nm hp 1:1 pattern
Development: 2.38% TMAH/2min

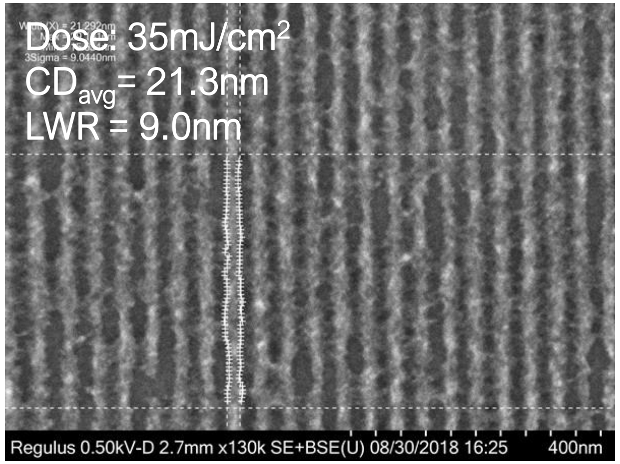
A : group to increase resin reactivity

Reference



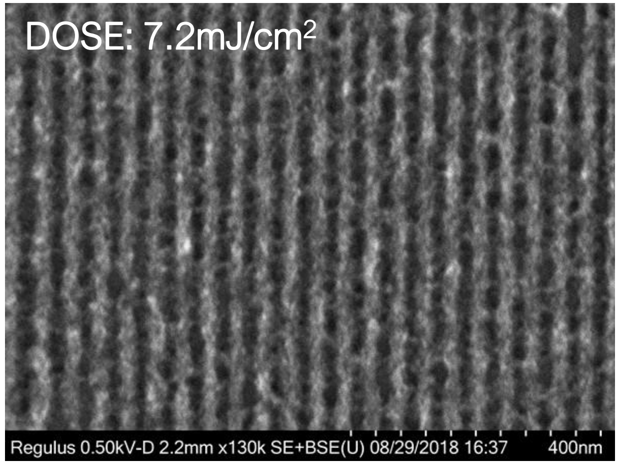
Dose: 63 mJ/cm^2
CD$_{avg}$= 20.1nm
LWR = 4.6nm

3.3% functional A
45% more sensitive

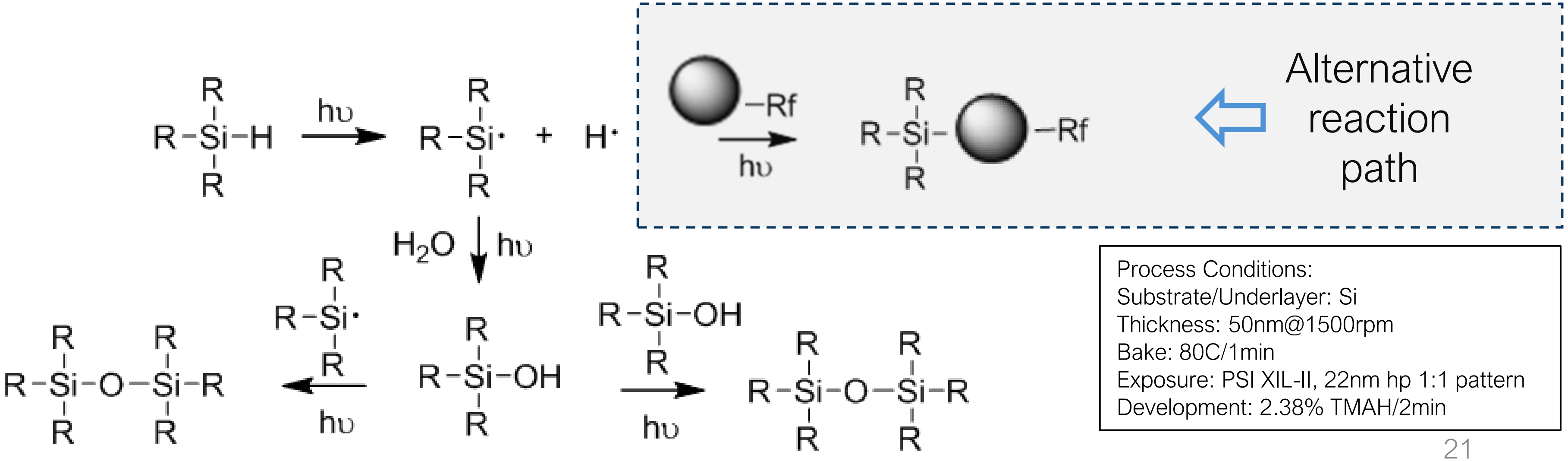


Dose: 35mJ/cm^2
CD$_{avg}$= 21.3nm
LWR = 9.0nm

10% functional A
89% more sensitive

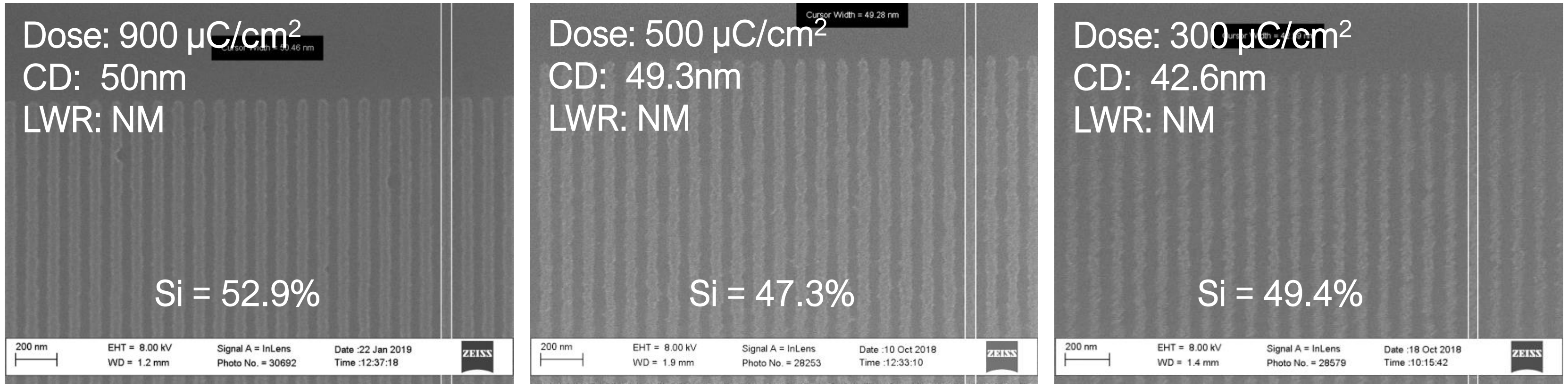


DOSE: 7.2mJ/cm^2



Process Conditions:
Substrate/Underlayer: Si
Thickness: 50nm@1500rpm
Bake: 80C/1min
Exposure: PSI XIL-II, 22nm hp 1:1 pattern
Development: 2.38% TMAH/2min

B : group to increase resin absorption



Reference

5% Functional A
42% more sensitive

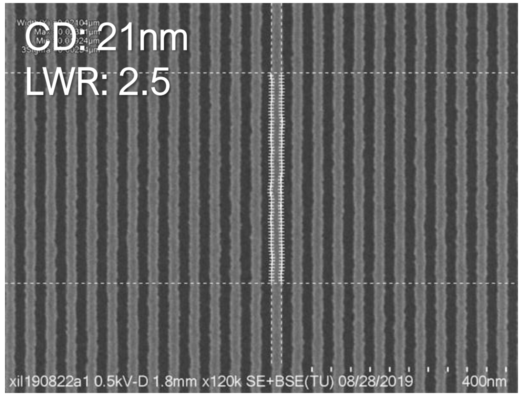
5% Functional B
70% more sensitive

- Effect of absorbing group C:
  - Increased functional group ⇨ significant improvement in sensitivity

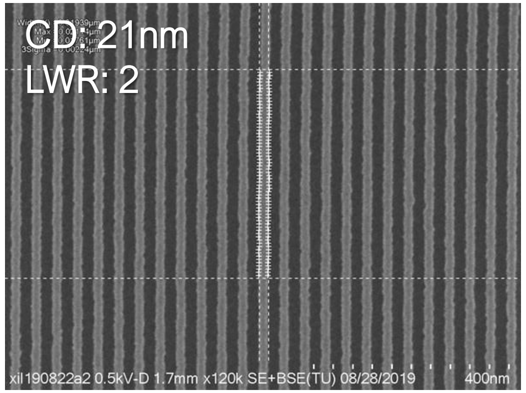
Process Conditions:
Substrate/Underlayer: Si
Thickness: 20nm@1500rpm
Bake: 80C/1min
Exposure:Vistec EBL 50nm hp 1:1 pattern
Development: 2.38% TMAH/2min

B : group to increase resin absorption

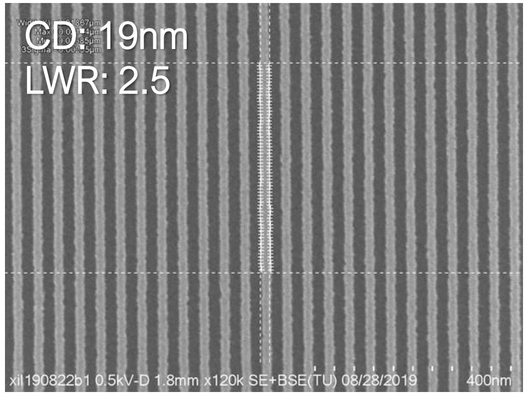
Reference
Development: 2.38% TMAH 3min



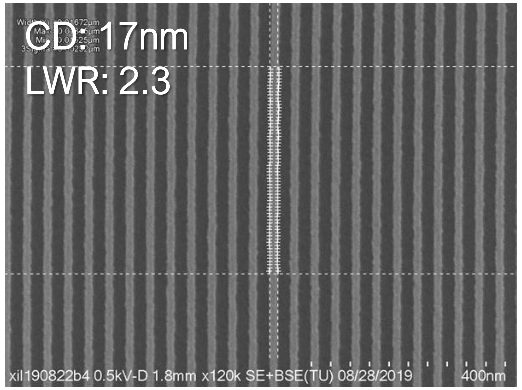
Reference
Development: 5% TMAH 3min



5% Functional B
Development: 2.38% TMAH 3min



5% Functional B
Development: 5% TMAH 3min

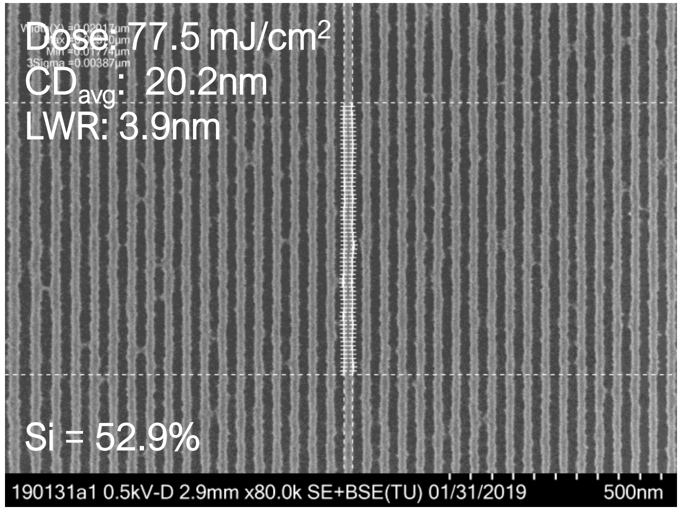


- Effect of absorbing group B:
  - Increased functional group ⇨ decrease in sensitivity
  - Increased dose needed to achieve same CD

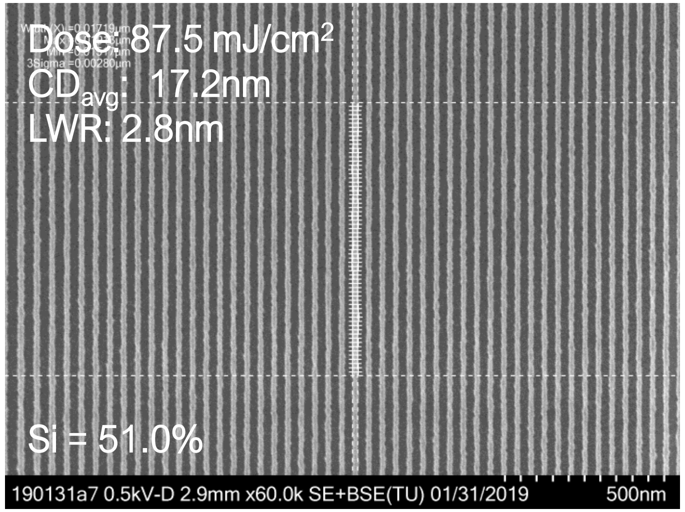
Process Conditions:
Substrate/Underlayer: Si
Thickness: 50nm@1500rpm
Bake: 80C/1min
Exposure: PSI XIL-II, 22nm hp 1:1 pattern
Development: see above

C : group to improve resin solubility

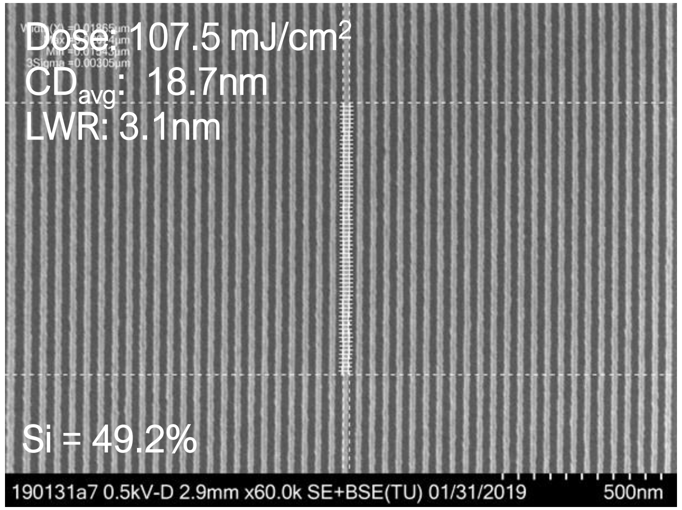
Reference


Dose: 77.5 mJ/cm^2
CD$_{avg}$: 20.2nm
LWR: 3.9nm
Si = 52.9%

1% Functional C


Dose: 87.5 mJ/cm^2
CD$_{avg}$: 17.2nm
LWR: 2.8nm
Si = 51.0%

2% Functional C

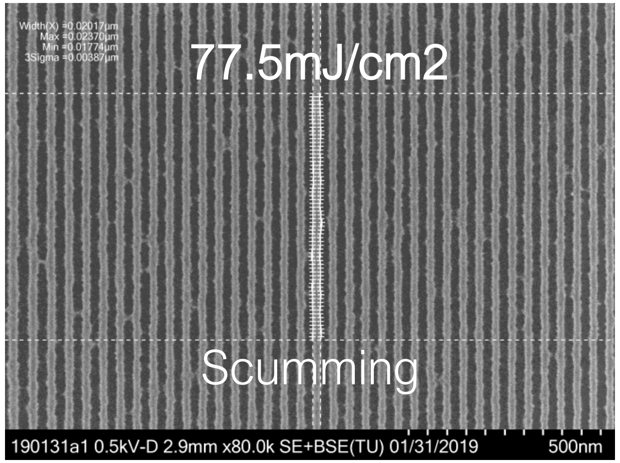

Dose: 107.5 mJ/cm^2
CD$_{avg}$: 18.7nm
LWR: 3.1nm
Si = 49.2%

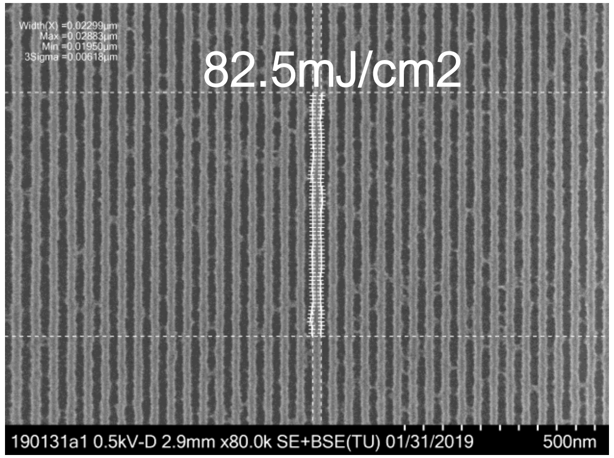
- Effect of functional group C:
  - Increased functional group ⇨ decreased sensitivity
  - Increased functional group ⇨ improved LWR, decreased scumming and bridging

Process Conditions:
Substrate/Underlayer: Si
Thickness: 20nm@1500rpm
Bake: 80C/1min
Exposure: PSI XIL-II, 22nm hp 1:1 pattern
Development: 2.38% TMAH/3min

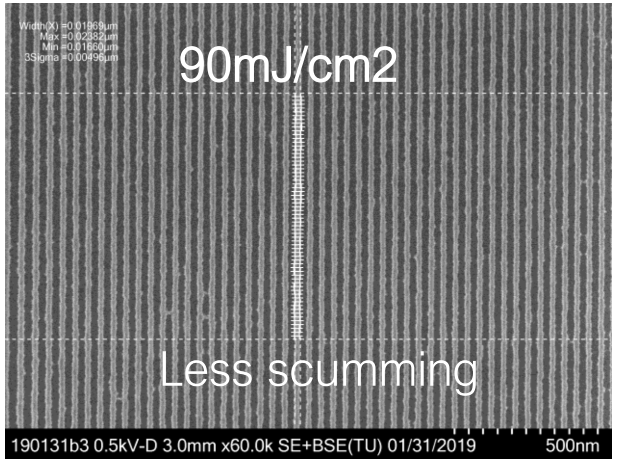
LER/Resolution improvements with different solubility enhancer EUV

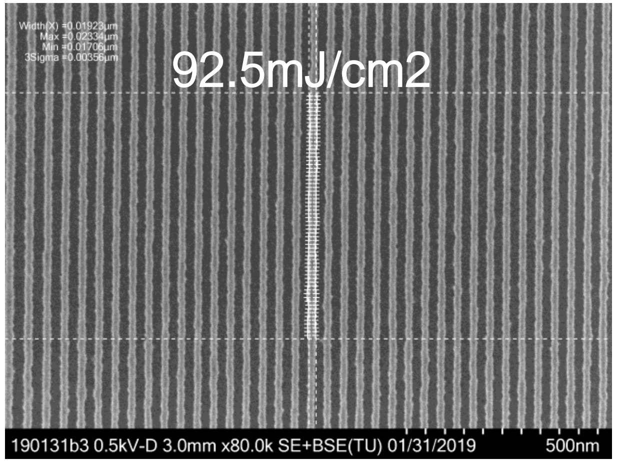
Reference sample



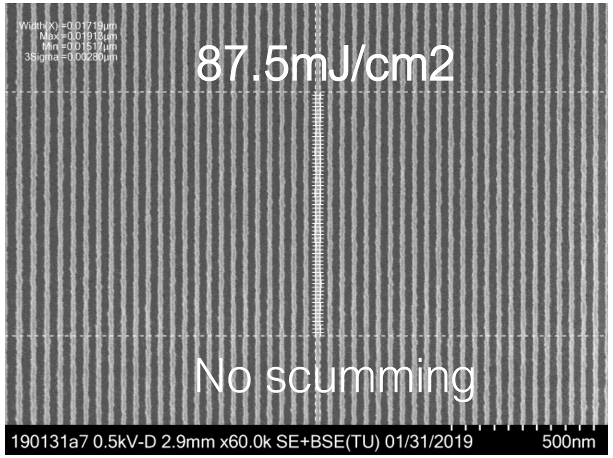


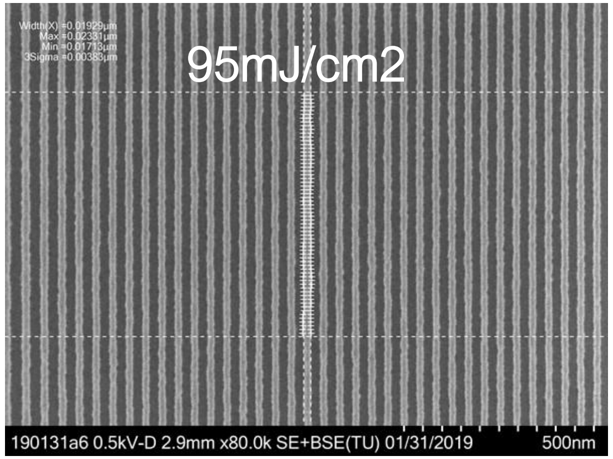
Solubility enhancer C1



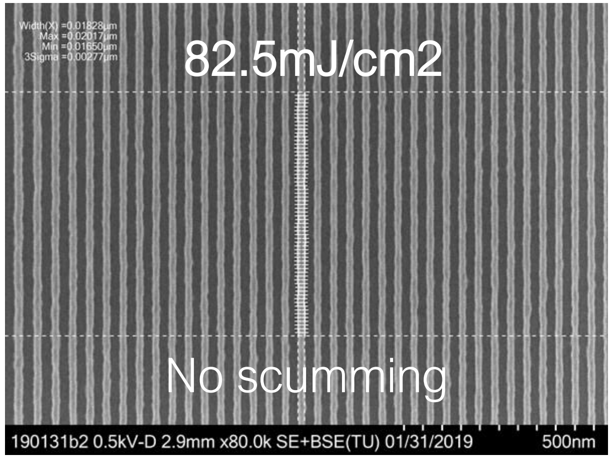


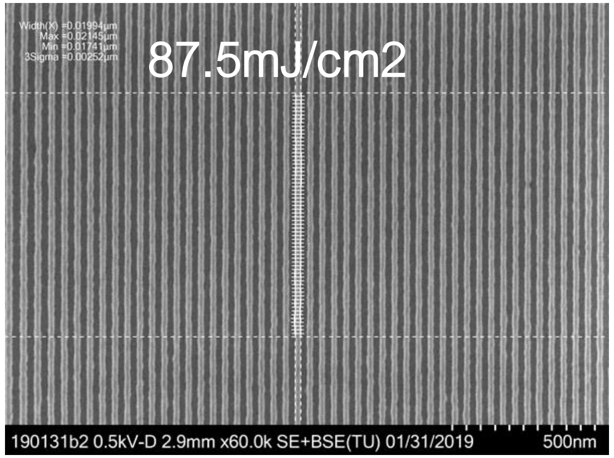
Solubility enhancer C2





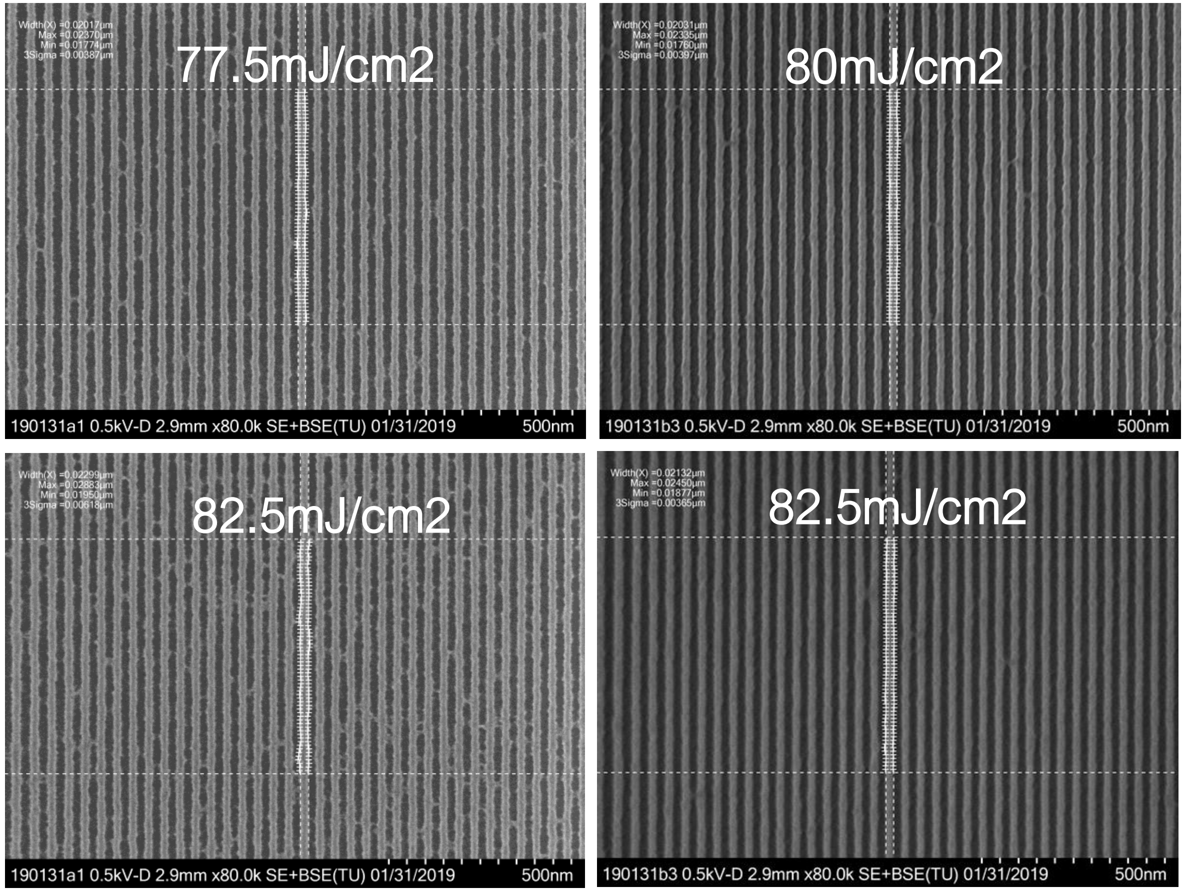
Solubility enhancer C3





Underlayer effect_ EUV

Si PiBond's OTL



Summary of PiBond’s siloxane resist

Main characteristics

- Simple and stable processing: aqueous development
- Simplified patterning: inorganic, excellent etch performance
- Risk-free: no metal contamination, low outgassing

Summary

Silicon based resist materials show promise as potential candidates in EUVL

High resolution demonstrated

Main challenge: sensitivity needs to be improved

Process parameters have significant effect on outcome

Improvement in resist performance can be obtained through chemical modifications

The underlayer effect is important and will affect results significantly

Thank You for your time!