Improvement of KrF photoresist performance by formulation and process optimization

HLMC Litho process：**Liang Cai**
2022.10.21

上海华力 HLMC

KEMPUR

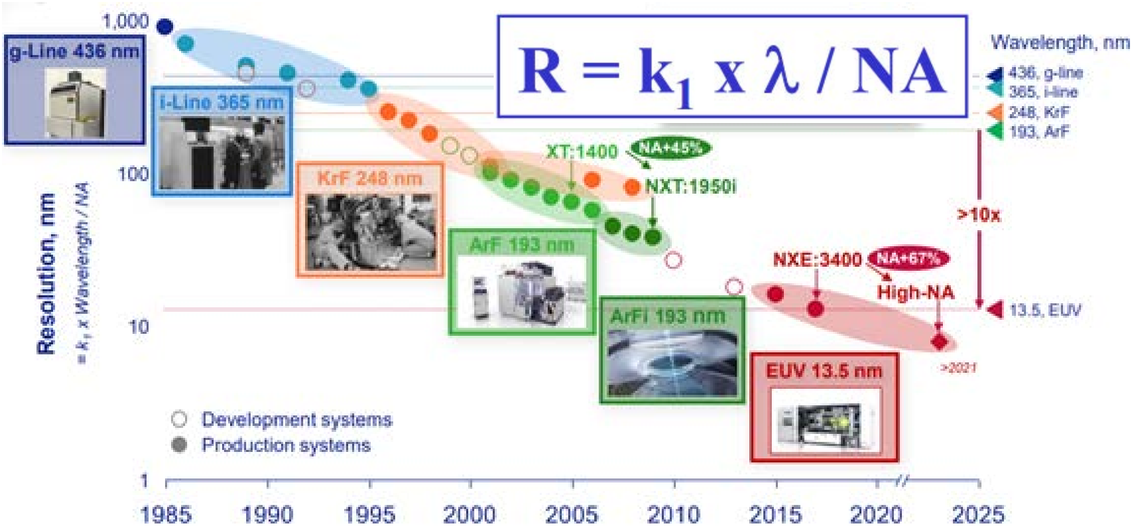
Red Avenue
彤 程 电 子

CATALOG

Part 1

INTRODUCTION

Lithography Development



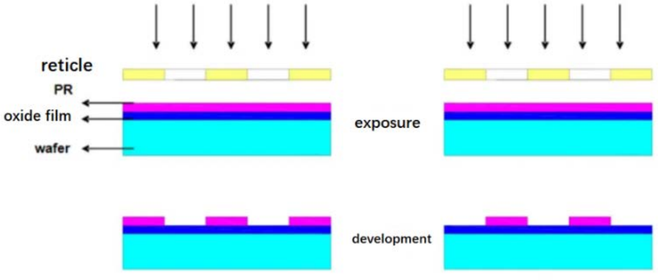
R : Resolution
k1 : depend on the process
λ : wavelength
NA : numerical aperture

3 ways to reduce Resolution

- ✓ Reduce λ : 436nm(G) => 365nm(I) => 248nm(KrF) => 193nm(ArF) => 13.5nm(EUV)
- ✓ Increase NA : 0.5 => 0.93 => 1.35
- ✓ Reduce K1 : Complex

Photoresist Classification

Classification by development



Positive

Negative

Classification by chemical structure

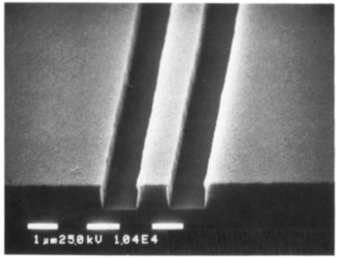
- ✓ polymerization
- ✓ decomposition
- ✓ crosslinking
- ✓ chemical amplify

Classification by exposure wavelength

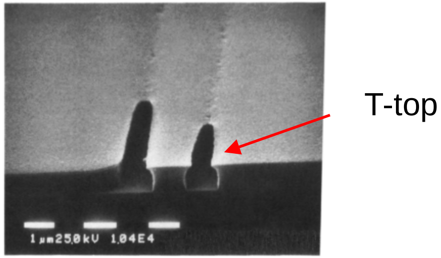
IC resist	Exposure wavelength	Technology node	FAB
I line	365nm (UV)	0.35um-0.5um	6’ 8‘
KrF	248nm (DUV)	0.13um-0.25um	8’ 12'
ArF	193nm (DUV)	7-130nm	12'
EUV	13.5nm (EUV)	< 7nm	12'

Basic chemistry of photoresist

- ***Reaction mechanism of ESCAP and Acetal polymer***

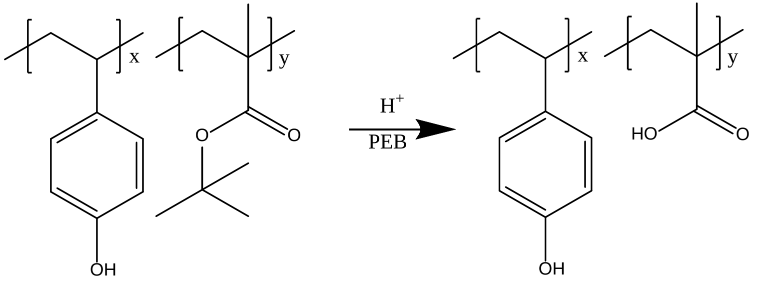


15 min in filtered air



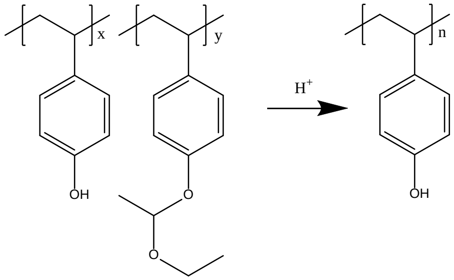
15 min in 10 ppb
NMP before exposure

ESCAP polymer



High Ea platform
HS(hydroxy styrene) and TBA(t-butyl acrylate) copolymer as main polymer good heat stability can withstand bake over 140℃

Acetal polymer



Low Ea platform
the block group is ethyl vinal ether (EVE)
can be deblocked at room temperature

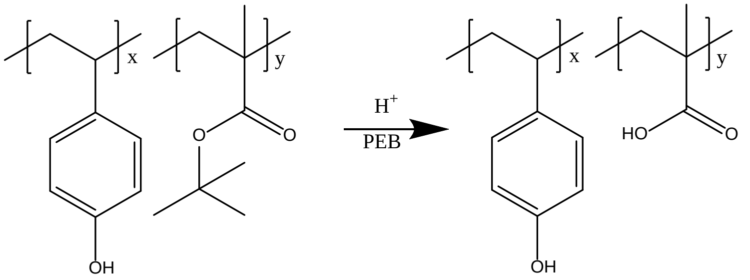
Part 2

DEVELOPMENT OF KRF PHOTORESIST OF HIGH ACTIVATION ENERGY(ESCAP)

DEVELOPMENT OF KRF PHOTORESIST OF HIGH ACTIVATION ENERGY(ESCAP)

ESCAP: Environmentally Stable Chemical Amplify Photoresist

Reaction mechanism of ESCAP polymer

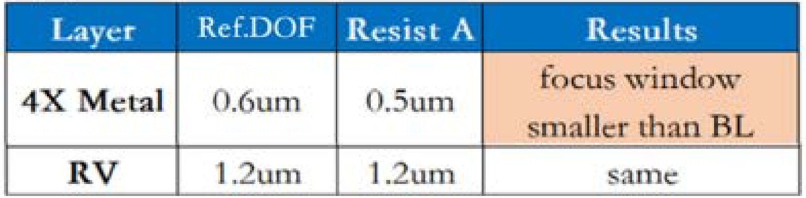


High Ea platform
Hydroxy styrene and t-butylacrylate copolymer as main polymer
good heat stability can withstand bake over 140℃

DEVELOPMENT OF KRF PHOTORESIST OF HIGH ACTIVATION ENERGY(ESCAP)

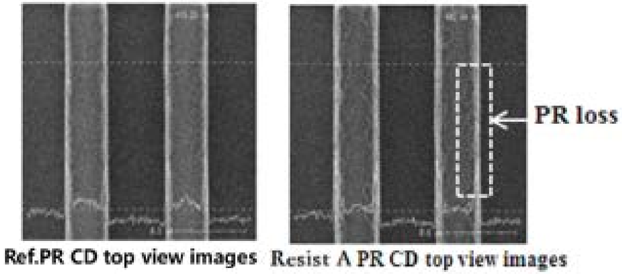
- ***Process verification***

(a)



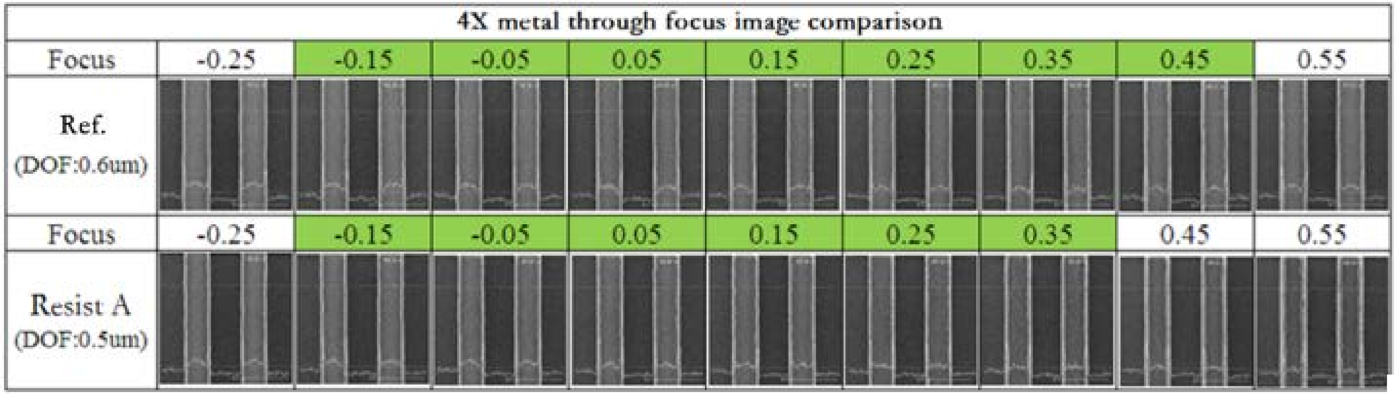
Layer	Ref.DOF	Resist A	Results
4X Metal	0.6um	0.5um	focus window smaller than BL
RV	1.2um	1.2um	same

(c)



Ref.PR CD top view images Resist A PR CD top view images

(b)

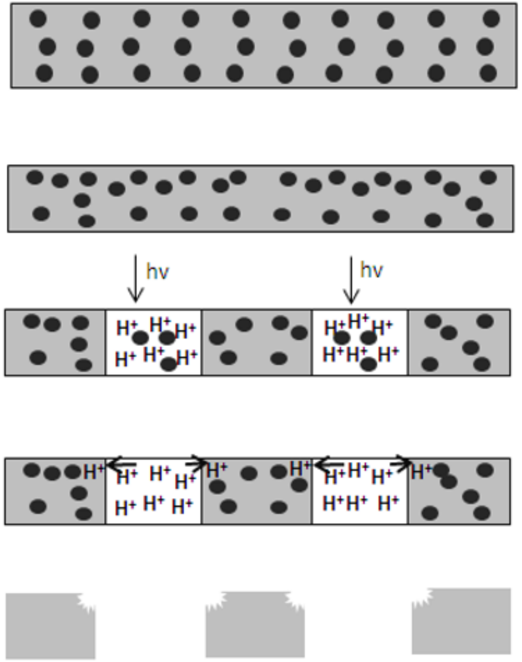


4X metal through focus image comparison									
Focus	-0.25	-0.15	-0.05	0.05	0.15	0.25	0.35	0.45	0.55
Ref. (DOF:0.6um)									
Focus	-0.25	-0.15	-0.05	0.05	0.15	0.25	0.35	0.45	0.55
Resist A (DOF:0.5um)									

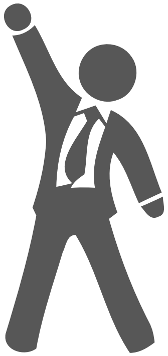
上海华力
HLMC

DEVELOPMENT OF KRF PHOTORESIST OF HIGH ACTIVATION ENERGY(ESCAP)

- ***Investigation of PR loss for top view images***



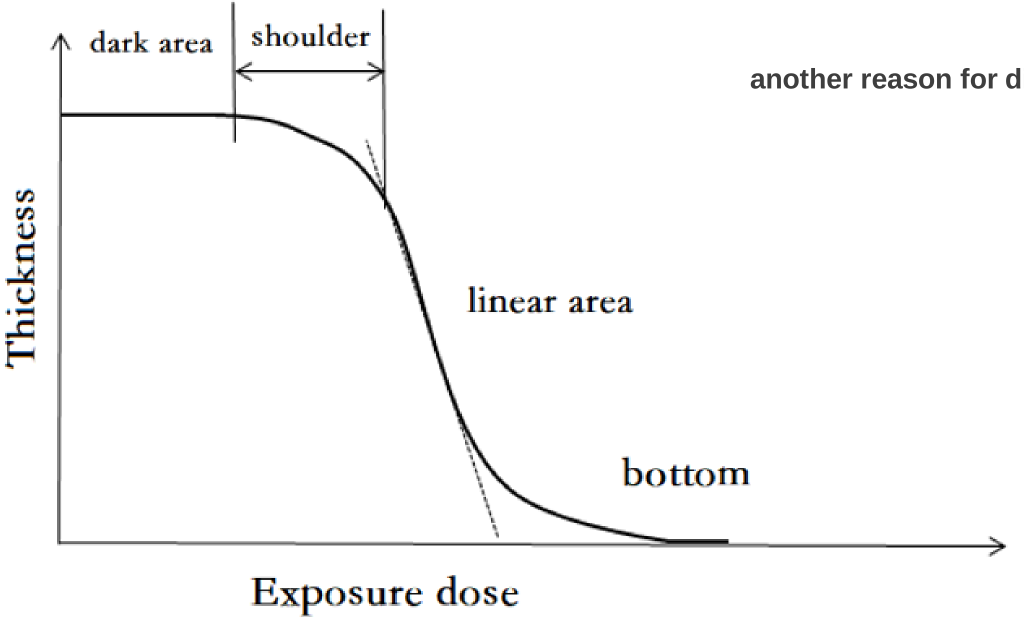
(a) After coating	● PAG
(b) After soft baking	Solvent volatilized and PAG was enriched on the surface
(c) After exposure	Generate H^+ after exposure
(d) After Baking	After baking, the high concentration of H^+ on the surface is more likely to diffuse to the non exposed area
(e) After development	After development, the top photoresist is lost



上海华力
HLMC

DEVELOPMENT OF KRF PHOTORESIST OF HIGH ACTIVATION ENERGY(ESCAP)

- ***Photoresist contrast curve***



another reason for dissolution on the top of photoresist pattern is that the poor contrast.

DEVELOPMENT OF KRF PHOTORESIST OF HIGH ACTIVATION ENERGY(ESCAP)

High activation energy of ESCAP KrF resist is more suitable for the process layer with less requirements for sharp profile.

For other process layers, further R&D verification is still needed.

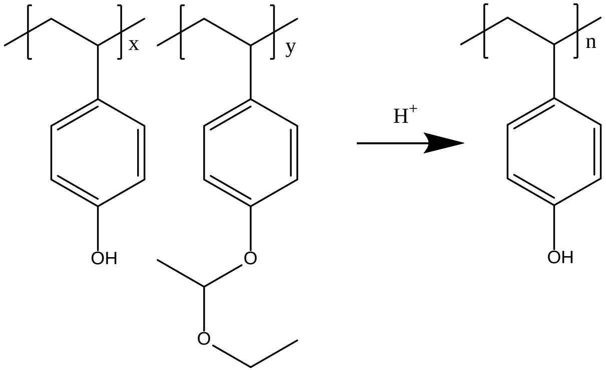
Part 3

DEVELOPMENT OF LOW ACTIVATION ENERGY KRF PHOTORESIST (ACETAL)

DEVELOPMENT OF LOW ACTIVATION ENERGY KRF PHOTORESIST (ACETAL)

- ***Acetal type polymer***

Reaction mechanism of Acetal polymer

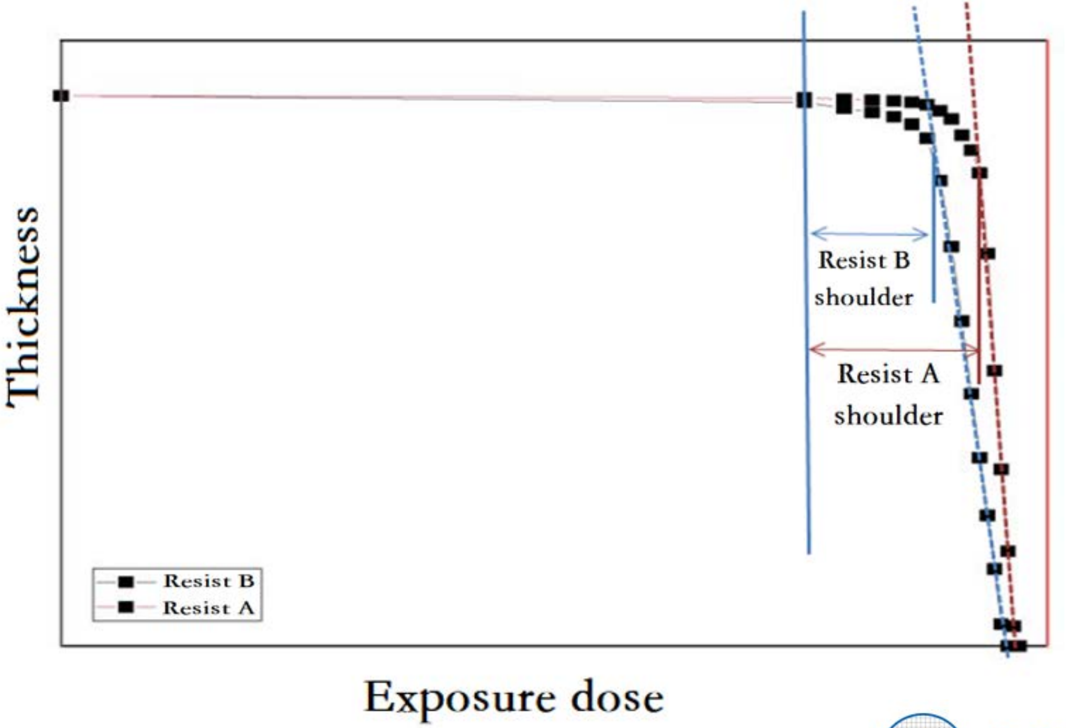


Low Ea platform
the block group is ethyl vinal ether (EVE)
can be deblocked at room temperature

DEVELOPMENT OF LOW ACTIVATION ENERGY KRF PHOTORESIST (ACETAL)

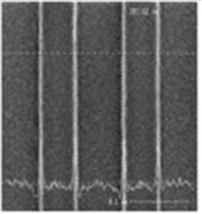
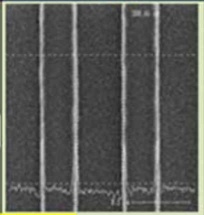
- ***Contrast curve of resist B (Acetal) and resist A(ESCAP)***

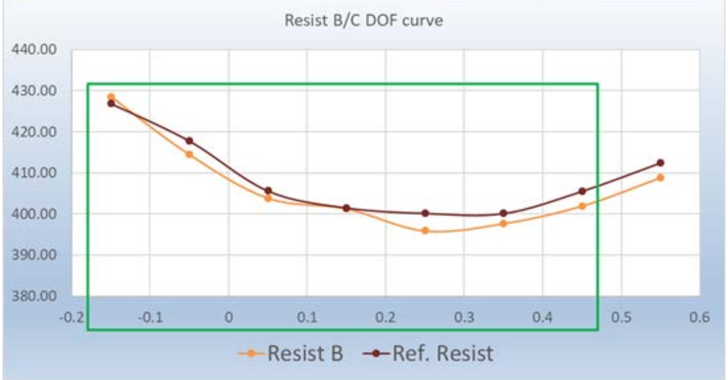
from the Acetal(Resist B) contrast curve, the shoulder is small.

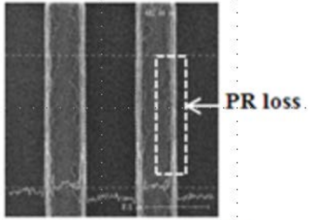


DEVELOPMENT OF LOW ACTIVATION ENERGY KRF PHOTORESIST (ACETAL)

DOF and image Results of resist B in 4x metal

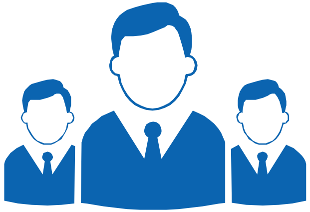
Layer	Ref. Resist		Resist B	
	DOF	Image	DOF	Image
4X Metal	0.6 um		0.6 um	 compare





Resist A PR CD top view images

Resist B 4X metal DOF is consistent with benchmark photoresist, and 4X metal top view images have no dissolution problem.

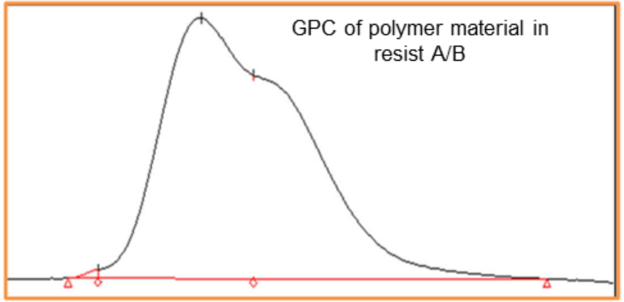


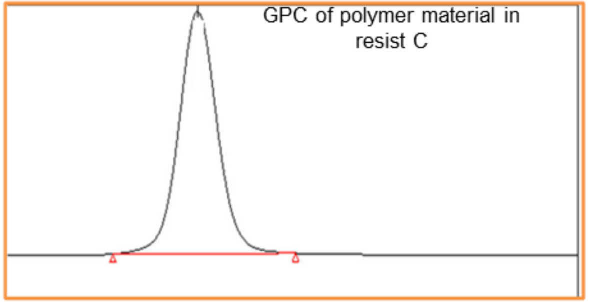
Part 4

ADVANCED PHOTORESIST DEVELOPMENT

ADVANCED PHOTORESIST DEVELOPMENT

Mechanism of photoresist improvement and optimization





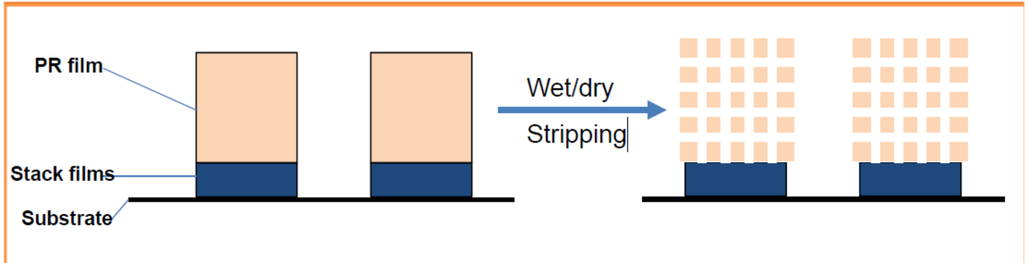
PDI
(Polymer dispersity index)

- High PDI, poor molecular size uniformity
- dissolution/ degradation rate of different polymer molecular is different

=> more ASI defect

- Low PDI, good molecular size uniformity
- dissolution/ degradation rate of different polymer molecular is similar

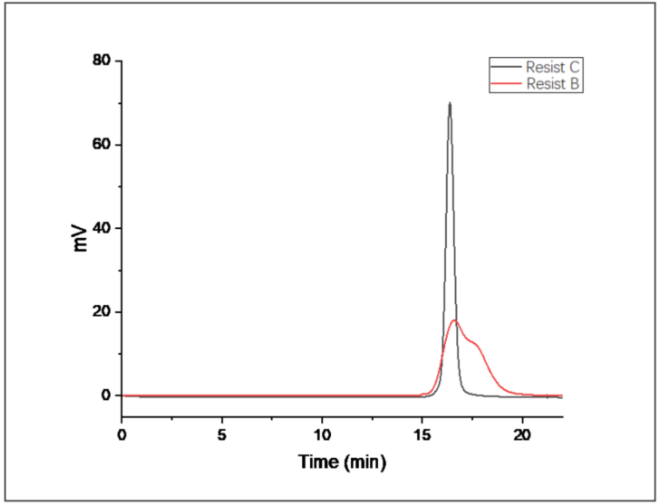
=> less ASI defect



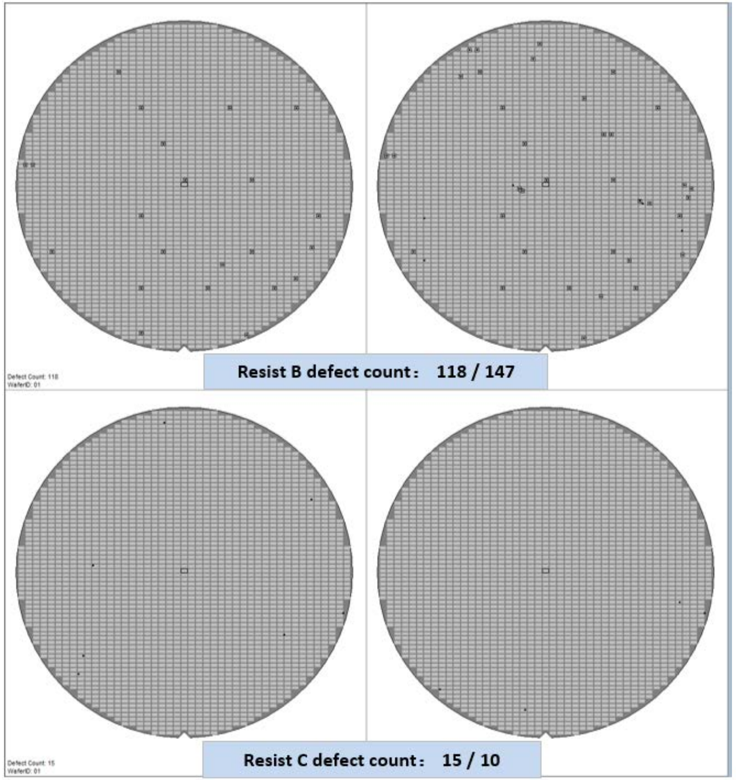
ADVANCED PHOTORESIST DEVELOPMENT

■ *Development of low PDI photoresist*

	Mn	Mw	PDI
Resist A	11450	20208	1.76
Resist B	8984	16028	1.48
Resist C	17673	18459	1.05



GPC of Resist B and Resist C



Resist B defect count： 118 / 147

Resist C defect count： 15 / 10

Part 5

COMPARISON OF THREE KINDS OF PHOTORESIST

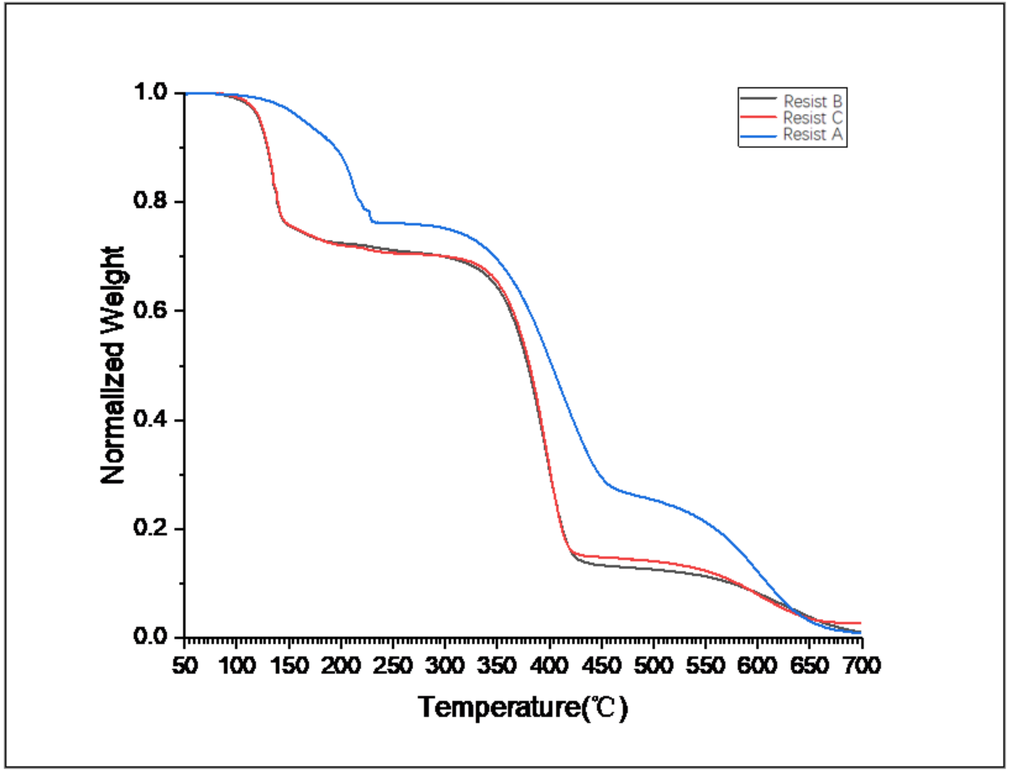
COMPARISON OF THREE KINDS OF PHOTORESIST

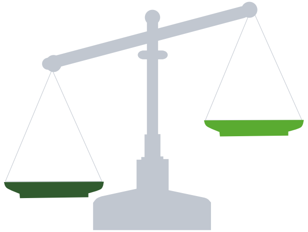
- ***Component comparison***

	Resist A	Resist B	Resist C
Polymer	Polymer1(ESCAP)	Polymer2(Acetal, Free radical polymerization)	Polymer3(Acetal, Anionic polymerization)
PAG	PAG1 (ionic)	PAG2 (nonionic)	PAG2(nonionic)
Solvent	PGMEA	PGMEA	PGMEA

COMPARISON OF THREE KINDS OF PHOTORESIST

- ***Thermal stability compare***



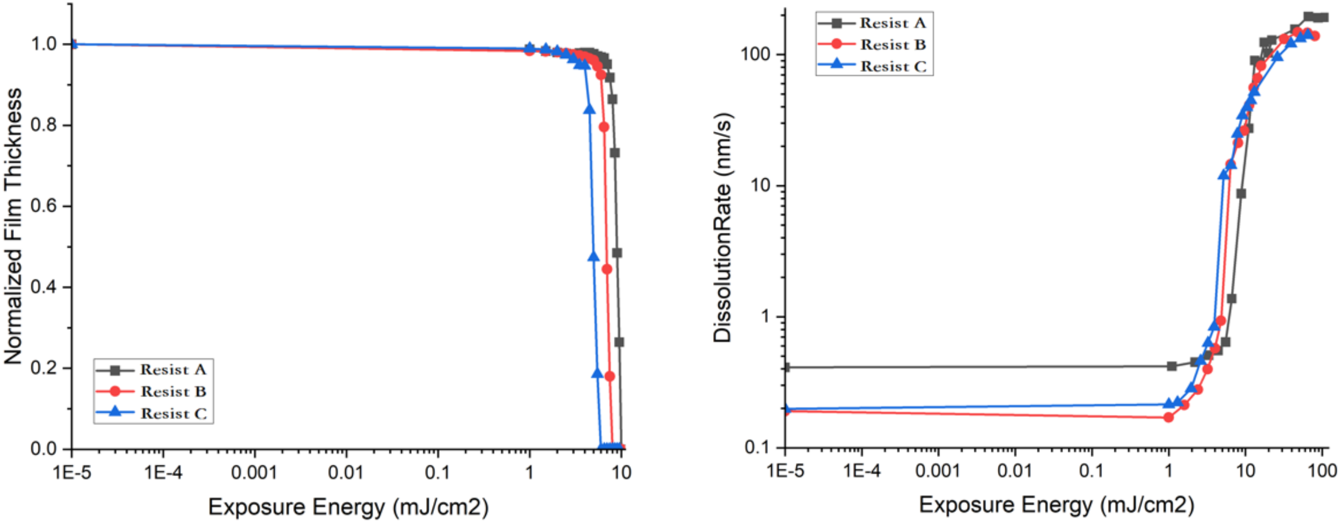


Resist A has higher decomposition temperature

Resist B and Resist C has lower decomposition temperature
even Resist B and Resist C has different PDI, the thermal performance is very close

COMPARISON OF THREE KINDS OF PHOTORESIST

- ***Dissolution rate compare***



	Resist A	Resist B	Resist C
R_{max}(nm/s)	192.43	138.89	140.64
R_{min}(nm/s)	0.41	0.19	0.20
Film thickness Contrast	0.40	0.62	0.65

Part 6

CONCLUSION AND PROSPECT

CONCLUSION AND PROSPECT

Close cooperation

Improve key parameters : DOF, profile, defect, etc.

Customer feedback

Reveal correlation

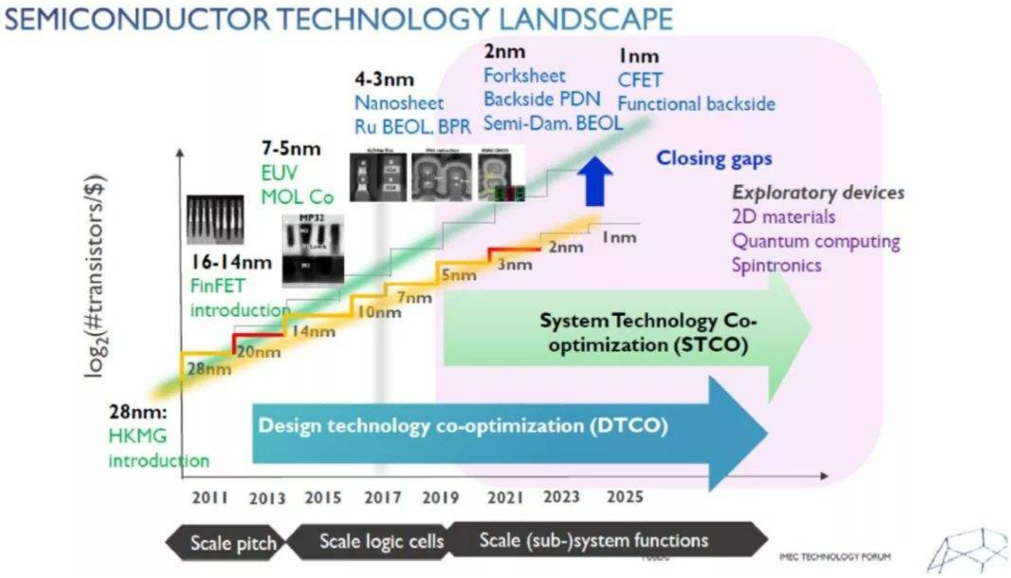
Continuous improvement

”

How We Achive Target

Closer cooperation, more thinking, more experiments, more summaries

CONCLUSION AND PROSPECT



Resist A (high activation energy) can basically meet the application of large CD and less sharp profile process;

Resist B (low activation energy) improves the contrast and obviously improves the profile top rounding on the basis of Resist A, which is suitable for the process requirement of small CD under same thickness.

Resist C (improved PDI) is a resist for higher requirement of ASI defect with specific layer. Finally, it meets the mass production requirements of manufacturing user for photoresist.

Keep moving!!

In the future, manufacturing users will work with photoresist manufacturers to R&D photoresist for KRF process with smaller CD.

REFERENCE

[1] Scott A. MacDonald, William D. Hinsberg, H.Russell Wendt, Cliton D. Snyder, “Airborne contamination of a chemically amplified resist”, Chem. Mater. 1993 (5), 348–356.
[2] Hiroshi Ito, Greg Breyta, Don Hofer, R.Sooriyakumaran, Karen Petrillo, David Seeger, “ Environmentally stable chemical amplification positive resist: principle, chemistry, contamination resistance, and lithographic feasibility”, Journal of Photopolymer Science and Technology 1994, 7 (3), 433–447.
[3] Yayi Wei, "Advanced Lithography Theory and Application for VLSI", BeiJing: Science Press,2016.

@ Huali Microelectronics Co., Ltd.
2022.10.22

THANKS

FOR YOUR WATCHING

上海华力
HLMC