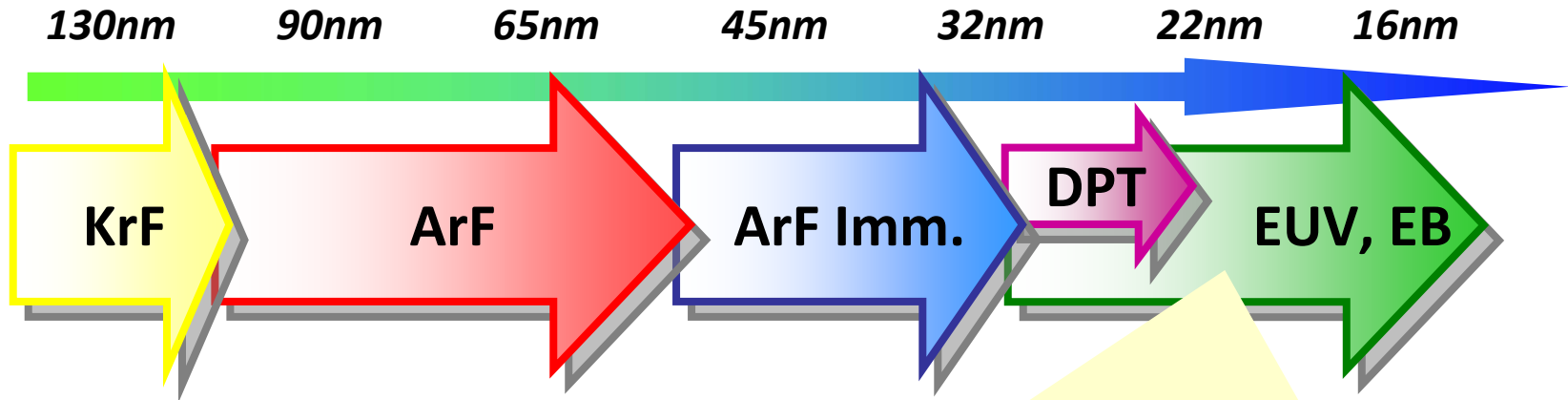


***New approach for reducing the Out of Band effect and  
outgassing by applying top coat materials  
(Outgassing and Ot-of-Band Protection Layer: OBPL)***

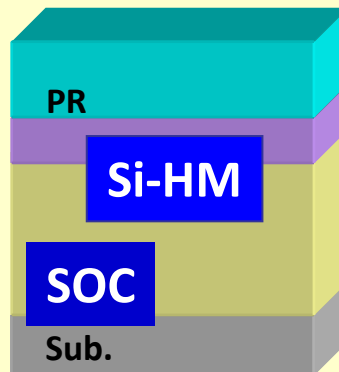
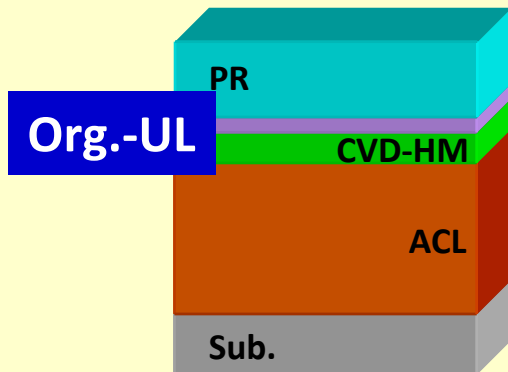
**Nissan Chemical Industries, LTD.**

# Outline

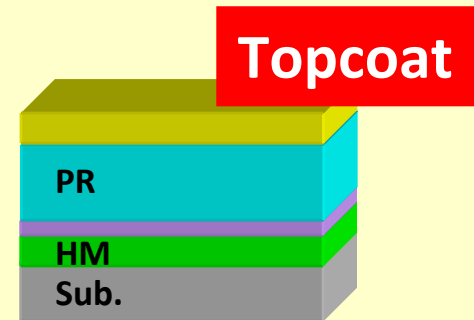
## Lithography Technology



## Nissan Chemical's activity for EUVL



## Today's talk



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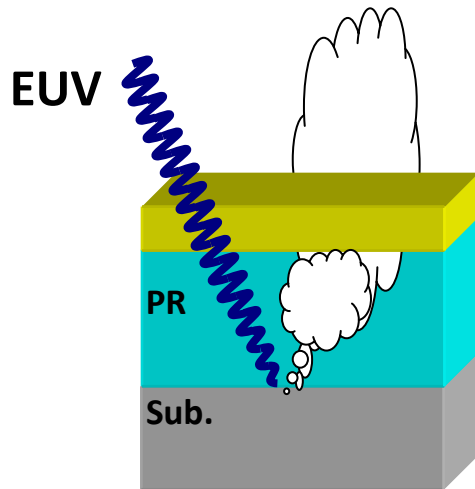
# *Nisan OBPL*

**OBPL (EUV-TC)**

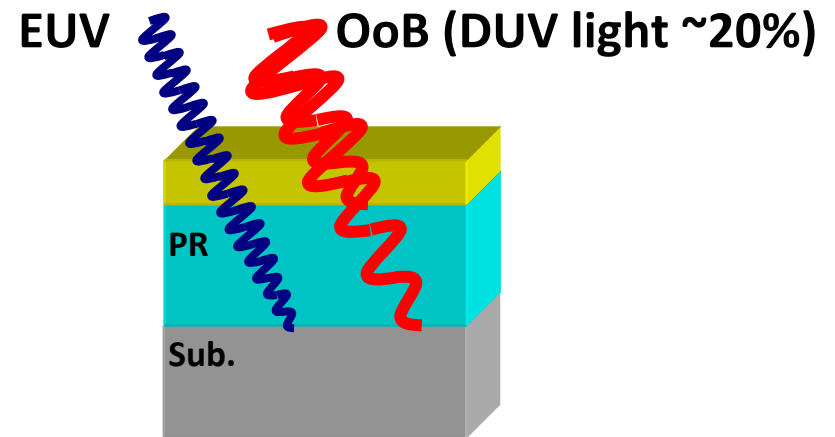


# OBPL

## Outgassing & Out-of-Band Protection Layer

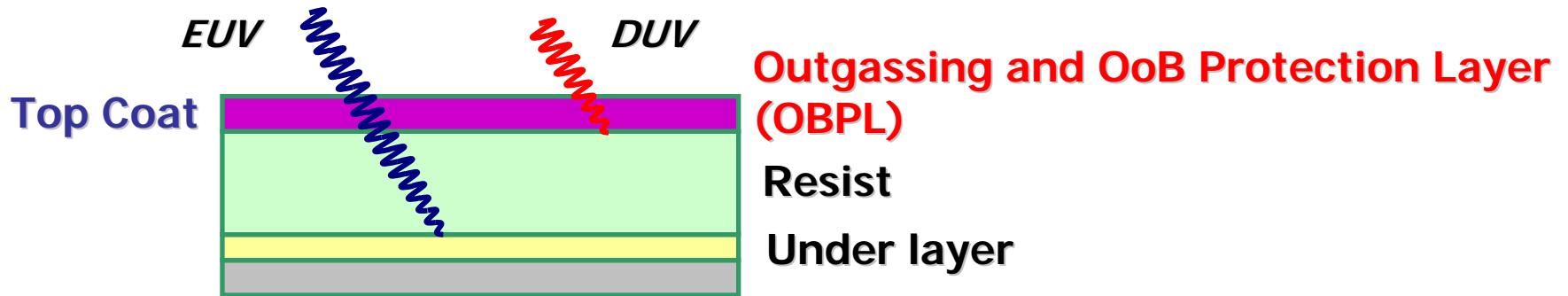


**Outgassing barrier**



**Out-of-Band filter**

# Concept of Top Coat material



## *Characteristic of OBPL :*

1. Low transmittance for OoB light
2. High transmittance for EUV light
3. Prevention of outgassing from resist

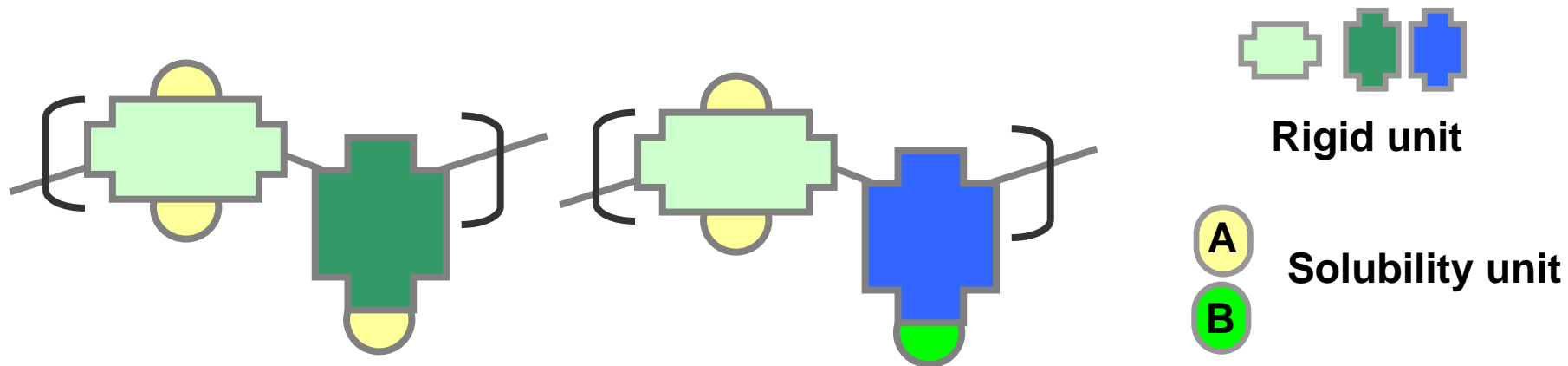
} Specific property for EUVL

4. No mixing with resist film
5. Removable by development and rinse process

} Common property with TARC and imm. TC

# Material design Concept

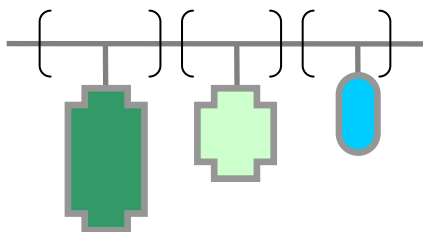
---



- **Ridged unit** : high outgassing barrier property and DUV abs.
- **Solubility unit A**: Developable unit into TMAH/DIW (For PTI)
- **Solubility unit B**: Solubility unit for OBPL Solvent (org.Solvent) and NBA (For NTI)

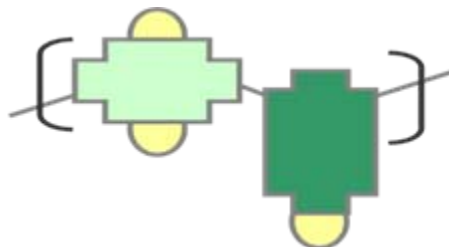
# Development road map

1<sup>st</sup> Generation



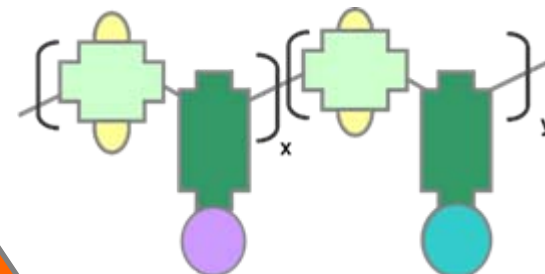
Polymer platform	<b>A</b>
OoB absorption	☺
Outgassing barrier	☹
Litho improvement	☹
Applicable for resist	Pure methacryl
Applicable for Dev. process	PTD

2<sup>nd</sup> Generation



Polymer platform	<b>B</b>
OoB absorption	☺
Outgassing barrier	☺
Litho improvement	☺
Applicable for resist	Pure methacryl
Applicable for Dev. process	PTD

3<sup>rd</sup> Generation  
(Current R&D)

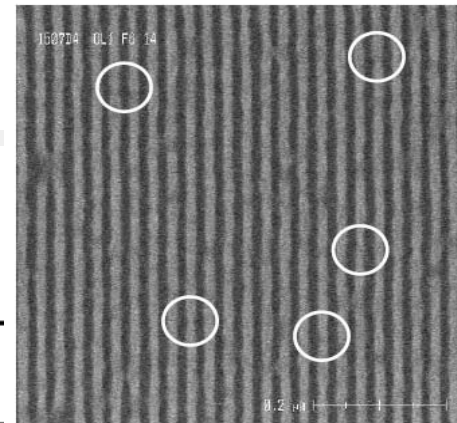


Polymer platform	<b>B</b>
OoB absorption	☺
Outgassing barrier	☺
Litho improvement	☺
Applicable for resist	All resist type
Applicable for Dev. process	PTD & NTD

---

# Outgassing

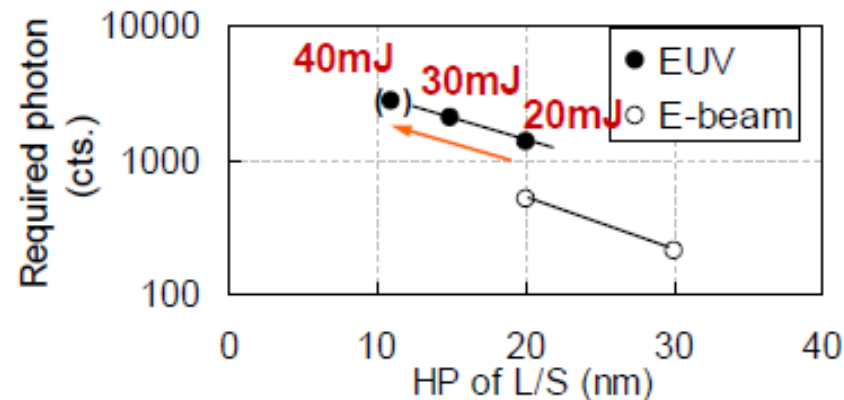




FUJIFILM Corporation

## PSN in EUVL

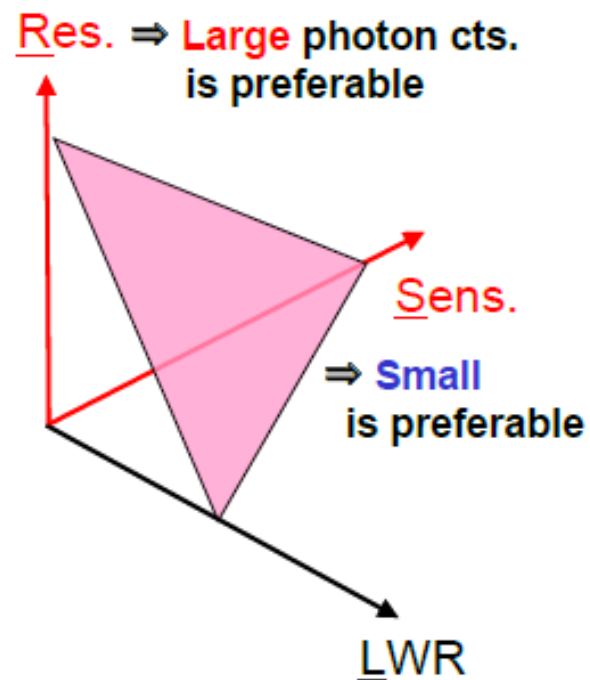
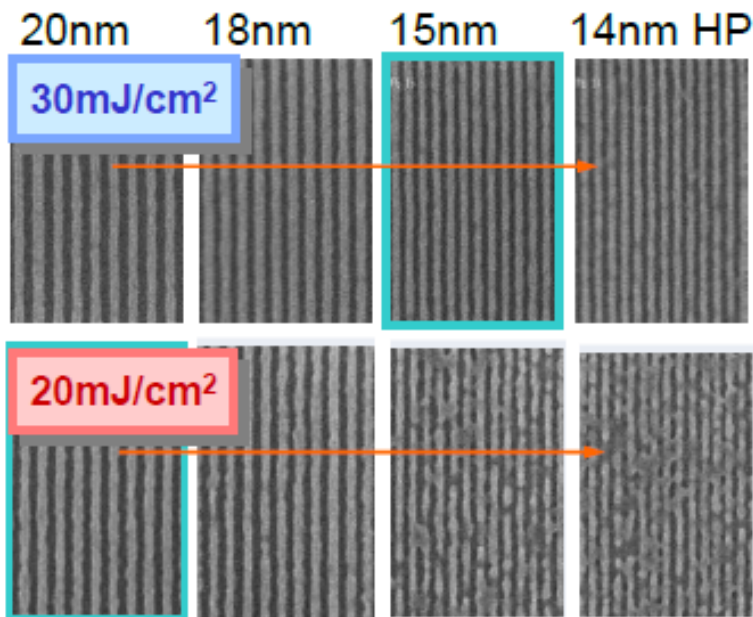
HP of L/S	Required photon cts. for resolution (pinching cts. < 10)	
	EUV (LBNL MET)	EB (50 keV)
30 nm	--	205
20 nm	1360	500
15 nm	2040	--
11 nm	2720 (estimated)	--



**20 mJ/cm<sup>2</sup> for 20 nm, 30 mJ/cm<sup>2</sup> for 15 nm are required**

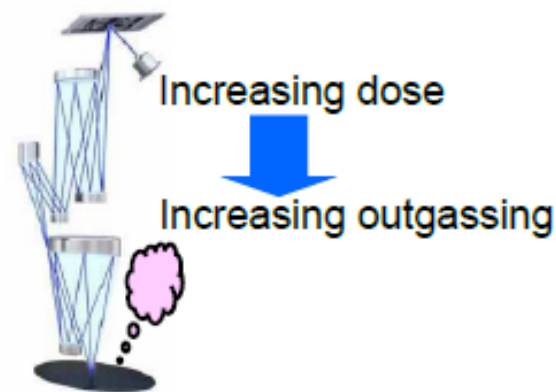
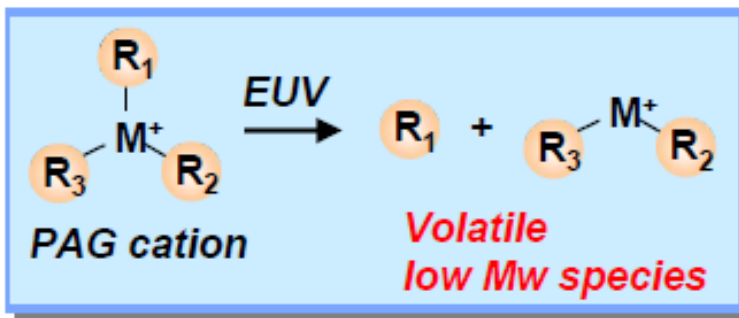
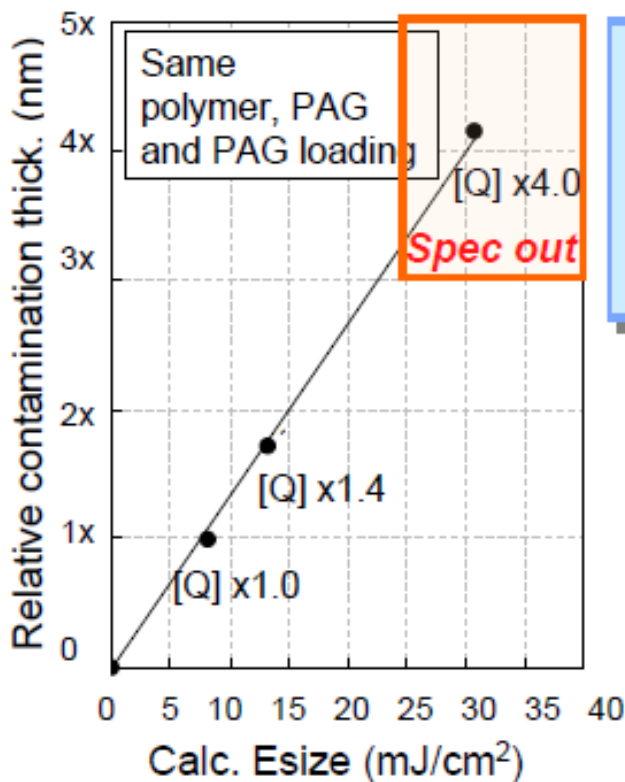
SPIE Advanced Lithography 2013 (February 25, 2013)

## Resolution – sensitivity tradeoff



PSN statistics causes res. – sens. tradeoff

## Resolution – outgassing tradeoff



→ Better resolution

**Slow Esize. for high res (1x nm). caused outgassing**

# ***Important message***

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## **Below Hp15 Generation.**

**More than 2000 photon will be required to get**

**The enough Resolution and imaging quality.**

**→ High dose (>30mJ) will be exposed to PR.**

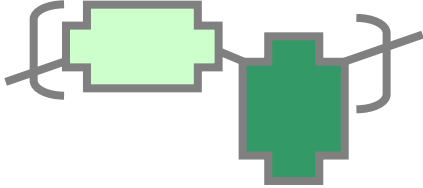
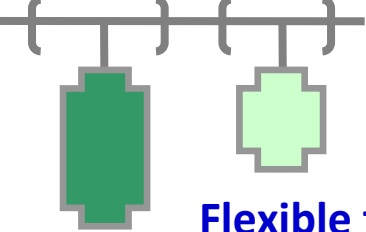
**→→ Outgass must be higher and higher.**

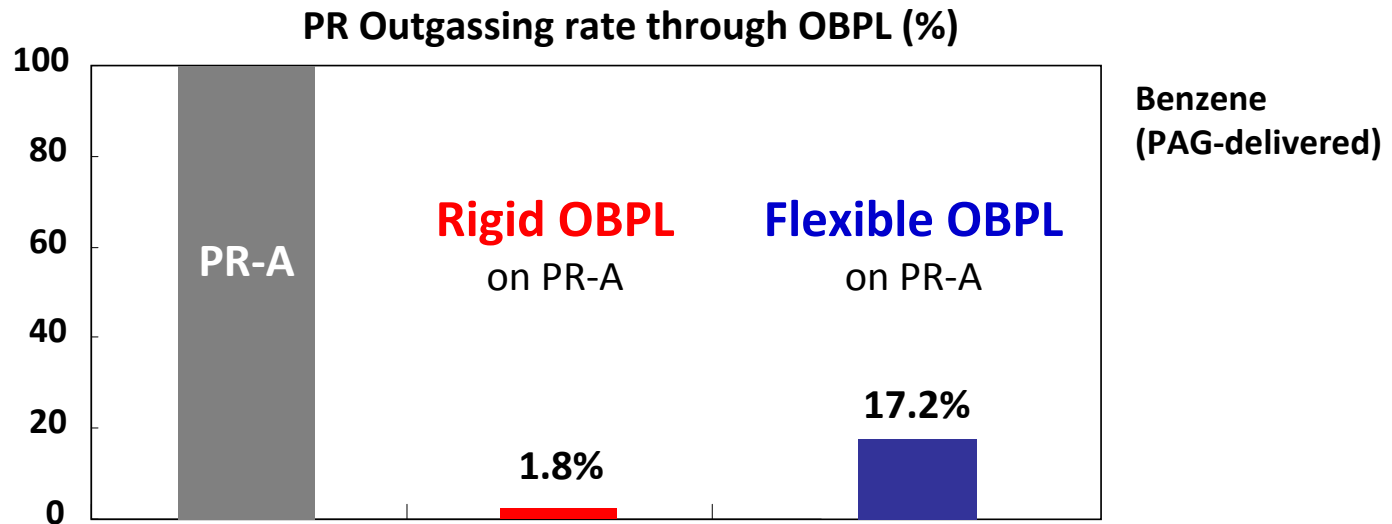
**Because of trade off between Res. & Outgass.**

**EUV-TC will be required for Hp15 and beyond**

# Previous study by RGA



	OBPL-1	OBPL-2
Polymer platform	 <b>Rigid type</b>	 <b>Flexible type</b>
Film density (g/cm <sup>3</sup> )	1.21	1.15

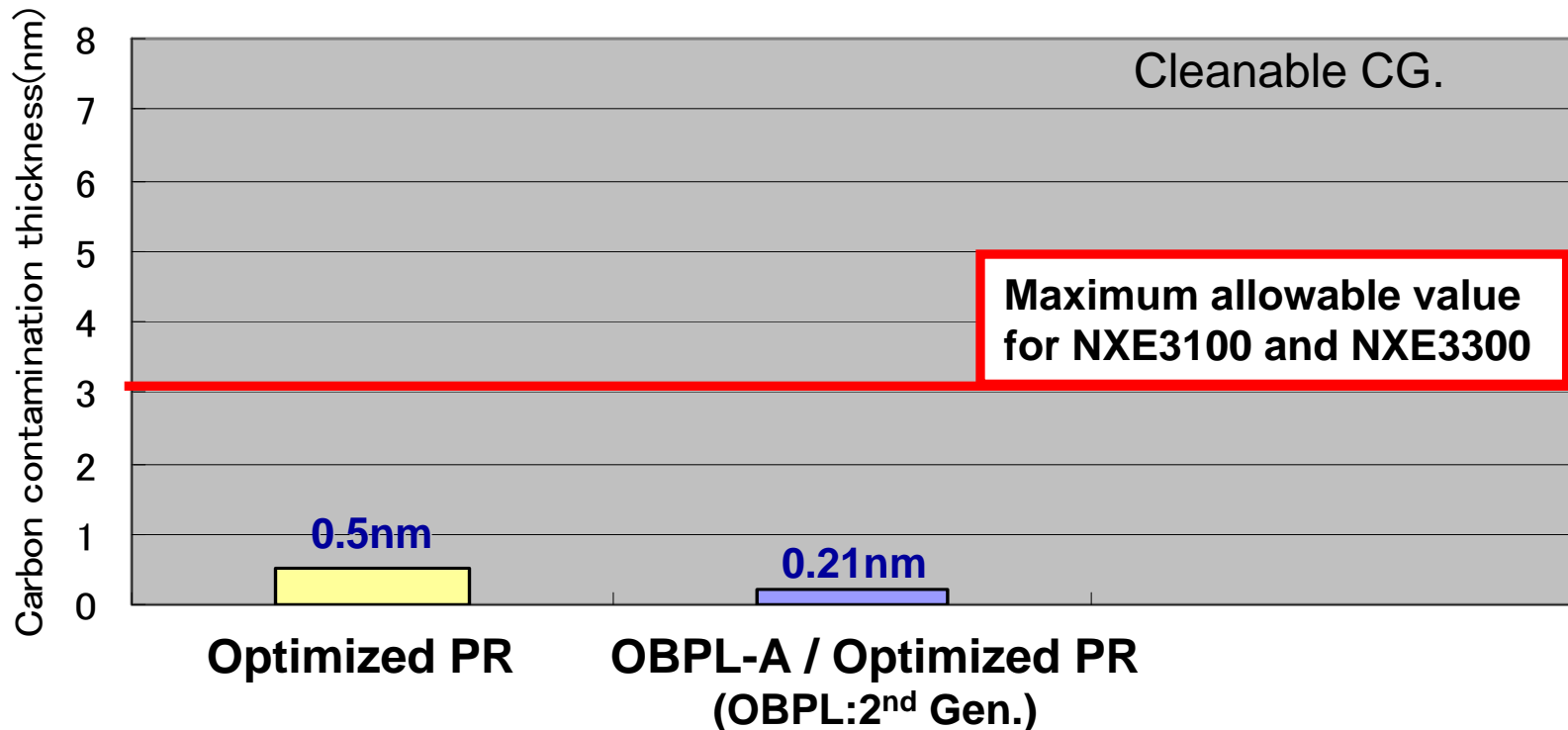


**Chemistry dependency for outgass barrier was confirmed,  
But applying OBPL could reduce the outgassing significantly.**

# Outgassing barrier test by WS

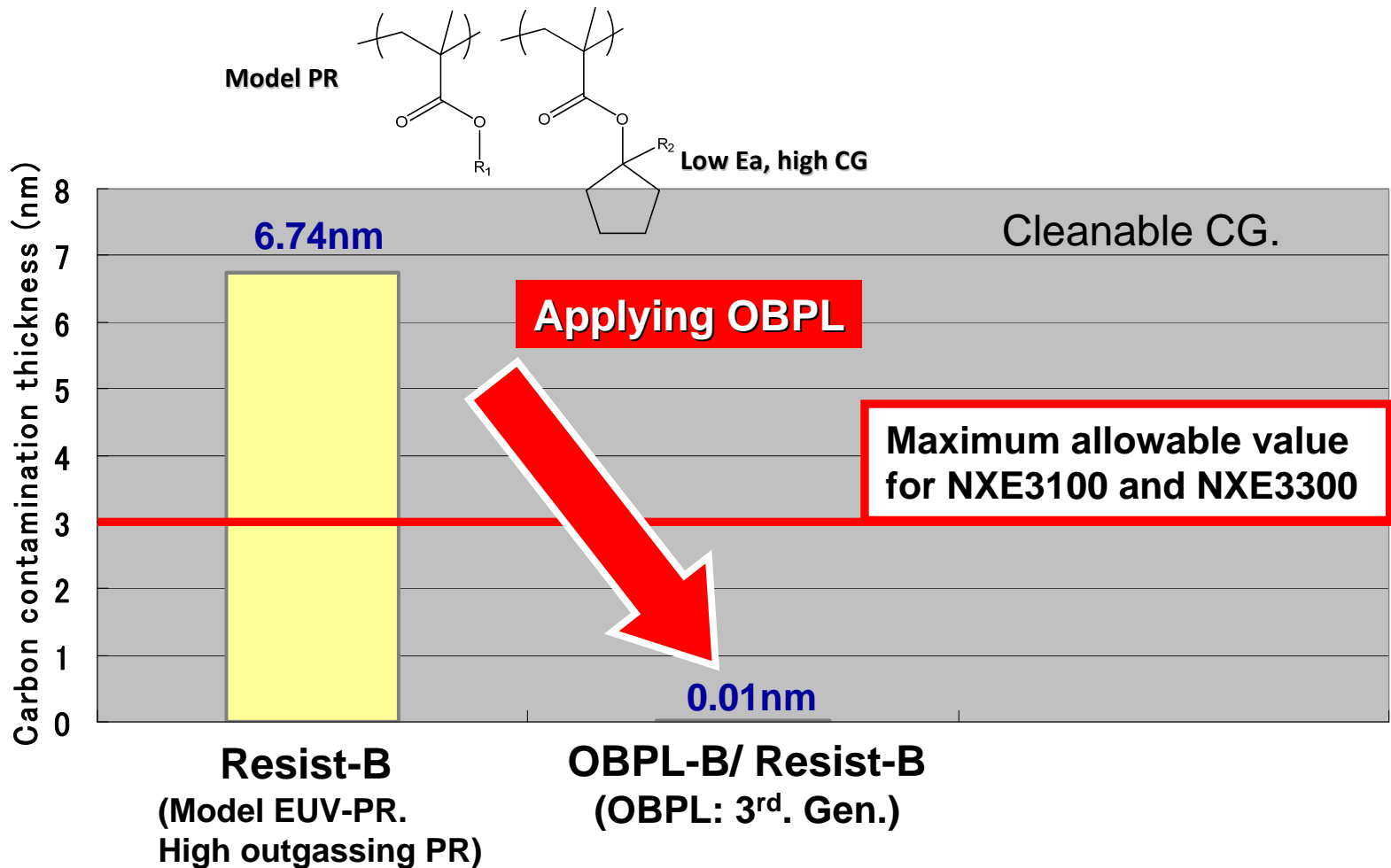


Tester / location: CNSE ROX (Witness)  
OBPL-A (FT: 30nm)



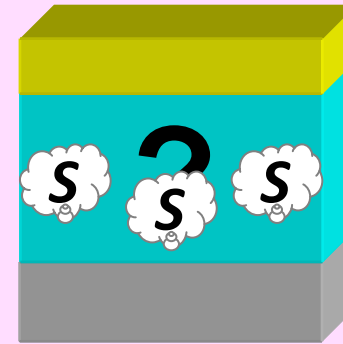
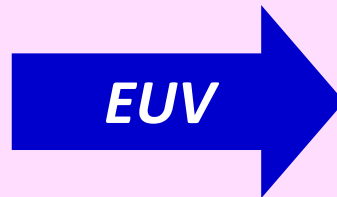
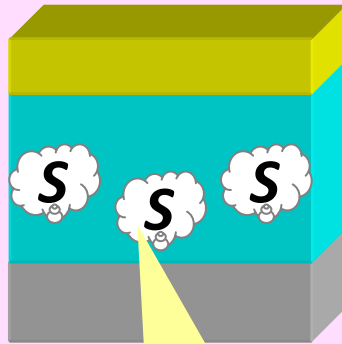
**There is no significant difference in outgassing level  
By using OBPL for optimized PR.**

# Outgassing barrier test

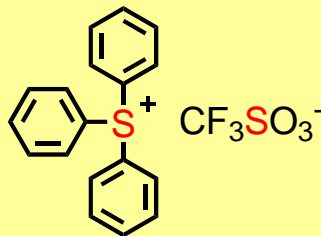


Perfect outgassing prevention by OBPL was confirmed.  
→ **SPEC-OUT PR** could be **SPEC-IN** by Applying OBPL.

# Contamination distributional analysis



PAG-delivered



Analysis method : Depth profile

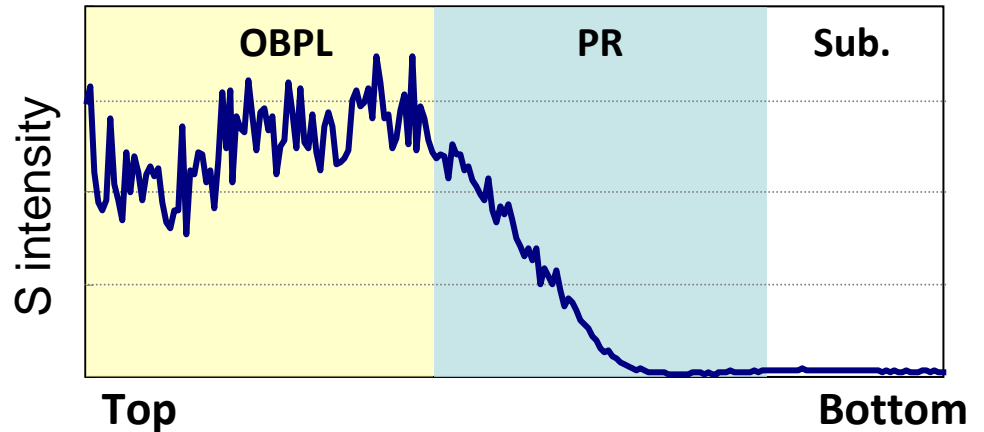
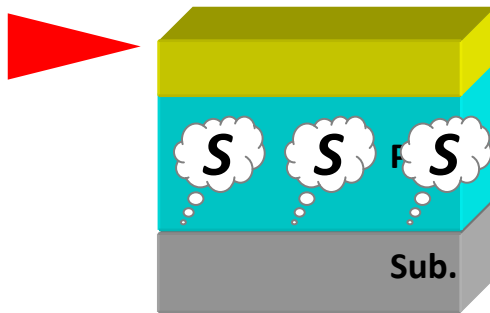
Tool : TOF-SIMS

Detection atom : Sulfur

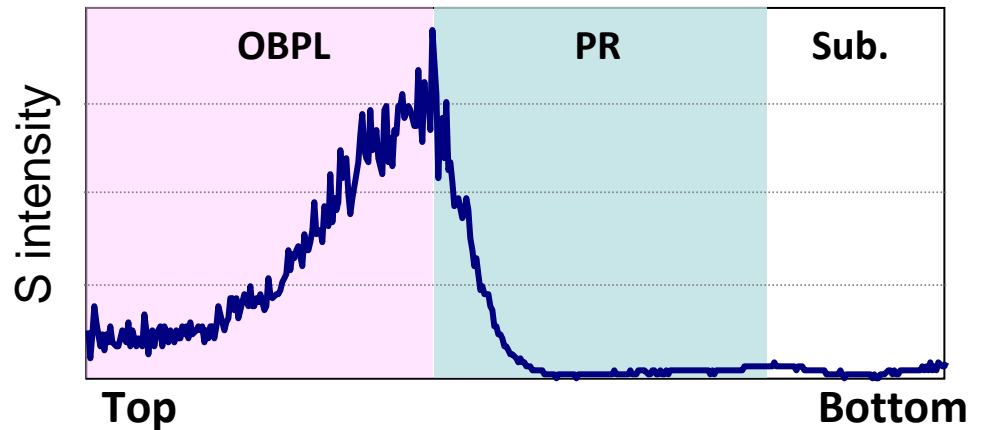
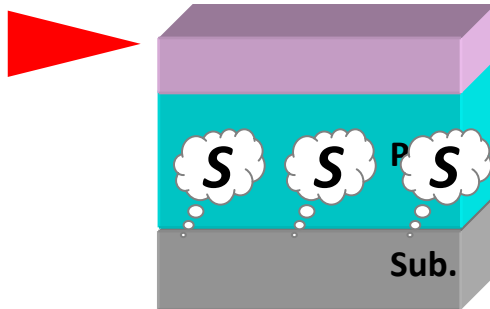


# Variation concentration of Sulfur atom

## Flexible OBPL



## Rigid OBPL



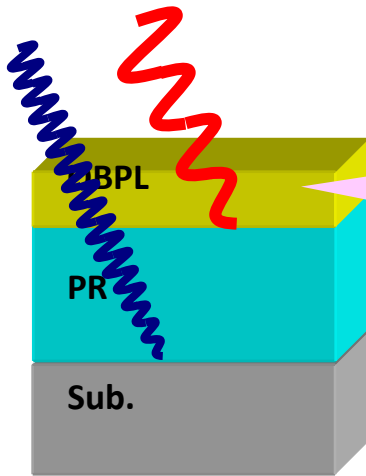
**Rigid OBPL blocks PR outgassing at interface.**

Research Laboratories.

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# OoB study

# Requirement of OBPL



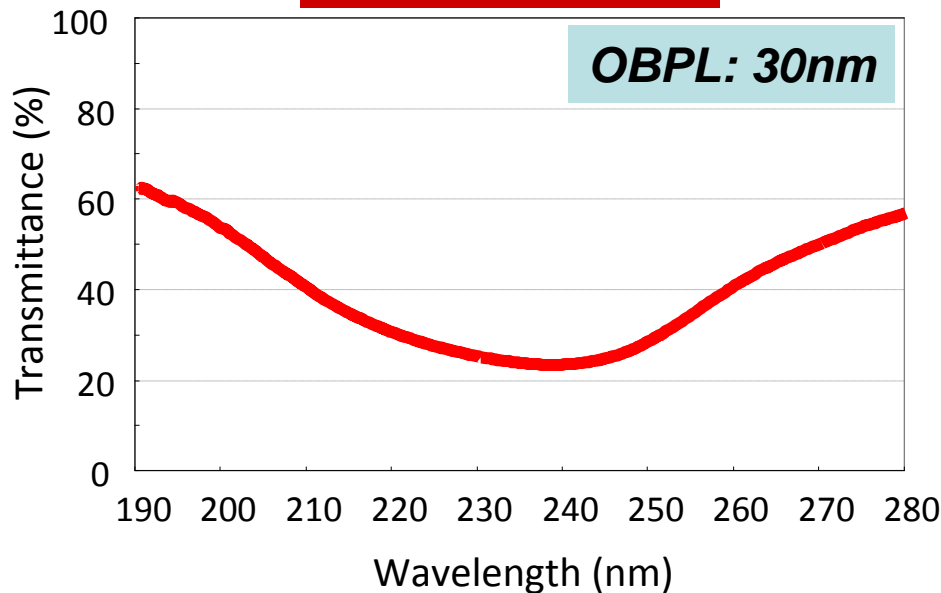
## Requirement of OBPL

- Low DUV transmittance
- High EUV transmittance

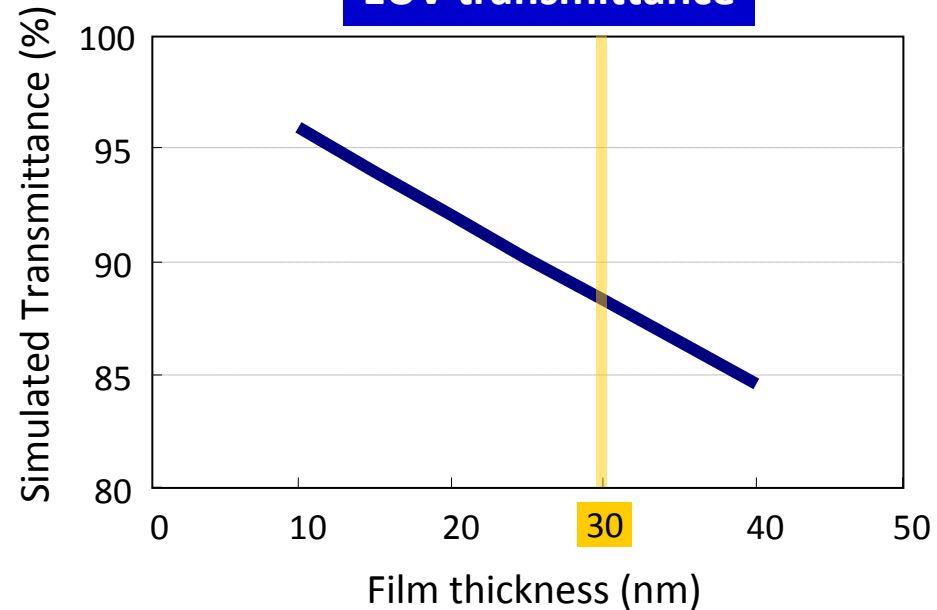
20~30%@min.

~90%

## DUV transmittance

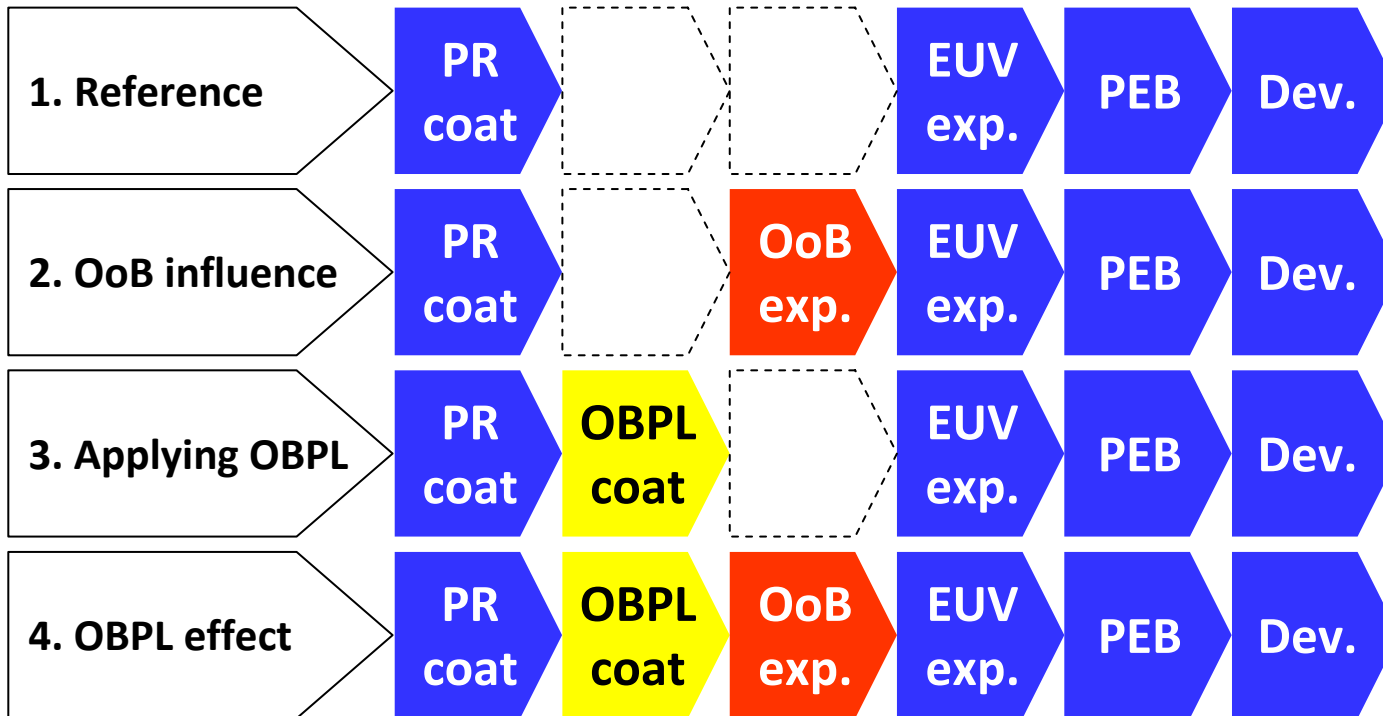


## EUV transmittance



# Investigation of OBPL effect

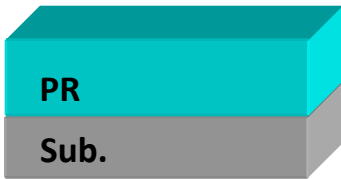
S.A. George *et al.*,  
SPIE (2011)



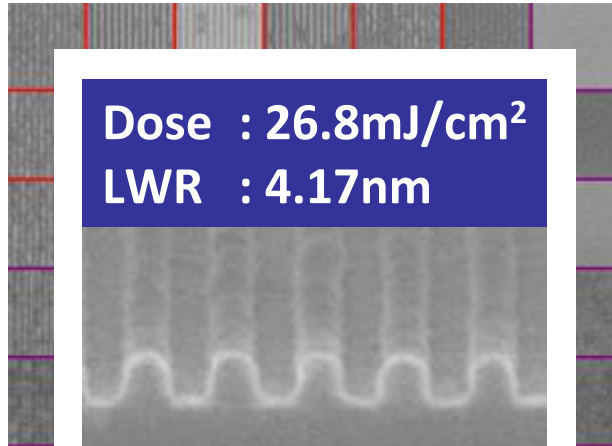
**OoB exposure condition**

Wavelength: 160~300nm (broad band)  
Dose: 5.0mJ/cm<sup>2</sup> (20% of EUV)

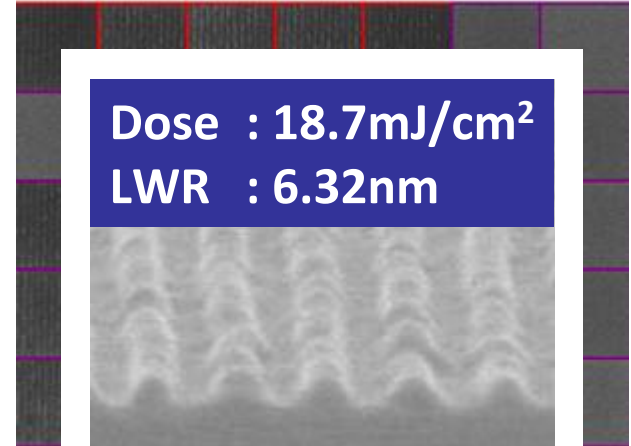
# OBPL effect results



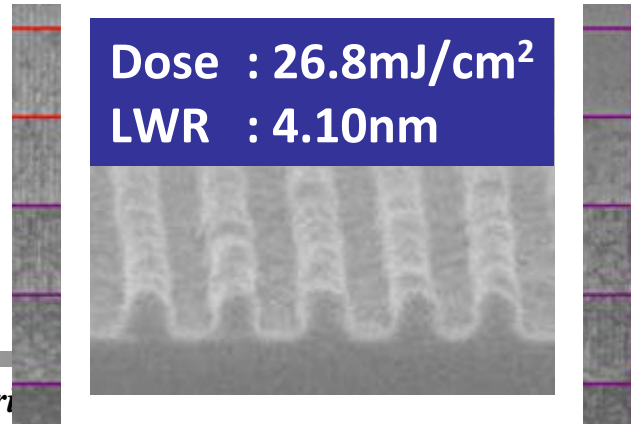
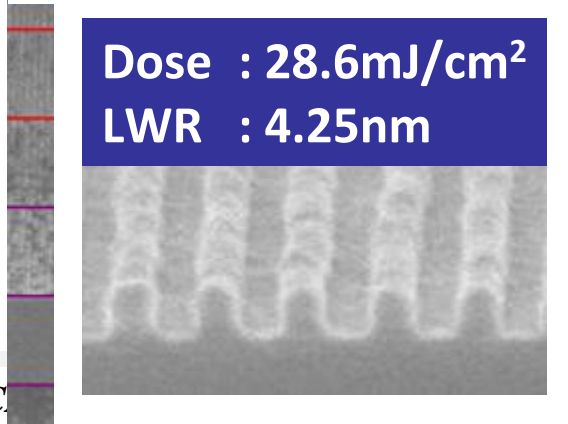
**EUV**



**EUV + OoB**






**OBPL behaves extremely well as OoB filter.**



# 3<sup>rd</sup> Generation (Current R&D)

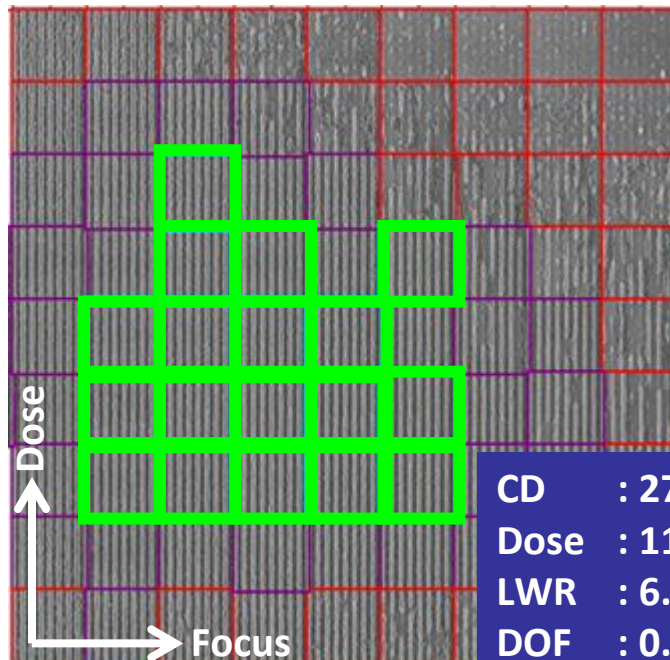
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## Concept: Universal TC for PR and process

Polymer platform	Rigid type
OoB absorption	
Outgassing barrier	
Litho improvement	
Applicable for resist	All resist type
Applicable for Dev. process	PTD & NTD

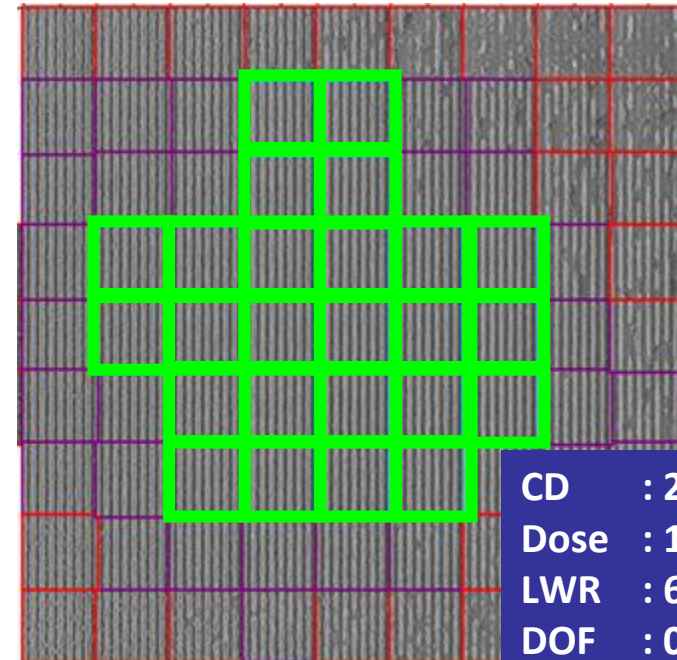
# Lithographic performance with NXE:3100

without OBPL



CD : 27.7nm  
Dose : 11.2mJ/cm<sup>2</sup>  
LWR : 6.4nm  
DOF : 0.20um

with OBPL



CD : 27.4nm  
Dose : 11.5mJ/cm<sup>2</sup>  
LWR : 6.6nm  
DOF : 0.22um

2<sup>nd</sup> gen. OBPL showed good compatibility with Methacrylate PR.

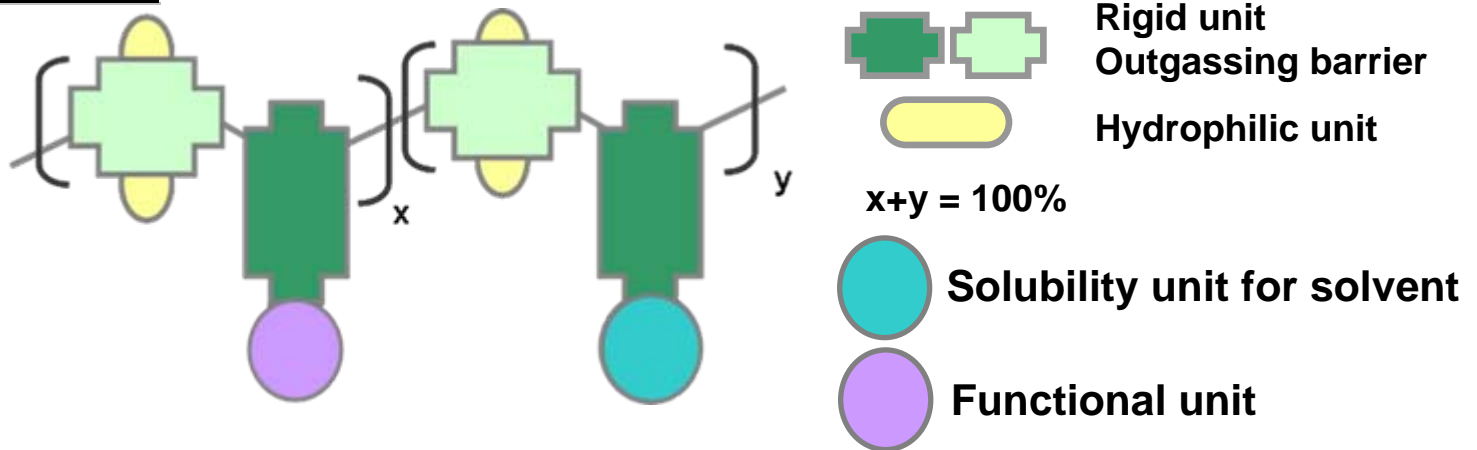
But, only with Methachylate PR.

# 3<sup>rd</sup> Generation OBPL

## *Target:*

Universal compatibility for PR (Methacrylate & PHS)  
and Dev. Process (PTD&NTD).

## Material design

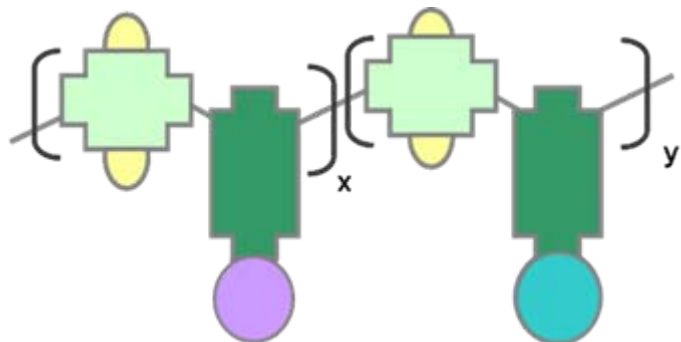


Sample design	Basis of materials	High rigidity resin
	Solvent	<b>Org. Solvent</b> <b>(non-mixing with Methacryl and PHS type PR)</b>
Process	Applicable for resist	All resist type
	Applicable for process	PTD (TMAH aq) & NTD (NBA)

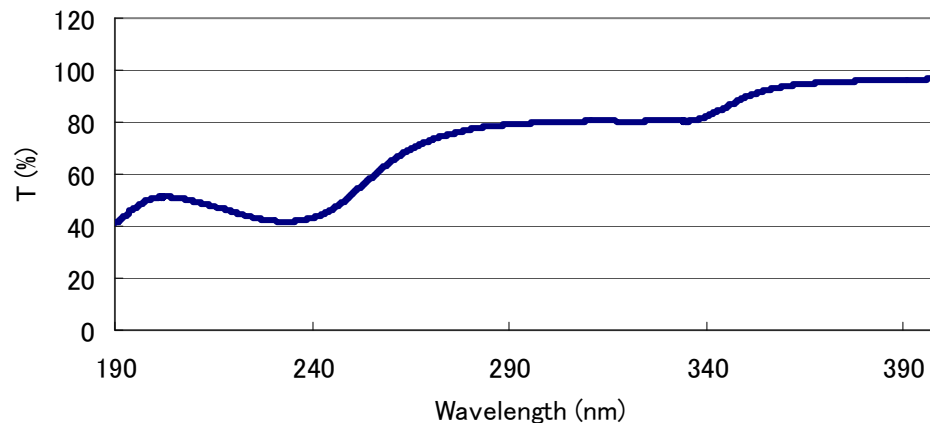


# Proposal sample (3<sup>rd</sup> Generation )

## Material design



DUV transmittance of 30nm OBPL



## Sample property (NCX2088)

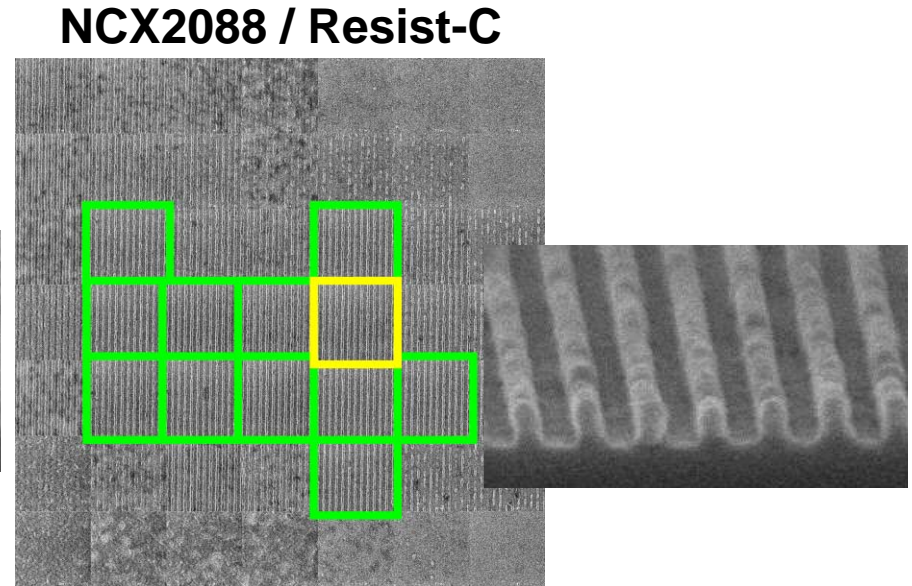
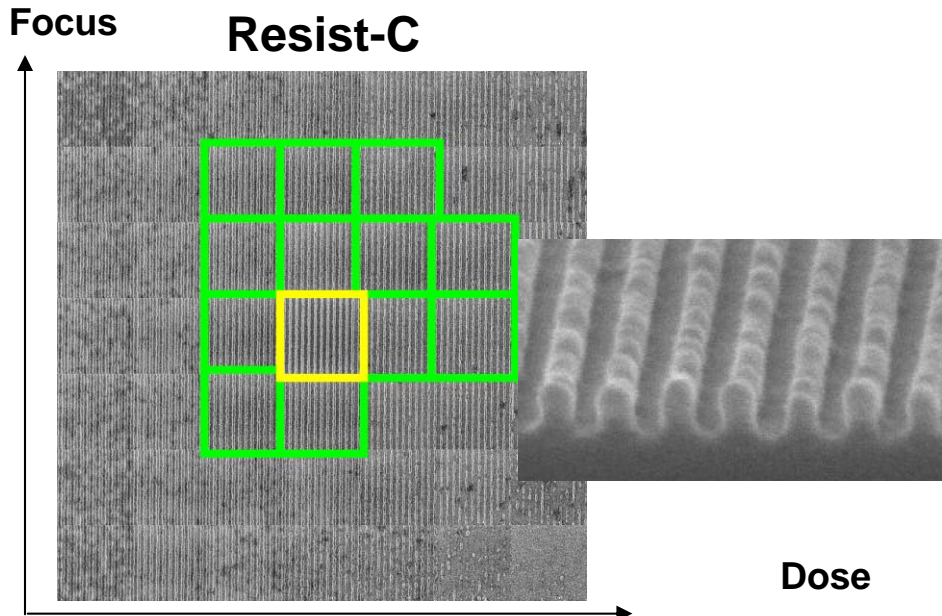
Sample name	Polymer platform	R unit	Outgassing qualification		Transmittance	
		Type	Qualification	Barrier test	13.5nm	240nm
NCX2088	B	High hydrophilic	Pass		81%	43%

**High DUV abs. and good outgass barrier property**

# Methacrylate type PR

Tester / location: Sematech (AMET)

Best shot
  Pattern standing



CD (nm)	27.3
Dose (mJ/cm <sup>2</sup> )	11.5
LWR (nm)	4.3
Max EL (%)	13.0
Max DOF (um)	0.20

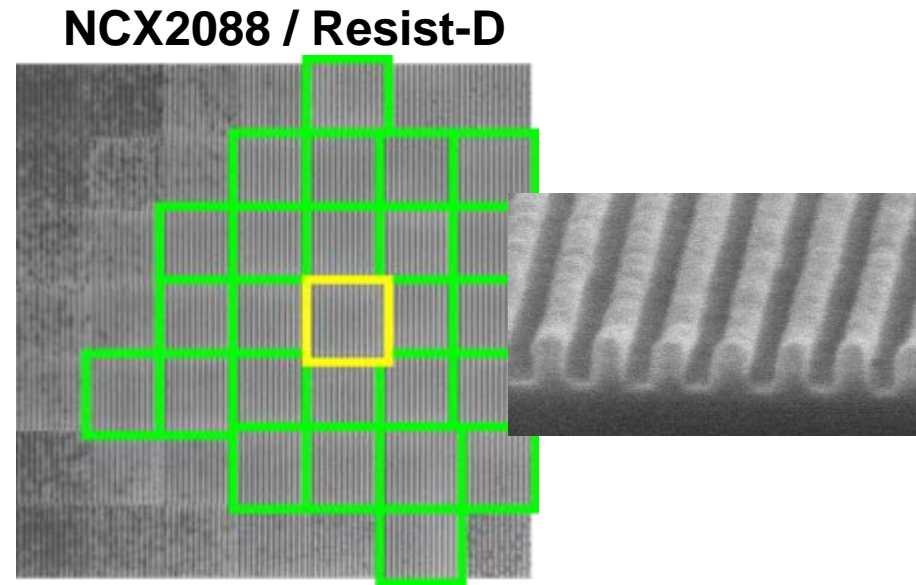
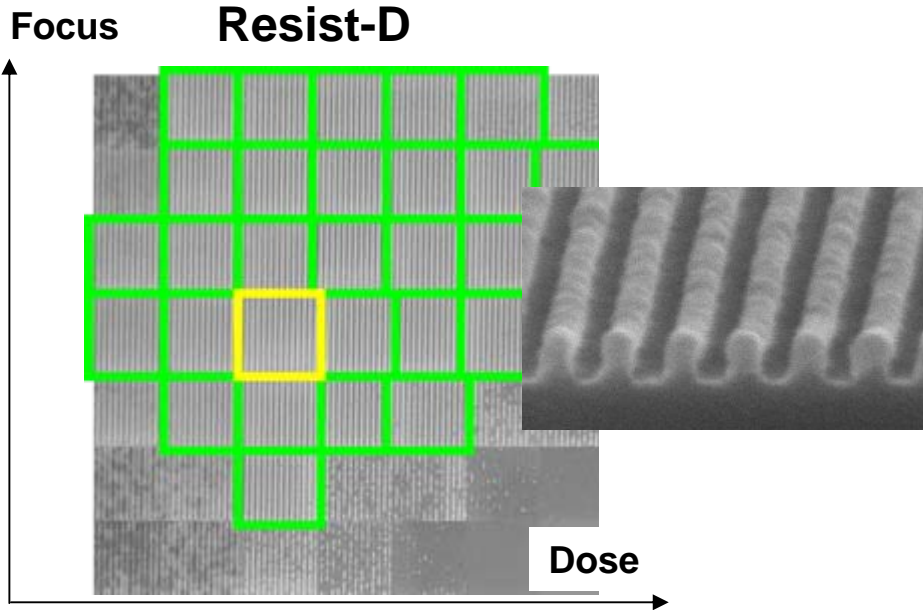
CD	28.1
Dose	14.0
LWR	4.5
Max EL	10.7
Max DOF	0.20

**Applying OBPL keep good process margin and LWR.**

# HS/Methacrylate hybrid type

Tester / location: Sematech (AMET)

Best shot
  Pattern standing



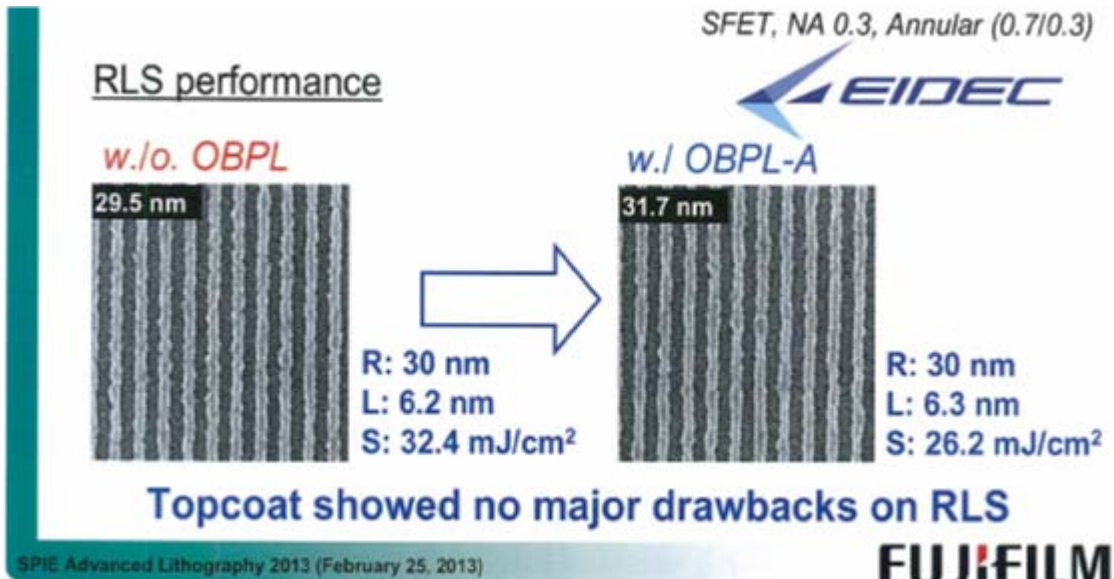
CD (nm)	26.1
Dose(mJ/cm <sup>2</sup> )	24.0
LWR (nm)	4.0
Max EL (%)	> 29.2
Max DOF (um)	> 0.30

CD	25.7
Dose	27.0
LWR	4.1
Max EL	> 18.5
Max DOF	> 0.30

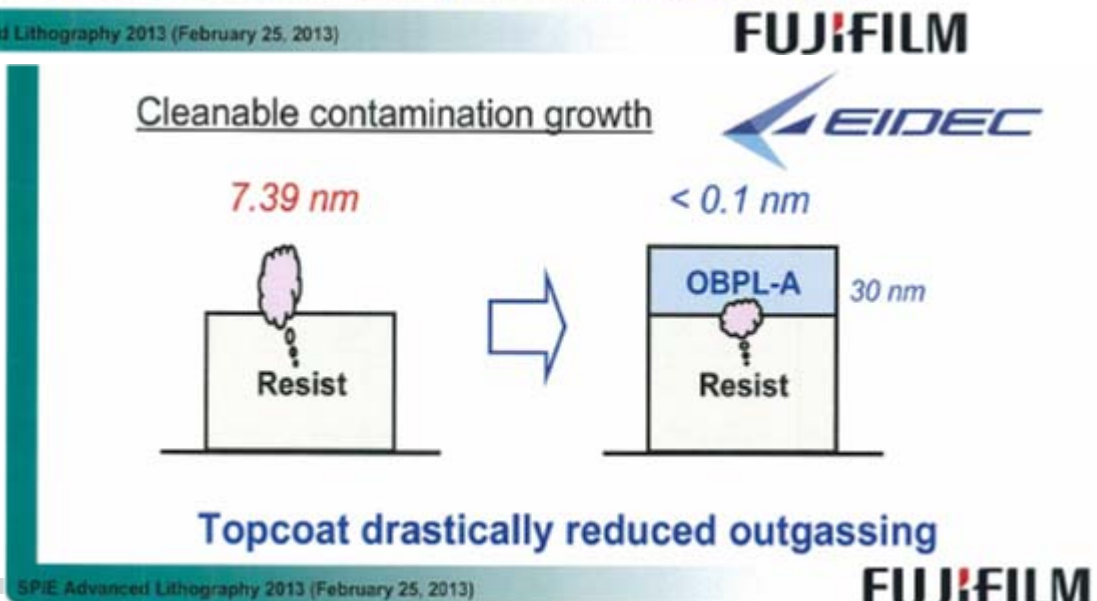
**Applying OBPL keep good process margin and LWR.**

# Performance for NTI

## Lithography performance



## Outgassing barrier performance



H. tsubaki, SPIE 2013

# Summary

---

## Outgassing

Perfect barrier property was confirmed.  
ROX qualification of Staked (PR/OBPL),  
**SPEC-OUT PR could be SPEC-IN by OBPL!!**

3<sup>rd</sup> Gen. OBPL

**NCX2088**

## Universality PR kinds and Process

Methacrylate type PR(PTI)

PHS hybrid type PR (PTI)

PHS hybrid type PR(NTI)

OoB

High DUV abs. could prevent  
OoB irradiation effect.

# Conclusion

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- Nissan Chemical has successfully developed **OBPL** for EUVL.
- OBPL has **PR outgassing barrier** property and **Out-of-Band filter** effect.
- **3<sup>rd</sup> Gen. OBPL** showed good PR universality and process compatibility.
- OBPL can be the key material for high volume manufacturing by EUVL.