Non PFOS & Non PFOA TARC Introduction

AZ AQUATAR-VIII-Series

~ for i-line, KrF, and ArF application ~

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Shizuoka Technology Center

R&D-1

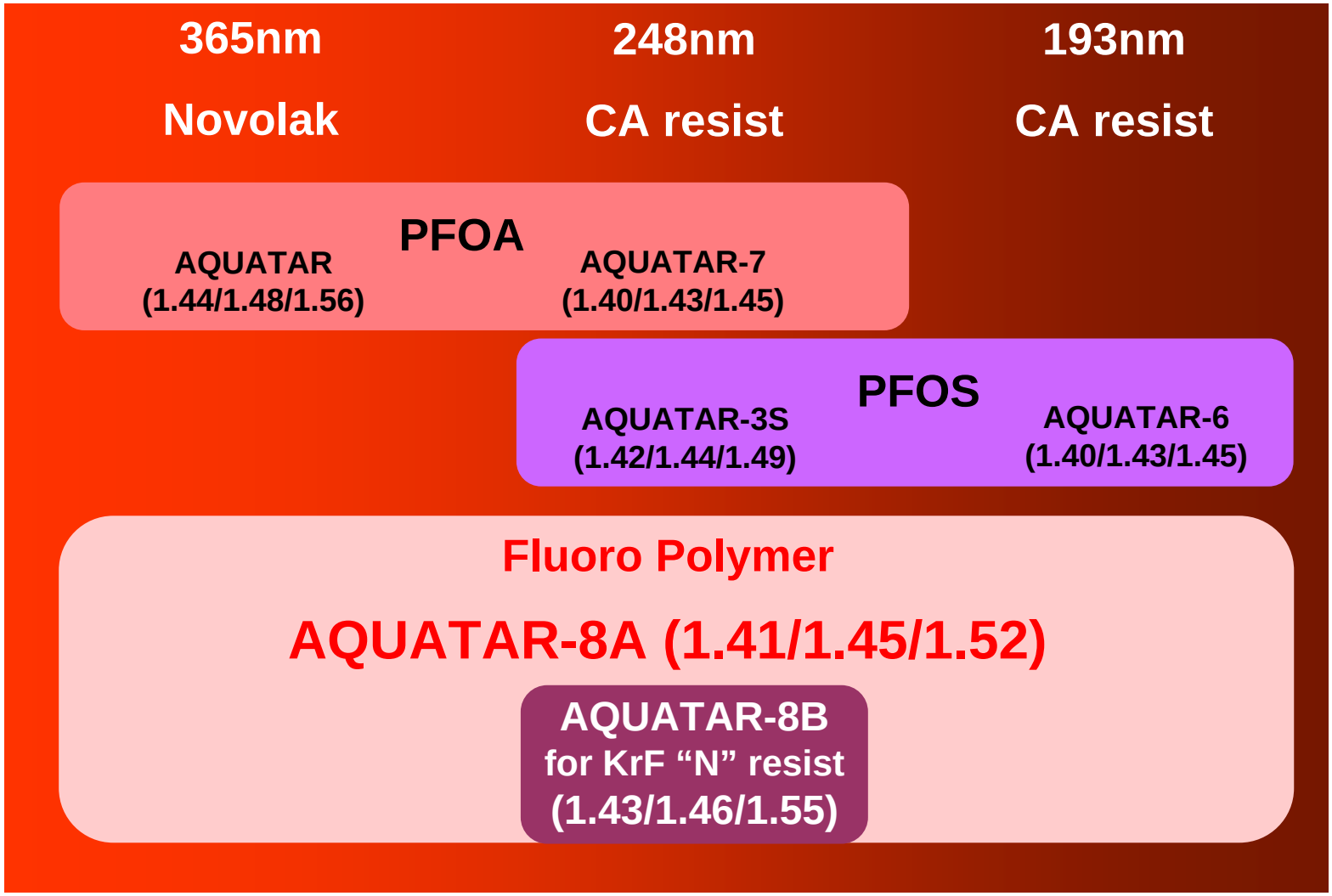
AZ Electronic Materials

1. General Introduction on AZ AQUATAR Family

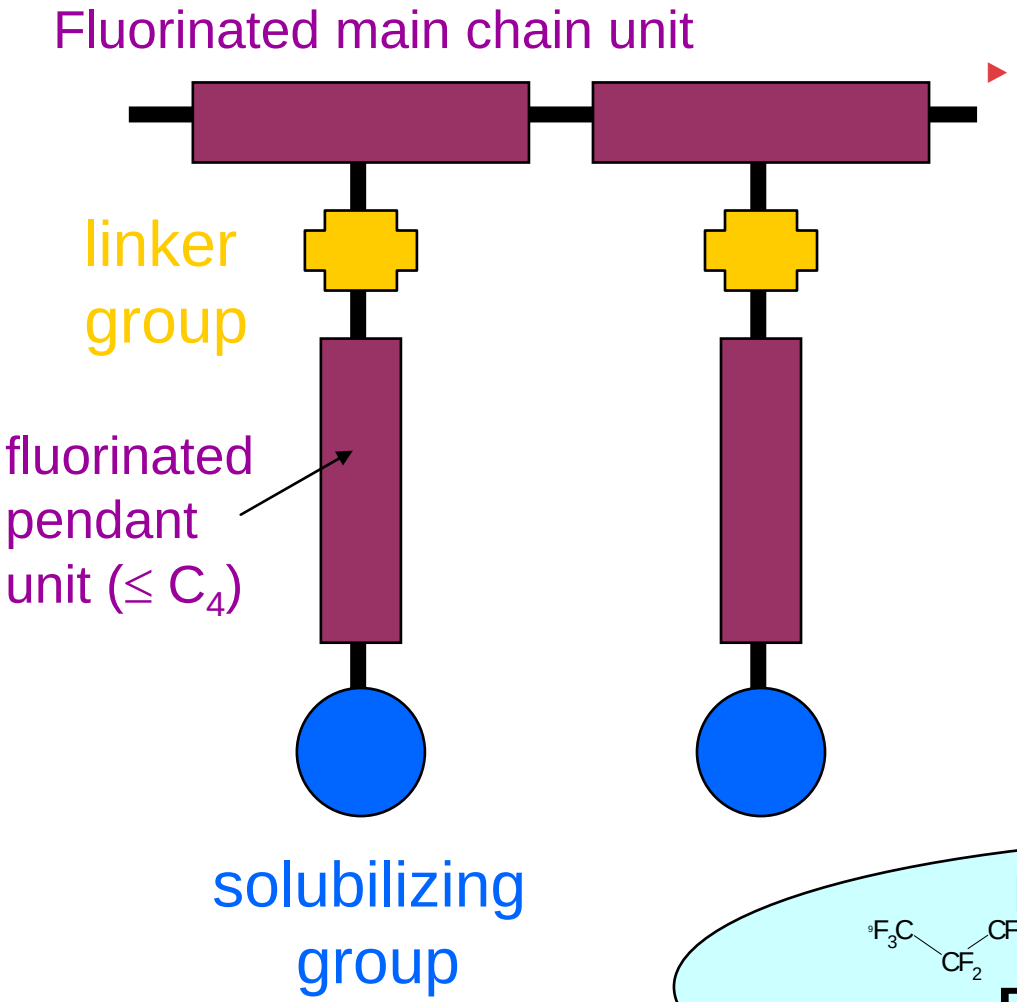
- **Providing TARC products as advanced implant or C/H solution to many customers in the world(80% of Market share)**
- **The 1st to commercialize "PFOX & Telomer free" TARC , "AZ AQ-8A" in the market (the safest material in EHS aspect)**
- **Long production history of AQ-8 for 3 years in the market**
- **AZ AQ-8B was developed for N type of KrF resist**

AZ TARCs	Refractive Index			Materials	Applications
	365nm	248nm	193nm		
AZ AQUATAR	1.44	1.48	1.56	PFOA	i-line
AZ AQUATAR-IIIS	1.42	1.44	1.49	PFOS	KrF&ArF
AZ AQUATAR-VI-A	1.40	1.43	1.45	PFOS	KrF&ArF
AZ AQUATAR-VII	1.40	1.43	1.50	PFOA	KrF&ArF
AZ AQUATAR-VIII-A	**1.41**	**1.45**	**1.52**	**Non PFOS Non PFOA**	**All**
AZ AQUATAR-VIII-B	**1.43**	**1.46**	**1.55**	**Non PFOS Non PFOA**	**i-line&KrF**

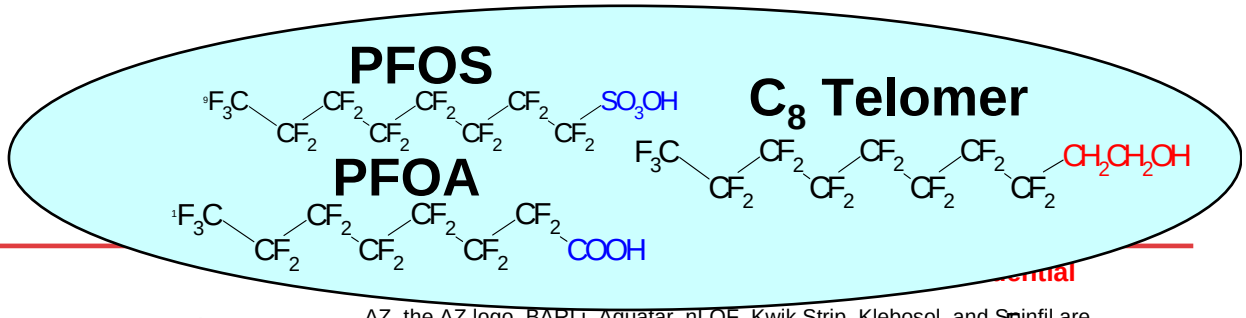
1. AZ TARC Technology Road Map



AZ AQUATAR-8 Series – PFOX & Telomer Free Chemistry

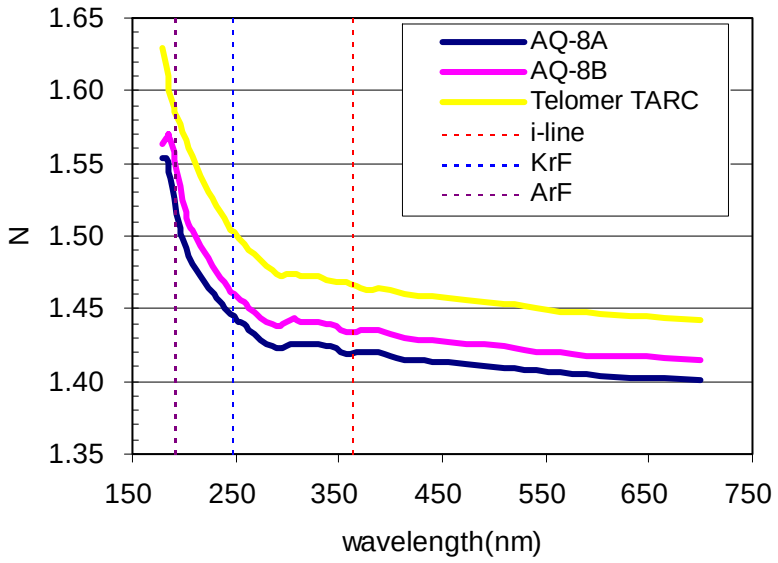


- Fluoropolymer platform
  - It is expected that acute bio effect is weak
  - Non telomer pendant platform
  - No biodegradation feature has been confirmed and low risk to release low molecular weight perfluoro substances
  - Low bioaccumulation feature
  - Length of the polymer pendant group is less than 4, so it does not yield any PBT compounds upon ultimate biodegradation

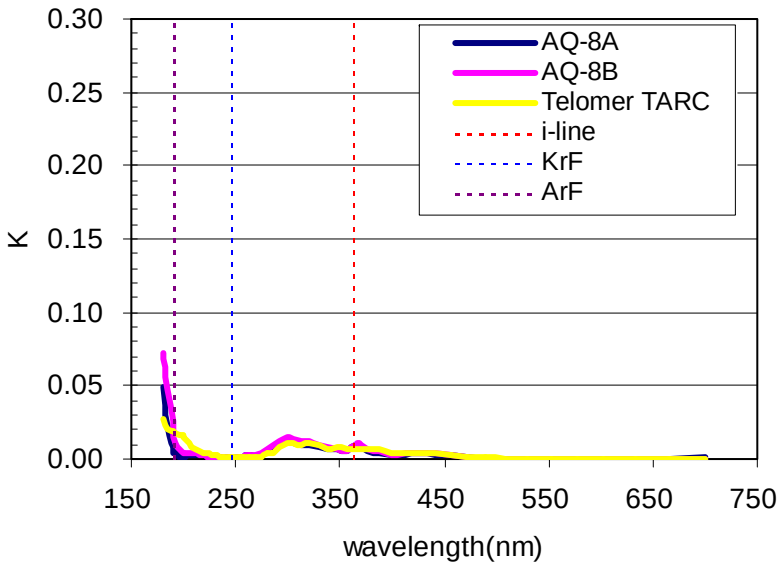


Optical Parameter

Index of Refraction "n"



Extinction Coefficient "k"



sample	cauchy coefficient			optical parameter						
	A	B(um^2)	C(um^4)	N@193nm	K@193nm	N@248nm	K@248nm	N@365nm	K@365nm	N@633nm
AQ-8A	1.3914	0.0046	0.0000	1.52	0.00	1.44	0.00	1.42	0.01	1.40
AQ-8B	1.4040	0.0051	0.0000	1.55	0.01	1.46	0.00	1.43	0.01	1.42
Telomer TARC	1.4093	0.0563	0.0000	1.58	0.02	1.50	0.00	1.47	0.01	1.44

Coating condition

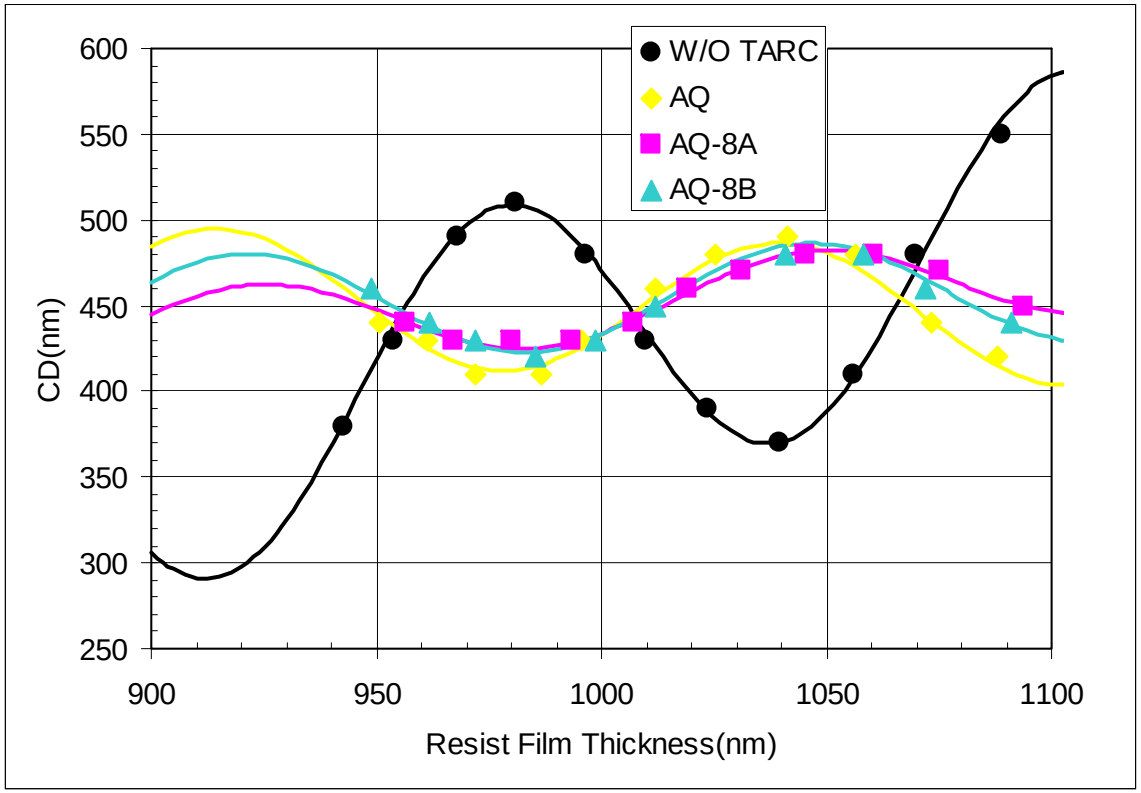
- **Track : TEL Mark 8**
- **Substrate : bare-Si, w/o adhesion**
- **Bake : 90ºC/60sec**
- **FT : 40nm**

Measurement condition

- **Ellipsometer : J.A.WOOLLAM VUV-VASE**

2.4 Resist swing reduction effect in 365nm application

Substrate	**: Silicon with HMDS(90C/60s)**	**Resist**	**: MiR703, Variable FT, 90C/60s PAB, 110C/60s PEB**
TARC	**: 64nm FT, NO PAB**	**Exposure**	**: Nikon NSR1755i7B NA=0.54, Conv.**
Develop	**: AZ 300MIF(2.38%) , puddle 60s**	**Mask pattern**	**: 450nm L/S(1:1), binary**



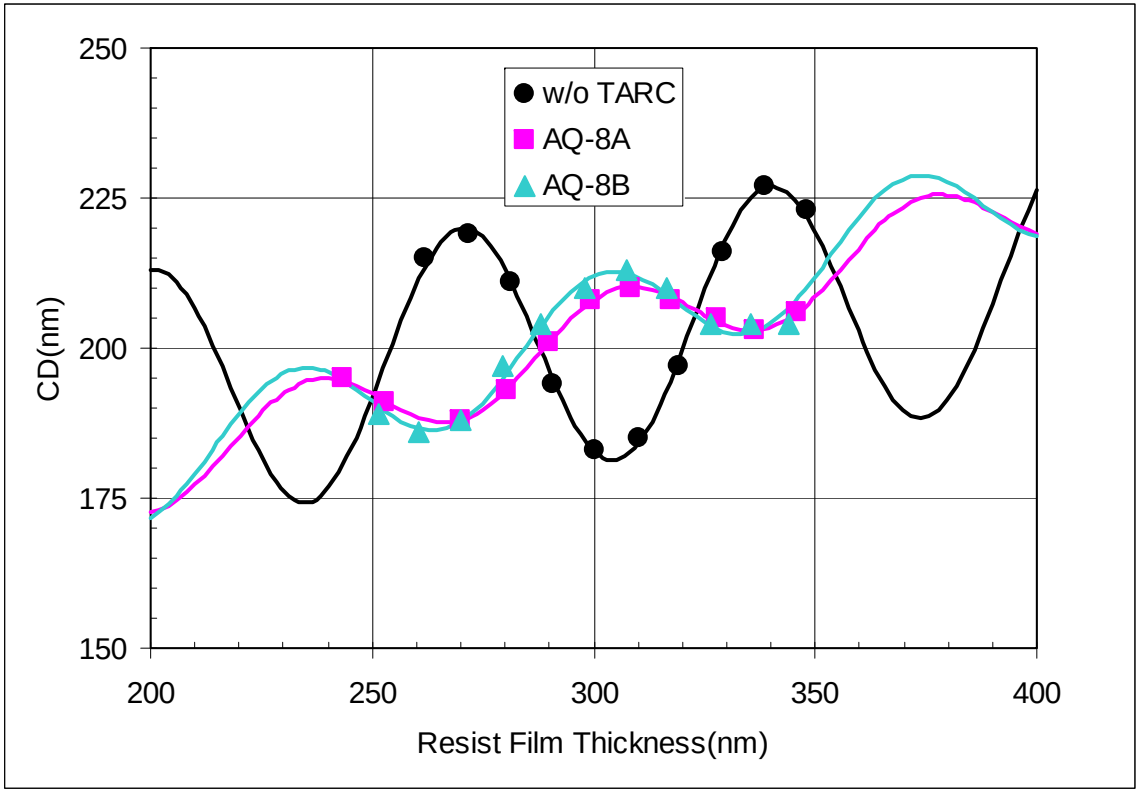
Swing Reduction Ratio

AZ AQ 45	**: 62%**
AZ AQ-8A 45	**: 83%**
AZ AQ-8B 45	**: 79%**

Swing Reduction Ratio = 1 – (A_{TARC} / $A_{w/o\ TARC}$)

2.5 Resist swing reduction effect in 248nm application

Substrate	**: BARC(90nm FT,180C60s PAB)**	**Resist**	**: DX7260P, Variable FT, 120C/60s PAB, 130C/60s PEB**
TARC	**: 43nm FT, 90C/60s PAB**	**Exposure**	**: Canon FPA-3000 EX-5, 0.63NA, 1/2Ann.**
Develop	**: AZ 300MIF(2.38%), puddle 60s**	**Mask pattern**	**: 200nm L/S(1:1), binary**



Swing Reduction Ratio

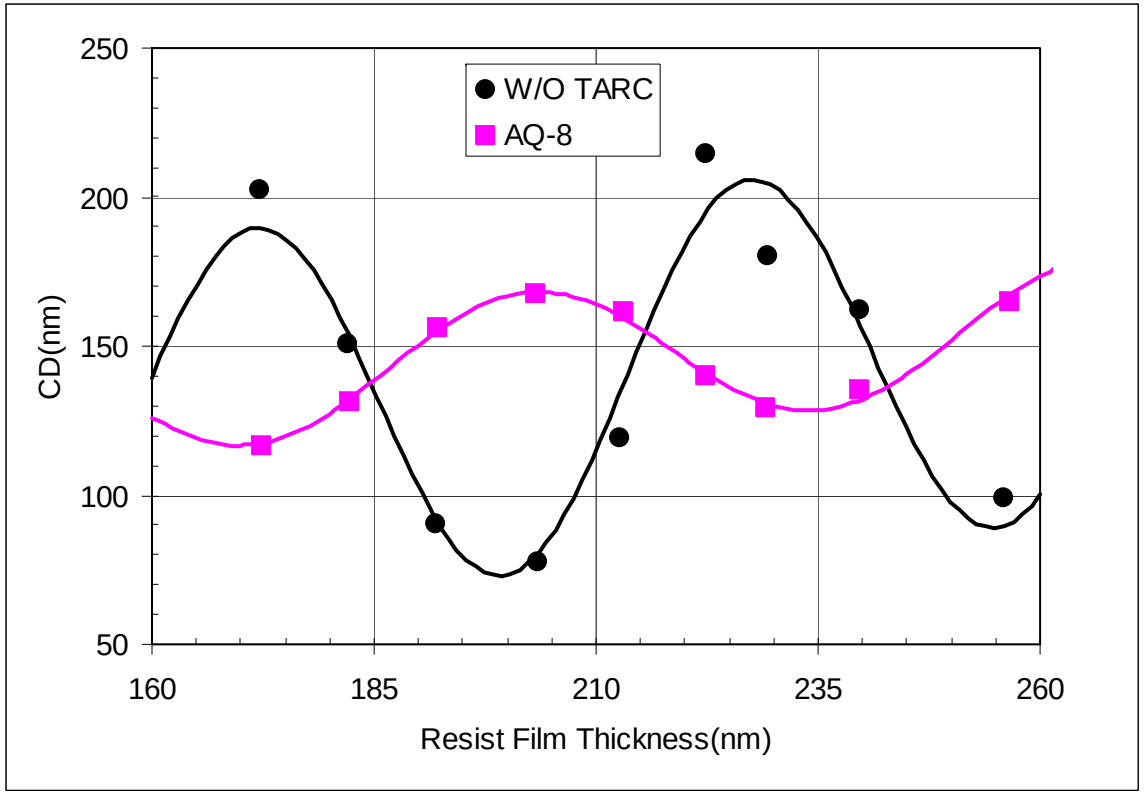
AZ AQ-8A 45 : 83%

AZ AQ-8B 45 : 79%

Swing Reduction Ratio = 1 – (A_{TARC} / $A_{w/o\ TARC}$)

2.6 Resist swing reduction effect in 193nm application

Substrate	**: Silicon with HMDS(90C/60s)**	**Resist**	**: AX1120P, Variable FT, 120C/90s PAB, 120C/90s PEB**
TARC	**: 32nm FT, 90C/60s PAB**	**Exposure**	**: Nikon NSR S306C, NA=0.78, 2/3Ann.**
Develop	**: AZ 300MIF(2.38%) , puddle 30s**	**Mask pattern**	**: 120nm L/S(1:1.5), binary**



Swing Reduction Ratio

AZ AQ-8A 25 : 70%

Swing Reduction Ratio = 1 – (A_{TARC} / $A_{w/o\ TARC}$)

6. Summary table of AZ AQUATAR Family

Products	wafer		N value(K=0) *ideal N value($\sqrt{N_{resist}}$)				Optimal FT(nm) λ /4N			**Mini.Dispense V(mL)		PH	Chemical
			633nm	365nm	248nm	193nm	365nm	248nm	193nm	8 inch	12 inch		
			-	1.33	1.33	1.30				on Resist			
AZ AQUATAR	8"	i-line	1.42	1.44	1.48	1.56	64	43	31	1.0	3.0	3.3	PFOA
AZ AQUATAR 45	12"												
AZ AQUATAR-IIIS 45	8"	KrF	1.41	1.42	1.44	1.49	65	43	32	2.5	5.0	2.2	PFOS
AZ AQUATAR-IIIS 33	12"												
AZ AQUATAR-VI-A-30	8"	ArF	1.38	1.40	1.43	1.45	65	43	33	2.0	4.5	2.9	PFOS
AZ AQUATAR-VI-A 25	12"												
AZ AQUATAR-VII-45	8"	KrF	1.39	1.40	1.43	1.50	65	43	32	1.0	3.0	3.4	PFOA
AZ AQUATAR-VII-A 30	12"												
AZ AQUATAR-VIII-A 45	**12"**	**i-line**	**1.40**	**1.41**	**1.45**	**1.52**	**65**	**43**	**32**	**2.5**	**5.0**	**1.8**	**F-polymer**
AZ AQUATAR-VIII-A 30	**12"**	**KrF**											
AZ AQUATAR-VIII-A 25	**12"**	**ArF**											

*Each ideal N was caluculated by using $N_{i\text{-}line\&KrF\ resist}$=1.77, $N_{ArF\ resist}$=1.70

**Minimal dispense volume was determined by visual inspection for 12 inch wafer.

AZ AQUATAR-8 series Process Recommendation

1. **Process recommendation** : "CBC" process
2. **Filter recommendation** : PE filter with wet treatment or pore size<0.05um

   Smaller pore size is BETTER for micro bubble, but need to adjust pump & dispense condition carefully.
3. **Coating method** : "Static Dispense"
4. **Coater recommendation** : Dedicated coater

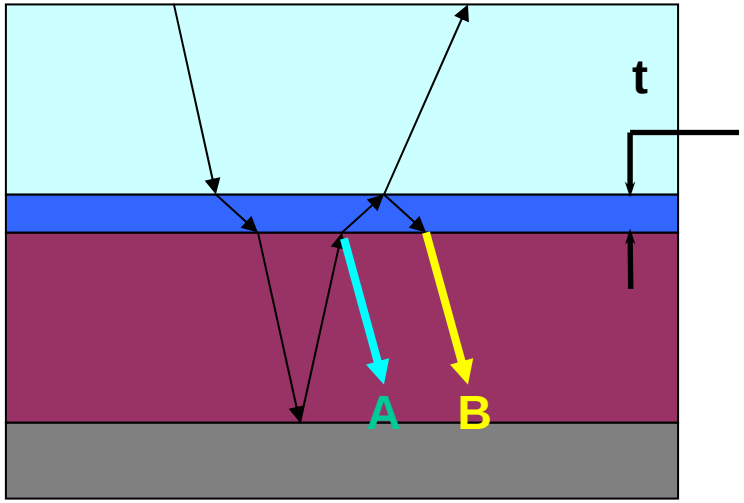
   DON'T SHARE with "RELACS"
5. **EBR recommendation** : DI water

Summary of “PFOX & Telomer FREE” TARC

- **AZ AQUATAR-8 Series**
  - only universal “PFOX & Telomer FREE” TARC product in the market
  - “the safest TARC in EHS aspect”
  - “>80% of market share” in “PFOS FREE” TARC
  - “Stable Supplibility” for 3 years
  - “Long Production History in many customers” for >2 years
  - “Broad Resist Compatibility” in 365 – 193nm
  - “Preferable Swing Control” in 365 – 193nm
  - “Long Shelf Life” 1 YEAR at 5 – 25C
  - “Less Defectivity” from customer feedback
  - “3 Grades of AQ-8, 25, 30, 45” fully can cover customer’s need
  - “AQ-8B” was developed for “N”-type of KrF resist

APPENDIX

Ap-1. Optical theory



Air (n=1)

TARC

Resist

Substrate

Required refractive index to be equalized light intensity in **A** and **B**

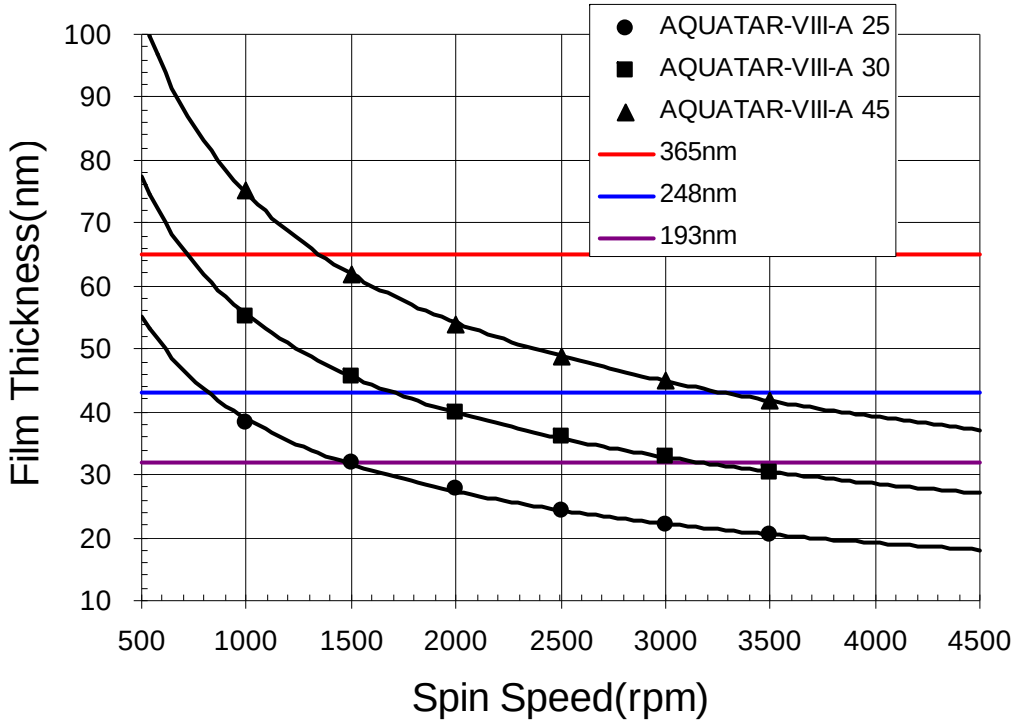
$n_{TARC} = (n_{air} \bullet n_{resist})^{1/2}$ ***n*** **:** Refractive index

Required thickness to be shifted optical phase at $1/2\,\pi$ in **A** and **B**

$t = \lambda / 4n_{TARC}$ ***t*** **:** Film thickness of TARC

λ **:** Wavelength

Ap-2. Material Information of AZ AQUATAR-VIII-A



Cauchy Parameter

Unit	um	nm	A
A	1.384	1.384	1.384
B	5.035E-03	5.035E+03	5.035E+05
C	0.000E+00	0.000E+00	0.000E+00
N_{633nm}	1.40		

	365nm	248nm	193nm
N	1.42	1.45	1.52
K	0.01	0.00	0.00
Optimal FT(nm)	64	43	32

N_{633nm} value is caluculated from A, B,C values
$N_{365nm,258nm,193nm}$ values are actual values measured by Ellipsometer

Optimal FT(nm) = $\lambda/4N$

Ap-3. AZ AQUATAR series install guide

Water based TARC is promising to provide a lot of benefits in the customer's process, but the customers need to pay close attention to the TARC install to make a good line condition without micro bubble issue. **This install guide is agreed to by TEL.**

a) TARC coater

Use a dedicated TARC coater system by a coater supplier (TEL, etc.).

b) Dummy dispense

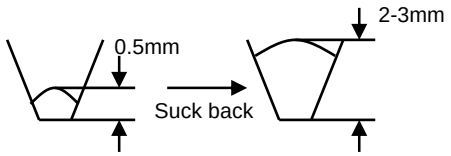
Keep the nozzle tip and line clean by periodical dummy dispense.

c) Suck back

Optimize the suck back condition.

EX.) Adjust the liquid breaking position to 0.5mm upper from the tip of nozzle, and then the final position after the suck back to 2-3mm upper for 2-3 sec.

Refer to a TARC coater operation guidance by your track maker on further detailed suck back adjustment. Suck back adjustment is one of KEY factors to achieve micro bubble free.



Ap-3. AZ AQUATAR series install guide

d) Filter

Use PE filter. PE filter requires hydrophilic treatment before the install (1 gallon of IPA flushing). Nylon filter is **NOT** suitable for some AQUATAR series with low pH(<2.0).
It is the most important to make a good filter condition.

e) Plumb in a virgin line (see SOP-1)

f) Tubing

From hydrodynamics view, use the same size of PFA tube and minimize the connection number in the line. Check if tube twist & bending, and some bubbles occur in the line visually.

g) Dispense rate

Adjust to preferable dispense rate(<1 mL/sec)

h) EBR / BSR

Use DI water or a hydrophilic solvent(EBR7030, PGME, etc.). Especially pay attention to rebounding back to a wafer choosing DI water as EBR/BSR.

Ap-3. AZ AQUATAR series install guide(SOP-1)

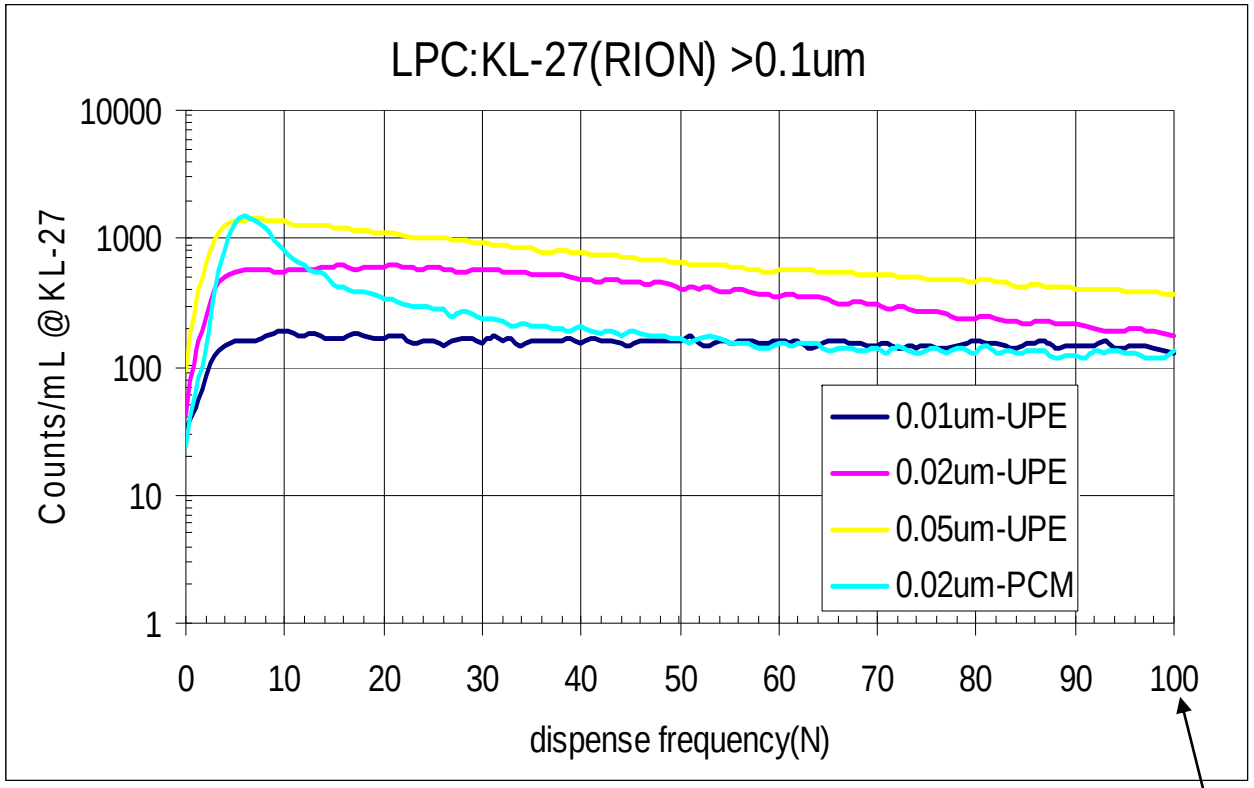
e) Plumb in a virgin line

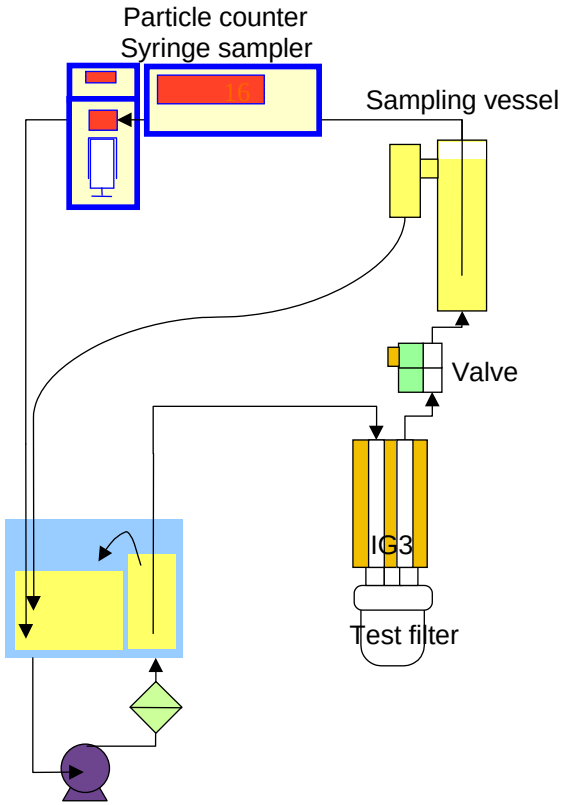
1. Leave 2 bottles of AQUATAR in CR chemical box for 1 day
2. Purge the line with 1 gallon of IPA (electronic grade)
3. Fill IPA in the line for 1-2 days
4. Empty the line
5. Install the filter
   - In PE filter case, purge 1 gallon of IPA with PE filter for hydrophilic treatment.
6. Check the line defectivity by a defect measurement tool (surface scanner etc.)
   - Inspect the wafer after IPA coating & spin dry
7. Purge the line with > 3 gallons of clean DI water
8. Install the TARC
9. Purge the line with 1 gallon of the TARC
   - After filling the TARC in the line and vent bubbles in the filter perfectly, take off N_2 pressure from the bottle, periodical vent from the filter would be effective to make a good line condition.
10. Install a new bottle of TARC
11. Check the line & filter carefully again after 1L of purge, and then setup your dispense.

Check the line cleanness carefully replacing from a resist or BARC line,
EX.) Purge > 1 gallons of thinner with strong solubility (NMP, etc.), and then fill it in the system for a week prior to the SOP-1.

Ap-4. Filter information on AQUATAR-VIII-A by Entegris

Dispense Frequency vs. LPC value for each filter by Entegris





Dispense condition: 1mL/sec ×7sec

700mL

Ap-5. AZ AQUATAR-VIII-A shaking test

Shake the samples for 30s

	initial	1H	3H	12H
AQ-8A				
AQ-3				

Ap-7. Material Compatibility-2

- AZ TARCs can mix with **“Hydrophilic”** solvents (PGME, EBR7030, EL, NMP,etc.).
- AZ TARCs can **NOT** mix with **“Hydrophobic”** solvents (PGMEA,EEP, etc.)

- **Recommend to separate TARC coater cup & drain tank from organic materials (BARC, resist, etc.).**

Ap-7. Material Compatibility-1

	TARC	R200	R500	R602/S680
PFOS TARC	☺		☹	☹
PFOA TARC			☺	
AQUATAR-VIII-A			☹	

TARC: AZ AQUATAR, AQUATAR-III, III-S, VI, VII, VIII-A
PFOS TARC: AZ AQUATAR-III, III-S
PFOA TARC: AZ AQUATAR, AQUATAR-VII

- "TARC/TARC" combination can mix freely.
- "TARC/RELACS" combination can **NOT** mix basically,

  except "TRAC/R200" & "PFOA TRARC/R500" combinations.
- **Recommend to separate TARC coater cup & drain tank from RELACS's**