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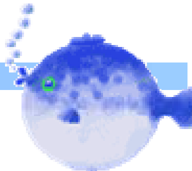

A New Monocyclic Fluoropolymer Structure For 157-nm Photoresists

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Semiconductor Leading Edge Technologies, Inc

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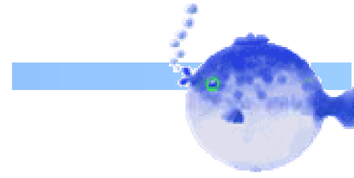
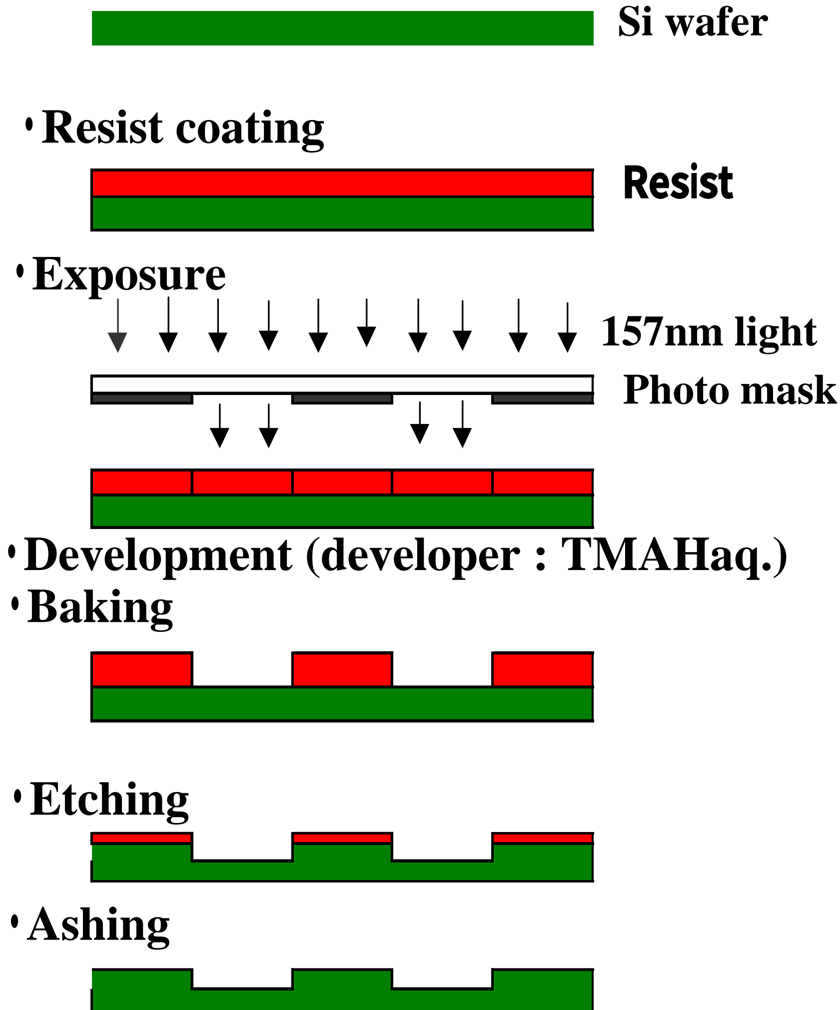
Requirements for 157nm Resist





Requirements for 157nm resist

- High transparency
- Solubility in alkaline soln.
- Heat resistance (higher Tg)
- Etching resistance

Our strategy

- Development of Monocyclic Polymer containing essential functions

1st generation polymer

FPR

Improvement of etching resistance & dissolution behavior retaining high transparency

New fluoropolymer

ASF-2

High transparency

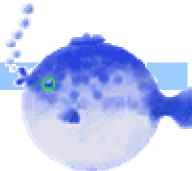
Improvement of etching resistance

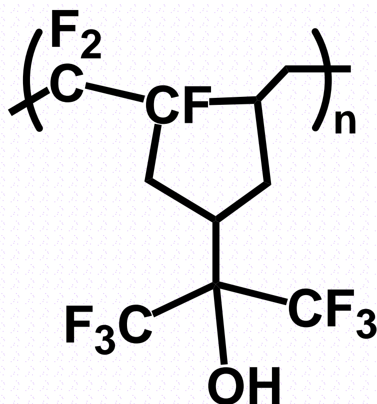
High transparency

Improvement of dissolution behavior

*Good transparency
*insufficient etching resistance & dissolution rate.

Characteristics of ASF-2





Great!!!

Improved

	abs. [µm-1]	dissolution rate [nm/sec]	etching rate [vs KrF resist]	refractive index n @157nm
ASF-2	0.1	>600	1.85	1.55
FPR(ref.)	0.4	80	2	1.55
target spec	0.2>	>500	1>	

- Soluble in : ketones(acetone, PGMEA)/ethers(THF)/esters(Ethyl acetate)/ alcohols(methanol,IPA)/fluorinated solvents(R-225)
- Not solble in : water/saturated hydrocarbon(Hexane etc.)

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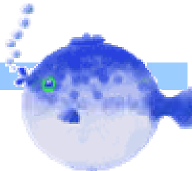
Characteristics of ASF-2



Tg changes vs molecular weight

Tg(°C)

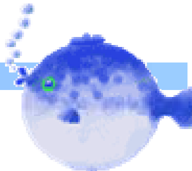
130
120
110
100
90

0
20000
40000
60000

Mw

Polymer Tg is affected by molecular weight, especially in the area of less than 20000 Mw.

For better dry-etching resistance and resolution



Co-polymerization

$$-\left(CF_2-CF(\text{ring})\right)_m-\left(CF_2-CF(\text{ring})\right)_n-\left(Y\right)_l-$$

(first unit ring substituent: $C(CF_3)_2OH$; second unit ring substituent: $C(CF_3)_2OR$)

Labels in structure: F_2, C, CF, F_3C, CF_3, OH, m, F_2, C, CF, F_3C, CF_3, OR, n, Y, l

Suitable Protecting groups

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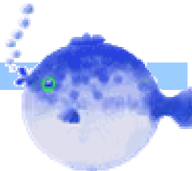
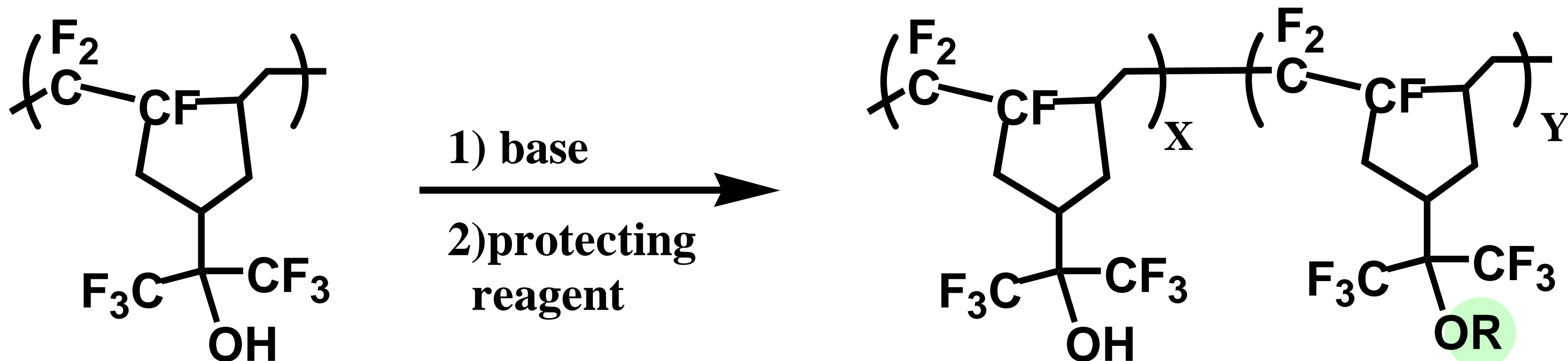
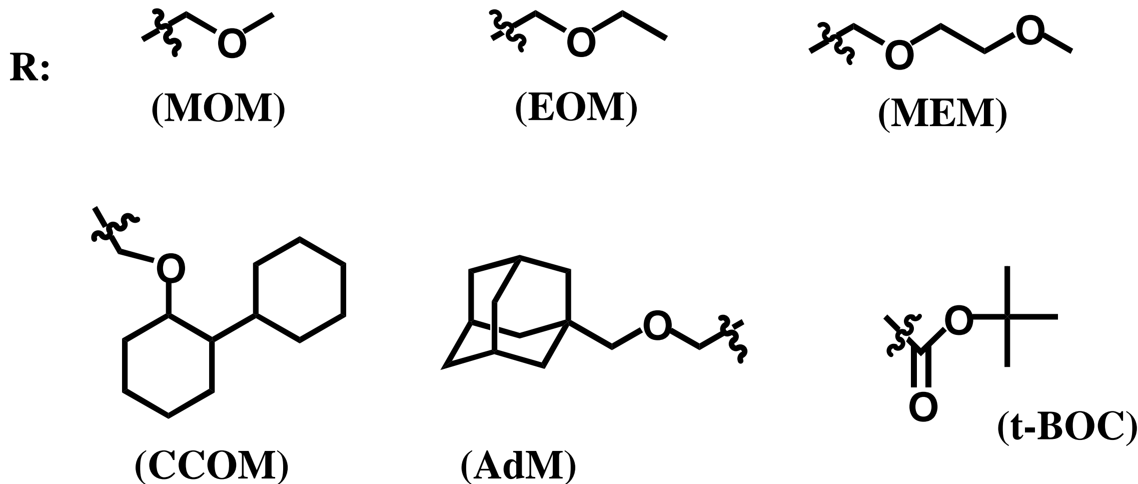
introduction of protecting group to ASF-2





Protecting group



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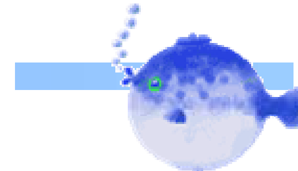
Characteristics of protected ASF-2



120
110
100
90

Tg(°C)

0 10 20 30 40 50

protection ratio(%)

t-BOC

AdM

MOM

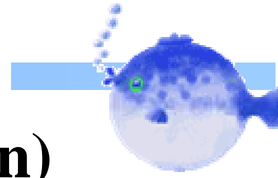
High Tg

EOM

MEM

CCOM

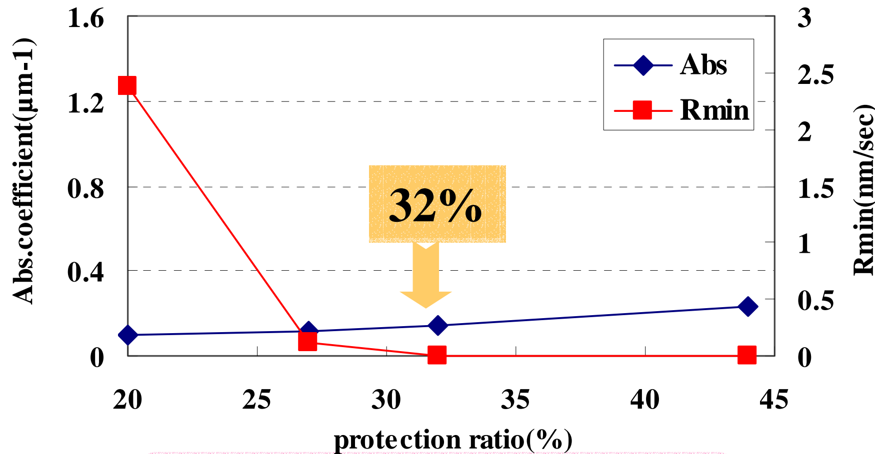
Decreasing Tg



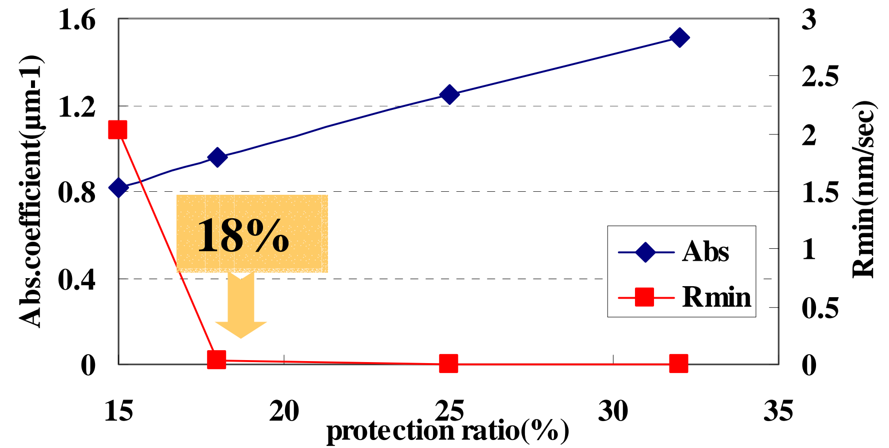
Characteristics of protected ASF-2

Transparency and Dark film thickness loss(Rmin)

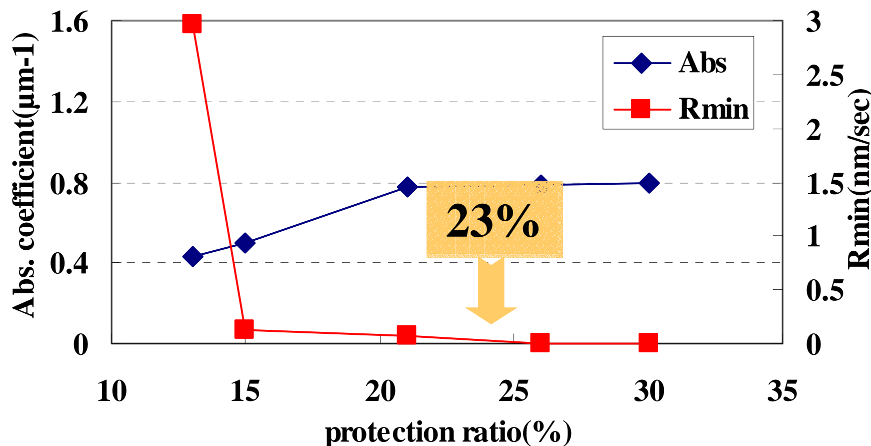
Estimation of proper protection ratio



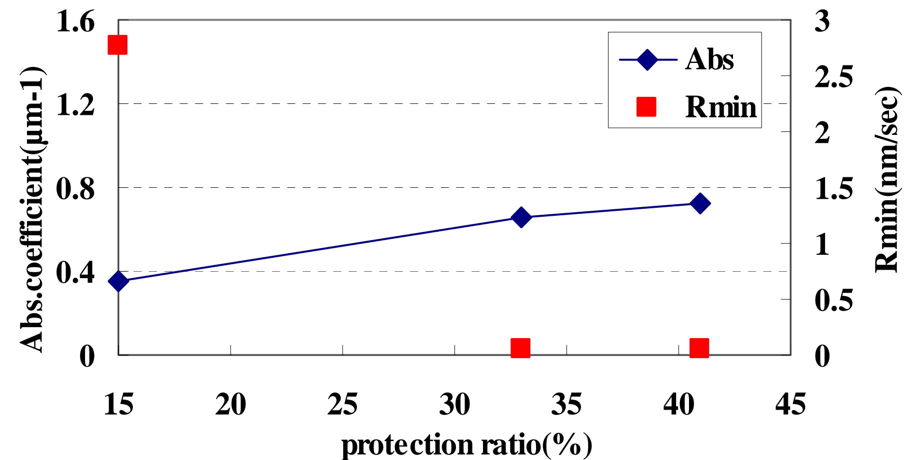
MOM-protected ASF-2



AdM-protected ASF-2



CCOM-protected ASF-2



tBOC-protected ASF-2

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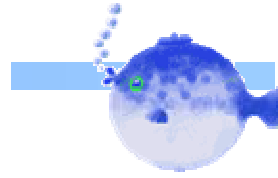
Characteristics of protected ASF-2



MOM
(68/32)
(80/20)
(85/15)
t-BOC
(59/41)
High transparency
(85/15)
(85/15)
AdM
(68/32)
(71/29)
CCOM
Good etching resistance
target
*(x/y): polymer composition ratio

Etching ratio (vs KrF)
2
1.75
1.5
1.25
1

0
0.5
1
1.5
2
Absorption coefficient.(/um)

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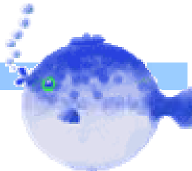
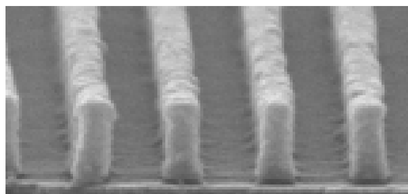
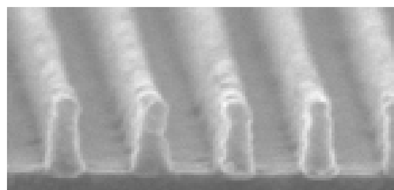
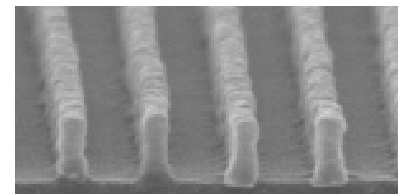
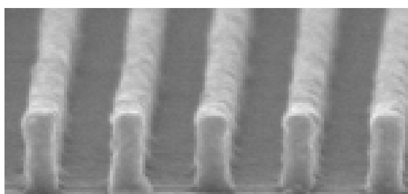
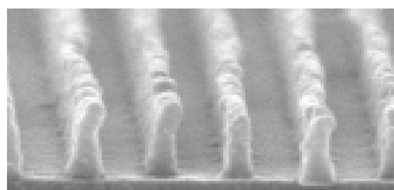
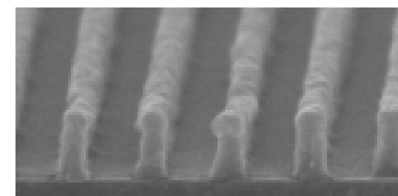
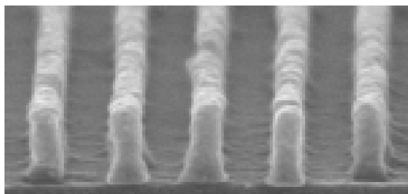
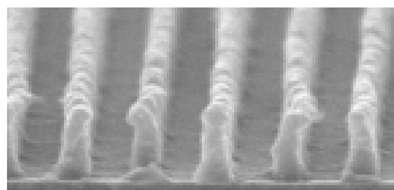
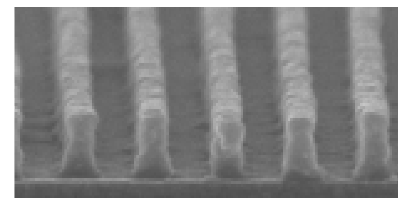
Patterning of ASF-2 based resist



MOM(32%) blocked ASF-2 based resist		AdM(32%) blocked ASF-2 based resist		CCOM (23%)blocked ASF-2 based resist	
75nm L/S		70nm L/S		80nm L/S	
70nm L/S		65nm L/S		75nm L/S	
65nm L/S		60nm L/S		70nm L/S	
PB 100℃ PEB 100 ℃		PB 90℃ PEB 80 ℃		PB 100℃ PEB 75 ℃	

150nm thickness
NA=0.9, 157nm microstepper, Alt-PSM

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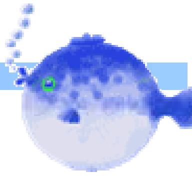
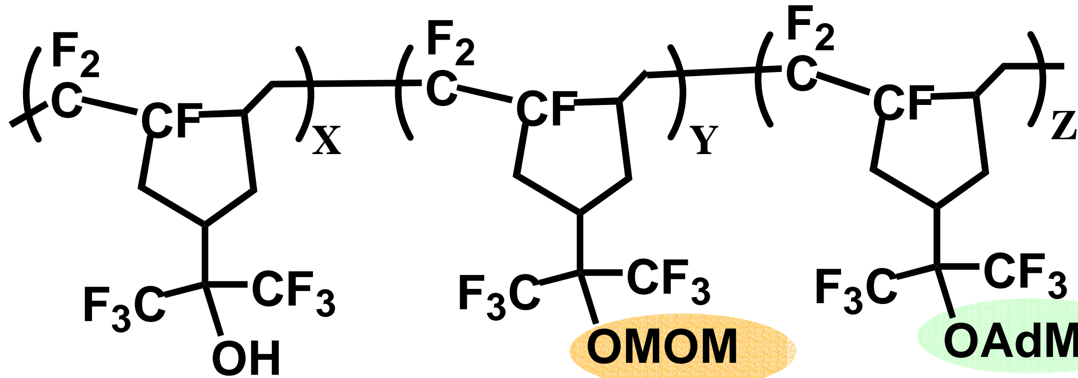


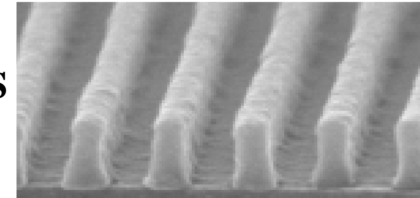
Characteristics of MOM and AdM protected ASF-2



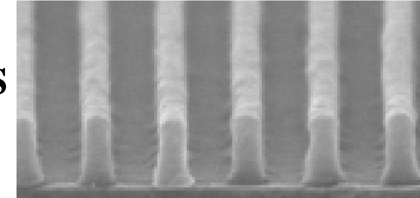
Improvement of dry-etching resistance

Keeping high transparency

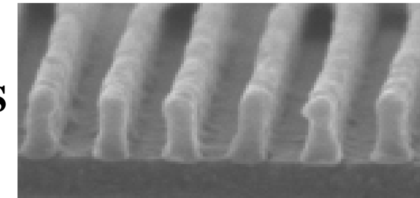
70nm L/S



65nm L/S



60nm L/S



Polymer composition (OH/MOM/AdM: mol%)	Absorption coefficient (μm-1)	dry-etching ratio (vs KrF resist)
ref.) 73 / 27 / 0	0.12	1.84
73.4 / 18.5 / 8.1	0.59	1.7
69.3 / 18.4 / 12.3	0.75	1.62
ref.) 68 / 0 / 32	1.51	1.43

both improved

PB 100℃/PEB 100 ℃

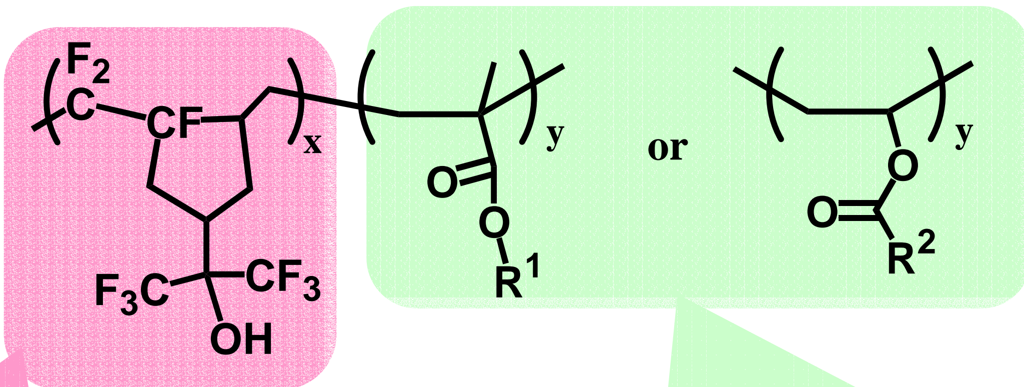
150nm thickness

NA=0.9, 157nm microstepper

Alt-PSM

Concept of copolymerization

Copolymerization of ASF-2 with acrylates or vinyl esters



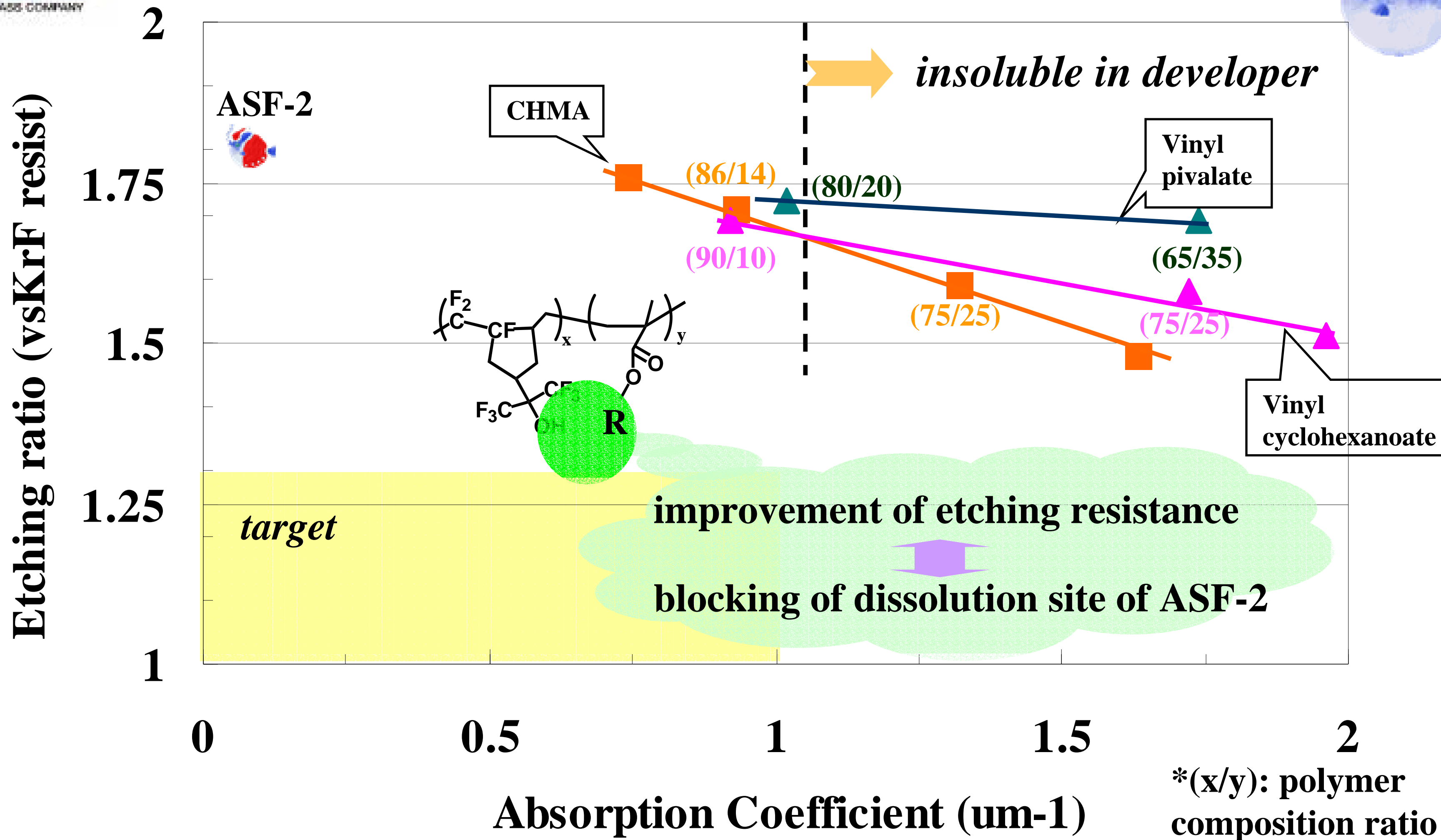
Transparency & Dissolution unit

Not acid deprotected type
Just for dry-etching resistance unit

monomer	R1	mol %	monomer	R2	mol %
CHMA	(cyclohexyl)	8~50	vinyl pivalate	(tert-butyl)	20~35
			vinyl cyclohexanoate	(cyclohexyl)	10~35

Comonomers can be introduced up to polymer dissolution limit in developer.

Characteristics of co-polymers



Next approach is ・・・

copolymerization with acid-deprotected type comonomers , having bulky group R.

we will show you new data at SPIE 2005

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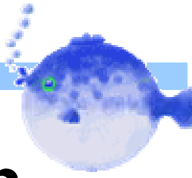
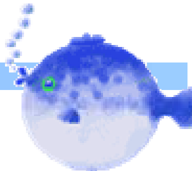
Summary



- **We have optimized new monocyclic fluoropolymer ASF-2, which has excellent transparency and dissolution behavior, for 157nm resist polymer. Protection of hydroxyl group by various protecting groups and copolymerizations of ASF-2 with some comonomers were studied.**
- **Etching resistance of ASF-2 was significantly improved when CCOM group or AdM group were used as protecting groups. And when both MOM and AdM group were introduced at the same polymer, etching resistance was also improved keeping high transparency.**
- **We examined the copolymerization with acrylates and vinyl esters.**
- **60-nm line and space pattern in a 150nm thick film was achieved.**



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SONY TOSHIBA