# High-sensitivity EUV resists based on Tetrafluoroethylene contained Fluoropolymers

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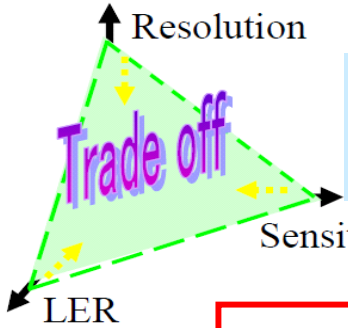
# Introduction

**Trade-off relationships between resolution, sensitivity, and LER**

Trade-off relationship




**Solution**

**Increase in pattern formation efficiency**

**Polymer absorption enhancement**

**Acid generation efficiency enhancement**
**ex. increasing AG conc.**

**Deprotection efficiency enhancement**
**ex. lowering $E_a$**

**Acid diffusion confinement**
**ex. control of acid diffusion by matrix**

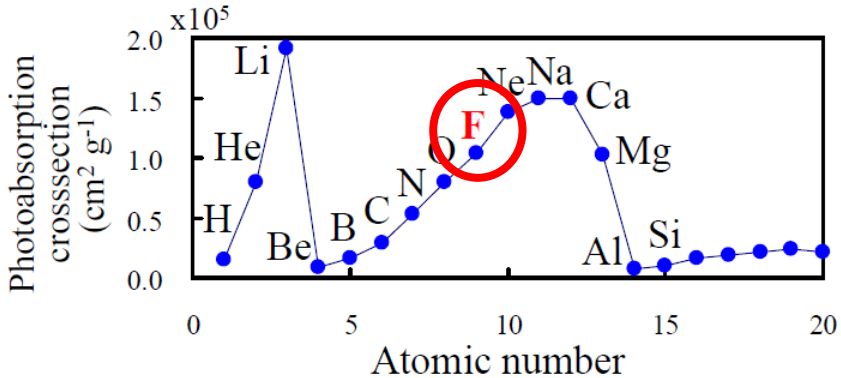
**T. Kozawa, et.al, Appl. Phys. Express 1 (2008), 067012**

**●Increase in pattern formation efficiency is one solution in improving the trade-off relationship in EUV resists.**

**●Increase in polymer absorption can enhance pattern formation efficiency.**

# Introduction

## How to increase resist absorption




B. L. Henke et al., At. Data Nucl. Data Tables **54** (1993) 181.

Increase in acid generator concentration [R. Hirose et al. JJAP 46 (2007) L979.]

| AG conc. (TPS-tf) | 5 | 10 | 20 |
|---|---|---|---|
| Abs. Coefficient | 3.8±0.2 | 3.8±0.2 | 3.8±0.2 |
| Q efficiency | 1.7 | 2.5 | 3.1 |

**Fluorination of polymer**

**Problem** **necessary for acid generation**

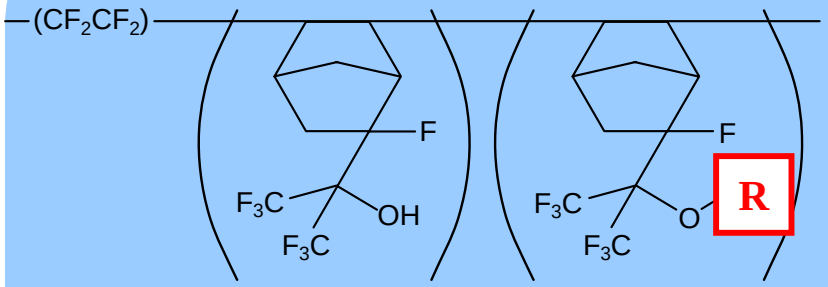
**Halogenated organic compound attract low energy electrons**
**Due to the high electron affinity of the halogen.**

**T. Kozawa, et.al, Appl. Phys. Express 1 (2008), 067012**

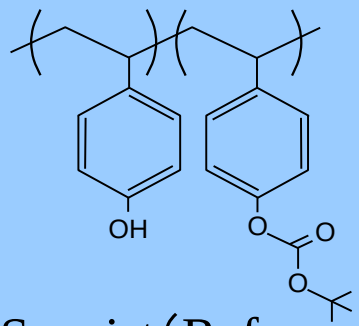
**Fluorination will increase polymer absorption to improve pattern formation efficiency.**

# Materials

## Polymer




**Mw : 4500 Mn : 3200**
**Mw / Mn=1.41**
**DR（2.38%TMAH）:890nm/s**
**Abs. coeff.* 8.28 μm$^{-1}$**

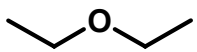



PHS resist（Reference） **4.27 μm$^{-1}$**

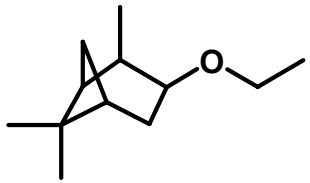
** Abs. coeff. calculated at assumed film density of 1.2 g/cm$^3$*

## Resists

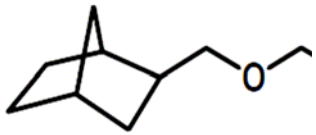
● **Protection group : R**



**Ethoxy-methyl (PG-A)**



**(2,6,6-Trimethyl-bicyclo [3.1.1]hept-3-yloxy)-methyl (PG-B)**



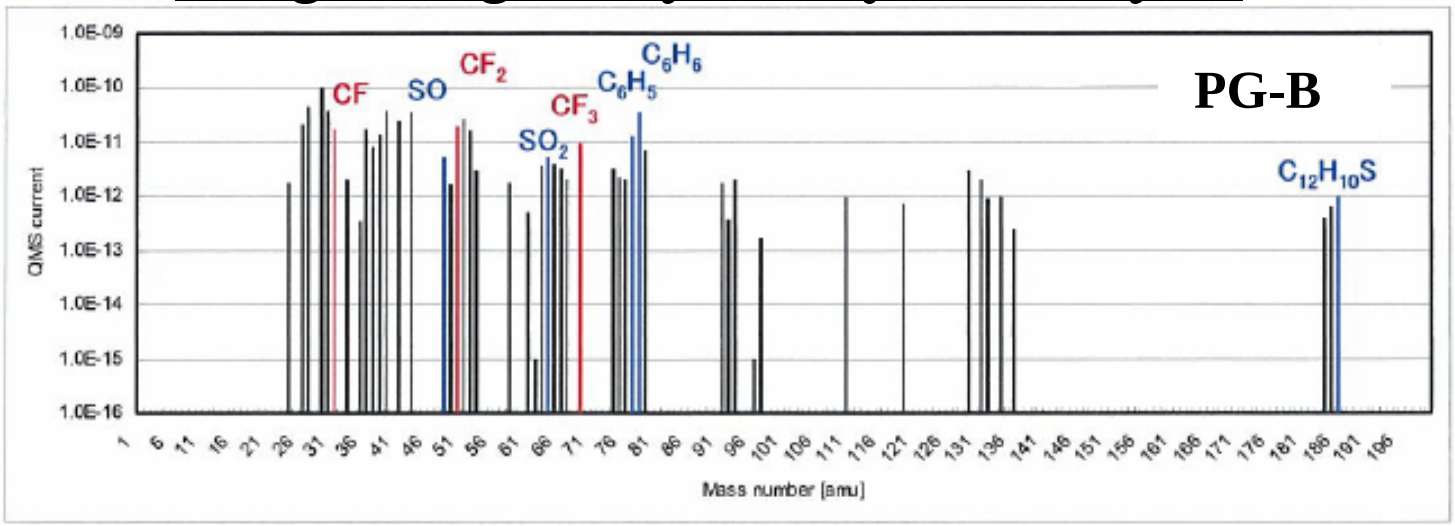
**(Bicyclo[2.2.1]hept-2-ylmethoxy) -methyl (PG-C)**

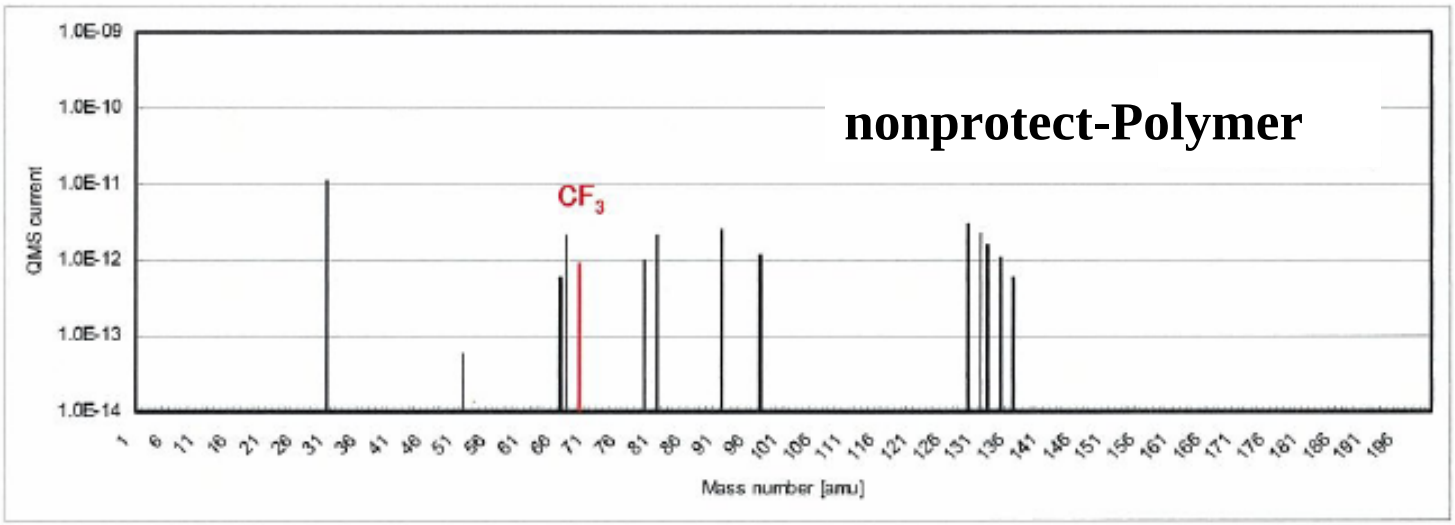
● **Quencher (8mol%)** : **Triethanolamine(TEA)**
**Tri-n-hexylamine(THA)**
**Tri-n-octylamine(TOA)**

● **PAG(20wt%)** : **TPS-PFBS**

● **Solvent** : **MAK**

# Outgassing analysis - QMS analysis




Hydrofluoric acids which are viewed as a possible harmful source of contamination were also not detected with QMS analysis. .

# Lithographic evaluation conditions

## Process conditions

Coater / Dev. : ACT-12

Substrate : Si with HMDS

Film thickness : 60nm

PAB / PEB : 110ºC 60s / 100ºC 90s

Developer : 2.38% TMAH (60s)

## Exposure Condition

Tool : SFET (Canon)

NA : 0.3

Illumination : Annular

$\sigma$ : 0.3/0.7

## SEM Condition

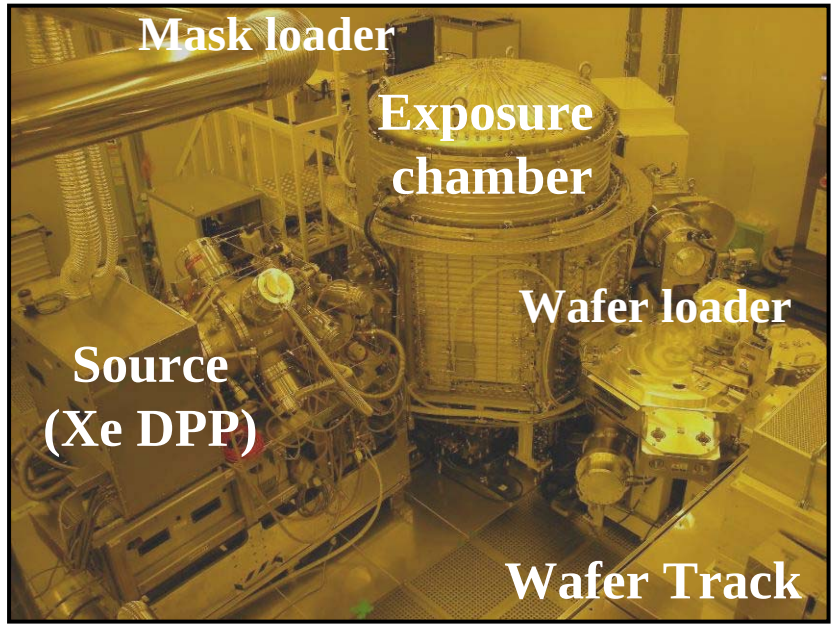
Tool : S-9380 Ⅱ (Hitachi)

Vacc : 800V

Ip : 5.0pA

Mag. : 200k

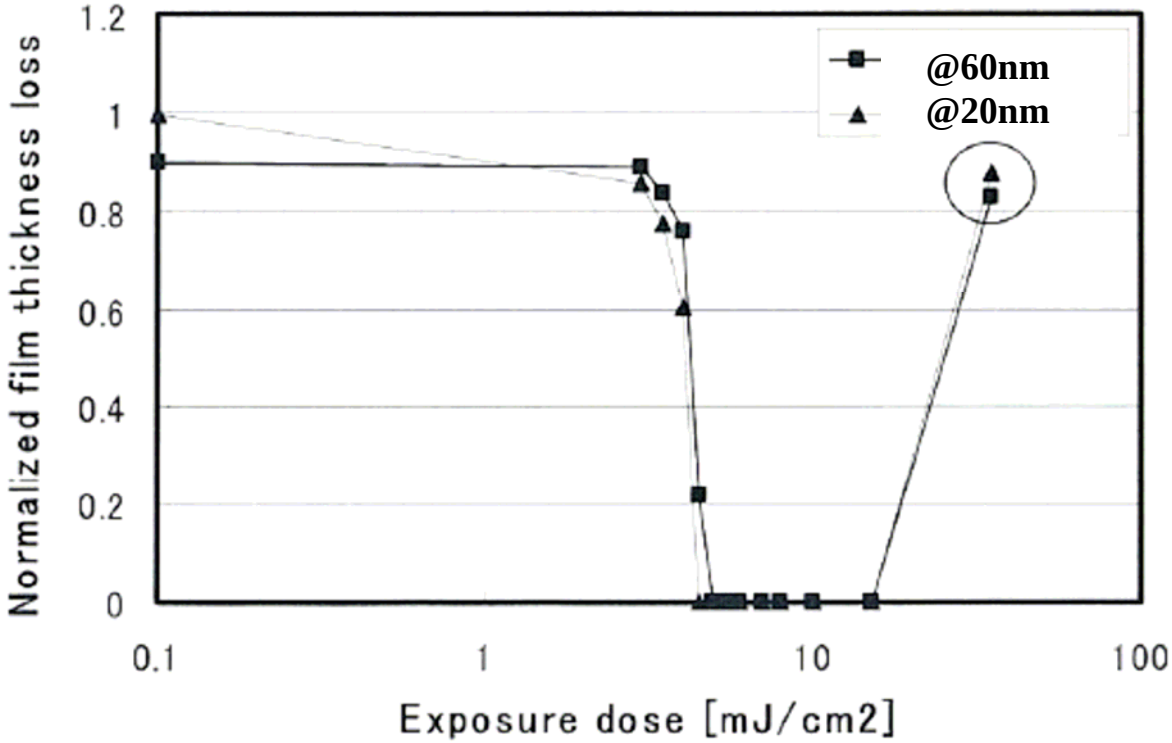
Frame : 32




| Item | Line Width | LWR |
|---|---|---|
| Inspection Area | 350pixels | |
| Measurement Point | 350pixels | |
| Sum Lines / Point | 32pixels | 17pixels |
| ACD | Auto / Target: 5 / Limit: 3 | |
| Method | Threshold: 50% | |
| Smoothing | 7 | 7 |
| Differential | - | 5 |

# Sensitivity:PG-A

## Protection ratio:17%

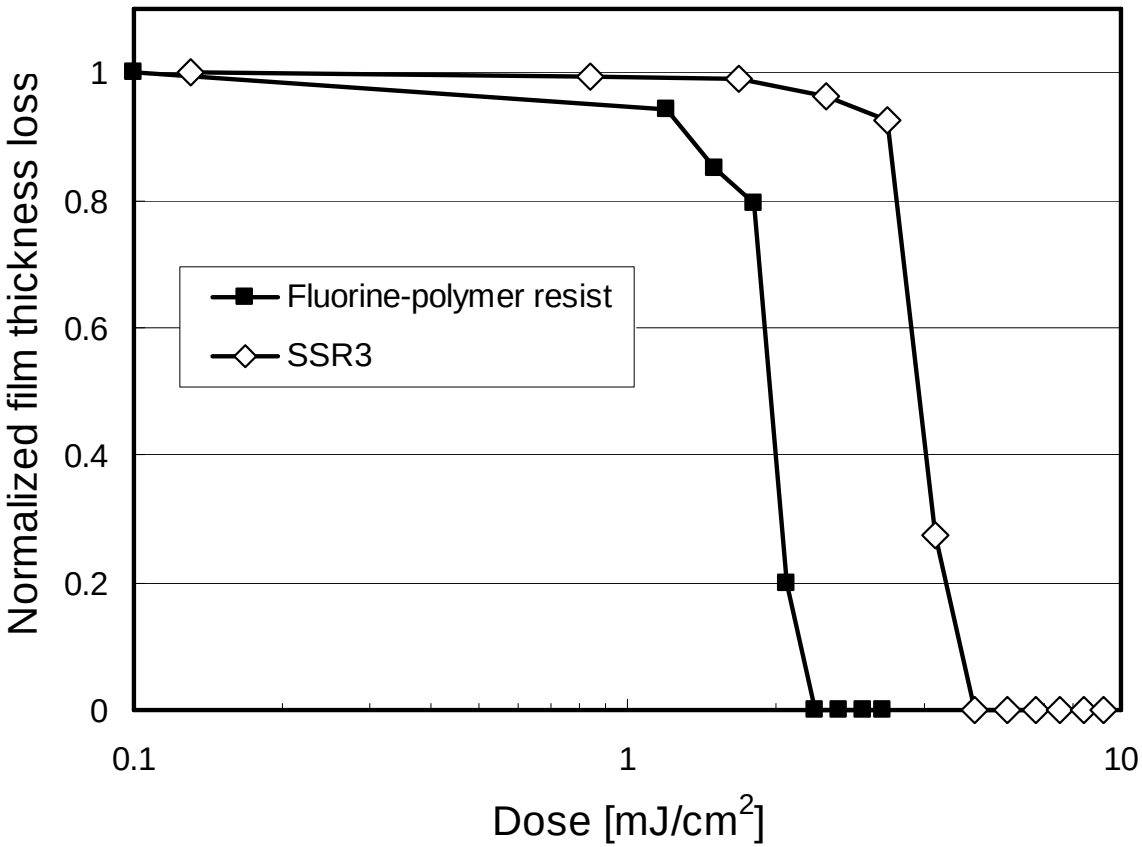



EUV Source : EQ-10MR
Power on Wafer : 0.03mW/cm$^2$
Exposure Area : 1.43cm$^2$

**High sensitivity ($E_0$=4.0mJ/cm$^2$) obtained for fluorinated polymer resist, but over dose appear the negative tone.**

# Sensitivity:PG-B

## Protection ratio:11%

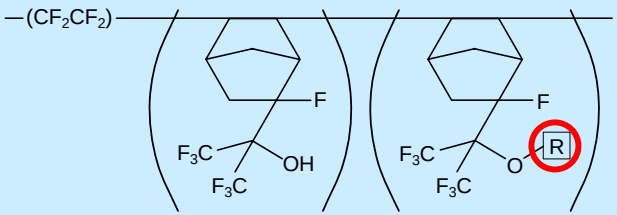



**EUV Source : EQ-10MR**
**Power on Wafer : 0.03mW/cm$^2$**
**Exposure Area : 1.43cm$^2$**

**Relatively high sensitivity obtained for fluorinated polymer resist compared to high performance SSR3 resist.**

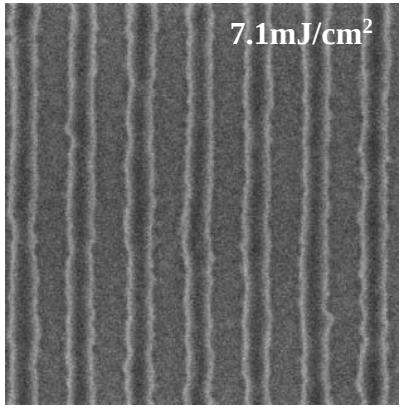
# Lithographic performance of Fluorinated polymer resist at optimized protection ratio

**R=PG-B**

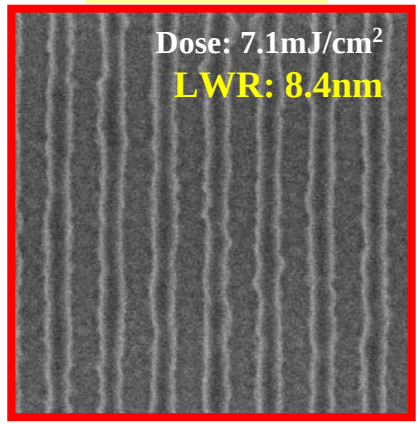



| | |
|---|---|
| PAG | : TPS-PFBS |
| Quencher | : tri-n-hexylamine |
| Solvent | : MAK |

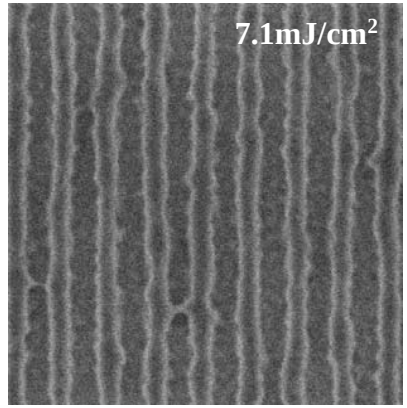
hp 50nm



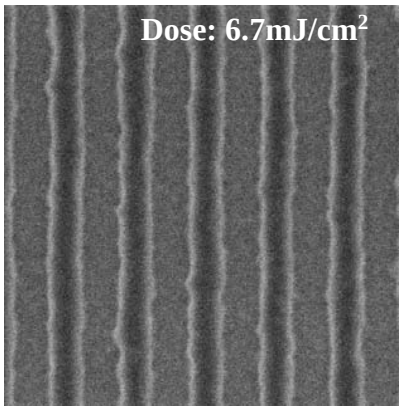

hp 45nm



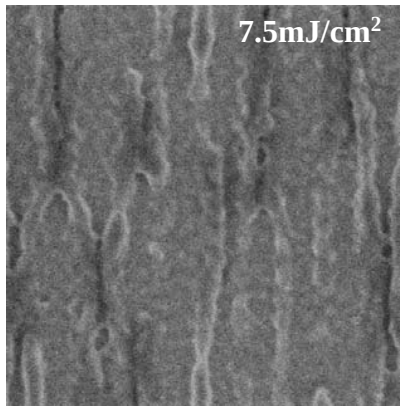

hp 40nm



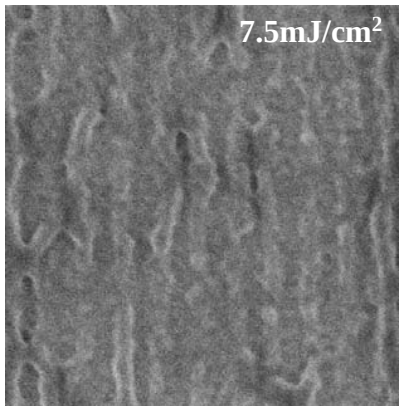

hp 60nm



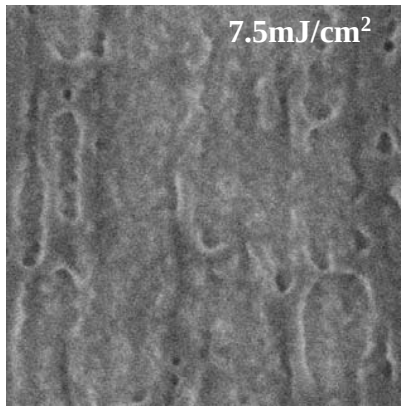

hp 35nm




hp 32nm



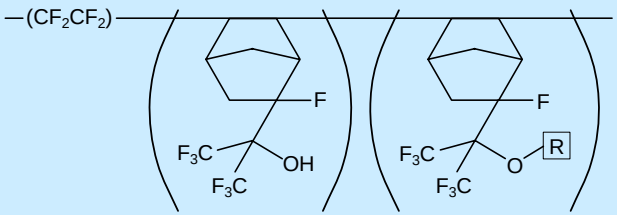

hp 30nm




**Improved LWR and partial resolution at hp 40nm.**
**Further improvement of LWR and resolution is necessary.**

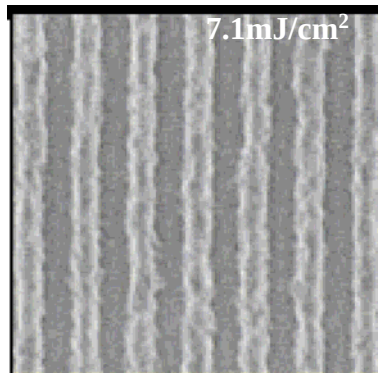
# Lithographic performance of Fluorinated polymer resist at Changed Quencher (triethanolamine→ tri-n-octylamine)

**R=PG-B**

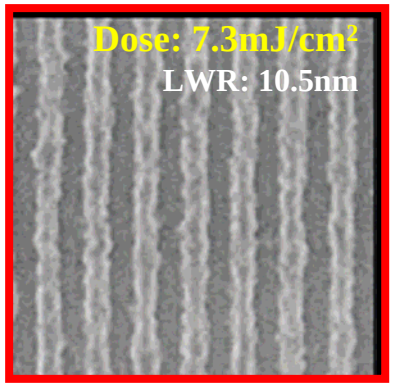



| | |
|---|---|
| PAG | : TPS-PFBS |
| Quencher | : **tri-n-octylamine** |
| Solvent | : MAK |

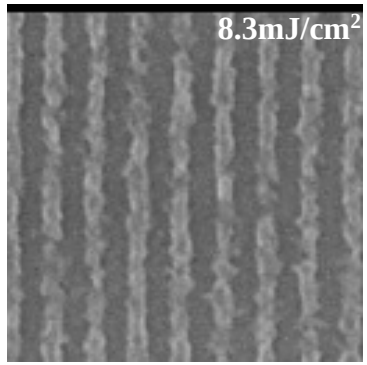
hp 50nm



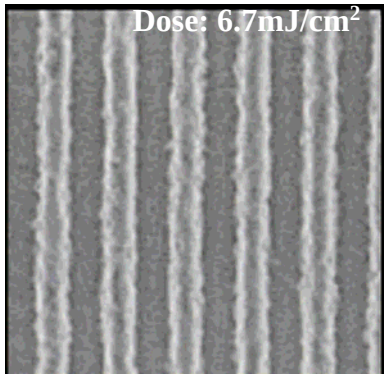

hp 45nm



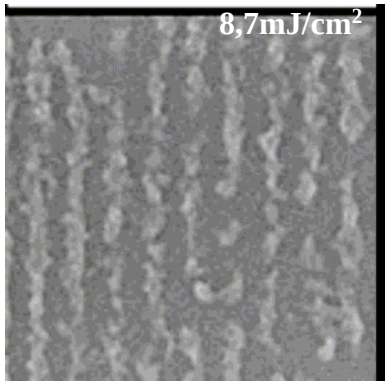

hp 40nm



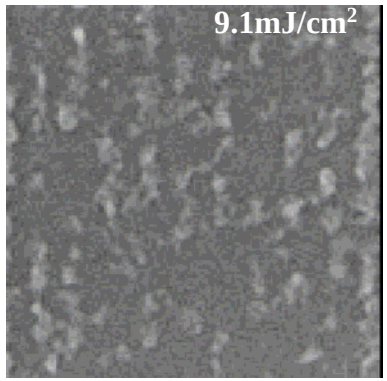

hp 60nm



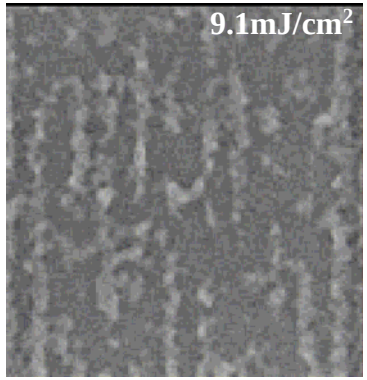

hp 35nm




hp 32nm



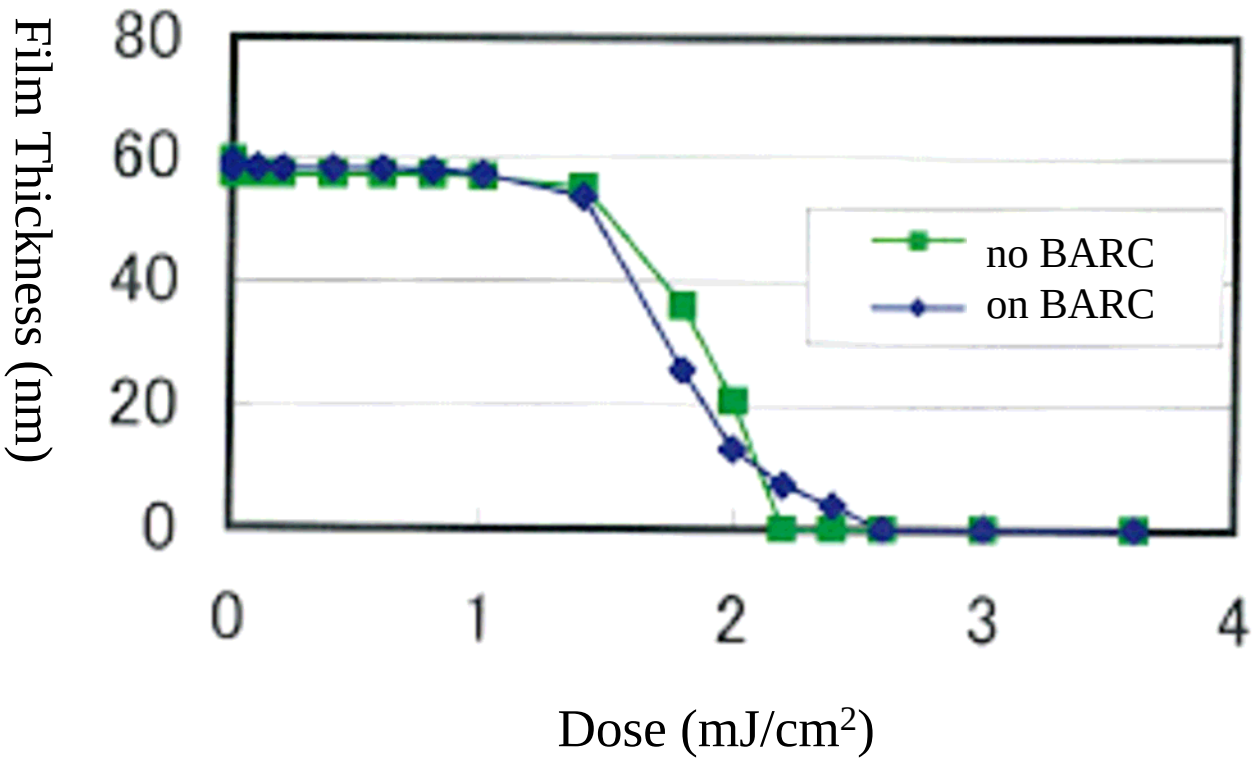

hp 30nm




**Quencher was changed for possible resolution and LWR improvement.**
**Improved resolution at hp 40nm with slight decrease of sensitivity and LWR.**

# Sensitivity:PG-C

## Protection ratio:14%

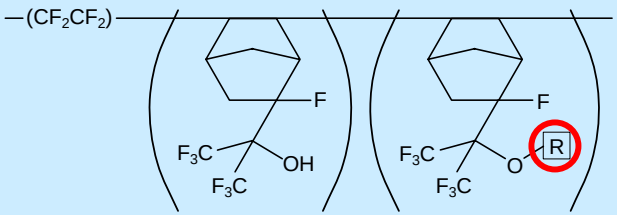



**EUV Source : EQ-10MR**
**Power on Wafer : 0.03mW/cm$^2$**
**Exposure Area : 1.43cm$^2$**

**Excellent high sensitivity obtained for changed protection group from PG-B to PG-C.**

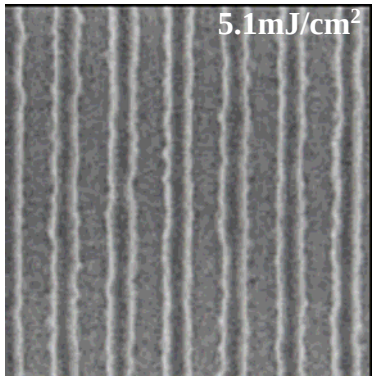
# Lithographic performance of Fluorinated polymer resist at Changed Protection Group PG-B→PG-C

**R=PG-C**

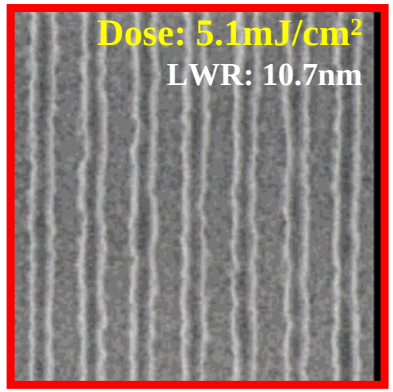



PAG : TPS-PFBS
Quencher : tri-n-octylamine
Solvent : MAK

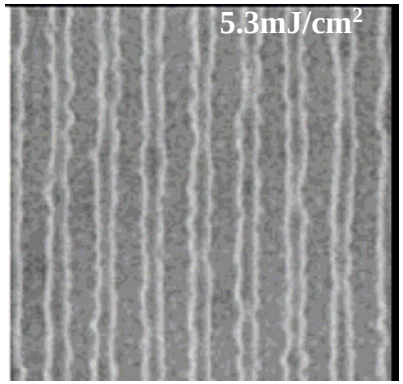
hp 50nm



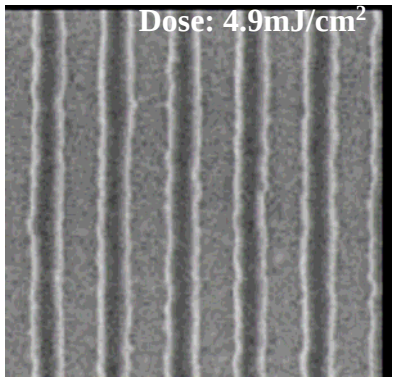

hp 45nm



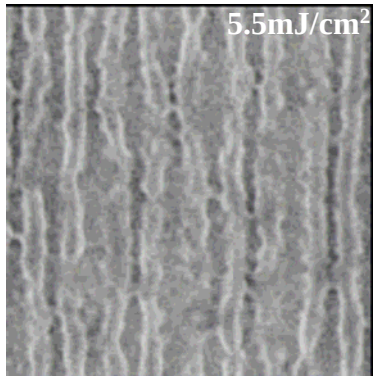

hp 40nm



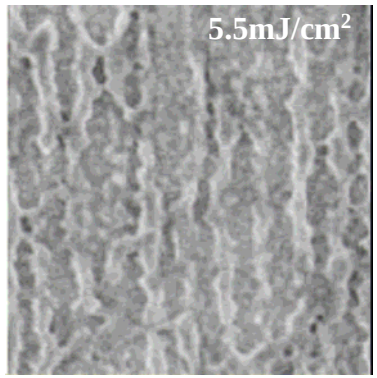

hp 60nm



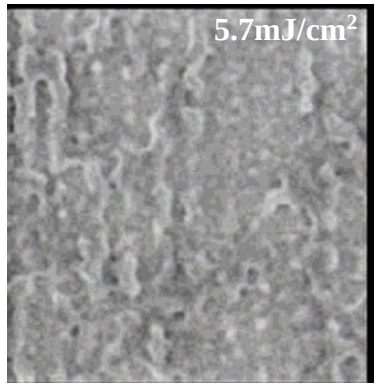

hp 35nm




hp 32nm




hp 30nm

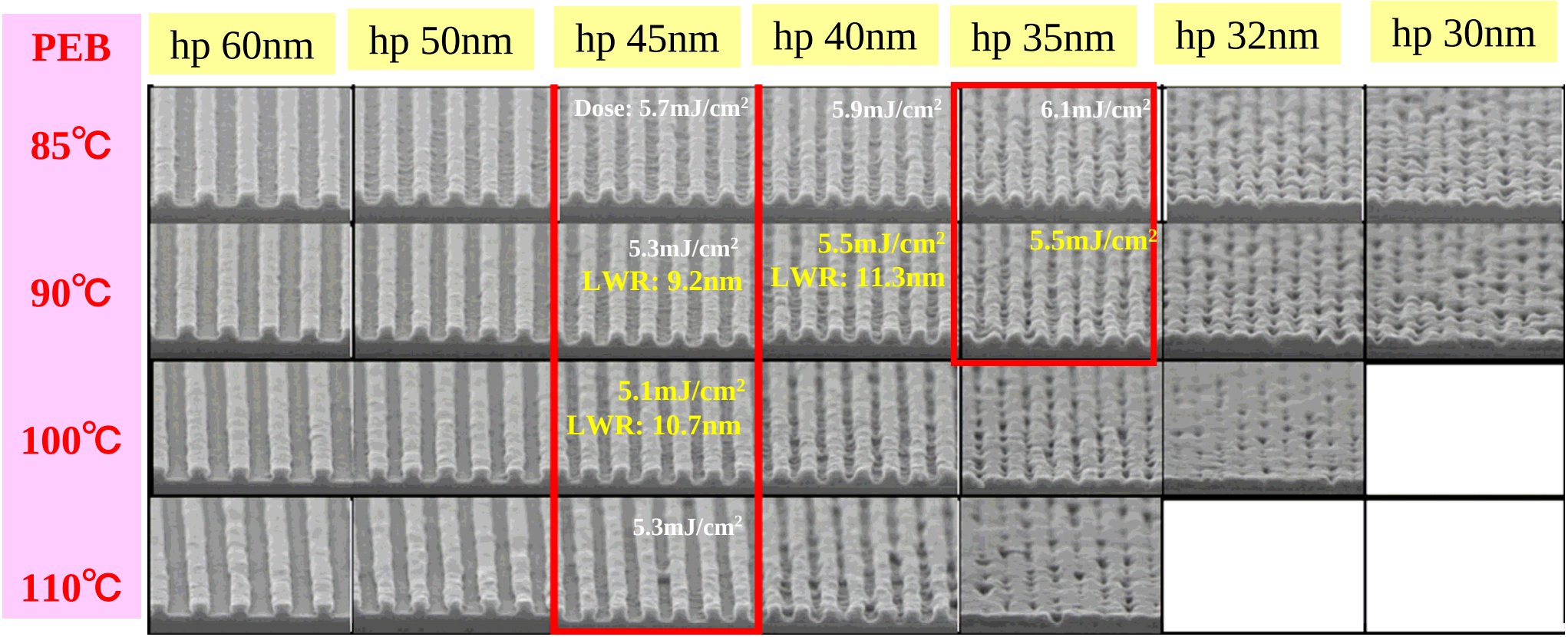



**Drastic Improved Sensitivity and partial resolution at hp 40nm.**
**But further improvement of LWR and resolution is necessary.**

# Lithographic performance of Fluorinated polymer resist

## Dependence of PEB Temperature

**R=PG-C**




**Improved sensitivity and partial resolution at hp 35nm with slight decrease of LWR.**

# Summary

- Feasibility of Fluorinated polymer as high sensitivity EUV resist was shown.
- Improved LWR and partial resolution at hp 40nm obtained through **protection ratio optimization**.
- **Change of quencher** improved resolution to hp 40nm with minimal change in sensitivity and LWR.
- **Change of Protection group ( PG-B→PG-C)** improved sensitivity.

  **Dose: 7.3mJ/cm$^2$→5.1mJ/cm$^2$ @ hp45nm**

- Improved LWR and partial resolution at hp 35nm obtained through **PEB Temperature optimization (100℃→90℃)**.

  **LWR: 10.7nm→9.2nm @ hp45nm**

## Future work

- Further improvement of **dissolution characteristics** necessary to improve resolution capability and possibly LWR.