

June 27, 2024

ICPST-41

A05-05, 10:50 – 11:10

Influence of the solvent in resist solution and thin films on aggregation size of chemical components

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1. Introduction

2. Results and Discussions

- Resist particle size analysis in solution
DLS measurement
- Aggregation size analysis in resist film
(Investigation of baking temperature effect)
Resonant Soft X-ray Scattering

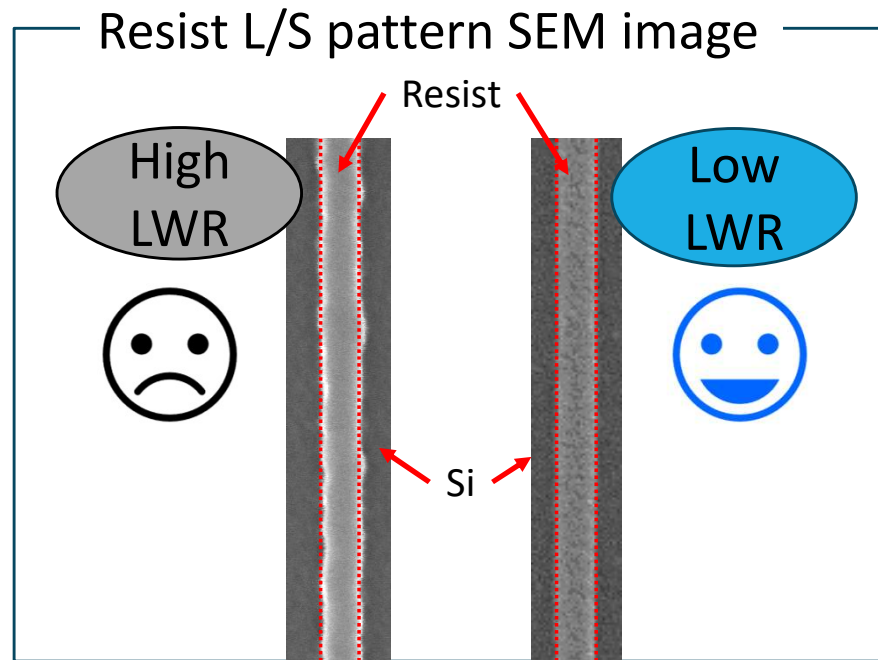
3. Summary

Critical issue of resist materials: Line Width Roughness

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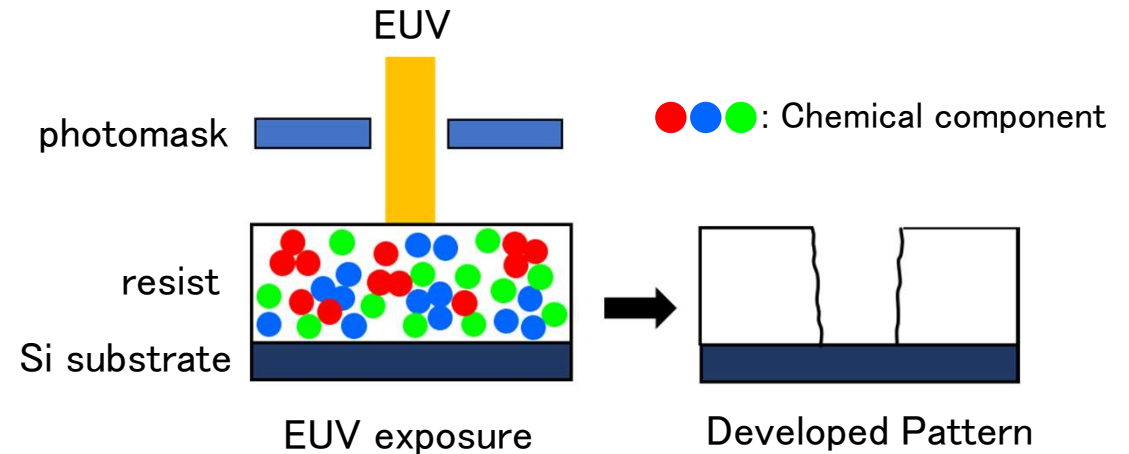
For next generation EUV lithography

- Resolution: < 10 nm
- Sensitivity: < 20 mJ/cm²
- **LWR (Line width roughness):**
 $< 1/10$ nm of pattern



One of the origin of LWR

- ✓ **Chemical composition distribution**
in the EUV resist film



The chemical composition distribution is not uniform.

→ The photochemical reaction is also not uniform

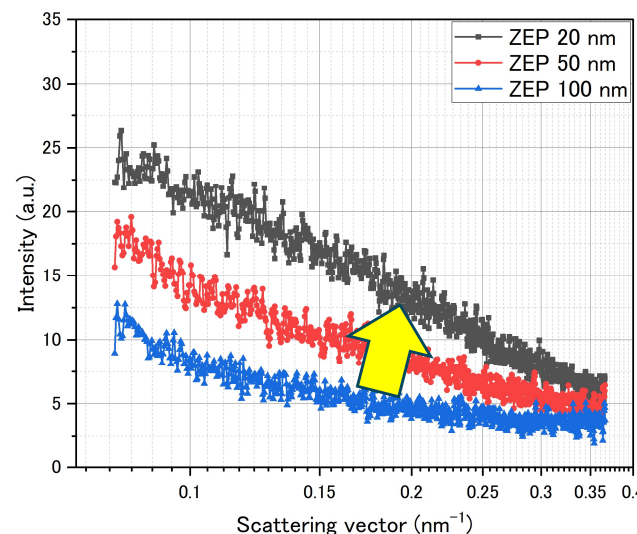
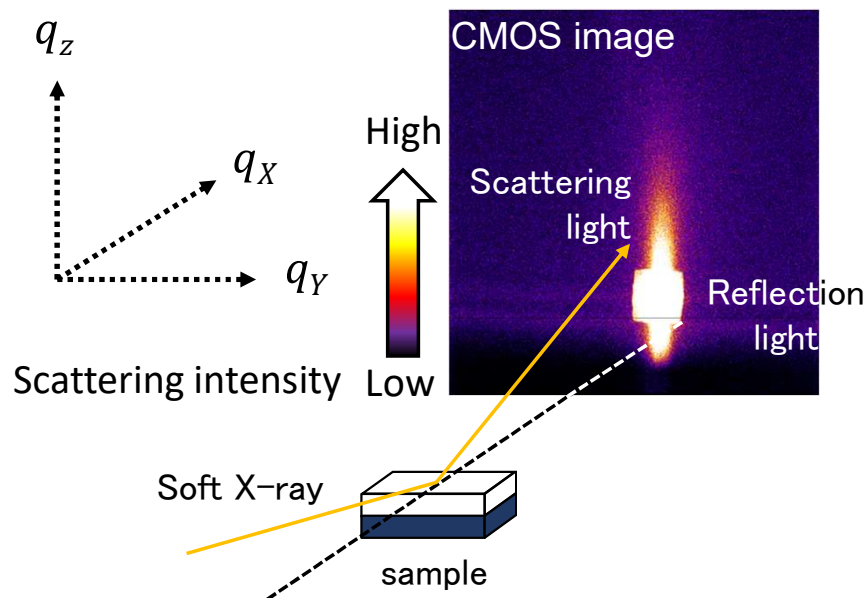


The chemical composition distribution analysis

Previous study (RSoXS at NewSUBARU BL10)

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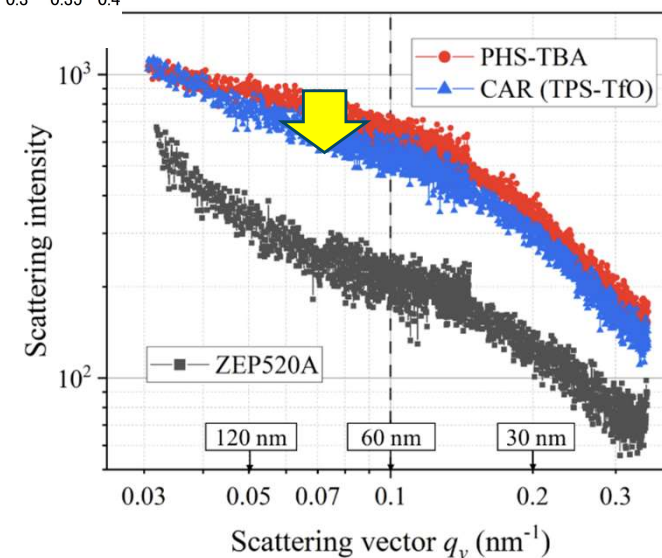
RSoXS (Resonant Soft X-ray Scattering)



<- Difference of thickness

Thinner film is more aggregate.

↓ Effect of PAG
aggregation was suppressed



Scattering light is translated scattering spectrum.

- X axis : **Size** of scattering source (scattering vector)
 - Y axis : **Amount** of scattering source (intensity)
- scattering source : aggregation and segregation

J. Photopolym. Sci. and Technol. (2022) p.61. & (2023) p.41.

The investigation whether the chemical composition distribution in the resist thin film is affected by the solvent.

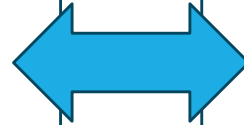
Solution



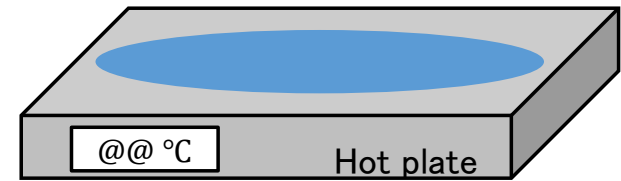
Resist solution

Dynamic light scattering (DLS) measurement

- Particle size
- Solvent parameter



Thin film



Resonant soft X-ray scattering (RSoXS) measurement

- Scattering spectrum
- Solvent parameter

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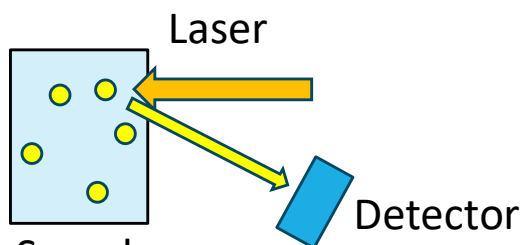
3. Summary

DLS (Dynamic Light Scattering) measurement setup

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DLS measurement

Litesizer500 (Anton Paar GmbH)
Range: 0.3nm~10μm (diameter)



Sample Solution Measuring fluctuations in scattering light intensity.

Hansen Solubility Parameter (HSP)

$$\delta^2 = \delta D^2 + \delta P^2 + \delta H^2$$

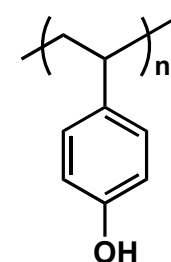
δD : Dispersion force

δP : Polar force

δH : Hydrogen bonding force

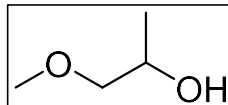
Samples

Base polymer
Poly hydroxy styrene (PHS)
 $M_w = 19,000$

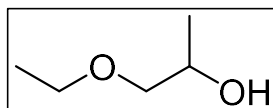


Solvents (8 samples)

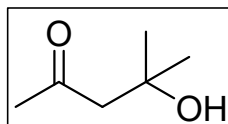
Alcohols



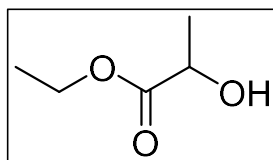
PGME



PE

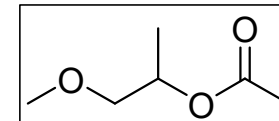


DAA

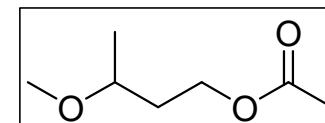


EL

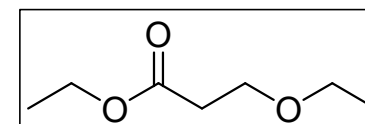
Esters



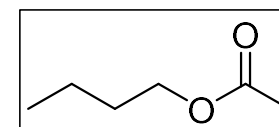
PGMEA



MBA



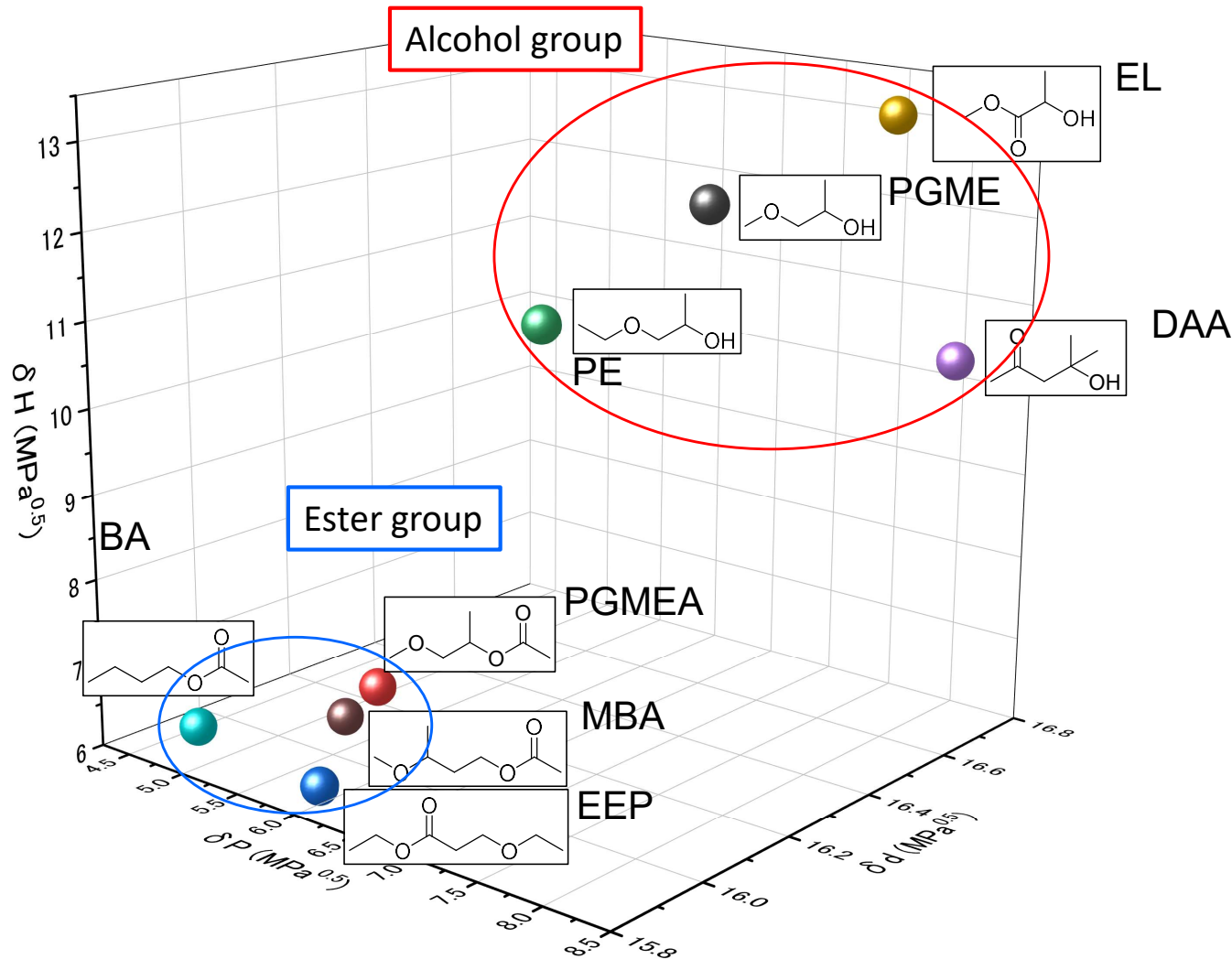
EEP



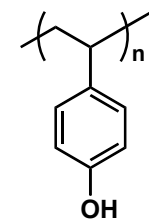
BA

Difference of solubility

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Solvent name
Particle size (nm)



δH (Hydrogen bond) and δD (dispersion)

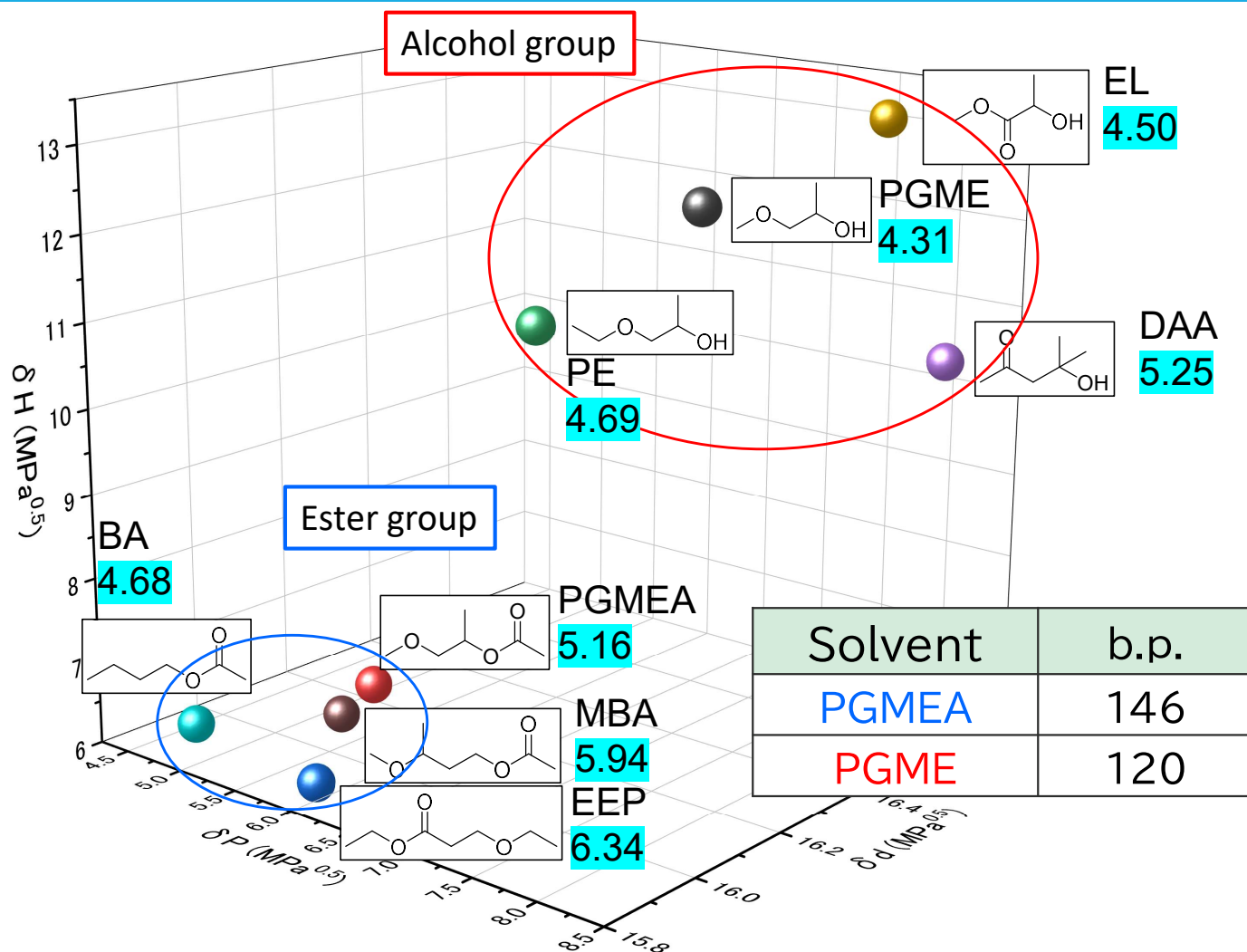
Alcohol groups: δH and δD are High

Ester groups: δH and δD are Low

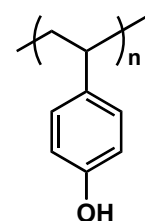
-> Alcohol groups has hydroxyl group.

HSP vs. Particle size

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Solvent name
Particle size (nm)



δH (Hydrogen bond) and δD (dispersion)

Alcohol groups: δH and δD are High

Ester groups: δH and δD are Low

-> Alcohol groups has hydroxyl group.

Particle size in

- alcohol solvent: 4~5 nm

- Ester solvent: 4~6 nm

-> slightly bigger (in ester solvent)

Ester solvent's affinity is stronger to PHS

Particle size is correlated to HSP value

Resist coating process

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Sample solution

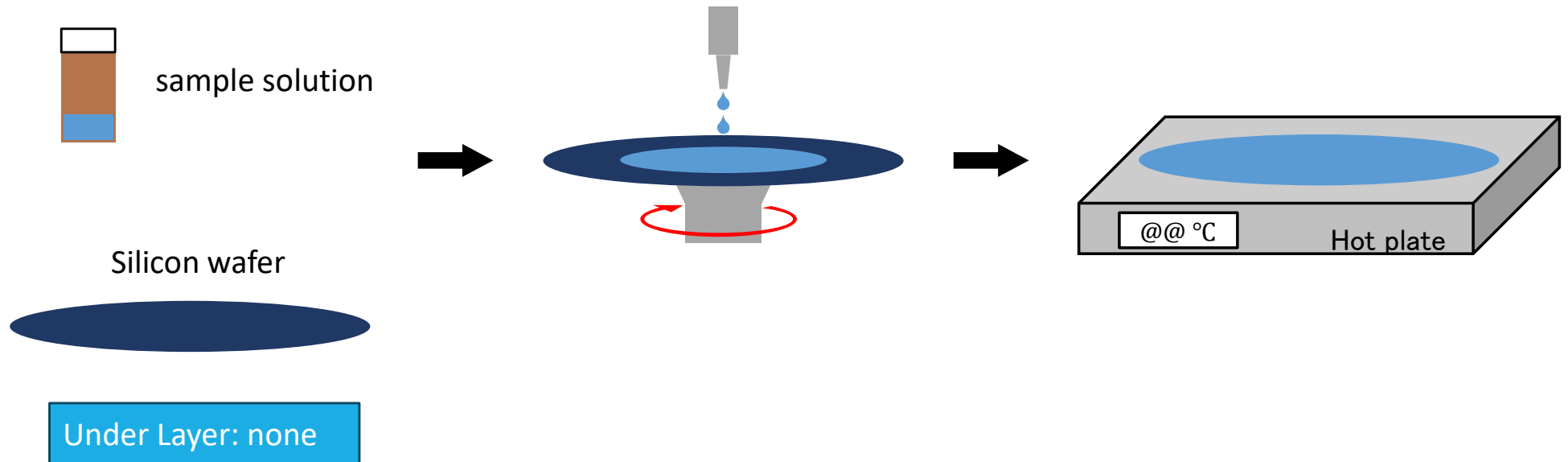
- PHS
- **Solvent**
(PGME, PGMEA)

Spin coating

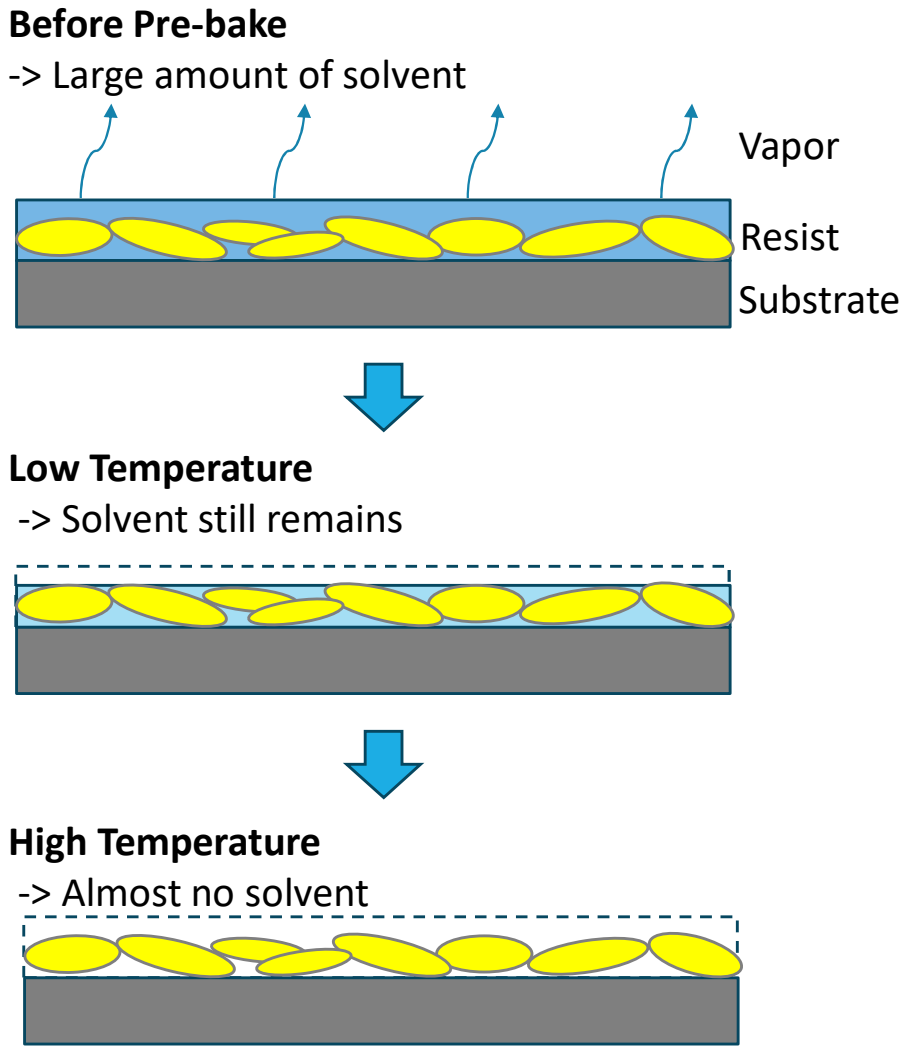
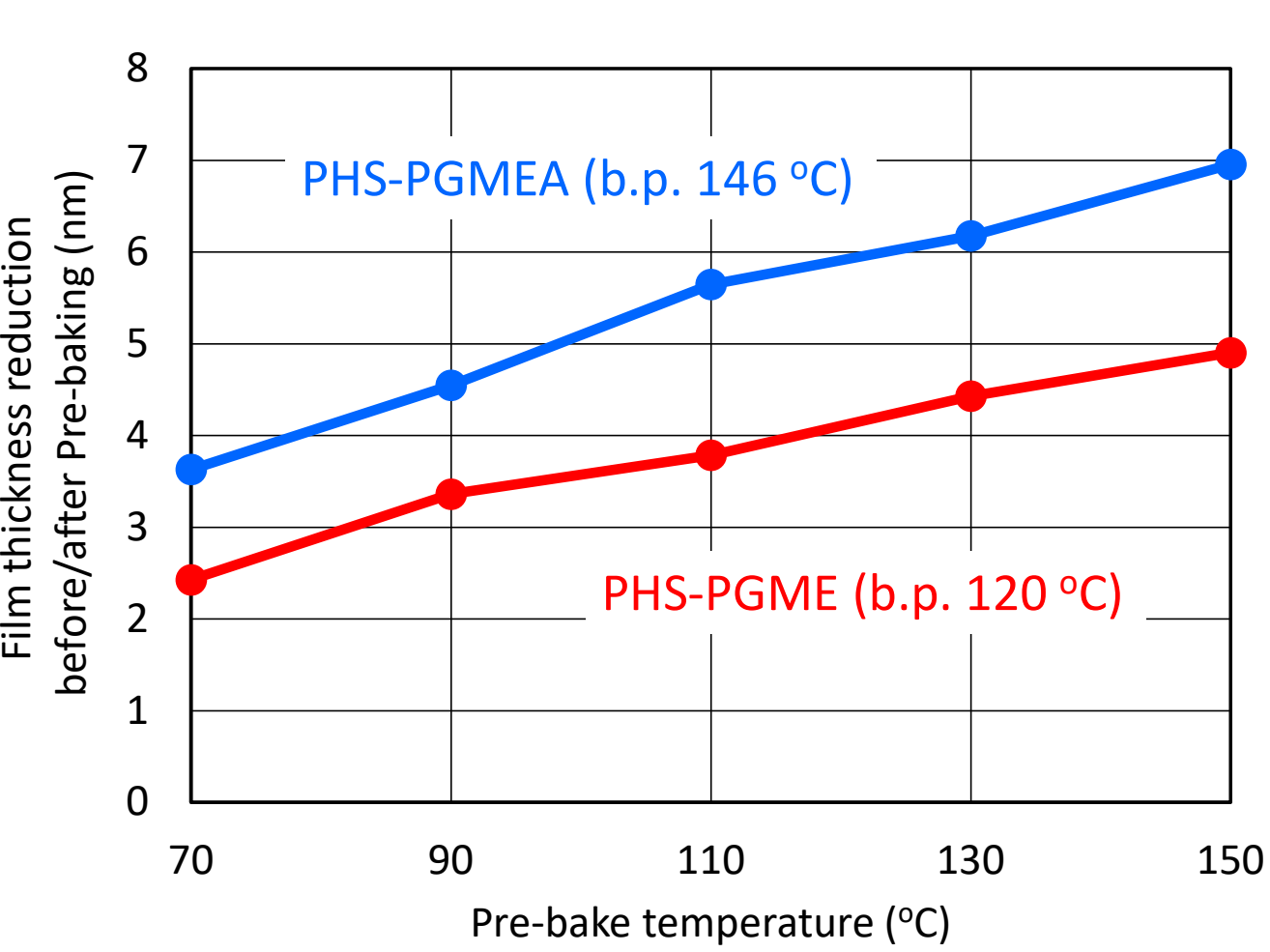
- 3000 rpm
- 30 s

Pre bake

- **70, 90, 110, 130, 150**
- 60 s



The relationship between remaining solvent and pre-baking temperature 10



1. Introduction

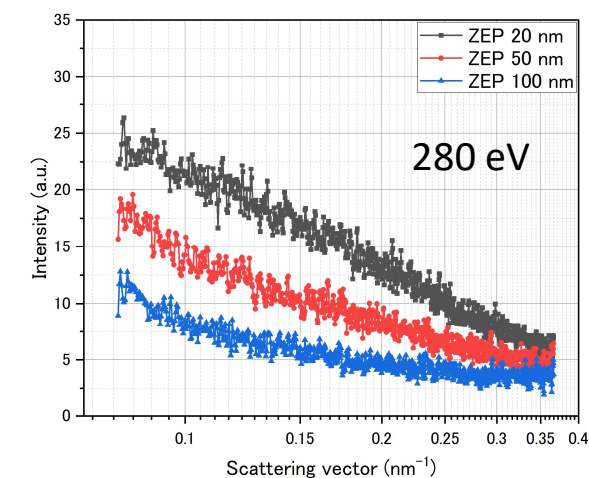
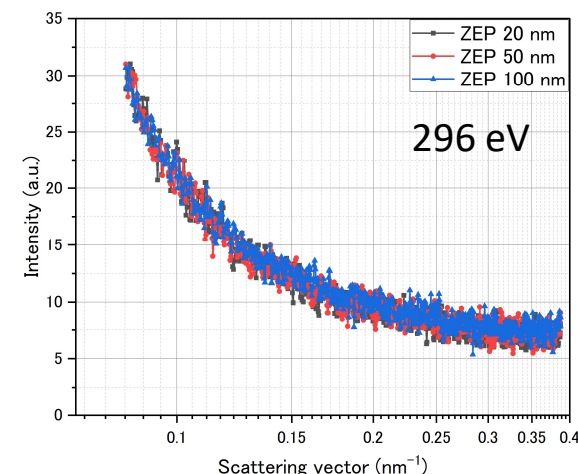
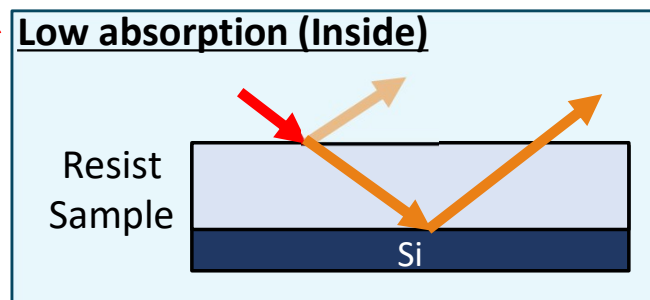
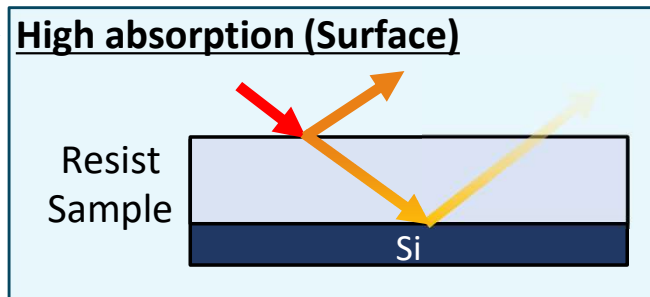
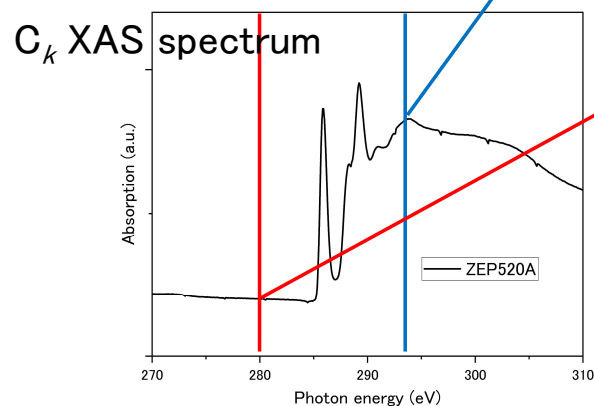
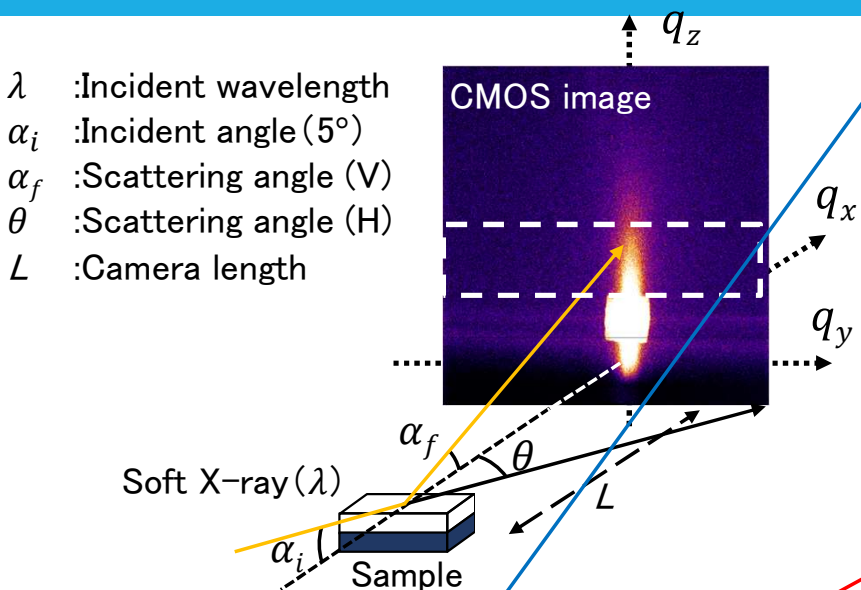
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3. Summary

Reflection-mode RSoXS at NewSUBARU BL10

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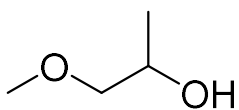
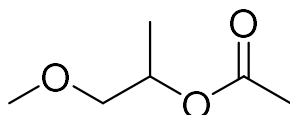
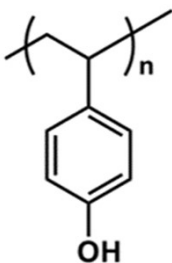
Incident photon energy (wavelength) choice is very important
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XAS results

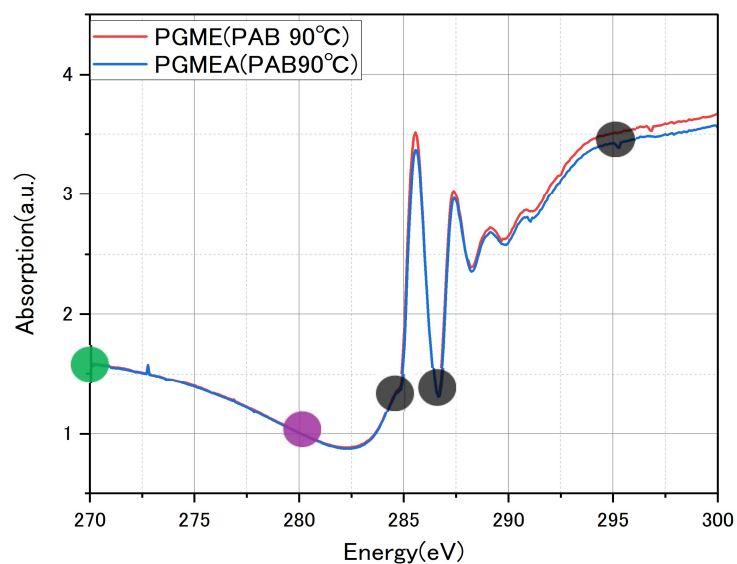
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Samples

**PGME****PGMEA****PHS**

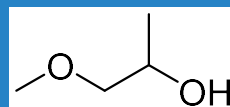
- Pre bake: 70, 90, 110, 130, 150 °C, 60 s
- Thickness: approximately 48 nm

C_K-XAS spectra of PHS

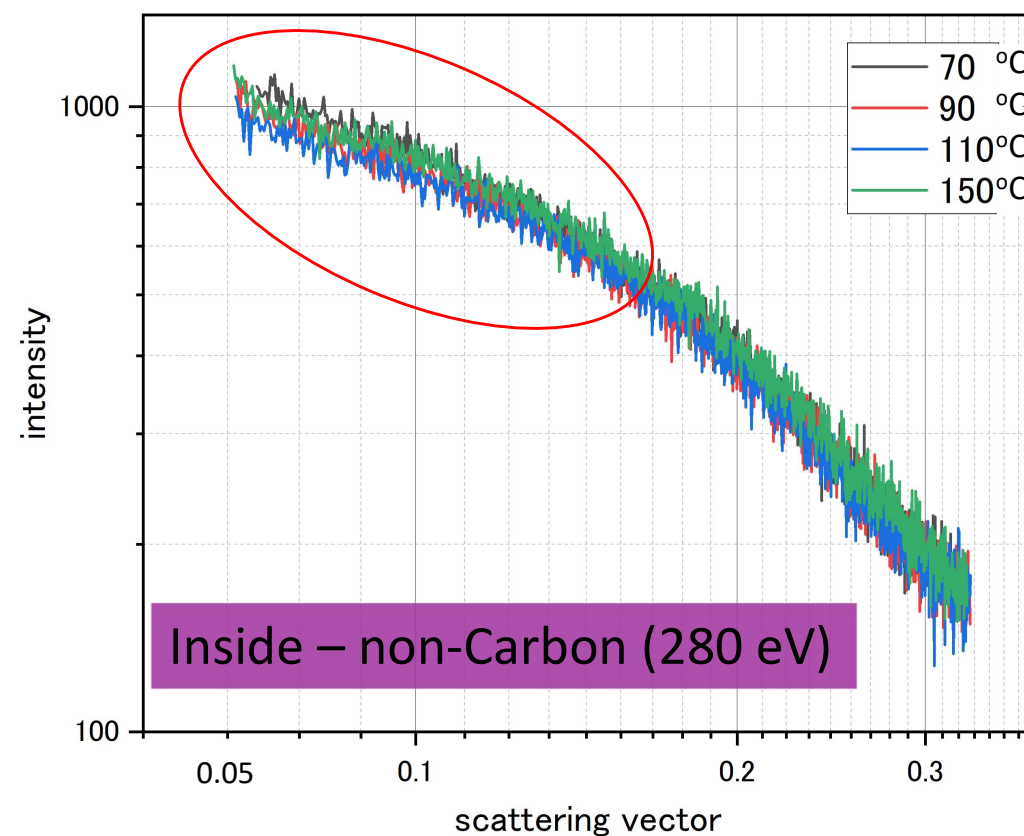
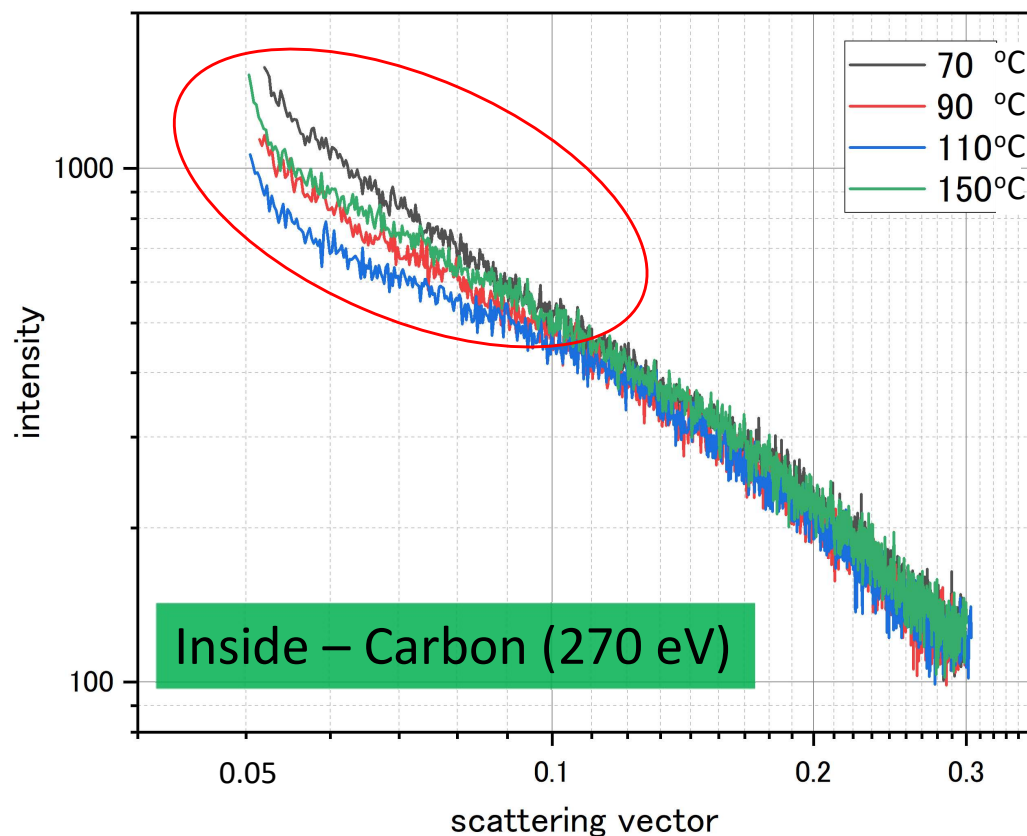


Photon energy	Information
270 eV	Inside – Carbon
280 eV	Inside – Non-Carbon
285 eV	Inside – Phenyl
287 eV	Inside – Acrylate
296 eV	Surface – Carbon

RSoXS result -1. PGME sample

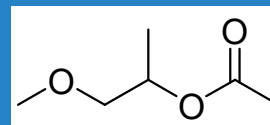


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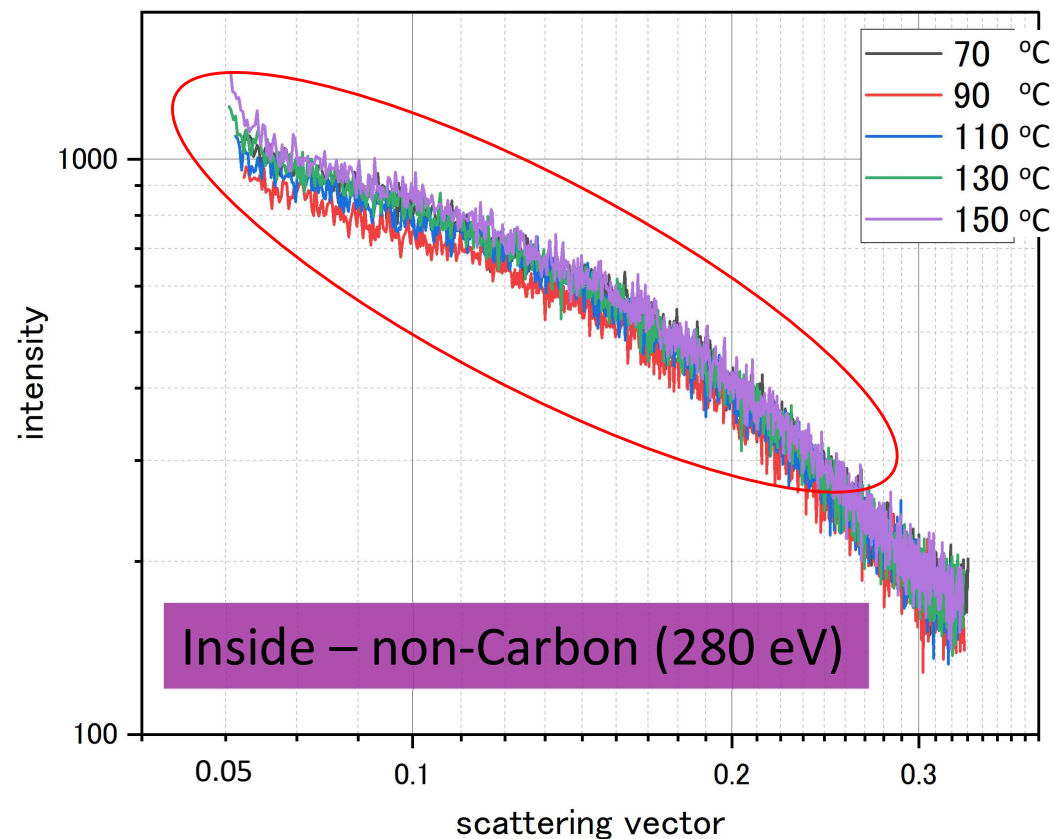
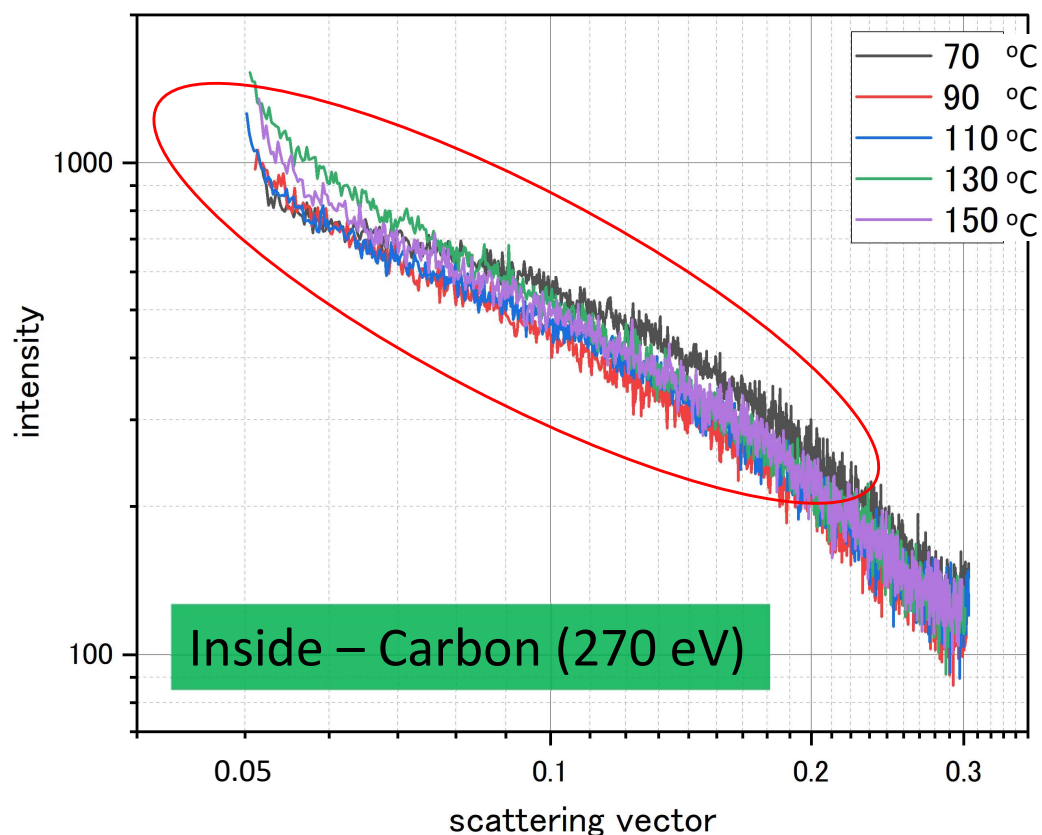


0.05 – 0.1 nm⁻¹ (120 - 60 nm spatial frequency) (\neq Polymer particle size: 4~5 nm)
The intensity of scattering spectra affected by pre-bake temperature.

RSoXS result -2. PGMEA sample



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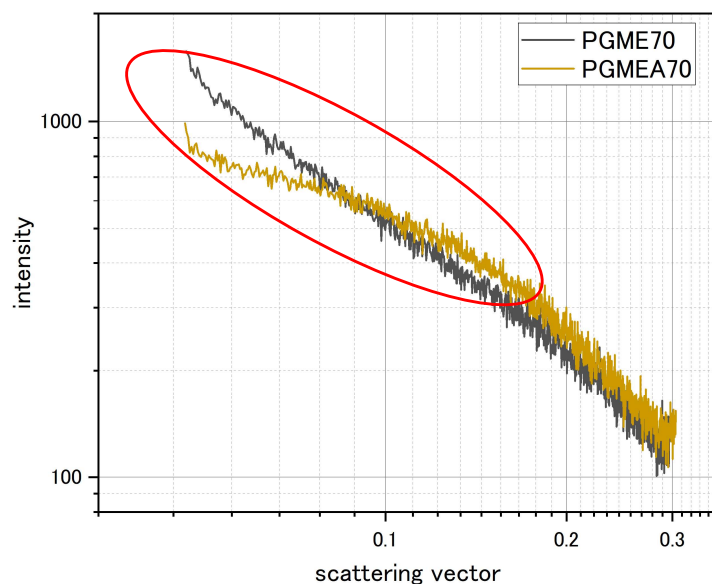
0.05 – 0.2 nm⁻¹ (120 - 30 nm spatial frequency) (≠ Polymer particle size: 4 ~ 6 nm)
→ Strong affinity of ester solvent?

RSoXS result -3. Aggregation source

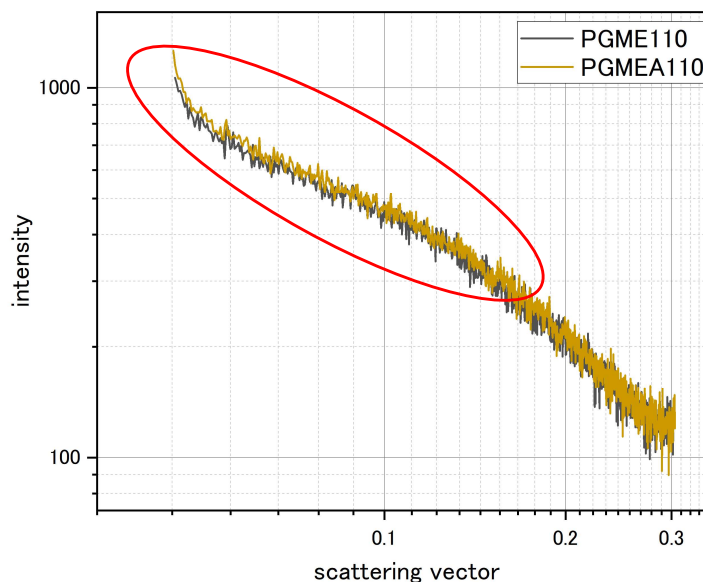
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Inside – Carbon (270 eV)

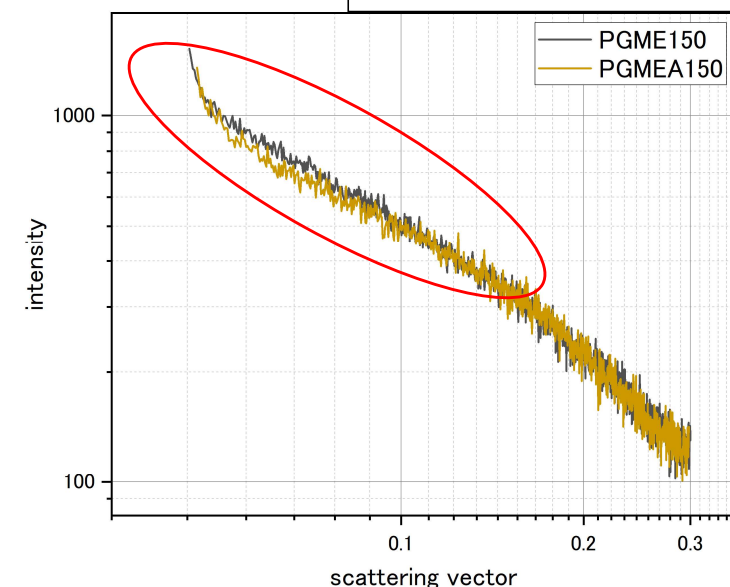
PAB Temperature **70 °C**



-> **110 °C**

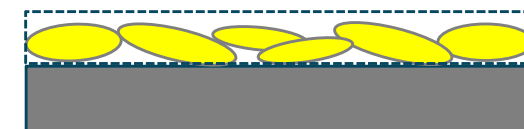
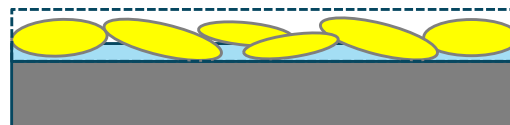
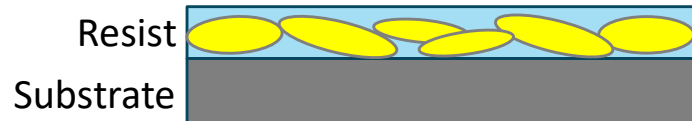


-> **150 °C**



Boiling point
PGMEA 146 °C
PGME 120 °C

Image



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-> Solvent and pre-baking temperature is affected to aggregation in the resist thin film.

The investigation whether the chemical composition distribution in the resist thin film is affected by the solvent. (purpose)

Solution

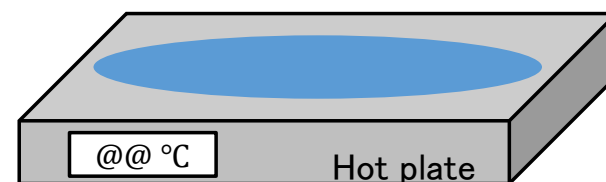


Resist solution

Dynamic light scattering (DLS)
measurement

- ✓ Particle size: 4-6 nm
- ✓ Ester solvent is more affinity to PHS

Thin film



Resonant soft X-ray scattering (RSoXS)
measurement

- ✓ Aggregation: 120 -30 nm (spatial frequency)
- ✓ Pre-baking temperature

The choice of solvents and pre-baking-temperature may also help to suppress the chemical aggregation.

Thank you for kind attention!