Investigation of Solvent Effects on the Distribution of Resist Compositions Using Resonant Soft X-ray Scattering

KH NeoChem

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Background and Objectives of the Research

Polarity mismatch between the polymer and Photoacid Generator (PAG) in the coating film causes aggregation, contributing to line width roughness (LWR).

We hypothesized that selecting the polarity of the solvent could be one method to homogenize the resist composition.

Resist L/S pattern SEM image

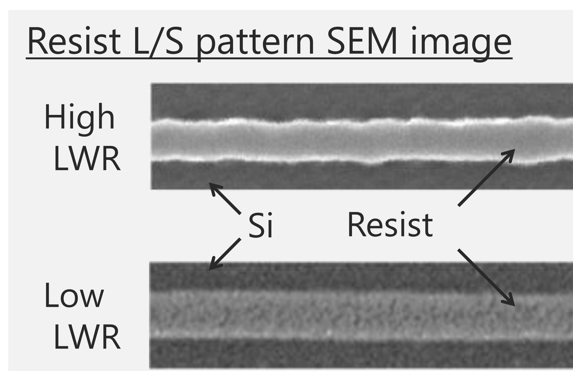
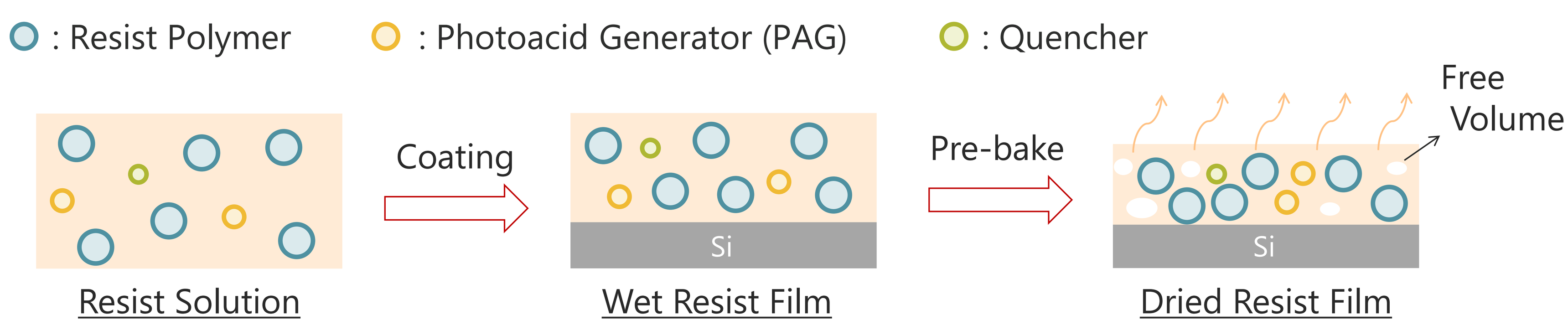


Image of the Resist Coating Process (Dispersion State)



-> Particle size measurement by Dynamic Light Scattering (DLS)

-> Scattering intensity measurement by Soft X-ray Resonant Scattering (RSoXS)

We examined the dispersion of resist compositions based on **solvent polarity** and **pre-bake conditions**.

DLS measurement

Measuring Instrument

Litesizer DLS 500 (Anton Paar GmbH)

- Principle : Dynamic Light Scattering (DLS)
- Range : 0.3nm to 10µm (particle diameter)
- Angles : 15˚, 90˚, 175˚

Hansen Solubility Parameter (HSP)

$$\delta^2 = \delta_d^{\ 2} + \delta p^2 + \delta_h^{\ 2}$$

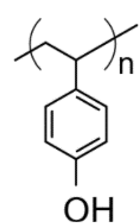
- δ_d : Dispersion force
- δ_p : Polar force
- δ_h : Hydrogen bonding force

Samples

Resist polymer :

Polyhydroxystyrene (PHS)

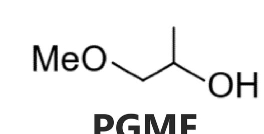
$Mw = 19{,}000$

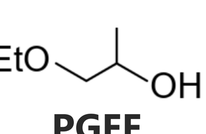


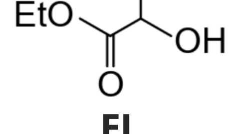
Conducted particle size analysis of the 10wt% PHS solution.

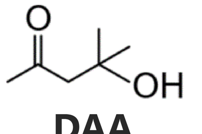
Solvents (8 samples) :

Alcohol

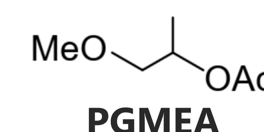


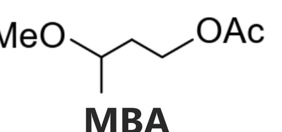


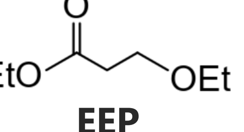


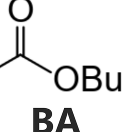


Ester

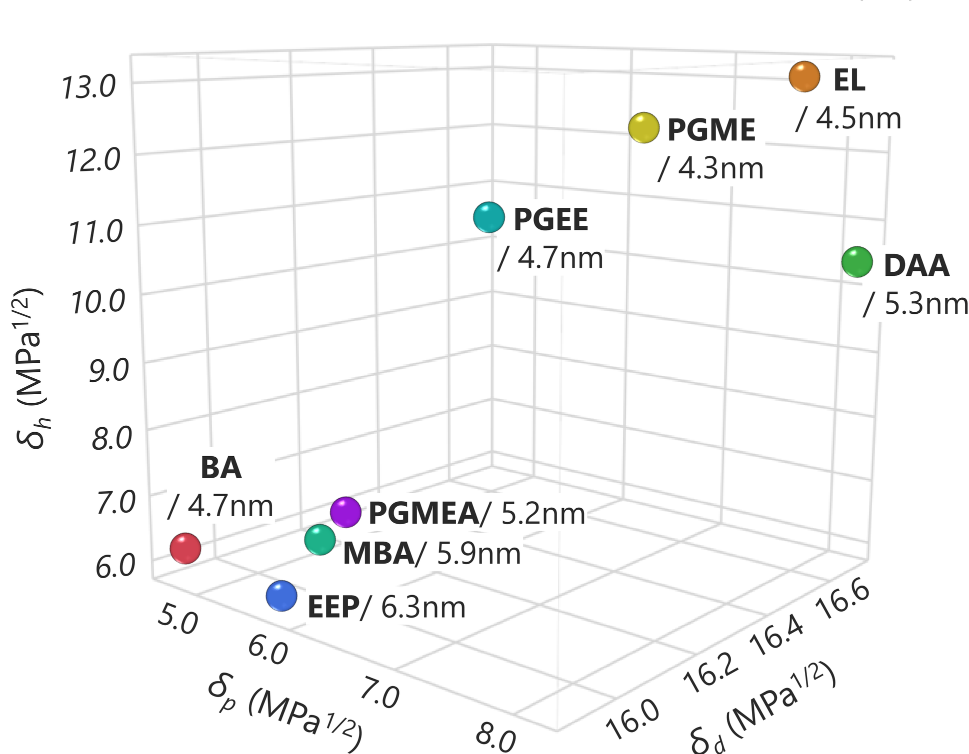








Particle size vs. HSP



Differences in HSP

- Alcohol : δ_h and δ_d are High
- Ester : δ_h and δ_d are Low

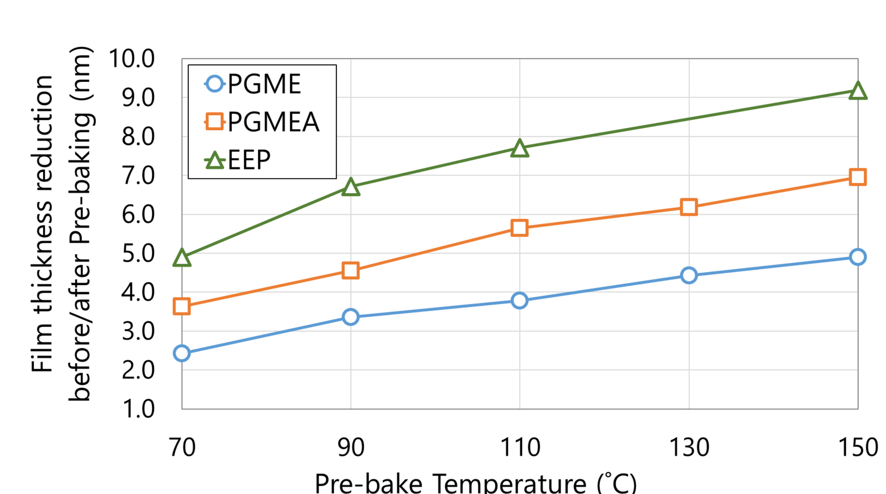
Particle size in

- Alcohol : 4 to 5 nm
- Ester : 5 to 6 nm

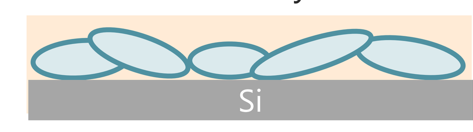
-> Particle size is correlated to HSP

Film Thickness Measurement

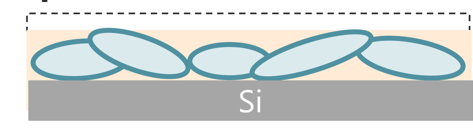
Relationship Between Residual Solvent and Pre-bake Temperature



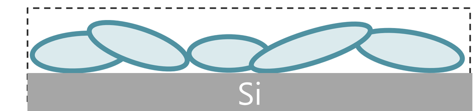
Before Pre-bake -> Many solvents are remaining



Low Temperature -> Residual solvent remains



High Temperature -> Residual solvent is minimal



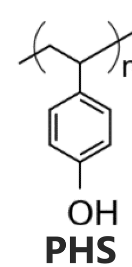
Solvent	Resist Solution Concentration (wt%)	Film thickness (nm@110 ˚C)	Solvent Properties	
			Boiling point (˚C)	Vapor pressure (kPa)
PGME	1.5	47	120	1.2@20 ˚C
PGMEA	2.3	47	146	0.5@20 ˚C
EEP	3.1	50	170	0.2@25 ˚C

- Higher boiling point tended to increase film thickness difference pre-/post-prebake.
- Higher vapor pressure tended to result in increased film thickness.

RSoXS Measurement

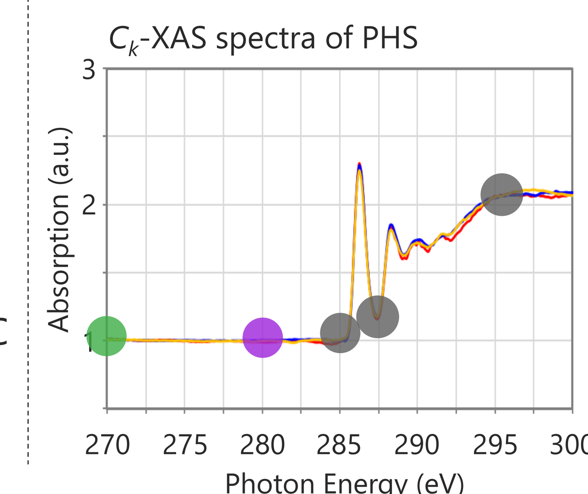
Samples

PGME
PGMEA +
EEP



- Pre-bake : 70, 90, 110, 130, 150 ˚C , 60s
- Film Thickness : ca.50nm

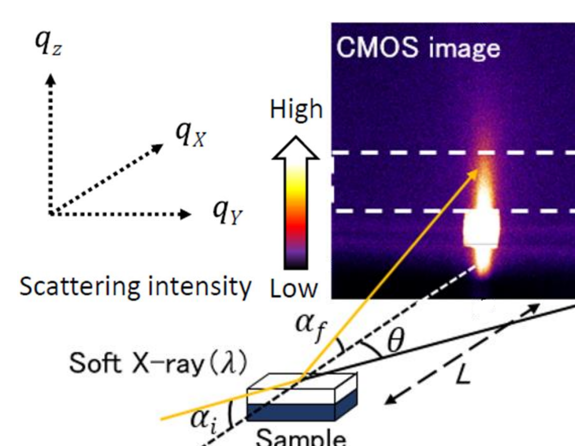
Measurement Conditions



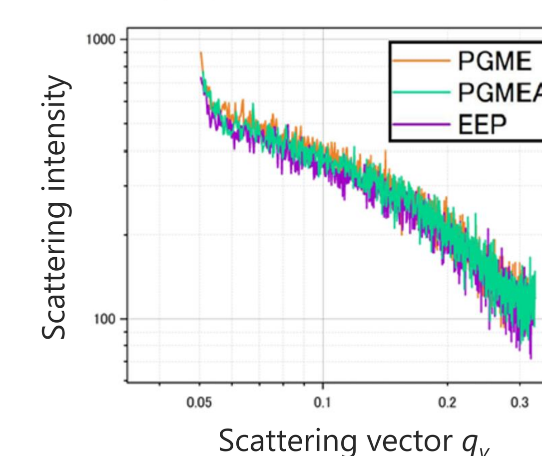
Photon Energy	Information
270 eV	Inside-Carbon
280 eV	Inside-non-Carbon
285 eV	Inside -Pheny
287 eV	Inside-Acrylate
296 eV	Surface-Carbon

Analysis of Scattering Spectra Obtained from RSoXS

Overview Diagram of RSoXS



Scattering Spectrum



Calculation of the Scattering Vector q_y

$$q_y = \frac{2\pi}{\lambda}(\sin\theta\cos\alpha_f)$$

λ : Incident wavelength

θ : Scattering angle (H)

α_f : Scattering angle (V)

- The scattering vector corresponds to the spatial frequency in scattering measurement analysis.
- q_y direction indicates spatial distribution in the sample plane, while scattering angle depends on structure size.

Scattering Intensity and Size of Scattering Sources

①Scattering Intensity：The scattering intensity decrease with smaller, uniformly dispersed aggregate sizes within the film.

②Size of Scattering Sources : The structural size d can be derived from Bragg's law.

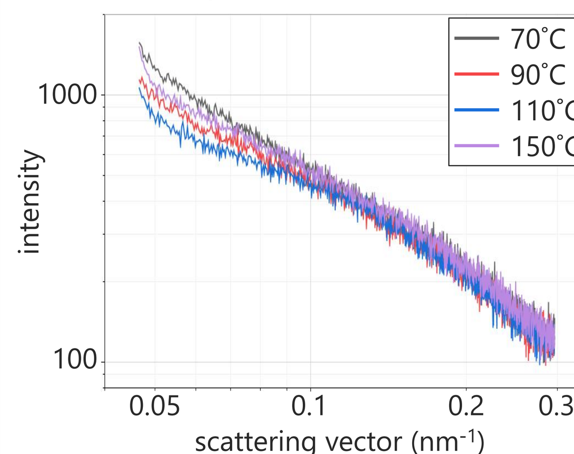
$$d = \frac{\lambda}{2\sin\theta} = \frac{2\pi}{q}$$

When q_y is 0.1 nm^{-1},the scattering source size are ca.60 nm.

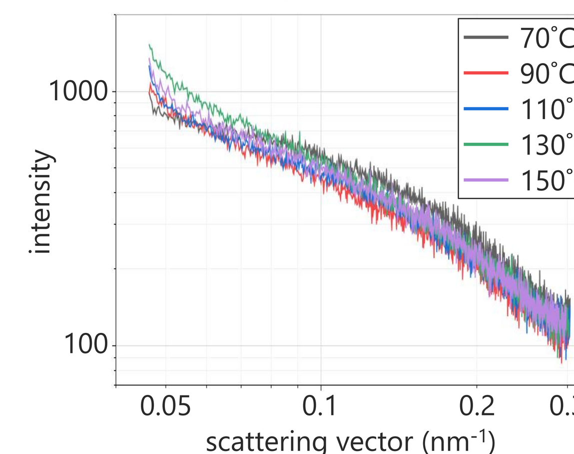
Results

RSoXS results-1. 270eV (Inside-Carbon)

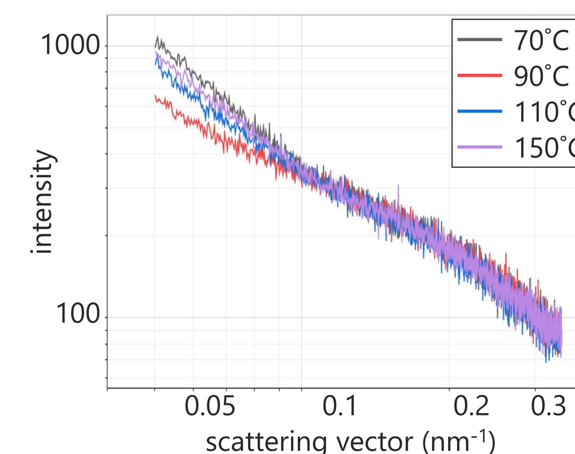
PGME sample



PGMEA sample



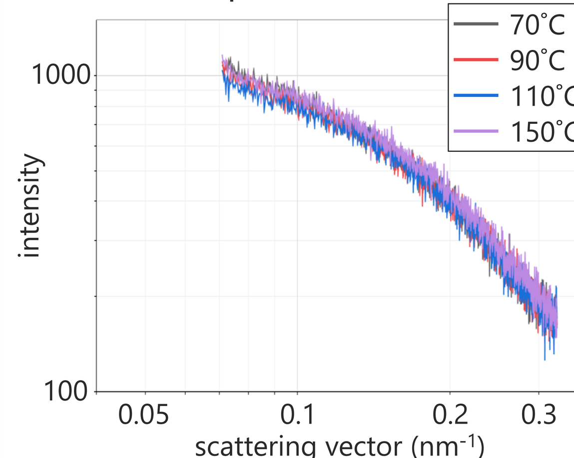
EEP sample



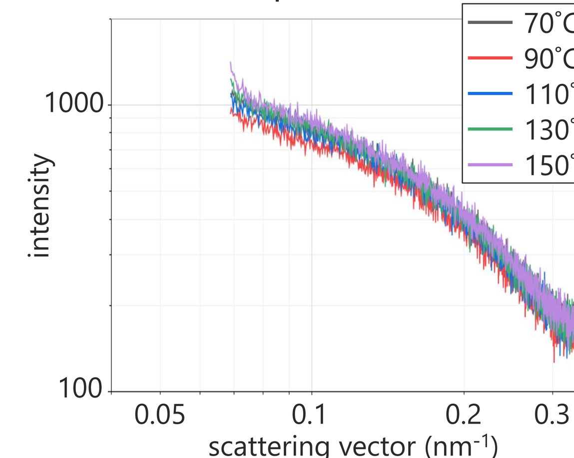
- The aggregation of inside-carbon was affected by temperature.
  -> The range of 0.05 to 0.1nm^{-1} (scattering source size are 120 to 60nm) was significantly affected.
- The result varied depending on the solvent, but the scattering intensity was lowest between 90 to 110 ˚C.

RSoXS results-2. 280eV (Inside-non-Carbon)

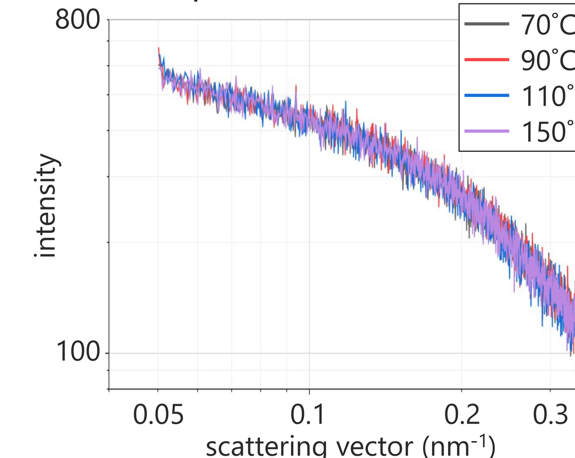
PGME sample



PGMEA sample



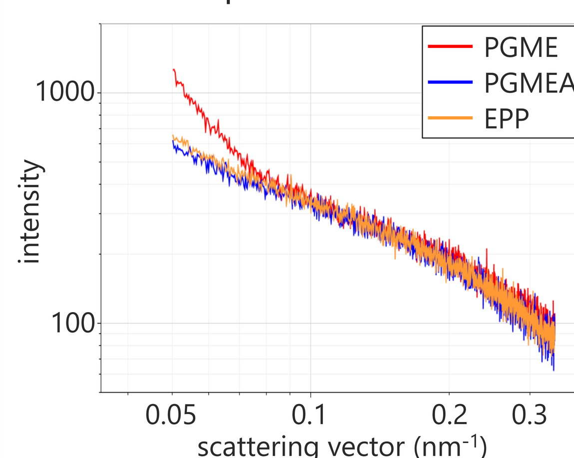
EEP sample



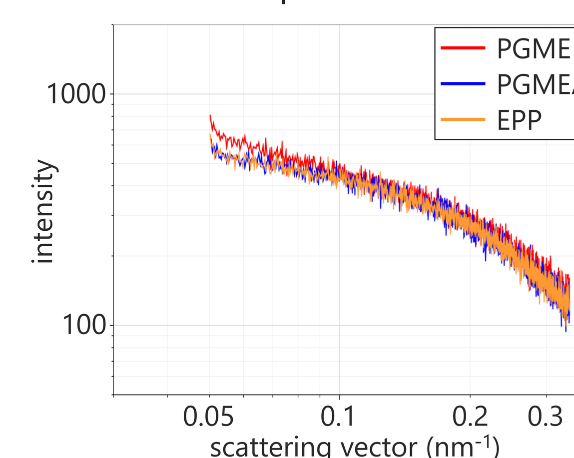
- Focusing on PGMEA in Results 1 and 2, variations in scattering intensity were observed the range from 0.05 to 0.2nm^{-1}.

RSoXS results-3. Comparison between solvents (pre-baking temperature is 90 ˚C)

270eV Sample



280eV Sample



A comparison between solvents showed that the scattering intensity of PGME was higher in the range from 0.05 to 0.08nm^{-1}.

Summary

- ✓ Differences in particle size in the resist solution and scattering intensity in the resist film were observed depending on the polarity of the solvent.
- ✓ The scattering intensity of the resist film also varied with temperature, suggesting the involvement of residual solvent or free volume.