Comparison of RSoXS-Based Chemical Non-Uniformity with EUV Contrast Curve in PHS-Boc Resist

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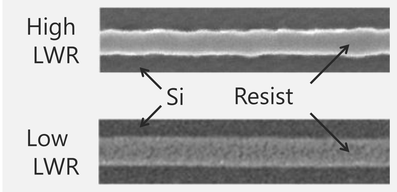
Background and Objectives of the Research

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



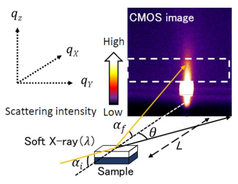
At MNC 2024, we reported solvent-dependent variations in resist film distribution using RSoXS (Resonant Soft X-ray Scattering) with a PHS polymer. In this study, a Boc-modified PHS polymer was used to examine the correlation between RSoXS scattering intensity and exposure sensitivity. In addition, the diffusion behavior of secondary electrons was investigated using LEEFET (Low Energy Electron Flood Exposure Tool) to evaluate the influence of solvent on film properties.

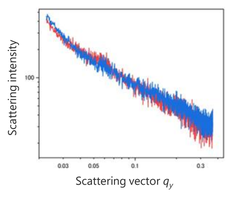
Structural and Property Evaluation of Resist Thin Films

Correlation between RSoXS and Sensitivity Characteristics

RSoXS is a useful technique for measuring the nanoscale spatial distribution within resist thin films. Yamakawa *et al.* clarified the relationship between the aggregation of resist components and sensitivity characteristics using a main-chain scission type resist.

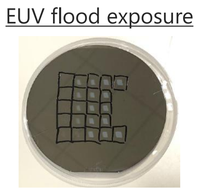
RSoXS Measurement

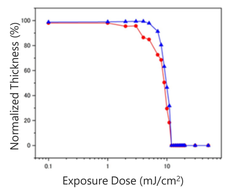




Scattering Intensity : **MwH** > **MwM**

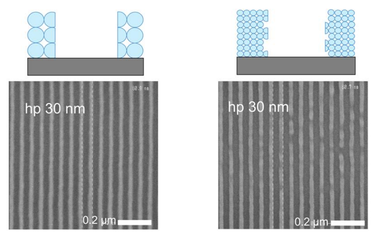
EUV flood exposure





Y value : **MwH** > **MwM**

MwH (Mw=73k) **MwM** (Mw=49k)

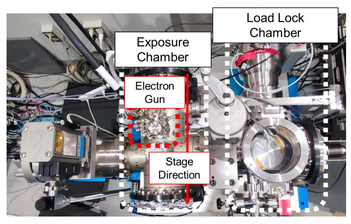


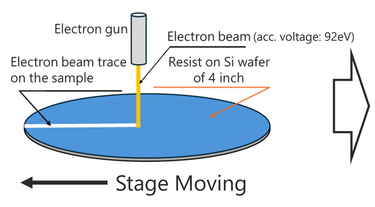
For the **MwH** sample:
- Increased scattering intensity (RSoXS)
- Improved contrast (Y value, L/Spattern) were observed.

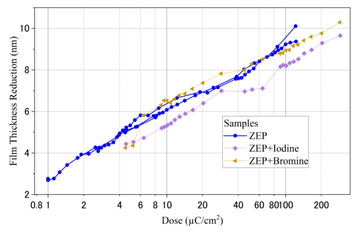
References
(1) J. Photopolym. Sci. Technol., 35 (2022) 61-65. (2) J. Photopolym. Sci. Technol., 36 (2023) 41-45. (3) Jpn. J. Appl. Phys., 64 (2025) 06SP24. (4) Jpn. Soc. Appl. Phys. Autumn Meeting, 2024, 17p-D62-3.

Characterization of Electron-Resist Interactions Using LEEFET

LEEFET is a device for evaluating the effects of electrons generated during EUV exposure. It irradiates samples with low-energy electrons accelerated at 92 eV and analyzes the secondary electron behavior based on the resulting development characteristics.







References
(1) ICPST-42, 2025, A05-08.

Co-author R. Yamasaki gave an oral presentation (Program No. 19A-1-3) at MNC2025.

Experimental

Materials

	PGME	PGMEA	EEP
b.p. (˚C)	120	146	170
v.p. (kPa)	1.2@20˚C	0.5@20˚C	0.2@25˚C

PHS-Boc (Mw 19k)

TPST

Fabrication of 50nm Evaluation Resist Films

Solution Preparation
- X wt% PHS-Boc
- 10wt% TPST (vs. Polymer)
- Solvent

⇨ Spin Coating: Film formation on Si substrate

⇨ Pre-bake (PAB): Solvent removal / Temp., 60 sec

⇨ Exposure/P.E.B: EUV flood or Electron gun / 110 ˚C, 90sec

⇨ Developer/Rinse: 2.38wt% TMAH / UPW

⇨ **Sensitivity Evaluation**

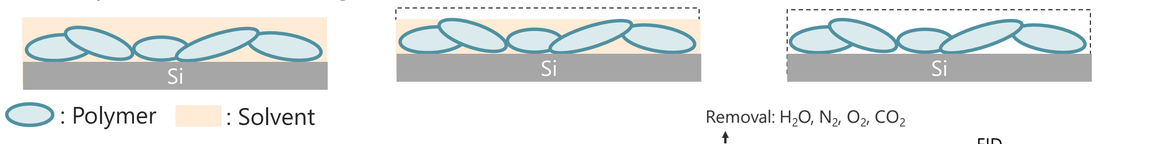
- **RSoXS** (Film Structure after PAB)
- **Residual Solvent** (after PAB)

Film Preparation and Residual Solv. Measurement Using Thermal Desorption GC–MS

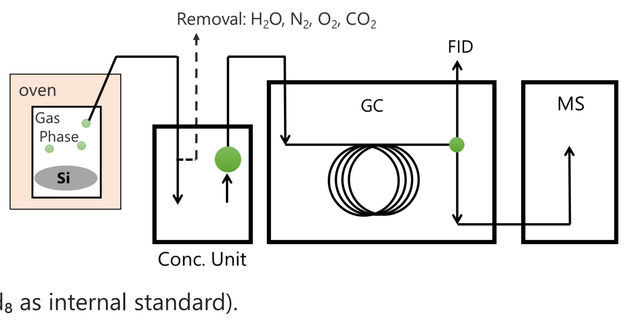
Before Pre-bake
-> Many solvents are remaining

Low Temperature
-> Residual solvent remains

High Temperature
-> Residual solvent is minimal



Solvent	Resist Conc. (wt%)	PAB Temp. (˚C)	Residual Solv.* (as PhMe eq., ppb)
PGME	1.5	70	8
PGMEA	2.2	70	64
PGMEA	2.2	120	29
EEP	3.1	70	85



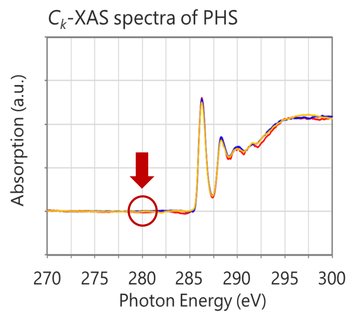
*: Quantified using N_2 standard gas (10 ppb toluene-d_8 as internal standard).

Residual solvent varied with solvent type and PAB temperature, following boiling point and vapor pressure trends.

RSoXS Measurement Results

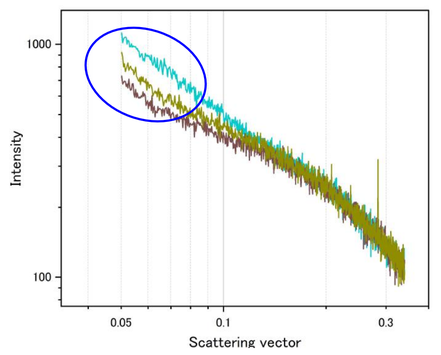
The effect of solvents on the aggregation structure of thin films was evaluated using RSoXS.

C_k-XAS spectra of PHS



Photon Energy
280 eV ··· Inside-non-Carbon
286 eV ··· C=C (π*)
289 eV ··· O-C=O (π*)
296 eV ··· C-C (δ*)

Samples (Solv. and PAB Temp.)
S01 : PGME, 90 ˚C
S02 : PGME, 120 ˚C
S03 : PGMEA, 90 ˚C



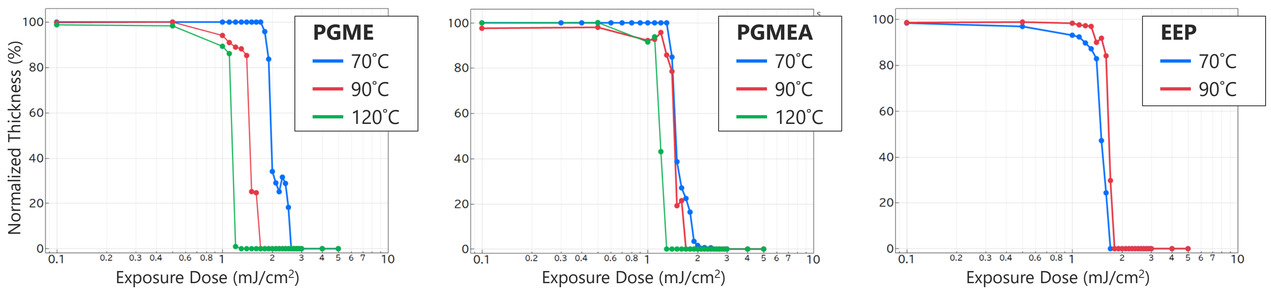
- The scattering intensity at 120˚C was higher than that at 90˚C.
- The scattering intensity of PGMEA was higher than that of PGME.

Features of RSoXS Measurement
- Resonant absorption: A phenomenon where absorption sharply increases at specific energies corresponding to chemical bonds.
- Reflective configuration: Enables the evaluation of resist thin films coated on Si wafers.
- Scattering intensity reflects the degree of aggregation—higher indicates more, lower indicates less.
- Energy selectivity: By tuning photon energy, scattering from specific functional groups, film surfaces, or internal regions can be analyzed.

Contrast Curve Measurement Results

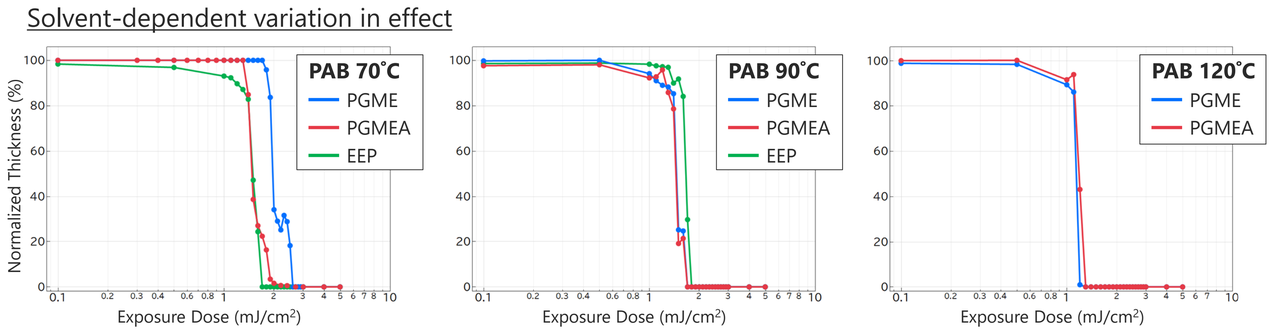
A contrast curve was generated to examine whether the residual solvent in the resist film affects sensitivity and how this influence varies depending on the solvent type.

Effect of residual solvent



- The PGME sample baked at 120 ˚C showed better contrast than the one baked at 90 ˚C.
- PGME, PGMEA showed increased sensitivity with higher PAB temp., while EEP exhibited the opposite trend.

Solvent-dependent variation in effect

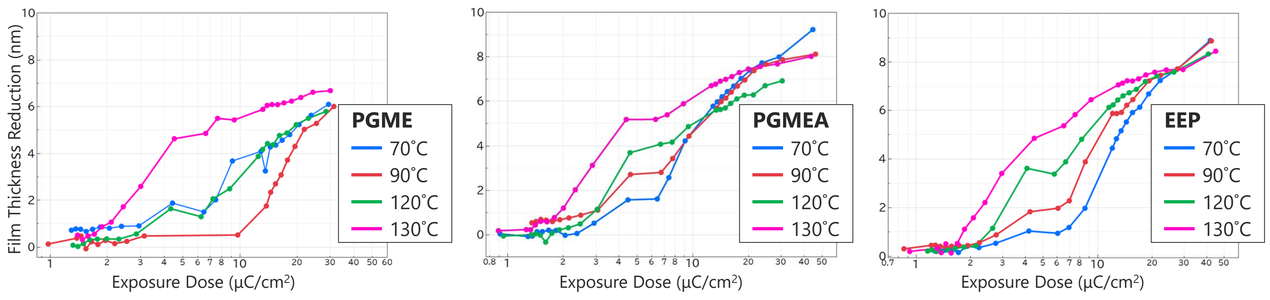


Sensitivity showed solvent-dependent PAB-temperature trends, indicating solvent-specific optimal PAB conditions.

LEEFET Measurement Results

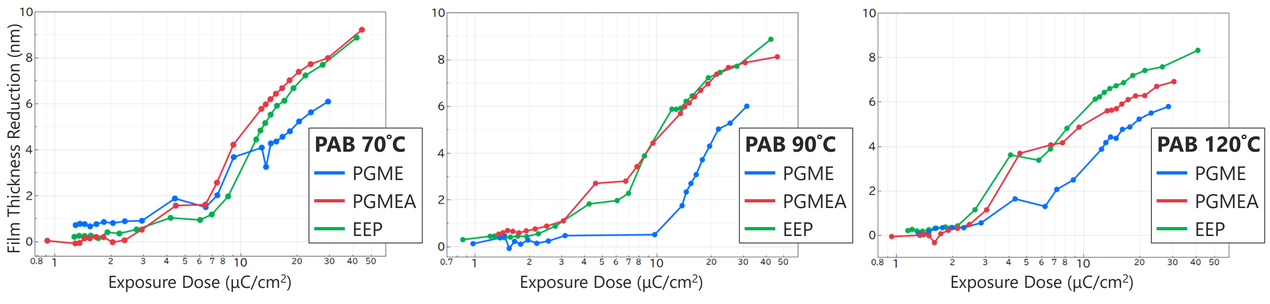
The effect of residual solvent in resist films on secondary electron diffusion was investigated.

Effect of residual solvent



All solvents showed increased sensitivity with higher PAB temperatures.
► Inference: At the same dose, electron diffusion length varies across samples (lower PAB → shorter).

Solvent-dependent variation in effect



At all PAB temperatures, the sensitivity followed the order PGME → PGMEA → EEP.

Summary

- ✓ From this study, it was found that residual solvent remains in the resist films after PAB, influencing both
  - the spatial distribution of resist components (RSoXS), and
  - the sensitivity and secondary electron diffusion (EUV flood exposure, LEEFET).
- ✓ Higher PAB temperatures resulted in improved sensitivity and stronger RSoXS scattering intensity, suggesting the formation of a more uniform film structure over a wider area.
- ✓ Residual solvent, once thought to be fully removed, was found to influence sensitivity; optimizing solvent conditions may improve LWR performance.