Soft X-ray Absorption Spectroscopy using SR for EUV Resist Chemical Reaction Analysis

Takeo Watanabe

Center for EUVL, University of Hyogo
Outline

1) Background

2) Principle of X-ray absorption spectroscopy (XAS)

3) X-ray absorption spectroscopy measurement of CAR for the chemical reaction analysis.

4) Photon energy extension for the EUV resist chemical reaction analysis
   - Probe photon energy region: 50 eV to 1,000 eV

5) Necessity of hard X-ray absorption spectroscopy

6) Summary
EUV lithography

Rayleigh equation

\[ R = k_1 \frac{\lambda}{NA} \]

Multi-exposure is complicated, and isn’t high cost efficient.

Single exposure is necessary for NGL.

EUVL is a promising lithographic technology.

Configuration of EUVL

Visible

UV

EUV

X-ray

- g-ray 436 nm (2.85 eV)
- i-ray 365 nm (3 eV)
- KrF 248 nm (5.0 eV)
- ArF 193 nm (6.5 eV)
- EUV 13.5 nm (91.8 eV)
How to solve the RLS trade off?

Achievement of high-quantum reaction yield of EUV resist is critical issue, for not only resolution, sensitivity, and LWR.

In order to develop high-sensitivity EUV resist, photo chemical reaction analysis using EUV exposure light is necessary!

It is very important to clarify the photo chemical reaction of EUV chemical amplified (CA) resist, by soft-x-ray absorption spectroscopy (XAS) for C, O, N, and F.
Necessity of the soft x-ray absorption spectroscopy

Achievement of the EUV Resist specification.

Since, chemical reaction of PAG does not detected by using FT-IR, FT-IR is not enough for analyzing chemical reaction of PAG.

Chemical reaction analysis using real EUV light of EUV resist is significant.

<Requirements specification>
The film thickness is 20～50 nm.
Chemical reaction analysis of EUV resist.
Probe photo energy region of 50 eV to 1,000 eV is required for CAR.

The soft x-ray absorption spectroscopy
The soft x-ray absorption spectroscopy

Synchrotron Radiation
NewSUBARU BL-7B

SR

Grating

Au Mesh

I

Intensity = I₂ / I₁

To measure the change of the chemical bonding, the specific energy of the incident energy required for the measurement.

For example,
Carbon 1s core
280~330 eV
Fluorine 1s core
690~730 eV

Powerful tool for evaluating the change of the chemical bonding
The absorption spectrum of “PHS-TBA”

The benzene in the PHS did not decompose.

The peak of $\pi^*$ bonding at 285.5 eV doesn’t change with increasing EUV dose.
The absorption spectrum of “PHS-TBA”

The decomposition reaction of TBA occurs with increasing EUV dose.
The low reflectivity of the conventional Ni-coating diffraction grating for the spectrometer causes the weak light intensity for XAS.

The new coating film on the grating is required!

For considering general usage of material analysis by XAS at BL-10 beamline, the target energy of the new grating is designed for the absorption edge region of fluorine and transition metal elements which corresponds to the photon high energy region from 500 to 1,000 eV in the soft X-ray.
Bragg condition of periodic W/Si multilayer

For the improvement of reflectance, multilayer film was coated on the grating.

The high reflectivity is obtained by multilayer film with constructive interference from each layer.

\[ m \lambda = 2d \sin \theta \]

- \( m = \text{Integer} (=1) \)
- \( \lambda = \text{Wavelength} \)
- \( d = \text{Periodic thickness} \)

W/Si multilayer was considered to use to obtain the most highest reflectivity in the photon energy region from 500 to 1,000 eV.
Aperiodic multilayer design for new grating

The designed W/Si multilayer has an aperiodic structure which consists of top two layers and ten periodic multilayer.

The top two layers widely reflects at the low-photon energy region below 800 eV.

The periodic structure reflects well at the high-photon energy region from 800 to 1,000 eV.

We developed this W/Si aperiodic multilayer to obtain the high reflectivity at the target photon energy region from 500 to 1,000 eV.
This magnetron sputtering system is generally used to deposit high quality Mo/Si multilayer for EUV optics.
The aperiodic W/Si-multilayer reflectivity

To estimate the reflectivity of W/Si multilayer deposited on the grating, the reflectivity of the witness W/Si multilayer on the Si substrate was measured.

Reflectivity measurement was carried out using the reflectometer of BL-10 beamline at NewSUBARU.

The aperiodic W/Si multilayer had high reflectivity of more than 10% for the photon energy region from 500 to 930 eV.
The photon intensity with new grating

The photon intensity was measured by the photodiode with the previous grating and the new grating.

We obtained the large photon intensity using the new diffraction grating in the target photon energy region.
Absorption spectrum of F 1s core level of Teflon
The model resist for the absorption spectroscopy

**PHS-TBA (Base polymer)**

![Chemical structure of PHS-TBA](image)

**poly (vinylphenol-co-tert butylacrylate)**

**PAG1: TPS-Imidate (30 wt%)**

![Chemical structure of PAG1](image)
EUV exposure dose dependency of the absorption spectra of PAG1 @ F 1s core level
EUV exposure dose dependency of the absorption spectra of PAG1 @ F 1s core level

Absorption (arb. unit) vs. Photon energy (eV)

0 mJ/cm²
5 mJ/cm²
10 mJ/cm²
20 mJ/cm²
40 mJ/cm²
80 mJ/cm²

Low energy bond is easier to decompose

High energy bond is not easy to decompose
Absorption Spectra of carbon 1s core level in TPS-Imidate

![Absorption Spectra Diagram](image)

Conventional reaction:

$$
\text{Conventional reaction}
$$
Chemical reaction of TPS-Imidate

Conventional reaction

\[
\text{EUV光 (hv)} \rightarrow \text{H}^+ + \text{e}^-
\]

Single reaction by one photon (Ionization reaction)

Additional reaction?

Multiple reaction by one photon (Direct excitation reaction)

SR absorption spectroscopy
C \( \pi^* \) bonding
F 1s orbit

\[
\text{EUV light (hv)} \rightarrow \text{H}^+ X_1^- + \text{H}^+ X_2^- + \text{H}^+ X_3^- + A_1^+ + A_2^+
\]
Absorption spectra of O, F, Co, Cu, and Zn using XAS with aperiodic grating

We performed XAS measurement at the target energy region. The absorption spectrum of Zn L shell (2s and 2p core level) around the photo energy of 1,020 eV was clearly resolved.

The XAS method using BL-10 beamline has a good capability to measure the absorption spectra to evaluate chemical bonding in the photon energy region from 50 to 1,000 eV.
The necessity to use hard X-ray absorption spectroscopy

The metal resist is one of the promising candidate for the use in EUV lithography.

In soft x-ray region can cover C, O, N, F,.....Zn.

For the metal resist containing Zr, Hf, Sn et al. , hard X-ray is required for the XAS.
Nano Particle Resist for EUVL

Figure 1. Schematic of the extreme-UV (EUV) nanoparticle photoresist with its core metal oxide and the organic ligand surrounding the core. ZrO$_2$: Zirconium dioxide. HfO$_2$: Hafnium oxide.

SPIE News Room
New oxide nanoparticle extreme-UV photoresists achieve high sensitivity
Christopher Ober and Emmanuel Giannelis
Cornell University
15 September 2014, SPIE Newsroom. DOI: 10.1117/2.1201409.005552
Figure 2. Schematic of the ligand-displacement patterning mechanism for negative-tone pattern formation. hv: Energy. H₂O: Water.
Analysis using SR and Computer Science

- Wide band X-ray can be produced by synchrotron radiation. The X-ray photon energy region depends on the electron energy of the storage ring.
- For the chemical reaction analysis using X-ray absorption spectroscopy, the photon energy is very significant for the analysis of the target atom of the EUV resist.
- For the analysis of the light element such as C, O, N, and F et al., soft X-ray absorption spectroscopy is an adequate method.
- For the analysis of the metal element such as Hf, Zr, and Zn et al., hard X-ray absorption spectroscopy is an adequate method.
- In addition, computational calculation such as first-principle calculation et. al, is very effective method to more understanding the results of the X-ray absorption spectroscopy.
- In Hyogo Prefecture, we can use NewSUBARU (soft X-ray) and SPring-8 (hard X-ray), FOCUS and KEI super computers.
Chemical analysis using SR and Computer Science

Synchrotron radiation

More precise structural analysis for the material development

Experiments based on simulation prediction result

Computer Science (Super computer)
SR Nanotech Center at University of Hyogo, Beamline at SPring-8

BL08B2 Beamline
Photon energy: 4 – 63keV

BL24XU Beamline
Undulator
Diamond Double Crystal Monochromator
Offset 2000 mm
Photon energy range: 8.8-12.8 keV

Diamond Double Crystal Monochromator
Offset 40 mm
Photon energy range: 4.7 – 37.8 keV

Bonse-Hart type
Ultra-Small-Angle X-ray Scattering

Experimental Hutch A1
Small angle X-ray Scattering

Experimental Hutch B1
High Accurate X-ray Diffractometry

Experimental Hutch A2
High Resolution XAFS

Objective Hutch
CT imaging
Small angle X-ray Scattering

Experimental Hutch 1
XAFS station
Homogeneous X-ray Topography

Experimental Hutch B2
Powder X-ray Diffractometry

Experimental Hutch 2
Small angle X-ray Scattering

Experimental Hutch B1
Micro-Beam X-ray Diffractometry

Experimental Hutch B2
Micro-Beam X-ray Diffractometry

Mirror
Monochromator
Bending magnet

Photon energy: 4 – 63keV
Lithium Ion 2ndry Battery (Li(NiCoAl)O₂)

LiMO₂ → Li₁₋ₓMO₂ + x Li⁺ + x e⁻
Li₁₋ₓCoO₂ + x Li⁺ + x e⁻ → LiCoO₂
Summary

・ We developed high reflective and wideband W/Si multilayer diffraction grating for the photon energy region from 500 to 1,100 eV. Thus now, the wide photon energy region from 50 eV to 11,00 eV can be support at BL10 beamline at NewSUBARU for the chemical reaction analysis in the soft X-ray region.

・ The reflectivity of this aperiodic W/Si multilayer was 13 times higher than that of the previous Ni single layer.

・ The photon intensity was significantly improved, more than 40 times at the absorption edge of fluorine 1s core level.

・ We measured the resist sample using XAS method. The fluorine decomposition reaction of the resist was clearly measured with good signal-to-noise ratio. And, the absorption structures of standard 3d transition metal compounds were also resolved clearly.

・ Soft X-ray absorption spectroscopy is effective method for the light element such as C, O, N, and F et al. at NewSUBARU light source at University of Hyogo.

・ Hard X-ray absorption spectroscopy is effective method for the metal element such as Hf, Zr and Zn et al. at SR Nanotech Center at University of Hyogo.
ACKNOWLEDGEMENT

1) The chemical reaction analysis was supported by Kaken B, MEXT, Japan.

2) The upgrade of the absorption spectroscopy beamline at NewSUBARU was supported by Project for Creation of Research Platforms and Sharing of Advanced Research Infrastructure, MEXT, Japan.

3) I would like to thank Dr. Kazufumi Sato and Dr. Katsumi Ohmori of Tokyo Ohka Kogyo for providing the model resist materials.

4) I would like to thank Dr. Kazushi Yokoyama of SR Nano Technology Center, Uni. of Hyogo, for providing the documents of hard X-ray absorption spectroscopy.
Thank you for your kind attention!!