Comparison of Resist Family Outgassing Characterization between EUV and EB

Isamu Takagi, Toshiya Takahashi, Norihiko Sugie, Kazuhiro Katayama, Yukiko Kikuchi, Eishi Shiobara, Hiroyuki Tanaka, Soichi Inoue, Takeo Watanabe*, Tetsuo Harada* and Hiroo Kinoshita*

EUVL Infrastructure Development Center, Inc.
16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
*Laboratory of Advanced Science and Technology for Industry, University of Hyogo
1-1-2 Koto, Kamigori, Ako, Hyogo 678-1205, Japan
isamu.takagi@eidec.co.jp

Witness-sample (WS) testing is the most favorable method for the simulation of EUV optics contamination by resist outgassing. Resists are expected to be correctly qualified with this method before they are used in HVM exposure tools. However, the present capacity of outgassing test facilities is insufficient for the total anticipated needs, based on the current capacity of existing EUV exposure tools. This paper defines a resist family for reducing the total number of required outgassing tests. The material contributions to outgassing are discussed on the basis of results obtained with model resists, where two types of WS test systems—high-power EUV light and EB sources—are used. A correlation between these light sources is also discussed.

Keywords: EUV, EB, outgassing, contamination, witness sample, resist family

1. Introduction

Extreme-ultraviolet (EUV) lithography is the most promising technology for sub-22-nm device manufacturing, and is being adapted to high-volume manufacturing (HVM). The EUV resists for these applications are required to produce excellent resolution, low line-width roughness (LWR), and high sensitivity. Research on resist materials is currently focused on the concurrent achievement of these requirements. However, difficulty is encountered with respect to the reported tradeoffs between these properties [1]. Another potentially significant factor being considered is the minimization or avoidance of outgassing from these resists, in order to prevent possible contamination of scanner optics. Thus, each of these resists must be screened or qualified before being used in a scanner.

Numerous resists will be tested when EUV lithography reaches the HVM stage. Hence, a practical and rapid qualification system that will allow direct quantification of optics contamination caused by resist outgassing is necessary. For this purpose, witness-sample (WS) testing has been proposed as the most acceptable method [2-5].

From the viewpoint of resists’ chemical composition, the primary components of resist outgases include the photoacid generator (PAG) cation and the degradation products of the protecting unit used in the resist base resin. However a wide variety of PAGs and protecting units are used for EUV resists, and the difficulty in predicting the actual resist outgassing behavior depends on the resist material being used. In addition, hydrogen-radical cleaning has recently been reported to not totally remove some types of PAG anions [6]. PAG anions had previously been considered a minor outgassing species [6]. For HVM applications, the number of EUV resists to be tested is expected to continue to increase. However, the present capacity of outgassing tests is insufficient for the total anticipated needs, based on the current capacity of EUV exposure tools.

This paper discusses the correlation between EUV light and EB sources for the resist family; the correlation was established to reduce the number...
of EUV resists to be tested by clarifying the dependence of outgassing on resist composition. The resist processes (e.g., pre-bake (PB) and post-exposure bake (PEB) processes) have been also reported to contribute substantially to the resulting outgassing [7-8]. However, further investigations are still necessary before these concepts can be used to reduce the total number of resist outgassing tests. This paper presents the application of resist family concepts focused on the characterization of resist outgassing on the basis of resist composition.

2. Experimental
2.1. EUV-based tester

The high-power EUV-based resist contamination (HERC) analysis tool, which uses EUV light to expose a WS and resist, has been installed at BL9c in the NewSUBARU synchrotron facility [6]. A high-power EUV light was produced by a 10.8-m-long undulator with a ring current of 300 mA. An Ru (5 nm)-capped Mo/Si multilayer mirror was used as the WS. The peak wavelength of the undulator light was tuned to match the center wavelength of the WS reflectivity spectrum, which was measured in advance by using the reflectometer located at BL10. The FWHM of the light used to expose the WS is less than 0.25 nm [9]. The spot size of the EUV light on the WS was approximately 4 mm × 1.1 mm. EUV light intensity was measured with a calibrated photodiode. Given the spot size, the calculated power on the WS was 320 mW/cm². The EUV light was reflected on the WS with an incidence angle of 27° to expose a resist-coated wafer with a diameter of 200 mm. The calculated power of the exposure on the wafer was approximately 120 mW/cm². Figure 1 shows a schematic of the HERC exposure chamber.

Before the contamination growth (CG) experiment, the E₀ (dose-to-clear) of the 60-nm-thick resists and the optimum post-application bake (PAB)/PEB conditions (100°C/100°C) were measured in the HERC using separate WSs devoted specifically to the E₀ evaluation. In the CG experiment, two 200 mm wafers were exposed with a dose of E₀ × 2.5. The total exposure area of the resist was approximately 74% of the full 300 mm wafer. The exposure chamber was pumped to ultrahigh vacuum (1–4 × 10⁻⁶ Pa) conditions before the exposure, in order to ensure a clean analysis environment. The vacuum pressure during the exposure was monitored by a cold cathode gauge (Pfeiffer). The pressure increase attributed to resist outgassing was 1–2 × 10⁻⁵ Pa.

2.2. EB-based tester

Figure 2 shows a schematic of the EUVOM-9000 (Litho Tech Japan Corporation) EB-based resist contamination analysis tool. Two electron guns at 5 and 0.9 keV were used as radiation sources for exposure of the resist and WS, respectively. The WS for an EB system (i.e., Ru (50 nm)/Si substrate) was positioned alongside the resist-coated wafer, as shown in Figure 2.

For the process flow, the E₀ of each resist (at 60 nm thickness and PAB/PEB = 100°C/100°C conditions) was first evaluated using EUVOM-9000. After these initial measurements, a fresh resist-coated wafer and a cleaned WS were prepared. Then, for the CG experiment, one resist-coated 300 mm wafer was exposed to a dose of E₀ × 2.5. The total exposure area of the resist was approximately 50% of the entire 300 mm wafer.

These experiments were performed at a base pressure of 2–4 × 10⁻⁶ Pa. During exposure, the base pressure increased to 1–2 × 10⁻⁵ Pa. These measured pressure values are similar to those
obtained during experiments conducted with the HERC analysis tool.

EUVOM-9000 was equipped with a hydrogen-based cleaning unit, which consists of a hot-wire filament and a hydrogen gas source. This unit was used to remove carbon-like contaminants from the WS surface before and after the CG exposure.

2.3. CG height evaluation

The actual contamination film thickness on the WS was measured with a spectroscopic ellipsometer (SE; M-2000X, J.A. Woollam Co.). Then, CG height was adjusted to achieve full exposure of a 300 mm full wafer.

2.4. Non-cleanable-element evaluation

After the contamination film thickness was measured, the WS was cleaned with hydrogen radicals to remove cleanable contamination. The atomic concentrations of the residual contaminants were quantified by X-ray photoelectron spectroscopy (XPS; PHI 5000 VersaProbe II, ULVAC-PHI, Inc.).

2.5. Resist family definition

Figures 3 and 4 show the composition and matrix of the “resist family” used in this study.

![Fig. 3. Composition of investigated resist family.](image)

The base resin was a PHS–methacrylate hybrid polymer, and the protecting group was methyl-adamantyl ester. TPS-nonaflate and tri-n-octylamine were used as the PAG and quencher, respectively. Formulation skew, where the protecting unit (PU) ratio of the base resin and the PAG loading ratio were changed, was employed because the primary components of resist outgassing include the PAG cation and the deprotecting-group derivative from the base resin.

The outgassing characteristics determined using an EB tool have been reported for this resist family [8]. Here we present the correlation between the outgassing characteristics determined using the EUV and EB methods, and suggest a new guideline for reducing the total number of outgassing tests.

3. Results and discussion

3.1. Cleanable contamination

3.1.1. Correlation between EUV and EB results

A correlative investigation between the HERC analysis tool (for the EUV method) and EUVOM-9000 (for the EB method) was performed. Figure 5 shows a linear correlation between the contamination film results obtained by the EUV and EB methods.

![Fig. 5. Correlation of contamination film thickness determined by EUV and EB methods.](image)

3.1.2. Comparison of the CG height trend between the EUV and EB methods

Figure 6 shows a strong correlation between the contamination film thickness and dominant outgas species (i.e., the deprotecting group and PAG) determined by the EUV and EB methods. Linear dependences of the contamination film thickness on the PU and PAG loading ratios were confirmed within the investigated range.

The contribution ratio of such components to the contamination film thickness was calculated under the assumption that all contaminants consist of decomposed species from the deprotecting groups and PAG. Figure 7 shows the contribution of the deprotecting groups and PAG determined by
the EUV and EB methods. The darker shades indicate contributions from the deprotecting groups, whereas brighter shades indicate contributions from PAG. The contribution ratios of deprotecting groups determined by the EUV and EB methods were 20%–84% and 25%–61%, respectively. The PAG contribution ratios determined by the EUV and EB methods were 16%–80% and 39%–75%, respectively. PAG was determined by both EUV and EB methods to contribute significantly to an increase in the contamination film thickness. As shown in Figure 7(a), the deprotecting group contribution at a 30% PU ratio is greater than that at a 40% PU ratio because the CG height of Resist-G is similar to that of Resist-D. A retest is planned for Resist-G.

3.2. Non-cleanable contamination

3.2.1. Correlation between EUV and EB results

After the cleaning process, the residual contaminants were analyzed by XPS. Figure 8 shows the detected non-cleanable elements determined by the EUV and EB methods. Sulfur, which is present in PAG, is assumed to be the main element among the non-cleanable elements, which is why it has been the focus of studies on non-cleanable elements. Figure 9 confirms a linear correlation between the sulfur concentrations determined by the EUV and EB methods. We found that the sulfur concentration does not depend on PAG loading.
3.2.2. Comparison of sulfur concentration trends determined by the EUV and EB methods

Figure 10 shows a clear correlation between the sulfur concentration and the dominant outgas species (i.e., deprotecting groups and PAG) determined by the EUV and EB methods. Non-cleanable elements exhibit a linear dependency on both PU and PAG loading ratios, as does the cleanable contamination film thickness.

Figure 11 shows the relationship between sulfur and the PAG contribution to the contamination film thickness. The sulfur concentration is considered to depend on the contribution of PAG to the contamination film thickness, as discussed in section 3.1.2. The difference in sulfur concentrations determined by the EUV and EB methods is due to the difference in the surface conditions of the WS. The WS for the EB tester was precleaned by hydrogen radicals to remove the carbon monolayer contamination before the CG

Fig. 8. Non-cleanable element on (a) EUV and (b) EB.

Fig. 9. Correlation of Sulfur between EUV and EB.

Fig. 10. Correlation between the sulfur concentration and the dominant outgas species (i.e., deprotecting groups and PAG) determined by (a) EUV and (b) EB.
test; however, this cleaning step was not possible with the EUV tester because of logistic limitations. Future tests are planned for EUV measurements using pre-cleaned WSs.

4. Conclusion

The use of formulation skew testing to change the PU ratio of the base resin and the PAG loading ratio of an EUV resist family was demonstrated as an approach for reducing the total number of outgassing samples to be tested. The outgassing was investigated using the WS method on EUV and EB testers: HERC analysis tool and EUVOM-9000, respectively. A linear correlation of contamination film thickness between EUV and EB was confirmed for the resist family. A strong correlation between the contamination film thickness and the composition ratio (i.e., the PU ratio and PAG loading) was confirmed by the results obtained using the EUV and EB methods. Non-cleanable contamination, especially sulfur, showed a similar tendency.

The results suggest that a resist outgassing trend can be predicted on the basis of resist composition. This prediction represents a significant step toward reducing the total number of required outgassing tests of EUV resists. However, we evaluated only one family in this study. Further investigations will be necessary to achieve the goal of a significant reduction in the number of EUV-resist outgassing tests.

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