Alternative Developer Solutions and Processes for EUV and ArFi Lithography

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The application of alternative developers for both extreme ultraviolet (EUV) and 193-nm immersion (“ArFi”) lithography is investigated by focusing on their effects on the “Defect-Not-Found” (*DNF*) margins. In case of EUV lithography, defects primarily comprise line bridging at the underdose region and line breaks at the overdose region. The application of a 0.26-N tetrabutylammonium hydroxide (TBAH) developer solution when compared to that of a 0.26-N tetramethylammonium hydroxide (TMAH) developer solution resulted in improved resist sensitivity while maintaining the same *DNF* margin. In case of ArFi lithography, defects primarily comprise line bridging at the underdose region and pattern collapse at the overdose region. The same improvement that has been mentioned above can be observed with respect to the resist sensitivity using the TBAH developer solution. However, the TBAH developer solution significantly minimizes the pattern collapse at the overdose region, further extending the minimum line pattern size. This translated to significant improvements in both the exposure latitude (*EL*) and overdose margin (*OM*) and resulted in a significant increase in the *DNF* margin. Furthermore, the application of a non-ionic surfactant type additive on the TMAH developer solution demonstrates resist sensitivity improvement and pattern collapse mitigation. Increased *EL* and *OM* values were observed, which also resulted in increased *DNF* margin. Results indicate the advantages of utilizing alternative developer solutions in improving the *DNF* margins.

Keywords: Developer solution, TMAH, TBAH, EUV lithography, ArFi lithography

1. Introduction

Ongoing and successful efforts in the development of lithographic technologies continue to be crucial to further extend the scaling targets for semiconductor devices [1-3]. 193-nm immersion (“ArFi”) and the recent extreme ultraviolet (EUV) lithography are the frontrunners in achieving critical patterning targets [1,2]. Resist materials are important in achieving the targeted resolution limits [4-6]. Here, advancement and, at times, drastic changes in resist materials have been performed to adapt and obtain the set targets [7-9]. However, currently, lithography is entering a generation of patterning, where resolution and stringent control of resist-based defects (e.g., residue, line bridge, line

break, and pattern collapse) are of utmost importance and must be prioritized [6,10-13]. Therefore, improving the resist processes is considered to be a potential solution.

This study explores the application of alternative resist processes in the form of developer solutions for both EUV and ArFi lithography resist materials.

2. Materials and processing

2.1. EUV lithography materials and processing

A chemically amplified resist (CAR) was utilized at a film thickness of 30 nm under optimal post application bake (PAB) and post exposure bake (PEB) conditions. The EUV CAR (typically a

hybrid of polyhydroxystyrene- and acryl-based polymers) was coated onto a 300-mm wafer coated with an organic underlayer at a thickness of 20 nm. The development process after PEB was performed at a development time of 30 s using several types of developer solutions as described in 2.3. The rinse process was performed using deionized water with a rinse time of approximately 19 s.

The resist processes from coating up to PEB were performed using the SOKUDO DUO coater/developer (SCREEN Semiconductor Solutions) at IMEC, Belgium. The development process was performed using the RFi coater/developer (SCREEN Semiconductor Solutions) in Hikone, Japan. The EUV patterning exposures were performed using the NXE-3300 (ASML) with a numerical aperture (NA) of 0.33 under optimal illumination conditions. All the SEM measurements were performed using CG5000 (Hitachi High Technologies).

2.2. ArFi lithography materials and processing

Another type of CAR was utilized (film thickness: 130 nm) under optimal PAB and PEB conditions. The ArFi CAR (typically acryl-based polymer) was coated onto a 300-mm wafer that was coated with a film stack of silicon hardmask (40 nm) and spin-on carbon (200 nm). The development process after PEB was performed with a development time of 60 s using several types of developer solutions. The rinse process was performed using deionized water with a rinse time of approximately 30 s. Note that the CAR film thickness was 30 nm thicker than the typical application conditions to realize accelerated testing for pattern collapse.

The resist processes from coating up to PEB were performed using a clean track coater/developer at the National Institute of Advanced Industrial Science and Technology (AIST) super clean room (SCR) facility in Tsukuba, Japan. Note that the ArFi lithographic patterning exposures were performed using the 1.3 NA NSR-S610C (Nikon) under optimal illumination conditions in the same facility. The development process was performed with a clean track coater/developer at the same facility. All the SEM measurements were performed using CG4000 (Hitachi High Technologies).

2.3. Developer solutions

Figure 1 denotes two types of aqueous developer solutions selected for both EUV and ArFi application. The tetramethylammonium hydroxide

Fig. 1. Selected aqueous alkali developer solutions.

(TMAH) developer solution, the present de facto standard in the lithography community, was utilized at a concentration of 0.26 N. Tetrabutylammonium hydroxide (TBAH; also utilized at a concentration of 0.26 N) was selected based on early reports describing its potential for minimizing the post-development process defects (e.g., pattern collapse) [14-18]. The TMAH developer solution had a contact angle (CA) of 79° as tested on the resist film surface. The TBAH developer solution had a CA of 66° (CA indicates the hydrophilicity or wettability of the developer solution on the resist film surface).

In addition, the application of a non-ionic type surfactant additive for the TMAH developer solution was explored for ArFi. In the past, surfactants have been used to improve the resist dissolution efficiency, especially for small patterns. This can be realized by increasing the wetting property of the developer to the resist surface [19,20]. For these investigations, the surfactant used was added at a concentration of 0.17 wt%, resulting in a developer solution CA of 40° when compared to the value of 79° that was observed when the developer solution did not contain any additive.

3. Results and discussion

3.1. EUV lithography: TMAH vs TBAH

Figure 2 depicts the EUV lithographic performance results obtained using the TMAH and TBAH developer solutions (broken lines indicate the ultimate resolution; line width roughness (LWR) and sensitivity were obtained with the 18-nm 1:1 lines/ spaces or L/S pattern). Using the TBAH developer solution, an obvious change as observed in resist sensitivity (28 mJ/cm² at TBAH compared to 32 mJ/cm² at TMAH). The ultimate resolution remained at 16-nm 1:1 L/S with some evidence of bridge defects at the 15-nm 1:1 L/S patterns. LWR was not significantly improved. A comparison of the process margin was conducted for the TMAH and TBAH developers.

Figure 3 denotes the SEM images obtained across the wafer exposed using NXE:3300 and developed using the TMAH and TBAH developer solutions.

Developer solution	Resolution (nm)	SEM image (design size, nm 1:1 L/S)				LWR (nm)	Sensitivity (mJ/cm ²)
		18	16	15	14		
TMAH	16					4.5	32
TBAH	16					4.2	28

Fig. 2. EUV lithographic performance results with TMAH and TBAH developer solutions (broken lines indicate ultimate resolution. LWR and sensitivity was obtained at the 18 nm 1:1 L/S pattern).

Fig. 3. SEM images obtained across the 300-mm wafer exposed using the NXE:3300 and developed using (a) TMAH and (b) TBAH developer solutions (black lines indicate the exposure area, where no line bridge or breaks were observed, and black broken lines indicate the best dose and focus condition).

These wafers were exposed as the focus-exposure matrices with dose on the x-coordinate and focus on the y-coordinate. For the wafer developed in TMAH, the center dose was 34 mJ/cm², whereas the center dose was 30 mJ/cm² for the wafer developed in TBAH. Note that the dose steps were fixed at 2 mJ/cm². Focus conditions were done at 25 nm per exposure step.

In Fig. 3, the black lines indicate the exposure area, where no line bridge or breaks were observed, and the black broken lines indicate the best dose and focus condition. Subsequent analyses were

$$EL = \frac{Dose_{target-10\%} - Dose_{target+10\%}}{Dose_{target}} \quad (1)$$

$$OM = \frac{Dose_{<break} - Dose_{target}}{Dose_{target}} \quad (2)$$

performed based on these measurement results focusing on the 18-nm 1:1 L/S pattern. Exposure latitude (EL) and overdose margin (OM) were calculated using Eq. (1) and (2), respectively.

where $Dose_{target}$ is the exposure dose value where measured critical dimension (CD) is equal to the target design size (in this case 18 nm). $Dose_{target-10\%}$ and $Dose_{target+10\%}$ indicates the dose values at -10% and +10% of target CD, respectively. Calculations consider and exclude exposure conditions where bridge at the underdose region and line breaks at the overdose region occur. $Dose_{<break}$ is the maximum dose before line break occurrence due to overdose.

A calculation of the “Defect-Not-Found” (DNF) margin was made using Eq. (3). $CD_{<bridge}$ indicates

$$DNF = \frac{CD_{<bridge} - CD_{<break}}{CD_{target}} \quad (3)$$

the largest pattern size before bridge defects occur (at the underdose region). $CD_{<break}$ shows the smallest pattern size before line breaks occur (at the overdose region). CD_{target} indicates the target pattern size (in this case, 18 nm).

Table 1 shows the EL and OM dependence on developer solution type. These results denote that a slight improvement in EL was obtained using the TBAH developer solution. More significant is the increase in OM with the TBAH developer solution, which indicates that the overdose window size was maintained even as the sensitivity was improved.

Table 1. EUV: EL and OM dependence on developer solution type.

Developer solution	EL (%)	OM (%)
TMAH	14.6	24.6
TBAH	16.1	33.0

Table 2 presents the DNF margin dependence on the developer solution. The results show that even at improved sensitivity with the TBAH when compared with that of the TMAH developer solution, $CD_{<bridge}$ and $CD_{<break}$ remained approximately the same at ~ 20 and ~ 12 nm, respectively. Thus, DNF margin remained at $\sim 40\%$.

Table 2. EUV: DNF margin dependence on developer solution type.

Developer solution	$CD_{<bridge}$ (nm)	$CD_{<break}$ (nm)	DNF margin (%)
TMAH	20.1	12.8	41
TBAH	18.9	11.9	39

Note that further investigations are required to better understand the effect of TBAH developer solutions on the EUV lithography resist performance. However, these preliminary results demonstrate that there is minimal or no disadvantageous effect on the EUV patterning capability while using the TBAH developer solution.

3.2. ArFi lithography: TMAH vs. TBAH

Figure 4 depicts the ArFi lithographic performance results for the 40-nm 1:1 L/S pattern obtained using the TMAH and TBAH developer solutions. As mentioned previously, to realize accelerated testing, the utilized CAR film thickness was 30 nm thicker than the typical application conditions, i.e., 100 nm.

The results demonstrate the occurrence of improved sensitivity (similar to that observed in the EUVL results) with the best dose using the TBAH developer solution observed to be 15.4 mJ/cm^2 when compared with the value of 16.6 mJ/cm^2 with the TMAH developer solution. Note that no significant change was observed in LWR; however, there was an obvious difference in the occurrence of pattern collapse depending on the developer solution. For the TMAH developer solution, pattern collapse was observed at $CD_{<collapse} = 38$ nm, and, with the sample being developed in the TBAH developer solution, pattern collapse only occurred at $CD_{<collapse} = 32$ nm. When compared with the TMAH developer solution, this mitigation of pattern collapse for the ArFi resist is assumed to be caused by the effect of minimized resist swelling during the development process with the TBAH developer solution, as reported in the literature [21].

Using Eqs. (1)–(3) and by replacing $CD_{<breaks}$

Developer solution	SEM image (CD size (nm))						
	~ 52	~ 48	~ 42	~ 40	~ 38	~ 34	~ 32
TMAH
Dose(mJ/cm ²) / LWR (nm)	13.0 / 6.1	14.6 / 5.1	15.8 / 4.9	16.6 / 4.1	17.4 / 3.6	18.6 / *	19. / *
TBAH
Dose(mJ/cm ²) / LWR (nm)	12.2 / 4.9	13.0 / 5.7	14.6 / 4.3	15.4 / 4.0	15.8 / 4.5	17.4 / 3.4	17.8 / 3.8

Fig. 4. ArFi lithographic performance results for the 40 nm 1:1 L/S using TMAH and TBAH developer solutions (broken lines indicate optimal dose. Black solid outline indicates absence of pattern bridge or collapse).

Developer solution	SEM image (CD size (nm))						
	~52	~48	~42	~40	~38	~34	~32
NO Additive							
Dose(mJ/cm ²) / LWR (nm)	13.0 / 6.1	14.6 / 5.1	15.8 / 4.9	16.6 / 4.1	17.4 / 3.6	18.6 / *	19. / *
With Additive							
Dose(mJ/cm ²) / LWR (nm)	12.2 / 5.6	14.2 / 5.1	15.0 / 4.7	15.8 / 3.8	16.2 / 4.0	17.8 / 3.8	18.6 / 3.3

Fig. 5. ArFi lithographic performance results for the 40 nm 1:1 L/S using TMAH developer solution with and without additive. Broken lines indicate optimal dose. Black solid outlines indicate absence of pattern bridge or collapse.

with $CD_{<collapse}$, Table 3 shows the *EL* and *OM* dependence on the developer solution. Significant increases in *EL* and *OM* were observed using the TBAH developer solution. Table 4 presents the *DNF margin* dependence on the developer solution. The results demonstrate a significant improvement in the overdose region using the TBAH developer solution, where the minimum CD size before pattern collapse was $CD_{<collapse} = 34.1$ nm when compared to that obtained with TMAH at $CD_{<collapse} = 39.9$ nm. The $CD_{<bridge}$ values were similar for both the developer solutions, i.e., ~52 nm. This resulted in improved *DNF margin* when using the TBAH developer solution compared with the usage of the TMAH developer solution, i.e., 43.2% and 28.6%, respectively.

The results suggest a significant advantage observed while utilizing TBAH as an alternative developer for use in ArFi.

Table 3. ArFi: *EL* and *OM* dependence on developer solution type.

Developer solution	<i>EL</i> (%)	<i>OM</i> (%)
TMAH	6.4	0
TBAH	17.3	13.0

Table 4. ArFi: *DNF margin* dependence on developer solution type.

Developer solution	$CD_{<bridge}$ (nm)	$CD_{<collapse}$ (nm)	<i>DNF margin</i> (%)
TMAH	52.9	39.9	28.6
TBAH	51.4	34.1	43.2

3.3 Non-ionic type surfactant additives for ArFi

The application of surfactants during the development and rinse processes is considered to be effective to improve the exposure process margin because it mitigates defects, e.g., pattern collapse

[19]. This increases developer solution hydrophilicity to the resist film, improving the developer solution penetration efficiency.

Figure 5 depicts the ArFi lithographic results for the 40-nm 1:1 L/S pattern obtained using the TMAH developer solutions with and without a surfactant additive. The non-ionic type surfactant was added to the TMAH developer solution at 0.17 wt%, resulting in a developer solution CA of 40° (compared to 79° for the developer solution without additive). Therefore, significant pattern collapse mitigation improvement was achieved, e.g., patterns were observed to have no pattern collapse even at $CD_{<collapse} = 34$ nm. The resist sensitivity also improved due to the application of the surfactant additive on the TMAH developer solution (15.8 mJ/cm² for the developer solution with the surfactant and 16.6 mJ/cm² without the surfactant).

Table 5 presents the ArFi lithographic performance results for the 40-nm 1:1 L/S pattern (*EL* and *OM* dependence on the developer solution with a surfactant additive). The results demonstrate an improvement in both *EL* and *OM* (*EL*: 16.7% and *OM*: 15.8% using developer solution with a surfactant additive when compared with *EL*: 6.4% and *OM*: 0% without any surfactant additive).

Table 6 presents the ArFi lithographic performance results for the 40-nm 1:1 L/S pattern (*DNF margin* dependence on the developer solution with a surfactant additive).

These results further confirm the effectiveness of the developer solution with a surfactant additive relative to improving the *DNF margin*, where the minimum CD size achieved before pattern collapse was $CD_{<collapse} = 33.7$ nm when compared with that obtained at TMAH without surfactant at $CD_{<collapse} = 39.9$ nm. Here, $CD_{<bridge}$ improved to 52 nm for the developer solution with a surfactant additive when compared to 54 nm without any surfactant additive. These results translate to an approximately

twice improved *DNF margin* (51% using the developer solution with a surfactant additive and 28.6% without any surfactant additive).

Table 5. ArFi: *EL* and *OM* for TMAH developer solution with and without surfactant additive.

Developer solution	<i>EL</i> (%)	<i>OM</i> (%)
No Additive	6.4	0
With Additive	16.7	15.8

Table 6. ArFi: *DNF margin* for TMAH developer solution with and without surfactant additive.

Developer solution	<i>CD</i> _{<bridge} (nm)	<i>CD</i> _{<collapse} (nm)	<i>DNF margin</i> (%)
No Additive	54.1	39.9	28.6
With Additive	51.4	33.7	51.0

4. Summary

The application of alternative developers in case of both EUV and ArFi were investigated by focusing on their effects on the *DNF margin*. In case of EUV lithography, defects were classified as comprising mostly line bridging at the underdose region and line breaks at the overdose region. In case of ArFi lithography, the defects were classified as line bridging at the underdose region and pattern collapse at the overdose region.

The application of alternative developers, such as TBAH, in both the EUV and ArFi lithographic technologies resulted in higher sensitivity when compared with that in TMAH. In case of EUV, this sensitivity improvement was obtained while maintaining the same *DNF margin*. In contrast, applying the TBAH developer solution to ArFi resulted in a significant reduction of the pattern collapse defects at the overdose region, which translated to a significant increase in the *DNF margins*. Furthermore, in case of ArFi, the application of a non-ionic surfactant type additive on the TMAH developer solution resulted in resist sensitivity improvement and pattern collapse mitigation, resulting in increased *DNF margin*.

These results demonstrate the advantages of utilizing TBAH and non-ionic type surfactant additives for improving the *DNF margins*.

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