Novel EUV Resist Materials for 7 nm Node and Beyond

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For semiconductor device manufacturing, line width roughness (LWR) and defect reduction of resists is one of the most important items to obtain high yield. In this study, we described the development of novel high absorption resists for use in extreme ultra violet (EUV) lithography system and its LWR and nano-bridge reduction capability. Herein decomposition rates of photo acid generator (PAG) and several high EUV absorption compounds were studied to clarify inefficient pass on acid generation mechanism. As a result, it is revealed that existence of decomposition pass on high EUV absorption compounds degenerates PAG decomposition efficiency. New high absorption materials were synthesized with taking into account its decomposition durability and its lithographic performance were investigated. 15-20% dose reduction keeping its LWR value and nano-bridge reduction were observed even at lower dose condition compared to non-high absorption platform.

Keywords: EUV lithography, Chemically amplified resist, High absorption, LWR

1. Introduction

EUV lithography (EUVL) is most promising process for alternative to 193 nm-immersion multiple lithography, realizing 7 nm node manufacturing and beyond. With recent rapid progress on the source power improvement [1], process and material explorations are more and more accelerated to achieve High Volume Manufacture (HVM) requirements. It has been thought that the main challenge of EUVL is satisfying Resolution (R) –LWR (L) –Sensitivity (S) requirements simultaneously for EUV resists [2]. On the other hand, recent reports indicate defectivity caused by stochastic effect have to be considered as well as RLS-tradeoff improvement [3].

For 7 nm node application, traditional chemically amplified resist (CAR) system is first candidate because of its well-studied property through KrF and ArF manufacturing process for many years, e.g. stability, metal contamination

and post-litho process compatibility. However, its low EUV absorption property enhancing photon-shot-noise (PSN) effect is one major disadvantage of conventional CAR system, especially for low dose resist process construction [4]. In the past, several researches aiming high EUV absorption CAR system were reported [5-8], but material design and its lithographic performance still need detailed investigation.

The present study aims to clarify how we can overcome RLS-tradeoff and reduce defects. Accordingly, we investigated the PSN effect using process dependency study and material design requirements to achieve high EUV absorption resists. Lithographic results of high EUV absorption resists based on the study were also described.

2. Experimental

2.1. Materials

Both standard and high-absorption unit introduced protected co-polymers were synthesized according to the conventional polymerization methods [9]. A series of photoresist were prepared by mixing organic solvents, the protected co-polymers, optimized amount of PAG and organic quencher. The resulting solution was filtered using 0.03 μm polyethylene filter before lithographic performance evaluation.

2.2. Lithography performance evaluation

The photoresist solution was spin-coated on a silicon wafer that was treated with an organic under layer (UL) or spin on glass (SOG) stacked with spin on carbon (SOC), and the resulting film was pre-baked at appropriate temperature for 60 sec to give a specific film thickness for each patterning features. The wafer was exposed with EUV light (13.5 nm) from an ASML NXE:3300 with 0.33 NA. After exposure, the wafer was post-exposure-baked (PEB) at moderate temperature for 60 sec, and developed with 2.38% TMAH aq. for moderate time. The resulting wafer was rinsed with a surfactant rinse material. CD-SEM measurements were performed with a Hitachi CG5000 at imec.

2.3. Decomposition rate measurement

To determine decomposition rate of PAG and EUV high absorption compounds, solutions containing polymer and PAG or EUV high absorption compounds were prepared and filtered with 0.03 μm polyethylene filter. The resulting solution was spin-coated on silicon wafer, and prebaked at appropriate temperature for 60 sec to give a film thickness of 100 nm. The film was exposed by open-frame EB exposure tool for 300 sec, and extracted by an organic solvent. Obtained solution was analyzed by high performance liquid chromatography (HPLC) and remaining PAG or high absorption compounds ratio were determined. The decomposition rates were calculated from the decomposed amount and the exposure time.

3. Results and discussion

3.1. Pitch and dose reduction effect

PSN effect on EUV lithography is well-known issue and various studies have emphasized its impact on LWR performance [10-12]. As well as LWR, the PSN effect on defectivity have to be considered to obtain pattern quality satisfying HVM requirements.

Tables 1a and 1b show patterning results with different pitch and dose using Fujifilm standard

Table 1a. HP16 nm L/S patterning results with different sensitivity resists. (Resist: FEVS-P series, Exposure: NXE:3300 with customized ill., Dev.: 2.38% TMAH aq., surfactant rinse, film thickness: 30 nm.)

Resist	HP 16 nm	HP 15 nm	HP 14 nm	HP 13 nm
Sensitivity (mJ/cm ²)	46.1	45.2	43.3	42.1
LWR (nm)	4.45	4.44	4.81	5.3
1:1 L/S Top-down CD-SEM image

Table 1b. L/S patterning results at different pitches. (Resist: FEVS-P series, Exposure: NXE:3300 with a dipole 45X of $\sigma_{0/i} = 0.902 / 0.671$, Dev.: 2.38% TMAH aq., surfactant rinse, film thickness: 30 nm.)

Resist	Std	Fast PR-1	Fast PR-2	Fast PR-3
Sensitivity (mJ/cm ²)	42.6	29.8	25.6	21.4
LWR (nm)	5.01	5.44	5.70	6.01
HP 16 nm L/S Top-down CD-SEM image

CAR PTI resists. Both pitch and dose reduction accompanies bridge appearance on space region as well as LWR increment. Since lower dose (high throughput) and tighten pitch (fine resolution) patterning is necessary for spreading EUV system as general exposure method, such deteriorated pattern quality, especially “nano-bridge defect”, is getting a large obstacle for EUV lithography application.

To use more photons for pattern formation, we applied thicker resist condition and Table 2 shows results of them. Thicker resist condition shows better LWR and nano-bridge performance, but accompanies pattern collapse. To overcome this collapse-LWR trade-off, high EUV absorption CAR material, which is able to increase absorbed photon number with the same film thickness is necessary.

3.2 Strategy for high EUV absorption material

Acid generation mechanism in EUV

lithography has been well investigated by many researchers and it is widely recognized it includes steps of absorption, ionization, reductive electron transfer to PAG, PAG decomposition and proton donation from polymer [7,13]. It is also well known that the EUV absorption coefficient of resist material is dependent on elements of the resist components (Fig. 1) [14]. As we previously reported, high absorption CAR material have a issue of acid generation efficiency degeneration, which implies wasting absorbed photon via energy loss pass and some previous reports suggested existence of decomposition pass on high absorption material as the degeneration pass [5,7]. To establish efficient EUV absorption CAR system, such energy loss pass must be removed. In this study, we investigated the influence of the decomposition pass on acid generation more in detail by focusing on energy transfer process.

To evaluate decomposition rate, we adopted EB-exposure and HPLC analysis described in Fig.

Table 2. HP16 nm L/S patterning results with different film thickness.
(Resist: FEVS-P series, Exposure: NXE:3300 with customized ill., Dev.: 2.38% TMAH aq., surfactant rinse.)

Film thickness (nm)	30 nm	35 nm	40nm
Sensitivity (mJ/cm ²)	27.8	28.0	(28.8)*
LWR (nm)	5.82	5.31	(4.96)*
HP 16 nm L/S Top-down CD-SEM image

*calculated from non-collapsed region

Fig. 1. EUV absorption coefficient per atom.

2 instead of widely used acid measurement method [5,15] so that eliminate the impact of absorption and proton donation pass.

Figure 3 shows results of the PAG decomposition rate in various polymer films including polyhydroxystyrene (PHS) and three polymers with high absorption unit. It was found out that the PAG decomposition rate is much slower in fluorophenyl type polymer (Polymer **B**) matrix, which is well-known high EUV absorption organic compound [7]. This result supports existence of the decomposition pass on fluorinated polymers through radical anion form which was suggested in previous reports [7,16,17]. To clarify the decomposition pass existence in a resist film, we tested the decomposition rate evaluation on low molecular model compounds of the evaluated polymers. Three compounds with different high absorption units attached to phenyl unit including

fluorophenyl type (Additive **A**) were added in polymer solution instead of PAG and the same EB exposure, extraction, and HPLC analysis were operated. The results were summarized in Fig. 4. Higher decomposition rate of Additive **A** on EB-exposure were confirmed. To investigate the impact of the decomposition in detail, both Additive **A** and PAG **A** were added to PHS film and the PAG decomposition rate evaluation was operated. As a result, the degenerated PAG decomposition rate was observed in Additive **A** including polymer film (Fig. 5). It clearly indicates the decomposition of high absorption unit is competitive to PAG decomposition, therefore the existence of the decomposition pass results in losing its advantage of high absorption property by wasting generated secondary electron (Fig. 6). To construct high EUV absorption CAR resist, stability on high energy beam exposure must be examined.

Fig. 2. Experimental method for decomposition rate evaluation.

Fig. 3. PAG decomposition rate in different polymer matrices.

Fig. 4. Decomposition rate of additives with different high absorption units.

Fig. 5. PAG decomposition rate with and without decomposable additive A.

Fig. 6. PAG decomposition mechanism.

3.3. Lithographic performance of High EUV absorption resists

For lithographic performance evaluation, we synthesized new polymer using high absorption monomer unit which shows stability on EB exposure based on the knowledge obtained in the

last section. Table 3 shows the results of the resist. High absorption resist showed 15-20% dose reduction with keeping its LWR value. Besides that, nano-bridge is clearly decreased on the high absorption resist. To quantify the impact on the nano-bridge reduction, we analyzed the

Table 3. HP16 nm L/S patterning results with high EUV absorption resists.

(Resist: FEVS-P series, Exposure: NXE:3300 with a dipole 45X of $\sigma_{o/i} = 0.902 / 0.671$, Dev.: 2.38% TMAH aq., surfactant rinse, film thickness: 30 nm.)

Resist	Non High Abs.	High Abs.-PR 1	High Abs.-PR 2	High Abs.-PR 3
Sensitivity (mJ/cm ²)	42.3	31.9	31.7	35.8
LWR (nm)	4.72	4.88	4.97	4.71
HP 16 nm L/S Top-down CD-SEM image

Non High Abs.	34.8 mJ 19.03 nm	36.0 mJ 17.71 nm	37.2 mJ 17.39 nm	38.4 mJ 16.63 nm
High Abs.-PR 1	27.6 mJ 18.52 nm	28.7 mJ 17.73 nm	29.8 mJ 17.09 nm	30.9 mJ 16.45 nm

Fig. 7. Relation between %NOK value (obtained by Stochalis analysis) and CD with non high abs. PR and high abs.PR-1.

SEM images by a software package called Stochalis, which is developed by imec [18]. Finally obtained percent not OK (written as %NOK) value shows how much of percentage the failure mode occupies in the analyzed SEM images [3]. Figure 7 shows the results and reduction of %NOK value by high absorption resist application were observed especially at higher CD range.

4. Conclusion

This study showed the progress of acid generation mechanism analysis and lithographic performance improvement on high EUV absorption CAR system. The study suggests suitable advantages of the system on RLS tradeoff improvement and defect reduction. Appropriate high absorption unit selection by suppressing polymer decomposition pass is necessary to obtain potential advantage of high absorption. This high EUV absorption CAR system is expected to become a fundamental technology for HVM stage of 7 nm node and beyond.

Acknowledgements

The full-field EUV exposures were done on the ASML NXE:3300 scanner at imec, as part of the imec Advanced Lithography Program. We would like to thank Danilo De Simone and Geert Vandenberghe for their support with the experiments at imec and helpful discussions.

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