PAG Study of PAG Bonded Resist for EUV and EB Lithography

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In order to reduce line edge roughness and to increase sensitivity, PAG-bonded chemically amplified resist was developed and was evaluated in extreme ultraviolet lithography (EUVL) and electron beam (EB) lithography. We investigated various kinds of photo acid generators (PAGs) which are on the basis of the sulfonium salts to find the beneficial photo acid generator (PAG) for our designed PAG-bonded resist. It was confirmed that not only the structure of anion of PAG but also the structure of cation of PAG are important to achieve the resist specification. It is confirmed that by a selected PAG system, high E_0 sensitivity was achieved under the EUV exposure. In addition, LER of 3.5 nm (3σ) was achieved by an EB writing tool.

Keywords: sensitivity, LER, PAG bonded CA resist, EUVL, EB

1. Introduction

The formulation of fine pattern of less than 32 nm is required around 2011. Extreme ultraviolet lithography (EUVL)¹⁾ is the expected to be the most promising semiconductor fabrication technology. Table 1 shows the requirement specification²⁾ of resist development. The resist development is the second top issue to realize the EUVL technology. The resist which satisfies the specification of the sensitivity and LER simultaneously has not been developed yet.

Table 1. The resist specification

	2011
Resolution-Gate (nm)	21
Resolution-1/2 pitch (nm)	32
LER (nm)	< 1.2
Sensitivity(mJ/cm ²)	< 10
Outgassing (molecules/cm ² /s)	< 5×10^{13}

If the resist sensitivity of 10 mJ/cm² is required, EUV light source power required to be 180-220 W at an intermediate focus position. However, it seems very challenging to achieve a high source

power. Thus the high sensitive resist such as 5 mJ/cm² to 10 mJ/cm² is required to alleviate a burden of the specification of the high power EUV light source. In addition, it is significant to reduce LER. The accuracy of the LER of less than 1.2 nm is required because of the LER being effective with the LSI circuit characteristics deviation.

In recent years, there is low molecular resist as a method to reduce LER.³⁻⁵⁾ Although the molecular size of a low molecular resist is smaller than that of polymer generally used as the base resin, low molecular resist has not satisfied the specification yet. Other methods of reducing LER are shown as follows; 1) the acid diffusion length is controlled during post exposure bake (PEB). 2) The molecular weight distribution is reduced close to 1. 3) The density distribution of photo acid generator (PAG) in resist film has to be uniformed. The methods of 1) and 2) have been studied in the many other institutes, however the resist which satisfied specifications of sensitivity and LER has not been developed yet.

For the major method of settlement of 3), there is the method of adding PAG to side chain of the

base resin^{6,7)}. The PAG density distribution is not uniform in the conventional resist because of the mixture in the solvent with polymers⁸⁾. Thus, we call this resist as the “PAG-blended resist”. On the other hand, in the resist that is synthesized PAG to back-bone of the base resin, there is a report that PAG exist uniformly in the resist film. Then, we call this resist the “PAG-bonded resist” which is chemically amplified (CA)⁹⁾ resist. We have already reported that LER of PAG-bonded resist has smaller than that of PAG-blended resist.¹⁰⁾ Then it seems to achieve a higher uniformity of PAG density distribution than a PAG-blended resist.

Recently, it gets to become active area of research gradually. We have developed and evaluated the PAG-bonded resist¹⁰⁾ for EUV. Sensitivity, resolution and LER is strongly influenced by the chemical structure of PAG from the current experiments. Thus we have been evaluated a various kind of PAGs on the basis of sulfonium salts to satisfy the sensitivity and LER simultaneously. The mitigation of the selection of PAG is focused on this paper and the evaluation results are described.

2. Experiment Procedure

2.1. Samples

Figure 1 shows the polymer structure of the PAG-bonded resist. Polyhydroxy styrene which has the outstanding accomplishment in lithography was used as base resin. The molecular weight of base resin is 16400, the molecular weight distribution is 1.09, the ratio of the protection group (R) is about 30 mol%, and the addition rate of PAG is less than 1 mol%.

Table 2 shows the chemical structure of PAG used in this experiment. All the PAGs employed in this experiments were on the basis of tri-phenyl sulfonium (TPS) type PAGs. The benzene of TPS was bonded to base resin. R, R' and R₁₋₅ of PAGs are functional group. TPS-nonaflate which is the general type was used as a PAG of resist A. Anions of PAGs employed in resists A and B have a different chemical structures. Anions of PAGs employed in resists B, C, and D have a same chemical structure. The cations of PAGs differences employed in resists B, C, and D are the number of functional group of benzene of cation of

Figure 1. The polymer structure of PAG-bonded CA resist.

PAG. In addition, anions of PAG employed in resists E and F are same. These PAGs were chosen to find the optimal PAG chemical structure and to investigate not only the influence a PAG of an anion but also that of a cation because the sensitivity, LER, and the resolution depend to the selection of an anion of PAG and a cation of PAG.¹¹⁾ Therefore, resists A, B, and E were prepared to compare the influences of the anion of PAG. In addition, resists B, C, D, E, and F were prepared to compare the effectiveness of the cation of PAG.

Table 2. PAG samples used in the experiment.

Resist A	Resist B	Resist C
Resist D	Resist E	Resist F

2.2. Process Condition

Propylene glycol monomethylether acetate (PGMEA) was used as solvent. The resist film was spin-coated on a silicon wafer and prebake was carried out on a hot plate at the temperature of 120°C for 90 s. The resist film thickness was controlled at 100 nm and measured by a multi-wavelength-interference-thickness measurement tool Nanospec model 6100A (NANOmetrics Co. Ltd.). Post-exposure bake (PEB) was carried out on a hot plate at the temperature of 90°C for 60 s after the exposure. Aqueous 2.38 wt% of tetramethyl ammonium hydroxide (TMAH) was used as developer at the temperature of 23°C for 30 s and rinsed with de-ionized water at the temperature of 23°C for 30 s.

2.3. Evaluation method

Resist pattern was performed by an electron beam (EB) writing system to evaluated resolution and LER. The acceleration voltages of EB writing system was 30 kV. The resist pattern image was obtained using scanning electron microscope (SEM S4500 Hitachi, Ltd.), and LER of resist pattern was measured with graphic processing PC computer software SuMMIT¹²⁾. LER was measured along the distance of 1.5 μm in the

longitudinal direction of the resist line pattern with interval of 10 nm in size.

The sensitivity and outgassing experiment were carried out under EUV exposure using resist evaluation system¹³⁾ installed at the BL3 beamline of NewSUBARU synchrotron radiation (SR) facility. Resist evaluation system can be simulating a six-mirror imaging optics for practical used for EUVL. Then SR light was monochromated to 13.5 nm wavelength by seven times reflection of concave mirror and two plane mirrors of Mo/Si multilayer. The centroid wavelength is 13.67 nm. The intensity flux on a wafer was 0.28 mW/cm² at the electron beam current of 200 mA of the electron storage ring. The outgassing is measured using a high sensitive quadrupole mass spectrometer (Model HAL/3F/PIC 501 RC, Hiden Analytical, Ltd.). Total outgassing displacement between before exposure and after exposure was measured. The measured mass range was 1 amu to 500 amu.

3. Results and discussion

The resolution and LER of resists A to F were evaluated with EB writing system. Tables 2, 3, and 4 show the photographs of SEM image and LER values for resists A to F.

Table 3. SEM images of resist patterns and LER values of resist A and B.

	Resist A	Resist B
150 nm L/S
100 nm L/S
75 nm L/S	No image
50 nm L/S	No image
LER(nm)	2.1	5.5

The resolution of resist A was limited to 100 nm. In resists B and C, a 50 nm line and space (L/S) pattern were replicated. However, resolution of

less than 100 nm was not observed in resist D. Resists E and F were limited to 75 nm. In the 100 nm L/S, LER of resists A, B, C, E, and F were 2.1 nm, 5.5 nm, 3.5 nm, 13.6 nm, and 9.6 nm, respectively.

Table 4. SEM images of resist patterns and LER values of resist C and D.

	Resist C	Resist D
150 nm L/S
100 nm L/S		No image
75 nm L/S		No image
50 nm L/S		No image
LER(nm)	3.5	

Table 5. SEM images of resist patterns and LER values of resist E and F.

	Resist E	Resist F
150 nm L/S
100 nm L/S
75 nm L/S
50 nm L/S	No image	No image
LER(nm)	13.6	9.6

As the results, the alternation of anion have a large impact on the sensitivity, LER, and resolution in comparison between resists A, B, C, E, and F, because strength and diffusion of the acid are difference. In addition, in comparison between resists B and C, and resists E and F, it was considered that appending functional group to benzene of TPS was little effective in the resolution. Figure 2 shows the sensitivity curves of resist A, B, and C under the EUV exposure.

Figure 2. Sensitivity curves of resists A, B, and C under EUV exposure

E_0 sensitivity of resists A, B, and C are 1.9 mJ/cm², 3.0 mJ/cm², and 5.0 mJ/cm², respectively. In comparison between the sensitivity of resist A and B, the difference of sensitivity is own to the anion of the PAG. It was thought the sensitivity difference is origin to the difference of acid strength and acid diffusion length. The difference of sensitivity between A and B is own to anion of PAG. In the case of resist C, the functional group which is electron donor group is bonding to the benzene of the cation. For this reason, the acid strength of resist C is weaker than that of resist B even if the same anion as resist B is used, and the sensitivity of resist C is lower than that of resist B. From the trade-off of the sensitivity and LER, LER of resist C is better than resist B. The total outgassing pressure of resists A, B and C are 2.71×10^{-6} Pa, 2.63×10^{-6} Pa, and 3.46×10^{-6} Pa, respectively. Total outgassing of resists are on the order of 10^{-6} Pa and all the resists satisfy the outgassing specification. As the results, it was confirmed that PAG of resist C has the best performance in the evaluated resist.

4. Conclusion

We developed and evaluated PAG-bonded CA resist to reduce LER and to increase sensitivity for EUVL. We investigated many samples to find the beneficial PAG for PAG-bonded resist. It was confirmed that the effect of anion and cation of

PAG on resolution and LER and sensitivity. It was considered vital to develop the PAG-bonded resist that anion and cation of PAG were designed. In addition, it is compared that LER and resolution of between PAG-bonded resist and PAG-blended resist which using same PAG and base resin for EB exposure. LER of 3.5 nm (3σ) was achieved by PAG bonded resist, which was improved LER of PAG-blended resist.

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