Study of PAG Size Effect on Lithographic Performance of 157 nm Resists

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Lithographic performances of 157 nm resists prepared by partially protected NBHFA-MOM polymer were compared by using different size of anion of TPS PAG. Vacuum ultraviolet spectroscopy measurement, discrimination curve measurements by 157 nm open flame exposure, 193 nm and 157 nm imaging results were examined. Higher resolution and better profile was observed for larger anion size of TPS PAG.

Keywords: 157 nm Resists, chemically amplified resists, protected polynorbornane polymer, anion size of TPS type PAG

1. Introduction

157 nm lithography is considered as the most promising candidate to fill the gap between 193 nm lithography and EUV lithography, and is expected to apply for 70 nm node technology.

The development of 157 nm resists has been very challenging due to the high energy of photon (7.9 eV). It is quite obvious that chemical amplification (CA) type resist is necessary also for 157 nm lithography, as same as 248 nm and 193 nm due to throughput demand. As major solid content of CA resists is partially protected polymer, absorption property of base polymer at the exposure wavelength is quite significant. Most common polymers used for 248 nm and 193 nm resists can not provide good imaging profile by 157 nm exposure due to their strong absorption at 157 nm, therefore several polymers having fluorine and silicone have been proposed to achieve lower absorption demand on 157 nm resists. [1-7]

The base polymer of 157 nm resists must provide not only higher transparency and other significant lithographic performances but also comparable reactive ion etching resistance with existing 248 nm or 193 nm resists.

Poly Norbornen hexafluoro alcohol (NBHFA) partially protected by methoxymethyl (MOM) is considered as one of the potential candidates for the base polymer of 157 nm resists, because of its lower absorbance about 2.0 μm⁻¹ together with preferable etching resistance. [3, 4]

While the majority of work has been concentrated on development of suitable resists to meet the various daunting requirements, the impact of photoacid generator (PAG) structure has been relatively ignored along the line of 157 nm resists research effort. In this contribution, we intended to examine the effect of anion size on lithographic performances, particularly of the system which consists of NBHFA-MOM polymer based resists and a conventional triphenylsulfonium (TPS) perfluorosulfonate designed for 157 nm application.

Results were discussed by comparing vacuum ultraviolet (VUV) spectroscopy, dissolution rate measurement, 157 nm open flame exposure, 193 nm imaging and 157 nm imaging examinations.

2. Method

2.1. Materials for polymer synthesis

All starting materials were procured from Aldrich except hexafluoroacetone (Tokyokasei) and used as received.

-3-(5-Bicyclo[2.2.1]hepten-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanol (NBHFA) was prepared according to Chiba et al. [8]
2.2 Instruments for polymer analysis

NMR spectra were obtained using a JEOL GX-270 spectrometer. Molecular weight (Mw) and polydispersity (Mw/Mn) were measured from THF solutions using a Tosoh GPC8020 and are reported relative to polystyrene standards.

2.3 Polymerization of NBHFA [9]

Typical NBHFA polymer was prepared as below. To a solution of 75.0 g NBHFA in 75 ml 1,2-dichloroethane, was added drop wise a catalyst solution, which was prepared by adding 2.0 g of allylpalladium chloride dimer in 1,2-dichloroethane to 4.3 g of silver tetrafluoroborate in 1,2-dichloroethane for 30 minutes and then filtering off the resulting silver chloride precipitate, under nitrogen at room temperature. The stirred reaction mixture was allowed to run for 24 hours. Upon adding the solution to hexane the polymer precipitated as a white powder. The polymer was washed with excess hexane and dried. The yield of polymer was 60.7 g. The polymer was found to have Mw of 11000 g/mol and a Mw/Mn of 2.0.

2.4 MOM Protection of poly NBHFA

To a solution of poly NBHFA (6.0 g), diisopropylethylamine (7.5 g) and 4-methyl-2-pentanone (MIBK) (60.0 g) was added drop wise a methoxymethyl chloride (3.9 g) under nitrogen at room temperature. The stirred reaction mixture was allowed to run for 24 hours. The solution was diluted with MIBK and washed 6 times and evaporated. The concentrated polymer solution was diluted with acetone and added to methanol/water mixture drop wise to precipitate the polymer. Filtration and drying under vacuum afforded the product as a white solid. The protection ratio of hydroxyl group is substituted with the methoxymethyl (MOM) group was 25 % according to the NMR measurement.

2.5 PAG synthesis and calculations

TPS PAG was prepared by a common method. Fig.2 shows structures of Triphenylsulfonium trifluoromethanesulfonate (TPS-C1), Triphenylsulfonium perfluorobutanesulfonate (TPS-C4), Triphenylsulfonium perfluorooctanesulfonate (TPS-C8), and Triphenylsulfonium 1,2,2,3,4,5,5,6,6-decafluoro 4-(pentafluoroethyl) cyclo hexane-

sulfonate (TPS-Cy).

We calculated pKa of PAG by ACD/pKa DB Ver. 3.00 (Advanced Chemistry Development Inc.). We estimated an Anion size of PAG using geometry optimization by PM3 method of WINMOPAC Ver.3.0 (Fujitsu Ltd.), wherein molecular charge of -1 was used for calculations. Results were shown on Table 1.

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**Table 1. Estimated Anion size and pKa**

<table>
<thead>
<tr>
<th>Anion size</th>
<th>L(Å)</th>
<th>W(Å)</th>
<th>H(Å)</th>
<th>V(Å³)</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS-C1</td>
<td>3.1</td>
<td>2.3</td>
<td>2.3</td>
<td>16</td>
<td>-6.85</td>
</tr>
<tr>
<td>TPS-C4</td>
<td>7.6</td>
<td>2.3</td>
<td>2.7</td>
<td>47</td>
<td>-5.96</td>
</tr>
<tr>
<td>TPS-C8</td>
<td>13.1</td>
<td>2.3</td>
<td>2.7</td>
<td>81</td>
<td>-5.08</td>
</tr>
<tr>
<td>TPS-Cy</td>
<td>9.5</td>
<td>3.3</td>
<td>4.7</td>
<td>147</td>
<td>-6.31</td>
</tr>
</tbody>
</table>

*Nominal volume by rectangular approximation*
2.6 Resists preparation for PAG study
Molar equivalent amount of PAG were added to NBHFA-MOM polymer, small amount of amines was added as a quencher, and propyleneglycol-monomethyl ether acetate (PGMEA) was used as a solvent. Typical PAG content was 1.1 wt% relative to NBHFA-MOM polymer in the case of TPS-C1.

2.7 Film thickness measurement of resists
Lambda Ace (Dainippon Screen Mfg. Co., Ltd.) was used for film thickness measurement of resists. Refractive index of 1.502 for the film thickness measurement was decided by spectroscopic ellipsometer ESVG-DUV (SOPRA S.A.).

2.8 Vacuum UV Spectroscopy
Resists were spin coated on MgF2 disks and baked at 90°C 60s prior to analysis. Spin speed was adjusted to produce about 100nm thickness of resist film. VUV spectra of resists films were measured by VUV-200 (JASCO) vacuum ultraviolet spectrophotometer.

2.9 Lithographic evaluation
Imaging tests by 193 nm and 157 nm exposures was made on 160 nm thickness of organic BARC DUV-30J (Brewer Science Inc.), which was baked at 215°C. Common 0.262 N tetramethylammonium hydroxide (TMAH) aqueous solution was used for development. We used 0.55 NA micro-stepper (Nikon corporation) for 193 nm imaging with binary mask to expose 200 nm resists film. 157 nm imaging test was made by the courtesy of Semiconductor Leading Edge Technologies, Inc. (Selete). 0.60 NA micro-stepper (Ultratech Stepper) was used for 157 nm exposure of 150 nm resist film on DUV-30J with alternating phase shift mask.

2.10 Discrimination curve
We measured dissolution rate of resist film of 350 nm thickness coated on silicon wafer by using dissolution rate monitor RDA-790 (Litho Tech Japan Co.). 157 nm exposure was made by open flame exposure equipment VUVES-4500 (Litho Tech Japan Co.). 0.262 N TMAH was also used for the measurement.

3. Results
3.1 Mw and protection ratio study

Before starting the PAG study, we examined bake condition, Mw and protection ratio of the NBHFA-MOM polymer to lithographic performance by 193 nm imaging test. We used TPS-C8 PAG for the preliminary study. We found 160°C of postapply bake (PAB) and 130°C of postexposure bake (PEB) was the optimum condition to achieve higher resolution and avoiding t-top shape. It was concluded that Mw around 11000 and protection ratio around 25 % was optimum for NBHFA-MOM polymer based resists.

3.2 Vacuum UV Spectroscopy
Fig.3 shows vacuum UV spectra of resists for PAG study. We didn’t observe remarkable influence of anion type on spectra.
We measured dissolution rate of resists for PAG study by changing dose of 157 nm exposures (Fig. 4). For the purpose of minimizing dissolution rate measurement error accompanied with thinner film thickness, we coated resists with 350 nm thickness. Resulted discrimination curves were quite similar regarding maximum and minimum dissolution rates, and contrast defined by \( \frac{d(\log R)}{d(\log E)} \), wherein \( R \) is dissolution rate and \( E \) is exposure dose.

**By the courtesy of Selete**

Fig. 6. 157 nm Imaging Results
150 nm resist film on 160 nm of DUV-30J. PAB 160°C, PEB 130°C, 157 nm exposures by 0.60 NA, sigma 0.30, Alt. PSM
Therefore we concluded that dissolution rate of resists based on NBHFA-MOM polymer was not affected by difference of anion type of PTS-PAG.

3.4 Imaging property

Fig. 5 showed results obtained by 193 nm imaging experiments. We found significant difference of resolution capability between anions of PTS-PAG. PTS-C8 and PTS-Cy showed higher resolution capability and better profile than those of PTS-C1 and PTS-C4 though photo speed did not show remarkable difference.

Quite similar results were obtained by 157 nm exposures (Fig.6) except profile. In general, we observed more round profile for the 157nm imaging. We supposed the observed difference of profiles was caused by difference in types of exposure field. In 193 nm imaging we used so called “dark field reticle” wherein printed pattern was surrounded by unexposed area. The dark field reticle usually gave t-top pattern comparing with “bright field reticle” wherein pattern is surrounded by exposed area.

As no remarkable difference was observed in the vacuum UV spectra and the discrimination curves, the results clearly suggested that differences of resolution capability and profile were caused by difference of anion of PTS-PAG.

4. Discussion

Considering reported works [10, 11], we recognized that interaction between PAG and polymer was quite significant to explain our experimental results. We supposed that difference of anion of TPS PAG likely provided difference of polar interaction of PAG with NBHFA-MOM polymer, and differences of diffusion behavior of PAG and photo generated acid in the polymer matrix. Also we assumed that larger anions could affect Tg of resists. However due to lack of thermal analyses of NBHFA-MOM polymer, TPS-PAG and resists examined, we could not made precise discussions.

When we just considered the calculated pKα and anion size of examined four PTS PAG on Table 1, the observed imaging results could be explained by difference of diffusion length of TPS PAG. We assumed that large anion of TPS-Cy might give appropriate diffusion length than TPS-C4. When we decreased PEB temperature for TPS-C4, which caused less diffusion length of PAG, a little bit of improvement of resolution was observed. But it was still worse than that observed for TPS-Cy. Less resolution observed for TPS-C1 also suggested that unfavorable excess diffusion into unexposed small pattern.

5. Conclusion

It was found that larger anion size of PTS PAG could provide higher resolution capability and better profile for resists based on NBHFA-MOM polymer. Further studies, especially thermal analyses will be required to recognize the role of anion of TPS PAG, and to design high performance 157 nm resists.

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