Evaluation of Non-ionic Photoacid Generators for Chemically Amplified Photoresists

Toshikage Asakura, Hitoshi Yamato, and Masaki Ohwa

*Technology Center Electronic Materials, Coating Effects Segment,
Ciba Specialty Chemicals K.K., 7-1-13, Doi-cho, Amagasaki, Japan 660-0083*

As reported previously, we developed a novel oxime sulfonate type of photoacid generator (PAG), 2-[2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1-(nonafluorobutylsulfonyloxyimino)-heptyl]-fluorene (DNHF), which generates a strong acid (nonaflc acid) by light irradiation and is applicable to chemically amplified ArF photoresists. Recently we have prepared two DNHF analogues with different fluoroalkyl chains adjacent to the oxime moiety, 2-[2,2,3,3,4,4,4-heptafluoro-1-(nonafluorobutylsulfonyloxyimino)-butyl]-fluorene (HNBF) and 2-[2,2,3,3,4,4,5,5-octafluoro-1-(nonafluorobutylsulfonyloxyimino)-pentyl]-fluorene (ONPF), and investigated the structure effect. The change of the fluoroalkyl chain did not have a strong impact on photo-efficiency and transparency at 193nm and these PAGs demonstrated superiority to triphenylsulfonium nonaflate (TPSNF) with respect to these criteria. On the other hand, different behaviors were observed in the coating property and contact angle measurement of the photoresists containing these PAGs. The hydrogen atom at the end of the fluoroalkyl chains of DNHF and ONPF was found to have a role in improving the coating property. These non-ionic PAGs were less risky for contamination on the surface of the lens due to insolubility in water. In addition, the effect by these PAGs on increasing hydrophobicity of the photoresist surface was identified. These results suggest that the newly developed non-ionic PAGs are suitable for ArF immersion lithography.

Keywords: non-ionic, photoacid generator, ArF, strong acid, chemically amplified resist

1. Introduction

The development of ArF immersion lithography is proceeding with an astonishing speed, and has eliminated F₂ lithography from the roadmap of semiconductor manufacturing for design rule of 45nm node (hp 65nm) and below [1]. This dynamic movement is due to the fact that a lot of key technology components of ArF dry lithography can be utilized in ArF immersion lithography, e.g., lens material and resist materials. However, the critical difference between ArF dry and ArF immersion lies

in the contact of the resist layer with a liquid medium in immersion lithography. For the 1st generation of ArF immersion, water is applied as the liquid medium due to its high refractive index ($n = 1.44$) and high transparency at 193nm. Hence the interaction of the resist layer with water may cause leaching of hydrophilic resist components, e.g., photoacid generator (PAG) and amine, into water or penetration of water into the resist layer. These potential phenomena raise the concerns of optical property change of the liquid medium and lens

contamination by leaching components from the resist layer, and change of resist performance. Owa et al have investigated the influence of chemical contamination on a projection lens under irradiation, and proposed the specifications for the leaching of PAG and amine to be below $2.5\text{ng}/\text{cm}^2/\text{s}$ and $1.0\text{ng}/\text{cm}^2/\text{s}$, respectively [2]. One of the approaches to solve the issue is an application of topcoat on the resist layer. There are several studies to develop the topcoat. It is sure that the PAG leaching can be depressed by applying topcoat. However, the topcoat has introduced a new problem in that PAG leaching to the topcoat layer is accompanied by a T-top profile in the resist layer [3]. On the other hand, an interesting result was reported that immersion specific defects were decreased to a large extent by increasing hydrophobicity of the topcoat, indicating that ArF immersion lithography with topcoat is coming close to practical use [4]. However, the lithography with topcoat is not the best option from the view points of cost and throughput, and a topcoat-less process is demanded for future ArF immersion lithography.

For ArF dry lithography, sulfonium salts like triphenylsulfonium (TPS) nonaflate are widely employed. These ionic PAGs were not expected to leach easily to water, but there are several reports on the leaching of sulfonium salts [5-7]. Dammel et al investigated the leaching of TPS with different anions, i.e., triflate, nonaflate and perfluorooctanesulfonate [5]. They observed a significant amount of leaching of these PAGs and found that more hydrophobic anions can lead to a decrease in saturation concentration. To decrease the PAG leaching, an increase in hydrophobicity of PAG is thought to be effective approach, and a non-ionic PAG looks promising to realize topcoat-less ArF lithography. There are several non-ionic PAGs for KrF lithography such as imidosulfonate, diazomethanedisulfone, and o-nitrobenzylsulfonate. However, few non-ionic PAGs are applicable for ArF lithography because a strong acid is needed to catalyze the cleavage of an ester group in a hydrophobic polymer matrix [8]. It is quite a challenge to make a stable non-ionic PAG that releases strong acid upon light exposure.

We have been investigating various oxime sulfonates type PAGs [9-14], which are adjustable to the target applications and exposure wavelength range by modification of chromophores and acid moieties. Additionally, non-ionic oxime sulfonates show good solubility in various solvents. Recently, we have newly developed and reported a thermally and storage stable non-ionic PAG, DNHF, which can release strong acid, i.e. perfluorobutanesulfonic

acid [12-14]. We have prepared a series of DNHF analogues with different fluoroalkyl chains adjacent to the oxime moiety, and we have investigated the influence of the structure on resist sensitivity, coating property and hydrophobicity of the resist formulation.

2. Experimental

2.1 Photochemical Properties in Model Formulation

2.1.1 Evaluation in ArF Model Formulation

Photochemical properties, such as sensitivity and DRM, were measured in an ArF model resist formulation with VUVES 4500 mini, Litho Tech Japan, as an exposure tool. The positive tone resist utilized a copolymer of γ -butyrolactone methacrylate and 2-methyladamantyl methacrylate (62/38mol-%, Mitsubishi Rayon Co., Ltd) having a weight average molecular weight of 11800. The composition of the formulation is described in Table 1.1.

The resist was spin-coated at 370nm thickness on silicon wafers on which the bottom antireflection coating with ARC-29, Nissan Chemical, was applied in advance at 82nm thickness and prebaked at 120°C for 60seconds. After exposure with various exposure doses, a post exposure bake was applied at 120°C for 60seconds and the resist was then developed in 2.38% aqueous tetramethyl ammonium hydroxide solution for 120seconds.

The PAGs in the model formulation were coated on quartz plates at 370nm thickness and the absorbance of the formulation at 193nm was measured with an Hitachi U-3300 spectrometer.

Dissolution rate monitoring (DRM) was carried out with the ArF model resist formulation described above. The resist was exposed with VUVES 4500 mini under dry condition. After post exposure bake, dissolution rate of the resist was monitored by RDA-790, Litho Tech Japan.

Table 1. 1. Composition of the formulation

Components	Parts
Binder polymer	100
PAG	2
PGMEA	700

2.1.2 Evaluation in EB Model Formulation

Photo speed and dark erosion were measured in an EB model resist formulation with JBX-5000SI, JEOL, as an EB exposure tool. The positive tone resist utilized a copolymer of a copolymer of (4-hydroxystyrene), styrene and tert-butyl acrylate (69/22/9 mol-%, Maruzen Petrochemical Co., Ltd) having a weight average molecular weight of 9850. The composition of the formulation is described in Table 1.2.

The resist was spin-coated at 200nm thickness on silicon wafers treated with hexamethyldisilazane and prebaked at 120°C for 60seconds. After exposure with various strength of electron beam (e-beam), a post exposure bake was applied at 120°C for 60seconds and the resist was then developed in 2.38% aqueous tetramethyl ammonium hydroxide solution for 60seconds.

Remaining thickness of the resist was measured optically with an Axiospeed film thickness measurement instrument from Zeiss. The resist comprising ONPF was compared with TPSNF and bis(p-tert-butylphenyl)iodonium trifluoromethanesulfonate (BTINF)

Table 1. 2. Composition of the formulation

Components	Parts
Binder polymer	100
PAG	4
PGMEA	1175

BTINF

2.2 Coating property

For the evaluation of coating property of the photoresist formulations containing these PAGs, the ArF model formulation mentioned above was employed except for a PAG loading of 6parts instead of 2parts. In order to investigate the effect of surfactants on the coating property, 0.07parts of a surfactant was added into the formulation. The formulation was spin-coated at a 370nm thickness on silicon wafers on which ARC-29 was applied and prebaked as described above. The evaluation of striations was carried out by visual observation.

2.3 Contact angle measurement

Water contact angles on the photoresist, which

was spin-coated on silicon wafer and prebaked at the condition described above, were measured with contact angle measurement equipment (CA-VE) from Kyowa Interface Science using deionized water at room temperature, ca. 23 °C.

In case of the contact angle measurement, the two types of base resins as shown below were employed. In addition to Polymer A mentioned above, Polymer B was radically synthesized in-house from the corresponding monomers purchased from Daicel, Idemitsu and Osaka Yuki. The weight average molecular weight of Polymer B was 14900. PAG content was 10% of resin.

Polymer A

(m: n = 62: 38)

Polymer B

(p: q: r = 50: 20: 30)

2.4 Chemical contamination under exposure

Five mg of PAG was put into 1ml of deionized water and stirred over night. In the case of TPSNF, the PAG was completely dissolved to give a clear solution at the concentration of 0.5wt %. In contrast, there remained insoluble PAG in water in the case of HNBF, ONPF and DNHF. The residual PAG was removed by filtration with a 0.2μm membrane filter and the filtrate saturated with PAG was employed for the experiment of contamination under exposure.

On a 1-inch quartz plate, an o-ring (Echo®-Oring P-20 from AWI MACH) made with fluoro resin was set. Then the solution was poured into the ring, covered with a 1-inch quartz glass and exposed with an ArF excimer laser at 1mW intensity for 30minutes. The evaluation of contamination was carried out by visual observation.

3. Results and Discussion

3.1 Absorption and sensitivity in ArF model formulation

In order to investigate the physical and photochemical property of a PAG for resist application, each PAG was formulated in an ArF model formulation with 2wt% against polymer. As the polymer matrix, a polymethacrylate platform was employed, which has high transparency at 193nm. The resist layer was exposed by ArF laser (193nm) for the estimation of sensitivity. In lithography studies, the "Dose to Clear" (E_0) is commonly used as a measure of resist sensitivity. The E_0 is the dose just sufficient to completely remove the resist film with 60seconds development. A smaller required dose means the resist formulation is more sensitive. The three non-ionic PAGs, HNBF, ONPF and DNHF, showed similar sensitivity but are less sensitive than TPSNF as shown in Table 2. The higher sensitivity of TPSNF is probably attributable to the high absorption of the formulation. The non-ionic PAGs show superiority in transparency at 193nm compared with TPSNF and their absorption in the formulation is about one-third that of TPSNF.

As mentioned above, the high sensitivity of TPSNF is due to its high absorption. However,

the photochemical efficiency of a PAG can't be determined only by sensitivity because the light intensity absorbed by each PAG is not identical. In order to estimate a relative photo-efficiency of a PAG in the formulation, the P-parameter is a simple and useful index, which was introduced by G. Pohlers et al [15]. The P-parameter is derived from the equation: $P = E_0 \times [\text{fraction of incident light absorbed by PAG}]$. A smaller P-parameter indicates higher photo-efficiency of the resist formulation. It is obvious from Table 2 that the three non-ionic PAGs more effectively generate acid in the formulation than TPSNF. ONPF showed less photo-efficiency than the other two non-ionic PAGs to a small extent but the reason has not been elucidated.

3.2 DRM measurement

For the evaluation of the photoresist performance without a stepper, dissolution rate monitoring (DRM) is a good tool to predict the photoresist profile. In addition, DRM is useful to analyze the dissolution property of the photoresist from a fundamental viewpoint. The DRM measurements were conducted for the ArF model formulations composed of the typical polymethacrylate polymer with HNBF, ONPF or DNHF, respectively. Figure 1 represents the

Table 2. Absorbance, E_0 and P-parameter

PAG	E_0 (mJ/cm ²)	Abs(193nm) in formulation (μm^{-1})	P-parameter
HNBF	2.7	0.08	0.22
ONPF	2.9	0.10	0.29
DNHF	3.0	0.07	0.21
TPSNF	1.6	0.29	0.46

Figure 1. DRM results of ArF model formulations with non-ionic PAGs

Figure 2. Sensitivity measurement of PAGs in EB model formulations

dissolution rate of the photoresists as a function of the exposure dose. A significant difference was not observed in $R_{\max}$, $R_{\min}$, and the slope of the discrimination curves in the current model formulation, suggesting that the three non-ionic PAGs give a similar photoresist performance.

3.3 Sensitivity in EB model formulation

In order to investigate the applicability of a PAG into EB resist application, the three PAG, ONPF, TPSNF and BTINF was formulated in a model formulation. As for the polymer matrix, a copolymer of (4-hydroxystyrene), styrene and tert-butyl acrylate commercially available from Maruzen Petrochemical Co., Ltd was employed, which is known as a base polymer for DUV resists. In this case of the EB resist, E_0 is used as a measure of resist sensitivity as well. The experimental results, contrast curves, were shown in Figure 2. The remaining resist thickness was plotted against the applied energy of e-beam. Among the three PAGs, TPSNF showed highest sensitivity. ONPF and BTINF, showed similar sensitivity but dark erosion of ONPF is more than that of BTINF. This erosion would be decreased by employing more hydrophobic polymer matrix, such as a copolymer with more ratio of tert-butyl acrylate. Interestingly Fedynyshn et al. found that the dissolution inhibition effect of PAG is responsible for the increase of the innate material roughness in the ESCAP type of photoresist as employed here. [16] Therefore the less dissolution inhibition with ONPF than BTINF observed here might positively affect lithography profile in terms of roughness.

Szmanda et al. reported the evaluation results of several PAGs in the exposure of EUV and e-beam. [17] In the report, EUV exposures yielded very similar trends to those seen in e-beam irradiation.

Thus the fact that ONPF is sensitive to EB tells us that the oxime sulfonates would be applicable to the resists for EUV lithography.

3.4 Coating property

Solubility of PAG in common organic solvents employed for resist application is one of the basic criteria. As reported previously, DNHF showed very high solubility (> 30wt/v %) in PGMEA, ethyl lactate and cyclohexanone. Similarly, HNBF and ONPF were very soluble in these solvents as summarized in Table 3. The high solubility of PAG in the organic solvents enlarges the flexibility of formulation and reduces a risk of particle generation during resist storage. However, it was found that a high loading amount of DNHF in the formulation with Polymer A caused an issue in coating property, i.e., a few striation patterns appeared by spin-coating of the formulation at the loading amount of 6% against polymer content, while no striation was observed at the loading amount of 2 and 4%. The coating property of HNBF and ONPF (Figure 3) was also examined at the loading amount of 6% in the combination of Polymer A. A similar result was obtained when comparing an ONPF containing film to a film with DNHF. However, a film with HNBF clearly showed much striation under the same condition as shown in Figure 3(b). The difference of HNBF from the other two PAGs is the lack of a hydrogen atom at the end of the fluoroalkyl chain. Hence, it is assumed that this hydrogen atom has a critical role to improve the compatibility of PAG with Polymer A.

Generally speaking, the coating property of the resist layer can be improved by the addition of a small amount of surfactant and/or leveling reagents. We have investigated the effect of commercially available surfactants on the coating property. One

Table 3. Solubility in organic solvents

PAG	PGMEA	Ethyl lactate	Cyclohexanone
HNBF	> 30 %	12 %	> 30 %
ONPF	> 30 %	> 30 %	> 30 %
DNHF	> 30 %	> 30 %	> 30 %

(a) ONPF without surfactant

(b) HNBF without surfactant

(c) HNBF with Fluorolink L

Figure 3. Coating property of photoresist formulations

Surfactant	X group	Molecular weight
Fluorolink A10	-CONHC ₁₈ H ₃₇	1200 - 2000
Fluorolink L	-COOCH ₃	1900 - 2300
Fluorolink L10	-COOCH ₃	1000 - 1500
Fluorolink T	-CH ₂ OCH ₂ CH(OH)CH ₂ OH	2200 - 2400

Scheme. Structures of Fluorolink**Table 4. Coating property of formulations including PAG**

Surfactant	PAG		
	HNBF	ONPF	DNHF
None	NG	Moderate	Moderate
Megafac R-08 (DIC)	NG	Good	Good
Megafac R-30 (DIC)	NG	Good	Good
Surflon KH-40 (Seimi Chem)	NG	Good	Moderate
Surflon S-381 (Seimi Chem)	NG	Good	Good
Surflon S-393 (Seimi Chem)	NG	Good	Good
Surflon S-141 (Seimi Chem)	NG	Moderate	Moderate
Surflon S-145 (Seimi Chem)	NG	Moderate	Moderate
Fluorolink A10 (Solvay)	Moderate	Good	Good
Fluorolink L (Solvay)	Moderate	Good	Good
Fluorolink L10 (Solvay)	Moderate	Good	Good
Fluorolink T (Solvay)	Moderate	Good	Good
Eftop EF-351 (Jemco)	NG	Good	Good
Eftop EF-352 (Jemco)	NG	Good	Good
Eftop EF-802 (Jemco)	NG	Good	Moderate

Good: No visible striation, Moderate: Moderate striation, NG: Much striation

example is displayed in Figure 3(c), which obviously demonstrates that the poor coating property of HNBF is improved by the addition of the small amount of Fluorolink L in the formulation. Other results are summarized in Table 4. Several surfactants have been found to be effective in

improving the coating property. Although the information on chemical structures of almost all surfactants is not available, the structures of Fluorolink are published as shown in the scheme below, which have fluoroalkyleneoxide units as the main component.

Figure 4. Contact angle of water on ArF model formulations

3.5 Contact angle measurement

On the development of immersion lithography, defect generation is one of the most critical issues. Water droplets that remain on the surface of resist or topcoat materials after exposure and stage scanning is one of the causes for the immersion specific defects. Hydrophobicity of the resist and topcoat surface has been found to play an important role in reducing the immersion specific defects. In addition, the high hydrophobic property of the surface enables high stage scan speed, leading to high throughput [2a]. Hence the effect of the non-ionic PAGs on the resist surface property has been investigated.

Three non-ionic PAGs, HNBF, ONPF, DNHF, and ionic PAG, TPSNF, were each formulated with two polymer systems. Compared to Polymer A, Polymer B is less hydrophobic due to a hydroxyl group on the adamantyl moiety. The hydrophobicity of the resist surface was estimated by the contact angle of a water droplet on the surface. The results are represented in Figure 4(a) and 4(b). In the case of Polymer A, the effect to increase the hydrophobicity by the addition of a non-ionic PAG was observed but was not so large because the hydrophobicity of Polymer A itself was rather high. On the other hand, in the case of Polymer B, the impact of the non-ionic PAG on the surface property was significant. The hydrophobicity was drastically increased especially by the addition of HNBF. The other two non-ionic PAGs have a smaller effect on the hydrophobicity compared with HNBF. This suggests that the hydrogen atom on the end of the fluoroalkyl chain of ONPF and DNHF has an influence to reduce the hydrophobicity of the fluoroalkyl chain. TPSNF was confirmed to have the effect of decreasing the hydrophobicity by its ionic characteristic in the formulation with Polymer A. However, the hydrophobicity of Polymer B itself was not so high that the decrease of hydrophobicity

by the addition of TPSNF was not substantial. It was found that novel non-ionic PAGs work well to increase the hydrophobicity of the resist surface, especially when the resist is comprised of a hydrophilic polymer matrix.

3.6 Chemical contamination under exposure

There still remains the concern that chemical components may come out of the resist into a liquid medium, resulting in a contamination on the surface of the bottom lens of the exposure tool. Since the leaching components are water-soluble, they may be washed out by water flow and thereby avoid contamination of the exposure tool. However, the products derived from decomposition of the leaching components by light exposure may contaminate the lens surface. The chemical contamination on the quartz glass substrate by a PAG has been investigated under light exposure. TPSNF was dissolved in water with the concentration of 0.5% and monochromatic 193nm light was exposed to the solution through quartz glass. After the light of 1mW intensity was applied for 30minutes, contamination was observed on the quartz substrate as shown in Figure 5. It seems that TPSNF decomposed by light to produce water-insoluble materials, which adhered to the surface of the quartz glass. On the other hand, the non-ionic PAGs, HNBF, ONPF, DNHF, do not dissolve in water at the concentration of 0.5% [12]. Hence, the water solutions saturated with each non-ionic PAG were prepared and the monochromatic light was exposed to each one separately. However, no contamination was observed on the surface of the quartz. As reported previously [13, 14], any significant leaching of HNBF and DNHF was not detected in the water medium from a model formulation ($< 2.6 \times 10^{-12}$ mol/cm²; detection limit). These results suggest a low risk of chemical contamination on the surface of the bottom lens by

Figure 5. Contamination on quartz by TPSNF after light irradiation

the newly developed non-ionic PAGs.

4. Conclusion

The oxime sulfonate type of PAGs, HNBF, ONPF and DNHF, were found to be superior to the conventional ionic PAG, TPSNF, with respect to transparency and photo-efficiency at 193nm. In addition, these non-ionic PAGs have the effect to increase the hydrophobicity of the photoresist formulation, and they are less risky for contamination on the surface of the lens due to insolubility in water. Our results suggest that these non-ionic PAGs are suitable for ArF immersion lithography. They have different fluoroalkyl chains adjacent to the oxime moiety. This difference did not have a strong effect on photo-efficiency and transparency at 193nm. However, the hydrogen atom at the end of fluoroalkyl chains of DNHF and ONPF played a role in improving the coating property.

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