

# Oxime Sulfonate Chemistry for Advanced Microlithography

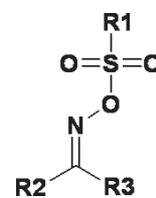
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Oxime sulfonate compounds are one of the important chemistries as a photoacid generator for advanced lithography application and practically used in mass production of semiconductor chips. This chemistry is adjustable for various applications like g-/h-/i-line, KrF and ArF lithography. This paper describes an overview of oxime sulfonate chemistry for semiconductor resist applications.

## Introduction

The development of semiconductor chips is making progress with astonishing speed, producing electronic apparatuses that are smaller, have higher speeds, and offer better performance. This dynamic advancement is significantly attributable from the development of photolithography technology. In an early era of integrated circuits (IC), a manufacturing lithography technique was introduced with a light source of g-line wavelength (436 nm). For further miniaturization of IC, the light source wavelength gets shorter and shorter [i.e., i-line (365 nm), KrF (248 nm) and ArF (193 nm)]. Currently, ArF immersion is actively investigated as the most advanced technology, and EUV (13.5 nm) is discussed as the next generation lithography. When the g-line and i-line light sources were used, the resist comprised diazonaphthoquinone (DNQ) as a photosensitive component.<sup>1</sup> However, after introduction of KrF laser, the DNQ resist cannot be employed for advanced lithography because the

absorption of DNQ resist at 248 nm and 193 nm is too high to transmit the light throughout the resist to the bottom. As an alternative technology, a chemically amplified (CA) resist was developed.<sup>2</sup> The CA resist is composed of polymer bearing acid-labile groups and photoacid generator (PAG). Photolytic decomposition of PAG during light exposure generates acids in the CA resist. This acid acts as catalyst to facilitate de-protection reaction of ester group or acetal group of polymer, rendering polymer matrix alkaline-soluble. For achieving desired resist performance such as resolution, depth-of-focus, line edge roughness and etching resistance, the acid-labile polymers were intensively studied and developed notably. For further improvement of the CA resist, a PAG was the key ingredient. Several chemistries were extensively investigated as the photoactive component for the CA resists (e.g., iodonium sulfonate, sulfonium sulfonate, diazomethane-disulfone, N-sulfonyloxymido compounds, nitrobenzyl sulfonate, etc.).<sup>3</sup> Oxime sulfonate chemistry was used due to its potential ability as latent acid and its wide structure variation.



*Oxime sulfonate*

TABLE 1

## PAG ABC series

PAG	Photoacid generated
A	n-Propanesulfonic acid
B	n-Octanesulfonic acid
C	p-Toluenesulfonic acid

Several oxime sulfonate compounds, aiming to g-/h-/i-line, KrF and ArF lithography, were developed. In addition, a sensitization of oxime sulfonate was investigated. These studies are described in this paper.

## PAG for g-/h-/i-line Application

Recently, there have been demands for broadband and i-line resist with high sensitivity, high resolution and thickness. DNQ resist has been widely used for broadband and i-line applications so far, but its performance does not satisfy such new demands. The CA resist is suitable for these applications. Chloromethyl triazines with extended conjugation are known as suitable PAGs for g-/h-/i-line exposure.<sup>4</sup> However, hydrochloric acid, photochemically generated from chloromethyl triazine, is highly volatile

and corrosive and is a concern with potential damage of the manufacturing equipment. Since sulfonic acids are less volatile, less mobile and less corrosive, they were therefore preferred over hydrochloric acid in the resist applications. Though only a few sulfonic acid generators sensitive up to g-line were known, oxime sulfonate type PAG was investigated. This chemistry was adjusted to the target applications and exposure wavelength range by selecting from a wide range of chromophores and acid moieties.

Berner *et. al.* reported oxime sulfonate as a latent acid catalyst for coating application<sup>5</sup>, but such compounds do not have absorption in a longer wavelength. Aiming for g-/h-/i-line application, IRGACURE<sup>®</sup> PAG ABC series (Table 1) was

developed.<sup>6</sup> Figure 1 shows UV absorption spectrum, indicating sufficiently red-shifted absorption profile over g-line (436 nm) with the  $\lambda_{max}$  at 405 nm. This red-shifted profile is attributable from the extended conjugated system by combination of phenyl ring and quinoide structure of thiophene ring. With the negative tone model formulation, the PAG ABC series showed a good sensitivity not only with i-line exposure, but also with g-line exposure.

As  $\pi$ -conjugation of an organic molecule is extended, the solubility of the molecule usually becomes lower. However, PAG ABC series retained a good solubility above 15% in PGMEA as summarized in Table 2. The good solubility of PAG minimized the risk of particle generation during resist storage and improved formulation flexibility.

Figure 2 displays a change of UV absorption in acetonitrile solution upon exposure to 436 nm monochromatic light. A distinctive absorption at 255 nm emerged and the absorption above 420 nm completely disappeared during exposure. The quantum yield of photolysis,  $\phi_d$ , was determined from the absorption decrease at 436 nm, indicating that PAG A was 0.13. Similarly the amount of acid generated upon exposure was determined by the indicator dye method. In Figure 3, the decrease of the normalized absorption at 436 nm and the normalized molar acid concentration (relative to initial molar PAG concentration) of the photochemically generated acid were plotted against exposure time. It was found that the decrease of absorption at 436 nm (photobleaching) was equal to the generated acid concentration when both were normalized to the initial molar PAG concentration. This suggests that photodecomposition of PAG ABC series quantitatively generates acid. Therefore, the quantum yield of photolysis,  $\phi_d$ , corresponds

FIGURE 1

## UV absorption of PAG A

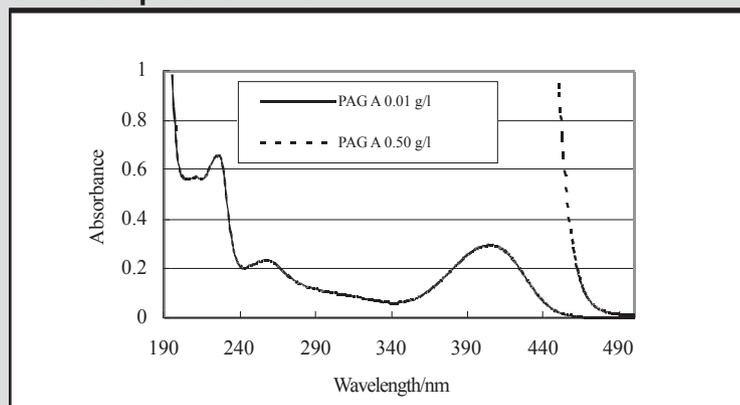


TABLE 2

Solubility in PGMEA

PAG	Solubility (%)
A	20
B	> 30
C	17

directly to that for acid formation,  $\phi_a$ , thus  $\phi_a/\phi_d = 1$ .

The reported  $\phi_a/\phi_d$  ratios for oxime sulfonates were found in the range of 0.6-0.8.<sup>7</sup> Hence, it was concluded that the PAG ABC series provides good or superior photoacid generation efficiency, based on good acid conversion yield.

The storage stability of PAG is one of the critical requirements for CA resist application because even a small amount of acid can cause degradation of CA resist. The stability of the PAG ABC series was evaluated by monitoring acid concentration in the sample stored at various temperature at frequent intervals (Figure 4). No acid formation was observed after more than one-year in storage even at 40°C. When the sample was stored at 4°C, the PAG ABC series was stable for more than five years. This evaluation is continuing.

PAG for KrF Application

When KrF excimer-laser (248 nm) was introduced as the light source for resist application, the conventional DNQ resist could not be employed due to a high absorption of novolak polymer matrix and DNQ molecules. Therefore, the CA resist, comprising polyhydroxystyrene (PHS)-based polymer and PAG, was developed for KrF lithography. There are two polymer platforms with different acid-labile groups. One is acetal-type polymer (i.e., PHS partially protected with acetal group). The other is

ESCAP-type polymer (i.e., co-polymer of PHS and tert-butyl methacrylate). The acetal-type polymer can be deprotected below 110°C at post-exposure baking (PEB), while the ESCAP-type

polymer needed to be heated in the range of 120-130°C.

The PAG ABC series was thermally stable up to 155°C in the neat form, but the stability was lowered to 140°C in a polymer matrix. This PAG was stable enough for the application of acetal-type KrF resist. On the other hand, there is a risk in its application for ESCAP-type formulation in terms of thermal decomposition of PAG at PEB.

The thermal stability of oxime sulfonate was studied and a thermally stable KrF PAG D was developed.<sup>8</sup> This compound possessed trifluoromethyl group adjacent to oxime group, which

FIGURE 2

UV absorption of change of PAG ABC series upon exposure

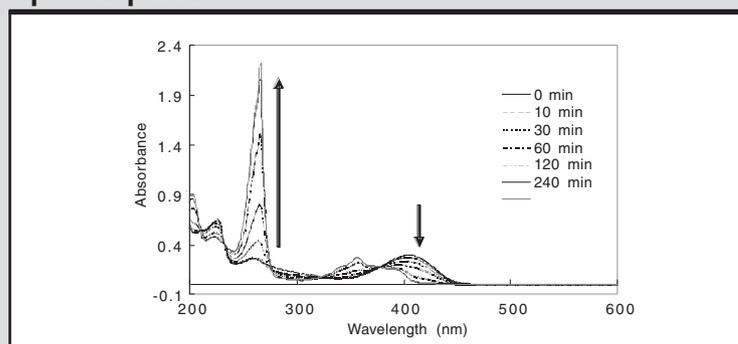
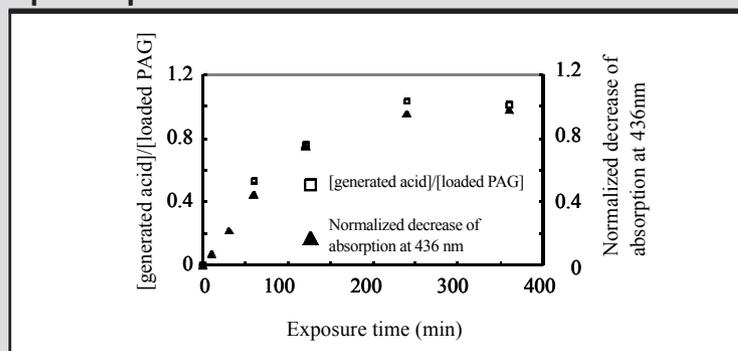
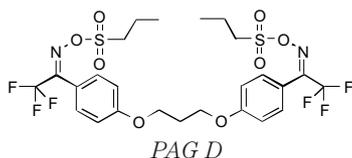


FIGURE 3

Acid generation and UV change of PAG ABC series upon exposure



stabilizes this molecule. PAG D was stable up to 188°C even in a polymer matrix and more than 200°C in a neat form as shown in Figure 5. Therefore, this PAG can be employed in both acetal- and ESCAP-type formulations.



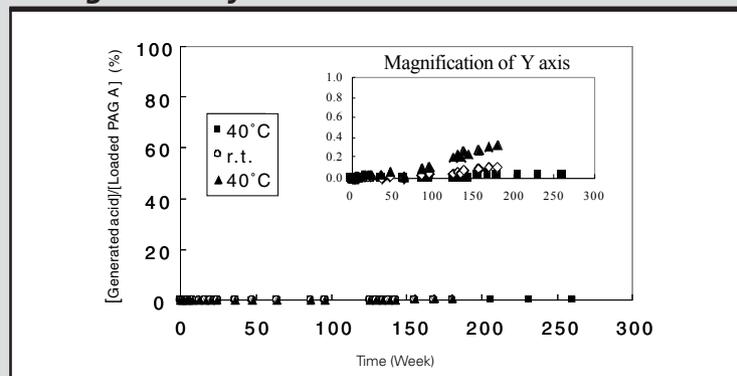
As can be seen from the UV absorption spectrum in Figure 6, PAG D had an absorption valley around 248 nm and showed a relatively low absorption at the wavelength of KrF lithography. Such a low absorption combined with high sensitivity is a highly desired property, because a low-overall absorbance ensures uniform exposure throughout the whole thickness of the resist. Compared to other PAGs typically used for KrF lithography such as triphenyl-sulfonium salt (TPS) and diazodisulfone (DAS), PAG D showed balanced behavior with respect to a number of application-relevant properties as KrF PAG as summarized in Table 3.

### PAG for ArF Application

With the polymer development for ArF formulation, a methacrylate unit, bearing aliphatic cyclic group such as adamantyl, was incorporated as an acid-labile group to improve etch resistance and transparency at 193 nm. As a result, PAG with a strong acid release was required, because the cleavage of ester bonding of the polymer matrix (e.g., 2-methyl-adamantyl methacrylate) was a key reaction during the lithography process. The oxime sulfonate compounds with a strong acid such as perfluoroalkyl-sulfonate were investigated. Usually such compounds were found to not be so stable because the perfluoroalkyl-sulfonate is a good leaving group. For

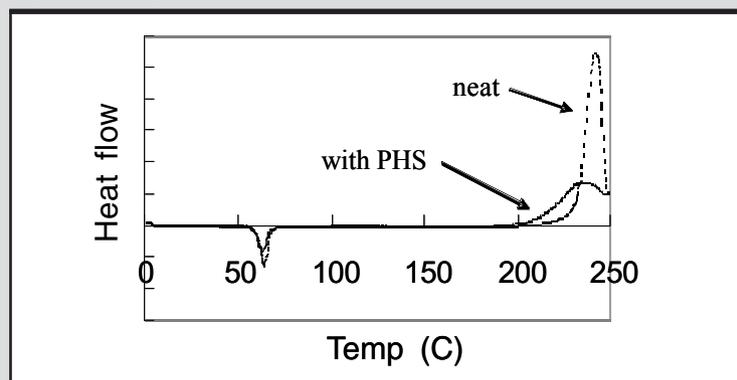
## FIGURE 4

### Storage stability of PAG A in neat form



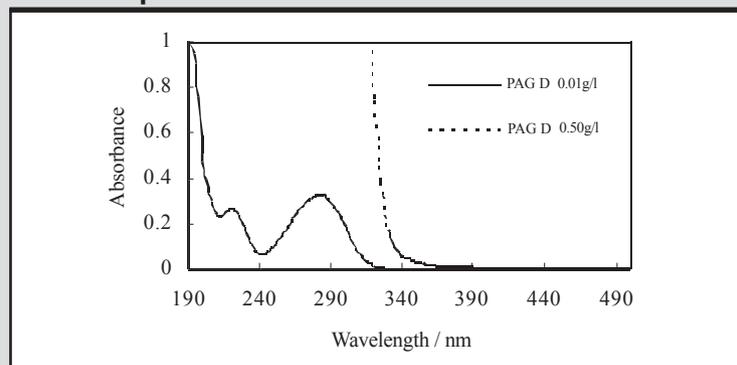
## FIGURE 5

### DSC curves of PAG D



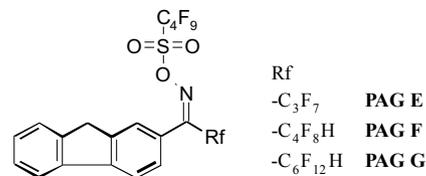
## FIGURE 6

### UV absorption of PAG D



instance, an attempt was made to synthesize the PAG ABC series with perfluoroalkylsulfonate, but the target compound was degraded during the purification and not

isolated as a pure material. In the case of PAG D analogue with trifluoromethanesulfonate, the pure compound was obtained, but it was not stable in the presence of amine in solution.



Long perfluoroalkyl group with oxime sulfonate

A fine-tuning of the structure has improved the stability of oxime sulfonate with perfluoroalkylsulfonate, resulting in PAG EFG series compounds.<sup>9</sup> The key structure was a long perfluoroalkyl group next to oxime sulfonate, which stabilized the molecule.

As shown in Figure 7, PAG EFG series was as stable as TPS in the presence of triethanolamine in PGMEA stored at 40°C, while PAG D analogue with trifluoromethanesulfonate degraded to approximately 40% after 28 days. This result suggests that the PAG EFG series is applicable for resist formulation.

The UV absorption spectra of PAG EFG series and TPS at equivalent weight percentage in acetonitrile are presented in Figure 8. The absorbance of PAG EFG series at 193 nm was about one third of that of TPS. The low absorption of PAG EFG facilitated a better resist profile as compared to TPS. The upper limit of PAG concentration in a given resist was a function both of PAG solubility and absorption. Thus, the low absorption and good solubility of the PAG EFG series means increased formulation flexibility for ArF resist.

By monitoring the remaining amount of PAG by HPLC analysis during exposure at 193 nm, the quantum yield of PAG G was estimated as compared with TPS and BPI (di-tertbutylphenyliodonium salt). The result is summarized in Table 4. PAG G gave the highest quantum yield (0.27), which was superior to TPS by 46%. On the other hand, the quantum yield of BPI was quite low, 0.06. The iodonium

TABLE 3

Screening results of PAG D

PAG	Abs <sub>248</sub> <sup>1)</sup> (wt/v%)	Solubility <sup>2)</sup> (wt/v%)	Td in PHS <sup>3)</sup> (C)	E <sub>0</sub> <sup>posi</sup> (mJ/cm <sup>2</sup> )
PAG D	0.091	25	188	1.73
cf. TPS	0.329	1.4	>200	0.27
DAS	0.019	ND	142	5.06

1) 0.01 g/l in AcCN

2) in PGMEA

3) Determined by DSC with equal amount of PHS

FIGURE 7

Storage stability of PAG G in the presence of amine in PGMEA at 40°C

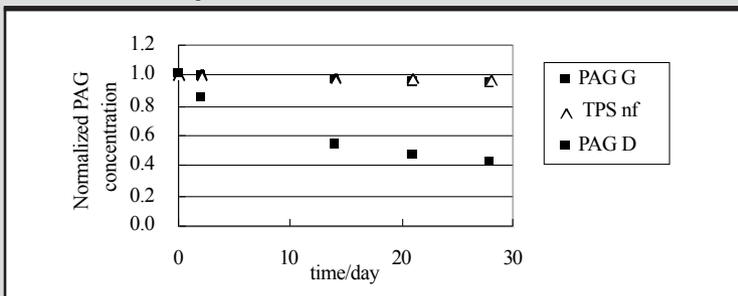
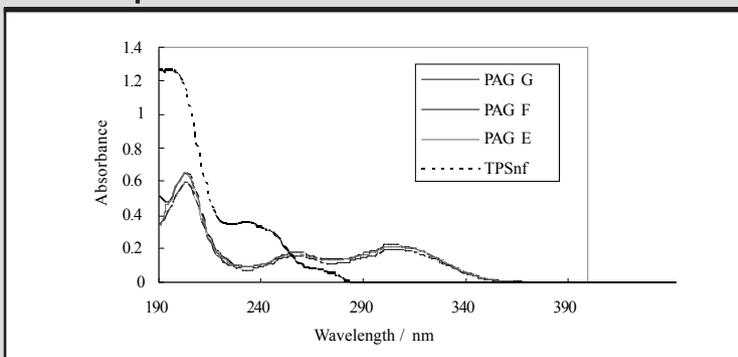


FIGURE 8

UV absorption of PAG EFG series



chromophore was not suitable for ArF lithography from the viewpoint of photospeed.

ArF immersion lithography is becoming the major technology of the next generation for 45 nm node. Water was employed as the immersion medium due to its high-refractive index ( $n=1.44$ ) and high transparency at 193 nm. The demanded properties for PAG in immersion application are non-leaching to water and contribution to reduce immersion specific defects. The evaluation of PAG leaching from ArF model formulation to water revealed that TPS had significant leaching behavior,  $2-9 \times 10^{-11} \text{mol/cm}^2$ . On the other hand, no leaching of PAG EFG series was observed (below detection limit:  $< 2.6 \times 10^{-12} \text{mol/cm}^2$ ) due to non-ionic property.

Water droplets remained on the surface of resist after exposure and stage scanning was one of the causes for the immersion specific defects. Hydrophobicity of the resist surface was found to play an important role to reduce the immersion specific defects. In addition, the high hydrophobic property of the surface enabled high-stage scan speed, leading to high throughput.<sup>10</sup> Figure 9 displays the contact angle of water on ArF model formulation including various PAGs. The addition of PAG EFG series increases the hydrophobicity of resist surface, while the addition of TPS decreases the hydrophobicity. PAG EFG series can contribute to reduce the defects and increase the scan speed. These results suggest that PAG EFG is suitable for ArF immersion lithography.

### Sensitization of Oxime Sulfonate

As described, the use of photolithography with light source of g-/h-/i-line was extensively studied besides the front-end process of

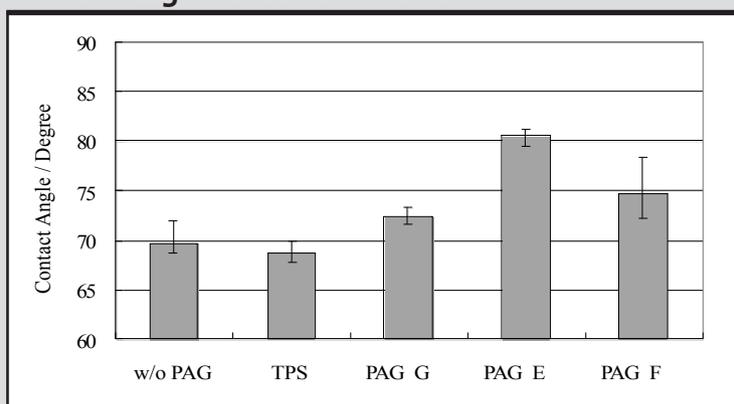
## TABLE 4

### Quantum yield of PAG in acetonitrile

PAG	Quantum yield in solution
PAG G	0.27
TPSnf	0.18
BPInf	0.06

## FIGURE 9

### Contact angle of water on ArF resist



## FIGURE 10

### Sensitivity of PAG D in combination with sensitizers at i-line

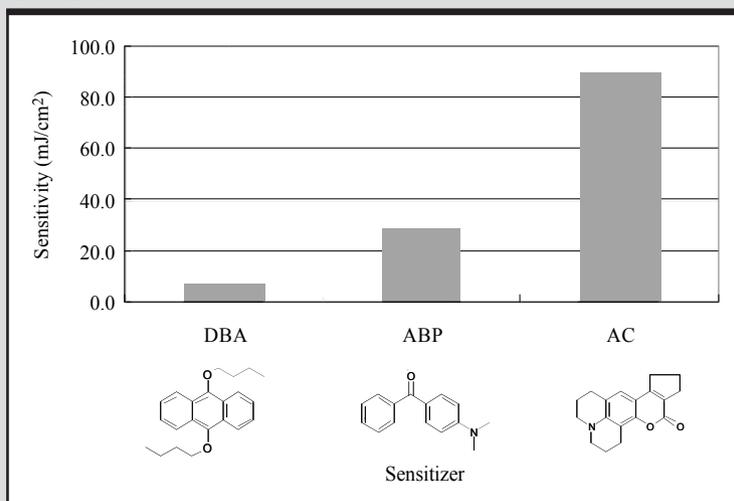
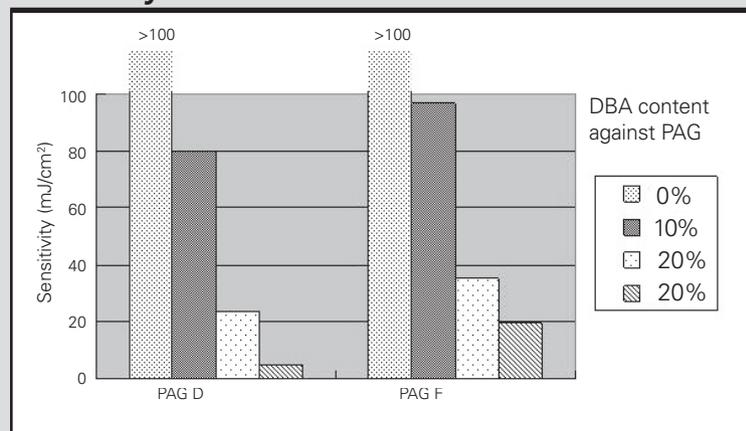


FIGURE 11

## Sensitivity of PAG in combination with DBA at i-line



semiconductor manufacturing. They are aimed for new fields like MEMS (Micro Electro Mechanical Systems), dielectric layer, buffer layer of semiconductor chip, display applications, etc. PAG ABC series was used for these applications, which has red-shifted absorption profile, leading to the direct excitation at a longer wavelength. As an alternative approach, the sensitization ability of oxime sulfonate compounds was investigated.

PAG D had no significant absorption at 365 nm. It did not give any sensitivity with the negative tone formulation upon i-line exposure. To this formulation, various sensitizers with 50 wt% against PAG were added and their sensitivity at i-line was measured, respectively. The result of the sensitivity was presented in Figure 10. Amino-coumarin (AC), aminobenzophenone (ABP), and anthracene (DBA) compounds had an effect on the sensitization of PAG D, and triggered the decomposition of PAG, giving photosensitivity of the formulation at i-line. Among them, 9, 10-dibutoxy-anthracene most effectively sensitized PAG D. The sensitization mechanism assumed an

electron transfer from the sensitizers to the oxime sulfonate molecule, but further studies are necessary for the mechanism elucidation. Another oxime sulfonate compound, PAG F, was also studied with respect to sensitization by DBA as shown in Figure 11. This PAG showed a good sensitivity at i-line in combination with DBA. It is worthwhile to mention that anthracene compounds work well as the sensitizer for oxime sulfonate compounds.

### Conclusion

The oxime sulfonate compounds have great potential as PAGs and they are adjustable for various demands such as high thermal and storage stability, red-shifted absorption profile, etc. Several oxime sulfonate type PAGs for g-/h-/i-line, KrF and ArF lithography applications have been developed. They are currently used in the mass production of semiconductor chips.

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