

Design and lithographic performances of 193-specific photoacid generators

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ABSTRACT

The improvement of the transparency of photoacid generators (PAGs) has an researchers' attention for 193-resist application. In this study, sulfonium salt was chosen as a target PAG. Triphenyl sulfonium salt (TPS) showing strong absorption at 193 nm was selected as a standard PAG. Starting from the ordinary compound, designing several 193-specific PAGs was attempted. Molecular orbital (MO) calculation was used for the estimation of transparency of PAGs. The calculated absorption results fit in with observed absorption spectra of synthesized PAGs in poly(methyl methacrylate) matrix. Furthermore, MO calculation illustrated that polycyclic aromatic systems based on π -system extension concept should be preferable in terms of transparency at 193 nm. A new PAG was synthesized based on the π -extended concept. The resist comprising the new PAG was evaluated in order to verify the effect of transparency improvement. The resist provide good lithographic performances, vertical wall angle without deterioration of photospeed. The MO calculations have materialized a 193-specific PAG for further improvement of resist performances.

Keywords: photoacid generator, transparency, molecular orbital calculation, and ZINDO

1. INTRODUCTION

Optical property of the resist material is, in general, one of the crucial factors for the improvement of resist performances. Transparency especially influences in resolution, resist profile, process window etc.. Higher transparency would be preferable in many respects to resist performances. Although much attention has been paid to the transparency of base resin material from the early stage of 193 resist development, there are a few papers on the transparency of PAGs at 193 nm; study on bis(tert-butyl)phenyl idonium salts by IBM¹, cyclic alkyl sulfonium salts proposed by NEC², and naphthalene-containing PAGs with band shift concept by Toshiba³.

The objective of this paper is to propose the method to predict 193-specific PAG structure. MO calculation was taken into advantage as a useful tool regarding sulfonium salts designing. Another objective of this paper is to clarify that the transparency improvement is valid in terms of resist performances.

2. METHODS

2.1. Calculation

For the estimation of the absorption wavelength and oscillator strength, singly excited configuration interaction (SECI) calculations were performed using ZINDO⁵ program, which is a semi-empirical MO calculation module in Gaussian 98 program package. The parameters implemented in ZINDO program of Gaussian 98 were used without further modification. In the SECI calculation, all molecular orbitals were taken into consideration. The geometry of every PAG was optimized by MOPAC AM1⁶ method. Only the cationic parts of sulfonium salt PAGs were considered for ZINDO calculations without considering counter anionic parts. Up to 40th peaks from the lowest excitation energy were calculated for all compounds (except for compound **5**, for which up to 70th peaks were calculated) to ensure that every peak down to 170 nm could be calculated. Peaks existing between 180 nm and 240 nm were shown in the figures in this paper.

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2.2. Measurement

Absorption spectrum of PAG in acetonitrile was measured with VUV-2010. Transparency of each PAG in poly(methyl methacrylate), PMMA film matrix was measured with JASCO VUV-200. The film matrix was obtained by the following method; sample solution was formulated with PAG, PMMA, and PGMEA. The same molar level of PAG was loaded into each sample solution. The solution was spin-coated on a quartz substrate and baked at 130 °C for 90 seconds.

2.3. Imaging performance evaluation

Two 193-nm photoresist was formulated with poly(cyclic olefin-*alt*-maleic anhydride) and a new transparent PAG and TPST, respectively. The formulated photoresist was spin-coated on a silicon wafer pre-coated by organic BARC. Each spin-coated wafer was soft baked on a hotplate at 130 °C for 90 seconds. The resist film was exposed on an ArF exposure tool (Nikon; 0.55NA, 0.7 σ), post-baked at 130 °C for 90 seconds, developed with a 0.26N TMAH aqueous solution for 40 seconds, and rinsed with deionized water for 5 seconds.

3. RESULT & DISCUSSION

3.1. Introduction of electron-donating and electron-withdrawing group to triphenylsulfonium salt (1)

The calculated UV spectrum of triphenylsulfonium salt (1) is shown in Figure 1 (a). The wavelength (λ_{\max}) and the oscillator strength for each absorption peak were estimated by ZINDO calculation. The height of the line in the figure indicates the value of the oscillator strength for the corresponding peak. There are two significant peaks in the deep UV region, *i.e.*, 203.58 nm and 209.67 nm, respectively. These peaks are considered to be allowed π - π^* electron transitions of the benzene ring. Absence of significant peaks around 193 nm indicates that experimentally detected UV absorption at 193 nm arises from the broadened UV absorption which has a peak top in the longer wavelength region. Therefore it was supposed that new transparent PAGs would be possible if these two peaks could be shifted to a longer wavelength or if the intensity of these two peaks could be diminished.

At first, introduction of some substituents to benzene ring was attempted to examine the effect on the UV absorption around 193 nm. Figure 1 (b), (c), and (d) show the calculated UV spectra of compound 2, 3, and 4 substituted with electron-donating groups in the benzene moieties, *i.e.*, -OMe, -Me, and -OH, respectively. Two significant peaks corresponding to the peaks of compound 1 slightly shifted to a longer wavelength region (red shift) and the oscillator strength of two peaks slightly decreased. However, the extent of the shift and the decrement of the oscillator strength are small, so it was concluded that the introduction of the substituent would not lead to so outstanding improvement of the transparency at 193 nm. Figure 1 (e) shows the calculated UV spectrum of compound 5 substituted with electron-withdrawing nitro groups in its benzene moieties. There are also two major peaks (205.95 nm and 214.10 nm) like the other compounds, while unlike the cases of introduction of electron-donating groups, many peaks of small intensity appeared between 190 and 200 nm region. Therefore, it was expected that the introduction of electron-withdrawing group like nitro group would bring an adverse effect to the transparency at 193 nm.

3.2. Number of benzene moieties in PAG

The effect of the number of the benzene moieties in PAGs on the transparency at 193 nm was also examined. Figure 2 (a) shows the calculated UV spectrum of compound 6 having two phenyl rings. In this case, four significant peaks appear around the deep UV region, *i.e.*, 199.76 nm, 205.01 nm, 206.02 nm, and 209.25 nm, respectively. The peak with the highest energy of four peaks located in a higher energy region than the highest peak for compound 1. Therefore, it was estimated that the two benzene rings system would be more opaque at 193 nm. Figure 2 (b) shows the calculated UV spectrum of compound 7, which was structured with one benzene moiety and two alkyl groups (R1 and R2). It was indicated that the oscillator strength of the significant two peaks decreased to some extent compared with the corresponding two peaks of compound 1, but no remarkable shift was observed about the two peaks of compound 7. The calculated result indicated that the absorption of the deep UV region of compound 7 will be slightly decreased and therefore it was estimated that the absorption at 193 nm should decrease with decreasing the absorption of peak top compared with compound 1. The calculation indicated that the system with one benzene moiety such as compound 7 would have better transparency than the system with multiple benzene moieties.

3.3. Introduction of electron-donating group to PAGs containing one phenyl group

In previous section, it was indicated that sulfonium salts containing only one phenyl group like compound 7 could provide high transparency at 193 nm. Starting with compound 7 as a leading compound, we attempted the introduction of some electron-donating and electron-withdrawing groups onto the structure for the next step. As expected from the previous

calculation results, the introduction of electron-withdrawing groups like nitro group had no effect for the transparency improvement at 193 nm. So, we attempted the introduction of two or three electron-donating groups to PAGs. Figure 3 (a), and (b) show the calculated UV spectra of compound **8**, and **9** respectively, having multiple methyl, hydroxyl, and methoxy groups in their structure. The calculated wavelength of major two peaks shifted to a longer wavelength region (red shift) in all compounds. The oscillator strength of two major peaks of these compounds were increased compared with two peaks of compound **7**. Therefore, it is obscure whether the transparency of these compounds should be increased.

3.4. Extension of π -system

It is well known that the UV absorption of aromatic group can be shifted to a longer wavelength region by extension of π -system. Previous section showed the PAGs with one benzene moiety like compound **7** should improve the transparency at 193 nm, so that it could be easily conceived that the PAGs with only one of π -extended aromatic system should demonstrate further improvement of transparency at 193 nm. We examined the transparency at 193 nm of a π -extended polycyclic aromatic, a naphthalene derivative **10**. Figure 4 shows its calculated UV spectrum. The calculated spectrum shows that only one significant peak appeared in the deep UV region (223.87 nm), which was located about 20nm longer wavelength region compared with the peaks of compound **1**. The oscillator strength decreased about one-third extent of compound **1**, indicating that the transparency at 193 nm for this compound will remarkably improve. The calculated results indicated that compound **10** is fairly effective for the improvement of transparency at 193 nm.

3.5. Comparison of experimental and calculated λ_{\max}

Judging from the calculation results, PAGs **7**, **8**, **9**, and **10** were synthesized according to synthetic scheme described in a previous paper⁷. Triphenylsulfonium salt **1** was also synthesized as a reference compound. The calculated absorption maximum λ_{\max} (calc.) and experimental absorption maximum λ_{\max} (exp.) in acetonitrile (0.2×10^{-4} M) were summarized in Table 1. λ_{\max} (calc.) was defined as wavelength of the highest oscillator strength peak. Compound **10** showed no clear maximum absorption, *i.e.* only shoulder peak was observed in the deep UV region, in other compounds, λ_{\max} (calc.) were in good agreement with experimental results λ_{\max} (exp.). Therefore, it was concluded that the calculation using ZINDO program were valid enough to make an accurate estimation of UV spectra.

3.6. Transparency at 193 nm

The transmittance at 193 nm of PAG was measured in PMMA resin matrix. The thickness of the resin film was adjusted to 5000 angstroms and the concentration of PAG was constant in each measurement. The UV spectrum of each PAG is shown in Figure 5. The shape of spectrum for compound **1** indicated that the transparency around 193 nm was very low because the peak top existed near the 193 nm. On the other hand, newly designed PAG, compound **10**, have high transparency around 193 nm, because the peak top shifted to a longer wavelength region and the absorption around 193 nm decreased as expected the calculations. The transmittance at 193 nm of compound **10** was also shown in Figure 5. The transmittance of compound **1** at 193 nm is 44.18 %, while the transmittance of compound **10** is 72.47 %, indicating we succeeded in the development of PAG which have high transparency at 193 nm.

3.7. Lithographic performance

Lithographic performance of compound **10** was evaluated. Figure 6 shows the cross section SEM of the resist comprising **10** and TPS, respectively. The resist containing TPS showed tapered pattern because of the strong absorption. On the contrary, the new PAG gave good pattern profile with vertical side-wall angle. The result clearly implied the effect of the transparency improvement. In addition to the transparency, photospeed of the new PAG is worth mentioning. This new PAG was realized high transparency with keeping acceptable photospeed.

4. CONCLUSION

We estimated the absorption of various compounds by MO calculation and designed, synthesized newly developed 193-specific PAG which has lower absorption than the conventional PAG, TPS. We evaluated the lithographic performance of this designed PAG. A resist which utilized the newly designed 193-specific PAG has shown a good performance. This result suggests that 193-specific PAG with higher transparency is one of the key factor for the further improvement of 193 resist performance.

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REFERENCES

1. R. R. Kunz, R. D. Allen, W. D. Hinsberg, and G. M. Wallraff, *Proc. SPIE*, **1925**, 167, 1993.
2. K. Nakano, K. Maeda, S. Iwasa, J. Yano, Y. Ogura, and E. Hasegawa, *Proc. SPIE*, **2195**, 194, 1994; K. Nakano, K. Maeda, S. Iwasa, Takeshi. Ohfuji, and E. Hasegawa, *Proc. SPIE*, **2438**, 433, 1995.
3. M. Nakase, T. Naito, K. Asakawa, A. Hongu, N. Shida, and T. Ushirogouchi, *Proc. SPIE*, **2438**, 445, 1995.
4. T. Ushirogouchi, N. Kihara, S. Saito, T. Naito, K. Asakawa, T. Tada, and M. Nakase, *J. Photopolymer Sci. Tech.*, **7**, 3, 423, 1994.
5. J. Redley, M. Zerner, *Theor. Chim. Acta.*, **32**, 111, 1973,
6. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902, 1985.
7. S. R. Akhtar, J. V. Crivello, and J. L. Lee, *J. Org. Chem.*, **55**, 4222, 1990.

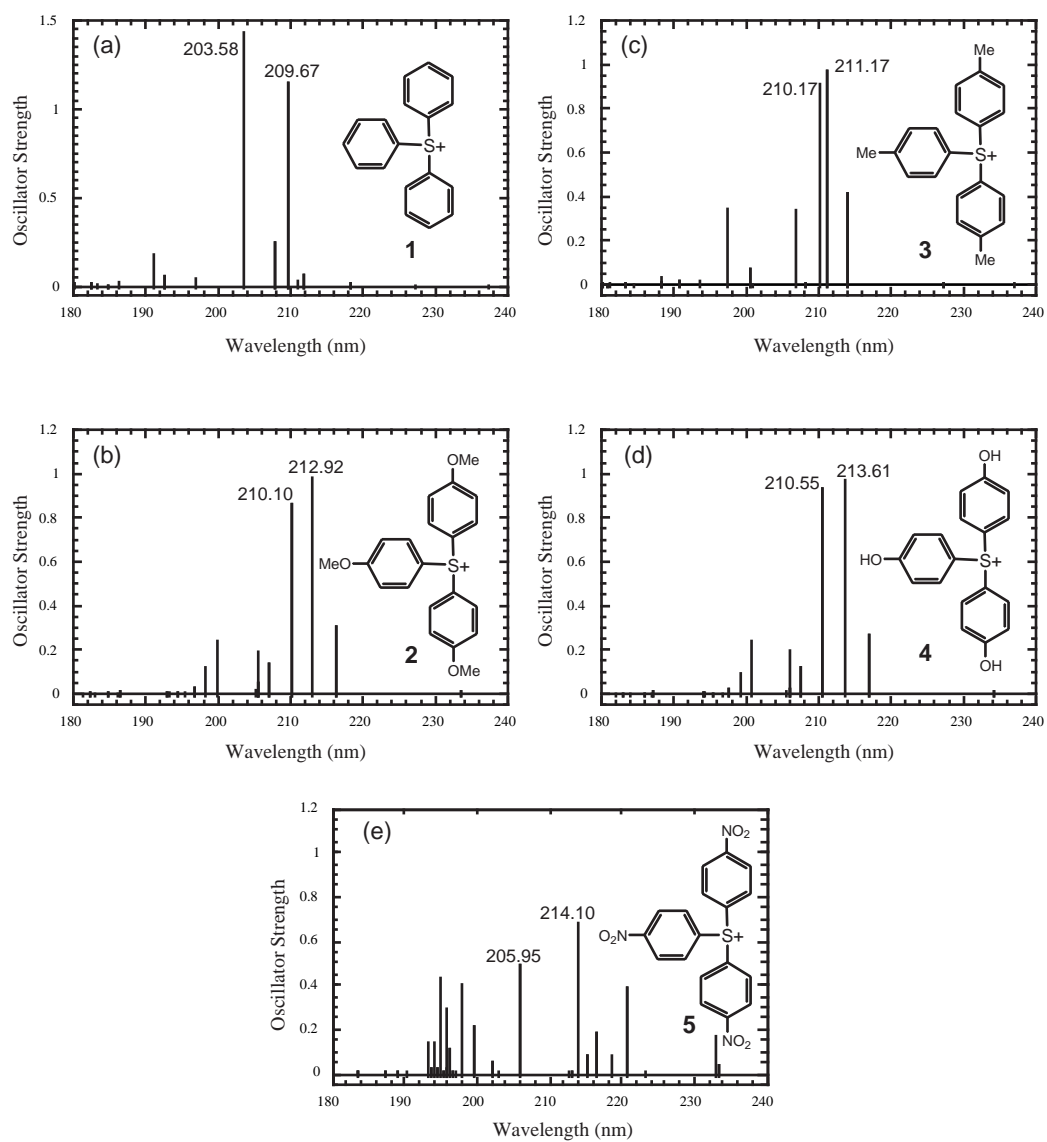


Figure 1. The calculated UV spectra of **1**, **2**, **3**, **4**, and **5**. The numerical values in the spectra indicate the wavelength of the peaks.

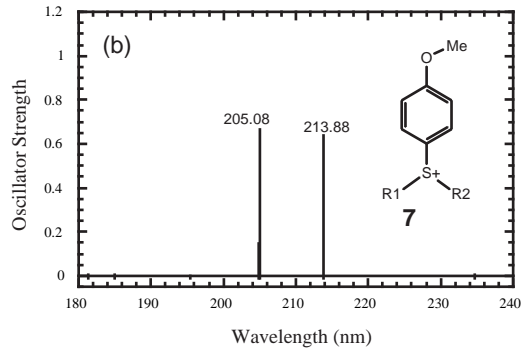
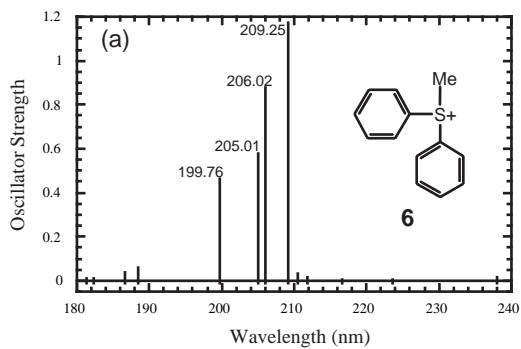


Figure 2. The calculated UV spectra of **6** and **7**. The numerical values in the spectra indicate the wavelength of the peaks.

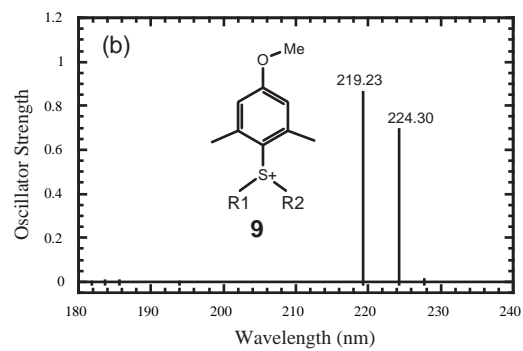
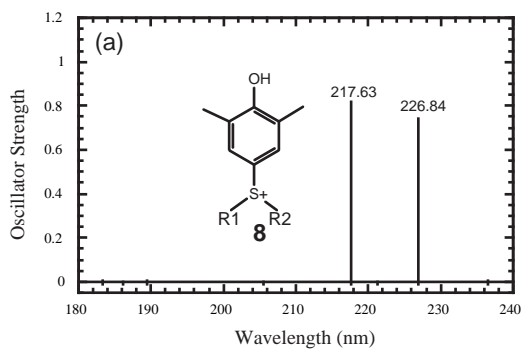


Figure 3. The calculated UV spectra of **8** and **9**. The numerical values in the spectra indicate the wavelength of the peaks.

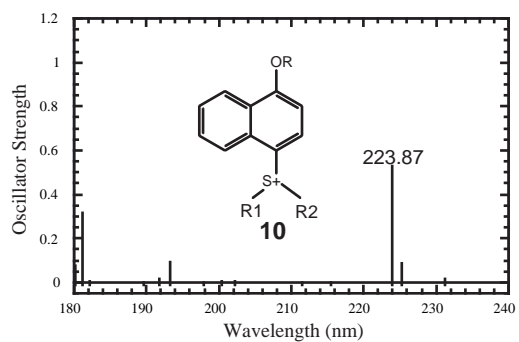


Figure 4. The calculated UV spectrum of **10**. The numerical value in the spectrum indicates the wavelength of the peak.

Table 1. Calculated and experimental UV data

| | λ_{max} /nm (exp.) | λ_{max} /nm (calc.) | Oscillator Strength (calc.) |
|-----------|-----------------------------------|------------------------------------|-----------------------------|
| 1 | 201.6 | 203.58 | 1.4303 |
| 7 | 204.4 | 205.08 | 0.6628 |
| 8 | 211.6 | 217.67 | 0.8189 |
| 9 | 215.4 | 219.80 | 0.8630 |
| 10 | (a) | 223.87 | 0.5286 |

(a) Only shoulder was observed in the deep UV region.

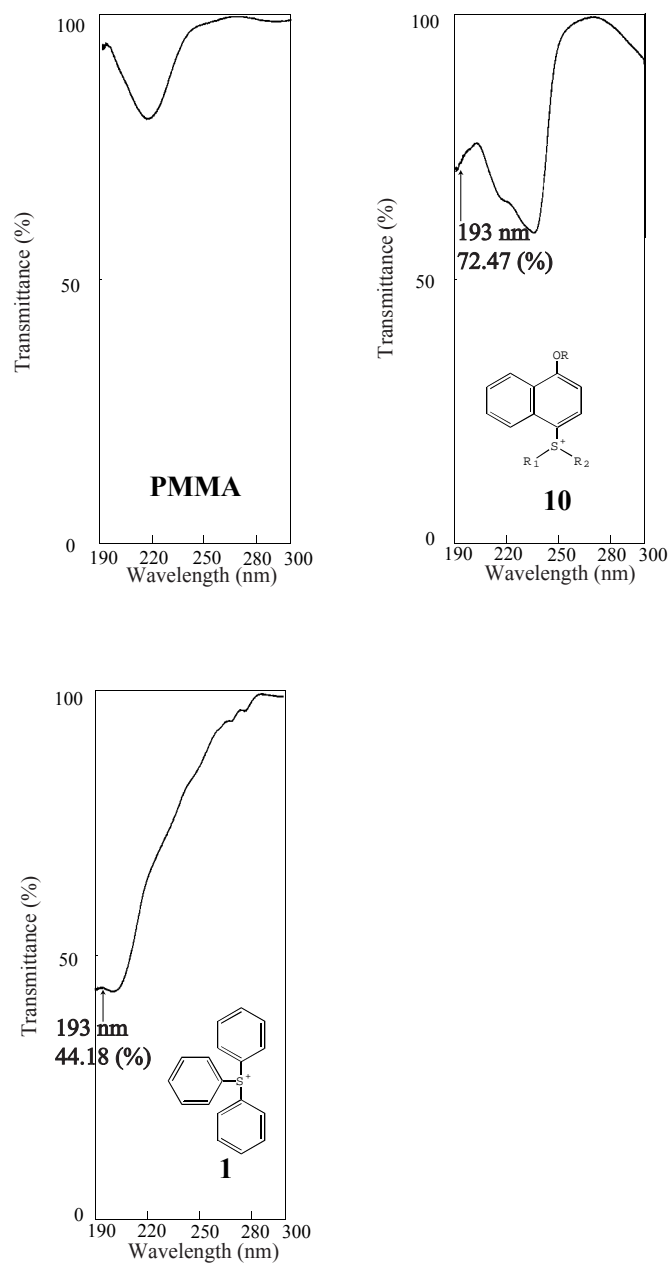
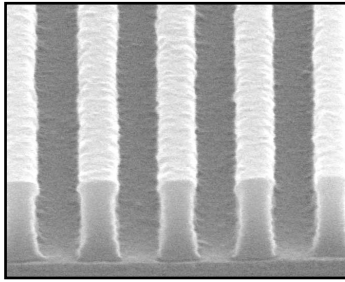
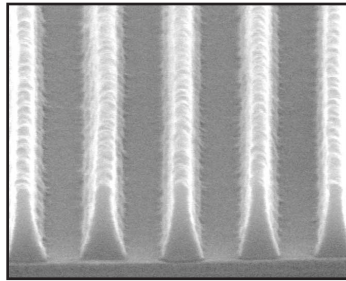


Figure 5. Transmittance of newly synthesized PAG and TPS



(a) newly designed PAG
18.5 mJ/cm²



(b) TPS - Trifrate

Evaluation Conditions

Thickness: 0.34 μ m on Organic BARC

Soft Bake: 130°C, 90 sec

Exposure: Nikon ArF Exposure Tool (0.55NA, 0.70 σ)

Post Exposure Bake: 130°C, 90 sec

Development: 40 sec (Developer: 0.26N TMAHq)

Figure 6. SEM photographs (size: 0.16 μ m) of 193-photoresist containing 5 % (by weight)
(a) newly designed PAG and (b) TPS, respectively.