Theoretical Study on Reactivity of Photoacid Generators for EUV Lithography

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We have investigated the reactivity of photoacid generators for extreme ultraviolet (EUV) exposure. Quantum chemical calculation was performed. As the secondary electrons from the polymer in a resist cause the reaction of the photoacid generator, the reactivity of the photoacid generator is determined as its electron affinity. We optimized the molecular structure of the photoacid generator and calculated the electron affinity of the photoacid generator. Through the calculation of the electron affinity and population analysis of added electrons, we found that incorporation of electron withdrawing group increases the reactivity of photoacid generators.

\textbf{Keyword:} lithography, EUV, resist, photoacid generator, reactivity, quantum chemical calculation

1. Introduction
With the increase in the density of semiconductors, the minimum feature size of patterns will be scaled down to 22nm. The development of extreme ultraviolet (EUV) lithography, which has an advantage of resolution in terms of its shorter wavelength, is accelerated to meet the requirements. The development of resists is one of the key technologies to realize this lithography. In particular, the sensitivity of resists has to be improved to compensate for a low exposure source power.

Upon EUV exposure to the polymer in the resist, the ionization of the polymer occurs and secondary electrons are generated. The secondary electrons from the polymer cause the reaction of photoacid generator and photoacid generation [1]. Thus, the sensitivity of the resist for EUV depends on the ionization of the polymer and the electron affinity of the photoacid generator.

In this paper, we investigated the reactivity of photoacid generators for EUV exposure. Structural dependence of photoacid generators and the effect of substituent on photoacid generators were studied.

2. Calculation
2.1. Method
Gaussian 09 calculation program based on density functional theory (DFT) was used. A high-order basis function of molecules of 6-31G polarized was applied to quantitatively calculate the molecular energy.

Upon EUV exposure to the polymer in the resist, secondary electrons are generated. Because the secondary electrons from the polymer cause the reaction of onium salt and photoacid generation, the reactivity of onium salt is determined as its electron affinity.

We performed optimization of the molecular structures with and without electron addition to the onium salt and
calculated the molecular energy of each structure. As the molecular structure is more stable with electron addition, we defined the absolute value of the difference in molecular energy between structures with and without electron addition as the stabilization energy. It corresponds to the electron affinity of onium salt. In the calculation, electric constant is 1.0.

The correlation between the electron affinity of onium salt and the observed resist sensitivity is reported [2]. A high reduction potential makes the electron affinity of onium salt higher. More acid generation is observed with a higher reduction potential.

The electron population was calculated after optimization of the molecular structure with electron addition to the onium salt. There are electron populations in the cation (sulfur atom and carbon atoms), the anion (sulfonate), and substituent in the cation part, and fluorine in the anion part.

2.2. Materials
The onium salts studied here are as followings:
- triphenylsulfonium methanesulfonate: A fluorine atom is substituted for a hydrogen atom in the anion part.
- triphenylsulfonium methanesulfonate, triphenylsulfonium n-butanesulfonate, triphenylsulfonium n-hexanesulfonate, triphenylsulfonium n-octanesulfonate
- tricyclopropylsulfonium trifluoromethane sulfonate, tricyclobutylsulfonium trifluoro methanesulfonate, tricyclohexylsulfonium trifluoromethanesulfonate
- triphenylsulfonium trifluoromethane sulfonate, tricyclohexylsulfonium trifluoro methanesulfonate: Methyl, methoxy, fluorne or cyano group is substituted as tri(4-substituted phenyl)sulfonium trifluoro methanesulfonate, respectively (Fig.1). Methyl, methoxy, nitro, oxo or thioxy group is substituted as (2-substituted cyclohexyl)dicyclohexylsulfonium trifluoromethane sulfonate, respectively (Fig.2). Di(2-oxo cyclohexyl)cyclohexylsulfonium trifluoro methanesulfonate and tri(2-oxocyclohexyl) sulfonium trifluoromethanesulfonate were also investigated.
- (2-oxocyclohexyl)dicyclohexylsulfonium toluenesulfonate, (2-thioxycyclohexyl)dicyclohexylsulfonium methanesulfonate

Figure 1. Chemical structure of tri(4-substituted phenyl)sulfonium trifluoro methanesulfonate.

Figure 2. Chemical structure of (2-substituted cyclohexyl)dicyclohexylsulfonium trifluoro methanesulfonate.

3. Results and Discussion
3.1. Effect of the electric constant
Figure 3 shows the relationship between the number of fluorine atoms substituted in the anion part and the stabilization energy for triphenylsulfonium methanesulfonate in the electric constant of 1.0 (vacuum) and 18.3 (cyclohexane). It is found that the incorporation of fluorine atoms increases the stabilization energy and the addition of more fluorine atoms further increases it in both cases. As the tendency of the increment is almost same for both cases, it means that the remaining solvent in a polymer does not influence the tendency of the stabilization energy.

3.2. Effect of the number of carbon atoms in the anion part
Figure 4 shows the relationship between the number of carbon atoms in the anion part
3.3 Effect of the number of cyclic carbon atoms in the cation part

Figure 5 shows the relationship between the number of cyclic carbon atoms in the cation part and the stabilization energy for tricyclopentylsulfonium trifluoromethanesulfonate, tricyclobutylsulfonium trifluoro methanesulfonate, and tricyclohexyl sulfonium trifluoromethanesulfonate. The smaller number of cyclic carbon atoms shows less stabilization energy. The instability due to the structural strain leads to the result.

3.4 Effect of the substituent in the cation part

Figure 6 shows the relationship between tri(4-substituted phenyl)sulfonium trifluoromethanesulfonate and the stabilization energy. It is found that cyano group most increases the stabilization energy. Electron withdrawing group such as cyano and fluorine substituent shows this tendency. More cationation of the onium salts by electron withdrawing group leads to a higher electron affinity. As the results, the stabilization energy is much enhanced as compared with the other substituents.

The stabilization energy, which was obtained in Fig.6, and the substituent constant [4] for tri(4-substituted phenyl)sulfonium trifluoromethanesulfonate are compared in Fig.7. The stabilization energy represents the substituent constant, which is proportional to the electron withdrawing capability.
The population of the added electrons for tri(4-substituted phenyl)sulphonium trifluoromethanesulphonate is shown in Fig. 8. In any substituent, the added electrons are largely populated in the cation and the substituent in the cation part. The total added electrons in the cation and the substituent in the cation part are summarized in Fig. 9. There is little difference of the total added electrons by the different substituents. Triphenylsulfonium has π conjugation, therefore it is thought that the added electrons are uniformly distributed among the cation and the substituent in the cation part, even if the substituent has electron withdrawing capability.

Figure 10 and 11 show the relationship between (2-substituted cyclohexyl) dicyclohexylsulphonium trifluoromethanesulphonate and the stabilization energy, in which the substituent is electron providing group (methyl, methoxy) or electron withdrawing group (nitro, oxo or thioxy), respectively. It can be seen that electron withdrawing group greatly enhances the stabilization energy. Electron withdrawing effect is larger than for tri(4-substituted phenyl)sulphonium trifluoromethanesulphonate.
The stabilization energy is a measure of the stability of a molecule. It is defined as the energy required to remove one electron from the molecule. The stabilization energy is calculated as the difference between the total energy of the ion and the sum of the energies of the neutral molecule and the electron. The stabilization energy is a useful measure of the stability of a molecule because it is related to the electronic structure of the molecule.

The stabilization energy is also affected by the substituent on the molecule. A substituent that is electron withdrawing will increase the stabilization energy, while a substituent that is electron donating will decrease the stabilization energy. This is because electron withdrawing groups stabilize the cation by withdrawing electron density from the molecule, while electron donating groups destabilize the cation by donating electron density to the molecule.

The quantitative effect of the substituent is investigated in Fig.12. This figure compares the stabilization energy of

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\text{Stabilization Energy (kcal/mol)} = E_{\text{cation}} - (E_{\text{neutral}} + E_{\text{electron}})
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where \(E_{\text{cation}}\) is the energy of the cation, \(E_{\text{neutral}}\) is the energy of the neutral molecule, and \(E_{\text{electron}}\) is the energy of the electron.

The population of the added electrons for (2-substituted cyclohexyl)dicyclohexylsulfonium trifluoromethanesulfonate is shown in Fig.13. For electron withdrawing group of nitro, oxy and thioxy, the added electrons are largely populated in the cation and the substituent in the cation part. The total added electrons in the cation and the substituent in the cation part are summarized in Fig.14. It can be seen that the added electrons do not distribute in the cation and the substituent in the cation part for electron providing group. The added electrons can be stable in the cation and the substituent in the cation part by the electron withdrawing. As the results, the balance between the cation part and the anion part becomes better, therefore the stabilization energy greatly increases.

Figure 15 shows the effect of the anion part (trifluoromethanesulfonate, toluenesulfonate, methanesulfonate) on the stabilization energy. The substituent is electron withdrawing group (oxo, thioxy). It can be seen that trifluoromethane sulfonate, which has the stable electron condition of the anion part, enhances the stabilization energy. The balance of the electrons-added molecule between the cation part and the anion part will be better for trifluoromethanesulfonate, so the stabilization energy increases.
EUV lithography was evaluated theoretically. Through the calculation of the stabilization energy and the population analysis of the added electrons, we found that incorporation of electron withdrawing group increases the reactivity.

The substituent of electron withdrawing group for (2-substituted cyclohexyl)dicyclohexylsulfonium trifluoromethanesulfonate is most effective. Trifluoromethanesulfonate contributes to the reactivity. By localizing the added electrons in the cation and the substituent in the cation part under the unstable electron condition of the cation part and the stable condition of the anion part, the balance of the electrons-added molecule becomes better and the electron affinity increases.

References