

Study on Reaction Mechanisms in Electron Beam and X-Ray Resists Using Time-Resolved Absorption Spectroscopy

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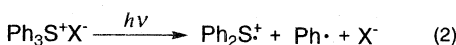
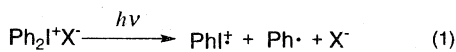
Abstract

Acid generation from onium salt acid generators in EB and X-ray chemically amplified (CA) resists was investigated using nanosecond time-resolved absorption spectroscopy (pulse radiolysis). The results indicate that an acid may generate through the one electron reduction of the onium salts. The behavior of protic acid generated in the CA resists was also analyzed using both conventional steady-state optical absorption spectroscopy and the pulse radiolysis. The results indicate that the protons are transferred from the proton adducts (acid precursors) of matrix polymers to other composition of CA resists. The proton transfer to a melamine crosslinker in a CA negative resist was much faster than that to a dissolution inhibitor in a CA positive resist.

1. Introduction

Electron Beam (EB) lithography and X-ray lithography using synchrotron radiation (SR) can be used for production of ultra-large-scale integrated circuits (ULSI) with very high integration. In such lithography, chemically amplified (CA) resists can provide high performance with high sensitivity. The CA resist employs the photogeneration of an acid which catalyzes many subsequent chemical event such as deblocking of a protecting group or cross-linking of a matrix resin.

Onium salts play an important role as the acid generator (AG) in the CA resists. Photochemistry of the onium salts has been widely investigated using product analysis, flash photolysis techniques, and so on[1-5]. It was reported that iodobenzene and diphenylsulfide cation radicals ($\text{PhI}^{\cdot+}$ and $\text{Ph}_2\text{S}^{\cdot+}$) are formed in the photolysis of diphenyliodonium salt ($\text{Ph}_2\text{I}^+\text{X}^-$) and triphenylsulfonium salt ($\text{Ph}_3\text{S}^+\text{X}^-$) according to reactions (1) and (2)[5]. On the other hand, the radiation-in-



duced acid generation mechanism via onium salt decomposition has not been clarified yet. To improve capabilities of AGs for EB or X-ray CA resists, we investigated the radiation-induced acid generation mechanism of iodonium and sulfonium salts using EB pulse radiolysis experiments[6].

In most CA systems, deformation of resist pattern easily occurs and the effect is most readily seen by increasing the time between the exposure and post-exposure bake process steps (post-exposure delay; PED). To solve the problems and to design a new CA resist system, it is essential to understand the behavior of acids in the resist films. Another objective of the present work is to investigate the behavior of protic acid in EB and X-ray CA resists[7,8].

2. Experimental

The nanosecond pulse radiolysis experiments were carried out using the 28 MeV L-band linear accelerator (LINAC) located at the Institute of Scientific and Industrial Research, Osaka University. The system is described in the previous literature[7]. The width of an electron beam pulse from the LINAC is 8 ns and the absorption dose per pulse is 70 Gy (J/kg). The sample solutions in quartz cells with 10-mm optical path length were bubbled with Ar gas before they were set in the system. These experiments were carried out at room temperature.

X-ray exposure to the resist film on quartz substrates was done using a SORTEC SR ring[9] in 1 atm He ambient. The peak wavelength of the X-ray was about 0.7 nm and the exposure dose was 540 mJ/cm². UV-visible absorption spectra of the resist films were measured before and 5 min after exposure. The spectra were normalized for a film thickness of 1 μm . These experiments were carried out in the clean room (CR) at SORTEC.

3. Results and Discussion

3.1 Acid Generation Reaction Mechanism in EB and X-ray CA resists

Figure 1 shows the optical absorption spectra obtained immediately after the electron pulse irradiation of *m*-cresol solution with and without onium salt ($\text{Ph}_2\text{I}^+\text{CF}_3\text{SO}_3^-$ or $\text{Ph}_3\text{S}^+\text{CF}_3\text{SO}_3^-$). *m*-Cresol was used as a model of phenolic

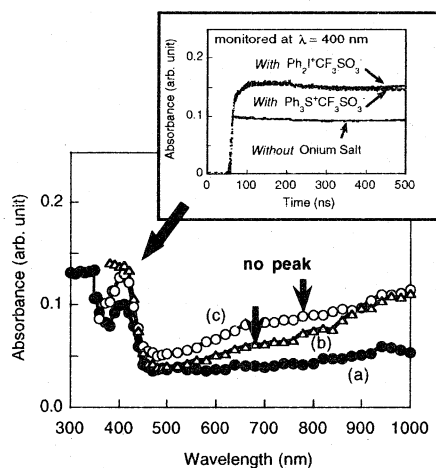


Fig.1 Optical absorption spectra of *m*-cresol solution obtained immediately after 8 ns electron pulses; (a) without onium salt (b) with $\text{Ph}_2\text{I}^+\text{CF}_3\text{SO}_3^-$ (100 mM) and (c) with $\text{Ph}_3\text{S}^+\text{CF}_3\text{SO}_3^-$ (100 mM). The insert shows the time dependent behavior of phenoxy radicals of *m*-cresol ($\lambda = 400$ nm).

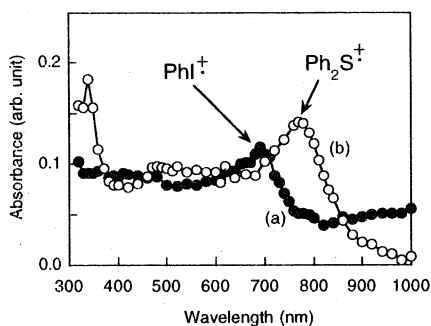


Fig. 2 Optical absorption spectra immediately after an 8 ns electron pulse irradiation of (a) PhI (10 mM) and (b) Ph₂S (10 mM) in dichloromethane solution.

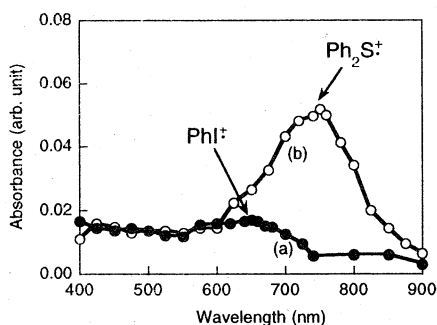
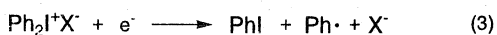


Fig. 3 Optical absorption spectra immediately after an 8 ns electron pulse irradiation of (a) Ph₂I⁺CF₃SO₃⁻ (200 mM) and (b) Ph₃S⁺CF₃SO₃⁻ (200 mM) in acetonitrile solution.

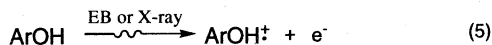
matrix resins in CA resists. Figure 2 shows the transient absorption spectra obtained immediately after the electron pulse irradiation of 10 mM iodobenzene (PhI) and 10 mM diphenylsulfide (Ph₂S) in dichloromethane solution. The absorption peaks of PhI⁺ and Ph₂S⁺ are observed at 690 nm and 770 nm, respectively. In Fig. 1, there were no absorption peaks of PhI⁺ and Ph₂S⁺ in the presence of onium salts. One reason of the result is that the contribution of the cleavage of C-I or C-S bond via excited states of the onium salts (reactions (1) and (2)) is small in the case of electron beam irradiation. And another reason may be that electrons transferred from *m*-cresols to the cation radicals (PhI⁺ and Ph₂S⁺) during the electron pulse width. Figure 3 shows the optical absorption spectra obtained immediately after an 8 ns electron pulse irradiation of the onium salts in acetonitrile solution where the electron transfer from the solution does not occur. When the onium salt concentration is high in the acetonitrile solution, the absorption peak of the cation radicals was observed. However, the yield of the cation radicals is low.

The main reaction pathway of acid generation in EB and X-ray CA resists is considered to be one-electron reduction of the salts as reported earlier [10]. The decomposition of the onium salts induced by electron reduction is considered to be reactions (3) and (4) [11,12]. The electron in reactions (3) and



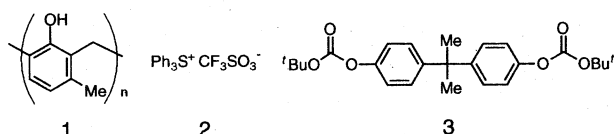
(4) is mainly generated by the radiation-induced ionization

of a matrix polymer (ArOH), and a cation radical of a matrix polymer (ArOH⁺) is formed as shown in reaction (5). In Fig.



1 insert, phenoxy radicals ($\lambda=400$ nm) of *m*-cresols increased by the addition of onium salts. This may indicate that the acids are formed from hydroxyl groups of phenolic compounds (ArOH) as the reaction (6) (or (7)).

3.2 Behavior of Acids in EB and X-Ray CA Positive Resists



For 1- μm -thick films of CA resists, optical absorption spectra of the films were measured before and after X-ray exposure. Figure 4 shows the absorption spectra of a novolac (1) film which contains 10 wt% onium salt AG (2). Before

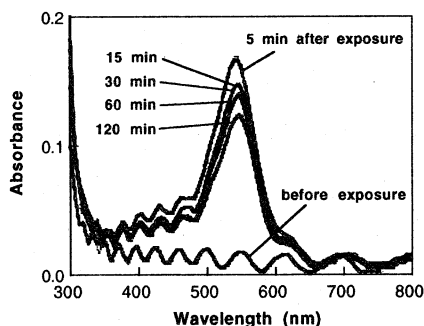


Fig. 4 Optical absorption spectra of a resist film; novolac resin (1) / AG (2) = 10 / 90 (wt ratio).

exposure, there was no absorption peak in the wavelength range 300 nm to 800 nm. However, after exposure, an absorption peak appeared at around 540 nm. The absorption peak at 540 nm is attributed to a proton adduct of *m*-cresol novolac resin (1) [12]. The proton adduct may be a trapping site of proton and is considered to be a precursor of an acid which catalyzes subsequent chain reactions to change solubility to the alkaline developer. As shown in Fig. 4, the value of absorbance at 540 nm decreases as the PED time increases and reduced 29% in CR1 during the period from 5 min to 120 min after exposure. This experiment was carried out in CR1 where the concentration of NH₄⁺ is 5-10 ppb. On the contrary, the value of absorbance reduced 22% during the same period in CR2 where the concentration of NH₄⁺ is less than 1 ppb. From the above results, it is considered that the proton adducts were captured by airborne basic contaminants in some extent.

In order to investigate the effect of a dissolution inhibitor on proton adducts in CA positive resists, optical absorption spectra of the films containing a dissolution inhibitor were measured before and after X-ray exposure. The composition

of the resist film was novolac resin (1) / AG (2) / dissolution inhibitor (3) = 60/10/30 (wt ratio). The absorption peak of proton adducts also appeared at 540 nm in the film. The value of absorbance reduced 38 % in CR1 during the period from 5 min to 130 min after exposure. This decrease is faster than that in the absence of a dissolution inhibitor. Therefore, the decrease might be partly due to migration of a proton to a dissolution inhibitor.

3.3 Behavior of Acids in EB and X-Ray CA Negative Resists

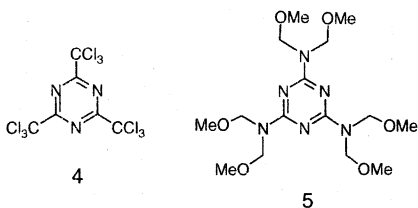


Figure 5 (a) shows the optical absorption spectra of the film which consists of novolac resin (1) / AG (4) = 60 / 10 (wt ratio) and does not contain any crosslinker. After X-ray exposure, an absorption peak of the proton adduct of novolac resin (1) appears at 540 nm.

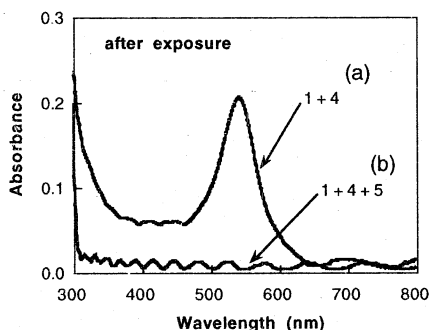


Fig.5 Optical absorption spectra of resist films; (a) novolac resin (1) / AG (4) = 60 / 10 (wt ratio) (b) novolac resin (1) / AG (4) / crosslinker (5) = 60 / 10 / 30 (wt ratio).

posure, an absorption peak of the proton adduct of novolac resin (1) appears at 540 nm. Figure 5 (b) shows the optical absorption spectra of the film of which the composition is novolac resin (1) / AG (4) / crosslinker (5) = 60 / 10 / 30 (wt ratio). This resist formulation provides excellent resolution in EB and X-ray lithographies. For this film, there is no strong absorption peak at around 540 nm before X-ray exposure nor after X-ray exposure. These results suggest that the proton transfer from the proton adducts of matrix polymers to crosslinker (5) is fast, and completed until the absorption measurement.

We analyzed the proton transfer using pulse radiolysis because the transfer is very fast. Figure 6 shows the time-dependent behavior of the absorption peak at 540 nm obtained by electron beam pulse radiolysis of novolac resin (1) (3 base mol/l) with an AG (200 m mol/l Ph₂IPF₆) in acetone solution. The absorption of proton adducts initially produced by the electron pulse has differs little between the cases of acetone solution with and that without crosslinker (5). This means that approximately the same amounts of proton adducts were

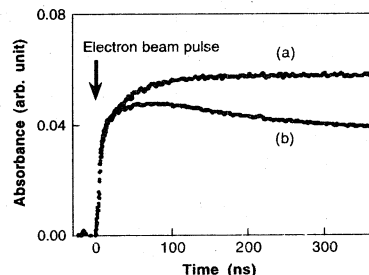


Fig.6 The time-dependent behavior of intermediates obtained in the pulse radiolysis of novolac resin (1) (3 base M) with an AG (200 mM Ph₂IPF₆) in acetone solutions; (a) without a crosslinker (b) with a crosslinker (5) (300 mM).

initially formed in those solutions by the irradiation. However, the intensity of the absorption of the proton adducts decreased thereafter. This is considered to have been due to the transfer of protons from proton adducts of novolac resin (1) to crosslinker (5). This proton transfer is apparently fast in the solution containing crosslinker (5), compared to that in the case for the CA positive resists containing dissolution inhibitor (3). This fast proton transfer may be due to high proton affinity of crosslinker (5) and may contribute to the environmental stability of this type of CA negative resist.

4. Conclusion

From the results of pulse radiolysis experiments, we can conclude that the decomposition of an onium salt via excited states is not the main reaction path of acid generation in EB and X-ray CA resists. The main path is considered to be the onium salt decomposition via electron transfer from a matrix polymer to an onium salt.

We observed the transfer of protons from the proton adducts of matrix polymers to other resist composition in CA resists using the combination of conventional steady state optical absorption spectroscopy and nanosecond pulse radiolysis. The rate of proton transfer to the crosslinker (5) in CA negative resist was much higher than that to the dissolution inhibitor (3) in CA positive resist.

Acknowledgments

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