Radiation Chemistry of Triphenylsulfonium Salts in EB and X-Ray Chemically Amplified Resists -Proton Generation Mechanisms

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1. Introduction

After ArF excimer laser lithography, it is necessary to use a higher energy (shorter wavelength) exposure source for the mass production of ultra-large-scale integrated circuits (ULSIs). There are some candidates for the exposure source such as electron beams (EB), X-rays, ion beams and so on. These emerging exposure sources have enough energy to ionize resist materials. It is therefore necessary to understand the radiation chemistry in the resists.

In EB and X-ray lithography, most of the radiation energy goes through without energy deposition in the resists. Hence, the chemically amplified (CA) resists are useful because the sensitivity of the resists can be enhanced by acid catalytic chain reactions. At the present time, the sensitivity of the EB and X-ray CA resists is not high enough. For the improvement of the resist sensitivity, investigation of the acid generation reactions induced by the ionizing radiation is essential.

Onium salts [1-5] play an important role as the acid generator (AG) in the CA resists. From the results of our research, the reaction mechanisms of the acid generation have been proposed for EB and X-ray CA resists [6]. It is proposed that the main reaction path of the acid generation is considered to be the path through the ionization of a matrix polymer because the energy of the ionizing radiation is absorbed mostly by the matrix polymer. The contribution of direct excitation of the AG is considered to be less important. In this work, we obtained further supporting results for our estimation by the product analysis after γ -ray irradiation and the EB pulse radiolysis.

2. Experiments

2.1. Materials

Triphenylsulfonium triflate (TPS-Tf) and infinite pure grade acetonitrile (CH_3CN) were obtained from Midori Kagaku Co., Ltd. and Wako Pure Chemical Industries, Ltd, respectively, and used in the whole experiments.

2.2. γ -Ray Radiolysis

The irradiation of γ -rays was carried out at room temperature for Ar-saturated acetonitrile solutions by using a ^{60}Co source. The molar hydrogen-ion (H^+) concentration after γ -ray irradiation of TPS-Tf solutions in acetonitrile was measured with a digital pH meter. The measurement of pH was done after the solution was diluted with water and the original concentration of H^+ in acetonitrile was calculated. Absorbed doses were determined with a ferrous sulfate (Fricke) dosimeter.

2.3. EB Pulse Radiolysis

The nanosecond EB radiolysis experiments were carried out using the L-band linear accelerator (LINAC) at the Institute of Scientific and Industrial Research, Osaka University. The changes in transient absorption of the samples after EB pulses were observed using the time-resolved absorption spectroscopy. The details of this system are described in the previous paper [7]. The width and energy of an EB pulse from the LINAC were 8 ns and 28 MeV, respectively. The absorbed dose per pulse was measured to be 93.1 Gy (J/kg) by monitoring the transient absorption of hydrated electrons ($\lambda_{\text{max}} = 720$ nm). The values used in the dosimetry were $1.85 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ for the molar extinction coefficient of e_s^- and 2.8 for $G(\text{e}_s^-)$ value [8]. (The symbol G represents the radiation-chemical yield of particles

produced per 100 eV radiation energy absorbed by the medium.) The sample solutions in quartz cells with 20-mm optical path length were bubbled with Ar gas prior to the pulse radiolysis measurement. To prevent decomposition of the samples by ultraviolet light from the Xe flash monitor lamp, the monitor light shorter than $\lambda = 400$ nm was cut off by a UV40 filter. All experiments were carried out at room temperature.

3. Results and Discussion

3.1. Proton Yield Determination

The yield of protons induced by the ionizing radiation was determined for solutions containing a sulfonium salt. Fig.1 shows H^+ concentration after the γ -ray radiolysis of TPS-Tf solutions in acetonitrile as a function of absorbed doses. The concentration of H^+ in the solution of 10 mM TPS-Tf increases almost linearly with increasing absorbed doses up to about 2 mM. The $G(H^+)$ value for 10 mM solution determined from the initial slope of the plot was 2.3. The H^+ concentration in the solution of 100 mM TPS-Tf also increases linearly with absorbed doses up to over 10 mM. The $G(H^+)$ value for 100 mM solution was evaluated from the slope of the straight line to be 2.6, which is close to the $G(H^+)$ value for 10 mM solution.

3.2. Contribution of Ionization Process to the Acid Generation

When the acetonitrile solution is exposed to the ionizing radiation, the acids can be generated by the ionization process and excitation process.

In the ionization process, solvent acetonitrile is mainly ionized by radiation because it absorbs most of the radiation energy. The primary processes occurring in the irradiated neat acetonitrile have been proposed [9] as follows:

Irradiation of liquid acetonitrile produces an electron and CH_3CN^{*+} (reaction (1)). The electron leads to $CH_3CN^{\bullet-}$ (reaction (2)), and the CH_3CN^{*+} leads to $\bullet CH_2CN$ by releasing H^+ to CH_3CN (reaction (3)). In the presence of sulfonium salt, the electrons and radical anions ($CH_3CN^{\bullet-}$) are scavenged through the one-electron reduction of the onium salts [6,10,11], and the salts are decomposed (reaction (4) and (5)):

Fig.1. Concentration of hydrogen ion generated by the γ -ray radiolysis of acetonitrile solution containing 10 mM (●) and 100 mM (○) TPS-Tf as a function of absorbed doses.

As a result of reaction (4) and (5), the recombination of CH_3CNH^+ and anionic species (electrons or radical anions of acetonitrile) (reaction (6) or (7)) are prohibited:

Thus, the yield and lifetime of H^+ (existing as CH_3CNH^+ in acetonitrile) are increased by adding sulfonium salts.

As the decomposition of onium salts is very fast, we observed transient intermediates by nanosecond EB pulse radiolysis. Fig.2A (a) shows the transient absorption spectrum of intermediates for neat acetonitrile at 20 ns after EB pulses. There is a broad absorption with a maximum at 550 nm in the visible region. Broad absorption also exists in the infrared region. These transient species were assigned to the radical anions of acetonitrile. [9] The radical anions exist as a monomeric form ($CH_3CN^{\bullet-}$) ($\lambda_{max} = 1450$ nm) or dimeric form ($(CH_3CN^{\bullet-})_2$) ($\lambda_{max} = 550$ nm). [9] The absorption at around 550 nm is superpositioned with these two species. Fig. 2B (a) illustrates the formation and decay behavior of the anion radicals. By adding 10 mM sulfonium salt to the acetonitrile, almost all anionic species were scavenged within 20 ns (Fig. 2A(b) and 2B(b)). This is considered to be due to reaction (4) and (5). Reported $G(CH_3CN^{\bullet-})$ value was 2.0 [12] and this value is close to the $G(H^+)$ (2.3 for 10 mM TPS-Tf solution). This indicates that anion scavenging by onium salts contributes greatly to the acid generation.

Fig.2. EB pulse radiolysis of (a) neat acetonitrile and (b) acetonitrile solution of 10 mM TPS-Tf: (A) transient absorption spectra obtained 20 ns after EB pulses; (B) time dependent behavior of the absorbance at $\lambda = 550$ and 1000 nm after EB pulses.

3.3. Contribution of Excitation Process to the Acid Generation

As shown in Fig. 2A(b), a small absorption maximum at about 750 nm appeared by adding 10 mM TPS-Tf to the acetonitrile. The absorption maximum became larger as the concentration of TPS-Tf became higher as shown in Fig.3. This absorption at 750 nm can be assigned to diphenylsulfide radical cation ($\text{Ph}_2\text{S}^{\bullet+}$), based on the previous results obtained by γ -radiolysis of diphenylsulfide in halocarbon matrices at 77 K. [13] The transient absorption ($\lambda_{\text{max}} = 750$ nm) was also observed in laser-flash photolysis of the acetonitrile solution of diphenyl(4-phenylthiophenyl) triphenylsulfonium salt and assigned to $\text{Ph}_2\text{S}^{\bullet+}$. [14] The $\text{Ph}_2\text{S}^{\bullet+}$ is considered to be the intermediate from the decomposition via excited states of TPS-Tf [1-5]. This means that the excitation of sulfonium salt occurred by the EB pulse irradiation. Decomposition from excited states of a onium salt in the radiation-induced reaction is thought to be similar to that in the light-induced reaction (reaction (8) and (9)) [3-5]:

Fig.3. EB pulse radiolysis of acetonitrile solutions of (a) 100 mM, (b) 200 mM, (c) 300 mM and (d) 500 mM TPS-Tf: (A) transient absorption spectra obtained immediately after EB pulses; (B) time dependent behavior of the absorbance at $\lambda = 750$ nm after EB pulses.

The decomposition from excited states results in the homolytic (reaction (8)) and heterolytic (reaction (9)) cleavage of C-S bond. [4] Homolytic cleavage directly produces the $\text{Ph}_2\text{S}^{\bullet+}$ - $\text{Ph}^\bullet$ pair. In contrast, heterolytic cleavage produces Ph_2S - Ph^+ pair. [4] In the heterolytic cleavage, Ph_2S - Ph^+ pair is energetically less stable than the $\text{Ph}_2\text{S}^{\bullet+}$ - $\text{Ph}^\bullet$ pair, and, therefore, electron transfer from Ph_2S to Ph^+ partly occurs, resulting in $\text{Ph}_2\text{S}^{\bullet+}$ - $\text{Ph}^\bullet$ pair (reaction (10)) [4]:

Thus, the absorption at 750 nm observed in the pulse radiolysis is considered to be due to the $\text{Ph}_2\text{S}^{\bullet+}$ from homolytic cleavage and also from heterolytic cleavage of C-S bond. After $\text{Ph}_2\text{S}^{\bullet+}$ is generated, the acid can be generated by hydrogen abstraction from solvent (reaction (11)) or addition of $\text{Ph}^\bullet$ to $\text{Ph}_2\text{S}^{\bullet+}$ (reaction (12)). [4]

Fig.4. Yields of $\text{Ph}_2\text{S}^{\bullet+}$ in the EB pulse radiolysis of TPS-Tf in acetonitrile plotted as a function of concentration of TPS-Tf.

$\text{Ph}_2\text{S}^{\bullet+}$ generated by EB pulse radiolysis has enough lifetime to evaluate the yield as shown in Fig.3B. Thus, we estimated the yields of $\text{Ph}_2\text{S}^{\bullet+}$ in acetonitrile by varying the concentration of the onium salt. Fig.4 shows $G(\text{Ph}_2\text{S}^{\bullet+})$ value in the EB pulse radiolysis of TPS-Tf in acetonitrile plotted as a function of concentration of TPS-Tf. To calculate the $G(\text{Ph}_2\text{S}^{\bullet+})$, the molar extinction coefficient of $\text{Ph}_2\text{S}^{\bullet+}$ was evaluated by the comparison between absorption of $\text{Ph}_2\text{S}^{\bullet+}$ and biphenyl radical cation after EB pulse irradiation in dichloromethane. The reported value for the molar extinction coefficient of biphenyl radical cation is $1.66 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at $\lambda = 690 \text{ nm}$. [15] Using this value, the molar extinction coefficient of $\text{Ph}_2\text{S}^{\bullet+}$ was calculated to be $1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. In Fig. 4, the $G(\text{Ph}_2\text{S}^{\bullet+})$ value increases with the TPS-Tf concentration. This means that excitation of onium salt increases with the TPS-Tf concentration. The $G(\text{Ph}_2\text{S}^{\bullet+})$ values for 10 mM and 100 mM TPS-Tf solutions were 0.04 and 0.2, respectively. This value is quite small compared to the acid yield, the $G(\text{H}^+) = 2.3$ and 2.6 for 10 mM and 100 mM TPS-Tf solutions, respectively. The increased $G(\text{H}^+)$ value for 100 mM TPS-Tf solution compared to 10 mM TPS-Tf solution can be explained by the increase in acid generation from decomposition through excited state of onium salts (reaction (8) and (9)) in addition to the increase in efficiency of the electron scavenging (reaction (4) or (5)).

4. Conclusion

The radiation chemical yields of protons and intermediates from sulfonium salt decomposition were determined in acetonitrile solutions. These results

support our estimation that the main path of acid generation induced by ionizing radiation is the onium salt decomposition through the ionization of a matrix. The contribution of the sulfonium salt decomposition through excited states increased with concentration of onium salts but it was much lower than that through ionization of the matrix.

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