Analysis of the Generating Action of the Acid from PAG using Acid Sensitive Dyes (2)

Atsushi Sekiguchi, Yoko Matsumoto, Kengo Moriyasu¹,
Yukihiro Morimoto¹ and John J. Biafor²

Litho Tech Japan Corporation

2-6-6-201, Namiki, Kawaguchi, Saitama 332-0034, Japan

¹ *Ushio Corporation*

1194 Tosa, Bessho, Himeji-city, Hyogo 671-0224, Japan.

² *KLA-Tencor Corporation, PCI Division*

8834 N. Capital of Texas Hwy #301 Austin, TX 78759, USA

Researchers are currently exploring the use of acid-sensitive dyes to determine the quantity of acid generated from a photoacid generator (PAG) and to analyze acid-generating reactions. Requiring merely the addition to the resist of an acid-sensitive dye, which reacts with the acid generated from the PAG during the exposure and generates a color, this method makes it easier to grasp the PAG acid-generating action. The process involves applying a resist containing an acid-sensitive dye to a sample quartz substrate; making the exposure; and measuring and evaluating the absorbance of a chromogenic substance near 530 nm using a spectroscope. The method determines the rate constant for acid generation (the Dill C parameter) during the exposure based on the relationship between transmissivity at 530 nm and the exposure dose. However, the chromogenic substance used in this method gradually degrades after the exposure, resulting in time-dependent variations in transmissivity. With this in mind, we devised a measurement system capable of *in situ* measurements of absorbance at 530 nm during exposures of a 193-nm light beam. Using this system, we obtained rate constants for acid generation, C parameters, and compared the effects of ArF resist polymer (with and without blocking groups) of different structures and various PAG types, as well as the dependence on the quantity of the quencher. The results of our experiments indicate a new model that accounts for the quencher concentration parameter would be useful in analyzing dependence on the quantity of quencher. This paper presents these findings.

Keywords: Chemically amplified resist, photoacid generator, quencher concentration parameter, acid sensitive dyes, coumarin, 193-nm excimer lamp

1. Introduction

Researchers are currently exploring the use of acid-sensitive dyes to determine the quantity of acid [1-5] generated from PAG and to analyze acid-generating reactions [6-7]. Requiring merely the addition to the resist of an acid-sensitive dye, which reacts with the acid generated from the PAG during the exposure and generates a color, this method makes it easier to grasp the PAG acid-generating action. After applying a resist containing an acid-sensitive dye to the quartz substrate, we expose it so that the dye generates a color, then measure and evaluate absorbance near 530 nm using a spectroscope. The

photoacid generator typically used for this purpose is coumarin 6. The method lets us determine the rate constant for acid generation (the Dill C parameter) during the exposure, based on the relationship between transmissivity at 530 nm and the exposure dose [8]. However, the chromogenic reaction of coumarin 6 is reversible: the chromogenic substance degrades over time after the exposure, resulting in color fading. This results in time-dependent variations between the completion of the exposure and measurements of transmissivity. With this in mind, we devised a measurement system capable of *in situ*

measurements of absorbance at 530 nm during exposures of a 193-nm light beam. Using this system, we obtained rate constants for acid generation (Dill C parameter values) and compared the effects of ArF resist polymers (with and without blocking groups) of different structures and various PAG types, as well as dependence on the quantity of the quencher. The results of our experiments indicate a new model that accounts for the quencher concentration parameter would be useful in analyzing dependence on the quantity of quencher. This paper presents our findings.

2. Experimental

Figure 1 is a schematic diagram of our measurement system. This system incorporates a 193-nm excimer lamp to make the exposures and a halogen lamp for spectrometry. It also incorporates a power meter to measure 193-nm exposure doses and a spectroscopy for spectrometry [9]. The spectroscopy is an ISO32 model manufactured by Ocean Optics.

The light source used in our experiments is an ArF excimer lamp (manufactured by Ushio), which generates a monochromatic 193-nm vacuum ultraviolet light beam [10]. This lamp consists of a lamp bulb containing argon and fluorine and a power supply unit that applies a high-voltage pulse. The argon and fluorine sealed in the lamp bulb form an ArF* exciplex when excited by the high-voltage pulse applied to the pair of electrodes located outside the lamp barrier, which emits a 193-nm VUV light beam, then goes back to the ground state. Figure 2 is a photo of the exterior of the measurement system.

Figure 1 Schematic diagram of measurement system

Figure 2 Exterior of the measurement system and exposed sample

We prepared resist samples (quasi-resists) by adding PAG and coumarin 6 in amounts twice the molecular amount of PAG to acrylic polymer for ArF resists (to a thickness of 400 nm at 3,000 rpm; target film thickness: 400 nm). We then measured transmissivity during the ArF exposure. The substrate was synthetic quartz. The resin used was a polymer for ArF resists (manufactured by Mitsubishi rayon) [11-13].

GMH (With blocking group)

GAH (Without blocking group)

Figure 3 Polymer structures

GBLMA/MAdMA/HAdMA 40/40/20 (mol%) (hereafter referred to as "GMH")

GBLMA/AdMA/HAdMA 40/40/20 (mol%) (hereafter referred to as "GAH")

Figure 4 PAG structures

Figure 3 illustrates the structures of the polymers used in our experiments. GMH has a blocking group. GAH lacks blocking groups. We used the following three types of triphenylsulfonium-based PAG having various molecular weights (see Figure 4): TPS-TF (triphenylsulfonium triflate; MW = 412.45), TPS-PFBS (triphenylsulfonium perfluorobutanesulfonate; MW = 562.47), TBPDPs-PFBuS (triphenylbutyl-diphenylsulfonate-perfluorobutanesulfonate; MW = 618.57) (All manufactured by Toyo Gosei)

The amount of PAG was 4% of the resin by weight. We used coumarin 6 (MW = 160.17; manufactured by Tokyo Chemical Industry) as the acid-sensitive dye [14-15]. (See Figure 5.)

The amount of coumarin 6 added was twice the molecular amount of PAG. As a quencher, we used triethanolamine (MW = 149.19). The quantity added was varied to 0, 0.05, 0.1, 0.5, and 0.75% of the molecular amount of PAG.

Figure 5 Structure and chromogenic reaction of coumarin 6

Applying the resist

We applied the resist to a thickness of 400 nm without HMDS. The pre-bake was performed at 100°C for 60 seconds. After using a Si substrate to adjust film thickness, we applied the resist to a quartz substrate.

Figure 6 Relationship between transmissivity at 530 nm and exposure dose obtained using differing PAG types (Resin: GMH; quantity of coumarin 6: twice the molecular amount of PAG)

3. Results and discussion

3.1 Effect of PAG type

Figure 6 shows the relationship between trans-

Figure 7 Relationship between normalized acid concentration $[H^+]$ and exposure dose obtained using different types of PAG (Resin: GMH; quantity of coumarin 6: twice the molar amount of PAG)

Table 1 Dill C parameters obtained using different types of PAG

PAG	Polymer	The amount of addition of coumarin (mol)	Dill C parameter (cm^2/mJ)
A	GMH	2	0.0674
B	GMH	2	0.0678
C	GMH	2	0.0567
A	GAH	2	0.0545
B	GAH	2	0.0578
C	GAH	2	0.0497

missivity and exposure dose obtained with different types of PAG. In all cases, the PAG concentration was 4%, the amount of coumarin 6 was twice the molecular amount of PAG, and the resin was GMH.

The results showed that PAG types of higher molecular weights suppress the decrease in transmissivity. We believe that adding PAG in amounts equal to 4% of the resin reduces the relative amount of acid generated when the PAG is of high molecular weight. Figure 7 shows the relationship between the concentration of acid generated and the exposure dose. Table 1 gives Dill C parameters calculated using Equation (1).

$$[H^+] = 1 - \exp(-C \cdot E) \quad (1)$$

where $[H^+]$ is the normalized acid concentration, C the

acid-generation reaction rate constant (cm^2/mJ), and E the exposure dose (mJ/cm^2).

When the polymer has a blocking group (GMH), the value calculated for the Dill C parameter is approximately 0.06, regardless of PAG type. When the polymer has no blocking group (GAH), the Dill C parameter calculated is approximately 0.05, regardless of PAG type.

3.2 Effect of the amount of added quencher

Figure 8 shows the relationship between transmissivity and the exposure dose when we added a quencher in amounts equal to 0 to 0.75% of the molecular amount of PAG. We used only PAG A in this experiment. The amount of coumarin added was twice the molecular amount of PAG.

(b) Polymer GAH

Figure 8 Relationship between transmissivity (at 530 nm) and exposure dose obtained with varying amounts of added quencher

Figure 8 shows that increasing the amount of added quencher rendered a decrease in transmissivity less dependent on exposure dose. We believe this was due to quencher consumption of the generated acid. Figure 9 shows the relationship between the absorbance coefficient $[A]$ and the quencher quantity. The absorbance coefficient $[A]$ is proportional to concentrations in a manner consistent with the Lambert-Beer law. The relationship between the amount of acid consumed by the quencher and the amount of quencher added is linear.

$$A = -\log T = \varepsilon cl \quad (2)$$

A : Absorbance (AU)

c : Concentration of substance

ε : Specific absorbance coefficient of substance

l : Thickness of medium (400 nm)

Figure 9 Relationship between absorbance $[A]$ and quencher quantity

Figure 10 shows the amounts of added quencher and the relationship between the acid concentration $[H^+]_q$ after quenching and exposure dose. We established a standard acid concentration level of 1 based on the absorbance resulting from the $100\text{mJ}/\text{cm}^2$ exposure when no quencher was added. We then used the absorbance ratio to calculate normalized acid concentrations under different conditions. The results obtained with polymer GMH (with blocking group) are shown in (a). The results obtained with polymer GAH (without blocking group) are shown in (b). Table 2 gives the Dill C parameters calculated using the

conventional formula (1) expressing the relationship between acid concentration and exposure dose.

(a) Polymer: GMH

(a) Polymer: GAH

Figure 10 Relationship between acid concentration $[H^+]_q$ after quenching and exposure dose obtained with varying amounts of added quencher (fitted results based on the conventional formula)

Table 2 C parameters obtained using varied quencher concentrations (old formula)

PAG	Polymer	The amount of addition of quencher (mol)	Dill C parameter (cm^2/mJ)
A	GMH	0.00	0.0631
A	GMH	0.05	0.0329
A	GMH	0.10	0.0235
A	GMH	0.50	0.0069
A	GMH	0.75	0.0027

PAG	Polymer	The amount of addition of quencher (mol)	Dill C parameter (cm^2/mJ)
A	GAH	0.00	0.0527
A	GAH	0.05	0.0343
A	GAH	0.10	0.0208
A	GAH	0.50	0.0074
A	GAH	0.75	0.0031

The Dill C parameter should remain consistent because of the PAG. However, since the quencher consumes the acid, the apparent amount of acid generated decreases. Thus, the Dill C parameter value changes depending on the amount of added quencher. With these results in mind, we developed a new formula to express the relationship between acid concentration $[H^+]_q$ after quenching and the exposure dose [17-18]

The reaction between acid and quencher is bimolecular. The rate law that acid is neutralized by quencher is

$$\frac{d[H^+]_0}{dt} = -k_q \cdot [H^+]_0 \cdot [Q] \quad (3)$$

where k_q is the rate constant of neutralization. Also

$$\frac{d[Q]}{dt} = -k_q \cdot [Q] \cdot [H^+]_0 \quad (4)$$

where k_q is the same in both expressions.

The difference between the concentration of $[H]$ and $[Q]$ at any time during the reaction is constant.

$$\frac{d[H^+]_0}{dt} - \frac{d[Q]}{dt} = 0 \quad (5)$$

and

$$[H^+]_{(t)} - [Q]_{(t)} = \text{constant} = [H^+]_0 - [Q]_0 \quad (6)$$

where $[H^+]_0$ and $[Q]_0$ are the concentrations after exposure (initial concentrations) and $[H^+]_{(t)}$ and $[Q]_{(t)}$ are the concentrations of $[H]$ and $[Q]$ at a time t during the reaction. The expression for $[H]_{(t)}$ is based on the integrated rate law for a bimolecular reaction, while accounting for the quencher parameter (quenching rate constant). This formula is given below as Equation (7).

$$[H^+]_q = \frac{([H^+]_0 - [Q]_0)}{\left(1 - \left(\frac{[Q]_0}{[H^+]_0}\right) \cdot e^{(-k_q \cdot ([H^+]_0 - [Q]_0) \cdot E)}\right)} \quad (7)$$

$[H^+]_q$: Normalized acid concentration level after quenching

$[H^+]_0$: Concentration of acid generated by the

exposure

$[Q]$: Quenching rate parameter

k_q : Quenching rate constant

E : Exposure rate (mJ/cm^2)

The quantity inside the exponential has to be greater than 0 and less than 1 and have no units

$$0 < e^{(-k_q) \cdot ([H^+]_0 - [Q]_0) \cdot E} < 1 \quad (8)$$

Therefore the units of k_q have to cancel the product of the units of concentration and time

(a) Polymer: GMH

(b) Polymer: GAH

Figure 11 Relationship between acid concentration $[H^+]_q$ after quenching and exposure dose obtained using varying amounts of added quencher (fitted results based on the new formula).

Figure 11 shows the fitted results obtained using the new formula. Table 3 gives the quenching rate parameters.

Table 3 C parameters obtained using different quencher concentrations (new formula), GMH: $C = 0.0631 \text{ (mJ/cm}^2\text{)}$ CGAH: $C = 0.0527 \text{ (mJ/cm}^2\text{)}$

PAG	Polymer	The amount of addition of quencher (mol)	Quencher concentration parameter
A	GMH	0.00	0.00
A	GMH	0.05	0.123
A	GMH	0.10	0.219
A	GMH	0.50	0.585
A	GMH	0.75	0.820

PAG	Polymer	The amount of addition of quencher (mol)	Quencher concentration parameter
A	GAH	0.00	0.00
A	GAH	0.05	0.111
A	GAH	0.10	0.208
A	GAH	0.50	0.573
A	GAH	0.75	0.774

These results indicate the new formula enables fitting that accounts for the quencher concentration parameter.

4. Conclusions

We obtained the Dill C parameter using three types of PAG. The results show the C parameter remains virtually unchanged ($C = 0.05$ to 0.06), although the value differs slightly between PAG with a blocking group and PAG without a blocking group. We varied the amount of quencher added, then obtained the Dill C parameter. We discovered that the Dill C parameter changes based on the amount of added quencher in accordance with the conventional formula. This happens because the quencher consumes the generated acid, reducing the apparent amount of acid. We developed a new acid concentration formula that accounts for the quencher concentration parameter and confirmed that the new formula lets us calculate acid concentrations by incorporating the quencher concentration parameter.

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