Profile Simulation of SU-8 Thick Film Resist

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XP SU-8 3000 (hereinafter referred to as “SU-8”) thick-film resist is a chemically amplified negative resist based on epoxy resin. Here, we report on the profile simulation for this resist. Profile simulation is an important technique for planning experiments. Thus, there have been many reports on simulation techniques. In particular, many studies have been conducted on chemically amplified positive resists, as they are major resist materials used in the IC industry. However, there have been few simulation studies concerning chemically amplified negative resists.

Thus, we conducted studies on the two-stage PEB process for a chemically amplified negative resist and reported the results [1]. In this article, the process is modified from the previous two-stage PEB process to a single-stage PEB process, the effects of the crosslinking reaction are measured, and a simulation technique is studied.

Keywords: Chemically amplified negative resist, Thick-film resist, Crosslink, Lithography simulation

1. Introduction

SU-8 (Kayaku Microchem Co., Ltd.) provides well-defined resist profiles with high aspect ratios, and is also suitable for use as a permanent resist. SU-8 has been widely used in the MEMS (Micro Electro Mechanical System), IC package (bump, insulator, encapsulation), soft lithography (micro mold, imprint), micro fluid (inkjet, micro reactor, biochips), and optical device (waveguide, optical switch) fields. SU-8 is a chemically amplified negative resist based on epoxy resin. This resist generates a strong acid during exposure, and PEB (Post Exposure Baking) induces the crosslinking reaction of the resin with the acid working as a catalyst to insolubilize the resist.

In recent years, the increased demand for chemically amplified negative resists in the field of MEMS has increased the need for simulation. The first study on lithography simulation was conducted by Dill in 1975 [2-5], and many studies have followed [6-11]. In particular, many researchers have studied simulation techniques for chemically amplified positive resists. However, few simulation studies have been conducted on chemically amplified negative resists. Thus, we report here our studies on the simulation technique for the single-stage PEB process with SU-8, a chemically amplified negative resist. The study is conducted as follows. First, the following parameters necessary for the simulation are measured:

(1) Photosensitivity parameters for exposure
(2) Crosslinking reaction parameters for PEB
(3) Development parameters for development

Next, the resist profile simulation is performed with the obtained parameters used as the input. Further, patterns are actually produced and the SEM observation results are compared with the simulation results.

2. Equipment for measuring parameters and the simulation system

Figure 1 shows the configuration of the equipment

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used in this study to measure the parameters. The photosensitivity measurement is performed using the ABC analyzer (manufactured by Lithotech Japan) [12], the crosslinking reaction parameters are measured using the PAGA-100 deprotection reaction analysis system (manufactured by Lithotech Japan) [13], and the development parameters are measured using RDA (manufactured by Lithotech Japan) [14]. The resist profile simulation is performed using PROLITH (produced by KLA-Tencor) software [15]. Each piece of the equipment is outlined below.

![Figure 1. Equipment for measuring parameters](image)

2.1. Equipment for measuring the photosensitivity parameters A and B (Exposure)

The equipment consists of hardware that exposes the resist and measures the transmittance, and software that calculates photosensitivity parameters A and B [12].

2.2. Equipment for measuring the crosslinking reaction parameters (PEB)

This equipment measures the crosslinking reaction during PEB. The hardware is an FT-IR spectrometer with bakeplates and an exposure function included in the measurement chamber. The software includes a program for analyzing changes in the absorbance of the functional group due to the crosslinking reaction, based on the spectral data obtained as a function of the PEB time [13]. Another program is also installed for calculating photosensitivity parameter C and the crosslinking reaction parameters.

2.3. Equipment for measuring the development parameters (Development)

This equipment measures the development rate. It consists of hardware that measures the reflectance as the development proceeds and software that calculates the development rate [14]. The development rates for several exposure values are measured in advance. This procedure makes it possible to determine the development rate, R, for the given exposure, E, thereby producing R(E) data. Further, the development parameters are calculated using the development rate data, R(E), and photo-sensitivity parameters A, B, and C [12]. This system can also calculate Eth, which expresses the resist sensitivity, the γ value, which is an indicator of the resolution, and tan θ, which is the gradient of the solution velocity curve.

2.4. Resist-profile simulation software

This software calculates the light intensity distribution in the resist film when the laser beam from the exposure system passes through the projection lens and forms the image in the resist film. This software calculates the resist profile using the light intensity distribution data, photosensitivity parameters A, B, and C for exposure, the crosslinking reaction parameters for PEB, and the development parameters for development [15].

![Figure 2. Process flow for sample preparation](image)

3. Measurement of parameters

3.1. Measurement conditions

The samples were prepared in the laboratory under conditions of a temperature of 24.3 °C and humidity of 37%. Figure 2 shows the process flow. SU-8 chemically amplified
negative resist (Kayaku Microchem Co., Ltd.) was coated on Si wafers 50 μm in thickness. Prebaking was performed using the proximity method at 65 °C for 5 minutes, followed by 95 °C for 15 minutes. After prebaking, the samples were allowed to stand in the laboratory for 30 minutes (Relaxation).

3.2. Photosensitivity parameter measurement

Photosensitivity parameters A and B for the resist exposure were calculated based on the measurement made using a quartz substrate. The substrate was coated with the resist and prebaked, and the change in transmittance with respect to the exposure time was then measured using the ABC analyzer. The i-line (365 nm) was selected as the exposure wavelength, and the exposure duration was set to 1000 seconds (6000 mJ/cm²). On the other hand, photosensitivity parameter C was calculated from the ring-opening reaction of the epoxy measured using PAGA-100 during PEB.

3.3. Crosslinking-reaction parameter measurement

After exposing the sample to an exposure dose of 125 mJ/cm², the PEB temperature is set to 45 °C, 65 °C, 75 °C, 85 °C, 95 °C, 105 °C, 115 °C, 125 °C, and 145 °C with measurement performed for 20 minutes at each temperature. Here, the IR absorption of the epoxy ring was measured at 910 cm⁻¹ to evaluate the crosslinking reaction of the epoxy resin.

3.4. Development conditions and development rate measurement

SU-8 developer (Kayaku Microchem Co., Ltd.) is used to develop the samples at 24 °C by the dip method. The samples were exposed at varied exposure values, and the development rate was measured using RDA for each exposure values to calculate the development parameters. The development rate was measured at a monitor wavelength of 950 nm.

3.5. Resist profile simulation

The photosensitivity parameters of the resist, the crosslinking reaction parameters, and the development parameters were input into the resist-profile simulation software, PROLITH to perform the simulation. The simulation conditions were NA: 0.63 and the coherence factor of the illumination system was 0.6. The resist line width was set to 20 μm (Line:Space = 1:1 and 1:2). The exposure dose is set to 125 mJ/cm², at which the resist pattern is resolved under a PEB condition of 95 °C for 6 minutes with a mask line width of 20 μm (Line:Space = 1:2). The defocus value was assumed to be the optimal focus. The resolution and the resist profile were simulated at different PEB temperatures.

3.6. Patterning

Patterning was performed using the Nikon stepper, NSR-220511D (NA: 0.63, coherence factor of the illumination system: 0.6), as the exposure system. The sample was dip developed in SU-8 developer at 24 °C for 8 minutes. The resist line width was set to 20 μm (Line:Space = 1:1 and 1:2). The exposure dose is set to 125 mJ/cm², at which the resist pattern is resolved under a PEB condition of 95 °C for 6 minutes with a mask line width of 20 μm (Line:Space = 1:2). The defocus value was assumed to be the optimal focus. The PEB temperature was varied in the formation of the patterns. The resist profiles were imaged using an SEM, and the resolution and resist profile were observed.

4. Results of parameter measurement and reaction analysis

4.1. Results of photosensitivity parameter measurement

The results of the A and B parameter measurement from ABC analyzer. From this result photosensitivity parameters A and B are estimated to be -0.001 μm⁻¹, and 0.007 μm⁻¹, respectively. Photosensitivity parameter C is estimated to be 0.011 cm²/mJ from the PAGA-100 measurement.

4.2 Results of the crosslinking reaction parameter measurement

(1) Observation of crosslinking reaction

While the Si wafer sample coated with 50 μm of SU-8 was exposed using the exposure function of PAGA-100, the change in the spectral absorption was measured in the transmittance measurement mode. Figure 3 shows the scheme for the crosslinking reaction of SU-8. Figure 4 shows the measurement results with PAGA-100. When SU-8 is exposed to ultraviolet light, the photoreaction initiator decomposes and generates an acid, which causes the ring opening reaction of the epoxy group. The polymerization reaction of the
epoxized oligomer due to the acid catalyst progresses the crosslinking reaction. Thus, measuring the change in the absorption by the epoxy group (910 cm⁻¹) during exposure and PEB provides a means for evaluating the relationship between the exposure and the crosslinking ratio of the resin, as well as the relationship between the PEB time and the crosslinking ratio of the resin.

Figure 3. Reaction scheme of SU-8

Figure 4. Change in the spectra before and after exposure (a), and change in absorption by the epoxy group at 910 cm⁻¹ (b)

Absorption by the epoxy group is observed near 910 cm⁻¹ in the spectrum. This result demonstrates that the cross-linking reaction of the functional group occurs due to the exposure and the PEB. The illumination energy of the exposure is 1 mW/cm², which amounts to 1 mJ/cm² in 1 second of exposure. Normalizing the crosslinking ratio by taking the peak area for the unexposed resin as 0 and the peak area for the sufficiently exposed and PEB processed resin as 100, the relationship between the exposure and the crosslinking ratio is obtained (Figure 5). Figure 5 shows that exposure alone can cause crosslinking. Exposure of 125 mJ/cm² results in a cross-linking ratio of approximately 9%.

Figure 5. Relationship between exposure and crosslinking ratio

(2) Crosslinking reaction model and crosslinking reaction parameter

The crosslinking reaction of chemically amplified negative resists is modeled as follows [16]. First, the crosslinking reaction due to the photon energy generated in the exposure is expressed as

$$\frac{\partial [S_{cl}]}{\partial t} = -K_{\text{photo}} I \cdot [S_{cl}]$$

(1)

Here, $K_{\text{photo}}$ is the crosslinking reaction constant for the crosslinking reaction due to the photon energy generated by the exposure, I is the illuminance of the exposure light, and $[S_{cl}]$ is the normalized concentration of the reactive groups in the crosslinking agent. Then, the crosslinking reaction of the unreacted reactive group after exposure during the PEB is expressed as

$$\frac{\partial [S_{cl}]}{\partial t'} = -K_{cl} \left[H^+\right]^m \cdot [S_{cl}]$$

(2)

$$\frac{\partial [H^+]}{\partial t'} = -K_{\text{loss}} \left[H^+\right] + D_{\text{acid}} \nabla^2 [H^+]$$

(3)

Here, $[S_{cl}]$ is the normalized crosslinking ratio, $t'$ is the PEB time (sec), m is the order of the crosslinking reaction, $K_{cl}$ is the crosslinking reaction constant, $K_{\text{loss}}$ is the constant corresponding to the deactivation of the acid in the PEB, and $D_{\text{acid}}$ is the diffusion constant of
the acid. Equation (2) indicates that the crosslinking reaction occurs in proportion to the crosslinking ratio, \([S_{ci}]\), and the acid concentration, \([H]^+\). Equation (3) indicates that the acid exponentially decreases with respect to the PEB time. The constants, \(K_{ci}\), \(K_{loss}\), and \(D\) are generally functions of the temperature and can be approximated from the Arrhenius plots as Equations (4), (5), and (6).

\[
K_{ci} = K_{ci0} \exp\left(\frac{-E_{aci}}{RT}\right)
\]

(4)

\[
K_{loss} = K_{loss0} \exp\left(\frac{-E_{aloss}}{RT}\right)
\]

(5)

\[
D_{acid} = D_{acid0} \exp\left(\frac{-E_{acid}}{RT}\right)
\]

(6)

Here, \(E_{aci}\), \(E_{aloss}\), and \(E_{acid}\) indicate the activation energies. Assuming the concentration of the generated acid to be expressed as

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

(7)

the general equation for the crosslinking reaction is expressed as

\[
[S_{ci}] = \exp\left[-K_{ci}\left(1 - \exp(-CE)\right)^m \cdot t\right]
\]

(8)

Here, \([S_{ci}]\) is the crosslinking ratio, \(K_{ci}\) is the crosslinking reaction constant, \(m\) is the order of the crosslinking reaction, \(C\) is the acid-generation reaction constant, \(E\) is the exposure energy, and \(t\) is the PEB time. The acid deactivation constant, \(K_{loss}\), is calculated from \(\tau\).

\[
K_{loss} = 1/\tau
\]

(9)

Yoshino et al. of NEC released this model in 1992 [16]. The current study uses this model.

When the exposure is 125 mJ/cm² approximately 9% of crosslinking occurs during the exposure. Figure 6 shows the relationship between the crosslinking ratio and the PEB time for SU-8 at various PEB temperatures. The crosslinking attributed to the PEB starts at 9% and eventually reaches 100%. Equation (8) is applied to the measurement results of the relationship between the crosslinking ratio and the PEB time at various PEB temperatures in order to calculate the crosslinking reaction constant.

Figure 6. Relationship between the crosslinking ratio and the PEB time (Exposure: 125 mJ/cm²)

Figure 7 shows the obtained Arrhenius plot for the crosslinking reaction constant. At a PEB temperature of 74°C, the gradient of the plot changes. This behavior indicates that regions with different activation energies exist. Table 1 shows the cross-linking reaction parameter and the acid diffusion parameter obtained from the Arrhenius plot for the crosslinking reaction constant.

Figure 7. Arrhenius plot
Table 1. Results of the crosslinking parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplification Reaction Order</td>
<td>1.0000</td>
</tr>
<tr>
<td>Amplification Reaction $E_a$ (kcal/mol)</td>
<td>3.9900</td>
</tr>
<tr>
<td>Amplification Reaction $\ln(A_r)$ (1/sec)</td>
<td>5.6812</td>
</tr>
<tr>
<td>Diffusion-Controlled Reaction $E_a$ (kcal/mol)</td>
<td>3.4040</td>
</tr>
<tr>
<td>Diffusion-Controlled Reaction $\ln(A_r)$ (1/sec)</td>
<td>5.8767</td>
</tr>
<tr>
<td>Bulk Acid Loss $E_a$ (kcal/mol)</td>
<td>7.2300</td>
</tr>
<tr>
<td>Bulk Acid Loss $\ln(A_r)$ (1/sec)</td>
<td>9.5390</td>
</tr>
</tbody>
</table>

4.3 Results of development parameter measurement

Table 2 shows the results of the development parameter measurement from RDA system.

Table 2. Results of the development parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development $R_{max}$ (nm/sec)</td>
<td>250.00</td>
</tr>
<tr>
<td>Development $R_{min}$ (nm/sec)</td>
<td>0.09</td>
</tr>
<tr>
<td>Development $M_{th}$</td>
<td>0.31</td>
</tr>
<tr>
<td>Development $n$</td>
<td>20.00</td>
</tr>
<tr>
<td>Relative Surface Rate</td>
<td>1.00</td>
</tr>
<tr>
<td>Inhibition Depth (nm)</td>
<td>10000.00</td>
</tr>
</tbody>
</table>

5. Discussion

5.1. Resist profile simulation

Figure 8 shows the results of the resist profile simulation and SEM observation. For 20 μm lines (Line:Space = 1:1) in the simulation, the patterns were resolved at PEB temperatures from 65 °C to 115 °C, and the simulation results almost agree with the SEM observation results. However, in the simulation, the patterns were also resolved at PEB temperatures from 125 °C to 145 °C, whereas the SEM observation reveals that the lines join with the adjacent lines at the top edge at these temperatures, so the results disagree between the simulation and SEM observation in this respect. The results of the simulation and the SEM observation also disagree with PEB at 45 °C.

For 20 μm lines (Line:Space = 1:2) in the simulation, the patterns were resolved at PEB temperatures from 65 °C to 145 °C, and the simulation results almost agree with the SEM observation results. However, the simulation produces increasing line width with increasing temperature at PEB temperatures from 115 °C to 145 °C, forming linear taper shaped resist sidewalls. On the other hand, the SEM observation reveals a thick line width at the top edge of the pattern, so the results disagree between the simulation and SEM observation in this respect.

The cause of the disagreement between the simulation results and the SEM observations is considered to be the divergence of the crosslinking reaction model equation from the measured values and the inability of the simulation to include the resist swelling reaction.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>L/S=20/20 μm</th>
<th>L/S=20/40 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>45°C</td>
<td></td>
<td></td>
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<tr>
<td>65°C</td>
<td></td>
<td></td>
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<tr>
<td>75°C</td>
<td></td>
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<td>85°C</td>
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<tr>
<td>95°C</td>
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<tr>
<td>105°C</td>
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<td></td>
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<tr>
<td>115°C</td>
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<td></td>
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<tr>
<td>125°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>145°C</td>
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<td></td>
</tr>
</tbody>
</table>

Figure 8. Results of SEM observation and resist profile simulation

5.2. Patterning (SEM observation)

Figure 8 shows the actually fabricated patterns
observed using an SEM. Regarding the resolution, the patterns resolve at PEB temperatures from 65°C to 115°C for 20 µm lines (Line:Space = 1:1). At PEB temperatures from 125°C to 145°C, the line width starts to increase near the middle of the resist film depth toward the top edge where the lines join together, and the patterns are not resolved. At a PEB temperature of 45°C, the resist pattern disintegrates and contacts with adjoining lines, and thus the pattern is not resolved. This result indicates that 48% of crosslinking is insufficient. The crosslinking reaction condition necessary to resolve the patterns corresponds to PEB temperatures from 65°C to 115°C. Thus, the range of crosslinking reaction for resolving 20 µm lines (Line:Space = 1:1) is considered to be from 81% to 87%.

For 20 µm lines (Line:Space = 1:2), the patterns resolve at PEB temperatures from 65°C to 145°C. At PEB temperatures from 115°C to 145°C, the line width at the top edge is greater for higher temperatures. Increasing the space width prevents the line top edges from joining together. For conditions without PEB and with PEB at 45°C, the results are similar to those for 20 µm lines (Line:Space = 1:1). The crosslinking reaction condition necessary for resolving the patterns corresponds to PEB temperatures from 65°C to 145°C. Thus, the range of crosslinking reaction for resolving the 20 µm lines (Line:Space = 1:2) is considered to be from 81% to 95%.

6. Summary
The simulation parameters for SU-8, a chemically amplified negative resist based on epoxy resin, are measured, and profile simulations are performed. The simulation results are compared with patterning results. The results do not completely agree. The cause of this observation is considered to be the divergence of the present crosslinking reaction model from the measured values and the inability of the simulation to include the resist swelling reaction and other related factors. Consideration of a new crosslinking reaction model is necessary to solve these problems in the future.

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References


