Study of Outgassing from the ArF CA Resist During ArF (193 nm) Exposure

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In recent years, we have seen growing numbers of reports on problems associated with outgas generated from resists during ArF exposure, including contaminating the exposure equipment lens [1]. Scanner manufacturers have reportedly begun taking countermeasures—for example, establishing criteria for outgas generated by resists during exposure. In the near future, resist manufacturers will likely be required to attach documents regarding outgassing to their products at the time of shipment. In our earlier studies, we tried to establish methods for evaluating outgassing from KrF resists during KrF (248 nm) exposure [2, 3]. This paper examines an approach to evaluating outgassing from ArF chemically-amplified resists during ArF exposure, with a special focus on sulfate ions (SO4^2-) derived from PAG, based on the outgas analytical techniques that we have built up to date. We used ion chromatography (IC) as the method of analysis.

Keywords: Outgassing, ArF exposure, Ion chromatography, Open-frame exposure, TPS-TF

1. Introduction

In recent years, we have seen growing numbers of reported cases on problems associated with outgas generated from resists during ArF exposure, including contaminating of the exposure equipment lens [1]. Scanner manufacturers have reportedly begun taking countermeasures—for example, establishing criteria for outgas generated by resists during exposure. In the near future, resist manufacturers will likely be required to attach documents regarding outgassing to their products at the time of shipment. In our earlier studies, we tried to establish methods for evaluating outgassing from KrF resists during KrF (248 nm) exposure [2, 3]. This paper examines an approach to evaluating outgassing from ArF chemically-amplified resists during ArF exposure, with a special focus on sulfate ions (SO4^2-) derived from PAG, which exceeded the estimated specification values in our previous report, based on the outgas analytical techniques that we have built up to date. The paper also discusses improvements of the outgas collection method for a more complete outgas collection and confirmation of the resulting collection accuracy, by re-examining outgassing from the ArF resists investigated in our previous study [4].

2. Experimental

2.1. Materials condition

We used an acrylic-based ArF resist with a lactone ring to collect and analyze the outgas generated during exposure. The PAG used was TPS-TF manufactured by Toyo Gosei. The protective group was adamantyl (MAdMA) [5-7]. This test resist was applied onto a 6 inch Si substrate to a thickness of 300 nm. Pre-bake was performed at 100 °C for 60 sec. Three types of solvents, PGMEA, PGME, and γ-butyrolactone, were used.

Figure 1 presents the scheme of the photochemical reactions of TPS-TF. Figure 2 shows the structure of the polymer.

2.2. Collection method

Figure 3 shows a schematic diagram of the outgas collection pathway. Figures 4 and 5, respectively, show a schematic diagram and a photograph of capture chamber.

A Si substrate coated with test resist is set inside
Fig. 1. Photochemical reactions of TPS-TF.

Fig. 2. Structure of the polymer used.

The outgas generated during the exposure was captured in the collection liquid. We placed 2 impingers in series along the collection pathway. On completion of outgas collection, we combined and diluted their contents to 50 mL. The collection liquid was 0.01% H₂O₂ aqueous solution. Analytical-grade high-purity nitrogen served as the carrier gas. As a blank test, collection was performed without setting a Si substrate inside the capture chamber.

Fig. 3. Schematic diagram of the outgas collection pathway.

Fig. 4. Schematic diagram of capture chamber.

Fig. 5. Photograph of capture chamber.
2.3. Method of analysis

We analyzed the outgas collection liquid described above by anion chromatography [5] with the HIC-20A SUPER ion chromatography system manufactured by Shimadzu Corporation. The detector was an electrical conductivity meter. The eluant was a 1.8 mM sodium carbonate /1.7 mM sodium hydrogen carbonate aqueous solution. The separation column was the Shim-pack IC-SA2 manufactured by Shimadzu Corporation.

2.4. PAG concentration dependence

To investigate the relationship between PAG concentrations and the amount of collected sulfate ions derived from PAG, we produced test resists at the PAG concentrations presented in Table 1 and determined the energy threshold ($E_{th}$) for each concentration. We then compared the amounts of sulfate ions generated during exposure for each resist type at 100 times its $E_{th}$.

| PAG concentration [wt% for polymer] | Exposure dose ($E_{th} \times 100$) [mJ/cm²] |
|-----------------------------------|----------------------------------------|
| 5                                 | 320                                    |
| 10                                | 250                                    |
| 20                                | 140                                    |

2.5. Exposure dose dependence

To investigate the relationship between the amount of collected sulfate ions derived from PAG and exposure doses, we investigated the 20%-PAG test resist to compare the amount of sulfate ions generated at the exposure doses shown in Table 2.

Table 2. Exposure doses for investigating exposure dose dependence.

| $E_{th} \times$ | Exposure dose [mJ/cm²] |
|----------------|------------------------|
| 10             | 14                     |
| 50             | 70                     |
| 100            | 140                    |
| 250            | 350                    |
| 500            | 700                    |
| 1000           | 1400                   |
| 2000           | 2800                   |
| 3000           | 4200                   |

2.6. Improving the outgas collection instrument and environment and reproducibility validation

We modified and improved the capture chamber and the pathway and environment of the outgas collection instrument to achieve a more complete outgas collection under more tightly sealed conditions. The modifications involved securing the quartz window of the capture chamber inside an O-ring and an outer ring using screws and positioning a screw at the connection between the chamber and the tube for the gas flow. Figure 7 is comparison of the new and old capture chambers.

Flow meters were placed at the intake and the outlet of the collection pathway (see Fig. 3) to check to confirm that the gas flow at the intake and outlet remained nearly the same throughout the collection.

Additionally, to ensure the cleanliness of the collection environment, we prepared a positive pressure collection room equipped with HEPA filters. We also installed a facility for washing instruments with ultra-pure water.

Five outgas collection runs were performed under identical conditions to validate the reproducibility of outgas collection achieved with these improvements.
3. Results

3.1. PAG concentration dependence

The amount of sulfate ions detected was converted into units of weight per surface area of exposure. Table 3 presents data on its dependence on PAG concentrations. Figure 8 shows this data.

Table 3. Exposure doses and amounts of sulfate ions detected at different PAG concentrations.

| PAG concentration [wt% for polymer] | Exposure dose [mJ/cm²] | Amount of detected sulfate ions [ng/cm²] |
|------------------------------------|------------------------|----------------------------------------|
| 5                                  | 320                    | 3.756                                  |
| 10                                 | 250                    | 4.630                                  |
| 20                                 | 140                    | 5.602                                  |

3.2. Exposure dose dependence

The amount of sulfate ions detected was converted into units of weight per surface exposure area. Table 4 gives data on its dependence on the exposure dose. Figure 9 shows this data.

Table 4. Amounts of sulfate ions detected at different exposure doses.

| Exposure dose [mJ/cm²] | Amount of detected sulfate ions [ng/cm²] |
|------------------------|----------------------------------------|
| 0                      | 1.822                                  |
| 14                     | N.D.                                   |
| 70                     | 3.519                                  |
| 140                    | 5.121                                  |
| 350                    | 11.454                                 |
| 700                    | 13.415                                 |
| 1400                   | 18.713                                 |
| 2800                   | 25.960                                 |
| 4200                   | 33.669                                 |

3.3. Validation of reproducibility

Table 5 gives the data for 5 outgas collection runs at a PAG concentration of 20% during exposure of 700 mJ/cm² ($E_{th} \times 500$). Figure 10 presents a graph of the average values of analysis performed twice for each collection specimen. Due to variations in collection conditions and in the analyzed values, average values were taken for 2 measurement runs.
Table 5. Data on amounts of sulfate ions detected in 5 collection runs.

| n   | 1st measurement run | 2nd measurement run | Average of two runs |
|-----|---------------------|---------------------|---------------------|
| 1   | 15.471              | 13.846              | 14.658              |
| 2   | 13.341              | 12.764              | 13.053              |
| 3   | 13.624              | 13.393              | 13.508              |
| 4   | 12.639              | 12.457              | 12.548              |
| 5   | 13.460              | 13.154              | 13.307              |

Average: 13.707, 13.123, 13.415

%RSD: 7.699, 4.118, 5.833

Max.: 15.471, 13.846, 14.658

Min.: 12.639, 12.457, 12.548

σ: 1.055, 0.540, 0.783

Fig. 10. Amounts of sulfate ions detected in 5 collection runs (average values of 2 measurement runs).

4. Discussion

We found a positive correlation between PAG concentrations and the amount of sulfate ions in data for PAG concentrations of up to 20%.

In the data for Eth × 3000 (4200 mJ/cm²), we found a positive correlation between exposure doses and the amount of sulfate ions.

Improvements in the instrument and environment resulted in high reproducibility.

5. Conclusion

We investigated a method for collecting outgas generated by ArF resists during ArF (193 nm) exposure and an analytical method with a special focus on sulfate ions in PAG. For the model resist, the results show positive correlations between the amount of sulfate ions and PAG concentrations and between the amount of sulfate ions and exposure doses. Based on what we learned from past studies, we achieved a relative standard deviation of 5.8%
through improvements in the outgas collection instrument and environment and confirmed that the instrument provided satisfactory collection accuracy. We believe the outgas collection and analytical method presented here will be useful in evaluating sulfate ions in outgas generated from ArF resists during exposure.

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