Role of Metal Sensitizers for Sensitivity Improvement in EUV Chemically Amplified Resist

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The requirements for next generation resist materials in extreme ultraviolet (EUV) lithography are very challenging. Therefore, the development of new resist materials and processes has been expected to meet strict requirements. In order to increase the sensitivity of EUV resists without losing resolution and line width roughness (LWR), it is essential to design new resist concept, which can increase pattern formation efficiency. Recently, metal sensitizers containing metal elements of high EUV absorbance have gained growing attention due to significant sensitivity improvement. However, the role of metal sensitizers for sensitivity improvement has been still unclear because of the absence of the fundamental study of the metal sensitizer. Therefore, it is very important to clarify the role of metal sensitizer for sensitivity improvement. In this study, we investigated the effect of metal sensitizers in the resist materials on acid yields using the acid dye method. The introduction of metal sensitizer leads to higher acid generation efficiency per unit volume. In addition, the dissolution behavior and the patterning performances of the resists containing metal sensitizer were investigated using quartz crystal microbalance (QCM) and electron beam (EB) lithography system. These results indicate metal sensitizers are promising method for the improvement of resist performance.

Keywords: Extreme ultraviolet, Metal sensitizer, Chemically amplified resist, Acid yield, Quartz crystal microbalance (QCM)

1. Introduction

A photolithography such as ArF excimer laser lithography (λ=193 nm) has increased resolution beyond expectations by using an immersion lithography and a double patterning technique. However, photolithography will approach its limitation as the pattern size shrinks to below the 16 nm node. Beyond the 16 nm node, extreme ultraviolet (EUV, λ=13.5 nm) lithography is regarded as the most promising next-generation lithography (NGL) technology [1-4]. So far, some excellent EUV resists have been reported, but the requirements for resist materials for NGL are so strict that technical solutions are still unknown. In particular, the trade-off among sensitivity, resolution, and line width roughness (LWR) is the most serious problem for the realization of EUV lithography. In order to overcome this trade-off problem, the increase in pattern formation efficiency is required to increase the chemical gradient without increasing dose. Pattern formation efficiency is very important because the available energy is limited. We need to clarify the chemistry and physics of EUV resists in details at each resist processes because we have to increase each factor to its physical limit. Therefore, fundamental understanding of pattern formation reactions is strongly needed. In order to increase pattern
formation efficiency, it is important to enhance acid generation efficiency per unit volume. Up to now, the effect of the absorption coefficients of the resist on acid generation efficiency has reported [5-8].

Recently, metal sensitizer containing metal elements of high EUV absorbance, which increase EUV photon absorption, have gained growing attention. To date, the metal sensitizer showed significant sensitivity improvement [9], potentially affecting patterning performances [10]. Further, it is known that a higher acid generation lead to higher sensitivity [11]. However, the role of metal sensitizers for sensitivity improvement has been still unclear because of the absence of the fundamental study of the metal sensitizer. Therefore, it is very important to clarify the role of metal sensitizer for sensitivity improvement.

In this study, we investigated the effect of metal sensitizer in the resist on acid yields using the acid dye method and alkaline earth metal salts as sensitizer in chemically amplified resist to better understand the mechanism underlying this sensitivity improvement. In addition, the dissolution behavior and the patterning performances of the resists containing metal sensitizer were investigated using quartz crystal microbalance (QCM) and electron beam (EB) lithography system.

2. Experimental

Two photoresist platforms were used. In the first one, 2 different loadings of sensitizer A were added. In the second platform, three different loadings of sensitizer B were added. The resist NXE1631, without sensitizer, will be called A0. ALow contains 7.5 wt% sensitizer A loading and AHigh has 11.3 wt% sensitizer A loading. The second platform is NXE1716, and B0 is the resist without sensitizer. BLow contains 0.7 wt% sensitizer B loading, BHigh has 2.1 wt% sensitizer loading and BVeryHigh has a loading of 6.7 wt% of sensitizer B. Propylene glycol monomethyl ether acetate (PGMEA) and Propylene glycol monomethyl ether (PGME) was used as a casting solvent without further purification. Coumarin 6 (C6, Aldrich Chem.) was used as an indicator to evaluate the acid yield [12-15]. 5 wt% C6 was added to the NXE 1631 and NXE 1716.

In the sample preparation for the evaluation of resist performance, NXE1631 and NXE1716 resist solutions with and without metal sensitizers A and B were spin-coated on quartz substrates, HMDS-treated n-type Si wafers or QCM substrates. The resist solutions were filtered through a 0.20 μm PTFE syringe filter prior to spin-coating on these wafers. For all coating steps, platform A resist was coated at 1500 rpm and baked for 60 s at 105°C. On the other hand, platform B resist was coated at 1500 rpm and baked for 60 s at 90 °C. Different dilution of the photoresist in casting solvent were prepared for acid yield measurement, QCM measurement, and EB patterning measurement. The film thickness was adjusted for each experimental. 100 nm film thickness resists were used for acid yield measurement and QCM. On the other hand, 30 nm film thickness resists were used for EB patterning experiment. The resist film thickness was measured with an ET200 surface profiler and a film thickness measurement system (spectroscopic ellipsometer).

The films were exposed to EUV (Energetic, EQ-10M) [16] for acid yield measurement and QCM measurement. The exposed area was approximately 1 × 1 cm². In acid yield measurement, after the exposure, absorption spectra were recorded using a JASCO V-670 spectrophotometer to quantify the acid yield in thin sample films by measuring the characteristic absorption of the protonated form of C6 (533 nm). The experimental procedure has been reported in detail elsewhere [13-15]. In QCM measurements, after the exposure, they were baked at 90 °C for 60 s. The exposed films were subjected to QCM analysis in tetramethylammonium hydroxide (TMAH) (2.38 wt%) developer solvents. Dissolution behavior of resist with and without sensitizer was investigated by using the QCM-based analyzer (RDA-Qz3). The experimental procedure has been reported in detail elsewhere [17].

In EB patterning measurement, the films were exposed to a 125 kV EB (ELIONIX, ELS-F125). After the exposure, they were baked at 90 °C to for 60 s. They were developed by dipping in 2.38 N TMAH solutions for 30 s at 23 °C and then rinsed in deionized water for 30 s before drying. Patterns were observed using a Hitachi S5500 scanning electron microscope (SEM; Hitachi-hitec S5500). LWR measurements were performed using the standard LWR measurement algorithm on the Hitachi S5500 SEM. In LWR measurement, the reported LWR values were taken as the average values from ten different lines with a 1 μm inspection length.
3. Results and discussion

We measured the amount of acid generated at the end of the exposure step in order to clarify the improvement in sensitivity due to metal sensitizers. Figure 1 shows representative absorption spectra of C6-containing A₀ upon exposure to EUV. The neutral form of C6 shows a characteristic absorption at 460 nm. By EUV exposure, the absorption of C6 proton adducts appeared at 533 nm [13] as shown in Fig. 1. The absorption intensity of C6 proton adducts increased with exposure dose. For the resists containing metal sensitizers, similar absorptions were observed.

Figures 2 (a) and (b) show the exposure dose dependence of the acid yield generated in two resist films ((a) platform A and (b) platform B) upon EUV exposure. Using the measured absorption coefficient, we can estimate the number of acid generated per absorbed photon. The number of acid molecules generated by a single EUV photon in resist films with and without sensitizer was estimated as shown in Fig. 2. The increase of acid yield was observed at all dose when a metal sensitizer was added to the resist films. We observed a mean 14% increase of acid yield for A₀Low and up to 66% increase for A₀High compared to A₀. Similarly, we observed the average 35% and 66% increase of acid yield for B₀Low and B₀High, respectively compared to B₀. Apart for A₀Low, these number was in line with the sensitivity improvement observed. Thus, the metal sensitizer loading was significantly improving the acid yield in both case. In addition, we measured the acid yield of a sample composed only of the polymer and the sensitizer in order to confirm whether the sensitizer itself played the role of an acid generator. As shown in Figs. 2 (a) and (b), no acid was generated without an acid generator. Thus, the sensitizer did not act as an acid generator by itself. By adding metal sensitizers higher acid yield was achieved, and the increased acid amount can quantitatively explain the dose-to-size reduction observed.

In previous study, we clarified that the metal sensitizer does not increase the absorption of EUV photon [18]. In order to examine the cause of sensitivity improvement of the resist, the patterning properties were investigated by EB exposure tool in Platform A. Figure 3 shows SEM micrographs of line and space patterns of A₀, A₀Low, and A₀High after PEB at 90 °C for 60 s. The area dose of electron beam exposure were required from 140 \( \mu \)C/cm² (A₀) to 60 \( \mu \)C/cm² (A₀High). We observed a dose reduction of 43% for A₀Low and 57% for A₀High. Similar trend with EUV patterning was observed from 125 kV EB patterning results. In both A₀ and A₀Low, clear line and space patterns could be obtained with resolutions of half-pitch 40 nm. At high sensitizer loading, we observed a clear degradation of the pattern quality. Nevertheless, the addition of a metal sensitizer does not necessarily lead to pattern degradation as shown in A₀Low where the line width roughness was reduced compared to A₀. This result indicates that an optimized loading of sensitizer can lead to a simultaneous reduction of dose and roughness, at
Thus, the sensitizer plays their role, with significant dose reduction. Perhaps, the presence of metal sensitizer helps achieving higher pattern formation efficiency. Possible explanation for this is that the addition of sensitizer could increase the secondary electron generation, or the presence of an ionic salt in the vicinity of acid generators could facilitate the reaction leading to acid generation.

QCM measurement was also carried out on platform A. In QCM, the film mass change during development is obtained by measuring the change in frequency of a quartz crystal resonator. Converted into film thickness, the relationship between resist thickness and development time were obtained in resists. Figures 4 (a) and (b) show the relationship between resist thickness and development time was obtained in A0 and ALow, respectively. The difference in dissolution behaviors between A0 and ALow was clearly observed. Swelling of the resist in unexposed and partially exposed film with very small dose was also observed in ALow. Furthermore, the development rate of ALow is faster than A0, which is consistent with dissolution rate monitor (DRM) measurement [18]. This is due to higher acid yield of ALow compared to A0 thanks to the presence of the metal salt.

| Sample | A₀ | A₁₅₀⁺ | A₁₅₀⁻ |
|--------|----|-------|-------|
| Picture HP 40nm | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| Dose-to-size (µC/cm²) | 140 | 80 | 60 |
| LWR (nm) | 3.1 | 2.3 | NA |

Fig. 3. SEM micrographs of line and space patterns of A₀, A₁₅₀⁺, and A₁₅₀⁻ after PEB at 90 °C for 60 s.

Fig. 4. Relationship between resist thickness and development time obtained in (a) A₀ and (b) A₁₅₀⁺, respectively.
4. Conclusion
Sensitivity improvement by adding metal sensitizer was observed by using EB as well as EUV. The sensitivity improvement comes from not higher EUV photon absorption but higher acid yield and electron efficiency. The metal sensitizer salts impact significantly acid yield and dissolution properties. They improve resist performance of resists by selecting properly a sensitizer and optimizing its loading. Actually, the addition of sensitizer (A_Low) showed the sensitivity improvement of 43% simultaneously with a reduction of roughness. The sensitivity improvement is mainly due to the higher acid yield and electron efficiency.

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