TRANSIENT SPECIES INDUCED IN X-RAY CHEMICALLY AMPLIFIED POSITIVE RESISTS: POST-EXPOSURE DELAY EFFECT

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The post exposure delay (PED) effect on transient species induced in X-ray chemically amplified positive resist was investigated. The resist consisted of m-cresol novolac (matrix polymer), bisphenol A protected with tert-butoxycarbonyl groups (dissolution inhibitor), and triphenylsulfonium triflate (acid generator). In order to analyze the PED effect, the changes in optical absorption were measured with a conventional spectrophotometer. For the resist system, it was observed that the absorbance of protonated intermediates of a matrix polymer decreased with PED time. The rate of decrease was accelerated by air borne contaminants, and was also affected by dissolution inhibitor.

1. Introduction

Synchrotron radiation-based X-ray lithography (SRL) can realize the resolution below 0.1 µm with precise line width control and simple processes [1]. Therefore, SRL is the most promising alternative to the optical lithography. In the SRL, chemically amplified resists [2] have demonstrated high performance [3,4]. For such systems, acid which is generated by X-ray exposure causes many subsequent reactions. In most chemically amplified systems, undesired side reactions prematurely destroy the acid, that is, the acid reacts with contaminants. The most notable contaminants are airborne amines [5-7]. The amines prematurely neutralize the acid. This depletion of acid results in a developer insoluble surface layer which leads to T-shaped lines (T-topping). The airborne contamination may occur at any time during the resist processes. However, its effect is most readily seen by increasing the time between the exposure and post-exposure bake process steps (post-exposure delay; PED) [5-7]. To solve this serious problem, various methods have been demonstrated. Reduction of the resist film free volume [8], protection by overcoats [9], and filtering the impurities from air [10] were carried out to reduce the PED effect. On the other hand, the reactions and intermediates in the X-ray chemically amplified resist are not fully understood. The understanding of the reactions and intermediates would be helpful in the design of a new X-ray chemically amplified resist system.
which is less susceptible to the PED effect.

It was observed that the protonated intermediates of a matrix polymer were formed upon X-ray exposure [11,12]. The protonated intermediates may be a trapping site of proton (acid) and are considered to be the precursor of acid.

In this article, we describe the PED effect on the protonated intermediates in model films of X-ray chemically amplified positive resists by monitoring the absorption of the protonated intermediates.

2. Experimental

Materials

The composition of the model film of X-ray chemically amplified positive resists were shown in Figure 1. The matrix polymer was m-cresol novolac supplied by Sumitomo Durez Co. The dissolution inhibitor was bisphenol A protected with tert-butoxycarbonyl groups (tBOC-BA) purchased from EIWEISS Chemical Co. The acid generator compound triphenylsulfonium triflate (TPS-OTf) was obtained from Midori Kagaku Co.

![Chemical structures of a matrix polymer (m-cresol novolac), an acid generator (TPS-OTf), and a dissolution inhibitor (tBOC-BA).](image)

Methods

Resist films were dissolved in methyl 3-methoxypropionate (MMP) and spin-coated at 1500 rpm for 2 min on 3-inch-diameter quartz wafers. Prebake and post exposure bake (PEB) were done on a hot plate at 100 °C for 5 min. X-ray exposure was conducted in a 1 atm He environment with a SORTEC synchrotron radiation (SR) ring [13]. An oscillating Pt mirror and a 40-µm-thick Be window were used in the SR beam line. The peak power wavelength of the X-rays was about 0.7 nm and the intensity on the wafer was about 540 mJ/cm² at 500 mA.

UV-visible absorption spectra of the films were measured with a Hitachi U3410 spectrophotometer. The measurements were started at 5 min after the X-ray exposure because it took a few minutes to take out a wafer from a chamber and set it in the spectrophotometer. The spectra were measured before and after X-ray exposure and after PEB. IR measurements were also taken before and after X-
ray exposure and after PEB using a Perkin Elmer 2000 FTIR spectrometer. These spectra were normalized for a film thickness of 1 µm. The film thicknesses were measured using Dektak ST surface profiler.

Environment

Our work was carried out in two types of clean rooms, CR1 and CR2, and a clean bench (CR3) [6]. CR1 was used for coating and development of resists; thus the room was heavily base-contaminated. CR2 was used as an exposure and inspection room; thus no base-containing materials were used. CR3 was equipped with a chemical filter; thus the base free environment was achieved. The main contaminant was NH₄⁺ in these clean rooms [6]. The concentrations of NH₄⁺ in CR1, CR2 and CR3 were measured to be 50-80 ppb, 5-10 ppb and less than 1 ppb, respectively [6].

3. Results and Discussion

The PED Effect on Protonated Intermediates in the Film of m-Cresol Novolac with an Acid Generator

For 1-µm-thick model films of chemically amplified resists, optical absorption spectra of the films were measured before and after X-ray exposure and after PEB by a conventional spectrophotometer. For a film of m-cresol novolac which did not contain an acid generator or a dissolution inhibitor, absorption peak was not observed in the wavelength range 300 nm to 800 nm. Figure 2 (a) shows the absorption spectra of a m-cresol novolac film which contains 10 wt% acid generator (TPS-OTf). Before exposure, there was no absorption peak in the wavelength range 300 nm to 800 nm. However, after exposure, a absorption peak appeared at around 540 nm. The position of the absorption peak is not affected by acid generators [12]. The absorption peak at 540 nm is attributed to a protonated intermediate of m-cresol novolac [12]. The protonated intermediate may be a trapping site of proton and is considered to be a precursor of acid which catalyzes subsequent chain reactions to change solubility to the alkaline developer. After PEB, the absorption peak at 540 nm decreased. One reason for this is considered that protons were set free from m-cresol novolac by PEB.

Fig. 2 Spectral change in m-cresol novolac films containing 10 wt% TPS-OTf.
The absorption at 540 nm was weakened by adding amines [12]. Therefore, the protonated intermediates can be affected by the basic contaminant in the air. We observed the PED effect on the protonated intermediates. Figure 2 (b) shows the spectral change due to PED in a m-cresol novolac film containing 10 wt% TPS-OTf. This experiment was carried out in CR2.

Figure 3 demonstrates the change in absorbance at 540 nm as a function of PED time in the film shown in Figure 2 (b). As shown in Figure 3, the value of absorbance at 540 nm decreases as the PED time increases. From this experiment, it turned out that the value of absorbance reduced to 71% in CR2 during the period from 5 min to 120 min after exposure. On the contrary, the value of absorbance reduced to 78% during the same period in CR3 which contains less basic contaminants than CR2.

From the above results, it is considered that the protonated intermediates were captured by airborne basic contaminants in some extent. Another reason of the decrease is considered that protons were set free from m-cresol novolac by PEB. Therefore, it is concluded that the condition of proton is changing after exposure in time range of minutes or hours.

**The Effect of Dissolution Inhibitor on Protonated Intermediates in Chemically Amplified Positive Resists**

In order to investigate the effect of a dissolution inhibitor on protonated intermediates in chemically amplified positive resists, optical absorption spectra of the films were measured before and after X-ray exposure and after PEB. The composition of the model resist films was TPS-OTf/tBOC-BA/m-cresol novolac=10/x/60 (weight ratio). The weight ratio of a dissolution inhibitor (tBOC-BA) (x) was changed from zero to 30. Spectral change of the film without dissolution inhibitor (tBOC-BA) is shown in Figure 4 (a). The absorption peak of protonated intermediates appeared at 540 nm after exposure. The absorption decreased after PEB. This is in the same way as Figure 2 (a). The absorption peak of protonated intermediates also appeared in the film containing 30 wt% dissolution inhibitor (tBOC-BA) as shown in Figure 4 (b). However, the value of absorbance increased after PEB. This result is different from that in Figure 4 (a). One possible reason of the increase after PEB is that the protons once trapped by the dissolution inhibitor returned to the novolac matrix polymer after the catalytic chain reaction. The IR peak at 1757 cm\(^{-1}\) (C=O stretching mode) was completely disappeared.
This means that a complete deprotection of tBOC was achieved for the exposure dose, as applied in this experiment. Figure 5 shows the change of absorbance of protonated intermediates as a function of the concentration of tBOC-BA in the model films of a chemically amplified resist. The composition was TPS-OTf/tBOC-BA/m-cresol novolac=10/x/60 (weight ratio). The increase of absorbance after PEB was found in the resist TPS-OTf/tBOC-BA/m-cresol novolac=10/5/60 (weight ratio) as shown in Figure 5. The change of absorbance after PEB from decrease to increase occurred between the tBOC-BA weight ratio (x) of zero and five.
The PED Effect on Protonated Intermediates in a Chemically Amplified Positive Resist

Figure 6 shows the spectral change due to time delay in a film of a chemically amplified positive resist. PED was carried out in CR2. The model composition of the resist film was TPS-OTf/tBOC-BA/m-cresol novolac=10/30/60 (weight ratio). The composition is the same as that in Figure 4 (b).

Fig. 6 Spectral change in a model film of a chemically amplified positive resist.
Resist composition : TPS-OTf / tBOC-BA / m-cresol novolac = 10 / 30 / 60 (weight ratio).

The absorption peak of protonated intermediates also appeared at 540 nm in the film. The value of absorbance decreased with increasing PED time, which is the similar manner as Figure 2 (b). Figure 7 illustrates the decrease of the absorbance at 540 nm with PED time. The value of absorbance reduced to 62 % in CR2 during the period from 5 min to 130 min after exposure. This might be partly due to the airborne contamination in the same way shown in Figure 2 (b). Moreover, the decrease might be partly due to migration of a proton (acid) to a dissolution inhibitor because the absorption of protonated intermediates in the presence of a dissolution inhibitor decreases faster than in the absence
of a dissolution inhibitor.

From the above observation, we can conclude that the condition of acid is changing during PED in the chemically amplified positive resist.

4. Conclusion

For the model films of chemically amplified positive resists, the behavior of protonated intermediates of a matrix polymer were observed by monitoring the absorbance with a conventional spectrophotometer. PED effect on the protonated intermediates were investigated.

The protonated intermediates formed by X-ray exposure decreased during PED. One reason of decrease is air borne contamination because the decrease was accelerated in the room which contains more air borne contaminants, that is, NH$_4^+$. Another reason of the decrease is considered to be due to migration of proton (acid) from the matrix polymer to the dissolution inhibitor. It can be also considered that the protons were set free from the matrix polymer by way of other reactions.

From the results, it might be concluded that the trapping states of proton (acid) are changing during the PED time. The lack of stability in the chemically amplified positive resist can be brought by the change of the trapping states of proton (acid).

References