Time delay effect on a positive deep UV resist using partially tetrahydropyran-protected polyvinylphenol

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Chemical amplification positive resists using partially tetrahydropyran-protected polyvinylphenol (THP-M) were investigated for deep UV lithography. A resist formulated from 20% THP-protected polyvinylphenol and bis(tert-butylphenyl) iodonium triflate resolved 0.30-µm line-and-space patterns with the aqueous base development using a KrF excimer laser stepper with a dose of 46 mJ/cm². Post-exposure delay effect of this resist system was studied. The deprotection reaction of THP-M for lower dose during the holding time at room temperature and incomplete deprotection reaction for higher dose were found to deteriorate the exposure characteristics.

1. Introduction

Recently, much attention has been focused on chemically amplified resist systems for deep UV lithography originally reported by Ito and Willson.1 We showed in a previous article that polyvinylphenol protected with a tetrahydropyran group (THP-M) is deprotected by photo-generated acid from an ionium salt.2 Since this resist system has the difficulty in obtaining fine patterns with a pure aqueous base development, it is necessary to add some n-propanol to the aqueous base developer. We found this difficulty is caused by incomplete deprotection of THP-group and use of partially tetrahydropyran (THP)-protected polyvinylphenol as a base polymer can improve the developability in the pure aqueous base developer.3

In this paper we describe a lithographic performance and time delay effect of the two-component resist system composed of a partially THP-protected polyvinylphenol and an acid generator.

2. Experimental

THP-M was synthesized as previously reported4 by an acid-catalyzed protection reaction of polyvinylphenol (Mw=6500, Mw/Mn=1.89) obtained from Maruzen Petrochemical Co. with 3,4-dihydropyran. To obtain THP-M with different degrees of protection, we changed the amount of added 3,4-dihydropyran. An acid generator bis(tert-butylphenyl)iodonium triflate (TBIT) was synthesized according to the literature.5 The chemical structures of the materials are shown in Fig.
1. The developer was an aqueous base NMD-3 (tetramethylammonium hydroxide: 2.38 wt % and 5 wt %, Tokyo Ohka Co.).

The THP-protection degree was determined by 1H-NMR spectroscopy. Infrared spectroscopy was also used to determine the THP-protection degree of cast films on sodium chloride substrates. To determine the THP-protection degree by infrared spectroscopy, we made a calibration curve between the ratio of peak height (C-O stretching of aromatic ether 969 cm⁻¹ / C-H vibration of para-substituted benzene ring 829 cm⁻¹) and the THP-protection degree determined by 1H-NMR.

Resist formulations were prepared by dissolving THP-M and 3 wt % TBIT in 2-methoxy ethylacetate. Resist films were spin-coated from solutions onto silicon substrates and prebaked on a hot-plate at 80 °C for 10 min or 2 min and exposed to 248-nm radiation from a Xe-Hg lamp through an interference filter. After post-exposure baking (PEB) at 100 °C, the films were developed in NMD-3 (2.38%) for 2 min. Film thickness measurements were made with a Tencor Instruments alpha-step 200. Dissolution rate was determined by measuring the time to clear the resist film in the developer. Lithographic evaluations were made with a Canon KrF excimer laser stepper (0.45 NA).

![Chemical structures of THP-M x% and the acid generator.](image)

3. Results & Discussion

3.1 Dependence of the dissolution rate on the THP-protection degree

To obtain aqueous base developable resists, we examined the dependence of the dissolution rate on the THP-protection degree in developers. The dissolution rate of THP-M films for two developers is plotted as a function of the THP-protection degree in Fig. 2. It is clear from Fig. 2 that the dissolution rate decreases with increasing THP-protection degree as expected and the change of dissolution rate depends on the developer. The THP-protection degrees for negligible small dissolution rate (0.1 nm/sec) are 28% for NMD-3 (2.38%) and 40% for NMD-3 (5%). Moreover, NMD-3 (2.38%) gives the larger change in dissolution rate with change in protection degree than NMD-3 (5%). Therefore, partially protected THP-Ms below 28% protection degree are evaluated as a base polymer for NMD-3 (2.38%) developer in the following experiment.
3.2 Resist containing partially THP-protected polyvinylphenol

We evaluated two-component resist systems composed of partially protected THP-M and bis(tert-butylphenyl)iodonium triflate (TBIT). From Fig. 2, 28% THP-protection leads to negligible small dissolution rate for NMD-3 (2.38%) developer. Therefore, it is reasonable to examine the resist systems composed of THP-M with lower THP-protection degree than 28%, since the onium salt TBIT has a dissolution inhibition effect. The results are shown in Fig. 3. It can be seen that a higher sensitivity of 10 mJ/cm² is obtained for the lower THP-protection degree of 20% without remarkable film thickness loss. In the following experiments THP-M with 20% of THP-protection degree is used.

The absorbance of the resist at 248 nm is 0.41 µm⁻¹ (T=39%). This is due to the relatively high absorbance of the onium salt TBIT at 248 nm and the polyvinylphenol used to synthesize THP-M. The lower THP-protection degree also leads to higher absorbance than fully protected THP-M. However, the absorbance of this resist system is improved compared to three component resist systems composed of novolak, THP-M and an acid generator.⁶

![Fig. 2 Dissolution rate as a function of THP-protection degree for the developers.](image1)

![Fig. 3 Exposure characteristic curves for THP-M x%/TBIT resist (100/3 wt ratio). PEB: 100 °C/10 min; Development: NMD-3 (2.38%) 2 min.](image2)
3.3 Lithographic performance evaluation

Patterning of the resist composed of THP-M 20% and TBIT (100/3 wt ratio) was carried out with a Canon KrF excimer laser stepper (0.45 NA). A PEB of 100 °C/2 min and a development in NMD-3 (2.38%) for 2 min were used. As shown in Fig. 4, 0.30-µm line-and-space patterns with a vertical profile were achieved for a resist film thickness of 1.0 µm with a dose of 46 mJ/cm². Although 0.25-µm line-and-space patterns were not resolved with this dose, they were separated with higher dose of 52 mJ/cm².

![Exposure Dose: 46 mJ/cm²](image1)

![Exposure Dose: 52 mJ/cm²](image2)

Fig. 4  SEM photographs of line-and-space patterns produced by Canon KrF excimer laser stepper (0.45 NA) with the resist composed of THP-M 20%/TBIT. Film thickness: 1.0 µm; PEB: 100 °C/2 min.

3.4 Post-exposure delay time effect

In chemically amplified resist systems, holding time between exposure and post-exposure baking often affects the sensitivity and the resolution. Some previous reports showed that this is due to basic vapor contaminants which deactivate photogenerated acid.7,8

We examined this post-exposure delay time effect on the THP-M 20%/TBIT resist system. In this experiment, resist films were left in air without any treatment. Exposure characteristic curves with different post-exposure delay time are shown in Fig. 5. The contrast of this resist was found to become deteriorated with the post-exposure delay time. With the post-exposure delay time of 16 hours this effect become more pronounced. The SEM photographs of patterns for immediate PEB and PEB after 1 hour delay time are shown in Fig. 6. Although T-top is not observed for 1-hour delay, the pattern profile is slightly deteriorated.
Fig. 5  Post-exposure delay effect on exposure characteristic curves of THP-M 20%/TBIT resist. PEB: 100 °C/2 min.

Fig. 6  Post-exposure delay effect on 0.30-µm line-and-space patterns of the resist composed of THP-M 20%/TBIT. Film thickness: 1.0 µm; PEB: 100 °C/2 min.

Fig. 7  Post-exposure delay effect on dissolution rate of THP-M 20%/TBIT. PEB: 100°C/2 min.
In Fig. 7 the dissolution rate of the resist film were plotted as a function of exposure dose. The dissolution rate in the range of 20-100 mJ/cm² decreases with 16 hours of post-exposure delay time. In contrast, the dissolution rate in the range of 1-20 mJ/cm² is found to increase. The decrease in dissolution rate for higher dose with 16 hours delay time can be explained by the deactivation of the photogenerated acid during the post-exposure delay time, while the increase in the dissolution rate for lower dose cannot be explained.

To investigate the dissolution characteristic behavior described above, we examined THP-protection degree of exposed resist film by infrared spectroscopy as shown in Fig. 8. When a post exposure bake is carried out immediately after exposure, the sharp change of THP-protection degree is observed in the range of 5-100 mJ/cm², and no change of the THP-protection degree is observed in the range of 0-5 mJ/cm². On the other hand, the deprotection reaction of THP-M occurs in 17 hours after exposure without PEB. It is surprising that this reaction occurs even in the range of 1-10 mJ/cm². During PEB after 17 hours holding time, the deprotection reaction proceeds further at 100 mJ/cm², though the THP-protection degree in the range of 1-50 mJ/cm² hardly changes by PEB. As a result, the deprotection reaction proceeds less in the range of 20-100 mJ/cm² and proceeds more in the range of 1-20 mJ/cm² with 17 hours of post-exposure delay time compared to immediate PEB. Therefore, the reason for the dissolution rate increase in the range of 1-10 mJ/cm² with post-exposure delay is revealed to be deprotection reaction of THP-M at room temperature.
Since the activation energy of the deprotection reaction of THP-M is low, it is reasonable that the deprotection reaction proceeds at room temperature. As shown in scheme 1, the deprotection reaction of THP-M is a equilibrium reaction and water is involved in this reaction. While it is impossible to explain the whole behavior described above due to the complicated reaction scheme, it is considered that water penetration into the resist film might promote the deprotection reaction during the holding time at room temperature even for the lower exposure dose area after exposure. This results in poor contrast in exposure characteristic curves. Further study is necessary for complete understanding for the delay time effect of THP-M resist systems.

Scheme 1 Acid-catalyzed reaction of THP-M

4. Conclusion

Partially tetrahydropyranyl-protected polyvinylphenol (THP-M) has been studied for chemical amplification positive resist for deep UV lithography. The investigation of the dissolution rate of THP-M films with different protection degrees indicates that 28% THP-protection degree shows negligible small dissolution rate in an aqueous base developer NMD-3 (2.38%). A resist formulated from THP-M 20% and TBIT resolved 0.30-µm line-and-space patterns with the aqueous base development using a KrF excimer laser stepper with 46 mJ/cm² dose. Post-exposure delay time was found to deteriorate the exposure characteristic of this resist. This is due to the deprotection reaction of THP-M during the holding time after exposure at room temperature and the difference in the final protection degree compared to immediate PEB.
References


