

Alcohol-Assisted Photocrosslinking of Poly(vinyl alcohol) for Water-Soluble Photoresists

Sang-Yeon Shim[†] and Jong-Man Kim^{*}

[†]*Department of Industrial Chemistry, College of Engineering, Kangnung National University,
123 Chibyon-dong, Kangnung, Kangwondo 210-702, Korea*

*Department of Chemical Engineering, Center for Ultra-microchemical Process Systems, Hanyang University,
17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea*

Received April 4, 2001

Patterned negative-tone images on the polymer film have been prepared based on the photoinduced crosslinking of water soluble poly(vinyl alcohol) (PVA) in the presence of various alcohols. Irradiation of a polymer film containing PVA, a photoacid generator and an alcohol as a crosslinker with 254-nm UV through a photomask followed post-exposure bake (PEB) allowed generation of negative-tone relief images at 5 μm resolution in the polymer film. Among various alcohols tested, aromatic alcohols such as pyrogallol and resorcinol were found to be superior to aliphatic alcohols such as sucrose and inositol in terms of resist sensitivity.

Keywords : Photoresist, Polymer, Water-soluble, Image.

Introduction

Photoresists are photosensitive coating materials which are in use for the generation of relief images on solid substrates.¹⁻⁵ They are essential components for the fabrication of semiconducting memory chips, television screens, and many other display panels. In principle, the photoresists undergo chemical modification upon irradiation and result in different solubility properties between the exposed and unexposed area. The relief images are obtained after development of the exposed substrates in developing solvents. When the exposed areas of the film are removed during the development, positive-tone images are obtained. Negative-tone images are generated in reverse ways. In general, photoresists are formulated in organic solvents for spincoating on solid substrates and developed in strong alkaline aqueous solutions after irradiation. Recently, the development of photoresists based on water-based polymers has gained much attention.⁶⁻⁸ The water-based resist systems are attractive because they can avoid the two separate solvent systems and can simplify the imaging processes. In addition, the water-based resists are environmentally more desirable than the conventional resist systems. As part of our ongoing efforts for the development of relief and functional images in the polymer film,⁹ we now report generation of negative-tone relief images based on water-soluble poly(vinyl alcohol) (PVA) with alcohols as cross-linkers.

Experimental Section

Materials. Poly(vinyl alcohol) (87-89% hydrolyzed with an average Mw of 13000), inositol, sucrose, pyrogallol, and

resorcinol were purchased from Aldrich Chemical Company and used as received. (2,4-Dihydroxyphenyl)dimethylsulfonium triflate was synthesized as previous described.¹⁰ Distilled and deionized water was used throughout.

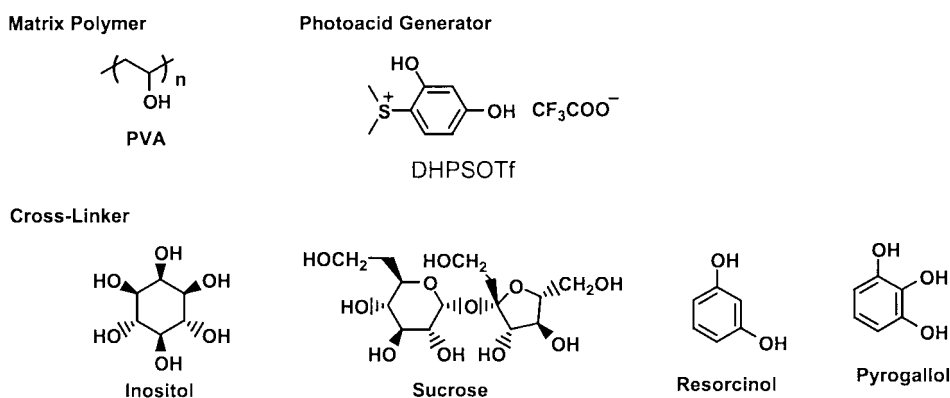
Resist formulation and lithographic evaluation. A general procedure for the formulation of three-component resists consisted of PVA (10 wt%), cross-linker (10 wt%), and (2,4-dihydroxyphenyl)dimethylsulfonium triflate (10 wt%). The solution was spin coated onto silicone wafers to give 0.6 μm thick resists. Deep UV exposures were performed using an UV exposure system. The resist films were post-exposure baked (PEB) on a hot plate and developed in deionized water.

Results and Discussion

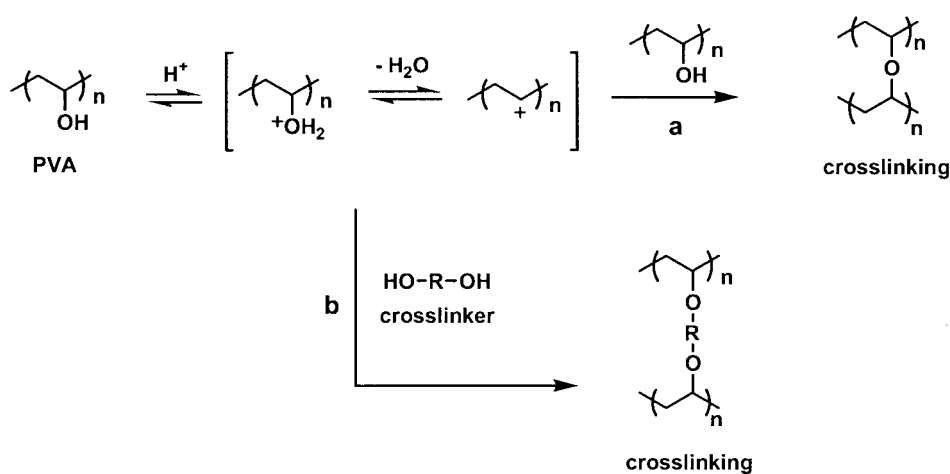
The structures of a matrix polymer, cross-linkers, and a photoacid generator used in this study are shown in Scheme 1. The water-soluble poly(vinyl alcohol) (PVA) which has an average Mw of 13000 was employed as a matrix polymer. Several aliphatic and aromatic alcohols were investigated as cross-linkers. Since photoinduced generation of relief images with PVA requires a water-soluble photoacid generator (PAG), (2,4-dihydroxyphenyl)dimethyl sulfonium triflate DHPSOTf was also used. The matrix polymer and cross-linkers were commercially available. The photoacid generator was prepared according to the reported procedures.¹⁰

The water-soluble PVA resist system operates *via* photoacid-induced cross-linking of the matrix polymer (Scheme 2). Accordingly, irradiation of a resist film initially produces a trace amount of strong acid from the photoacid generator. Protonation of the matrix polymer PVA by photo-generated acid produces cation intermediates. The cation intermediates, then can undergo two different pathways. In the absence of a cross-linker, the cationic intermediates can be captured by

^{*}To whom correspondence should be addressed. Tel: +82-2-2290-0522; Fax: +82-2-2298-4101; e-mail: jmk@hanyang.ac.kr



Scheme 1. Structures of a matrix polymer, cross-linkers, and a photoacid generator.



Scheme 2. A schematic representation of photoinduced crosslinking of PVA in the resist film.

neighboring poly(vinyl alcohol) to form cross-linked polymers (pathway a). In the presence of cross-linkers, the cation intermediates can react either with adjacent PVA (pathway a) or with cross-linkers (pathway b). When the cross-linkers are more reactive than the PVA the pathway b will be the dominant pathway to form cross-linked polymers.⁶

In order to investigate the effect of cross-linkers on the resist properties, a series of resist solutions containing the matrix polymer, a cross-linker and the photoacid generator were prepared. The resist solutions were spin-coated (1500 rpm, 40 sec) on silicon wafers and the resulting films were prebaked for 5 min at 90 °C to make 0.6- μm thick polymer films. The resist films were irradiated with 254 nm UV-light and followed by PEB at 120 °C for 2 min. A resist solution without a cross-linker was also prepared for a control experiment. Negative-tone images were obtained after incubation of the exposed films in deionized water for 60 sec (Figure 1). The dark areas are the portions exposed through the photo-mask.

The sensitivity data for the resists are shown in Table 1. The sensitivity was determined by plotting the film thickness remaining after development for various exposure doses. Thus, the sensitivity value in Table 1 is the minimum dose needed to maintain full thickness in the exposed areas

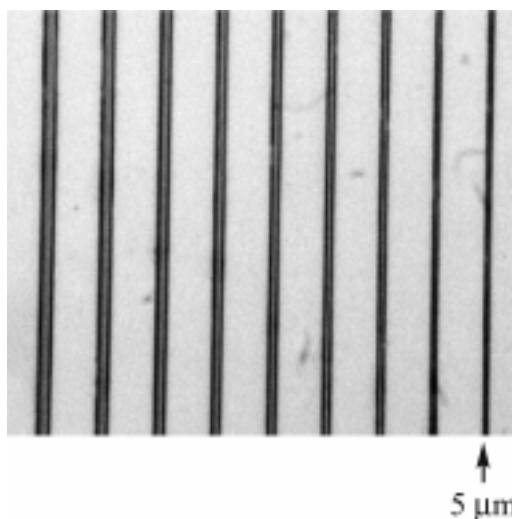


Figure 1. The negative-tone image pattern obtained with a 0.6- μm thick resist film containing PVA (10 wt%), resorcinol (10 wt%) and PAG (10 wt%) after irradiation with 254 nm UV-light (165 mJ/cm²) followed by PEB (120 °C, 2 min) and development (60 sec) in deionized water.

of the resist film.

As can be seen in the Table 1, the sensitivity of the resist

Table 1. Sensitivity of resist films upon deep-UV irradiation

Cross-linker (10 wt%)	PAG (%)	Sensitivity (mJ/cm ²) ^a
None	10	255
Inositol	10	225
Sucrose	10	210
Resorcinol	10	165
Pyrogallol	10	165

^aIrradiation at 254 nm, PEB of 2 min at 120 °C, and development in deionized water for 60 sec for all cases.

film varies depending on the cross-linkers used. Without any cross-linkers, highest dose of exposure is required. Aromatic cross-linkers such as resorcinol and pyrogallol are superior to the aliphatic cross-linkers such as inositol and sucrose. The observed sensitivity between the two aromatic alcohols were found to be the same.

In summary, we have investigated the effect of cross-linkers on the sensitivity of water-soluble resist films. Thus, resist films containing poly(vinyl alcohol) (PVA), cross-linker and photoacid generator were irradiated with 254-nm UV. Postexposure bake (PEB) followed by development in deionized water gave negative tone images. Among several alcohols investigated, aromatic alcohols such as pyrogallol and resorcinol were found to be superior to aliphatic alcohols such as sucrose and inositol in terms of cross-linking ability.

Acknowledgment. This research was funded by Center for Ultramicrochemical Process Systems (2001- 2002).

References

- Ito, H. *IBM J. Res. Develop.* **1997**, *41*, 69.
- Vekselman, A. M.; Zhang, C.; Darling, G. D. *Chem. Mater.* **1995**, *7*, 850.
- (a) Ahn, K.-D.; Koo, D.-I.; Wilson, C. G. *Polymer* **1995**, *36*, 2621. (b) Kim, S.-T.; Kim, J.-B.; Chung, C.-M.; Ahn, K.-D. *J. Appl. Polym. Sci.* **1997**, *66*, 2507.
- Frechét, J. M. J.; Eichler, E.; Ito, H.; Wilson, C. G. *Polymer* **1983**, *24*, 995.
- (a) Chung, C.-M.; Ahn, K.-D. *Reac. Func. Polym.* **1999**, *40*, 1. (b) Harvard, J. M.; Shim, S.-Y.; Frechét, J. M. J.; Lin, Q.; Medeiros, D. R.; Wilson, C. G.; Byers, J. D. *Chem. Mater.* **1999**, *11*, 719. (c) Frechét, J. M. J.; Eichler, E.; Ito, H.; Wilson, C. G. *Polymer* **1983**, *24*, 995. (d) Harvard, J. M.; Shim, S.-Y.; Frechét, J. M. J.; Lin, Q.; Medeiros, D. R.; Wilson, C. G.; Byers, J. D. *Chem. Mater.* **1999**, *11*, 719.
- Harvard, J. M.; Vladimirov, N.; Frechét, J. M. J.; Yamada, S.; Wilson, C. G.; Byers, J. D. *Macromolecules* **1999**, *32*, 86.
- Aoki, H.; Tokuda, T.; Nagasaki, Y.; Kato, M. *J. Polym. Sci., Polym. Chem.* **1997**, *A35*, 2827.
- Shrai, M.; Katsuta, N.; Tsunooka, M.; Tanaka, M. *Makromol. Chem., Macromol. Chem. Phys.* **1989**, *190*, 2099.
- (a) Kim, J.-M.; Chang, T.-E.; Kang, J.-H.; Park, K. H.; Han, D. K.; Ahn, K.-D. *Angew. Chem. Int. Ed.* **2000**, *39*, 1780. (b) Kim, J.-M.; Chang, T.-E.; Kang, J.-H.; Han, D. K.; Ahn, K. D. *Adv. Mater.* **1999**, *11*, 1499. (c) Kim, J.-M.; Kang, J.-H.; Han, D. K.; Lee, C.-W.; Ahn, K.-D. *Chem. Mater.* **1998**, *10*, 2332. (d) Kim, J.-M.; Kim, J.-Y.; Kim, T.-H.; Han, D.-K.; Ahn, K.-D. *Chem. Lett.* **2000**, 360. (e) Lee, C.-W.; Shin, J.-H.; Kang, J.-H.; Kim, J.-M.; Han, D.-K.; Ahn, K.-D. *J. Photopolym. Sci. Technol.* **1998**, *11*, 405. (f) Ahn, K. D.; Kang, J.-H.; Lee, C.-W.; Kim, J.-M.; Han, D.-K.; Lee, J.-H.; Cho, I.; Moon, S.-Y.; Koo, J.-S.; Lee, S.-K. *J. Photopolym. Sci. Technol.* **1998**, *11*, 499.
- Frechét, J. M. J.; Shim, S.-Y. U.S. Patent 5,648,196 (1997).