Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A New Positive Resist Based on Poly(4-Hydroxystyrene) for KrF Excimer Laser Lithography

Ilho Kim [a], Sang-Jin Park [a], Si-Hyung Lee [b], Eung-Ryul Kim [a], Kyoung-Chul Kim [a] & Haiwon Lee [a]

[a] Department of Chemistry, Hanyang University, Seoul, 133-791, Korea

[b] Semiconductor R&D Center, Samsung Electronics, Yongin-City, Korea

Version of record first published: 24 Sep 2006

To cite this article: Ilho Kim, Sang-Jin Park, Si-Hyung Lee, Eung-Ryul Kim, Kyoung-Chul Kim & Haiwon Lee (2000): A New Positive Resist Based on Poly(4-Hydroxystyrene) for KrF Excimer Laser Lithography, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 179-182

To link to this article: http://dx.doi.org/10.1080/10587250008024894

Mol. Cryst. Liq. Cryst., 2000, Vol. 349, pp. 179-182
Reprints available directly from the publisher
Photocopying permitted by license only

A New Positive Resist Based on Poly(4-Hydroxystyrene) for KrF Excimer Laser Lithography

ILHO KIM[a], SANG-JIN PARK[a], SI-HYUNG LEE[b], EUNG-RYUL KIM[a], KYOUNG-CHUL KIM[a] and HAIWON LEE[a]

[a]*Department of Chemistry, Hanyang University, Seoul 133–791, Korea and* [b]*Semiconductor R&D Center, Samsung Electronics, Yongin-City, Korea*

A positive acrylic silicon containing polymer was synthesized with 1,3-bis(trimethylsilyl)isopropyl methacrylate (BPMA) and 4-hydroxy styrene (4-HST) for KrF lithography. Lithographic evaluation shows the capability of 0.2 μm line and space with 2 wt% PAG concentration.

Keywords: KrF lithography; photoresist; etch resistance

INTRODUCTION

The explosive growth in performance of semiconductor devices has been made possible by steady advances in microlithography and photoresist technology. Several approaches are being pursued to extend the 248 nm lithography to achieve sub-200 nm features.[1] The enhancement in the resolution capability stems simply from the reduced resist film thickness because the depth of focus is improved by decreasing resist film thickness.[2] However the thin resist layer is insufficient in dry etch resistance. Silicon in polymer chains is converted silicon dioxide while it is bombarded with O_2 plasma. The

silicon dioxide serves as a barrier to dry etching.

The general resists for KrF excimer laser lithography are polyhydroxystyrene (PHST) backbone resists that contain various deprotecting groups.[3] BPMA is a silicon containing monomer and designed to enhance dry etch resistance. We have synthesized silicon containing methacrylate polymers, poly(4-HST_x-$BPMA_y$), that have an acid labile group. This paper reports the physical properties and lithographic performance of the copolymer.

EXPERIMENTAL

BPMA was synthesized according to the method described in the previous report.[4] The polymerization was carried out by free radical polymerization using AIBN in THF solvent with 4-acetoxystyrene (4-AST) and BPMA as shown in Figure 1. The pattern formation was carried out with resist solution by dissolving the copolymer and photoacid generator (PAG) in propylene glycol methyl ether acetate (PGMEA). Exposure was carried out by using KrF proto-type stepper. The exposed film was post-exposure baked (PEB) and developed in 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution.

RESULTS AND DISCUSSION

The synthesized BPMA and copolymer were confirmed by ^{1}H-NMR and FT-IR spectra. Molecular weight of synthesized copolymer, poly(4-HST_7-$BPMA_3$), was about 9800 and polydispersity (PDI) was 1.66. Figure 2 shows TGA thermodiagrams and UV transmittance of poly(4-HST_7-$BPMA_3$) with PAG concentration of 0, 1 and 5 wt%.

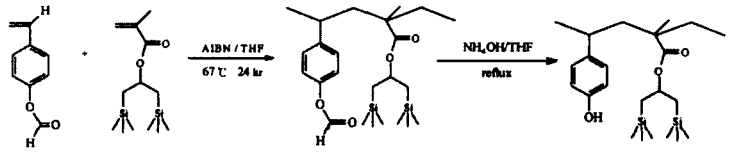

FIGURE 1. Synthetic scheme of copolymer, poly(4-HST$_x$-BPMA$_y$).

The pure unexposed copolymer, poly(4-HST$_7$-BPMA$_3$), was thermally stable up to about 150 ℃ and began to decompose at the temperature. From this temperature the total weight loss was 12% weight up to 180 ℃. It is due to deprotection of silicon group of BPMA. However, in the presence of PAG, the decomposition of silicon group started at about 90-100 ℃. And the spectroscopic analysis of exposed copolymer showed an increment of –OH portion at 3500 cm^{-1} in FT-IR spectra and a disappearance of proton peak of silicon groups at 0 ppm in ^{1}H-NMR spectra. From these results we can suggest that BPMA is converted MAA by the acid catalyzed deprotection.

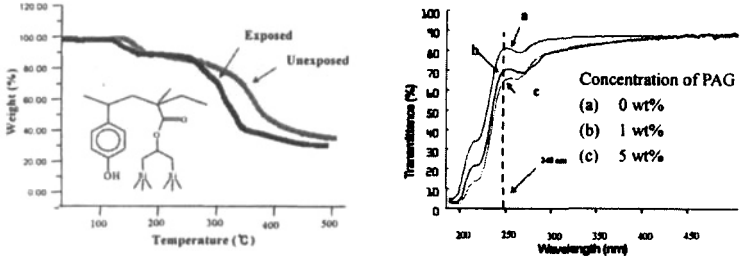

FIGURE 2. TGA curves and UV spectra of poly(4-HST$_7$-BPMA$_3$).

UV transmittance of polymer without PAG was about 88% at 248 nm wavelength. The lithographic performance of poly(4-HST$_7$-BPMA$_3$) resist was carried out by using various PAG concentrations and

exposure doses. A SEM micrograph of poly(4-HST_7-$BPMA_3$) is shown in Figure 3. The image shows 0.26 ㎛ line and space with 2 wt% of PAG. The exposed energy was 70 mJ/cm^2.

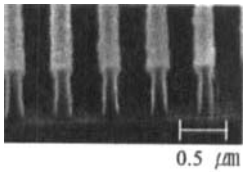

FIGURE 3. SEM micrograph of poly(4-HST_7-$BPMA_3$).

CONCLUSION

Poly(4-HST_7-$BPMA_3$) was synthesized with the BPMA and 4-AST. The copolymer has a good thermal stability up to 150 ℃ and UV transparency at KrF wavelength: The lithographic evaluations showed a resolution capability of 0.26 ㎛ feature with KrF exposure system.

Acknowledgements

This work is supported by Korea research foundation of Ministry of Education (9806-055).

References

[1] R. Sooriyakumaran, G. M. Wallraff, C. E. Larson, D. Fenzel-Alexander, R. A. DiPietro, J. Opits, D. C. Hofer, proc. SPIE **3333** 219 (1998).
[2] A. Azuma, T. Ohiwa, K. Okumura, T. Farrell, R. Nunes, D. Dobuzinsky, G. Fichtl, A. Gutmann, J. Vac. Sci. Technol. **B16** 4246 (1996).
[3] H. Ito, J. Photopolym. Sci. Technol. **11** 379 (1998).
[4] Y. J. Kang, H. Lee, E. R. Kim, S. J. Choi, C. G. Park, J. Photopolym. Sci. Technol. **10** 585 (1997).