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Synthesis of Triphenylsulfonium Triflate Bound Copolymer for Electron Beam Lithography

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Photoacid generator (PAG) has been widely used as a key component in photoresist for highresolution patterning with high sensitivity. A novel acrylic monomer, triphenylsulfonium salt methyl methacrylate (TPSMA), was synthesized and includes triphenylsulfonium triflate as a PAG. The poly(MMA-co-TPSMA) (PMT) as a polymer-bound PAG was synthesized with methyl methacrylate (MMA) and TPSMA for electron beam lithography. Characterization of PMT was carried out by NMR and FTIR. The molecular weight was analyzed by GPC. Thermal properties were studied using TGA and DSC. Thecharacterization results were in good agreement with corresponding chemical compositions and thermal stability. PMT was subsequently employed in electron beam lithography and its lithographic performance was confirmed by FE-SEM. This PMT was accomplished to improve the lithographic performance including sensitivity, line width roughness (LWR) and resolution. We found that PMT was capable of 20 nm negative tone patterns with better sensitivity than hydrogensilsesquioxane (HSQ) which is a conventional negative tone resist.

Keywords: Polymer-Bound PAG, Photoacid Generator, E-Beam Lithography, Negative Tone Photoresist.

1. INTRODUCTION

Lithography processing is important in the semiconductor industry for fabricating nanostructures. Electron beam lithography is one candidate that is able to reach below 10 nm resolution for device fabrication.¹ Next generation lithography is required to achieve critical lithographic performances such as high resolution, high sensitivity and low line width roughness (LWR). Photoresists have an important role in future lithographic performance, and photoacid generator (PAG) is a key component in photoresist for high-resolution patterning with high sensitivity. Most resists are prepared by mixing polymer, PAG and some additives. The polymer-blend PAG resist is known to have inherent incompatibility problems that can lead to PAG phase separation, PAG aggregation, and acid migration during the post-exposure baking (PEB) processes.²⁻⁵ These problems ultimately create a tradeoff among the desired characteristics of high resolution, high sensitivity, and LWR.6,7 A polymer-bound PAG resist is expected to

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solve problems such as PAG aggregation and acid migration with the use of a polymer-blend PAG resist.⁸ Recently, it was reported that polymer-bound PAG resist showed an improved lithographic performance such as higher stability, lower out-gassing and lower LWR.^{9–11} In our previous studies, triphenylsulfonium triflate was bound to poly benzyl methacrylate (PBMA) and used to fabricate a pattern by using AFM lithography.^{12, 13} Polymer-bound PAG resist was subsequently employed in E-beam lithography and KrF lithography.¹⁴

In this paper, triphenylsulfonium methyl methacrylate (TPSMA) was polymerized as a polymer-bound PAG unit and was employed to study on the dose, pitch ratio and exposed line width for electron beam lithography.

2. EXPERIMENTAL DETAILS 2.1. Materials

Methyl methacrylate (MMA), diphenylsulfoxide (96%), NBS, CCl_4 , sodium methacrylate, acetonitrile, cyclohexanone and trifluoromethane sulfonic anhydride (99%) were

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purchased from Sigma Aldrich. 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Junsei Co., Japan and was recrystallized in methanol. Single-crystal silicon wafers of 4-inch-diameter with a polished face (*p*-type, 100) were obtained from LG Siltron Co.

2.2. Analytical Measurement

¹H-NMR spectra were recorded on a Varian UNITY INOVA (400 MHz for ¹H) spectrometer in acetone- d_6 using tetramethylsilane as an internal reference, and IR spectra were recorded on a Perkin Elmer spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were both carried out with SDT Q600 at a heating rate of 10 °C/min under a nitrogen atmosphere. The molecular weight of the polymer was determined by GPC using DMF as an eluent.

An SEM image was obtained with a HITACHI S-4800 field emission instrument using an accelerating voltage of 15.0 kV. The thickness of the resist film was measured by ellipsometer (Rudolph Auto EL 2, USA).

2.3. Synthesis of TPSMA

Synthesis of the TPSMA was summarized in Scheme 1. Diphenyl-4-methylphenylsulfonium triflate (1) was synthesized through a modified Friedel-Craft reaction. This compound could be conveniently isolated in 90% yield. Diphenyl-4-bromomethylphenylsulfonium triflate (2) was obtained in 95% yield by bromination. The solution of (1) and NBS in CCl₄ was refluxed for 72 hrs. Reaction of (2) with sodium methacrylate in acetonitrile was refluxed for 1 hrto afford TPSMA (3) in 65% yield.

2.4. Synthesis of Poly(MMA-co-TPSMA)(PMT)

PMT was prepared by free radical polymerization using AIBN in argon atmosphere. Monomers and AIBN were dissolved in THF (Scheme 2). Polymerization was performed at 65 °C for 14 h. The mixture was then poured into methanol, and the precipitate was filtered and dried. The white polymer was purified by redissolving in methylene chloride, precipitating in hexane/isopropanol (3/7) and then drying in a vacuum oven at 50 °C for 24 h.

2.5. Resist Processing

Silicon wafers were cleaned in isopropanol prior to use. The bare silicon wafer was first coated with a solution



Scheme 2. Synthetic scheme of PMT.

of 10 wt% hexamethyldisilazane (HMDS) in propylene glycol monomethyl ether acetate (PGMEA). Each silicon substrate was prepared by spin-coating of HMDS onto the wafer, followed by baking at 120 °C for 120 s. The resist was prepared by dissolving 5 wt% PMT in cyclohexanone and filtering through a 0.1 μ m-PTFE membrane filter (Whatman). Prime grade single-crystal silicon wafers (4 inch) were used as a substrate for electron beam lithography. The resist was applied directly by spin coating and was coated onto the silicon substrate at 3500 rpm for 40 seconds. Soft baking at 110 °C for 2 min vaporized the residual solvents and enhanced the hardness of the thin films. The thickness of the resist was measured about 80-90 nm using an ellipsometer. Irradiation with an electron beam was executed using a JBX9300FS-JEOL lithography system with a 100 keV acceleration voltage, a beam current of 100 pA and a step size of 2 nm. The coated film was developed inan isopropanol/DIwater (7/3) solution for 40 s to dissolve the non-exposed portion. After rinsing with DI water, the negative pattern was obtained. The image of the pattern was obtained by FE-SEM. The contrast curve of the resists was evaluated using atomic image projection electron-beam lithography (AIPEL).¹⁶

3. RESULTS AND DISCUSSION 3.1. Characteristics of PMT

The composition of TPSMA was characterized by ¹H NMR (400 MHz, CDCl₃) based on characteristic peaks at 7.97 (*m*, 14 H), 6.20 (*s*, 1 H), 5.65 (*s*, 1 H), 5.29 (*s*, 2 H), 1.97 (*s*, 3 H). The thermal stability of the polymer was estimated to be around 150 °C by TGA. The molecular weight and polydispersity index were 19000 and 2.0, respectively. Figure 1 shows the FT-IR spectra of their



Scheme 1. Synthesis of the triphenyl sulfonium methyl methacrylate (TPSMA).

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Figure 1. FT-IR spectra of PMT at exposure times: (a) unexposed, (b) exposed for 1 min in KrF.

radiation of PMT film on the NaCl plate. The formation of PMT was confirmed by the IR spectra and absorption characteristics of phenyl ring and sulfoxide group were appeared at 640–780 cm⁻¹ and at 1030 cm⁻¹, respectively. The absorption of the sulfate group appeared at 1450 cm⁻¹, and absorption of the carboxyl group appeared 1700– 1760 cm⁻¹, respectively. IR spectra exhibited a minor change in the majorpeaks. After exposure to triphenylsulfonium salt, the photolytic cleavage of the bond between phenyl group and sulfur was occurred, and cleaved phenyl ring was cross-rinked with the main chain of PMT externally and/or internally.¹⁵ No significant changes in IR spectra were observed due to the detection limit for confirming the absorption change of phenyl rings in cleavage and cross-rinking.

3.2. E-Beam Lithography

To evaluate the lithographic performance of the resist, PMT was employed to check the effect of dose, pitch ratio and exposed line width in electron beam lithography. Lithographic conditions were optimized by changing pitch and dose without employing a PEB process. Figure 2



Figure 2. Cross sectional SEM image of negative pattern in 20 nm resolution (1:2/line:space) by e-beam lithography.



Figure 3. The resist contrast curves under e-beam radiation.

showed a negative tone pattern at a 100 keV acceleration voltage. A 20 nm pattern was achieved with good LWR and line edge roughness (LER). Both LWR and LER were improved by controlling the acid diffusion length by using a bound PAG. The pattern height was 40 nm without any pattern collapse under high dose.

The contrast curve, which shows the sensitivity characteristics of a resist, is expressed by the relationship between exposure dose and residual resist thickness after development. To evaluate the e-beam sensitivity of new polymer-bound PAG, contrast curve of PMT was compared to that of conventional hydrogensilsesquioxane (HSQ) (Fig. 3). HSQ has been used as a negative tone resist for electron beam resist because of high resolution, sensitivity, good LWR, etching resistance and thermal stability.¹⁷ The γ values of PMT and HSQ were 4.33 and 5.67, respectively.

We expect that the polymer-bound PAG can achieve high resolution and high sensitivity patterns.

4. CONCLUSION

A new polymer-bound PAG was synthesized and characterized as a negative resist for e-beam lithography. A negative pattern was obtained with good LWR and high resolution (sub 20 nm). PMT showed a better contrast than HSQ. PMT will be studied for further investigations of reaction mechanisms and processing optimization.

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References and Notes

- 1. W. Hu, K. Sarveswran, M. Lieberman, and G. H. Bernstein, J. Vac. Sci. Technol. B 22, 1711 (2004).
- G. M. Schmid, M. D. Stewart, C. Y. Wang, B. D. Vogt, V. M. Prabhu, E. K. Lin, and C. G. Willson, *Proc. SPIE* 5376, 333 (2004).
- 3. Q. Lin, R. Sooriyakumaran, and W. S. Huang, *Proc. SPIE* 3999, 230 (2000).

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- 4. H. Fukuda, J. Photopolym. Sci. Technol. 15, 389 (2002).
- 5. T. Ogura and M. Ueda, J. Polym. Sci., Part A: Polym. Chem. 45, 661 (2007).
- 6. K. L. Covert and D. J. Russell, J. Appl. Polym. Sci. 49, 657 (1993).
- M. Wang, W. Yueh, and K. E. Gonsalves, *Macromolecules* 40, 8220 (2007).
- K. E. Gonsalves, M. Wang, C.-T. Lee, W. Yueh, M. T.-Tapia, N. Batina, and C. L. Henderson, J. Mater. Chem. 19, 2797 (2009).
- H. Tamaoki, S. Tarutani, H. Tsubaki, T. Takahashi, N. Inoue, T. Tsushihashi, H. Takizawa, and H. Takahashi, *Proc. SPIE* 7972, 79720A (2011).
- D. V. Steenwinckel, J. H. Lammers, L. H. A. Leunissen, and J. A. J. M. Kwinten, *Proc. SPIE* 5753, 269 (2005).
- J. B. Shin, H. S. Joo, S. D. Cho, H. S. Lim, J. H. Kim, S. J. Lee, D. H. Shin, J. H. Han, and D. C. Seo, *Proc. SPIE* 7969, 79692N (2011).

- 12. G. Kwun, E. Jang, G. Kwon, and H. Lee, *Current Applied Physics* 9, S121 (2009).
- 13. S. W. Park, H. J. Yoon, H. Y. Oh, Y. I. Kim, G. J. Kwun, and H. Lee, Solid State Phenomena 121, 697 (2007).
- 14. K. E. Lee, M. J. Kim, J. B. Yoo, H. S. Mondkar, K. Sohn, and H. Lee, J. Nanosci. Nanotechnol. 12, 725 (2012).
- M. Höfer and R. Liska, J. Polymsci. Part A: Polym. Chem. 47, 3419 (2009).
- 16. H. S. Lee, B. S. Kim, H. M. Kim, J. S. Wi, S. W. Nam, K. B. Jin, Y. Arai, and K. B. Kim, *Adv. Mater.* 19, 4189 (2007).
- W. Henschel, Y. M. Georgiev, and H. Kurz, J. Vac. Sci. Technol. B 21, 2018 (2003).
- B. M. Kim, D. W. Kang, C.H Jung, J. H. Choi, I. T. Hwang, S. K. Hong, and J. S. Lee, *J. Nanosci. Nanotechnol.* 11, 7390 (2011).
- W. Yue, Z. Wang, X. Wang, L. Chen, Y. Yang, B. Chew, A. Syed, K.-C. Wong, and X. Zhang, *J. Nanosci. Nanotechnol.* 12, 696 (2012).

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