Surface Tension Driven Flow in a Low Molecular Weight Photopolymer

Chae Bin Kim, Sunshine X. Zhou, Drew L. Heilman, Dustin W. Janes,† and Christopher J. Ellison*

McKetta Department of Chemical Engineering, The University of Texas at Austin, 200 E. Dean Keeton Stop C0400, Austin, TX 78712 USA

* ellison@che.utexas.edu

†Present Address: U.S. Food and Drug Administration, 10903 New Hampshire Avenue, Silver Spring, MD 20993 USA

Low molecular weight photopolymers are candidate materials for resists in Extreme Ultraviolet Lithography. The patterned chemical transformations used in photolithography generate a surface energy pattern that can induce flow in low molecular weight photopolymers via the Marangoni effect, due to their intrinsically higher translational mobility relative to larger polymers. To demonstrate this outcome, a low molecular weight photopolymer bearing acid-labile protecting groups was co-cast with a photo-acid generator and exposed through a contact mask. During a post-exposure bake above the film’s glass transition temperature, unexposed polymer flowed into deprotected regions since the deprotected polymers possess relatively higher surface tension compared to the unreacted polymers. After cooling, the film exhibited thickness variations of up to 90 nm, and the topographic profile reflected the mask pattern. An appreciation of this transport mechanism could be useful to those integrating low molecular weight photopolymers into lithographic process flows.

Keywords: Marangoni, Convection, Diffusion, Patterning, Photopolymer, Thin Film

1. Introduction

Microelectronics manufacturers hope to use Extreme Ultraviolet Lithography (EUVL) to manufacture devices with critical features less than 10 nm in width, a length scale commensurate with the molecular size of many photopolymers. [1] This presents a new challenge to achieving suitably low line edge roughness and line width variation in a lithography process because individual photopolymer molecules are either entirely dissolved or not dissolved by developer. The randomness of dissolution at the interface between exposed and unexposed polymer can yield unacceptable developed profiles. [2,3] Many working to develop new photoresist materials for EUVL are retaining existing chemical amplification chemistries already used in photoresists, but are tailoring the physical state of photomaterials to meet process requirements. Some candidate materials for EUVL are specifically described as low-molecular weight photopolymers [4-6] and/or molecular glasses. [7-9] By virtue of their lower molecular size, they achieved reduced line-edge roughness in the developed patterns.

However, the higher translational mobility possessed by low molar mass materials, [10,11] when heated above their softening point, may introduce unanticipated effects to photolithographic processes. [12] An appreciation of all possible transport phenomena in low-molecular weight photopolymer films could aid process scientists and engineers who are tasked with integrating EUVL into device manufacture. For example, typical lithographic flows use a "post exposure bake" (PEB) to make the light-activated acid diffuse and deprotect acid-labile groups in the photopolymer. Deprotection makes the light exposed regions more polar, and by extension increases the surface energy of the resist relative to the unexposed regions. [13] We note that flow in small molecule liquids towards regions of higher surface tension has been documented since 1855 [14], and can also occur in photopolymers heated above their thermal transition to a melt-state. This type of surface-tension driven flow is called the “Marangoni effect.” [15] This transport
mechanism is not relevant to photopolymers with high molecular weights and correspondingly high melt-viscosities, because the associated low translational mobility prevents flow during a PEB. In this work, we have synthesized a low molecular weight photopolymer and demonstrate that surface tension driven flow is physically possible, owing to a relatively high translational mobility. The result of flow caused by the PEB is film thickness variations reflective of the mask pattern, [16,17] which would be undesirable in a conventional photolithographic process.

2. Materials, Characterization, and Exposure Conditions

Unless described otherwise, all chemicals used in this study were purchased from Fisher Scientific or Sigma-Aldrich and used as received.

A low molecular weight copolymer of styrene and tert-butyl acrylate was synthesized by activator regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) as described elsewhere. [18] The molar feed ratio relative to initiator was 48 : 0.1 : 0.01 : 0.1 for monomers, ligand, catalyst, and reducing agent, respectively. The molar feed ratio of styrene to tert-butyl acrylate was 9 : 1, and the total mass of monomer was 40 g. The reaction was performed at 90 °C for 24 hrs in 70 wt.% solvent relative to all other components. A quantitative carbon nuclear magnetic resonance (13C-NMR) spectrum of the precipitated and dried polymer was used to determine the ratio of tert-butyl acrylate monomers to styrene monomers incorporated in the polymer. Tert-butyl acrylate has characteristic peaks at 28-30 ppm (methyl carbons) and at 79-81 ppm (tertiary carbon in the tert-butyl group), and styrene has characteristic peaks at 124-130 ppm (ortho, meta, and para benzyllic carbons). Based on the ratio of the areas of these characteristic peaks, the copolymer molar composition is approximately 10:1 for styrene and tert-butyl acrylate groups, respectively.

Subsequently, the copolymer was partially hydrolyzed [19] to obtain a terpolymer of styrene, tert-butyl acrylate, and acrylic acid, P(S-r-tBA-r-AA) (Mn = 4330 Da, D = 1.06, relative to PS standard, as characterized by size exclusion chromatography). The glass transition temperature of the bulk polymer sample was 82 °C (mid-point) as measured by differential scanning calorimetry with a 10 °C/min heating rate upon second heating. Methanol was used as the precipitating solvent after the polymerization and hydrolysis steps. Transmission mode Fourier transform spectroscopy (FTIR) analysis on the P(S-r-tBA-r-AA) film supported on double side polished silicon wafer indicated a composition ratio of tert-butyl acrylate to acrylic acid was 0.73 : 0.27. This estimate is based on a comparison of the area under ester peaks associated with the tert-butyl acrylate to the ester peaks associated to the acrylic acid. While they overlap slightly, their contributions were separated by fitting two Lorentz functions.

P(S-r-tBA-r-AA) and PAG (triphenylsulfonylum triflate, TPS) were spin-coated onto silicon wafers from diglyme solution. The PAG content was 5 wt. % of the total film solids. A dose of 42 J/cm² of broadband light was applied onto the films to convert PAG in the exposed areas into its acidic form. This exposure dose was measured from the entire spectral output of the metal halide broadband light source (200 nm to 600 nm). Since TPS absorbs only a fraction of the broadband output, significantly lower doses limited to effective wavelengths (i.e. < 300 nm), could give an equivalent result. The PEB conditions were 150 °C for 1 min.

Figure 1. A photochemical transformation scheme. Light activated acid diffuses upon post exposure heating and deprotects tert-butyl acrylates, yielding more acrylic acid subunits. Based on FTIR analysis, c = 0.02.

3. Results and Discussion

The photochemical transformation used to induce surface tension driven flow of the P(S-r-tBA-r-AA) film is shown in Figure 1. Upon PEB, light-activated PAG reacts with some tert-butyl acrylate groups, converting them to acrylic acid.
We anticipate this reaction would increase the surface energy (and the corresponding melt-state surface tension) in the light exposed region because acrylic acid is more polar than tert-butyl acrylate. [20] For example, a handbook value for poly(tert-butyl methacrylate) surface energy is 30.4 dyne/cm while that for poly(methacrylic acid) is 41.1 dyne/cm. [21]

This chemical transformation was confirmed using FTIR as shown in Figure 2. The sample for the FTIR analysis was made by spin coating the P(S-r-tBA-r-AA) and PAG onto a double side polished silicon wafer. This film possesses both $\nu_{\text{C=O}}$ signals associated with tert-butyl acrylate, 1730 cm$^{-1}$, and $\nu_{\text{C=O}}$ signals associated with acrylic acid, 1700 cm$^{-1}$. Once the film has been flood exposed and thermally annealed for 1 min at 150 °C, the area under the tert-butyl acrylate peak is reduced relative to the acrylic acid peak, consistent with deprotection. Normalized to the light insensitive aromatic C-C stretches at 1585-1600 cm$^{-1}$, the decrease in area under the tert-butyl acrylate peak represents 29% deprotection during the PEB.

A 260 nm thick film containing P(S-r-tBA-r-AA) and PAG was exposed through a photomask possessing an array of 45 µm wide, hexagonally shaped transparent regions and then heated for 1 min at 150 °C. A representative optical micrograph and profilometry trace of this film is shown in Figure 3. Different colors observed in the optical micrograph are light interference patterns resulting from the film thickness variations. As the profilometry trace below indicates, a film topography was created without any solvent development or etching. The film is thickest in the light unexposed regions nearest to the exposed regions, consistent with the polymer flowing towards the hexagonally exposed regions. This direction of flow is consistent with that characteristic for Marangoni flow, i.e. flow from low surface tension to high surface tension regions.

From the profilometry trace shown in Figure 3, two different pairs of local film thickness maxima are observed across one pattern periodicity: a pair with the same lateral dimension as the mask used during the light exposure step (indicated by dotted lines), and the other pair (dashed lines) located 12 µm outward from the original light exposed regions. We believe the latter maximum has resulted from lateral diffusion of photo-acid beyond the spatially-defined exposure area, coupled with the Marangoni convection of the film materials, as well. The length scale of photo-acid diffusion for this annealing time suggests a diffusion coefficient of $\sim 6 \times 10^{-9}$ cm$^2$s$^{-1}$ at 150 °C.

Admittedly, the PEB conditions used in this study were more aggressive than what would be used in a real photolithographic process. PEB conditions above the bulk glass transition temperature of the polymer, are often considered undesirable because of relatively fast acid...
diffusion which deteriorates pattern resolution. [22] However, some features could contribute to polymer flowing even below the bulk glass transition. Glass transition temperatures can be suppressed below the bulk value in thin polymer films due to contributions from a surface layer exhibiting enhanced mobility. [23] Additionally PAGs possess low-surface energy moities which concentrate at the air surface and could plasticize the top of the film. [24] For the small critical dimensions envisioned for EUVL technology, relatively small lateral displacements of unexposed polymer due to flow would represent a significant distortion from the intended chemical pattern.

4. Conclusions
In this work, a low molecular weight photopolymer containing an acid-labile group was synthesized, exposed through a photomask, and then baked. Due to the spatially-defined melt-state surface tension pattern, the Marangoni effect caused polymer to flow from light unexposed (low surface tension) to exposed (high surface tension) regions during the PEB, creating a film with a smoothly varying height profile. No solvent development or etching was performed. The resulting topographical patterns were larger in lateral size than the original light exposure patterns and we believe this was caused by acid diffusion outside of the exposed area, convoluted with the Marangoni convection of the film materials.

Line-edge roughness of the developed pattern has been considered as a stochastic effect in photoresists. [2,3] One of the known factors that deteriorates line-edge roughness is inhomogeneity in the distribution of light exposed and unexposed polymer chains at the interface of light exposed and unexposed regions. [2] When addressing this issue by using low molar weight photopolymers, scientists and engineers should also consider the possibility of spatial rearrangement due to the surface tension gradients imposed by the chemical transformation.

Acknowledgements
The authors thank Professor C. Grant Willson for use of his facilities and William K. Bell, Austin P. Lane, and Michael J. Maher for helpful discussions. Financial support was provided by the National Science Foundation CAREER Award (Grant no. DMR-1053293), Nissan Chemical Industries, Ltd., the Robert A. Welch Foundation (No. F-1709), the 3M Nontenured Faculty Award, and the DuPont Young Professor Award.

References
1. Naulleau, P.; Anderson, C.; Chao, W.; Bhattacharai, S.; Neureuther, A.; Cummings, K.; Jen, S.; Neisser, M.; Thomas, B. J. Photopolym. Sci. Technol. 27 (2014) 725–730.
2. Kozawa, T. J. Photopolym. Sci. Technol. 26 (2013), 643–648.
3. Kozawa, T.; Santillan, J. J.; Itani, T. J. Photopolym. Sci. Technol. 27 (2014), 11–19.
4. Simone, D. D.; Goethals, A.; Roey, F. V.; Zheng, T.; Foubert, P.; Hendrickx, E.; Vandenbergh, G.; Ronse, K. J. Photopolym. Sci. Technol. 27 (2014) 601–610.
5. Saito, S.; Nakasugi, T. J. Photopolym. Sci. Technol. 16 (2003) 459–461.
6. Hirayama, T.; Shiono, D.; Hada, H.; Onodera, J.; Ueda, M. J. Photopolym. Sci. Technol. 17 (2004) 435–440.
7. Yoshiwai, M.; Kageyama, H.; Shirota, Y.; Wakaya, F.; Gamo, K.; Takai, M. Appl. Phys. Lett. 69 (1996) 2605–2607.
8. Dai, J.; Chang, S. W.; Hamad, A.; Yang, D.; Felix, N.; Ober, C. K. Chem. Mater. 18 (2006) 3404–3411.
9. Silva, A. D.; Felix, N.; Sha, J.; Lee, J.; Ober, C. K. Proc. SPIE 6923 (2008) 69231L-69231L-14.
10. Ubukata, T.; Moriya, Y.; Yokoyama, Y. Polym. J. 44 (2012) 966–972.
11. Okada, K.; Tokudome, Y.; Makiura, R.; Konstas, K.; Malfatti, L.; Innocenzi, P.; Ogawa, H.; Kanaya, T.; Falcaro, P.; Takahashi, M. Adv. Funct. Mater. 24 (2014) 2801–2809.
12. Yamaguchi, T.; Yamazaki, K.; Namatsu, H. J. Vac. Sci. Technol. B 22 (2004) 2604–2610.
13. Ito, H. Microlithography/Molecular Imprinting (Springer, Heidelberg, 2005) Advances in Polymer Science Series, 172, 37.
14. J. Thomson, London Edinburgh Philos. Mag. J. Sci. 10 (1855) 330–333.
15. Scriven, L. E.; Sterling, C. V. Nature 187 (1960) 186–188.
16. Arshad, T. A.; Kim, C. B.; Prisco, N. A.; Katzenstein, J. M.; Janes, D. W.; Bonnecaze, R. T.; Ellison, C. J. Soft Matter 10 (2014) 8043–8050.
17. Kim, C. B.; Janes, D. W.; McGuffin, D. L.; Ellison, C. J. J. of Polym. Sci. Part B: Polym. Phys 52 (2014) 1195–1202.
18. Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J. Y.; Braunecker, W. A.; Tsarevsky, N. V. Proc. Natl. Acad. Sci. U. S. A. 103 (2006) 15309–15314.
19. Davis, K. A.; Matyjaszewski, K. Macromolecules 33 (2000) 4039–4047.
20. Feng, C. L.; Vancso, G. J.; Schonherr, H. *Langmuir*, **21** (2005) 2356–2363.

21. J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe and D. R. Bloch, Polymer Handbook, John Wiley & Sons, Hoboken, 4th edn, 2005.

22. Nakagawa, H.; Naruoka, T.; Nagai, T. *J. Photopolym. Sci. Technol.* **27** (2014), 739–746.

23. Ellison, C. J.; Torkelson, J. M. *Nature Mater.* **2** (2003), 695–700.

24. Lenhart, J. L.; Jones, R. L.; Lin, E. K.; Soles, C. L.; Wu, W.; Fischer, D. A.; Sambasivan, S.; Goldfarb, D. L.; Angelopoulos, M. *J. Vac. Sci. Technol. B* **20** (2002) 2920–2926.