

Task ID: 425.030

Task Title: Supercritical Carbon Dioxide Compatible Additives: Design, Synthesis, and Application of an Environmentally Friendly Development Process to Next Generation Lithography: Resists and Additives

Deliverable: Report on new development additives including silazanes

Christine Y. Ouyang, Christopher K. Ober, Department of Materials Science and Engineering, Cornell University, Ithaca NY 14853

Abstract:

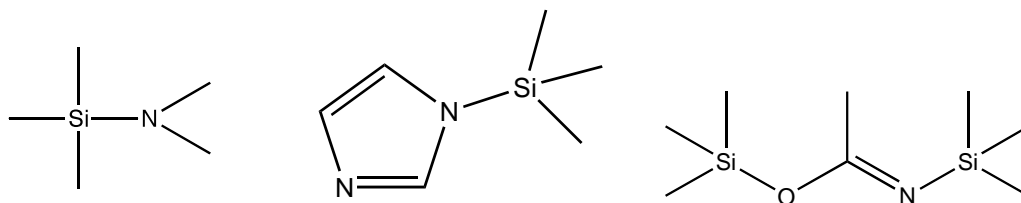
Supercritical carbon dioxide (scCO<sub>2</sub>) is considered as an environmentally benign replacement for organic solvents in many microelectronic applications. Its unique properties are also beneficial for it to be used as a developing solvent for photoresists patterning. However, most conventional photoresists are generally not soluble in scCO<sub>2</sub>. Previously, we have reported the use of fluorinated quaternary ammonium salts to assist in the dissolution of photoresists in scCO<sub>2</sub>. In order to make the process more environmentally benign, it is desirable to eliminate fluorine. In this report, we present several non-fluorinated additives to develop photoresists in scCO<sub>2</sub> and the proposed dissolution mechanism.

Introduction:

Carbon dioxide is nontoxic, nonflammable, inert under most conditions and has been used as an environmentally benign replacement for organic solvents in many microelectronic applications [1]. Supercritical carbon dioxide (scCO<sub>2</sub>) exhibits the unique properties as combining liquid-like densities with gas-like diffusivities and zero surface tension. Therefore, it could be utilized as a developer for photoresist processing. However, conventional photoresists are generally not soluble in scCO<sub>2</sub>, which limits its practical use. For pure scCO<sub>2</sub> processing, certain fluorinated or silicon containing polymers have been used. Ober et al. have showed the ability to develop fluorinated photoresists in scCO<sub>2</sub> [2,3]. It is believed that the presence of fluorine increases the solubility of polymers in scCO<sub>2</sub>, but high content of fluorine has an adverse effect on the etch resistance. Therefore, conventional photoresists generally are not fluorinated and require additives such as cosolvents to be developed in scCO<sub>2</sub>[4].

In the previous report, we have shown the development of two conventional photoresists, poly(4-*t*-butoxycarbonyloxystyrene) (PBOCST) and poly(hydroxystyrene-co-styrene-co-*t*-butylacrylate)(PHS-co-PS-co-PtBA)(ESCAP) in scCO<sub>2</sub> with quaternary ammonium salts(QAS). However, it is desirable to make the process more environmentally friendly by eliminating the use of fluorinated compounds. Therefore, many non-fluorinated additives have been considered and tested for developing photoresists in scCO<sub>2</sub>.

## Experimental:



(N,N-Dimethyl)trimethyl silane 1-(trimethylsilyl)imidazole N,O-Bis-(trimethylsilyl)-acetamide

**Figure 1 Chemical structures of new development additives**

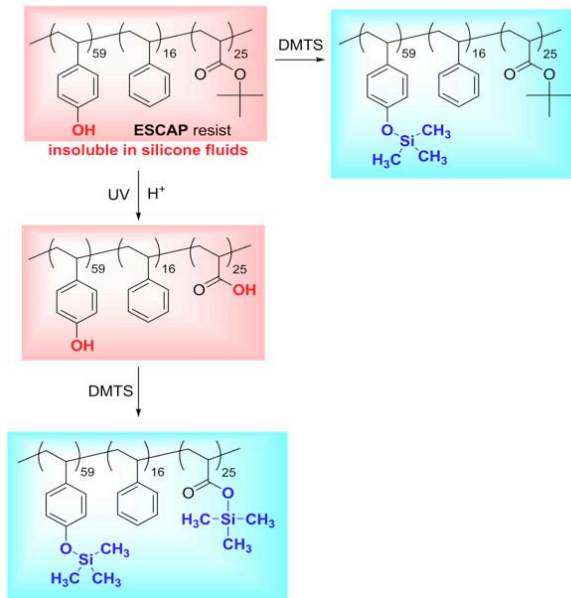
*Lithographic Evaluation.* Each resist film was spin-coated on an HMDS-primed silicon wafer and baked at 130°C for 60 seconds. Dose testing was performed by using a GCA Autostep 200 DSW i-line Wafer Stepper (500mW/cm<sup>2</sup>). After exposure, ESCAP and PBOCST were baked at 115°C and 90°C for 60 seconds, respectively.

*Development in Supercritical CO<sub>2</sub>.* The chemical structures of new development additives are shown in Figure 1. Each additive was dissolved in scCO<sub>2</sub> at 50°C and 5000 psi for 10-15 minutes and was subsequently used to develop each resist film for 5-15 minutes by using a scCO<sub>2</sub> dissolution rate monitor described elsewhere [6].

*Metrology.* A Tencor P10 profilometer was used to measure the film thickness of each photoresist before and after development. The developed patterns were examined using the Nikon Digital Sight D5-5M-L1 optical microscope and the LEO 1550 FESEM scanning electron microscope.

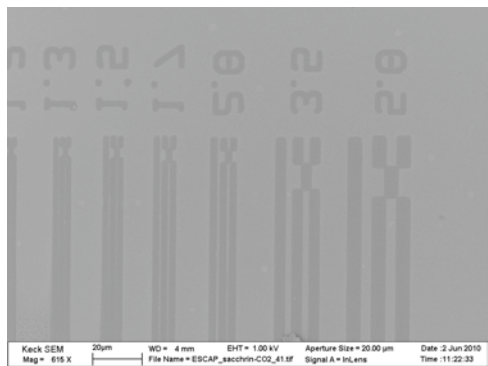
## Results and Discussion:

The additives are able to react with the hydroxy groups in each photoresist and increase their solubility in scCO<sub>2</sub>. As shown in Figure 2, the hydroxy groups in unexposed ESCAP could react with (N,N-dimethyl)trimethyl silane(DMTS) and form trimethylsilyl (TMS) groups to increase the solubility of the resist in scCO<sub>2</sub>.



**Figure 2 Reaction of ESCAP with DMTS**

It was found that ESCAP wasn't completely silylated by only using DMTS. Therefore, saccharin or 1-(trimethylsilyl)imidazole(TMSI) were mixed with DMTS as catalysts to increase the amount of silylation. The result of ESCAP developed in scCO<sub>2</sub> using DMTS and saccharin is shown in Figure 3. As the unexposed ESCAP dissolved in scCO<sub>2</sub>, a negative-tone image was developed.



**Figure 3 ESCAP developed in scCO<sub>2</sub> using DMTS**

N,O-Bis-(trimethylsilyl)-acetamide (BSA) is a stronger silylating reagent compared to DMTS and does not require any catalyst to develop ESCAP in scCO<sub>2</sub>. However, both exposed and unexposed ESCAP dissolved in scCO<sub>2</sub> with the aid of BSA and therefore requires more optimization.

#### References:

- 1.G. L. Weibel and C.K. Ober, *Microelec. Eng.* **2003**, 65, 145-152
- 2.A. H. Gabor, R. D. Allen, P. M. Gallagher-Wetmore, and C. K. Ober, *Proc. Of SPIE* **1996**, 2724, 410-417

3. N. Sundararajan, S. Yang, K. Ogino, S. Valiyaveetil, J. Wang, X. Zhou, and C. K. Ober, *Chem. Mater.* **2000**, 12, 41-48
4. Y. Mao, N. M. Felix, P. T. Nguyen, C. K. Ober, *Chemical Vapor Deposition* **2006**, 12,(5), 259
5. M. Tanaka, A. Rastogi, G. N. Toepperwein, R. Riggelman, N. M. Felix, J. J. de Pablo, and C. K. Ober, *Chem. Mater.* **2009**, 21(14) 3125-3135
6. V. Q. Pham, N. Rao, and C. K. Ober, *Journal of Supercritical Fluids* **2004**, 31(3), 323-328