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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 the Preparation and Lithographic Evaluation of New QAS Resist Systems and Processes for scCO$_2$ Development

Abstract:
        Supercritical carbon dioxide (scCO$_2$) has been 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 photoresist patterning. However, most conventional photoresists are not soluble in scCO$_2$. We have synthesized a series of quaternary ammonium salts to assist in the dissolution of photoresists in scCO$_2$. In this report, we present the lithographic evaluation of using QAS as additives to develop photoresists in scCO$_2$. The results have shown the potential of PBOCST and PHS-co-PS-co-PtBA (ESCAP) to be used as negative-tone photoresists in scCO$_2$.

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$_2$) 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 photoresists processing. However, conventional photoresists are generally not soluble in scCO$_2$, which limits its practical use. For pure scCO$_2$ processing, certain fluorinated or silicon containing polymers have been used. Ober et al. have shown the ability to develop flourinated photoresists in scCO$_2$ [2,3]. It is believed that the presence of fluorine increases the solubility of polymers in scCO$_2$, but high levels 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$_2$[4].
        Wagner et al. at Micell Integrated Systems have reported the use of CO$_2$ compatible salts to develop polar polymers in scCO$_2$ [5]. This work has permitted the negative tone development in scCO$_2$ of EUV and DUV photoresists that are normally positive tone under aqueous development. This technique has shown impressive contrast and dense L/S features with aspect ratios>12[6]. These results have encouraged the study of the scCO$_2$ compatible quaternary ammonium salts.

Results and Discussion:
        A series of quaternary ammonium salts (QAS) was synthesized and tested on the development of conventional photoresists in scCO$_2$. The conventional photoresists used were poly(4-t-butoxycarbonyloxystyrene) (PBOCST), poly(hydroxystyrene-co-styrene-co-t-butylacrylate)(PHS-co-PS-co-PtBA)(ESCAP),   and   poly(methyladamantane

methacrylate-co-α-methacryloxy-γ-butyrolactone) (PMAMA-co-PGBLMA), as shown in Figure 1. A commercial resist donated by TOK was also evaluated in this report.

PHS-co-PS-co-PtBA

PBOCST

PMAMA-co-PGBLMA
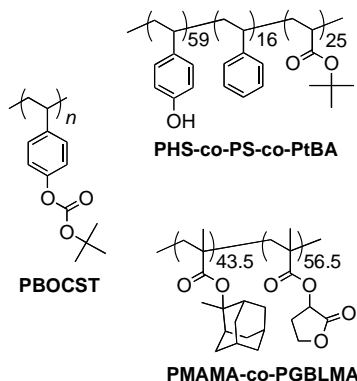
Figure 1 Chemical structures of conventional photoresists

Solubility Test of Conventional Photoresists in scCO$_2$ with QAS

All the conventional photoresists used were insoluble in scCO$_2$ before and after exposure without the additives. The QAS was put into the preheating vessel to help dissolve the polymer films in scCO$_2$, and the polymer films were monitored using laser interferometry. It was shown that PBOCST, ESCAP and TOK resist with QAS-4 were dissolved in scCO$_2$, and the dissolution rates are shown in Table 1. However, ESCAP did not show solubility in the QAS-4/scCO$_2$ solution. On the other hand, QAS-7 did not assist in the dissolution of PBOCST, ESCAP or PMAMA-co-GBLMA in scCO$_2$, but was able to assist the dissolution of TOK resist in scCO$_2$.

The exposed (deprotected) photoresists were also developed in the QAS/scCO$_2$ solutions. It was shown that ESCAP became insoluble in the QAS-4/scCO$_2$ solution after exposure at doses of 0.71 to 14.2 mJ/cm^2. The deprotected PBOCST and TOK resist also showed much slower dissolution than the unexposed resists. These results indicate that these resists are potential negative-tone photoresists in scCO$_2$. On the other hand, PMAMA-co-PGBLMA did not show any solubility in 1.25 mM QAS-4/scCO$_2$ solution at 50°C and 5000 psi after processing for 30 minutes.

| QAS	Resist	Unexposed	Exposed	note
QAS-4 (1.25 mM)	PBOCST	**Dissolution** (40 nm/min)	**Slow dissolution** (1-4 nm/min)	*Negative tone resist*
	ESCAP (Du Pont)	**Dissolution** (25 nm/min)	**No dissolution**	*Negative tone resist*
	PMAMA-co-GBLMA (Mitsubishi Rayon)	No dissolution	No dissolution	
	EUV-P568 (TOK)	**Dissolution** (15 nm/min)	**Slow dissolution** (1-2 nm/min)	*Negative tone resist*
QAS-7 (1.25 mM)	PBOCST	No dissolution	No dissolution	
	ESCAP (Du Pont)	No dissolution	No dissolution	
	PMAMA-co-GBLMA (Mitsubishi Rayon)	No dissolution	No dissolution	
	EUV-P568 (TOK)	**Dissolution** (45 nm/min)	**Slow dissolution** (<1 nm/min)	*Negative tone resist*

Table 1 Solubility results of the photoresists

Lithographic Evaluation

A commercial photoresist donated by TOK was used to evaluate the lithographic performance. The protected TOK photoresists showed a constant dissolution rate of

15nm/min in scCO$_2$ with either QAS-4 or QAS-7. On the other hand, the deprotected TOK photoresist showed a slow dissolution rate of 1 nm/min. The contrast curves of the TOK photoresist developed in both QAS-4/scCO$_2$ and 0.26 N tetramethylammonium hydroxide(TMAH) solutions are shown in Figure 2. The dissolution test of the TOK photoresist in the QAS-7/scCO$_2$ has also revealed a negative-tone behavior.
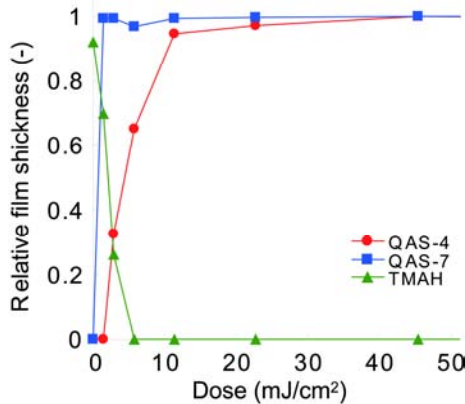
Figure 2 Contrast curves of TOK photoresist
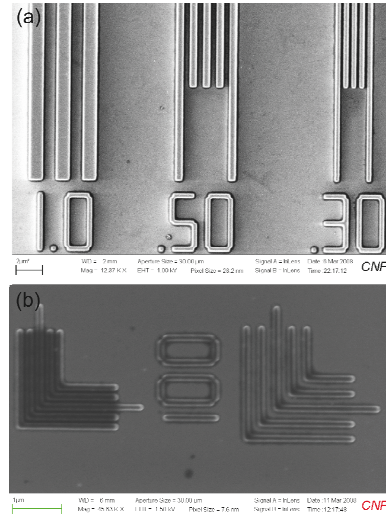
Figure 3 (a)SEM image of TOK photoresist patterned by e-beam lithography with an exposure dose of 107 μC/cm^2 and developed in the 1.25mM QAS-4/scCO$_2$ solution for 60 min at 50°C and 5000 psi (b) in QAS-7/scCO$_2$

The results of e-beam patterned TOK photoresists developed in the QAS/scCO$_2$ solutions are shown in Figure 3.

Discussion

The interactions between the QAS and photoresists depend on the ion pair energy, the shape and size of the mobility of the ions. Good solubility of protected PBOCST in scCO$_2$ has been demonstrated in the presence of the QAS. The electro-negative oxygen atom in the carbonate group can easily interact with the electro-positive ammonium center to provide a CO$_2$-friendly environment, which allows the salt to pull the polymer into scCO$_2$. It was found that as the polymer chains dissolved into scCO$_2$ from the film, each chain formed its own spherical globule with the *tert*-butyl tails of each monomer creating a non-polar outer shell. The QAS molecules bind to the surface of the polymer film, but have limited interactions with the dissolved species. These micelles do not form freely in the absence of QAS, which indicates the micelle stabilization by the QAS. For the deprotected PBOCST, removing the t-BOC group increases polymer-polymer dipole interactions by the resulting hydroxyl groups, which lowers the interaction with the QAS and decreases its solubility in scCO$_2$.

The oxygen atoms in the hydroxyl group and carbonyl group of the unexposed ESCAP can undergo electrostatic interaction with the ammonium cations. The reason that ESCAP did not dissolve in QAS-7/scCO$_2$ in contrast to QAS-4/scCO$_2$ was due to the ion pair energy of the salt, which depends on the basic nature of the anion. The fluoroalkyl carboxylate anion in QAS-7 is less basic than the carboxylate anion in QAS-4 because of the inductive effect of the fluorine substitution. There was a weaker interaction between QAS-7 and the polymer, so it is unable to shield the hydroxyl group of ESCAP and the polymer was still insoluble in scCO$_2$. For the deprotected ESCAP, removing the *tert*-butyl group made it more polar and thus did not dissolve in scCO$_2$.

Future Work:

In order to make the process more environmentally benign, the possibility to design non-fluorinated additives will be considered. Beckman [8] has reported that the interactions between oxygen-containing functional groups and CO$_2$ such as acetate groups are important for designing non-fluorinated CO$_2$-soluble molecules. Previously, Kazarian et al. [9] has also reported the existence of Lewis acid-base interactions between CO$_2$ and the oxygen of a carbonyl. Therefore, non-fluorinated additives based on carbonyl and silicon-containing groups will be tested in scCO$_2$. Besides conventional photoresists, other resist systems such as molecular glass resists will also be studied in scCO$_2$.

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. Valiyaveettil, 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.J. DeYoung, M. Wagner, C. Harbinson,M. Miles, A. E. Zweber,R. G. Carbonell, *Proc. of SPIE* **2006**, 6153, 615345-1
6.M. Wagner, J. DeYoung, C. Harbinson, *Proc. of SPIE* **2006**, 6153, 615311-1
7. M. Tanaka, A. Rastogi, G. N. Toepperwein, R. Riggleman, N. M. Felix, J. J. de Pablo, and C. K. Ober, *Chem. Mater.* 21(14) 3125-3135 (**2009**)
8. E.J. Beckman, *ChemComm* **2004**,1885-1888
9. S.G. Kazarian, M. F. Vincent, F. V. Bright, C. L. Liotta and C. A. Eckert, *J. Am. Chem. Soc.* **1999**, 118, 1729