

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 the Preparation and Lithographic Evaluation of New QAS Resist Systems and Processes for scCO₂ Development

Abstract:

Supercritical carbon dioxide (scCO₂) 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 scCO₂. We have synthesized a series of quaternary ammonium salts to assist in the dissolution of photoresists in scCO₂. In this report, we present the lithographic evaluation of using QAS as additives to develop photoresists in scCO₂. The results have shown the potential of PBOCST and PHS-co-PS-co-PtBA (ESCAP) to be used as negative-tone photoresists in scCO₂.

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 (scCO₂) 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 scCO₂, which limits its practical use. For pure scCO₂ processing, certain fluorinated or silicon containing polymers have been used. Ober et al. have shown the ability to develop fluorinated photoresists in scCO₂ [2,3]. It is believed that the presence of fluorine increases the solubility of polymers in scCO₂, 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 scCO₂[4].

Wagner et al. at Micell Integrated Systems have reported the use of CO₂ compatible salts to develop polar polymers in scCO₂ [5]. This work has permitted the negative tone development in scCO₂ 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 scCO₂ 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 scCO₂. 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.

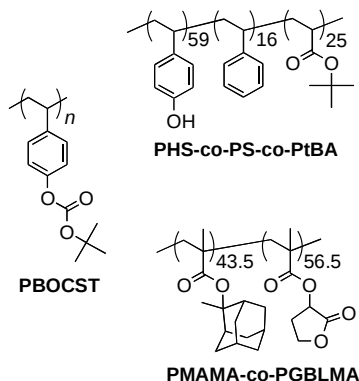


Figure 1 Chemical structures of conventional photoresists

Solubility Test of Conventional Photoresists in scCO₂ with QAS

All the conventional photoresists used were insoluble in scCO₂ before and after exposure without the additives. The QAS was put into the preheating vessel to help dissolve the polymer films in scCO₂, and the polymer films were monitored using laser interferometry. It was shown that PBOCST, ESCAP and TOK resist with QAS-4 were dissolved in scCO₂, and the dissolution rates are shown in Table 1. However, ESCAP did not show solubility in the QAS-4/scCO₂ solution. On the other hand, QAS-7 did not assist in the dissolution of PBOCST, ESCAP or PMAMA-co-PGBLMA in scCO₂, but was able to assist the dissolution of TOK resist in scCO₂.

The exposed (deprotected) photoresists were also developed in the QAS/scCO₂ solutions. It was shown that ESCAP became insoluble in the QAS-4/scCO₂ solution after exposure at doses of 0.71 to 14.2 mJ/cm². 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 scCO₂. On the other hand, PMAMA-co-PGBLMA did not show any solubility in 1.25 mM QAS-4/scCO₂ 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-PGBLMA (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-PGBLMA (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 scCO₂ 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/scCO₂ and 0.26 N tetramethylammonium hydroxide(TMAH) solutions are shown in Figure 2. The dissolution test of the TOK photoresist in the QAS-7/scCO₂ has also revealed a negative-tone behavior.

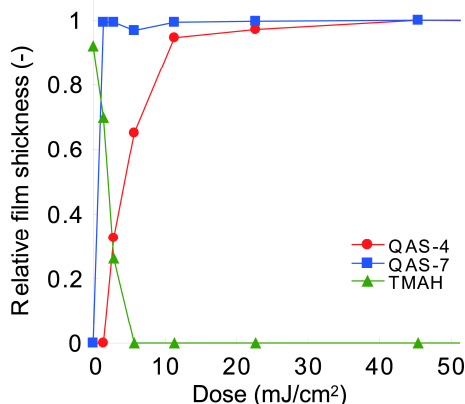


Figure 2 Contrast curves of TOK photoresist

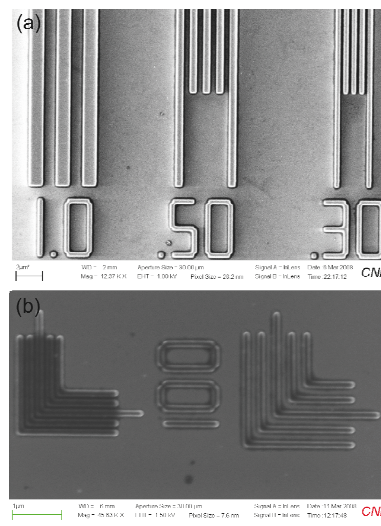


Figure 3 (a)SEM image of TOK photoresist patterned by e-beam lithography with an exposure dose of 107 $\mu\text{C}/\text{cm}^2$ and developed in the 1.25mM QAS-4/scCO₂ solution for 60 min at 50°C and 5000 psi (b) in QAS-7/scCO₂

The results of e-beam patterned TOK photoresists developed in the QAS/scCO₂ 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 scCO₂ 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 CO₂-friendly environment, which allows the salt to pull the polymer into scCO₂. It was found that as the polymer chains dissolved into scCO₂ 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 scCO₂.

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/scCO₂ in contrast to QAS-4/scCO₂ 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 scCO₂. For the deprotected ESCAP, removing the *tert*-butyl group made it more polar and thus did not dissolve in scCO₂.

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 CO₂ such as acetate groups are important for designing non-fluorinated CO₂-soluble molecules. Previously, Kazarian et al. [9] has also reported the existence of Lewis acid-base interactions between CO₂ and the oxygen of a carbonyl. Therefore, non-fluorinated additives based on carbonyl and silicon-containing groups will be tested in scCO₂. Besides conventional photoresists, other resist systems such as molecular glass resists will also be studied in scCO₂.

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