Supercritical Carbon Dioxide Compatible Salts: Synthesis and Application to Next Generation Lithography

Manabu Tanaka,^{1,†} Abhinav Rastogi,^{1,2,†} Nelson M. Felix,^{1,3} Christopher K. Ober^{1,*}

¹ Department of Materials Science and Engineering,

² Department of Chemistry and Chemical Biology,

³ Department of Chemical and Biomolecular Engineering,

Cornell University, Ithaca, NY 14853 USA

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1. Introduction

The continuous advancement and evolution of microelectronic devices has been based on their miniaturization. This reduction in minimum feature size is often described by “Moore’s Law”. As part of this effort, significant progress has been made in the area of photolithography in the last couple of decades. The wavelength of imaging has evolved from 365 to 248 nm and more recently to 193 nm to achieve higher resolution. As microelectronic features progress to the 45 nm node and smaller, extreme ultraviolet (EUV) lithography is being explored as the next generation lithographic process. However image collapse and line edge roughness (LER) become increasingly problematic for sub-50 nm features. At these small dimensions, conventional aqueous-base development can cause the pattern to collapse inwards due to high surface tension. Thus a solution to these problems is of utmost importance to the microelectronic industry. Besides these technical issues of image collapse and LER, “wet” processes have high environmental impact and potentially pose an occupational risk for line workers.¹

Supercritical carbon dioxide (scCO₂) development is a potential alternative process to aqueous-base or organic-solvent development for

high resolution patterning. Supercritical carbon dioxide is defined as carbon dioxide that is in a single fluid state above its critical temperature and pressure ($T_c=31.1\text{ }^\circ\text{C}$, $P_c=1070\text{ psi}$). Carbon dioxide is nontoxic, nonflammable and unreactive under most conditions. Supercritical CO₂ is a solvent with zero surface tension and gas-like diffusivity. These characteristics make scCO₂ an ideal candidate for development of small scale structures (a few nm in size) without suffering from the strong capillary forces that lead to pattern distortion. Previously Ober et al. demonstrated the ability to develop custom polymeric photoresists in pure scCO₂ using otherwise conventional resist chemistries with the inclusion of fluorinated moieties to impart scCO₂ solubility.² Examining the possibility to process fluorine-free resists, Ober and coworkers have demonstrated the ability to develop a variety of small molecular resists (molecular glasses) in pure scCO₂.³

scCO₂ is a good solvent for many non-polar molecules with low molecular weights. However, it is generally a very poor solvent for high molecular weight photoresists. Certain fluorinated or silicone containing photoresists have been shown to be soluble at moderate supercritical conditions.⁴ Recently researchers have reported the ability to develop conventional polymeric resists in scCO₂ using tailored soluble additives. Mao et al. showed that fluorinated and non-fluorinated resists can be developed in scCO₂ using a cosolvent such as acetone or alcohols.⁵

[†] These authors contributed equally to this work.

*To whom correspondence should be addressed.

Tel: (607) 255-8417 Fax: (607) 255-2365

E-mail: cober@ccmr.cornell.edu

Researchers at Micell Technologies have reported the use of fluorinated surfactants as development aids.⁶ This work has permitted the negative tone development in scCO_2 of EUV and DUV resists that are normally positive tone under aqueous-base development. This technique has shown impressive contrast and dense L/S features with aspect ratios > 12. This method does have disadvantages of excessive line thinning and a small process window but opens up the possibility of exploring other additives to impart solubility in scCO_2 . The mechanism of dissolution of a photoresist in scCO_2 in the presence of the nitrogen-containing additives is clearly at a very early stage of understanding. In order to design newer additives with improved performance, we need to know the specific interactions that these quaternary ammonium salts (QAS) have with the different groups on the photoresist. For this purpose we synthesized a series of scCO_2 compatible QAS based on the findings of Micell Technologies. We report herein preliminary results with *t*-Boc protected poly(hydroxystyrene) and EUV/DUV type model resists.

Fig. 1. Comparison between the conventional aqueous-base development and the scCO_2 development. Using scCO_2 , a positive tone resist can be transformed into a negative tone resist.

2. Experimental

2.1 Materials

All chemicals except resists were purchased from Sigma-Aldrich, Synquest, and Oakwood Products, and were used as received. Fluoroalkyl substituted QAS were synthesized in six steps. Partially fluorinated alkyl iodide was synthesized from perfluoroalkyl iodide and olefin alcohol, as described elsewhere. Amination of partially

fluorinated alkyl iodide with a secondary amine under basic conditions followed by reaction with partially fluorinated alkyl iodide formed di-fluoroalkyl quarterly ammonium iodide. Ion exchange reaction yielded quarterly ammonium salt with carboxylate or fluorocarboxylate anion. ^1H -, ^{13}C -, ^{19}F -NMR (Varian Mercury-300) and ESI-Mass (Micromass Quattro I) spectra supported the formation of these compounds.

Poly(4-*t*-butoxycarbonyloxystyrene) (PBOCST) was prepared by protecting poly(4-hydroxystyrene) ($M_n = 8000$, Aldrich) with di-*t*-butyldicarbonate. Poly(hydroxystyrene-co-styrene-co-*t*-butylacrylate) (ESCAP) and Poly(methyladamantane methacrylate-co- α -methacryloxy- γ -butyrolactone) (PMAMA-co-GBLMA) resists were obtained from DuPont Electric polymers Inc. and Mitsubishi Rayon America Inc., respectively.

Fig. 2. The chemical structures of QAS, PBOCST, ESCAP, and PMAMA-co-GBLMA.

2.2 Film Preparation and Exposure

Films of PBOCST, ESCAP, and PMAMA-co-GBLMA (100 and 400 nm thickness) were spin-cast onto HMDS-primed silicon wafers from 5 or 10wt% (v/v) solutions of propylene glycol methyl ether acetate with 5wt% (v/v, with respect to polymers) loading of triphenylsulfonium nonaflate photoacid generator. After spin casting, post apply bake (PAB) at 130°C for 90 s was performed on all wafers.

Each wafer was exposed using an ABM mask aligner with 254 nm light source (7.1 mW/cm²) for varied time from 0.1 to 20 s. High resolution patterning was done using a Leica VB6B-HR

e-beam lithography system operation at 100 kV. After exposure, post exposure bake at 115°C for 30 s was performed on all wafers.

2.3 Development using scCO₂

A series of films were developed in QAS/scCO₂ solutions using a scCO₂ dissolution-rate monitor apparatus, as described in previous papers.^{7,8} Briefly, a piece of silicon wafer coated with polymer resist film was placed into a 25 ml observation vessel, which was aligned with a HeNe laser (632.8 nm wavelength) and fitted with a quartz glass observation window for the laser beams to pass through. A known amount of QAS was dissolved in a 25 ml preheating vessel that connects the observation vessel and the CO₂ pump. CO₂ was introduced into the preheating vessel and kept for 15 min at the desired temperature and pressure to dissolve QAS into scCO₂ with stirring. Then, the QAS/scCO₂ solution was quickly introduced into the observation vessel. The reflected intensity of the laser on the film was continuously monitored until complete dissolution. The dissolution rate was calculated from the dissolution time and the film thickness. After development with CCS/scCO₂ solution, pure CO₂ was injected into each vessel to flush out the dissolving polymer resist and QAS.

2.4 Instrumentation

Tencor P10 profilometer was used to measure the film thickness of each polymer resist before and after development. Optical microscopy and scanning electron microscopy (SEM) imaging were performed using the Nikon Digital Sight DS-5M-L1 and the Zeiss Ultra 55 SEM, respectively.

3. Results and discussion

Solubility of a series of QAS in scCO₂ was examined at various temperatures and pressures. The QAS with short alkyl carboxylate or fluoroalkyl carboxylate anion showed good solubility in scCO₂ over a wide range of temperature and pressure (50-70°C and 5000-7000 psi). These salts showed dissolution at concentrations up to 5 mM at 50°C and 5000 psi. The QAS with halide anion showed poor solubility in scCO₂ even at high temperature and pressure (70°C, 7000 psi).

The solubility of spin-cast model polymer resist films was tested in scCO₂ without any salts. PBOCST, ESCAP, and PMAMA-co-GBLMA were all insoluble in scCO₂ before and after

exposure.

Then, scCO₂-soluble QAS was put into the preheating vessel to help dissolve the polymer resist films into scCO₂. The dissolution rate monitor plots of PBOCST, ESCAP, and PMAMA-co-GBLMA resists in 1.25 mM QAS(carboxylate)/scCO₂ solution at 50°C and 5000 psi were obtained (Fig. 3). The laser reflected intensity of PBOCST film (470 nm thickness) showed a gentle elevation along with the development time to reach to a constant value. The laser intensity plots of ESCAP resists (340 nm) gave a complex sine wave, representing a complicated nonconstant dissolution rate. The dissolution rate of PBOCST and ESCAP in 1.25 mM QAS(carboxylate)/scCO₂ solution at 50°C and 5000 psi were calculated to be ca. 40 and 25 nm/min, respectively. Profilometry and optical microscopy also supported the bulk removal of PBOCST and ESCAP resists into scCO₂ after development.

Fig. 3. Representative dissolution rate monitor plots of unexposed (a) PBOCST, (b) ESCAP, and (c) PMAMA-co-GBLMA in scCO₂ including 1.25 mM QAS with carboxylate anion at 50°C and 5000 psi. The thickness of polymer resist films are all around 400 nm.

Exposed resists were also developed in the QAS(carboxylate)/scCO₂ solutions. All the exposed ESCAP resists turned insoluble in the QAS/scCO₂ solutions after exposure with different doses (0.71 – 14.2 mJ/cm²). The exposed PBOCST films showed very slow dissolution at 1-4 nm/min. These results indicate

that the PBOCST and ESCAP resists have potential to be used as negative tone resists in scCO_2 development with the QAS(carboxylate). In contrast, both the unexposed and exposed PMAMA-co-GBLMA resists were insoluble in QAS(carboxylate)/ scCO_2 solution at 50°C and 5000 psi after 30 min development, as depicted from its flat reflected intensity plots in Fig. 3.

Dissolution test of these model polymer resists with QAS(fluoroalkyl carboxylate) were also performed at 50°C and 5000 psi. The QAS(fluoroalkyl carboxylate) did not help dissolve any model polymer resists into scCO_2 . The solubility results of the unexposed/exposed model resists are summarized in Table 1.

Table 1. Summary of dissolution of the model polymer resists with QAS/ scCO_2 solutions.

QAS (1.25 mM)	Resist	Solubility (Dissolution rate)	
		Unexposed	Exposed
$\begin{array}{c} \text{R}^{\oplus} \\ \\ \text{Rf}-\text{N}-\text{R} \quad \text{X}^{\ominus} \\ \\ \text{Rf} \\ \text{X: Carboxylate} \end{array}$	PBOCST	Dissolution (40 nm/min)	Slow dissolution (1-4 nm/min)
	ESCAP	Dissolution (25 nm/min)	No dissolution
	PMAMA-co-GBLMA	No dissolution	No dissolution
$\begin{array}{c} \text{R}^{\oplus} \\ \\ \text{Rf}-\text{N}-\text{R} \quad \text{X}^{\ominus} \\ \\ \text{Rf} \\ \text{X: Fluoroalkyl carboxylate} \end{array}$	PBOCST	No dissolution	No dissolution
	ESCAP	No dissolution	No dissolution
	PMAMA-co-GBLMA	No dissolution	No dissolution

Here, we discuss the reasons for the differing effect of the two QAS. We believe that a balance between the ion pair energy of the QAS and the basicity of the counter anion is important for the QAS to help dissolution. We tried two different QAS having anions with different basicity. Fluoroalkyl carboxylate anion is less basic than the carboxylate anion. Hence, it has lesser ability to deprotonate the hydroxyl and/or carboxyl groups or to bind electrostatically to the polar groups in the polymer resists. A detailed discussion on the mechanism will be reported elsewhere.

We demonstrate the preliminary results of e-beam patterned PBOCST and ESCAP resists. Fig. 4 is optical and SEM images of ESCAP resist film that was patterned by e-beam lithography with an exposure dose of $39 \mu\text{C}/\text{cm}^2$ and developed in 1.25mM QAS(carboxylate)/ scCO_2 solution for 60 min at 50°C and 5000 psi. Bulk of the polymer was removed leaving behind small amount of residues which can be removed by optimizing the development conditions. These experiments are currently underway.

Fig. 4. Optical and SEM images of the e-beam patterned ESCAP resist film (exposed with $39 \mu\text{C}/\text{cm}^2$, developed in 1.25 mM QAS(carboxylate)/ scCO_2 solution for 60 min at 50°C and 5000 psi).

4. Conclusion

We have synthesized a series of QAS and examined their ability to help the dissolution of model polymer resists in scCO_2 . QAS (carboxylate) showed good solubility in scCO_2 and assisted in the dissolution of PBOCST and ESCAP resists. The exposed PBOCST and ESCAP resists showed very slow or no dissolution in QAS(carboxylate)/ scCO_2 . These results indicate that the PBOCST and ESCAP resists could be used as negative tone resists in scCO_2 in the presence of QAS(carboxylate).

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