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Fluorinated Quaternary Ammonium Salts as Dissolution Aids for Polar Polymers in Environmentally Benign Supercritical Carbon Dioxide

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Environmentally benign supercritical carbon dioxide ($scCO_2$) has been utilized as an "ecologically responsible" solvent for a wide variety of applications. However, nonpolar $scCO_2$ is generally a very poor solvent for polar polymers which limits its use as a processing solvent in high resolution photolithography. In this paper, we report the synthesis of fluorinated $scCO_2$ compatible additives and demonstrate their utility to help dissolve polar polymers in $scCO_2$. We have designed and synthesized a series of quaternary ammonium salts (QAS) as $scCO_2$ additives. The ability of these salts to assist in the dissolution of model acidic and protected polar polymers has been compared. For our studies we have chosen three different polar reference polymers. Addition of millimolar quantities of the QAS to the $scCO_2$ solvent helped to dissolve the protected model polymer under moderate supercritical conditions. To explicitly investigate the interactions between the QAS additive and the various functionalities on the polymers we have carried out computational simulations using a fully atomistic force field adapted from optimized potentials for liquid simulations (OPLS). These studies combining both theory and experiment showed that the architecture of the cation and the basic nature and size of the anion are crucial in designing more efficient additives. Finally, on the basis of these findings we report the lithographic evaluation of a standard commercially available polymer photoresist using an appropriate $scCO_2$ compatible QAS additive after development in $scCO_2$. Well-resolved, negative-tone patterns as small as 100 nm were obtained by e-beam exposure, indicating the excellent potential of using $scCO_2$ as the processing solvent in the presence of the QAS additives to form high-resolution structures.

Introduction

Environmentally benign processes are gaining renewed interest and are being considered as promising alternatives to current industrial practices as a result of increasing awareness of environmental issues and the economic benefits of shifting to "greener" routes. Carbon dioxide is considered a "green" solvent, and since its first use in the 1950s it has attracted attention in academia and industry. Carbon dioxide is relatively nontoxic, nonflammable, and inert under most conditions and is a potential candidate for a more environmentally friendly replacement for organic solvents in the area of polymer synthesis, coatings, biomaterials, and microelectronic processing.[1−3] Like water, it is a naturally abundant material that can be removed from the environment, used in a process, and then recycled.

Supercritical fluids have been heavily investigated as environmentally benign solvents. A supercritical fluid is a substance at a temperature and pressure above its thermodynamic critical point. Under these conditions, these substances exhibit properties such as high gas-like diffusivity, zero surface tension, ease of solvent removal, and the ability to be recycled and can be tuned to achieve the desired density and solvent properties. However, the critical temperatures (T_c) of possible solvents can be inconveniently high (T_c of water is 374.2 °C, P_c = 221.2 atm). In contrast, supercritical carbon dioxide ($scCO_2$) has the advantage of having an easily accessible critical point (T_c = 31.1 °C, P_c = 72.8 atm). It is inexpensive and environmentally benign, and it combines the best properties of both a gas and a liquid, which makes it easy to separate from solutes. These unique properties associated with supercritical fluids offer a range of possibilities in polymer chemistry. DeSimone et al. showed that high molar mass fluoropolymers could be synthesized by using homogeneous free radical polymerization methods in $scCO_2$.[4]

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Here $scCO_2$ helped circumvent the environmental concerns of chlorofluorocarbons. DuPont has prepared a range of fluoropolymers using $scCO_2$ as a reaction medium.[5] Several copolymerizations via living free radical polymerization reactions (reversible addition−fragmentation chain transfer (RAFT) and atom transfer radical polymerization (ATRP)) have been successfully carried out in $scCO_2$.[6,7] Supercritical CO_2 has also been used for the production of microcellular biodegradable composite materials. Mistele et al. described the ring-opening metathesis polymerization (ROMP) of norbornene in $scCO_2$.[8] Bien Tan et al. developed a new approach for producing inexpensive and biodegradable polymer surfactants for use in $scCO_2$.[9] They synthesized CO_2-soluble surfactants from oligomeric poly(vinyl acetate) that produced stable CO_2-in-water emulsions, which were then used to produce emulsion templated materials. For a more detailed study of polymerizations in $scCO_2$, the reader is directed to the review article by Kendall et al.[10]

Over the last couple of decades the unique properties of $scCO_2$ have led to its application in the area of microelectronics. Industrial and academic researchers have shown that $scCO_2$ has been explored for multiple aspects of device fabrication including drying, cleaning, deposition, and etching.[11−14] More recently $scCO_2$ has been used for the synthesis and processing of organic materials in the area of flexible electronics. Progress of the semiconductor industry is based on the ever increasing demand of miniaturization of devices as described by Moore's Law.[15] As microelectronic features progress to the 45 nm node and smaller, overcoming the inherent challenges at such small dimensions becomes more difficult. At these resolutions, development of photoresist images in an aqueous base can cause the pattern to collapse inward due to high surface tension of the aqueous solution.[16,17] As the rinse solution evaporates from the narrow openings, it pulls the features together. In addition, line edge roughness (LER) becomes increasingly problematic for sub-50 nm features as the acceptable tolerance of edge roughness of the patterns decreases with smaller features.[18,19] Both these issues need to be addressed in lithography. Thus, the use of multiple layers of varied materials in organic electronics and high performance transistors requires a solvent system that is selective and benign to maintain the integrity of the device. It has been established that $scCO_2$ can be used for the development of small scale structures without suffering from the very strong capillary forces that lead to pattern distortion. In particular, Goldfarb et al. have explored in greater depth, the direct use of $scCO_2$ as a means of avoiding pattern collapse.[20,21] Johnston and co-workers have reported the use of hydrocarbon surfactants to dry photoresists directly in $scCO_2$.[22] Development in $scCO_2$ can lead to a dramatic decrease in the glass transition temperature of resists. It has been shown by various methods that CO_2 is a good plasticizing agent for a host of polymeric materials even at moderate pressures.[23] This can help in reducing LER by surface treating the photoresist with $scCO_2$ during and after development. The plasticized photoresist may be subjected to a heating step to reflow the photoresist. Meagley et al. have predicted that such a reflow process may help reduce LER of the patterned, developed photoresist.[24] Besides these technical issues of image collapse and LER, "wet" processes have high environmental implications and potentially pose an occupational risk for line workers. Williams et al. reported in 2002 that the production of a single 2 g 32 MB DRAM microchip requires about 1600 g of secondary fossil fuels and 72 g of chemical inputs. About 32 kg of water and 700 g of elemental gases (mainly nitrogen) are used in the fabrication stage.[25] A solution to this problem is of utmost importance. The advantages of $scCO_2$ development over conventional aqueous base development are summarized in Figure 1.

Even though liquid and supercritical CO_2 have attracted much interest as an environmentally benign solvent, its practical use has been limited due to the low solubility of many materials, particularly the polar polymers used in high-resolution photoresists. Generally CO_2 is a good solvent for many nonpolar molecules with low molecular weights. However, high CO_2 pressures are required to dissolve small amounts of polar, amphiphilic, or high molecular weight polymers. This restricts the type of polymers that can be processed in $scCO_2$ to experimental photoresists. The current lithographic imaging process involves the acid-catalyzed cleavage of pendent protecting groups, such as the *tert*-butoxycarbonyl (t-boc) group, *tert*-butyl, and methyl adamantyl groups to generate base-soluble acidic functionalities such as

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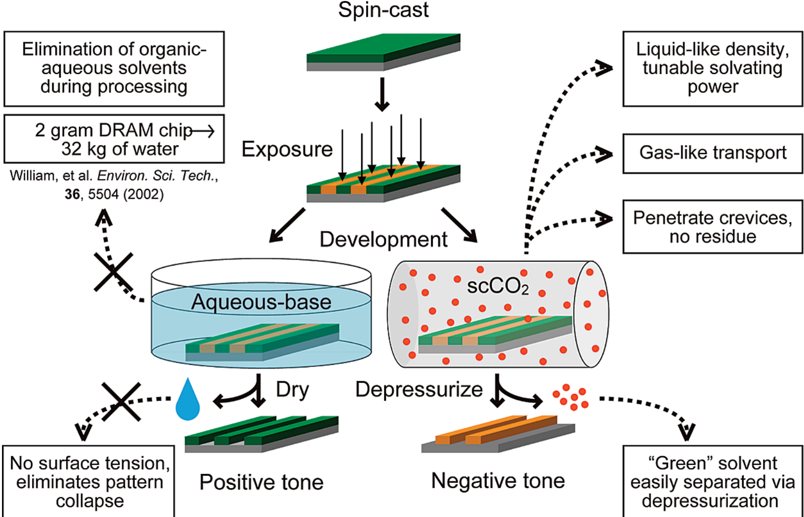

Figure 1. Comparison between conventional aqueous-base processing and $scCO_2$ processing. Processing in $scCO_2$ has several environmental and lithographical benefits.

hydroxyl and carboxylic acid groups. This imaging mechanism has drawn a great deal of attention because it provides the basis of designing aqueous base developable positive photoresists. However, these polar polymer photoresists are generally insoluble in $scCO_2$, making it extremely difficult for the required solubility switch to be observed in the $scCO_2$ solvent. For pure $scCO_2$ processing, certain fluorinated or silicone containing classes of polymers are typically used.[26] It is believed that the presence of fluorine creates molecules with weak self-interaction, thus increasing the solubility in $scCO_2$. Previously our group has demonstrated the ability to develop custom polymeric photoresists in pure $scCO_2$ using otherwise conventional photoresist chemistries with the inclusion of fluorinated moieties to impart $scCO_2$ solubility.[27] Unfortunately, the fluorination of polymers to achieve CO_2 solubility is relatively expensive and the high content of fluorine has an adverse effect on the etch resistance of the polymer matrix.[28] As a result of this characteristic, commercial photoresists generally do not have fluorinated components. Examining the possibility to process fluorine free photoresists, we have demonstrated the ability to develop a variety of small molecule, molecular glass resists in pure $scCO_2$ with easily achievable resolution down to 50 nm.[29,30] Felix et al. have reported a new type of acid-catalyzed, chain scission polymeric systems based on main-chain acetal linkages to produce high-resolution, $scCO_2$ processed positive tone patterns. Excellent solubility contrasts and feature sizes below 200 nm were obtained with this system.[31] Recently, several researchers have reported the ability to develop conventional polymeric resists in $scCO_2$ using cosolvents or tailored soluble additives. Mao et al. have shown that the addition of selected cosolvents such as acetone or alcohols allows for the development of fluorinated and nonfluorinated photoresists in $scCO_2$.[32,33] In addition, other researchers have shown that the inclusion of certain surfactants into $scCO_2$ imparts solubility to otherwise insoluble polymers.[34]

Wagner et al. at Micell Integrated Systems have recently reported a solution to the solubility of polar polymers in $scCO_2$ by use of surfactants they call CO_2 compatible salts.[35] They used these salts to get highly effective images with $scCO_2$ processing of a standard EUV photoresist. This technique has shown impressive contrast and dense L/S features with aspect ratios > 12.[36] These results encouraged us to study $scCO_2$ compatible quaternary ammonium salt additives. The mechanism of dissolution of polymers in $scCO_2$ in the presence of nitrogen containing additives is clearly at an early stage of understanding. In order to design highly efficient additives, it is crucial to understand the interactions that these additives have with the different functional groups on the chemical structures of the polar polymers commonly used as photoresist materials.

We report herein the synthesis of a series of fluorinated quaternary ammonium salts (QAS) as $scCO_2$ compatible additives and demonstrate their utility to help dissolve polar polymers in $scCO_2$. In particular, the effects of architecture (symmetric or asymmetric structure) of the cation and the effect of the basic nature and size of the counteranion of the salt on the efficiency of the $scCO_2$ compatible additive were studied in detail. The solubility

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of each QAS was tested in $scCO_2$ at various concentrations, temperatures, and pressures. The solubility enhancement parameter was calculated for each salt using computational methods. We describe the effect of these salts on the dissolution behavior of model polymers. For our studies, we chose three different protected acidic polymer systems. Poly(4-*t*-butoxycarbonyloxystyrene) (PBOCST), poly(hydroxystyrene-*co*-styrene-*co*-*t*-butylacrylate) (PHS-*co*-PS-*co*-PtBA), and poly(methyladamantane methylacrylate-*co*-α-methacryloxy-γ-butyrolactone) (PMAMA-*co*-PGBLMA); each have structures similar to what one would find in a chemically amplified photoresist. Without the QAS additive, all these polar polymers showed no dissolution in $scCO_2$ in the protected or deprotected acidic form. Addition of millimolar quantities of the QAS to the $scCO_2$ developer helped dissolve the protected polymers under moderate supercritical conditions. To explicitly investigate the interactions between the polymers, QAS additives, and the $scCO_2$ solvent, we carried out computational simulations using a fully atomistic force-field adapted from optimized potentials for liquid simulations (OPLS). On the basis of our experimental and computational results we identify the key interactions between the QAS additive and different functional groups on the solubilized polymer. Understanding these interactions is important if superior additives are to be designed. Finally based on these findings, we report the lithographic evaluation of a standard commercially available polymer photoresist using an appropriate $scCO_2$ compatible QAS additive in $scCO_2$. Well-resolved, negative tone patterns as small as 100 nm were obtained by e-beam lithography, indicating the potential of using $scCO_2$ as a process solvent for polar polymers in the presence of the QAS additives.

Experimental Section

Materials. All chemicals except resists were purchased from Sigma-Aldrich unless otherwise stated and were used without further purification. High purity carbon dioxide and argon were purchased from Airgas and used as received. Poly(4-*t*-butoxycarbonyloxystyrene] (PBOCST) was prepared by protecting poly(4-hydroxystyrene) (M_n=8000) with di-*t*-butyldicarbonate. Poly(hydroxystyrene-*co*-styrene-*co*-*t*-butylacrylate) (PHS-*co*-PS-*co*-PtBA) and Poly(methyladamantane methacrylate-*co*-α-methacryloxy-γ-butyrolactone) (PMAMA-*co*-PGBLMA) polymers were obtained from DuPont Electric polymers Inc. and Mitsubishi Rayon America Inc., respectively. A commercial photoresist used for lithographic evaluation was donated by Tokyo Ohka Kogyo (TOK) Co. Ltd.

Characterization. ^{1}H NMR spectra were recorded on a Varian Inova-400 (400 MHz) or Mercury-300 (300 MHz) spectrometer at room temperature, using the chemical shift of a residual protic solvent (chloroform at δ 7.24 ppm or acetonitrile at 2.10 ppm) as an internal reference. All shifts are quoted in parts per million (ppm) relative to chloroform or acetonitrile, and coupling constants J are measured in hertz. The multiplicity of the signal is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{19}F NMR spectra were recorded on a Varian Mercury-300 (300 MHz) spectrometer.

Synthesis of 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-9-iodononane (1). 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononan-1-ol (25 g, 66.1 mmol, purchased from SynQuest), triphenyl phosphine (26.0 g, 99.2 mmol), and imidazole (26.0 g, 99.2 mmol) were dissolved in 300 mL of anhydrous THF and cooled to −78 °C. Iodine (25.2 g, 99.2 mmol) was then added slowly to the solution at −78 °C. The mixture was stirred for 1 h at −78 °C and allowed to warm up to room temperature. After stirring for 2 h at room temperature, the mixture was quenched by adding 100 mL of water. The product was extracted with diethyl ether three times and washed with water. The solvent was evaporated, and then 300 mL of fresh diethyl ether was added to precipitate the byproduct, phosphonium oxide. After the precipitate was filtrated off, the product was purified by the distillation under vacuum. The product was obtained as a colorless viscous liquid (27.1 g, yield = 79.3%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.24 (t, J = 6.3 Hz, 2H, $-CF_2-CH_2-$), 2.20 (m, 2H, $-CH_2-$), 2.15 (t, J = 6 Hz, 2H, $-CH_2-I$). ^{19}F NMR (300 MHz, $CDCl_3$): δ = −82.0 (s, 3F, CF_3-), −114.7 (s, 2F, CF_3-CF_2-), −122.8 (s, 2F, $-CF_2-$), −123.8 (s, 2F, $-CF_2-$), −124.5 (s, 2F, $-CF_2-$), −127.1 (s, 2F, $-CF_2-CH_2-$).

Synthesis of *N*-Ethyl-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-*N*-methylnonan-1-amine (2). Ethyl methyl amine (5.5 g, 92.2 mmol) was added dropwise to a mixture of **1** (10 g, 20.5 mmol) and pyridine (20 mL). The mixture was stirred for 4 h at 80 °C after which the lower phase (yellow liquid) of the mixture solution was collected. The remaining upper phase (red liquid) was washed with 10 wt % NaOH aqueous solution for 1 h at 50 °C and allowed to stand. The lower phase was collected and combined to the previous yellow liquid. The collected liquid was washed with a 10 wt % NaOH aqueous solution and dried with magnesium sulfate. After distillation under vacuum, the product was obtained as colorless viscous liquid (6.29 g, yield = 73.2%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.42 (t, J=7.4 Hz, 2H, $-CH_2-N-$), 2.39 (t, J = 7.8 Hz, 2H, $-N-CH_2-$), 2.20 (s, 3H, $-N-CH_3$), 2.09 (m, 2H, $-CF_2-CH_2-$), 1.75 (m, 2H, $-CH_2-CH_2-CH_2-$), 1.04 (t, J = 7.2 Hz, 3H, $-CH_2-CH_3$). ^{19}F NMR (300 MHz, $CDCl_3$): δ = −81.3 (s, 3F, CF_3-), −114.7 (s, 2F, CF_3-CF_2-), −122.4 (s, 2F, $-CF_2-$), −123.4 (s, 2F, $-CF_2-$), −124.0 (s, 2F, $-CF_2-$), −126.7 (s, 2F, $-CF_2-CH_2-$).

Synthesis of *N*-Ethyl-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-*N*-methyl-*N*-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)nonan-1-aminium iodide (QAS-3). A mixture of **1** (9.06 g, 18.6 mmol) and **2** (6.77 g, 16.2 mmol) was stirred for 24 h at 80 °C. After the reaction, the crude product was washed with copious amount of diethyl ether to remove remaining reactants, and then dried under vacuum. The product was obtained as a white powder (11.8 g, yield = 80.4%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ=3.39−3.29 (m, 6H, $-N-CH_2-$), 3.00 (s, 3H, $-N-CH_3$), 2.31 (m, 4H, $-CH_2-$), 2.05 (m, 4H, $-CH_2-$), 1.32 (t, J = 6.9 Hz, 3H, $-CH_2-CH_3$). ^{19}F NMR (300 MHz, acetonitrile-d_3): δ= −81.9 (s, 6F, CF_3-), −115.0 (s, 4F, CF_3-CF_2-), −122.8 (s, 4F, $-CF_2-$), −123.8 (s, 4F, $-CF_2-$), −124.5 (s, 4F, $-CF_2-$), −127.1 (s, 4F, $-CF_2-CH_2-$).

Synthesis of QAS-1−QAS-10. The general synthetic procedure for QAS is described with the synthesis of **QAS-4** and **QAS-7** given in detail as representative. **QAS-5−QAS-10** were prepared using similar synthetic procedures as **QAS-7**, with their corresponding counteranion sodium salts. **QAS-1** was obtained from **1** and triethylamine. **QAS-2** was prepared using diethylamine instead of ethylmethylamine.

QAS-4. An acetic acid/water mixture solution (25 mL/25 mL) of **QAS-3** (0.50 g, 0.55 mmol) was passed slowly through an ion-exchange column filled with 500 g of an anion exchange resin

(Dowex 1 × 4 chloride form, 20−50 mesh), which was converted to acetate form using acetic acid/water before usage. After passing the **QAS-3** solution, the column was washed with 500 mL of acetic acid/water. The aqueous solution was concentrated and fully dried at 80 °C under vacuum to yield **QAS-4** as a white solid (0.46 g, yield=99.4%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ = 3.40−3.31 (m, 6H, −N−CH_2−), 3.02 (s, 3H, −N−CH_3), 2.32 (m, 4H, −CH_2−), 2.19 (s, 3H, CH_3−COO^-), 2.03 (m, 4H, −CH_2−), 1.32 (t, J=6.9 Hz, 3H, −CH_2−CH_3). ^{19}F NMR (300 MHz, acetonitrile-d_3): δ = −82.0 (s, 6F, CF_3−), −114.9 (s, 4F, CF_3−CF_2−), −122.8 (s, 4F, −CF_2−), −123.8 (s, 4F, −CF_2−), −124.4 (s, 4F, −CF_2−), −127.1 (s, 4F, −CF_2−CH_2−).

QAS-7. To an acetonitrile solution (5 mL) of **QAS-3** (1.5 g, 1.65 mmol) was added an aqueous solution (50 mL) of sodium perfluoropropionate (15.4 g, 82.7 mmol). After stirring the mixture solution for 7−10 days to ensure complete ion exchange, the solvent was removed under vacuum. The crude product was washed with 5 × 200 mL of water to remove excess amount of sodium perfluoropropionate and then dried under vacuum. The product was obtained as a white solid (1.09 g, yield=69.8%). ^{1}H NMR (300 MHz, acetonitrile-d_3): δ = 3.42−3.35 (m, 6H, −N−CH_2−), 3.03 (s, 3H, −N−CH_3), 2.31 (m, 4H, −CH_2−), 2.04 (m, 4H, −CH_2−), 1.32 (t, J=6.9 Hz, 3H, −CH_2−CH_3). ^{19}F NMR (300 MHz, acetonitrile-d_3): δ=−82.1 (s, 6F, CF_3−), −83.8 (s, 3F, CF_3−), −115.1 (s, 4F, CF_3−CF_2−), −120.1 (s, 2F, CF_3−CF_2−COO^-), −122.9 (s, 4F, −CF_2−), −123.9 (s, 4F, −CF_2−), −124.6 (s, 4F, −CF_2−), −127.2 (s, 4F, −CF_2−CH_2−).

NMR shifts for **QAS-1**, **QAS-2**, **QAS-5**, **QAS-6**, **QAS-8**, **QAS-9**, and **QAS-10** can be found in the Supporting Information.

Lithographic Procedure. A typical procedure is described as follows using PHS-*co*-PS-*co*-PtBA as an example. A 10 wt % solution of the resist and triphenylsulfonium perfluoro-1-butane sulfonate (5 wt % with respect to the photoresist) was prepared in propylene glycol monomethyl ether acetate (PGMEA). The solution was then spin-coated onto a HMDS-primed silicon wafer after being filtered through a 0.2 μm filter. The film (approximately 100 or 400 nm) was baked at 130 °C for 90 s. Parts of the wafers were exposed using an ABM mask aligner with 254 nm light source (7.1 mW/cm^2) for various times from 0.1 to 20 s. High resolution patterning was done using a Leica VB6B-HR e-beam lithography system operated at 100 kV. After exposure, post-exposure bake was performed at 115 °C for 30 s.

Supercritical Carbon Dioxide Development. A series of films were developed in QAS/$scCO_2$ solutions using a $scCO_2$ dissolution-rate monitor apparatus, as described in previous papers.[37,38] 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 CO_2 pump. CO_2 was introduced into the preheating vessel and kept for 15 min at the desired temperature and pressure to dissolve QAS into $scCO_2$ with stirring. Then, the QAS/$scCO_2$ 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 QAS/$scCO_2$ solution, pure CO_2 was injected into each vessel to flush out the dissolving polymer photoresist and QAS.

Metrology. Tencor P10 profilometer was used to measure the film thickness of each polymer photoresist 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.

Computational Simulation. A fully atomistic model of the photoresists was adapted from the optimized potentials for liquid simulations (OPLS) force field. Optimization of the model by calculating local charges for each species was performed using quantum mechanical calculations with the Gaussian simulation package. Thin films of each resist were equilibrated and simulated in GROMACS.

Results and Discussion

Design and Synthesis of the QAS. The fluoroalkyl-substituted quaternary ammonium salt (QAS) was designed as a $scCO_2$ compatible additive to dissolve standard protected acidic polymers in $scCO_2$. The rationale behind the design is that the additive should favorably interact with either the unexposed (protected) or exposed (acidic) photoresist and solubilize it into the $scCO_2$ phase. This solubility switch forms the basis of creating three-dimensional patterns in the resist film. The ammonium cation center has high affinity for the polar moieties of the polymer photoresist and the fluoroalkyl chain is expected to impart solubility to the salt itself in $scCO_2$. These electrostatic interactions between the additive and the polymer can assist in the dissolution of the polymer in $scCO_2$. For these QAS, the architecture of the salt and the ion pair energy are important factors to be considered. QAS with symmetrical and unsymmetrical cations were synthesized and their solubility performance was compared. The basic nature of the counteranion also plays an important role in controlling the solubility of the salt and the strength of the ion pair energy, which determines the interaction between QAS and photoresists. Figure 2 shows a series of QAS with various combinations of cations and anions that were synthesized and used for this study. Scheme 1 shows a typical synthetic route of QAS using **QAS-4** as an example. Amination of fluoroalkyl iodide **1**, which was synthesized in three steps with total yield of 40%, using ethylmethylamine yielded tertiary amine **2**. Reaction of the tertiary amine **2** and the fluoroalkyl iodide **1** formed quaternary ammonium salt with iodide anion (**QAS-3**). An acetic acid/water solution of **QAS-3** when passed through an ion-exchange yielded the anion-exchanged salt (**QAS-4**). To ensure complete conversion, the ion exchange column was washed with 500 mL of 50% acetic acid solution. Other salts were obtained from their corresponding counteranion sodium salts; for example **QAS-2** was synthesized using diethylamine instead of ethylmethylamine, and **QAS-7** bearing a fluorocarboxylate anion was prepared using the corresponding sodium perpropionate. The structure of each compound was characterized by ^{1}H- and ^{19}F-NMR.

Solubility of a series of QAS in $scCO_2$ was examined at various temperatures and pressures. Most of the QAS were highly soluble in $scCO_2$ under moderate conditions. In particular **QAS-4** and **QAS-7** showed good solubility

(37) Pham, V. Q.; Rao, N.; Ober, C. K. *J. Supercrit. Fluids* **2004**, *31*, 323.
(38) Tanaka, M.; Rastogi, A.; Felix, N. M.; Ober, C. K. *J. Photopolym. Sci. Technol.* **2008**, *21*(3), 393.

QAS-1 (Γ = -3.60) QAS-2 (Γ = -1.44) QAS-3 QAS-4 (Γ = +0.83)

QAS-5 QAS-6 (Γ = +0.14) QAS-7 (Γ = +2.08) QAS-8 (Γ = +2.39)

QAS-9 (Γ = +0.82) QAS-10 (Γ = +1.44)

Figure 2. Series of synthesized QAS. The computationally calculated Γ value represents the solubility enhancement factor, which predicts the solubility of QAS in $scCO_2$. QAS with positive Γ value are predicted to be soluble in $scCO_2$.

Scheme 1. Synthesis of the QAS-4 Additive; the other QAS's Were Obtained Similarly

in $scCO_2$ over a wide range of temperature and pressure (50−70 °C and 5000−7000 psi). These salts dissolved at concentrations up to 5 mM at 50 °C and 5000 psi. On the other hand, some of the QAS (**QAS-1**, **QAS-2**, **QAS-3**, and **QAS-5**) showed poor solubility in $scCO_2$ even at high temperature and pressure (70 °C, 7000 psi). These experimental observations were confirmed using computational simulations. The quaternary ammonium salts are amphiphilic as they have a polar ammonium cation and a relatively nonpolar fluoroalkyl chain. We expect that these salts form a reverse micelle structure in nonpolar $scCO_2$ with the polar headgroups at the center and the fluoroalkyl chains facing outward (water-in-oil micelle). The shape and size of a micelle depends on the architecture of its surfactant molecules and the solution conditions such as surfactant concentration, temperature and ionic strength. **QAS-1** was insoluble in $scCO_2$. This is somewhat expected due to the lower content of fluorine in the molecule. Psathas et al. have reported simulation results that also show that quaternary ammonium salts with a perfluoropolyether (PFPE) tail and a cationic trimethylammonium acetate headgroup form micelles in $scCO_2$.[39]

Fluorination is known to impart solubility in $scCO_2$. Modification of the **QAS-1** by adding another fluoroalkyl chain gave new salts with improved solubilities. However, **QAS-2** showed much lower solubility than **QAS-4** which is attributed to the symmetric molecular structure of **QAS-2**. Such symmetric molecules can aggregate and stratify onto each other, preventing the formation of micelles. The poor solubility of **QAS-3** and **QAS-5** can be explained by the fact that they both have rigid and bulky anions. The iodide and the heptanoate anions have

(39) Psathas, P. A.; Sander, E. A.; Lim, K. T.; Johnston, K. P. *J. Dispersion Sci. Technol.* **2002**, *23*(1−3), 65.

low mobility in the solvent. This decreased mobility of the anions coupled with their steric hindrance prevents the micelle formation. The asymmetric salts, **QAS-4** and **QAS-7**, showed high solubility in $scCO_2$. Thus the micelle formation in $scCO_2$ depends on the molecular architecture of the cation and size of the anion. Generally, it was observed that QAS with asymmetric cations are more easily soluble in $scCO_2$ compared to salts with symmetric cations.

These solubility properties of QAS were also studied using molecular simulations, where five QAS molecules were placed in a dense $scCO_2$ phase to examine micelle formation and determine solubility parameters. At the beginning of the simulation, the QAS molecules were widely spaced out in the simulation box; for **QAS-4** and **QAS-7**, the molecules quickly diffused toward each other and formed micelles. These micelles were stable for the duration of the simulation, corresponding to at least 1.5 ns. Other salts exhibiting relatively poor solubility in $scCO_2$, such as **QAS-1**, were slow to come together and were unable to form stable micelles. The solubilities in $scCO_2$ can be quantified from a simulation by calculating the solubility enhancement factor

$$\Gamma = \rho \int_0^\infty (g(r) - 1) 4\pi r^2 \, dr$$

where ρ is the density and $g(r)$ is the pair distribution function calculated between the QAS and the $scCO_2$ molecules. Γ represents the solubility of the species relative to a mixture of ideal gases, and large positive values of Γ indicate good solubility while large negative values indicate poor solubility. For **QAS-4** and **QAS-7**, we found $\Gamma = 1.01$ and 1.24, respectively; these values are consistent with the stable micelles observed in the simulations. **QAS-1**, on the other hand, had $\Gamma = -1.44$ and did not form long-lived, stable micelles.

Solubility Test of Reference Polymers in $scCO_2$ with QAS. Chemically amplified photoresists invented in the early 1980s enabled lithography to decrease the smallest accessible features of semiconductor devices. Today's advanced photoresists are exclusively built on the acid-catalyzed deprotection mechanism. Thus, we chose three different acidic reference polymer systems, namely, poly(4-*t*-butoxycarbonyloxystyrene) (PBOCST), poly(hydroxystyrene-*co*-styrene-*co*-*t*-butylacrylate) (PHS-*co*-PS-*co*-PtBA), and poly(methyladamantane methylacrylate-*co*-α-methacryloxy-γ-butyrolactone) (PMAMA-*co*-PGBLMA), that mimic many of the characteristics of a modern photoresist. In addition to these three model systems, we also examined the effect of our QAS additives on a commercial photoresist. The solubility of these spin-cast photoresist films shown in Figure 3 was tested in $scCO_2$ without any salts using a dissolution rate monitor. All these polymers were completely insoluble in $scCO_2$ before and after exposure without the addition of any additive.

The $scCO_2$-soluble QAS was put into the preheating vessel to help dissolve the polymer films into $scCO_2$. The solubilization of the polymer films (ca. 300 nm) was monitored using laser interferometry. PBOCST and

Figure 3. Chemical structures of PBOCST, PHS-*co*-PS-*co*-PtBA, and PMAMA-*co*-PGBLMA reference polymers.

PHS-*co*-PS-*co*-PtBA with **QAS-4** dissolved in $scCO_2$ and showed changes in laser reflected intensity that corresponds to the film thickness change. After keeping the film in a QAS/$scCO_2$ solution for a short period, the laser reflected intensity increased slowly and reached a constant value corresponding to the value of the silicon surface itself, indicating that the entire film dissolved in $scCO_2$. The dissolution rates of polymer films were calculated by dividing the film thickness (nm) by the total time (s) until full dissolution of the films occurs. The dissolution rates of PBOCST and PHS-*co*-PS-*co*-PtBA polymers in 1.25 mM **QAS-4**/$scCO_2$ solution at 50 °C and 5000 psi were approximately 40 and 25 nm/min, respectively. Profilometry and optical microscopy also support the bulk removal of these polymer films into $scCO_2$ after development. On the other hand, PMAMA-*co*-PGBLMA in the **QAS-4**/$scCO_2$ solution showed no change in reflected intensity value, suggesting the insolubility of this polymer in $scCO_2$. Table 1 shows the dissolution results of representative combinations of QAS and the selected polymers. The **QAS-7** did not help dissolve PBOCST, PHS-*co*-PS-*co*-PtBA, or PMAMA-*co*-GBLMA into $scCO_2$, in contrast to **QAS-4** which solubilizes PHS-*co*-PS-*co*-PtBA and PBOCST in $scCO_2$. Other combinations of QAS and reference polymers were also examined: most of the other QAS including **QAS-6**, **QAS-8**, **QAS-9**, and **QAS-10** helped dissolve PBOCST in $scCO_2$, but they had no effect on PHS-*co*-PS-*co*-PtBA and PMAMA-*co*-PGBLMA.

The exposed (deprotected) polymers were also developed in the QAS/$scCO_2$ solutions. The PHS-*co*-PS-*co*-PtBA copolymer 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 films showed very slow dissolution at 1−4 nm/min, which is much slower than that of the corresponding unexposed polymers. These results indicate that PBOCST and PHS-*co*-PS-*co*-PtBA have the potential to be utilized as negative-tone photoresists, processable in $scCO_2$. The PMAMA-*co*-PGBLMA copolymer however, did not show any solubility in 1.25 mM **QAS-4**/$scCO_2$ solution at 50 °C and 5000 psi after a processing for 30 min. It is worth mentioning that the salt may be recovered from the QAS/$scCO_2$ solution by depressurizing $scCO_2$.

Table 1. Summary of Dissolution of the Reference Polymers in 1.25 mM QAS-4/$scCO_2$ and QAS-7/$scCO_2$ Solutions[a]

QAS	Resist	Unexposed	Exposed	Note
$CH_3COO^{\ominus}$; $N^{\oplus}$–$(CH_2)_3$–$(CF_2)_5$–CF_3; $(CH_2)_3$; $(CF_2)_5$; CF_3 **QAS-4**	PBOCST	Dissolution (40 nm/min)	Slow dissolution (1-4 nm/min)	*Negative tone resist*
	PHS-co-PS -co-PtBA	Dissolution (25 nm/min)	No dissolution	*Negative tone resist*
	PMAMA-co-PGBLMA	No dissolution	No dissolution	
	TOK resist	Dissolution (15 nm/min)	Slow dissolution (1-2 nm/min)	*Negative tone resist*
$CF_3CF_2COO^{\ominus}$; $N^{\oplus}$–$(CH_2)_3$–$(CF_2)_5$–CF_3; $(CH_2)_3$; $(CF_2)_5$; CF_3 **QAS-7**	PBOCST	No dissolution	No dissolution	
	PHS-co-PS -co-PtBA	No dissolution	No dissolution	
	PMAMA-co-PGBLMA	No dissolution	No dissolution	
	TOK resist	Dissolution (45 nm/min)	Slow dissolution (<1 nm/min)	*Negative tone resist*

[a] The choice of counter anion is crucial to the QAS design. The basic nature and size of the counter anion is important. **QAS-4** with acetate anion helped dissolve polar protected polymers.

Computational Simulation. A number of polymers were simulated as thin films and exposed to various QAS additives in concert with this experimental work to provide a molecular level view of the systems and help elucidate the underlying mechanism at work. In that work, a fully atomistic model of the PHS-*co*-PS-*co*-PtBA and the PBOCST photoresists was adapted from the OPLS force field. In addition, we further optimized the model by calculating local charges for each species using quantum mechanical calculations with the Gaussian simulation package. The model of Harris and Yung was used for the $scCO_2$.[40] Thin films of each polymer were equilibrated and simulated in GROMACS. Each polymer was first equilibrated in the bulk and then exposed to $scCO_2$ to form a thin film. This film was further equilibrated at a constant density of 817 kg/m^3 (Figure 4). After equilibration, production runs were performed in the NVT ensemble at 340 K for 2 ns. Forces on each atom were recorded during the simulations. As a result of the high fluctuations on force during the course of a simulation, exact values at given positions were not statistically meaningful. However, by integrating the average force of each chain as a function of its position in the film, free energy curves for the removal of a polymer chain from the film in the presence of different QAS additives were obtained. The uncertainty in the energy at the surface of the film is less than 4 kT for all values shown. For further details on the molecular simulations, we refer the reader to another article.[41]

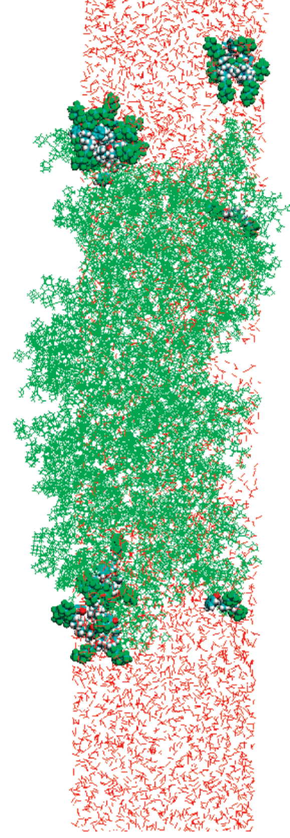

Figure 4. Example of equilibrated polymer film: PMAMA-*co*-PGBLMA with **QAS-10** in $scCO_2$. Box has periodic boundaries. Red lines are $scCO_2$, green lines are PMAMA-*co*-PGBLMA, and spheres are **QAS-10**.

Proposed Mechanism of Dissolution of Polymers in $scCO_2$. Here we discuss the interactions that the QAS have with the functional groups on the polymer to help them dissolve in $scCO_2$. As both **QAS-4** and **QAS-7** showed good solubility in $scCO_2$ but showed opposite effects on the dissolution of the reference polymers, we use these salts to explain the interactions involved in the dissolution process. It is known that standard polar photoresist polymers are generally insoluble in nonpolar $scCO_2$ solvent. We examined the solubility of acidic and protected polar polymers in the presence of additives and observed that the protected polymer is more soluble in $scCO_2$ than the acidic, deprotected polymer. The interactions between the QAS and the polymers depend on the ion pair energy, the shape and size, and the mobility of the ions.

(40) Harris, J. G.; Yung, K. H. *J. Phys. Chem.* **1995**, *99*(31), 12021.
(41) Rastogi, A; Toepperwein, G. N.; Tanaka, M.; Riggleman, R.A.; de Pablo, J. J.; Ober, C. K. *Proceedings of SPIE* **2009**, Volume *7273*, 72734F.

Protected PBOCST showed very good solubility in $scCO_2$ in the presence of most of QAS because the electronegative oxygen atom in the carbonate group can easily interact with the electro-positive ammonium center of QAS to provide a CO_2-friendly environment. This allows the fluorinated $scCO_2$ soluble salt to pull the polymer into the $scCO_2$. Simulation of PBOCST also predicted dissolution in **QAS-4** and **QAS-7**. We found that as polymer chains dissolved into the $scCO_2$ phase from the film, each chain formed its own spherical globule with the *tert*-butyl tails of each monomer creating a nonpolar outer shell for the chain. The QAS molecules bind to the surface of the polymer film but have limited interactions with the dissolved species. However, such micelles do not freely form in the absence of QAS, indicating that the QAS interactions stabilize the formation of these micelles by an unknown mechanism. E-beam exposure of the PBOCST polymer in the presence of an onium acid generator causes the deprotection of the acid labile *tert*-butoxycarbonyl groups to phenolic acid. Removal of the acid cleavable *t*-BOC group greatly increases polymer–polymer dipole interactions by the resulting hydroxy groups. This lowers the interaction with the QAS additive, and the solubility in $scCO_2$ sharply decreases.

In the case of the unexposed PHS-*co*-PS-*co*-PtBA polymer, oxygen atoms in the hydroxyl group and carbonyl group can undergo electrostatic interaction with ammonium cations. **QAS-7**/$scCO_2$ solution did not dissolve the PHS-*co*-PS-*co*-PtBA polymer in contrast to **QAS-4**/$scCO_2$ solution. This result is attributed 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. Therefore the anion in **QAS-7** is weak enough to deprotonate the hydroxyl groups and has weak electrostatic interaction with the electropositive carbon atom of the carbonyl group in the polymer. Simulations of this polymer provided results consistent with the experiments suggesting dissolution in the presence of **QAS-4** but not with **QAS-7** (Figure 5). While resist at any given position may tend more toward dissolution or stability, it is only the energy value at the surface of the film, denoted by the termination of the line, as compared to the center that determines thermodynamic stability. Note that values reported at a higher distance from the center are averaged over more data and are thus more accurate. Our molecular simulations show that the carbonyl group of PHS-*co*-PS-*co*-PtBA plays a much smaller role than the hydroxyl group. Contact analysis confirms that charged **QAS-4** anions bind strongly to the hydroxyl groups and that multiple hydroxyl groups coalesce around a single **QAS-4**. These structures are stable on time scales exceeding 500 ps.[41] Additionally, the **QAS-4** salt ions dissociate as additive penetrates into the polymer phase. **QAS-7** has a weaker interaction with this polymer on the film surface, and a substantial fraction of the additive remains in the $scCO_2$ phase. Thus, it is unable to shield the hydroxyl groups of PHS-*co*-PS-*co*-PtBA from the nonpolar $scCO_2$, causing the polymer to be insoluble in the solvent. This polymer has *tert*-butyl protecting groups, which are cleaved on deprotection. This deprotection reaction results in a more polar deprotected polymer bearing carboxylic acids and phenols that does not dissolve in $scCO_2$.

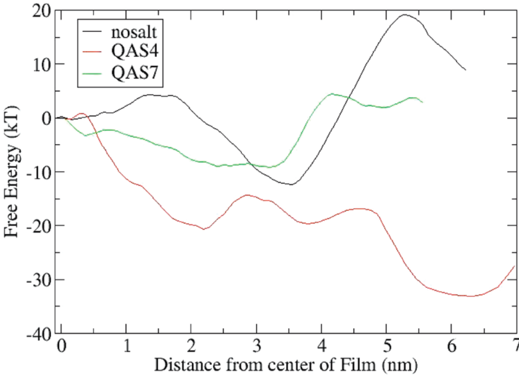

Figure 5. Free energy curves for $scCO_2$ system. Solid black, red, and green lines represent the PHS-*co*-PS-*co*-PtBA systems without an additive, with **QAS-4** and with **QAS-7** respectively. Results averaged over 1.0 ns. The free energy for the **QAS-4** system is lower at the interface of the film (end of the line) than at the center of the film, indicating a net driving force for polymer dissolution. The other lines show an opposite trend, indicating that the polymer remains insoluble in $scCO_2$.

QAS-4 turned out to be the best salt for our work. This superior performance is because the ion pair energy of **QAS-4** is such that the ammonium cation can interact with the oxygen atoms of the resist material. Its acetate anion is strong enough to deprotonate the Brønsted acid groups. On the basis of the idea, **QAS-10** bearing phenolate anion was prepared as a new QAS bearing more basic anion. However, **QAS-10** allowed only PBOCST to dissolve in $scCO_2$ similar to the results of **QAS-7**. It is conceivable that the stronger ion pair prevented **QAS-10** from having any favorable interactions with the polymer. We believe that a balance between the ion pair energy of the QAS and the basicity of the counteranion is important for the QAS to help dissolve the polymer. The protected PMAMA-*co*-PGBLMA polymer, which bears many ester groups and no carboxylic/phenol groups, was expected to dissolve in $scCO_2$ by using QAS. However, PMAMA-*co*-PGBLMA was fully insoluble in any QAS/$scCO_2$ solutions. Insolubility can be explained on the basis of steric effects. It is speculated that the bulky methyl adamantyl groups inhibit the polymer resist from interacting with the QAS. Simulation of PMAMA-*co*-PGBLMA in the presence of **QAS-10** also showed no solubility enhancement of the polymer. The QAS anion was bound immobile to the surface of the cation for the duration of the simulation. This is in contrast to other systems, whose QAS ions maintained some relative mobility, if not dissociating completely.

$scCO_2$ Development of an e-Beam Patterned Commercial Resist. On the basis of our findings, we used a TOK polymer photoresist to evaluate the lithographic performance of this standard commercial polymer using an appropriate $scCO_2$ compatible QAS additive in $scCO_2$. This polymer works as a positive-tone photoresist in

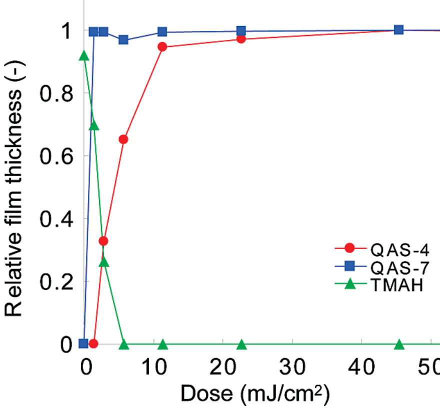

Figure 6. Contrast curves of the commercial TOK photoresist developed in $scCO_2$ with **QAS-4** or **QAS-7** (1.25 mM) at 50 °C, 5000 psi for 15 min, or developed in tetramethylammonium hydroxide (TMAH) aqueous solution (0.24 N) at room temperature for 30 s.

conventional aqueous base processing and is insoluble in $scCO_2$ without the use of the additive. Similar to the previously mentioned acidic polymers, the protected TOK polymer was processed in $scCO_2$ using the QAS additives. The protected polymer showed complete dissolution in $scCO_2$ with either **QAS-4** or **QAS-7**. The dissolution rate monitor studies with the protected polymer film gave sine wave response, indicating a constant dissolution rate of 15 nm/min. Most of the other salts had no effect on the polymer. It is worth mentioning that the polymer swelled in the **QAS-10**/$scCO_2$ solution. This result has encouraged us to design QAS additives with substituted phenolate counteranions to be used as dissolution aids for such commercial polymers. The deprotected TOK polymer film showed very slow dissolution at 1 nm/min, which is much slower than the corresponding protected polymer. The contrast curves of the TOK resist were studied with development in both **QAS-4**/$scCO_2$ and 0.26 N tetramethylammonium hydroxide solutions. The dissolution test of the TOK resist in $scCO_2$ in the presence of **QAS-7** revealed a similar negative tone behavior (Figure 6).

New lithographic technologies and materials are being developed to meet the growing demand for higher resolution. Electron-beam lithography enables the fabrication of nanometer-scale patterns as small as 20 nm. The primary advantage of e-beam lithography over photolithography is that it is one of the ways to beat the diffraction limit of light. Here we demonstrate the results of an e-beam patterned resist developed in QAS/$scCO_2$. Figure 7 a is a SEM image of a TOK resist film (90 nm thick) that was patterned by e-beam lithography with an exposure dose of 107 $\mu C/cm^2$ and developed in the 1.25 mM **QAS-4**/$scCO_2$ solution for 60 min at 50 °C and 5000 psi. In the same way, the **QAS-7**/$scCO_2$ development also gave negative-tone patterns with feature sizes down to 100 nm (Figure 7b).

Conclusion

A series of QAS were synthesized and examined as additives for $scCO_2$ to dissolve polar polymers in $scCO_2$. The chemical structures of QAS influence their solubility

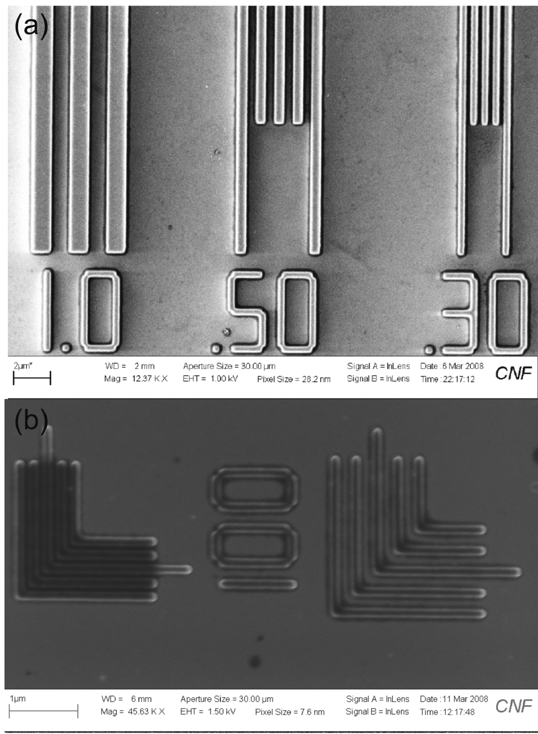

Figure 7. SEM images of the e-beam patterned commercial TOK polymer photoresist (a) exposed with 107 $\mu C/cm^2$ and developed in 1.25 mM **QAS-4**/$scCO_2$ solution for 60 min at 50 °C and 5000 psi and (b) exposed with 20 $\mu C/cm^2$ and developed in 1.25 mM **QAS-7**/$scCO_2$ solution for 60 min at 50 °C and 5000 psi.

in $scCO_2$. QAS with higher fluorination, less sterically hindered anion, and asymmetric structure of cation showed higher solubility. Such QAS proved to be very effective for dissolution of polar polymers in $scCO_2$. Addition of the $scCO_2$ compatible QAS greatly helped in the dissolution of polymers, especially PBOCST, PHS-*co*-PS-*co*-PtBA, and a commercially used photoresist, under moderate conditions (50 °C and 5000 psi). Solubility of the polymers in $scCO_2$ was examined at various combinations of polymer and QAS additive by using a dissolution rate monitor to observe the change in film thickness during dissolution. The key interactions between the additive and the photoresist material were discussed by comparing the experimental results and computational simulations. Understanding these interactions is important and will help in designing more efficient additives for polymer dissolution. Finally, on the basis of these studies the lithographic performance of a polymer photoresist in $scCO_2$ development using an appropriate QAS was shown. As $scCO_2$ development has various advantages in terms of environmental and lithographic benefits, the success of photoresist development in $scCO_2$ using QAS additives is a significant result in the advancement of this environmentally friendly process.

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Supporting Information Available: Characterization data for **QAS-1**, **QAS-2**, **QAS-5**, **QAS-6**, **QAS-8**, and **QAS-10** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.