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Supercritical CO_2 Processing for Submicron Imaging of Fluoropolymers

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To keep pace with the ever-shrinking feature sizes required in the microelectronics industry, suitable developers with high diffusivities, selectivity, and adjustable solvating power are required. Supercritical fluid (SCF) CO_2 possesses many of the above unique properties and could serve as an “environmentally responsible” alternative developer to aqueous base. In this study, the high solubility of fluorinated block copolymers in supercritical CO_2 and the selectivity of supercritical CO_2 to both polarity changes and the molecular structure of the polymer were utilized to develop an environmentally friendly lithographic process. Polymers with acid-cleavable tetrahydropyranyl groups and supercritical CO_2 soluble, fluoro-side-chain-containing methacrylate groups were synthesized with varying volume fractions of the components, and their solubilities in supercritical CO_2 were characterized. Chemical amplification was used to effect the polarity change leading to the solubility difference in supercritical CO_2, and the lithographic performance was evaluated. Important parameters such as sensitivity, contrast, and resolution were investigated, and 0.2 μm features using supercritical CO_2 development were demonstrated.

Introduction

Supercritical fluid (SCF) technology has been gaining considerable attention over the last two decades in the area of polymer synthesis and processing.[1] This has been due to the unique properties of supercritical fluids, such as their high diffusivities comparable to those of gases, their liquid-like densities, and also the ability to control their densities and hence their solvating powers by the simple manipulation of pressure and temperature conditions. SCF technology has been widely applied in the food and pharmaceutical industries to use in such techniques as supercritical fluid chromatography and extraction of toxic compounds from wastewater.

Carbon dioxide is rapidly becoming a very attractive candidate among the supercritical fluids for replacing traditional liquid organic solvents in various applications such as coatings, separations, polymerization, and antisolvents. Though SCF CO_2 has been found to be a very good solvent for small molecules, it acts as an extremely poor solvent for polymers. Very few classes of polymers have appreciable solubility in SCF CO_2 at the conditions $T < 100$ °C and $P < 5000$ psi.[2] In terms of their solubility in CO_2, polymers have been classified as CO_2-philic and CO_2-phobic. While conventional hydrophilic or lipophilic polymers are relatively insoluble in CO_2, fluoropolymers and silicon-containing polymers fall into the CO_2-philic category. For some time, fluorocopolymers have been known to be soluble in SCF CO_2, and in fact, a variety of acrylic and styrene fluoropolymers have been synthesized in SCF CO_2 using homogeneous free radical polymerization. Statistical copolymers containing up to 50 mol % of the hydrocarbon moiety with a second fluoropolymer component have been found to be soluble in SCF CO_2.[3,4]

The mechanism of solubility of polymers in SCF CO_2 has been the subject of much research in recent years. Some of the factors which have been identified as important parameters are the specific solute−solvent interactions between the polymers and CO_2, solute−

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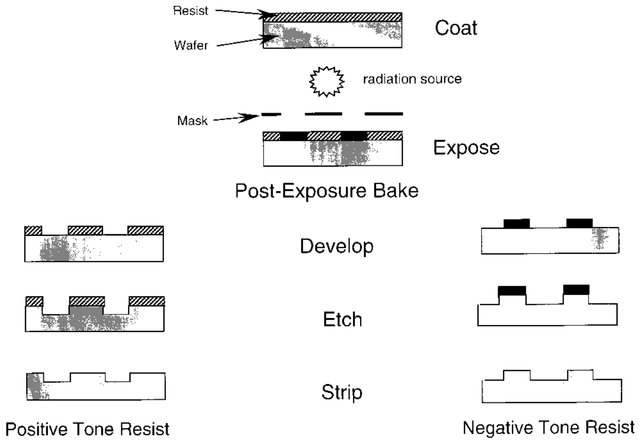

Figure 1. Scheme of the lithographic process showing both positive- and negative-tone imaging.

solute interactions, van der Waals interactions, Lewis acid−base interactions, the free volume and cohesive energy density of the polymer, and so forth.[5−14] It has been found that the solubility of a polymer in SCF CO_2 has a marked dependency on the structure of the polymer, including both the backbone and the side chain. Hence, manipulation of the polymer solubility in SCF CO_2 is indeed possible by careful tailoring of the molecular structure. Solubility switching phenomena obtained by controlling the molecular structure of a polymer has been utilized for over two decades in the electronics industry, in the lithographic process used to pattern integrated circuits.[15]

The lithography process is shown schematically in Figure 1. In this process, a polymeric material is spun onto a substrate such as a silicon wafer to form a uniform coating. Then, the polymer is exposed to a source of photons, electrons, or X-rays through a mask which has the pattern information to be transferred. The mask allows the radiation to pass through previously defined areas. The polymer exposed to the radiation undergoes a chemical change (cross-linking, chain-scission, or polarity change). The next step is the use of a solvent to selectively remove the exposed or the unexposed regions to successfully transfer the pattern onto the polymer layer. The polymer is called a positive-tone resist if the exposed regions become more soluble in the solvent and a negative-tone resist if the opposite is true. It is very important that the solvent used for the image transfer has the ability to distinguish between very small areas of chemical differences in the polymer structure.

Supercritical fluid CO_2 could thus be envisioned as an "environmentally responsible" solvent for solvent-intensive processes in lithography such as the spin-coating and development steps, wherein a polymer soluble in liquid CO_2 could be coated directly using liquid CO_2,[16] exposed, and then developed using supercritical/liquid CO_2. The initial experiments using SCF CO_2 as a solvent for microelectronics applications were conducted by Taylor et al.[17] They extracted unreacted siloxane compounds from an organic polymer matrix. From their work, a window of processing conditions for achieving 0.75-μm resolution for an X-ray-exposed lithography system was defined.

Allen et al.[18] used the selectivity of SCF CO_2 based on molecular weight differences to study the effect of molecular weight on the glass transition and the dissolution rate of novolac resin and thereby on the lithographic performance. In addition to their selectivity based on molecular weight differences, SCF CO_2 is also very sensitive to changes in the polarity of the polymer. Researchers at IBM and Phasex Corporation have used this concept in designing novel photoresists.[19−21] They accomplished the polarity switch needed for the solubility change in SCF CO_2 using the chemical amplification mechanism and demonstrated the solubility difference between the exposed and the unexposed regions of the polymeric photoresist film. A variety of fluoro- and silicon-containing polymers were tested in both positive- and negative-tone resist schemes where the film becomes more soluble in SCF CO_2 after exposure and vice-versa. Recently, our research group demonstrated the good contrast and excellent sensitivity of silicon-containing block copolymers as SCF CO_2 developable photoresists.[22] Other applications of SCF CO_2 in the area of microelectronics include surface cleaning and removal of the solvent remaining after processing and development. SCF CO_2 drying was found to be very effective in the case of high aspect ratio features due to the very low surface tension of supercritical fluids.

In this study, we utilized the high solubility of fluorinated block copolymers in SCF CO_2 and the selectivity of this solvent to polarity changes and the molecular structure of a polymer to develop an environmentally friendly lithographic process. Polymers with acid-cleavable tetrahydropyranyl groups and SCF CO_2 soluble perfluorinated methacrylate segments were synthesized with varying volume fractions of the components, and their solubilities in SCF CO_2 were characterized. Chemical amplification was used to effect the polarity change leading to the solubility difference in

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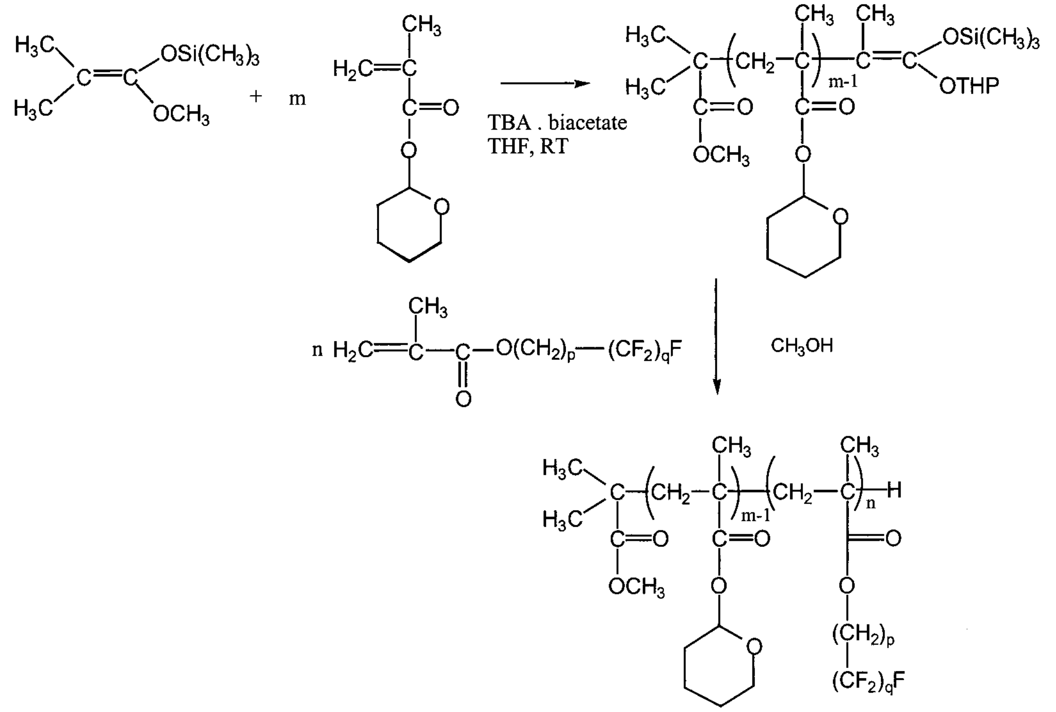

Figure 2. General scheme for synthesis of copolymers of tetrahydropyranyl methacrylate and fluorinated methacrylate using group-transfer polymerization.

SCF CO_2, and the lithographic performance of these new fluoropolymers was evaluated. Important parameters such as sensitivity, contrast, and resolution were investigated, and 0.2 μm features using SCF CO_2 development were demonstrated.

Experimental Section

Materials. Tetrahydrofuran (THF) (Aldrich) was freshly distilled from sodium/benzophenone under nitrogen before polymerization. The initiator methyl trimethylsilyl dimethylketene acetal {[(1-methoxy-2-methyl-1-propenyl)oxy]trimethylsilane, MTMS} (Aldrich) was distilled and stored under nitrogen. 2-Tetrahydropyranyl methacrylate (THPMA) was synthesized as described in the literature.[23] The commercially available monomers 1H,1H-perfluoro-*n*-butyl methacrylate (F3MA, Lancaster) and 1H,1H-perfluorooctyl methacrylate (F7MA, Lancaster) were first purified by stirring with CaH_2 for 24−48 h, followed by vacuum-distillation into a cold trap. The monomer was transferred to a monomer reservoir under nitrogen and stored at −20 °C. The catalyst tetrabutylammonium (TBA) biacetate was prepared as described in the literature[24] and was dissolved in freshly distilled THF to give a 0.04 M solution. A small amount of water (6 molar equiv) was added to facilitate dissolution.

Synthesis of Copolymers of Tetrahydropyranyl Methacrylate (THPMA) and Fluorinated Methacrylates. A detailed description of the synthetic procedures used is published in a separate paper.[25] A general reaction scheme for the synthesis of block copolymers of tetrahydropyranyl (THP) methacrylate and fluorinated methacrylates is shown in Figure 2. In this procedure, THPMA was always polymerized first. Methanol or hexane was used as a precipitation solvent.

A. Synthesis of Block Copolymers of THPMA and 1H,1H-Perfluorobutyl Methacrylate (F3MA): A typical example for the synthesis of THPMA-*b*−F3MA (F3-4) block copolymers is described below: After 8 mL of THF was distilled into the reactor, 67 μL (0.33 mmol) of MTDA and 8.3 μL (0.34×10^{-3} mmol) of TBA biacetate solution were added. After 5 min, 1.35 mL (8.32 mmol) of THPMA was added over a period of approximately 3 min. The temperature of the solution rose from 22.5 to 40.0 °C. With 30 min of stirring, the temperature was cooled back to room temperature. After the mixture was stirred for an additional 30 min, 1.35 mL (7.05 mmol) of F3MA was added all at once. The temperature did not change over approximately 2 min and then suddenly increased and reached a maximum of approximately 41.0 °C in 1 min. A milky solution was observed in the initial 2 or 3 s during the temperature rise. The reaction was quenched with approximately 1 mL of methanol and poured into 200 mL of methanol after stirring for 2 h. After filtration and washing with hexane, the polymer was air-dried at room temperature and then dried 12 h in a vacuum oven at room temperature. Block copolymer was obtained with a yield of 2.7 g (~82%). Table 1 shows the characteristics of THPMA-*b*-F3MA.

Table 1. Characteristics of THPMA-*b*-F3MA Block Copolymers

	THPMA/F3MA (% v/v)		molecular weight[a]			
sample	in feed	in polymer	$M_n/10^3$	$M_w/10^3$	polydispersity M_w/M_n	yield (%)
F3-1	75/25	89/11	8.52	8.88	1.04	79
F3-2	75/25	78/22	7.26	8.18	1.13	99
F3-3	65/35	68/32	7.43	7.93	1.09	93
F3-4	50/50	62/38	6.1	6.89	1.13	56
F3-5	50/50	54/46	5.51	6.94	1.26	89
F3-6	50/50	49/51	7.89	8.96	1.14	82
F3-7	50/50	47/53	6.55	7.27	1.11	93
F3-8	33/67	44/56	4.19	4.82	1.15	62
F3-9	33/67	38/62	5.9	6.9	1.17	74
F3-10	20/80	29/71	5.43	6.08	1.12	72

[a] Measured with GPC using refractive index detector, and PMMA as calibration standard.

B. Synthesis of Block Copolymers of THPMA and 1H,1H-Perfluorooctyl Methacrylate (F7MA). A typical procedure for the synthesis of THPMA-*b*−F7MA (50:50 vol %) is given below: After 10 mL of THF was distilled into a reactor, 56 μL (9.34 mmol) of MTDA and 10.4 μL of TBA biacetate solution

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Table 2. Characteristics of THPMA-*b*-F7MA Block Copolymers

	THPMA/F3MA (% v/v)		molecular weight[a]			
sample	in feed	in polymer	$M_n/10^3$	$M_w/10^3$	polydispersity M_w/M_n	yield (%)
F7-1	75/25	78/23	8.47	9.4	1.11	89
F7-2		50/50	8.85	9.5	1.07	
F7-3	50/50	46/54	10.1	11.11	1.1	89
F7-4	33/66	45/55	5.2	5.67	1.09	71
F7-5	40/60	37/63	8.2	8.77	1.07	92
F7-6		34/66	8.95	9.54	1.07	
F7-7	33/66	32/68	6.61	7.14	1.08	85
F7-8	27/73	23/77	7.7	8.32	1.08	92

[a] Measured with GPC using refractive index detector, and PMMA as calibration standard.

were added. After 5 min, 1.5 mL (9.34 mmol) of THPMA was added over 3 min. The temperature rose from 22.5 to 38.6 °C. With 30 min of stirring, the temperature was cooled back to room temperature. After the mixture was stirred for an additional 30 min, 1.5 mL (4.49 mmol) of predistilled F7MA was added to the living poly-THPMA solution. The temperature of the solution increased up to 28 °C within 1 min, and the solution was left stirring for another 2 h. The color of the solution changed to light blue and with time to pale yellow. The viscosity of the solution also seemed to change during the polymerization. The mixture was stirred for another 5 h, and the polymer was then precipitated into 250 mL of methanol. The solid polymer was filtered after 2 h of stirring and dried under vacuum at room-temperature overnight. Table 2 shows the characteristics of THPMA-*b*-F7MA copolymers.

C. Synthesis of a Random Copolymer of THPMA and 1H,1H-Perfluorooctyl Methacrylate (F7MA). The procedure used was the same as that for the synthesis of block copolymers. However, both monomers were added simultaneously into the reaction chamber using two different syringes. Polymerization was continued for 6 h, and a milky solution was obtained, possibly due to the low solubility of the polymer in THF.

Characterization. The number average molecular weights (M_ns) and polydispersities of the copolymers were determined by GPC (THF) using PMMA as the standard, a Waters Associates 510 Pump, a 410 refractive index detector, and 4.6 mm × 300 mm Styragel HT3, HT4, HT5, and HT6E columns. The copolymer compositions were verified by ^{1}H NMR studies carried out on a Varian 200 spectrometer using either $CDCl_3$ or deuterated $THF/CFCl_3$ as solvent. Compositions are reported in volume fractions rather than mole fractions, since these values are useful in predicting the microstructure of block copolymers. However, these values are estimates based on the experimentally measured density of the homopolymers (ρ_{THPMA}, 1.06; ρ_{F3MA}, 1.4; ρ_{F7MA}, 1.495; ρ_{HF4MA}, 1.28). The glass transition temperatures of the copolymers were measured using differential scanning calorimetry (DSC) measurement on a Perkin-Elmer DSC-7 Series instrument at a 10 °C/min heating rate under nitrogen.

Lithographic Processing. Polymer solutions for spin-casting were prepared by dissolving 15−20 wt % of polymer in propylene glycol methyl ether acetate (PGMEA). Photoacid generators (PAGs) were added as needed. Photoacid generators of different polarities were used with different polymeric matrixes. Typical PAG concentrations in the polymer matrixes were 1−2 wt % of the polymer concentration in the solution. The solutions were then filtered using 0.2 or 0.45 μm PTFE filters. The polymer solutions were manually dispensed using an Eppendorf pipet. Approximately 2 mL of solution was needed to form a uniform film for each 8 in. silicon wafer. The silicon wafers were pretreated by one of two procedures: (1) vapor-priming with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) at 120 °C for 25 s or (2) coating with Brewer Science DUV 18L antireflective coating and then baking at 120 °C for 25 s. Silicon wafers with the solution were then spun at appropriate speeds to obtain thin films of thickness ranging from 0.2 to 0.4 μm. The approximate range of speeds used was 1000−2000 rpm depending on the viscosity of the solutions. The samples were then baked at 120−150 °C for 60 s.

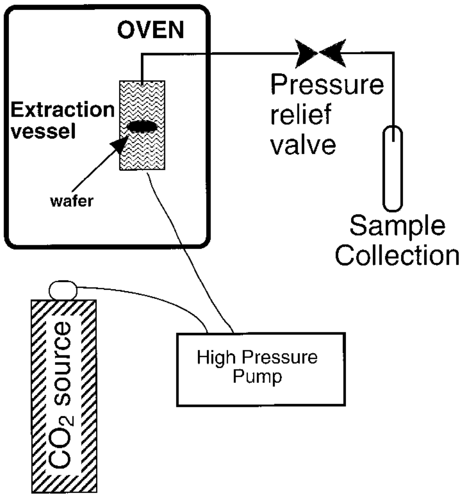

Figure 3. Schematic of the supercritical CO_2 development apparatus.

Resist processing was done either at the Class 1 cleanroom facility at SEMATECH, Austin, TX, or at the experimental cleanroom facility at IBM Almaden Research Center, San Jose, CA. Reported exposures were made using a 193 nm ArF excimer laser source (SEMATECH, IBM Almaden). Both the 193-nm stepper at SEMATECH and that at IBM Almaden had a lens of variable numerical aperture (NA) of 0.6, a field size diameter of 1.5 mm × 1.5 mm, and a partial coherence of 0.7. Exposure dose matrixes were used to determine the sensitivities of the various photoresists. Typical dose matrixes ranged from 1 to 60 mJ/cm^2 in steps of 1 mJ/cm^2, although different ranges and steps were used depending on the photoresist. The postexposure bake was done at 120 or 90 °C for 60 s. Development of the photoresists was carried out in the in-house SCF CO_2 resist-processing facility.

The polymer film thickness after the postapply bake was determined using a Prometrix SM-200 film thickness probe. The Prometrix measures the film thickness using constant angle reflection interference spectroscopy (CARIS). It was assumed that the variation of the index of refraction with wavelength for some of the block copolymers was comparable to that for the corresponding homopolymer or random copolymer methacrylates of similar composition. The thickness of each of the films was averaged over 49 measurements covering the entire wafer. The films were very uniform with standard deviation <1% of the thickness of the film. The film thicknesses were confirmed by profilometry [the thickness of the film was measured before and after development using a Sloan Dektak II Profilometer by dragging the tip over a scratch in the film] and were comparable with the Prometrix measurements within 10 nm. The film thicknesses after development in SCF CO_2 were measured using a surface-profiling measurement system.

Supercritical Fluid CO_2 Development. The supercritical CO_2 development was carried out using a setup shown schematically in Figure 3. The exposed wafers were cleaved into squares of dimensions <2.3 cm in order to fit inside the extraction vessel. The diced wafers were covered with cleanroom tissue paper and placed inside the extraction vessel. The extraction vessel had an inner diameter of 2.54 cm, a length of 9 cm, and an internal volume of 50 mL. The extraction vessel was double-ended, meaning there were two bolt−washer sets on either end to help withstand higher pressures. Carbon dioxide (SCF grade with a helium head pressure of 1500 psi, 99.99% pure) was passed through the extraction vessel at temperatures ranging from 30 to 70 °C and pressures ranging from 2800 to 6500 psi at a flow rate of ~2−4 L/min. As the gas passes through the extraction vessel with the exposed

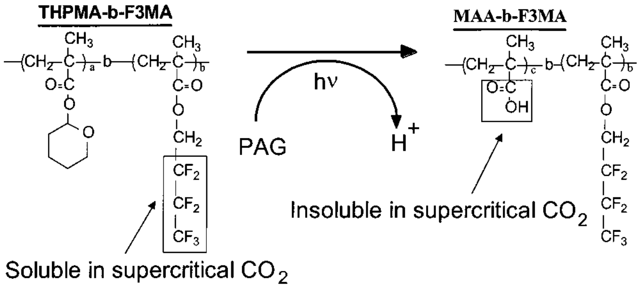

Figure 4. Imaging process of the negative-tone supercritical CO_2 developable resists used in this study.

wafer in it, it dissolves the polymer that is soluble under the particular conditions of operation. After leaving the extraction chamber, the gas flows through a pressure reduction valve that is normally maintained at a slightly higher temperature than the vessel to prevent clogging of the valve by condensation as the gas expands. The previously dissolved polymer precipitates out into a collection vessel. All the development was performed in a dynamic fashion; that is, there was a continuous flow of CO_2 throughout the development time. After the vessel was cooled and the carbon dioxide was vented, the samples were removed and examined using either a Leo or an AMRAY scanning electron microscope.

Table 3. Optimization of Dissolution Conditions for THPMA-*b*-F3MA Block Copolymers

temp (°C)	pressure (psi)	time (min)	percentage dissolution (%)[a]
	49/51 vol % (F3-6)		
60	2800	30	16
80	4000	30	22
100	6500	30	100
60	6500	30	100
50	5500	30	100
50	5000	30	100
45	4500	30	100
45	4500	15	100
45	4500	5	100
45	4500	2	100
	68/32 vol % (F3-3)		
45	4500	5	small
45	5000	15	7
60	6000	15	43
60	6500	20	47
80	6500	30	50
	78/22 vol % (F3-2)		
45	4500	5	small
45	5000	15	small
60	6000	15	10
60	6500	20	13
80	6500	30	16

[a] Calculated from the ratio of the thickness loss after development.

Results and Discussion

Fluoropolymers have been found to be highly soluble in SCF CO_2 under very mild conditions.[2,3,13,14] In this work, we utilized fluoro-containing groups as supercritical CO_2 solubilizers in designing photoresists developable by CO_2. The very nonpolar fluoromethacrylates, which are soluble in supercritical CO_2, were chosen for copolymerization with the acid-cleavable THPMA so that the classical chemically amplified polarity change in the presence of a proton could be utilized. After exposure to radiation, the THPMA block converts to a more polar methacrylic acid, which is insoluble in supercritical CO_2, giving rise to a solubility change. The imaging mechanism of these polymers is shown in Figure 4. Block copolymers of different ratios of the two components for both F3MA and F7MA (Tables 1 and 2) were synthesized as described in the Experimental Section.

Before these fluorinated polymers were used as photoresists, the effect of the molecular structure on the solubility and development characteristics needed to be investigated and optimized. These studies were performed using an in-house SC CO_2 processing facility described in the Experimental Section. The conditions at which the polymer dissolves in SC CO_2 are important criteria for the feasibility of the materials used. The optimization of dissolution conditions is important for the following reasons: (i) to avoid operating at unnecessarily high temperature, pressure, or time; (ii) to prevent blistering or swelling of the film after an exposure-induced solubility change; (iii) to obtain better contrast between the exposed and unexposed regions. There are various important parameters in a supercritical fluid development process. Some of them are the pressure and temperature of extraction or development, the time for development, and the flow rate of CO_2 through the development or extraction chamber. Various pressure, temperature, and time conditions were studied to find the most practical processing condition for the polymers. Upon optimization, the wafer was processed under the desired pressure and temperature conditions of carbon dioxide for a fixed time.

The most practical processing condition was fixed as the condition with the minimum balance of pressure, temperature, and time that completely dissolved the entire resist film from the silicon wafer. A variety of conditions from mild (2800 psi, 40 °C) to aggressive (7000 psi, 80 °C) were investigated.

The processing conditions of a particular polymer were determined as follows: the most severe conditions were studied at first, and then, if the polymer was found to be soluble, the pressure and temperature were progressively reduced until the mildest conditions at which the entire polymer film dissolved were reached. Then, the time of extraction or development was optimized to the shortest time possible. A typical list of processing conditions investigated for THPMA-*b*-F3MA polymers is given in Table 3.

One of the important parameters governing solubility in supercritical CO_2 of our photoresist fluoropolymers at modest conditions is the volume ratio of the THPMA versus the fluorinated methacrylate. In the case of copolymers of THPMA and either F3MA or F7MA, the competing interactions affecting solubility are the segment−segment interactions and the THPMA−solvent and perfluoromethacrylate−solvent interactions. Polar interactions are more pronounced at low temperatures and have a significant effect on the solubility of the polymer in supercritical CO_2.[27] It has been suggested that CO_2 may complex with the fluorine of the C−F bonds instead of the less polar C−H bonds,[11,12] and also, the high solubility of fluorinated acrylates in CO_2 has been attributed to their large free volumes and small cohesive energy densities.[14] As the F_nMA block increases

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Table 4. Dissolution Conditions for THPMA-*b*-F3MA Block Copolymers

polymer	volume fraction of fluorocomponent (%)	pressure (psi)	temp (°C)
F3-2	22	insoluble at conditions tested[a]	
F3-3	32	insoluble at conditions tested[a]	
F3-5	46	insoluble at conditions tested[a]	
F3-6	51	4500	45
F3-8	56	6500	65
F3-9	62	2800	45

[a] Conditions tested: 2800 psi, 40 °C, to 7000 psi, 80 °C.

Table 5. Dissolution Conditions for THPMA−F7MA Block Copolymers

polymer	volume fraction of fluorocomponent (%)	pressure (psi)	temp (°C)
F7-1	23	insoluble at conditions tested[a]	
F7-2	50	insoluble at conditions tested[a]	
F7-3	54	6500	75
F7-4	55	6500	65
F7-6	66	4000	40
random copolymer	66	insoluble at conditions tested[a]	

[a] Conditions tested: 2800 psi, 40 °C, to 7000 psi, 80 °C.

in length, the specific interactions between CO_2 and the fluorine increase, thereby rendering it soluble in supercritical CO_2. As the THPMA block length increases or the F_nMA block length decreases, the polar polymer segment−segment interactions dominate due to the polar nature of tetrahydropyranyl groups, thereby making the polymer insoluble in supercritical CO_2. Thus, a series of block copolymers were synthesized to investigate the ratio of the two blocks at which the polymer segment−segment interactions dominate over the specific interactions between the fluorinated side chain and CO_2 and the free volume effects such that the polymer becomes insoluble in CO_2. It is very well-known that 100% poly(1,1-dihydroperfluorooctyl acrylate) is soluble in CO_2 under very mild conditions,[14] so the volume fraction of the fluorinated methacrylate component was progressively reduced to investigate the limits at which the polymer becomes insoluble in supercritical CO_2.

Tables 4 and 5 describe the dissolution conditions for copolymers of both THPMA-*b*-F3MA and THPMA-*b*-F7MA with different block ratios, respectively, which were tested for their solubility in supercritical CO_2. From Table 4, it is seen that the THPMA-*b*-F3MA polymers become insoluble in supercritical CO_2 if they have <51 vol % of the fluorinated methacrylate moiety incorporated into the polymer. From Table 5, it can be seen that the THPMA-*b*-F7MA block copolymers become insoluble if the fluorinated methacrylate moiety volume fraction is <54%. It is also interesting to note that the random copolymer of THPMA−F7MA (34/66 vol %) did not dissolve even at 6000 psi and 60 °C while the corresponding block copolymer with the same volume fraction dissolved at much lower pressure and temperature conditions. This increased solubility of the block copolymer over the corresponding random copolymer has been observed previously in our research group[22] and is possibly due to the formation of micelles with a THPMA block in the core and the fluorinated block forming the corona of the micelle. In fact, micelle formation has been observed in block copolymers of similar structure such as poly(styrene-*b*-poly(1,1-dihydroperfluorooctylacrylate)) (PS−PFOA) in supercritical CO_2 using small-angle neutron and X-ray scattering.[28]

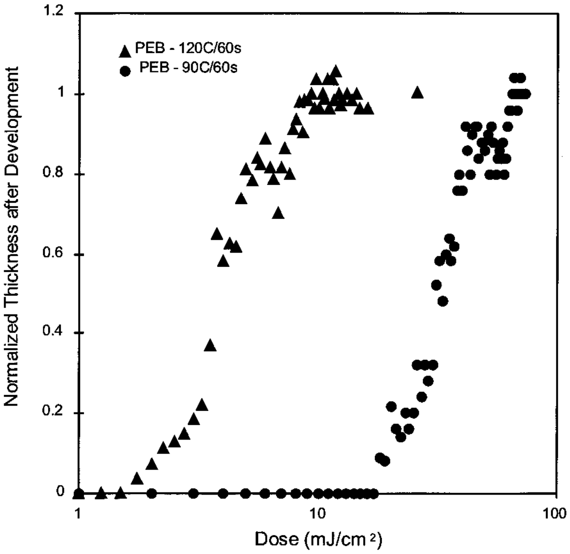

Figure 5. Sensitivity curve for a block copolymer of THPMA−F3MA (49/51 vol %) patterned with 193 nm radiation using the iodonium PAG and two different thermal cycles.

The solubility change in supercritical CO_2 was achieved by formulating the block copolymers of THPMA and F_nMA with small amounts (∼1 wt %) of photoacid generator before spinning and exposure. The imaging mechanism of these polymers is shown in Figure 4. During exposure, the photoacid generator dissociates into a proton that during a subsequent baking step cleaves the acid-cleavable tetrahydropyranyl group to convert the initial copolymer to a copolymer of polar methacrylic acid and F_nMA. Rindfleisch et al.[27] have shown that very polar or water soluble polymers are not soluble in CO_2 even at very high temperatures. Poly(acrylic acid) was found to be insoluble in CO_2 even at temperatures as high as 272 °C and pressures of 2220 bar. This is due to the strong segment−segment polar interactions resulting from hydrogen bonding that are pronounced at low temperatures. Hence, it is not surprising that the generation of polar methacrylic acid in the exposed regions makes the polymer insoluble in supercritical CO_2.

Lithographic Performance. *A. Sensitivity.* After the optimum conditions for dissolution and development of the unexposed polymer had been determined, sensitivity curves were obtained to gain information about the dose required to induce the solubility change and the contrast. A sensitivity curve is the plot of the energy dosage of the exposure radiation (mJ/cm² for optical radiation) versus the normalized thickness of the film remaining after development in an appropriate photoresist developer. The sensitivity curve provides an understanding of how much dose of the exposing radiation is necessary to render the entire film insoluble in supercritical CO_2.

The sensitivity curve at 193 nm for the block copolymer of THPMA−F3MA (49/51 vol %) is shown in Figure 5. The sensitivity curve was obtained by exposing the

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polymeric film to an array of increasing dosages and measuring the thickness of the remaining exposed insoluble film after a postexposure bake (PEB) and development in supercritical CO_2 at the optimum conditions of temperature and pressure previously determined. The sensitivity of a 49/51 vol % block copolymer of THPMA−F3MA was determined to be approximately 10 mJ/cm^2 at a postapply bake of 120 °C for 60 s and a PEB of 120 °C for 60 s. Despite the early state of research in these SCF CO_2-developable resists, it should be noted that this value of sensitivity is comparable to that obtained with current aqueous base-developed, chemically amplified photoresists. A more dramatic comparison can be made with the early work on t-BOC/styrene resists developed in anisole, where these fluorinated resists are much more sensitive. The processing conditions before and after exposure had a major effect on the sensitivity of the photoresist. When the PEB temperature was decreased to 90 °C, the sensitivity of the photoresist was >50 mJ/cm^2. Hence, finding the right processing conditions for exposure is critical to the performance of these photoresists.

The interactions between the various components of a photoresist play a very important role in the overall performance of the photoresist. In the case of a chemically amplified photoresist, the interactions and the polarity differences between the solvent, the polymer, and the PAG dictate their properties to an appreciable extent.[29] The polymer−PAG interactions have been studied previously using block copolymers of different components.[30] It was found that the PAG prefers to sequester in a particular microdomain depending on the polarity interactions.[28]

Hence, photoacid generators of different polarities that were expected to interact differently with the constituents of the THPMA-*b*−F7MA resists were blended and lithographically evaluated. The sensitivity of THPMA-*b*-F7MA with a polar PAG such as bis(*tert*-butyl phenyl) iodonium triflate (t-BIT) was 4 mJ/cm^2 whereas use of a nonpolar PAG, such as 2,6-dimethyl-4-(bromophenyl)perfluorooctylsulfonate, gave a sensitivity of approximately 23 mJ/cm^2. This is possibly due to the sequestering of the nonpolar PAG in the fluoro block microdomain, thereby reducing the effective concentration in the acid-cleavable regions to make them less sensitive.

B. Lithographic Resolution. After the photoresists were tested for solubility conditions and their sensitivities were determined, their lithographic resolution was studied. A test mask having different features of sizes ranging from 1 μm to sub-0.1 μm was used for resolution testing. The photoresist was coated, exposed, and baked either at SEMATECH Austin or at the IBM Almaden Research Center, as explained in the Experimental Section. The exposed wafers were then brought back to Cornell to be developed at the SC CO_2 facility. The developed features were then examined using an AMRAY scanning electron microscope. Figures 6 and 7 show the features resolved using fluorinated block copolymers and SC CO_2 development. The resolution obtained using THPMA-*b*-F3MA and THPMA-*b*-F7MA block copolymers was as small as 0.2 μm. A possible reason for the high resolution exhibited by these block copolymers compared to previous SCF CO_2-developable resists is their interfacial segregation characteristics.

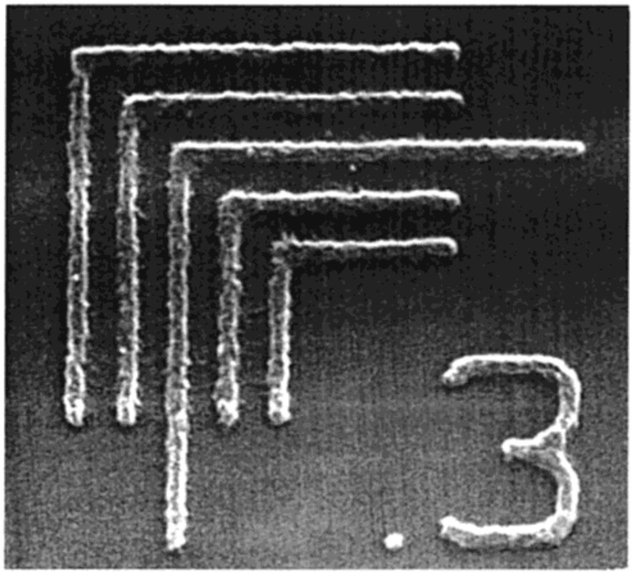

Figure 6. Features resolved using THPMA−F3MA copolymers using 193 nm exposure and SC CO_2 development.

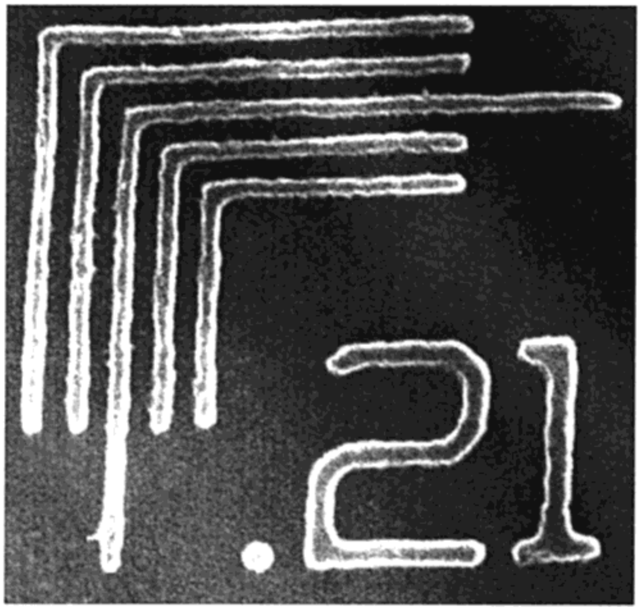

Figure 7. Features resolved using THPMA−F7MA copolymers using 193 nm exposure and SC CO_2 development.

Block copolymers possess the advantage of having two chemically different segments linked covalently, where each component prefers to segregate to a specific phase. In these block copolymers, the very nonpolar fluoromethacrylates have low surface energy and tend to populate the surface of the polymer film. Researchers have observed this surface energy-driven segregation of fluorinated components in block copolymers.[31,32]

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Incorporation of polar groups in the polymer has been shown to increase the adhesion of the film onto the substrate and the resolution achieved, possibly due to their favorable interaction with the substrate.[33] The THPMA block, due to its polar nature, can be assumed to segregate down to the internal interface between the silicon wafer and the polymer film, thereby increasing the adhesion of the film to the silicon wafer.

Developer−film interaction (penetration of the developer at the substrate−film interface) and the anchoring effect have been identified as important factors in the adhesion of the photoresist film and the substrate.[34−36] In this case, by using block copolymers with interfacial segregation characteristics, it is possible to tackle these two factors simultaneously. After exposure to radiation, the tetrahydropyranyl methacrylate block is converted to a more polar methacrylic acid. This polar methacrylic acid component provides excellent anchoring onto the silicon substrate. At the same time, it also prevents the penetration of the very nonpolar developer, that is supercritical CO_2, at the substrate−film interface, thereby reducing the likelihood of pattern collapse. This increased adhesion and decreased probability of failure at the interface increases the ultimate resolution achievable.

It should also be noted that these features were obtained with no optimization of the processing conditions or the photoresist/PAG combination for either of the two polymer systems investigated. This demonstrates the remarkable potential of using block copolymers and supercritical CO_2 development and shows that it may be possible to gain performance superior to that of aqueous-based systems with proper optimization. Supercritical CO_2 development could play an especially key role in the fabrication of high-aspect-ratio features due to its extremely low-surface-tension characteristics.

Conclusion

An environmentally friendly process for fabricating $\sim$0.2 μm features using fluorinated polymers and supercritical CO_2 was developed. A series of block copolymers containing acid-cleavable tetrahydropyranyl methacrylate and fluorinated methacrylates were synthesized by group-transfer polymerization. Their solubility characteristics in supercritical CO_2 were investigated using an in-house supercritical CO_2-processing facility. Block copolymers with more than 50 vol % fluorinated methacrylate component were found for both F3MA and F7MA to be soluble in SCF CO_2 under mild conditions at temperatures <80 °C and pressures <7000 psi. The polymers were lithographically evaluated using a 193 nm exposure source and were found to have sensitivities <10 mJ/cm^2 with appropriate photoacid generator combinations. The fluoropolymers were found to resolve features as small as 0.2 μm without any optimization, indicating the remarkable potential of this class of polymers as photoresists and the supercritical CO_2 development technique.

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