RAFT Technology for the Production of Advanced Photoresist Polymers

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ABSTRACT

Reversible **A**ddition **F**ragmentation Chain **T**ransfer (RAFT) technology has been developed for use in producing high yield low polydispersity (PD) polymers for many applications. RAFT technology is being used to produce low PD polymers and to allow control of the polymer architecture. A variety of polymers are being synthesized for use in advanced photoresists using this technique. By varying the RAFT reagent used we can modulate the system reactivity of the RAFT reagent and optimize it for use in acrylate or methacrylate monomer systems (193 and 193i photoresist polymers) or for use in styrenic monomer systems (248 nm photoresist polymers) to achieve PD as low as 1.05.

RAFT polymerization technology also allows us to produce block copolymers using a wide variety of monomers. These block copolymers have been shown to be useful in self assembly polymer applications to produce unique and very small feature sizes.

The mutual compatibilities of all the components within a single layer 193 photoresist are very important in order to achieve low LWR and low defect count. The advent of immersion imaging demands an additional element of protection at the solid/liquid interface. We have used RAFT technology to produce block copolymers comprising a random "resist" block with composition and size based on conventional dry photoresist materials, and a "low surface energy" block for use in 193i lithography. The relative block lengths and compositions may be varied to tune solution behavior, surface energy, contact angles, and solubility in developer. The use of this technique will be explored to produce polymers used in hydrophobic single layer resists as well as additives compatible with the main photoresist polymer.

Keywords: RAFT, photoresist, 193nm lithography, polydispersity, immersion, 193i, block copolymer

1. INTRODUCTION

RAFT (reversible addition fragmentation chain transfer) polymerization processes have been used for the preparation of low-polydispersity polymers from acrylic, styrenic and selected other vinyl monomers. The ability to polymerize monomers at high yields to the desired composition and molecular weight at low polydispersity is an advantage in RAFT polymerizations. This molecular length uniformity has been reported to enhance the dissolution characteristics of photoresists leading to lower LWR. Lower molecular weight polymers have also been reported to enable lower LWR photoresists. It is possible that lower Mw in combination with lower polydispersity would have a synergistic effect on the dissolution rate characteristics of photoresists and lead to even lower LWR due to lower degrees of irregular swelling and more uniform dissolution. While a lot of work has been done to take advantage of lower polydispersity, we have focused on using RAFT polymerization technology to control the polymer architecture of photoresist materials. Block copolymers can be produced and have shown usefulness in self assembly applications. A modification of block copolymers will be discussed in this paper where an A block of a random methacrylate copolymer is linked to a partially fluorinated B block to provide unique properties in a 193i photoresist.

2. EXPERIMENTAL

2.1 Synthesis of Bis-(dodecylsulfanylthiocarbonyl) disulfide

A 2000 mL 4-neck round bottom flask (fitted with mechanical stirrer, septum, thermocouple well, and reflux condenser with N_2 bubbler) was charged with heptane (1000 mL) and a solution of potassium t-butoxide in tetrahydrofuran (174.4 g, containing 34.7 g potassium t-butoxide, 0.31 mol). The resulting solution was cooled to ca. 5 °C and reacted with dodecanethiol (60.6 g, 0.30 mol). The resulting white slurry was stirred for 30 min at 5 - 10 °C and then reacted with carbon disulfide (23.5 g, 0.31 mol) over a 20 min period. The mixture was stirred at 5 °C for 10 min, allowed to warm to 20 –23 °C and stirred for 4 h. The resulting yellow slurry was reacted in portions with iodine (40.0 g, 0.158 mol) over a 40 min period at 16 –18 °C. The mixture was stirred at room temperature for 15 h. Distilled water was added, and the separated organic phase was washed with a solution of sodium chloride and sodium thiosulfate, then with sodium chloride solution. The organic layer was dried and the solvent was evaporated to provide 84.2 g (98%) of yellow solid.

2.2 Synthesis of 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid

A 2 liter, 3-neck flask fitted with reflux condenser, solids addition port, thermowell, and stir bar was charged with bis(dodecylsulfanylthiocarbonyl) disulfide (84.1 g, 151.6 mmol) and 760 mL ethyl acetate. The resulting solution was heated to gentle reflux and reacted with 4,4'-azobis(4-cyanopentanoic acid) (72.1 g, 257 mmol) over 3.75 h. The reaction mixture was heated for an additional 16 h. Ethyl acetate was removed under reduced pressure and the product

was allowed to crystallize from heptane. The solid was filtered, washed with water, and dried to provide 110.0 g (91% yield). Purity by NMR > 99%.

2.3 Synthesis of methyl 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoate

A solution of 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid ($C_{12}H_{25}SC(S)SC(Me)(CN)CH_2CH_2CO_2H$, 64.8 g, 160.5 mmol) in THF (195 mL) at 5 – 10 °C was treated with diazabicyclo[5.4.0]undec-7-ene (26.9 g, 176.6 mmol). The mixture was stirred for 5 min, then treated with methyl iodide (25.9 g, 182 mmol), and the resulting mixture was stirred for 18 h.

The reaction mixture was diluted with heptane, filtered, and the solid was rinsed with heptane. The filtrate was washed successively with dilute sodium chloride, 1N hydrochloric acid, dilute sodium bicarbonate solution, and water. The dried organic phase was evaporated to give 64.13 g (96%) of amber oil.

2.4 Synthesis of a block copolymer of α-GBLMA/MAdMA/ECPMA and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (C6Z)

A 3-neck flask fitted with condenser, addition funnel, N$_2$-inlet with adaptor to vacuum, thermowell, and stir-bar is charged with a random terpolymer of α-GBLMA/MAdMA/ECPMA (10.9 grams), (previously synthesized using the RAFT reagent methyl 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoate), methyl ethyl ketone (MEK, 15 mL), NaHCO$_3$ (50 mg), and V-601 (145 mg, 0.63 mmol). The weight average molecular weight of this polymer was 3,330 and the polydispersity was 1.17 as measured by GPC. A solution of 1*H*,1*H*,2*H*,2*H* -perfluorooctyl methacrylate (C6Z) (5.36 g) in MEK (4 mL) is charged to the addition funnel. A small volume of monomer solution (0.25 mL) is added, and the reaction mixture is heated to 70 °C. The remaining monomer is added over 3 h. The temperature is maintained for 22 h. The cooled reaction mixture is diluted with MEK (20 mL), filtered to remove sodium bicarbonate, and added dropwise to 800 mL methanol. The precipitated polymer is filtered, washed with methanol, and dried to give the desired block copolymer. Final weight average molecular weight was 4,981 and polydispersity was 1.15 as measured by GPC.

2.4.1 Reduction of trithiocarbonate end group from (α-GBLMA/MAdMA/ECPMA)-*b*-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate)

A 3-neck flask fitted with condenser, N$_2$-inlet with adaptor to vacuum, thermowell, and stir-bar is charged with block copolymer (α-GBLMA/MAdMA/ECPMA)-*b*-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate), 12.5g (2.5 mmol), MEK (30 mL), triethylammonium hypophosphite (2.74g, 16.4 mmol), and V-501 (0.52g, 1.8 mmol). The reaction mixture is heated to 70°C for 3 h. The colorless, cooled polymer solution is added to cold methanol (500 mL) to precipitate the polymer. The collected polymer is re-precipitated, filtered, and dried to provide 11.6 g of white solid. Conversion of trithiocarbonate is >99.9% (UV analysis). Final polymer purification is by conventional ion exchange processing.

2.5 Preparation of blends of 193 nm resist copolymer with fluorinated block copolymer additive

The fluorinated block copolymer (α-GBLMA/MAdMA/ECPMA)-*b*-(1*H*,1*H*,2*H*,2*H*-perfluoroctyl methacrylate) from 2.4.1 was used to prepare a series of 12 wt% solution blends with a copolymer of α-GBLMA/MAdMA/ECPMA (57/31/12 molar ratios) in a solvent mixture of 60/40 PGMEA/ethyl lactate. The weight fraction of fluorinated copolymer typically ranges from 0 to 100%, and includes specific compositions with 1/2, 1/4, 1/9, 1/29, 1/100, and 1/299 ratios. Films were prepared by spin-coating filtered (0.2 µm) solutions on silicon wafers at 1000 rpm. The films were thermally annealed in a 70 ºC oven before measurement of water contact angles (advancing and receding) using a Rame´- Hart standard automated goniometer employing DropImage® standard software equipped with an automated dispensing system.

3.   RESULTS AND DISCUSSION

A block copolymer for use as a 193 immersion photoresist additive consisting of an A block copolymer matching the composition of the main 193 nm photoresist polymer, for example α-GBLMA/MAdMA/ECPMA was prepared using RAFT polymerization technology. In a subsequent reaction, a block consisting of 1*H*,1*H*,2*H*,2*H* -perfluorooctyl methacrylate (C6Z) was reacted onto the A block again using RAFT technology. The resulting purified polymer (α-GBLMA/MAdMA/ECPMA)-*b*-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate) (F-block 1), as shown in figure 1, was added to a copolymer used in 193 nm photoresists consisting of α-GBLMA/MAdMA/ECPMA. The contact angle vs. % fraction (F-block 1) added are shown in figure 2. The fluoropolymer tail of this block copolymer tends to segregate at or near the surface of the resist when spun on the Si wafer and annealed in the post apply bake process as shown schematically in figure 3. The ability to produce the block A section having the same monomer and ratio composition of the commercial 193 resist provides excellent compatibility of the fluorinated 193 block copolymer while allowing for the fluoropolymer end cap to migrate to the surface to provide the desired contact angles for the immersion lithography system. This technique allows for selective exclusion of the immersion fluid and possibly minimal transport of contaminates from the resist (ex. PAG). Similarly, a block copolymer (F-block 2) was prepared matching the composition and M_w of a commercially available 193 nm photoresist polymer and a short block of 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate was reacted on one end of that copolymer using RAFT polymerization techniques.
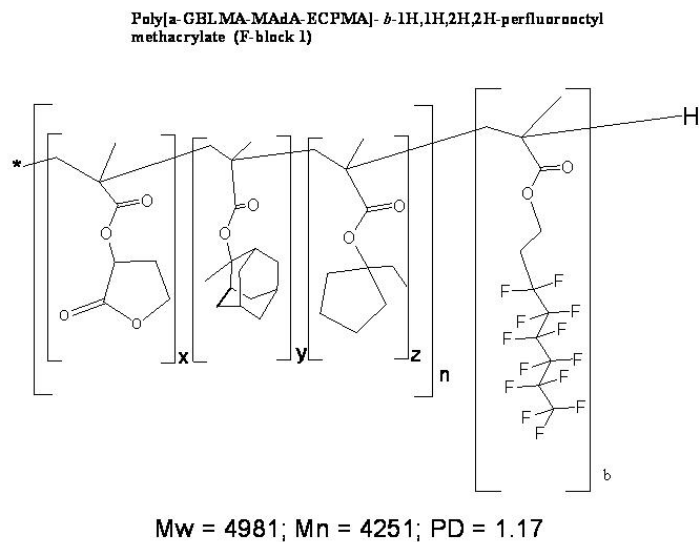
Figure 1. Structure of block copolymer [α-GBLMA-MAdMA-ECPMA]-*b*-[1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate] (F-block 1)
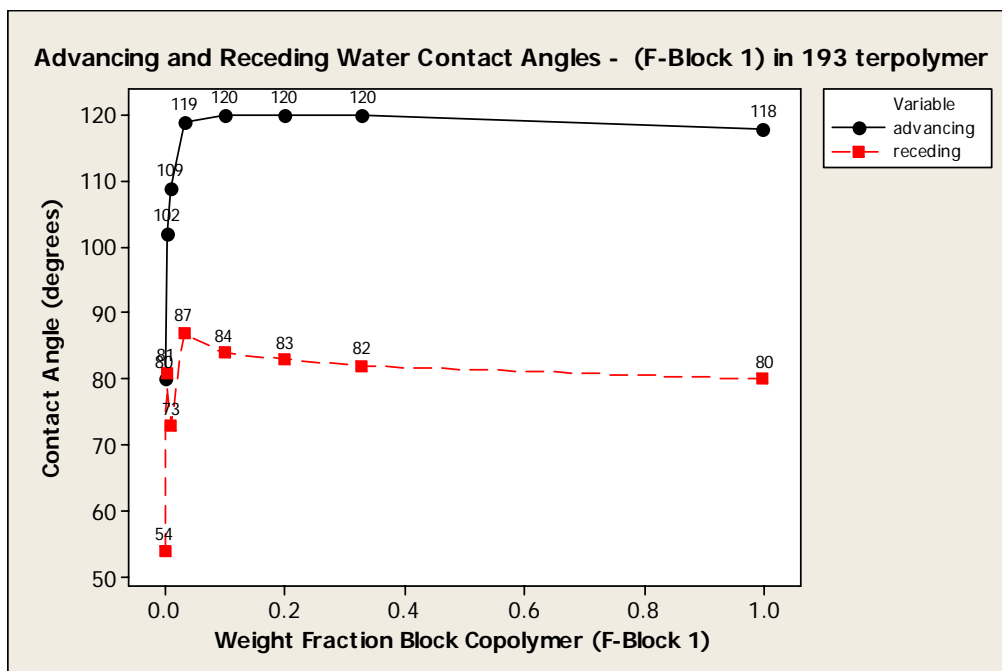

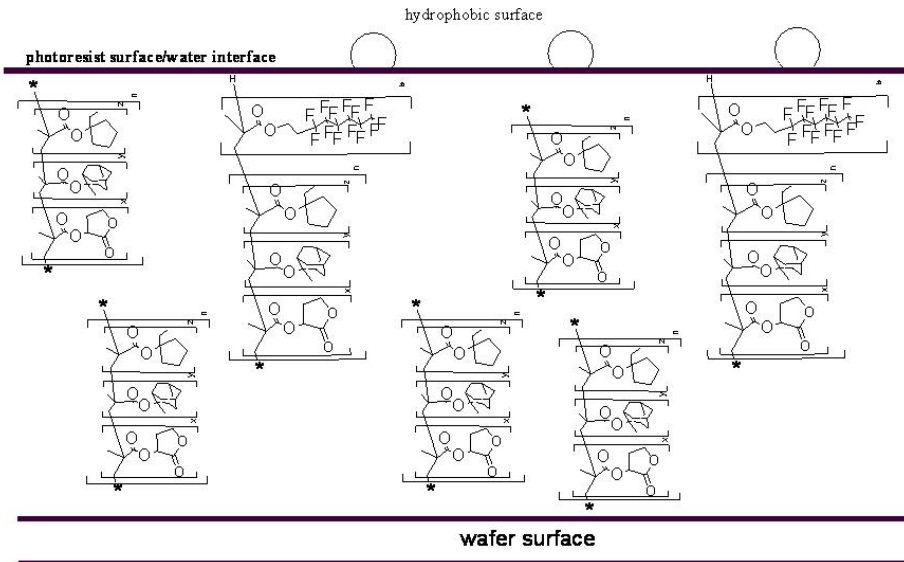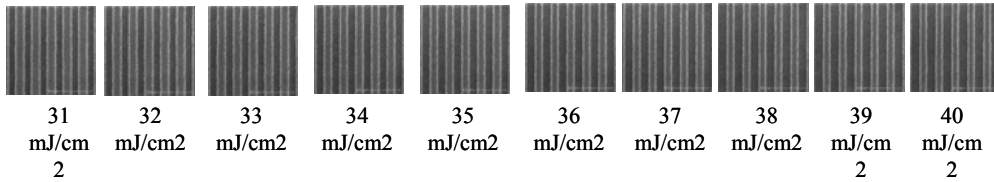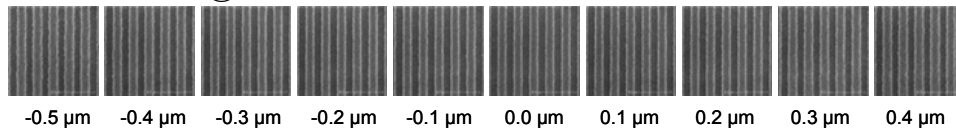Figure 2. Water contact angles of [α-GBLMA-MAdMA-ECPMA]-*b*-[1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate] (F-block 1)

Figure 3. Schematic of block copolymer [α-GBLMA-MAdMA-ECPMA]-*b*-[1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate] (F-block 1) in the resist on the Si wafer

1 wt.% (F-block 2) in a commercial 193 nm resist

120 nm L/S @ best focus

| 31 mJ/cm2 | 32 mJ/cm2 | 33 mJ/cm2 | 34 mJ/cm2 | 35 mJ/cm2 | 36 mJ/cm2 | 37 mJ/cm2 | 38 mJ/cm2 | 39 mJ/cm2 | 40 mJ/cm2 |

120 nm L/S @ 34.0 mJ/cm^2

| -0.5 µm | -0.4 µm | -0.3 µm | -0.2 µm | -0.1 µm | 0.0 µm | 0.1 µm | 0.2 µm | 0.3 µm | 0.4 µm |

Linearity @ 34.0 mJ/cm^2

| 137.0 | 122.4 | 122.7 | 123.9 | 126.7 | 131.9 |
| Mask CD 100 | Mask CD 110 | Mask CD 120 | Mask CD 130 | Mask CD 140 | Mask CD 150 |

Figure 4. SEM images of L/S microlithography from 1 wt. % block copolymer (F-block 2) added to a commercial 193 nm photoresist

3 wt.% (F-block 2) in a commercial 193 nm resist

120 nm L/S @ best focus

| 28 mJ/cm2 | 29 mJ/cm2 | 30 mJ/cm2 | 31 mJ/cm2 | 32 mJ/cm2 | 33 mJ/cm2 | 34 mJ/cm2 | 35 mJ/cm2 | 36 mJ/cm2 | 37 mJ/cm2 |

120 nm L/S @ 32.0 mJ/cm^2

| -0.5 μm | -0.4 μm | -0.3 μm | -0.2 μm | -0.1 μm | 0.0 μm | 0.1 μm | 0.2 μm | 0.3 μm | 0.4 μm | 0.5 μm |

Linearity @ 32.0 mJ/cm^2

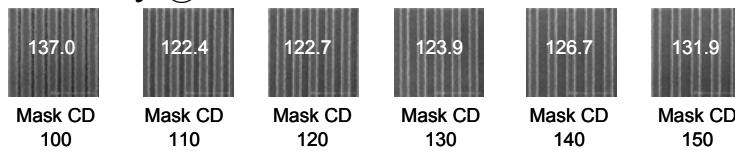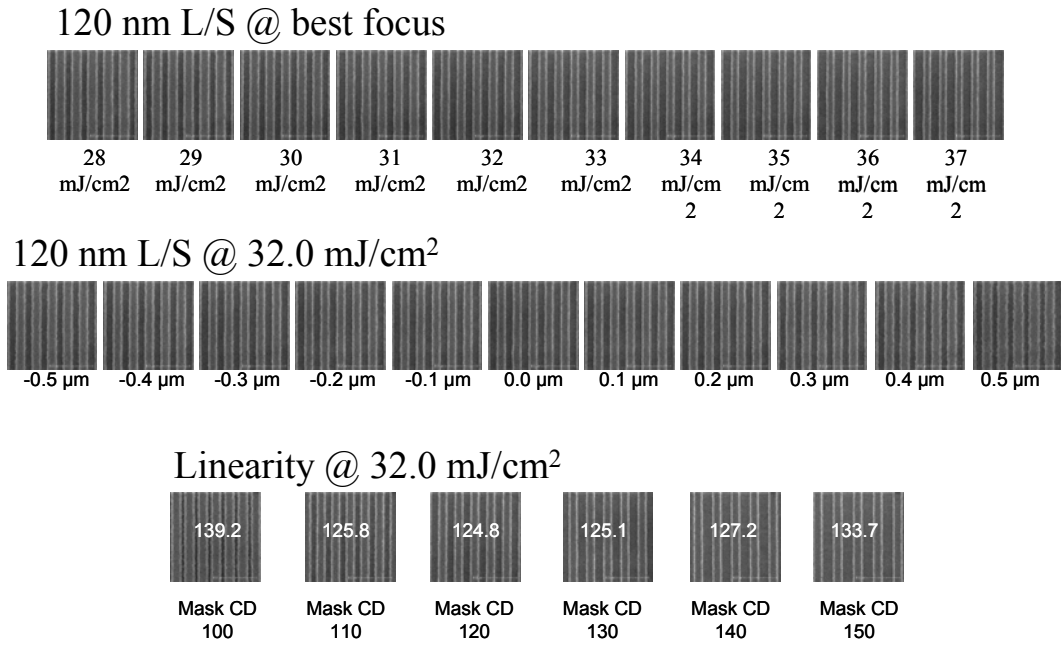| 139.2 | 125.8 | 124.8 | 125.1 | 127.2 | 133.7 |
| Mask CD 100 | Mask CD 110 | Mask CD 120 | Mask CD 130 | Mask CD 140 | Mask CD 150 |

Figure 5. SEM images of L/S microlithography from 3 wt. % block copolymer (F-block 2) added to a commercial 193 nm photoresist

5 wt.% (F-block 2) in a commercial 193 nm resist

120 nm L/S @ best focus

| 28 mJ/cm2 | 29 mJ/cm2 | 30 mJ/cm2 | 31 mJ/cm2 | 32 mJ/cm2 | 33 mJ/cm2 | 34 mJ/cm2 | 35 mJ/cm2 | 36 mJ/cm2 | 37 mJ/cm2 |

120 nm L/S @ 31.0 mJ/cm^2

| -0.4 μm | -0.3 μm | -0.2 μm | -0.1 μm | 0.0 μm | 0.1 μm | 0.2μm | 0.3 μm | 0.4 μm |

Linearity @ 31.0 mJ/cm^2

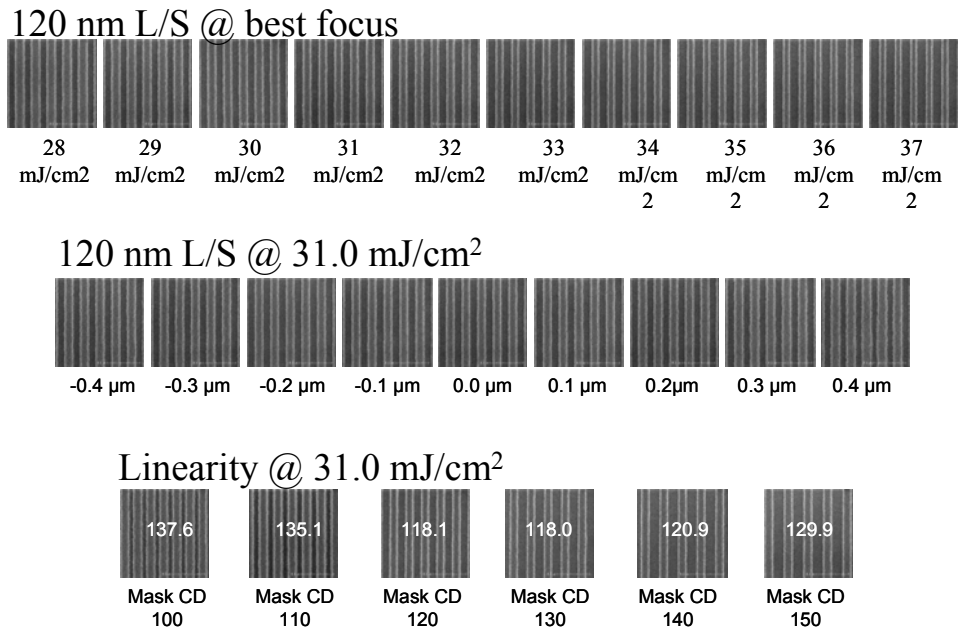| 137.6 | 135.1 | 118.1 | 118.0 | 120.9 | 129.9 |
| Mask CD 100 | Mask CD 110 | Mask CD 120 | Mask CD 130 | Mask CD 140 | Mask CD 150 |

Figure 6. SEM images of L/S microlithography from 5 wt. % block copolymer (F-block 2) added to a commercial 193 nm photoresist

4. CONCLUSION

The use of RAFT in free radical polymerization to produce low polydispersity polymers at high monomer conversions is well documented. Control of polymer architecture is a key advantage in RAFT polymerizations and is finding usefulness in unique applications where block, gradient, star, comb or other unique structures and properties are required. In this paper, we have shown the usefulness of RAFT polymerization techniques in preparing polymers of unique architecture for use in 193i photoresists. The random block A portion of the polymer in the photoresist combined with a controllable hydrophobic block B provides excellent compatibility with normal 193 dry polymers while the hydrophobic tail provides the needed hydrophobicity to form a 193i system when properly annealed. The annealing step allows the hydrophobic tail to concentrate on the surface to provide the proper protection in the 193 immersion resist system. By varying the specific monomers used for the hydrophobic B blocks the advancing and receding contact angles can be controlled. Selection of the specific fluorinated monomer in the block copolymer appears to be a key factor in controlling the advancing contact angle. Control of hysteresis remains an area for optimization in this system.

5. ACKNOWLEDGEMENTS

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