Aqueous Developable Dual Switching Photoresists for Nanolithography

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ABSTRACT: Photon-mediated switching of polymer solubility plays a crucial role in the manufacture of integrated circuits by photolithography. Conventional photoresists typically rely on a single switching mechanism based on either a change in polarity or, molecular weight of the polymer. Here we report a photoresist platform that uses both mechanisms. The molecular weight switch was achieved by using a poly(olefin sulfone) designed to undergo photo-induced chain scission. The polarity switch was achieved using pendant groups functionalized with *o*-nitrobenzyl esters. These are hydrophobic photosensitive-protecting groups for hydrophilic carboxylic acids. On irradiation, they are cleaved, making the polymer soluble in aqueous base. Importantly, the resists do not contain photoacid generator, so do not suffer from prob-

INTRODUCTION Photolithography is a critical step for manufacturing integrated circuits (ICs),¹ including digital devices such as microprocessors, memory, and systems on a chip. Analogue devices such as sensors, power management circuits, and operational amplifiers are also manufactured using this technology. Finally, photolithography is also used in the fabrication of other devices including photomasks,² plasmonic devices,³ micro/nano-fluidic devices,⁴ micro/nanoelectromechanical systems (M/NEMS),^{5,6} gene chips,⁷ and protein microarrays.⁸ Briefly, the process relies on having a suitably designed polymer that is blended with a small amount of a photoacid generator (PAG), which when exposed to light can undergo photoreaction to form a strong photoacid.⁹ This photoacid catalyzes the deprotection of pendant hydrophobic tertiary esters or carbonates in the polymer, yielding hydrophilic carboxylic acids or phenols. The deprotection reaction changes (switches) the aqueous base solubility of the irradiated regions. Major challenges in photolithography, of particular relevance to the fabrication of ICs, are

lems associated with acid diffusion that are detrimental to pattern fidelity. The 193 nm photochemistry of polymer thin films was followed using grazing angle attenuated total reflectance Fourier transform infrared spectroscopy, variable angle spectroscopic ellipsometry, and measurements of solubility in aqueous base. The nanoscale patterning performance of the polymers was also assessed using 193 nm interference lithography and electron-beam lithography. The implications of using dual switching mechanisms are discussed. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

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simultaneously achieving high resolution (print small features), with good pattern fidelity (printed feature matches the design) and high sensitivity. Recent research efforts have focused on achieving these aims for printed features with dimensions of 32 nm or less; however, acceptable pattern fidelity has been elusive using conventional photoresist formulations.¹⁰ The pattern fidelity can be quantified by measuring the average deviation, to three standard deviations, of a printed line edge compared to an ideal line edge (i.e., line edge roughness [LER]).¹¹ LER has been predicted to significantly degrade device performance at small feature sizes.¹² A major contributing factor to LER is diffusion of photoacids produced during irradiation of the photoresist.13,15 Random diffusion of the photoacid results in a nonuniform distribution of deprotection reactions that ultimately results in features with rough edges.^{16,18}

One approach to overcoming problems associated with photoacid diffusion is to use photoresists that do not use a PAG,

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but instead rely on direct photolysis of bonds in the backbone of the photoresist polymer to facilitate a switch in the polymers solubility. This class of resists, chain-scissioning resists, were widely studied for lithography at longer wavelengths,^{19,25} however, after the development of resists that use PAGs,^{9,26} commercial demand for manufacturing using this process diminished. More recently, however, as LER and high resolution patterning have become more important, interest in evaluating chain-scissioning resists has been renewed for 193 nm lithography and extreme ultraviolet lithography (EUVL). For example, the development and evaluation of chain scissioning positive tone resists based on poly(olefin sulmethacrylates,^{27,28} polycarbonates,^{29,31} fones),^{32,36} acetal-containing polymers,³⁷ molecular glasses,³⁸ and halogenated polymers^{39,41} have recently been reported for 193 nm and EUVL. Chain-scissioning resists have been shown to have excellent resolution in these applications. For example, trenches with widths between 3 and 10 nm were achieved using poly(methyl methacrylate) (PMMA) as a photoresist for electron-beam lithography^{42,45} and image quality was shown to be excellent using EUV interference lithography.²⁷ As a comparison, the resolution of photoresist formulations that use a PAG is limited to approximately 20 nm and image quality parameters, such as LER, are relatively poor.⁴⁶ A drawback of chain-scission resists is poor sensitivity, but increasing the absorbance of the polymers at the wavelength used for patterning, can improve sensitivity.^{30,34} More importantly for chain-scissioning resists is the requirement for development with organic solvents. This is undesirable because solvent developers are less compatible with manufacturing tools, can cause swelling of the polymer, and are less environmentally friendly.

Another option for achieving a solubility switch is to use a photochemical reaction that is not reliant on PAGs to change the polarity of the polymer. For example, photosensitive *o*-nitrobenzyl esters have been used as pendant side chains to function as a hydrophobic protecting group for hydrophilic carboxylic acids.^{47,49} Photoresists using this chemistry were evaluated for lithography using 248 nm light.^{47,49} While the quality of the patterning was good, the sensitivity of the resists was poor compared to resists using PAG chemistry. This chemistry has not been evaluated for 193 nm or EUVL.

Here a resist platform that does not have PAGs is introduced, where the polymers have been designed to use both molecular weight and polarity solubility switches. The polarity switch occurs through photolysis of pendant nitrobenzyl esters, and chain scission is achieved through the use of a poly(olefin sulfone) backbone, because this is inherently sensitive to chain scission by radiation.^{50,52} Spectroscopic and empirical evidence for the photochemistry at 193 nm is presented. Another attractive feature of poly(olefin sulfones) is that following irradiation they can undergo depolymerization when heated, that is, during a post-exposure baking (PEB) step, which can increase the effective sensitivity of the resist.^{32,53} The ability to undergo depolymerization depends on the structure of the repeat units. For example, absorbing

repeat units derived from allyl benzene were found to increase the sensitivity to photo-induced chain scission at 193 nm, but inhibited depolymerization in a subsequent baking step.³⁴ The polymers used in this study have been redesigned so that the absorbing repeat units do not interfere with depolymerization. The patterning performance of poly(-olefin sulfone)-based resists was assessed using 193 nm interference lithography and electron-beam lithography.

EXPERIMENTAL

Materials

Anhydrous sulfur dioxide (99%, BOC), 5-norbornen-2-ol (99%, Aldrich), allylbenzene (98%, Aldrich), 3-(bicyclo[2.2.2]hept-5-en-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol (98%, SynQuest) (NBHFA), bicyclo[2.2.1]hept-5ene-2-carboxylic acid (98%, Aldrich), ethyl chloroformate (97%, Aldrich), 2-nitrobenzyl alcohol (Fluka), pyridine (99%, Aldrich), 4-dimethylaminopyridine (99%, Aldrich), 3chloropropiophenone (98%, Aldrich), triethylamine (99%, Aldrich), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (Alfa Aesar), sodium bicarbonate (99.5%, Aldrich), sodium chloride (99.5%, Scharlau), hydrochloride acid (UNIVAR, 32%), (GC) n-hexane (Merck. 98%), (GC) diethyl ether (Merck, 99.7%), (GC) dichloromethane (Merck, 99.7%), (GC) chloroform (Merck, 99.4%), potassium t-butoxide (97%, Aldrich), (GC) tetrahydrofuran (THF) (Merck, 99.9%), cyclohexanone (Aldrich, 99.9%), (HPLC) 4-Methyl-2-pentanone (Aldrich, 99.5%), (AR), ethyl acetate (UNIVAR), (AR), methanol (UNIVAR), (AR), 2-propanol (UNIVAR), (AR), Methyl isobutyl ketone (UNIVAR), (AR), hydrochloric acid (UNIVAR, 32%), and (HPLC) tetrahydrofuran (LAB-SCAN, 99.8%) were obtained at the highest purity available and used without further purification unless otherwise stated. Tetramethylammonium hydroxide (TMAH, NMD-3, 2.38%) was purchased from Tokyo Uhka Kogyo, Co. and used without further purification unless stated. BARC29A bottom antireflective coating solutions were obtained from Brewer Science.

Bicyclo[2.2.1]hept-5-en-2-yl Ethyl Carbonate

Ethyl chloroformate (17.5 mL, 18.3 \times 10⁻² mol) was added in drops to a stirred solution of the 5-norbornene-ol (6.8 imes 10^{-2} mol), pyridine (22 mL, 27.2 \times 10^{-2} mol), and 4-dimethylaminopyridine (40 mg) in tetrahydrofuran (300 mL) at 0 °C. The resulting cloudy mixture was stirred for 12 h at room temperature (25 °C). Brine (60 mL) and diethyl ether (20 mL) were added, and the organic layers were separated, washed successively with 10 vol/vol% HCl_(aq) and brine, dried over magnesium sulfate, and concentrated to leave the crude product. Column chromatography over silica gel (10% ethyl acetate/90% n-hexane) provided the pure bicyclo[2.2.1]hept-5-en-2-yl ethyl carbonate as a clear, colorless oil. Yield 85%. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.87 (m), 1.26-1.31 (m), 1.45 (m)), 1.46 (m), 1.57 (m), 2-2.15 (m), 2.82 (s), 2.93(s), 3.15 (s), 4.1 (m), 4.5 (m), 5.18 (m), 5.94-5.99 (m), 6.21–6.33 (m). 13 C NMR (CDCl₃, 500 MHz, ppm): δ 14.7, 34.4, 40.4, 42.1, 45.7, 46.0, 47.5, 63.6, 78.4, 78.7, 131.2, 132.3, 138.7, 141.3, 141.3, 155.0.

Synthesis of 2-Nitrobenzyl Bicyclo[2.2.1]hept-5-ene-2carboxylate

In a round-bottle flask, bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1 eq.), (2-nitrobenzyl)methanol (1 eq.), triethylamine (1.2 eq.), 1-(3-dimethylaminopropyl)-3-ethylcardiimide hydrochloride (1.1 eq.), and 4-(dimethylamino)pyridine (0.1 eq.) were dissolved in dichloromethane. The reaction mixture was stirred at room temperature overnight. Afterwards, the mixture was washed three times with 1 N HCl_(aq), saturated $NaHCO_{3(aq)}$, and distilled water. The product was then recrystallized from 70:30 hexane:ethyl acetate (vol:vol), vielding vellowish solid (vield is \sim 80%). The compound was characterized by ¹H NMR (CDCl₃) 8.09 (CH), 7.71 (CH), 7.60 (CH), 7.43 (CH), 6.18 (CH), 5.88 (CH), 5.43 (CH₂), 3.0 (CH), 2.52 (CH), 1.95 (CH), 1.57–1.28 (CH); ¹³C NMR (CDCl₃) 174 (C=O), 138 (C-N), 134 (C=C), 133 (C=C), 132 (C=C), 130 (C=C), 129 (C=C), 128 (C=C), 125 (C=C), 63 (C-C), 50 (C--C), 46 (C--C), 43 (C--C), 42 (C--C), 29 (C--C).

Polymerization of Sulfur Dioxide with 2-Nitrobenzyl Bicyclo[2.2.1]hept-5-ene-2-carboxylate

In a typical polymerization, a mixture of 2-nitrobenzyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (NPBHC) (1 g, 3.66 mmol) in THF (2.67 mL) was transferred to a 50-mL Schlenk tube and deoxygenated by three successive freeze-evacuate-thaw cycles. The reaction vessel was then cooled with liquid nitrogen, and sulfur dioxide (\sim 25 mL) was added by condensation. The polymerization was carried out at -15 °C to -20°C for 2 h and was initiated with *t*-butyl hydroperoxide. Afterwards, the reaction vessel was warmed to room temperature and the polymer was purified through precipitation in diethyl ether. All other polymerizations were similarly carried out but with the addition of different monomers and compositions.

Polymer Characterization

¹H NMR spectroscopy was carried out using a Bruker Avance DRX 500 spectrometer operating at 500.13 MHz for protons and equipped with a 5 mm triple resonance z-gradient probe. Deuterated chloroform (CDCl₃) was used to dissolve the organic samples. An internal standard, either tetramethylsilane (TMS) or the residual proton signal of the deuterated solvent, was used. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C min⁻¹ in N₂ on a METTLER TOLEDO STAR^e thermogravimetric analyzer. Differential scanning calorimetry (DSC) was performed at a heating rate of 10 °C min⁻¹ on a METTLER TOLEDO STAR^e differential scanning calorimeter. Molecular weights of polymers were measured using gel permeation chromatography. The chromatographic system consisted of a 1515 isocratic pump (Waters), a 717 autosampler (Waters), Styragel HT 6E, and Styragel HT 3 columns (Waters) run in series, a light scattering detector DAWN 8+ (Wyatt Technology Corp.), and a 2414 differential refractive index detector (Waters). THF was used as the mobile phase at a flow rate of 1 mL min⁻¹. ASTRA (Wyatt Technology Corp.) and Empower 2 (Waters) were used for data collection and processing. To determine molar mass by conventional SEC, the columns were calibrated by polystyrene standards (Waters)

covering the molar mass range of 1060-1,320,000 Da. FTIR spectra of the thin films on silicon wafers were obtained using a Nicolet Nexus 5700 FTIR spectrometer (Thermo Electron Corp., Waltham, MA) equipped with a Harrick grazing angle attenuated total reflectance (GATR) accessory (Harrick Scientific Products, Pleasantville, NY) fitted with a KRS-5 MIR polarizer (Harrick Scientific Products, Pleasantville, NY). p-Polarized illumination was used. Spectra were recorded at 4 cm^{-1} resolution for at least 128 scans with an optical path difference (OPD) velocity of 1.899 cm s⁻¹. The thin film side of the Si wafer was pressed directly onto the germanium internal reflection element of the ATR accessory, and a pressure of 56 lbs in⁻² was applied. Spectra were manipulated using the OMNIC 7 software package (Thermo Electron Corp., Waltham, MA). Optical properties of the thin films, phi and delta, were measured using a J.A. Woollam VUV-VASE. A Cauchy model calculated film thickness, while an oscillator model was used to model refractive index and absorbance.

Resist Evaluation

Photoresist solutions were prepared by dissolving the polymers (typically 2 wt %) in cyclohexanone. The solutions were then spin-coated onto a BARC29A coated silicon wafer at 1500 rpm approximately 70 nm thick before a 120 °C post-apply bake (PAB) step. The wafers were then exposed to varying doses using a 193 nm ArF excimer laser (GAM Laser, Orlando, FL). Afterwards, the wafers underwent a PEB and were developed in 2.38 wt % TMAH solution. For specific details of the temperatures, see the Results and Discussion section. The contrast curves were normalized to the initial film thickness. Patterning was done by dry 193 nm interference lithography using an Amphibian XIS microstepper tool (Amphibian at Rochester Institute of Technology, USA) using a 0.32 numerical aperture.⁵⁴

Electron-beam lithography (EBL) was carried out using a Raith-150 system manufactured by Raith GmbH. Specifically, the wafers with a native oxide layer (2 nm) that were coated with 50 nm of the specified resist (Polymer B1, Polymer C, or Polymer D [PMMA]) were exposed with an electron beam with an acceleration voltage of 10-20 keV, an aperture of 20 μ m, a 6 mm working distance, and a beam current of ${\sim}100$ – 200 pA. Lithographic patterns consisting of line features with critical dimensions of 11-50 nm with 100-200 nm pitch and 100 μ m long were designed using L-Edit Pro V.14 (Tanner EDA tool) and scanned with an area dose of 380 μ C cm⁻² at 20 kV for Polymer B1, single pass line dose of 120 pC cm⁻¹ at 20 kV for Polymer C, and single pass line dose of 375 pC cm⁻¹ at 10 kV for Polymer D [PMMA]. The samples were then baked at the prescribed temperature for 60 s on a hot plate followed by development in 2.38 wt/vol% TMAH for 30 s at room temperature, followed by rinsing with deionized water for 15 s, and drying with a jet of N₂ (except for the PMMA, which did not have a PEB and for which development was performed using MIBK:IPA 1:3 for 30 s). Pattern fidelity was examined by scanning electron microscopy (SEM) at a magnification of 50,000 or $100,000 \times$ at 2 kV, with an aperture of 30 μ m and a working distance of 3 mm. The LER of the patterned features was analyzed using



Summit v7.5.1, a commercial lithography metrology software package from EUV Technology (Martinez, CA). The LER was determined along the full length of the line using a polynomial edge detection algorithm with a threshold value of 0.5 determined by the average line threshold reference.

RESULTS AND DISCUSSION

Design of Poly(olefin sulfones) Resist Polymers

The aim of this study was to develop photoresist polymers that do not require a PAG and function through two mechanisms: a molecular weight reduction and also a polarity solubility switch. In particular, after irradiation through a photomask, the polymers should be able to be selectively developed using a conventional aqueous base developer. Scheme 1 shows a polymer structure undergoing photoinduced chain scission and photodeprotection of a hydrophobic pendant group to yield a hydrophilic carboxylic acid. The structures of the poly(olefin sulfones) investigated are shown in Figure 1(A,B).



SCHEME 1 Schematic diagram of a poly(olefin sulfone)-based photoresist that functions through both a molecular weight and polarity solubility switch.



FIGURE 1 Structures of polymers used in this study.

Poly(olefin sulfones) can be prepared by free radical-initiated polymerization of sulfur dioxide with alkenes. The 2-nitrobenzyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (NBHC) repeat unit was selected because it contains an o-nitrobenzyl group, which can undergo photoreaction to yield a carboxylic acid.^{48,55} The norbornene component of this repeat unit was selected because the corresponding monomer undergoes alternating polymerization with sulfur dioxide⁵⁶ and the bicyclic structure should impart a higher T_{g} and etch resistance to the final polymer.⁵⁷ An alternating copolymer of sulfur dioxide and NBHC was prepared by free radical polymerization, (Polymer A), which had an absorbance of 7.7 μm^{-1} at 193 nm. This high absorbance is expected to degrade performance of 193 nm lithography by preventing sufficient light from penetrating the entire film thickness, so additional materials including two additional norbornene-based monomers were prepared for comparison. These monomers, bicyclo[2.2.1]hept-5-en-2-yl ethyl carbonate (BHEC) and 3-(bicyclo[2.2.2]hept-5-en-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol (NBHFA) are not expected to contribute significantly to the absorbance of the polymer at 193 nm.^{58,59} Thus, by varying the proportion of these non-absorbing monomers, it was found that the absorbance of the polymer could be tuned between 1.66 and 3.58 μm^{-1} and varied linearly with the NBHC content (see Table 1). This is significant because it has been demonstrated that the absorbance of poly(olefin sulfone)s at 193 nm dictates the sensitivity to chain scission when irradiated with this wavelength of light.³⁴

It was also found that the refractive index of the polymers systemically increases with increasing content of NBHC, lying between 1.71 and 1.83 at 193 nm. Typically, the refractive index of 193 nm photoresist polymers is 1.65–1.7. For 193 nm immersion lithography, an increased refractive index of photoresists can precipitate gains in lithography parameters

TABLE 1 Composition and Optical Properties of the Poly(olefin sulfones) Used in This Study

Polymer	<i>M</i> n (kDa) ^a	ÐM	Composition	<i>T</i> d ^b (°C)	n_{193 nm}	Abs (µm ⁻¹)
А	520	2.9	0:0:100	237	1.83	7.71
B1	48	2.3	50:21:29	231	1.74	3.58
B2	43	3.6	54:20:26	212	1.72	2.88
B3	47	4.2	56:25:19	226	1.71	1.66

^a Molecular weight parameters are reported relative to polystyrene standards.

 $^{\rm b}$ T_d is measured at the onset of decomposition.

such as exposure latitude.^{60,61} The higher refractive index observed here can be attributed to the nitrogen and sulfur content, as well as the nitrobenzyl ester group having an absorption edge close to 193 nm.^{62,66} Finally, BHEC is hydrophobic and NBHFA is hydrophilic,^{58,59,67} hence, varying the proportion of these monomers allows the polarity of the polymer and ultimately the interaction of the polymer with the developer to be controlled. The thermal decomposition temperature of all the synthesized polymers (unirradiated) was above 200 °C, thus the polymers should be able to withstand typical lithographic processing steps without thermal degradation.

Polarity Switch—Photochemistry of Nitrobenzyl Protecting Groups

The photodeprotection of nitrobenzyl groups by ultraviolet A (UVA) and 254 nm light has been well studied,^{55,68} but the behavior at 193 nm has not been investigated, for example, whether the same photoreactions occur, or if there is a change in the nature of photoproducts. Polymer A (see Fig. 1) was selected for in-depth studies to simplify spectroscopic interpretation. GATR FTIR was used to follow the photochemical changes that occur as a result of 193 nm irradiation. GATR FTIR allows analysis of thin films or monolayers coated on high refractive index substrates such as silicon,^{69,70} because of the enhanced electric field that occurs in the nano-gap between the germanium internal reflective element and the silicon wafer, when the film is less than ~70 nm thick.

Figure 2 shows the GATR spectra of Polymer A after 193 nm irradiation at doses ranging from 0 to 300 mJ cm^{-2} . Several changes in the spectra can be observed with increasing irradiation dose. The peaks at 1526 and 1345 cm⁻¹ are characteristic of the asymmetric and symmetric NO₂ stretching modes, respectively. These bands decreased with increasing irradiation dose, with approximately 75% of the nitro groups being removed at a dose of 300 mJ cm^{-2} . The carbonyl stretching region also underwent changes. The ester C=0 stretching band at 1734 cm^{-1} can be observed to decrease slightly and shift to 1722 cm⁻¹, consistent with the formation of carboxylic acids. Upon irradiation with UVA (~315-400 nm)^{55,68} and 254 nm light, nitrobenzyl esters are reported to undergo photoinduced reactions, in which the benzylic C-O bond is cleaved to yield a carboxylic acid and an o-nitrosobenzaldehyde (see Scheme 2). The photochemis-



FIGURE 2 GATR FTIR spectra of thin films of Polymer A after exposure to 193 nm light at doses of 0–300 mJ cm⁻².

try of the nitrobenzyl ester moiety at 193 nm has not previously been reported; the observed spectral changes described above, that is, the loss of the nitro and ester groups along with the formation of the carboxylic acids, are nevertheless consistent with the mechanism reported for longer wavelengths.



SCHEME 2 Schematic shows a reported mechanism for (i) photo-induced formation of a biradical in the nitrobenzyl group, (ii) subsequent chain transfer, and (iii) eventual deprotection to form a pendent carboxylic acid.^{55,68} (iv) It is proposed that chain scission of the poly(olefin sulfone) occurs as a consequence of the formation of the radical species; that is, eventual abstraction of a proton from a carbon on the polymer backbone results in chain scission. (iv) Heating following chain scission then results in depolymerization of the polysulfone backbone.



FIGURE 3 Absorbance spectra of thin films of Polymer A after irradiation with various doses at 193 nm (0–300 mJ cm⁻²). Optical constants were measured using a variable angle spectroscopic ellipsometer and data was fit using an oscillator model.

Deprotection of the nitrobenzyl esters was also confirmed by studying changes in the UV spectroscopic ellipsometry spectra of the thin films as a function of 193 nm irradiation dose (see Fig. 3). Before irradiation, a peak at 260 nm, due to the π - π * transition of the nitrobenzyl functional group can be observed. Upon irradiation, the intensity of this peak decreases and bands at 300 and 350 nm appear and increase in intensity with increasing dose. These later bands are consistent with the formation of nitrosobenzalde-hyde.^{71,72} This again is consistent with the mechanism described above.

The deprotection reaction can also be followed by monitoring the solubility of the polymer thin films in aqueous base solution as a function of dose. Figure 4 shows a contrast curve for Polymer A, which plots the relative film thickness as a function of 193 nm dose, following a post-exposure bake step at 120 $\,^\circ\text{C}$ and development with a 2.38 wt % aqueous solution of TMAH. Up to doses of approximately 30 mJ cm^{-2} , the film remains insoluble in the developer. At higher doses, the rate of film loss increases until total dissolution was observed at approximately 110 mJ cm⁻². From the GATR results, this corresponds to approximately 50% deprotection of the nitrobenzyl groups at a dose of 110 mJ cm^{-2} . The switch of the polymer solubility in the aqueous base developer solution can primarily be attributed to the formation of carboxylic acids, however chain scission during the post exposure bake step also plays a role in dictating polymer solubility (vide infra).

Molecular Weight Switch-Evidence for Chain Scission

Further inspection of the GATR spectra (Fig. 2) in regions characteristic of sulfone groups, that is, the asymmetric and symmetric SO_2 stretching modes at 1301 and 1134 cm⁻¹,

respectively, reveals a decrease in intensity of these peaks with increasing dose (a clearer 1D plot in color is shown in Fig. S2 in the Supporting Information). After irradiation to 300 mJ cm⁻², approximately 40% of the sulfone groups are lost. Purely aliphatic poly(olefin sulfones) such as poly(norbornene sulfone), (PNBS) also undergo loss of sulfone groups during 193 nm irradiation, but at the same dose only 10% of sulfone groups are lost.³² The increased loss of sulfone groups for Polymer A is attributed to its higher absorbance, which is 7.7 μm^{-1} , compared with PNBS which has an absorbance of only 0.17 $\mu m^{-1.32}$ Energy transfer from an excited state nitrobenzyl group to the sulfone group is ruled out as a possible mechanism, because there are no overlapping allowed transitions. Previously, it has been shown that incorporation of allyl benzene repeat units increases the 193 nm absorbance and also the sensitivity of the polymer to lose sulfone groups at this wavelength. For allyl benzene repeat units, the absorbing moiety is situated close to the polymer chain and upon irradiation a radical is expected to form on the carbon alpha to the aromatic ring.⁷³ This radical rearrangement is then likely to result in chain scission and loss of sulfur dioxide. A recognized photoreaction pathway for the nitrobenzyl group involves the formation of a reactive biradical that can participate in hydrogen abstraction.55,68 For Polymer A, however, the nitrobenzyl absorbing unit is separated from the backbone by a norbornene unit. To explain the loss of sulfone groups mediated by the presence of the nitrobenzyl groups, the radicals formed during irradiation must undergo a number of radical chain transfer steps and ultimately lead to abstraction of hydrogen atoms from C-H on or adjacent to the polymer backbone and then consequently to chain scission (see Scheme 2).



FIGURE 4 Plot of relative film thickness versus 193 nm dose for Polymer A, following a PEB step at 120 °C and development with 2.38% TMAH in water (contrast curves). Solid line shown to guide the eye.



FIGURE 5 Top down SEM micrographs of 1:1 line spaces of (a) Polymer B1 and (b) Polymer B1 with 15 wt % acridine that were obtained by patterning with 193 nm interference lithography (0.32 NA) and development with aqueous TMAH (2.38 wt %).

As well as loss of sulfone groups, the solubility of PNBS increases in organic solvents with increasing dose and this was interpreted as being due to a decreases in polymer molecular weight that was a consequence of photo-induced chain scission reactions.³² Similar solubility studies for Polymer A were confounded by the concurrent deprotection of the nitrobenzyl units, which also changes polymer solubility. Unfortunately, it was not possible to confirm the changes in molecular weight using size exclusion chromatography (SEC), because the thin films (70 nm) used in the irradiation study did not provide sufficient polymer for a measurement. The increased polarity of the polymer would also make comparative SEC analysis challenging. Nonetheless, GATR-FTIR results presented above provided evidence for chain scission and this is further strengthened by the occurrence of depolymerization during the post-exposure bake step (vide infra).

Patterning Performance and Evidence for Depolymerization

Initially, patterning performance of Polymer B1 (see Table 1) was assessed using 193 nm interference lithography. The process involved exposing different regions on a wafer to a range of doses, employing a PEB at 120 °C and development with a standard aqueous base solution (2.38% TMAH_(aq)). Under these conditions, 150 nm lines and spaces could be resolved at 170 mJ cm⁻² [see Fig. 5(a)]. Qualitatively, the LER was high, but could not be quantified due to poor image contrast. Clearly, the sensitivity of the system was also poor.

Valerials Views To enhance the sensitivity of this polymer, 15 wt % of acridine, a known sensitizer,⁷⁴ was added to the formulation. Interestingly, addition of acridine only marginally increased the absorbance at 193 nm by 0.1 μ m⁻¹ (to 3.68 μ m⁻¹), although a peak with a maxima at 250 nm was observed to appear (see Supporting Information Fig. S3). However, the sensitivity of the formulation at 193 nm was found to significantly improve. For example, Figure 5(b) shows that 1:1 150 nm lines could be resolved at a dose of 110 mJ cm^{-2} (120 °C PEB), which is an improvement of 60 mJ cm^{-2} compared to the performance without acridine. One cause of the increase in sensitivity is likely to be due to energy transfer from excited acridine molecules to the nitrobenzyl groups. However, it is also worth noting that patterning was not observed in the dose range used when the PEB step was omitted. This indicates that increased depolymerization is occurring in the irradiated regions during the PEB step and may be due to the acridine acting as a chain transfer agent. This result also shows that the molecular weight switch is contributing to the sensitivity of the resists.

To investigate the PEB effect further, the effect of 193 nm dose on line width was investigated for PEB temperatures of 120 and 130 °C (Fig. 6). At both temperatures the line width decreases with increasing dose. The reason for this is that the deposition of photons in the resist is non-uniform. Specifically, the intensity of light varies sinusoidally across the wafer, because by nature interference lithography occurs at the diffraction limit. A similar intensity variation can also be observed for lens-based manufacturing tools, because they also operate at the diffraction limit when patterning at high



FIGURE 6 Plots of line width (by 193 nm interference lithography) versus dose for PEB temperatures of 120 (filled circle) and 130 °C (crossed open square). The solid line is the linear regression for the 120 °C PEB data series ($r^2 = 0.89$, slope = -0.8 ± 0.2 nm cm² mJ⁻¹); the dotted line is the linear regression for the 130 °C PEB data series ($r^2 = 0.97$, slope = -1.3 ± 0.1 nm cm² mJ⁻¹).

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FIGURE 7 Plots of LER versus normalized dose obtained following 193 nm interference lithography (0.32 NA) after development with aqueous TMAH (2.38 wt %) (a) for Polymer B1 with added acridine (15 wt %) using a 120 °C PEB step (filled circle), 130 °C PEB step (crossed open square), and (c) a commercial 193 nm photoresist.

resolution. This variation in light intensity generates chemical gradients in the latent image formed in the resist film.⁷⁵ When the wafer is treated with developer, the soluble regions of polymer are selectively removed to reveal a physical pattern. There are regions of the remaining polymer film that have been exposed to light, but the local dose is insufficient to cause a solubility switch. However, when the total dose is increased, the chemical gradient formed changes, decreasing the observed line width after development. A similar decrease in line width was also observed as a function of increasing dose for a PAG-based commercial photoresist (see Supporting Information Fig. S4). This decrease of line width with increasing dose can be useful for double patterning,⁷⁶ a multistep process that is used to achieve high resolution patterning at resolutions well below the diffraction limit.

Also of note in Figure 6 is the difference in the gradients of the lines of best fit for the 120 and 130 °C data series, which are -0.8 ± 0.2 and -1.3 ± 0.1 nm cm² mJ⁻¹, respectively. The gradient quantifies the amount of line-width shrinkage per unit dose for the different PEB temperatures. The difference in the gradients can be attributed to the different rates of depolymerization of the poly(olefin sulfone) backbone at the two different PEB temperatures. Further evidence for depolymerization was obtained by comparing the GATR spectra of thin films of Polymer B that had been irradiated to a dose of 100 mJ cm⁻² and then annealed to 120 $^{\circ}$ C, where a decrease of sulfone and olefin repeat unit peaks was observed (see Supporting Information Fig. S3). A decrease in both peaks occurs as a result of the volatilization of both species at the elevated temperatures experience during the PEB step. Previously, the inclusion of certain absorbing comonomers, such as allyl benzene, has been shown to inhibit depolymerization.³⁴ Observing a depolymerization effect here indicates that absorbing groups such as nitrobenzyl esters can be included without inhibiting the depolymerization process. Consequently, gains in sensitivity are possible during a PEB step when appropriate absorbing units are selected.

To determine how the depolymerization step influences the quality of patterning, the LER values were determined as a function of dose and PEB temperature. Figure 7(a) shows plots of LER as a function of normalized dose for PEB temperatures of 120 and 130 °C. For the 130 °C PEB temperature, LER clearly decreases with increasing dose, while for the 120 °C PEB temperature this was less pronounced, although LER is significantly lower at the highest dose. This behavior differs from that observed for a conventional 193 nm PAG-based photoresist, for which the LER remains essentially unchanged with increasing dose [Fig. 7(b)]. It is hypothesized that LER decreases with increasing dose for Polymer B1 because two orthogonal chemical gradients are established upon irradiation. The first is a gradient of carboxylic acids that are formed due to photodeprotection of the nitrobenzyl esters, and the second is a gradient of chainscissioned polymer chains. The carboxylic acids should be unaffected by the PEB, however, the polymer chains that have undergone chain scission during irradiation will have radicals present that will initiate depolymerization on heating. Higher temperatures result in increased depolymerization.⁵⁰ The observation of decreased LER and increased rates of line-width shrinkage at higher PEB temperatures demonstrates that depolymerization can play a role in tuning the lithographic performance of these materials. The difference between the dose dependence of LER for the poly(olefin sulfone) and chemically amplified resists (CARs) may be due to the inherent differences in the physical and chemical processes involved. CARs rely on the catalytic deprotection of hydrophobic esters by a strong acid to yield hydrophilic carboxylic acids. Diffusion of the acid catalyst is a significant contributor to LER values.^{13,15} On the other hand, depolymerization of poly(olefin sulfones) is a radical process, in



FIGURE 8 Top-down SEM micrographs of approximately 32 nm trenches patterned in (a) Polymer B1, (b) Polymer D (PMMA), (c) Polymer C with 8.41 wt % triphenyl sulfonium triflate, and 1.44 wt % trioctyl amine using EBL.

which the small molecule products (sulfur dioxide and alkene) are non-radical, making their diffusion unimportant. Furthermore, depolymerization is initiated by radicals on the polymer chain, and can involve chain transfer of radicals between polymer chains. These processes are controlled by the dynamics of the polymer chain, as well as the ceiling temperature of the polymer. The length scales involved should be much less than those in PAG diffusion. Hence, the depolymerization reactions will not significantly spread beyond the regions of polymer that have been exposed to light and this is a possible reason why reduced LER was observed under certain conditions.

High Resolution Patterning Performance

EBL was used to test the high resolution patterning performance of Polymer B1. EBL can also be used as a good model for EUV lithography, because when EUV photons (13.5 nm, 92 eV) interact with a polymer, secondary electrons are responsible for the photo-induced chemical changes in the photoresist.⁷⁷ In addition, both EBL and EUVL are conducted under high vacuum conditions. EBL is extensively used in the manufacture of photomasks,² and multiple electron beam approaches⁷⁸ have also been proposed as alternative next generation lithography platforms. Figure 8 shows the topdown SEM micrographs for EBL patterning of trenches with a resolution of approximately 32 nm for Polymer B1 (30.5 nm trenches), Polymer D (PMMA, a commonly used e-beam resist; 33.6 nm trenches), and Polymer C, an open source EUVL resist polymer (32.6 nm trenches) (see Fig. 1 and Table 1 for compositions). The poly(olefin sulfone) and PMMA had comparable LER values of 2.7 \pm 0.6 nm and 3.0 \pm 0.2 nm, respectively, while the open source EUVL resist formulation (Polymer C) had a much higher LER of 7.4 \pm 0.9 nm. The LER value for this EUVL resist formulation is similar to values reported in the literature for patterning using EUVL.⁷⁹ Note that the minimum LER typically observed for optimized PAG-based EUVL resists, is approximately 4 nm.⁸⁰ The results here indicate that chain-scissioning resists can achieve much better LER values than standard resists for high resolution patterning. This is because the resists reported here do not rely on diffusion of a photoacid to cause the switch in polymer solubility. The performance of Polymer B1 was comparable to that of PMMA, however, an advantage of Polymer B1 was compatibility with aqueous

base development, which is better suited to manufacturing tools and more environmentally friendly.

ARTICLE

CONCLUSIONS

A novel photoresist platform based on a poly(olefin sulfone) polymer backbone functionalized with pendant nitrobenzyl esters was synthesized and its performance examined. The results from GATR FTIR and UV spectroscopic ellipsometry of the polymer thin films before and after 193 nm irradiation were consistent with the polymer undergoing both chain scission and also photodeprotection of the hydrophobic nitrobenzyl ester to yield hydrophilic carboxylic acids that were soluble in aqueous base. Following irradiation, depolymerization was also observed during an annealing step that served to increase the sensitivity of the resists. Patterning was possible using 193 nm interference lithography during which sensitivity increased as a result of using a photosensitizer (acridine). Depolymerization of the polymer was found to improve the LER during patterning when higher doses were used. High resolution patterning was carried out using EBL. While sensitivity could still be increased, LER was superior to an open source EUVL resist that used PAG chemistry. The patterning performance was comparable to PMMA, but with the advantage that aqueous developers could be used.

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