Photogenerated Acid-Catalyzed Formation of Phosphonic/Phosphoric Acids by Deprotection of Esters in Polymer Films

Marcia L. Schilling,* Howard E. Katz,* Francis M. Houlihan,* Janet M. Kometani, Susan M. Stein, and Omkaram Nalamasu

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

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ABSTRACT: A new class of photodefinable polymers based on phosphonic acid esters has been developed. Photogenerated acid catalysts convert the esters to phosphonic acids in the exposed regions of films during postexposure bake. These phosphonic acids, in addition to providing the base solubility necessary for positive-tone development, are also uniquely capable of binding metal ions and cations from solution. Preliminary lithographic evaluations indicate that these polymers generally show high contrast (~10), good sensitivity, low volume loss (<15%), and the potential for submicron resolution. More importantly, the patterned deposition of refractory metal ions has also been demonstrated, which could be useful for circuit fabrication via at-the-surface imaging schemes.

Introduction

The chemisorption of species from solution onto patterned polymer surfaces is of increasing interest for a variety of developing technologies. For example, at-the-surface imaging is being considered to achieve 0.1-μm lithography.[1] This process would involve formation of a refractory etch mask via selective surface binding of metal-containing compounds from solution. For example, zirconium/organodiphosphonate and pyrophosphate multilayers provide substantial etch resistance to underlying polymer films.[2] Growth of these multilayers was initiated by phosphorylation of hydroxyl groups in the polymer with phosphorus oxychloride and subsequent binding of Zr^{4+} ions to the phosphorylated polymer. Pattern definition in this scheme would depend on photogeneration or destruction of the hydroxyl groups, followed by an in situ phosphorylation step. Direct photogeneration of phosphonic acid groups would constitute a simpler approach to photodefined binding of Zr-rich material to the films.

Several metals, such as nickel, also form excellent reactive ion etch barriers. Metal film deposition for this purpose, as well as for lower resolution applications such as conductive lines, may be carried out by electroless plating. Current schemes for the patterned deposition of electroless metal[3] require many wet chemical steps and employ differently functionalized polymers for pattern formation by positive development and plating initiation, making them inappropriate for surface imaging. These schemes would be more attractive if one polymer could serve both purposes.

In addition, color filters for displays are currently produced by depositing and patterning films of the individual colors as pigmented photoresists or by the repetition of sequences that include dying, photo-crosslinking, and development of gelatin films.[4] These processes are cumbersome because the photopatterning and dye binding involve different functional groups and could be improved with photoselective chemisorption techniques.

The phosphonic acid group (PO_3H_2) confers unique chemical properties to materials.[5] It is an unusually strong ligand for transition-metal ions over a wide pH range. It ionizes readily to the conjugate mono- or dibase, either of which can bind cations from solution. This binding capability may be useful in the applications described above. Polymers containing the phosphonic acid group are known[6] but have not been photopatterned. Conversely, certain monomeric phosphonate esters have been photodeprotected in solution.[7] However, these transformations have quantum efficiencies that are insufficient for applications requiring high lithographic sensitivity.

One means of improving the sensitivity of a photochemical process is to employ chemical amplification, which involves the formation of a catalyst from a photoacid generator (PAG).[8] Generally, the acidic species formed catalyzes many subsequent thermal chemical events, increasing the overall quantum efficiency of the photoreactions. Typical resist polymers incorporate acid labile groups, such as *tert*-butyl or *tert*-butoxycarbonyl, which are removed selectively in the exposed regions of the polymer film to deprotect hydroxyl groups during a postexposure bake (PEB). The different chemical properties (chemical contrast) of the exposed and unexposed regions of the film can then be utilized in several different ways to develop an image. We reasoned that acid-labile phosphonate esters might undergo similar photoinduced deprotection in a polymer film, providing a means of generating patterned phosphonic acids.

In this paper, we describe a new class of polymers containing the monomers shown below, esters of phosphonic/phosphoric acids. We demonstrate by thermal gravimetric analysis, spectroscopy, and preliminary lithographic evaluation that these polymers can be deprotected by photoacid catalysis. We also report the selective binding of refractory materials and dyes from solution in the exposed regions of a photopatterned polymer film.

Experimental Section

General Procedures. The PAGs, triphenylsulfonium hexafluoroarsenate,[9] and a 2-nitrobenzyl arylsulfonate[10] were prepared as previously described. Thermal data were obtained on a Perkin-Elmer DSC7/TGA7 instrument interfaced with a TAC 7 thermal analysis controller and a DEC 325c data station. FTIR spectra were obtained on a Nicolet 510P spectrometer. NMR spectra were obtained on a Bruker AM360 spectrometer. GPC data were obtained on a Beckman system HPLC with a 10^4-Å μ-Spherogel column with 1,4-dioxane as eluant, with molecular weights referenced to polystyrene

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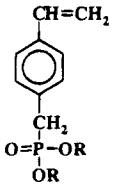
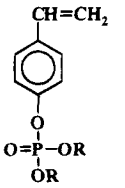


Dialkyl Vinylbenzylphosphonate

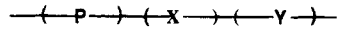
R = t-butyl (DBVBP)
R = isopropyl (DPVBP)



Dialkyl Vinylphenylphosphate

R = t- butyl (DBVPP)
R = isopropyl (DPVPP)

Vinylbenzylphosphonate Polymers



Poly(DBVBP)

Poly(DPVBP)

Poly(DBVBP-co-STY[a])

Poly(DBVBP-co-STY -co- SO_2[b])

Poly(DPVBP-co-STY- co- SO_2)

Poly(DPVBP-co-SO_2)

Poly(DBVBP-co-NMM[c])

Poly(DPVBP-co-NMM)

Poly(DBVPP)

Poly(DPVPP)

a. STY - styrene
b. NMM - N-methylmaleimide
c. SO_2 - sulfur dioxide

standards. ^{1}H NMR and GPC data for the vinylbenzylphosphonate polymers are listed in Table 1.

Di-*tert*-butyl 4-Vinylbenzylphosphonate [DBVBP]. Freshly distilled di-*tert*-butyl phosphite (40 g, 0.2 mol) was dissolved in toluene (40 mL) under a nitrogen atmosphere and cooled to 0 °C in an ice bath. Sodium hydride (7.2 g, 60% in mineral oil, 0.18 mol) was added portionwise over 30 min to the cold toluene solution.[11a] The solution was stirred under nitrogen overnight and allowed to warm gradually to room temperature. The 4-vinylbenzyl chloride (20 g, 0.12 mol) was added,[11b] and the solution was heated to 80 °C and stirred for 3 days under a nitrogen atmosphere. NMR analysis of an aliquot indicated that the reaction was >95% complete. The solution was then cooled to room temperature and washed twice with 50 mL of saturated sodium bicarbonate and then with 50 mL of water. The toluene layer was separated and dried over anhydrous sodium sulfate. The toluene was removed using a rotary evaporator and the remaining oil pumped under vacuum (0.1 mmHg) at 50 °C to remove excess phosphite. ^{1}H NMR showed the product to be DBVBP ($CDCl_3$): δ 1.50 (d, 18H, $C(CH_3)_3$), 3.03 (d, 2H, benzyl H), 5.22 (d, 1H, vinyl H), 5.75 (d, 1H, vinyl H), 6.71 (m, 1H, vinyl H), 7.25 (m, 4H, aromatic H).

Diisopropyl 4-Vinylbenzylphosphonate [DPVBP]. DPVBP was prepared by the procedure described above from diisopropyl phosphite (34 g, 0.2 mol). After the addition of the 4-vinylbenzyl chloride, only 4 h of heating at 80 °C was required to complete the reaction. ^{1}H NMR ($CDCl_3$): δ 1.20 (d of d, 12H, $CH(CH_3)_2$), 3.08 (d, 2H, benzyl H), 4.61 (m, 2H, $CH(CH_3)_2$), 5.22 (d, 1H, vinyl H), 5.75 (d, 1H, vinyl H), 6.71 (m, 1H, vinyl H), 7.30 (m, 4H, aromatic H).

Poly(DBVBP). DBVBP (7 g, 0.023 mol) was dissolved in toluene (100 mL), and nitrogen was bubbled through the solution for 15 min to deoxygenate the solution. An initiator, 2,2′-azobis(2-methylpropionitrile) (AIBN; 150 mg), was added to the solution, and the temperature was increased to 80 °C. The mixture was stirred under nitrogen for 16 h and then cooled to room temperature. The polymer was isolated by precipitation into hexane and purified by dissolution in toluene and reprecipitation in hexane (2×). Five grams of homopolymer were collected. TGA: *tert*-butyl loss, onset 180 °C (34% weight loss; theoretical, 36%). T_g: 83 °C.

Poly(DPVBP). Using a similar procedure, DPVBP (5 g, 0.02 mol) was polymerized in 15 mL of toluene at 80 °C for 5 h with AIBN (0.12 g, 0.7 mmol) as initiator. The polymer was purified by precipitation into hexane. TGA: isopropyl loss, onset 260 °C (30% weight loss; theoretical 30%).

Poly(DBVBP-*co*-styrene) [Poly(DBVBP-*co*-STY)]. DBVBP (10 g, 0.03 mol) and styrene (10 g, 0.09 mol, inhibitor removed) were dissolved in 50 mL of toluene, and argon was bubbled through the solution for 10 min. The mixture was heated to 80 °C, and AIBN (0.5 g, 3 mmol), dissolved in 5 mL of toluene, was added dropwise to the monomers via a slow-addition funnel over 2 h. The reaction mixture was heated overnight and cooled to room temperature. The polymer was isolated by precipitation into methanol (MeOH) and purified by redissolution in toluene and reprecipitation in MeOH (2×) to give 5 g of polymer. TGA: *tert*-butyl loss, onset 170 °C (weight loss 18%; theoretical 18% based on monomer feed). T_g: 90 °C.

Poly(DBVBP-*co*-styrene-*co*-sulfur dioxide) [Poly(DBVBP-*co*-STY-*co*-SO_2)]. DBVBP (15.2 g, 0.05 mol) and styrene (15.2 g, 0.15 mol, inhibitor removed) were combined in a modified Kjeldahl reactor flask and degassed by a freeze–thaw method. In a separate flask, AIBN (0.97 g, 6 mmol) in 15 mL of toluene was degassed and then transferred under vacuum to the reaction flask. Degassed sulfur dioxide (SO_2, 19.2 mL at −78 °C, 0.5 mol) was distilled into the reactor. The reactor flask was sealed and placed into a 60 °C bath for 6.5 h. After cooling to room temperature, the excess SO_2 was removed with stirring under vacuum. The polymer was isolated by precipitation of the reaction mixture into hexane. The polymer was

Table 1. ^{1}H NMR and Molecular Weights of Vinylbenzylphosphonate Polymers

	^{1}H NMR (ppm vs TMS)	M_w
poly(DBVBP)	1.3 (20H, t-Bu, CH_2), 2.4 (1H, CH), 2.8 (2H, benzylic CH_2), 6.3, 6.9 (4H, aromatic)	5 000
poly(DPVBP)	1.0 (2H, CH_2), 1.3 (12H, i-Pr CH_3), 2.5 (1H, CH), 3.0 (2H, benzylic CH_2), 4.5 (2H, i−Pr CH), 6.3, 7.0 (4H, aromatic)	24 500
poly(DBVBP-*co*-STY-*co*-SO_2)	1.1 (5H, CH_2), 1.3 (18H, t-Bu), 2.4 (2.5H, CH), 3.0 (2H, benzylic CH_2), 6.3, 6.9 (11.5H, aromatic)	10 000
poly(DPVBP-*co*-STY-*co*-SO_2)	1.1 (5H, CH_2), 1.3 (12H, i-Pr CH_3), 2.4 (2.5H, CH), 3.0 (2H, benzylic CH_2), 4.5 (2H, i-Pr CH), 6.6, 7.1 (11.5H, aromatic)	9 000
poly(DBVBP-*co*-NMM)	1.4 (20H, t-Bu, CH_2), 1.8 (3H, CH_3), 2.7 (3H, CH, maleimide CH), 2.9 (2H, benzylic CH_2), 6.5, 7.0 (4H, aromatic)	60 000
poly(DPVBP-*co*-NMM)	1.1 (2H, CH_2), 1.3 (12H, i-Pr CH_3), 2.2 (3H, CH_3), 2.7 (3H, CH, maleimide CH), 3.1 (2H, benzylic CH_2), 4.5 (2H, i-Pr CH), 6.6, 7.1 (4H, aromatic)	42 500

purified by redissolution in acetone followed by precipitation into hexane (2×). The purified polymer was dried in a vacuum oven overnight at room temperature to give the terpolymer in approximately 30% yield. TGA: *tert*-butyl loss, onset 125 °C (weight loss 18%; theoretical 21%). T_g: 125 °C. Residual acid was removed by dissolving the polymer in acetone and adjusting the pH to 5 with the dropwise addition of pyridine. The polymer was precipitated into hexane, filtered, and dried. TGA: *tert*-butyl loss, onset 150 °C. Anal. Found: C, 64.89; H, 6.95; P, 5.06; S, 5.95. This best corresponds to a 1:1.5:1 ratio of DBVBP/styrene/SO_2. Calcd: C, 65.7; H, 7.4; P, 5.8; S, 6.0.

Poly(DPVBP-*co*-STY-*co*-SO_2). Using the procedure described above, DPVBP (28 g, 0.1 mol), styrene (30.1 g, 0.3 mol), and SO_2 (39 mL at −78 °C, 1 mol) were reacted in 40 mL of toluene with AIBN (1.98 g, 0.012 mol) as initiator at 60 °C for 5 h. The polymer was isolated by precipitation of the reaction mixture into hexane and purified by redissolution in toluene followed by precipitation into hexane (2×). The purified polymer was dried in a vacuum oven at room temperature to give 13 g of the terpolymer. TGA: isopropyl loss, onset 280 °C. Anal. Found: C, 64.24; H, 6.79; P, 5.63; S, 6.12. Calcd for 1:1.5:1 DPVBP/styrene/SO_2: C, 64.5; H, 7.0; P, 6.2; S, 6.4.

Poly(DBVBP-*co*-*N*-methylmaleimide) [Poly(DBVBP-*co*-NMM)]. DBVBP (5 g, 0.016 mol) and *N*-methylmaleimide (1.8 g, 0.016 mol) were dissolved in 6.5 mL of cyclohexanone with gentle heating in a reaction flask. Nitrogen was bubbled through the solution for 30 min. The reaction mixture was heated to 60 °C, and AIBN (0.05 g, 0.3 mmol) was added. After 2 h at 60 °C, the mixture was cooled to room temperature and allowed to stir for 16 h. The polymer was isolated by precipitation into hexane and purified by redissolution in THF and precipitation in hexane (2×). The polymer was dried in a vacuum oven at room temperature. TGA: *tert*-butyl loss, onset 175 °C (weight loss 23%; theoretical: 1:1 DBVBP/NMM, 26.7%). T_g: ≥175 °C. Anal. Found: C, 60.73; H, 7.51; P, 7.23; N, 3.11. Calcd for 1:1 copolymer: C, 62.69; H, 7.65; P, 7.35; N, 3.32.

Poly(DPVBP-*co*-*N*-methylmaleimide) [Poly(DPVBP-*co*-NMM)]. DPVBP (5 g, 0.02 mol) and *N*-methylmaleimide (1.9 g, 0.02 mol) were dissolved in 15 mL of cyclohexanone with gentle heating in a reaction flask. Nitrogen was bubbled through the solution for 30 min. The reaction mixture was heated to 35 °C, and dodecanethiol[12] (0.14 g, 0.7 mmol) and AIBN (0.12 g, 0.7 mmol) were added in rapid succession. After 2 h of stirring in a N_2 atmosphere at 35 °C, the reaction mixture was cooled to room temperature and the polymer was isolated by precipitation into hexane. The polymer was purified by redissolution of the polymer in tetrahydrofuran (THF) followed by precipitation in hexane (2×). The purified polymer was dried overnight in a vacuum oven at room temperature. TGA: isopropyl loss, onset 258 °C (weight loss 21%; theoretical: 1:1 DPVBP/NMM, 21%). Anal. Found: C, 59.73; H, 7.38; P, 7.53; N, 3.36. Calcd for 1:1 copolymer: C, 61.06; H, 7.17; P, 7.87; N, 3.56.

Poly(di-*tert*-butyl 4-Vinylphenylphosphate) [Poly(DBVPP)]. Poly(4-hydroxystyrene) (1 g, 8.3 mmol) was treated with di-*tert*-butyl diethylphosphoramidite (2.9 g, 0.012 mol) and tetrazole (0.82 g, 0.012 mol) in 50 mL of anhydrous tetrahydrofuran to form poly(di-*tert*-butyl vinylphenylphosphite).[13] After 3 h, the mixture was cooled to −45 °C, and *m*-chloroperbenzoic acid (2.4 g, 0.014 mol) was then added to the solution to form poly(DBVPP). The mixture was allowed to warm to room temperature, and the polymer was precipitated from aqueous sodium sulfite (250 mL), redissolved in acetone (25 mL), and reprecipitated from water (125 mL). TGA: *tert*-butyl loss, onset 120 °C (40% weight loss; theoretical: 37%).

Poly(diisopropyl 4-vinylphenylphosphate) [Poly(DPVPP)]. Poly(4-hydroxystyrene) was treated as described above with diisopropyl diethylphosphoramidite. NMR showed nearly quantitative conversion of the hydroxy groups to diisopropylphosphoryl groups. TGA: isopropyl loss, onset 270 °C (25% weight loss; theoretical: 29%). ^{1}H NMR ($CDCl_3$): δ 1.2 (2H, CH_2), 1.5 (13H, i-Pr CH_3, CH), 4.65 (2H, i-Pr CH), 6.3, 6.9 (4H, aromatic).

Table 2. Resist Formulation and Lithographic Processing Conditions

resist polymer	w/v %, solvent[a]	PAG,[b] wt %	PEB time (min), temp (°C)
poly(DBVBP)	10, EEP	NBAS, 12	1, 60
poly(DPVBP)	10, CH	AsF_6, 12	1, 120
poly(DBVBP-*co*-STY)	15, EEP	NBAS, 12	20, 90
poly(DBVBP-*co*-STY-*co*-SO_2)	10, CH	NBAS, 15	1, 90
poly(DPVBP-*co*-STY-*co*-SO_2)	12.5, CH	AsF_6, 5	1, ≥150
poly(DBVBP-*co*-NMM)	3.3, CH	NBAS, 15	1, 120
poly(DPVBP-*co*-NMM)	15, CH	AsF_6, 15	1, 150

[a] EEP = ethyl 3-ethoxypropionate; CH = cyclohexanone. [b] NBAS = 2-nitrobenzyl arylsulfonate; AsF_6 = hexafluoroarsenate.

Resist Formulation. The polymer and PAG were sequentially dissolved in the appropriate solvent, and the solution was filtered through a series of 1-, 0.5-, and 0.2-μm Teflon filters (Millipore) three times before processing. The compositions of the resist formulation and the processing temperatures used for each polymer are summarized in Table 2.

Lithographic Processing. A silicon wafer was spin-coated with hexamethyldisilazane (HMDS) at 2000 rpm for 2 min. The resist solution was then spin-coated onto the substrate which was baked at the appropriate temperature (Table 2) for 30 s. Most of the films were imaged using a Süss MA56A contact aligner equipped with a Lambda Physik excimer laser operating at 248 nm, followed by a PEB (Table 2). Resist volume loss was evaluated by measuring the film thickness after exposure, and PEB, normalized to the thickness in the unexposed area, using a Nanospec film thickness gauge (Nanometrics, Inc.). The exposed film was developed with 0.26 N tetramethylammonium hydroxide (TMAH) in water.

For patterning films of poly(DPVBP-*co*-NMM) at 248 nm, a GCA XLS stepper (NA = 0.53, 4× reduction optics)/MTI Flexifab hot-plate track lithocell was used. Film thicknesses were determined with a Nanospec/AFT thickness gauge. SEM photomicrographs were obtained with a JEOL scanning electron microscope. No protective overcoat was used during the processing. Silicon wafers were primed with HMDS in an oven (Yield Engineering Systems, Inc.) for 3 min prior to the resist application. The resist was spin-coated at 2500 rpm to provide nominally 7900-Å-thick films. The coated wafers were prebaked at 120 °C/60 s with a PEB at 150 °C/60 s. The films were immersion developed in OPD 262 (0.26 N TMAH) for 60 s.

Zirconium Selectivity. Poly(DBVBP) (10 w/v %) in cyclopentanone was spin-coated (2000 rpm, 2 min) onto a silicon substrate. The substrate was divided into two pieces, and one piece was heated to 180 °C for 10 min in a vacuum oven to deprotect the polymer. Both the protected and deprotected polymer films were then immersed overnight in a 5 mM aqueous solution of zirconium oxychloride at pH 5. The substrates were removed from the solution, washed with deionized water, and spin-dried before XPS analysis to determine the composition of the polymer on the surface of the two substrates.

Patterned Refractory Metal Deposition. A resist solution of poly(DBVBP) was prepared, spin-coated onto a HMDS-treated silicon wafer, and processed (Table 1) without base development. The patterned polymer film was sequentially immersed in three solutions for the electroless plating of nickel onto the exposed regions of the polymer film:[14] first in an aqueous colloidal suspension of tin(II) fluoride (0.017 M; ultrasonicated 10 min) at room temperature for 5 min, then in an aqueous palladium chloride solution (1.5 mM $PdCl_2$, 0.028 M HCl) at room temperature for 5 min, and finally in an electroless nickel bath at 85 °C for 1 min. The electroless nickel bath (Fidelity Chemical Products Corp., electroless solution No. 4685) was prepared and used according to the manufacturer's instructions.

Selective Dye Adsorption. Poly(DPVBP) was spin-coated onto a glass substrate, and the substrate was cleaved in half. One portion was placed on the surface of a hot plate at 275 °C

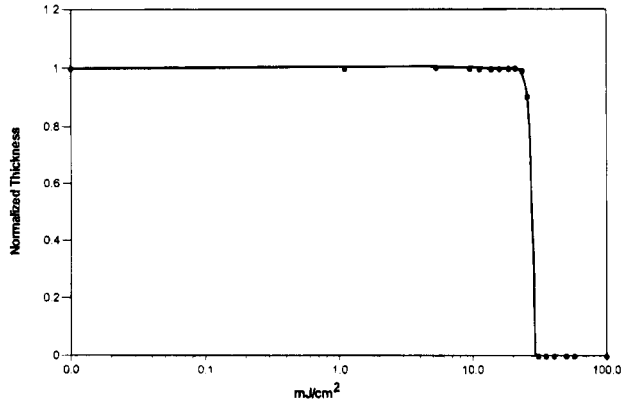


Figure 1. Contrast curve for a resist formulated with poly(DBVBP-*co*-STY-*co*-SO_2) and a 2-nitrobenzyl arylsulfonate PAG after a 1-min PEB at 90 °C and 1 min development in 0.26 N TMAH.

for 1 min in order to deprotect the polymer. The polymer on the other portion of the substrate was not thermally deprotected. Both substrates were then immersed in an aqueous thionin (0.02 w/v %) solution for 5 min. They were then removed, washed with water, and spin-dried.

Results and Discussion

Lithography. Deep UV imaging and conventional base development were carried out on a series of photoresists containing esters of phosphonic acids in order to evaluate patternability and determine processing conditions. Initial experiments were carried out on the homopolymer, poly(DBVBP). Although the T_g is lower than desirable for normal processing (77 °C), imaging and development could be demonstrated after a 1-min PEB at 60 °C. The resist had a clearing dose of 67 mJ/cm^2 for large features and a contrast of 6 with only 6% volume loss. In general, a shrinkage of less than 20% is desirable in order to avoid distortion of pattern features.[15]

A copolymer, poly(DBVBP-*co*-STY), was also prepared which was processed at 90 °C. Base development did not occur with aqueous TMAH alone but required a 20-min PEB and addition of 20% isopropyl alcohol for development. The use of isopropyl alcohol is undesirable for clean room processing.

In order to increase the T_g and processing latitude, poly(DBVBP-*co*-STY-*co*-SO_2) was prepared.[16] The higher T_g (125 °C) was sufficient to allow processing at 90 °C. After a 3-min PEB at 90 °C, the resist was developed with 0.26 N TMAH. The resist had a clearing dose of 22 mJ/cm^2, a contrast of 7 (Figure 1), and a 15% volume loss.

FTIR spectroscopy experiments monitoring the CH stretch band of the *tert*-butyl group at 2978 cm^{-1} were carried out for the three *tert*-butyl phosphonate polymers and a reference sample of poly[[(*tert*-butoxycarbonyl)oxy]styrene], poly(TBS), after irradiation at 248 nm and PEB at 90 °C for varying amounts of time (Figure 2). It was found that acidolytic cleavage of the *tert*-butoxycarbonyl (t-BOC) group follows first-order kinetics, while all three *tert*-butyl phosphonate polymers lose *tert*-butyl groups at a slower rate and follow second-order kinetics (Table 3). This reflects the more sluggish reaction of *tert*-butyl esters as compared to *tert*-butyl carbonates.[17]

Instability of the terpolymer was indicated by a comparison of TGA data for a sample as originally isolated with a sample that had been redissolved in acetone at pH 5 (pH adjusted with pyridine) and

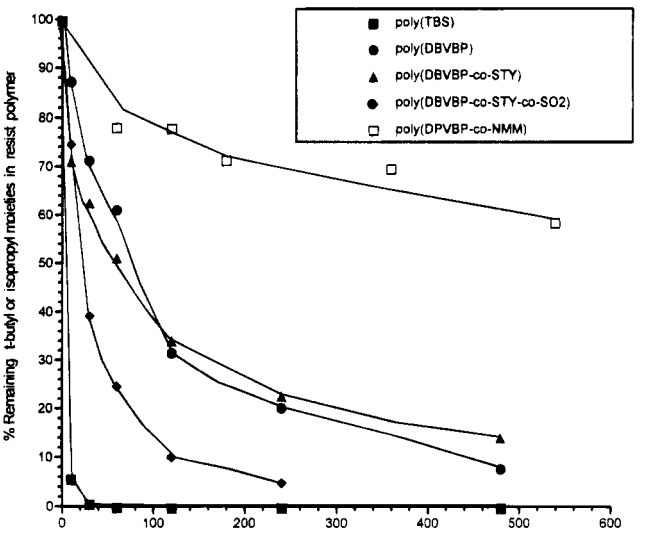


Figure 2. Comparison of the disappearance of alkyl groups in dialkyl phosphonate ester resists (formulated and processed as in Table 2) as a function of bake time, as determined by FTIR.

Table 3. Kinetics of Acidolytic Cleavage

resist polymer	relative rates of acidolytic cleavage	order of rate constant
poly(TBS)[a]	5.5×10^1	first
poly(DBVBP)[a]	1.0	second
poly(DBVBP-*co*-STY)[a]	7.4×10^{-1}	second
poly(DBVBP-*co*-STY-*co*-SO_2)[a]	4.7	second
poly(DPVBP-*co*-NMM)[b]	3.4×10^{-2}	second

[a] Resist formulated with a 2-nitrobenzyl arylsulfonate PAG and exposed to 200 mJ/cm^2 at 248 nm followed by a PEB at 90 °C. [b] Resist formulated with a hexafluoroarsenate PAG and exposed to 200 mJ/cm^2 at 248 nm followed by a PEB at 120 °C.

reprecipitated. After base-washing, the onset of *tert*-butyl loss was increased from 125 to 150 °C, suggesting the presence of residual acid in the isolated polymer. Repetition of the TGA measurements on base-washed polymer which had been aged for 3 months at room temperature shows the onset of weight loss shifting toward lower temperatures. The sulfone terpolymer decomposes slowly, releasing a sufficient quantity of acid to deprotect the phosphonic acid.

The incorporation of maleimide units into a polymer backbone has been shown to increase thermal stability and reduce weight loss.[12,18] A processed film of poly(DBVBP-*co*-NMM) was completely dissolved by 0.26 N TMAH in 5 s. A similar film that was unexposed to radiation did not dissolve under identical conditions, indicating that copolymerization of VBP monomers with *N*-methylmaleimide does provide thermal stability. This is in contrast to unexposed films of the sulfone terpolymer which dissolved after aging in the dark.

Another means of improving thermal stability is to change the acid-labile alkyl group on the phosphonate/phosphate esters. Isopropyl groups have been previously used instead of *tert*-butyl groups in chemical amplification processes where increased thermal stability was required.[19] We prepared several VBP polymers with isopropyl protecting groups in order to evaluate the feasibility of using these groups for lithographic imaging. The homopolymer, poly(DPVBP), has an onset for ester cleavage at 260 °C, 80 °C higher than that of the corresponding *tert*-butyl polymer. In the presence of acid, this is lowered to 170 °C. Initial lithographic experiments, using sulfonate ester PAGs in the resist formulation, showed that the produced acids are not

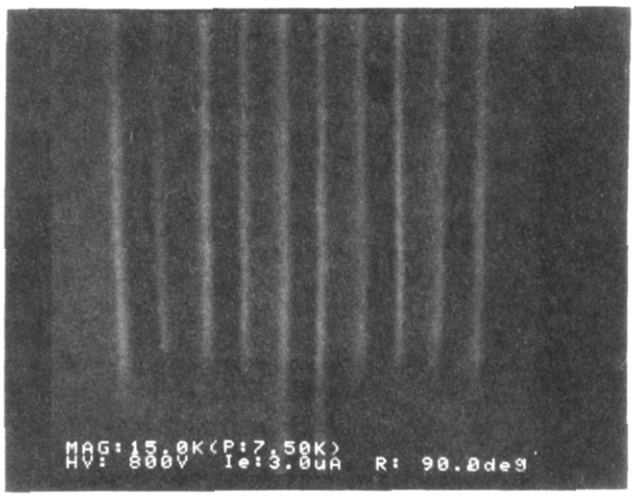


Figure 3. SEM photomicrograph of 0.8 μm line/1.1 μm spaces in 0.8-μm thickness of a poly(DPVBP-*co*-NMM) resist film. The resolution dose was 60 mJ/cm^2.

strong enough to catalyze isopropyl loss under reasonable processing conditions, but photopatterning can be done using hexafluoroarsenate salts. At 120 °C, a PEB of 12 min was required to remove 10% of the film thickness, corresponding to the removal of one isopropyl group from the diester. The film was developed with 0.26 N TMAH in <1 min. Longer heating times gave no additional thickness loss, indicating that the phosphonate monoester is stable. At shorter PEB times, development was poor, with film adhesion being lost before development. At 140 °C, a 1-min PEB gave development comparable to that at 120 °C for 12 min.

Films of poly(DPVBP-*co*-NMM) were patterned with a deep UV lithocell. Optical and SEM examination of the developed films revealed at least 0.8-μm resolution in 0.8-μm thickness at a dose of 60 mJ/cm^2 (Figure 3). The PEB induced shrinkage was 7–8%. Sub-0.5-μm features were distorted with the current unoptimized processing conditions, suggesting that the bake and development parameters need adjustment. However, it appears that further optimization of materials and processing should be able to give sub-0.5-μm resolution.

The acidolysis of poly(DPVBP-*co*-NMM) was also investigated by FTIR spectroscopy, monitoring the C–H stretch band of the isopropyl group at 2990 cm^{-1} after irradiation at 248 nm and a PEB at 120 °C for varying amounts of time (Figure 2). The cleavage of isopropyl groups follows second-order kinetics (Table 2), as was observed for the *tert*-butyl esters. However, because of the lower stability of the isopropyl cation relative to the *tert*-butyl cation, it is understandable that the rate of acidolysis of isopropyl groups is at least an order of magnitude lower, despite the use of a higher PEB temperature and a stronger acid (hexafluoroarsenic acid).

Poly(DPVBP-*co*-STY-*co*-SO_2) was found to be more stable than the analogous *tert*-butyl polymer. However, the conditions necessary for deprotection of the isopropyl groups (hexafluoroarsenate PAG, PEB ≥150 °C) were extreme enough to make the polymer insoluble in base. While this insolubility precludes use of this polymer for conventional lithography, it may have some utility for binding applications.

In order to demonstrate that analogous deprotection chemistry occurs with dialkyl arylphosphates, thermal gravimetric analyses were carried out on poly(DBVPP) and poly(DPVPP). The weight losses were in agreement with cleavage of the O–alkyl bonds as opposed to the O–aryl bond. The poly(DPVPP) showed an onset for ester loss at the same temperature as the analogous phosphonate ester; however, the *tert*-butyl phosphate was less stable than the corresponding phosphonate.

Using conventional base-development techniques, we have shown that poly(DPVBP-*co*-NMM) exhibits the best lithographic behavior of all of the vinylbenzylphosphonate polymers that we have prepared. Reaction of a vinylbenzylphosphonate ester with *N*-methylmaleimide yields a copolymer with the thermal stability necessary for lithographic processing. In addition, the use of the more stable isopropyl ester in place of the *tert*-butyl ester provides added stability. Deprotection of only one isopropyl group is sufficient for development and minimizes volume loss. Formulations of this copolymer with triphenylsulfonium hexafluoroarsenate give a resist which can be developed with submicron resolution.

Zirconium Selectivity. In order to determine the zirconium binding selectivity for the deprotected polymer as compared to the protected polymer, two films of poly(DBVBP), as spin-coated and as thermally deprotected, at 180 °C, respectively were simultaneously immersed in aqueous zirconium oxychloride overnight. After washing and spin drying, the surfaces of the polymer films were analyzed by XPS to determine the amount of adsorbed zirconium. The deprotected polymer adsorbed 7.34 atom % zirconium as compared to 1.44 atom % zirconium for the protected polymer film. Clearly, zirconium binds preferentially to the phosphonic acid groups of the deprotected polymer.

Patterned Refractory Metal Deposition. In the following experiment, we show that the *tert*-butyl phosphonate group, already determined to be patternable in the conventional sense, can be photogenerated acid-converted to a site at which electroless nickel can be plated. Resist films of poly(DBVBP) were imaged and postexposure baked, and the pattern was developed using an electroless nickel deposition process[14] initiated by colloidal tin(II) fluoride and catalyzed by palladium. The thickness of the nickel layer deposited on the exposed regions of the polymer was approximately 730 Å as measured by X-ray fluorescence. Only traces of nickel (13 Å) were deposited on the unexposed portions of the polymer. Although the selectivity was good, the resolution of the image (1 μm) was limited by the grain size of the deposited nickel. The polarity of the polymer film is important for initiator binding. Thermally deprotected films of poly(DBVBP-*co*-STY) were found to be too hydrophobic for adsorption of the tin colloid, and no metal deposition occurred.

Selective Dye Adsorption. Films of poly(DPVBP), as spin-coated and thermally deprotected at 275 °C, were simultaneously immersed in an aqueous thionin solution for 5 min. The substrate with the deprotected polymer was a dark purple color, indicating dye absorption (absorbance: 2 μm^{-1} at 580 nm). Rinsing does not remove any of the dye, suggesting that it may be possible to pattern with several colors on a single polymer film, making this process useful for color filter applications. The protected polymer showed no evidence of dye adsorption. Dye was also found to selectively absorb in the exposed regions of a patterned photoresist film with a boundary sharpness of less than a micron based on optical microscopy.

Conclusions

The selective, photoinitiated deprotection of phosphonate esters to form phosphonic acids in polymer films has been described. The process occurs in several types of styrene copolymers with good sensitivity and contrast and with low absorbance and shrinkage. Indications of fine resolution have been observed, and means of improving the resolution of positive-developed patterns are available, including the incorporation of moderately polar comonomers[20] and removal of low molecular weight fractions. Most importantly, chemical capabilities, unique to phosphorus acids, are observed in the photodefined regions, opening new possibilities for the finely resolved deposition of refractory inorganics, metals, and dyes. In addition to the microfabrication of silicon-based devices, the chemistry thus demonstrated may be applicable to the fabrication of circuits by additive metallization or to color filters.

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References and Notes

(1) (a) Nalamasu, O.; Baiocchi, F. A.; Taylor, G. N. In *Polymers in Microlithography*; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; ACS Symposium Series 412; American Chemical Society: Washington, DC, 1989; pp 189–209. (b) Calvert, J. M.; Dulcey, C. S.; Peckerar, M. C.; Schnur, J. M.; Calabrese, J. H.; Sricharoenchakikit, P. *Solid State Technol.* **1991**, *34* (10), 77.

(2) Taylor, G. N.; Hutton, R. S.; Stein, S. M.; Katz, H. E.; Schilling, M. L.; Putvinski, T. M. *Microelectron. Eng.* **1994**, *23*, 259–62.

(3) Sricharoenchaikit, P. *J. Electrochem. Soc.* **1993**, *140*, 1917–21.

(4) (a) Endo, A.; Otera, S.; Chiba, N.; Saeki, H.; Suzuki, S.; Tsubouchi, N. *J. Imaging Sci.* **1991**, *35*, 252–8. (b) Latham, W. J.; Hawley, D. W. *Solid State Technol.* **1988**, *31*, 223–6.

(5) Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420–7.

(6) (a) Muray, B. J. *J. Polym. Sci., Part C* **1967**, *16*, 1869–86. (b) Furukawa, J.; Kobayashi, E.; Wakui, T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, *20*, 551–4. (c) Hartmann, M.; Hipler, U.-Ch.; Carlsohn, H. *Acta Polym.* **1980**, *31*, 165–8. (d) Letourneur, D.; Douzon, C.; Jozefowicz, M. *J. Polym. Sci., Part A* **1991**, 1367–77. (e) Penczek, S.; Pretula, J. *Macromolecules* **1993**, *26*, 2228–33.

(7) (a) Givens, R. S.; Kueper, L. W., III *Chem. Rev.* **1993**, 55–66. (b) Furata, T.; Torigai, H.; Osawa, T.; Iwamura, M. *Chem. Lett.* **1993**, 1179–82.

(8) (a) Ito, H.; Willson, C. G. In *Polymers in Electronics*; Davidson, T., Ed.; ACS Symposium Series 242; American Chemical Society: Washington, DC, 1984; pp 11–23. (b) Ito, H.; Willson, C. G.; Frechet, J. M. J. U.S. Patent 4,491,628, 1985. (c) Willson, C. G.; Ito, H.; Frechet, J. M. J.; Tessier, T. G.; Houlihan, F. M. *J. Electrochem. Soc.* **1986**, *133*, 181–7.

(9) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977–99.

(10) Houlihan, F. M.; Neenan, T. X.; Reichmanis, E.; Kometani, J. M.; Chin, T. *Chem. Mater.* **1991**, *3*, 462–71.

(11) (a) Maruszewska-Wieczorkowska, E.; Michalski, J. *Rocz. Chem.* **1964**, *38*, 625–33. (b) Redmore, D. *J. Org. Chem.* **1969**, *34*, 1420–5.

(12) (a) Turner, S. R.; Anderson, C. C.; Kolterman, K. M. *J. Polym. Sci., Part C: Polym. Lett.* **1989**, *27*, 253–8. (b) Galvin, M. E.; Reichmanis, E.; Nalamasu, O. U.S. Patent pending.

(13) Kitas, E. A.; Knorr, R.; Trzrciak, A.; Bannwarth, W. *Helv. Chim. Acta* **1991**, *74*, 1314–28.

(14) Lowenheim, F. A., *Electroplating*; McGraw-Hill: New York, 1978; pp 389–425.

(15) Reichmanis, E.; Thompson, L. F.; Nalamasu, O.; Blakeney, A.; Slater, S. *Microlithogr. World* **1992**, *1*, 7–14.

(16) Tarascon, R. G.; Reichmanis, E.; Houlihan, F. M.; Shugard, A.; Thompson, L. F. *Polym. Eng. Sci.* **1989**, *29*, 850–5.

(17) MacDonald, S. A.; Willson, C. G.; Frechet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151–158.

(18) (a) Brunswold, W. R.; Conley, W. E.; Crockatt, M.; Iwamota, N. E. U.S. Patent 4,931,397, 1990. (b) Brunsvold, W. R.; Chow, M.; Conley, W. E.; Crockatt, D. M.; Frechet, J. M. J.; Heffron, G. J.; Ito, H.; Iwamoto, N. E.; Willson, C. G. U.S. Patent 4,939,070, 1990. (c) Wu, C.; Mooring, A. M.; McFarland, M. J.; Osuch, C. E.; Yardley, J. T. U.S. Patent 4,968,-581, 1990.

(19) Brunsvold, W. R.; Conley, W. E.; Crockatt, D. M.; Iwamoto, N. E. *Proc. SPIE* **1989**, *1086*, 357–62.

(20) Kometani, J. M.; Galvin, M. E.; Heffner, S. A.; Houlihan, F. M.; Nalamasu, O.; Chin, E.; Reichmanis, E. *Macromolecules* **1993**, *26*, 2165–70.

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