Photogenerated Base in Resist and Imaging Materials: Design of Functional Polymers Susceptible to Base Catalyzed Decarboxylation

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Received April 14, 1997. Revised Manuscript Received August 5, 1997[⊗]

A chemically amplified resist material consisting of poly[2-cyano-2-(*p*-vinylphenyl) butanoic acid] and bis[[(2-nitrobenzyl)oxy]carbonyl]hexane-1,6-diamine has been designed and tested in negative and positive tone imaging. The resist operates on the principle of base-catalyzed decarboxylation. Amine generated by exposure to UV radiation catalyzes the thermal loss of carbon dioxide from the polymer side chain thereby changing the solubility of the resist film in aqueous base developer. Image reversal is accomplished by in situ silylation of the exposed and thermolyzed film followed by dry development using an oxygen plasma. The resist shows high sensitivity to deep UV irradiation, ca. 10 mJ/cm^2, while image contrast is excellent.

Introduction

Chemically amplified imaging processes[1] have been increasingly integrated into resist systems because of their high sensitivity, excellent resolution, and ability to operate in the deep-UV. This concept was first demonstrated with the development of the poly (*t*-BOC−styrene) family[2] of imaging materials. This resist system utilized the photochemical formation of a strong acid to promote the catalytic thermolysis of the pendent carbonate groups in a process that drastically changed the solubility of the matrix polymer. Since this development, commercial implementation of this and analogous systems based on acid-catalyzed cross-linking[3] has been realized. Numerous resist systems based on these concepts, and therefore susceptible to cationic processes,[4] have since been investigated.

Despite the widespread use of base catalysis in organic chemistry, the design of analogous resist systems relying on the photochemical liberation of a basic species has received far less attention. This was due in part to the absence of functional sources of photogenerated base. Early work[5] in this area focused on the photolysis of cobalt−amine complexes in the formation of ammonia and the subsequent insolubilization of matrix polymers bearing pendent epoxide groups. More recently, however, a number of strategies[6] have been developed that enable the photogeneration of bases stronger and less volatile than ammonia, mainly amines and diamines, from photoactive carbamate precursors. The design of these materials offers the possibility of generating a wide range of amines in a reactive form while also maintaining an effective quantum efficiency. Some of these photobase generators have now been used in a variety of lithographic and other processes including for example the development of a photopatternable polyimide through an amine-catalyzed imidization process[7] that creates a patterned change in solubility in a precursor coating. Interest in this approach to imaging materials has led to reports of similar strategies[8] toward photogenerated basic species, including hydroxide and alkoxide ions,[9] as well as the development of various

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

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S0897-4756(97)00220-2 CCC: $14.00

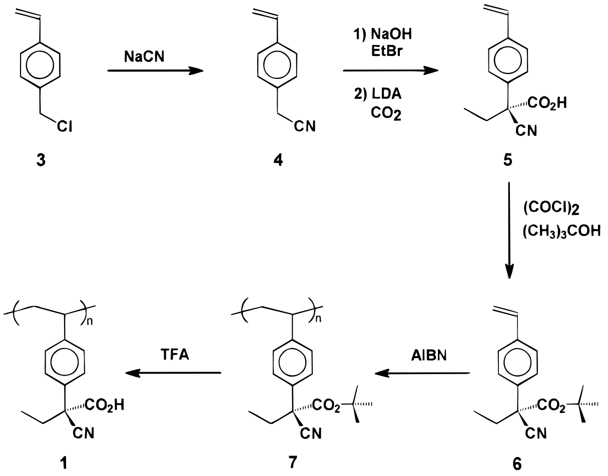
polymeric imaging systems[10] utilizing this mode of phototriggered stimulus.

After considering a number of base-catalyzed processes which might be incorporated into an imaging system, we chose to investigate a decarboxylation[11] reaction. Decarboxylation of carboxylic acids and their derivatives have been well studied in synthetic organic chemistry and biochemistry. This reaction is attractive in terms of an imaging process because in the presence of amines the decarboxylation often takes place at temperatures well below the thermal decomposition temperature of the free acid. In such systems, the rate of the decarboxylation reaction may be correlated to the stability of the carbanion formed[12] upon loss of carbon dioxide. This type of reaction is suitable for photopatterning processes as it is accompanied by a large change in the polarity of the medium undergoing decarboxylation; this is easily translated into differential dissolution for imaging purposes. The decarboxylation reaction, which occurs without excessive loss of weight since only carbon dioxide is evolved, affords a product that is insoluble in aqueous base while the unexposed areas of the film retain solubility in this development medium providing a negative tone image. Preferential loss of the carboxylic acid moieties from the exposed areas within the functionalized polymer film may also enable reversal of the image tone obtained via wet development through the use of an alternative dry development process. To investigate the feasibility of amine catalyzed decarboxylation processes in the context of imaging materials, we selected poly(2-cyano-2-(*p*-vinylphenyl)butanoic acid) (**1**) as the base-sensitive polymer matrix. This paper reports the use of this novel functional polymer and photogenerated base in the design of a chemically amplified resist material.

Results and Discussion

Since it is well-known[12] that the ease of decarboxylation of carboxylic acids is related to the stability of the carbanion formed by the loss of CO$_2$, 2-cyano-2-phenylpropanoic acid (**2**)[13] was selected as a model compound. This molecule, which includes both a cyano and a phenyl substituent α to the incipient carbanionic site, should be nearly ideal for our study since its phenyl ring can be easily elaborated into a polystyrene backbone. The thermogravimetric analysis (TGA) of carboxylic acid **2** demonstrates that the material is stable to elevated temperatures as the thermally induced decarboxylation reaction only occurs above 160 °C. However, when acid **2** is mixed with 1,10-diaminodecane, an amine selected for its relatively low volatility, the decarboxylation temperature is reduced significantly. Addition of as little as 1 mol % of this amine to **2** lowers the decomposition temperature by 30 °C. This simple model study clearly suggests that a similarly functionalized polymer matrix may possess both the thermal stability necessary for adequate shelf life and the reactivity needed for application as a resist in a photo-base-catalyzed decarboxylation reaction.

Scheme 1



Preparation of the Carboxylic Acid Functionalized Polymer. The synthetic route used for the preparation of poly(2-cyano-2-(*p*-vinylphenyl)butanoic acid) (**1**) is illustrated in Scheme 1. The starting material was commercial 4-vinylbenzyl chloride (**3**), which was converted to 4-vinylbenzyl cyanide (**4**) via nucleophilic substitution,[14] then alkylated in the benzylic position with ethyl bromide under basic conditions.[15] This alkylation was done to remove the acidic benzylic hydrogen which might create problems in the subsequent radical polymerization of the highly activated monomer. During this alkylation step, a relatively small amount of dialkylation product was also formed; however, it was carried through to the next step since it could be separated easily from the desired product **5**. Introduction of the carboxylic acid functionality of **5** was accomplished via deprotonation of the monoalkylated product with lithium diisopropylamide followed by quenching with dry ice. The crude product was extracted with dilute base which was then neutralized to provide the desired carboxylic acid functionalized styrenic monomer **5** free of any contamination from the bisethylated side product. Initial attempts at the free radical polymerization of **5** using AIBN as a radical source led to the isolation of a polymer which contained no carboxylic groups. Examination of the thermal stability of **5** in the absence of AIBN revealed that decarboxylation of this monomer occurs slowly at 70 °C

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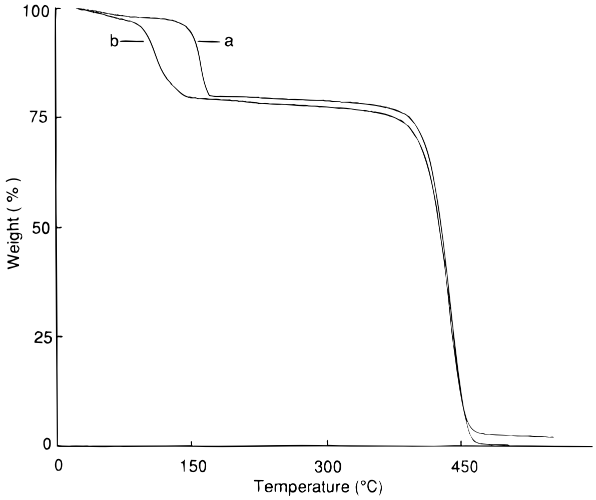
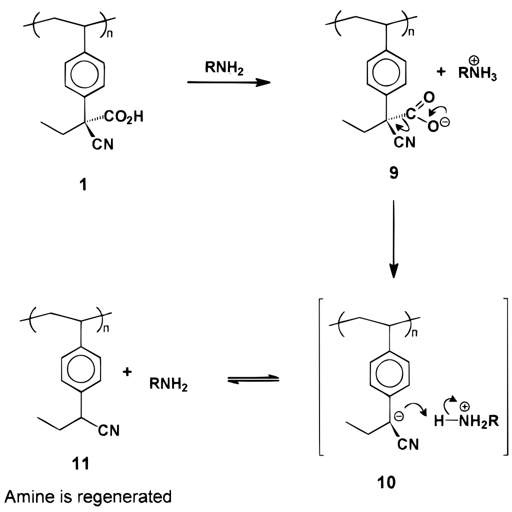


Figure 1. TGA curve for poly(2-cyano-2-(*p*-vinylphenyl) butanoic acid) (**1**): (a) without added amine (b) with 1.5 mol % of 1,10-diaminodecane added.

in toluene. This decomposition problem was remedied by protecting the carboxylic acid funtionality[16] as the *tert*-butyl ester (**6**) prior to polymerization. Radical polymerization of **6** was then carried out under standard conditions to provide the protected polymer **7**. Deprotection of the ester groups of **7** was achieved by reaction with trifluoroacetic acid at room temperature[17] to afford the free carboxylic acid-functionalized polymer **1**.

Thermal Stability of the Carboxylic Acid-Functionalized Polymer. For polymer **1** to function properly as an imaging material, it must be sufficiently stable to the processing conditions used in the film casting and image formation process. These conditions typically include baking at temperatures ranging between 100 and 130 °C over a period of minutes. The polymer must also be reactive enough to undergo amine-catalyzed decarboxylation at temperatures well below the uncatalyzed thermal decomposition temperature to provide maximum contrast between the exposed and unexposed areas of the polymer film. Thermogravimetric (TGA) analysis of polymer **1** reveals a two-step decomposition (Figure 1) in which the initial weight loss, corresponding to loss of carbon dioxide as a result of the decarboxylation reaction, is then followed by additional degradation of the polymer. The results of the TGA analysis suggest that the thermally induced loss of carbon dioxide from polymer **1** does not effectively take place until the polymer is heated above 140 °C (curve a). However, the transition is not as sharp as that seen for model compound **2**, suggesting that some decomposition of the polymer may take place below this temperature. Differential scanning calorimetry (DSC) confirms the results of the TGA experiment with a broad endothermic transition observed in the same temperature range from 130 to 150 °C. To examine the effect of added amine on the thermal behavior of polymer **1**, the TGA measurement was repeated with polymer **1** containing 1.5 mol % of 1,10-diaminodecane (Figure 1, curve b). As expected, addition of the amine to polymer **1** did result in a lowering of the decarboxylation temperature to approximately 100 °C. It is this modest shift in the decarboxylation temperature in the presence of base that should enable the preferential decarboxylation within the exposed areas of the resist film with concomitant image formation.

Scheme 2



Mechanism of Chemical Amplification and Lithographic Evaluation. Resist films containing 90 wt % polymer **1** and 10 wt % bis[[(2,6-dinitrobenzyl)oxy]carbonyl]hexane-1,6-diamine (**8**) were spin-coated onto silicon substrates and exposed to 254 nm radiation to evaluate the ability of photogenerated amines to effect the decarboxylation of the matrix polymer. Exposure of the resist film to ultraviolet irradiation liberates 1,6-diaminohexane within the polymer matrix, which, upon subsequent baking, can catalyze the loss of carbon dioxide from the polymer film.

Scheme 2 outlines the mechanism of the base-catalyzed decarboxylation process. Acid−base reaction between polymer **1** and the amine leads to the carboxylate salt **9** which losses carbon dioxide to afford the polymer-bound anion **10**. A key feature of the design of polymer **1** is the relative stability of anion **10** which is stabilized by both the α-cyano and -phenyl groups. Chemical amplification is achieved as the starting amine may be regenerated from **10** in a process that also affords the nonpolar decarboxylated polymer **11**.

Monitoring the resist films using FTIR spectroscopy (Figure 2) provided valuable information on the decarboxylation process. The FTIR spectrum of a nonirradiated resist film baked at 130 °C for 10 min shows the characteristic absorptions of the carboxylic acid functional group (curve a). A similar film exposed to ca. 44 mJ/cm^2 of 254 nm irradiation and baked under identical conditions has an IR spectrum in which the bands at 1700, 1753, and 2500−3500 cm^{-1} characteristic of the free carboxylic acid group have all disappeared (curve b). The disappearance of these characteristic absorptions indicates that the amine formed upon exposure of the resist film does indeed promote the decarboxylation process effectively within the polymer matrix. However, polymer **1** is not thermally stable to baking over an extended period of time at these temperatures and it undergoes a very slow thermally induced decarboxylation even in the absence of photogenerated base. Figure 3 shows the results of monitoring the intensity of the IR carbonyl absorption (1753 cm^{-1}) of the carboxylic acid group within polymer **1** while heating the unexposed

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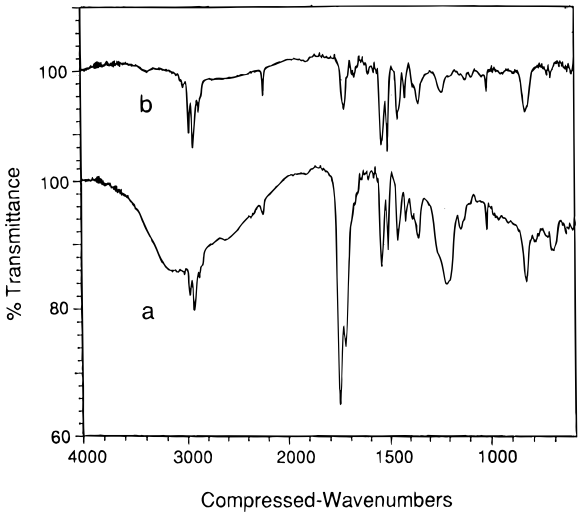

Figure 2. FTIR spectra for a resist containing 90 wt % polymer **1** and 10 wt % photobase generator **8**: (a) baked at 130 °C for 10 min without exposure to UV irradiation (b) after exposure to 44 mJ/cm^2 of 254 nm irradiation and baking at 130 °C for 10 min.

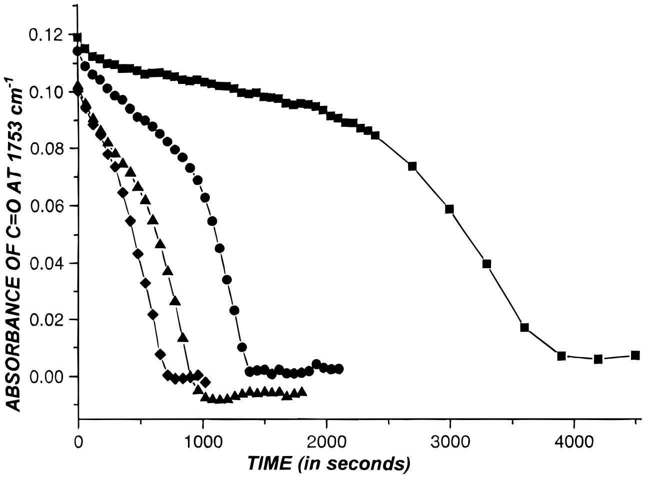

Figure 3. Change in the IR carbonyl absorption (1753 cm^{-1}) with time for a film of polymer **1** containing amine photogenerator and heated to 120 °C. (□) Unexposed polymer film; (○) O after exposure to 50 mJ/cm^2; (◇) after exposure to 100 mJ/cm^2; (△) after exposure to 200 mJ/cm^2.

resist film at 120 °C for a variable amount of time. These results confirm that there is slow but definite loss of the carbonyl intensity over time while baking at this elevated temperature. This accounts for the slow weight loss and broad transition observed during TGA analysis of polymer **1** (Figure 1). However, it must be emphasized that exposure to 254 nm irradiation (10−50 mJ/cm^2) and liberation of the amine base within the resist film significantly accelerates the rate of decarboxylation leading to a complete loss of the carbonyl absorption after about 25 min at this temperature. In contrast, the unexposed film still retains approximately 85% of its carboxyl moieties after baking at the same temperature for the same period of time.

Table 1. Deep-UV Sensitivity Values of Resist[a] upon Development with Dilute AZ312MIF (0.10% V/V)

	sensitivity, mJ/cm^2 (contrast) after various baking times	
postbake temp (°C)	5 min	10 min
130	24.7 (4.4)	8.5 (11.9)
125	46.3 (10.9)	

[a] Resist film (1 μm) of polymer **1** containing bis[[(2,6-dinitrobenzyl)oxy]carbonyl]hexane-1,6-diamine (**8**) was exposed to 254 nm irradiation, baked, and developed in dilute AZ312MIF (0.10% V/V) for 2.5 min.

Table 2. Deep-UV Sensitivity Values of Resist[a] upon Development with Aqueous Triethanolamine (1.06 g/L)

	sensitivity, mJ/cm^2 (contrast) after various baking times	
postbake temp (°C)	8 min	14 min
130	13.5 (13.7)	
125	16.9 (6.1)	13.6 (15.0)[b]

[a] Resist film (1μm) of polymer **1** containing bis[[(2,6-dinitrobenzyl)oxy]carbonyl]hexane-1,6-diamine (**8**) was exposed to 254 nm irradiation, baked, and developed in aqueous triethanolamine (1.06 g/L) for 30 s. [b]Concentration of the developer was 2.6 g/L.

The large difference in functionalization between the exposed and unexposed regions of the resist film translates into a solubility difference in dilute aqueous base that can be used in the development of the latent image. The unexposed regions of the resist film, which contain a large amount of carboxylic acid groups, are highly soluble in dilute aqueous base. The amine-promoted decarboxylation process within the exposed areas of the film renders them insoluble in aqueous base and generates the negative tone image of the mask upon using this form of development. To evaluate the sensitivity of the previously described resist film, contrast curves for the resist were obtained under various postexposure bake (PEB) and development conditions. Tables1 and 2 summarize the sensitivity and contrast results obtained from these measurements. The general trend seen from the data suggests that as the PEB temperature was increased from 125 to 130 °C, the measured sensitivity was also increased. Increasing the PEB temperature above 135 °C destroys the differential solubility created between the exposed and unexposed areas of the film as the thermal decarboxylation process becomes prevalent. The sensitivity and contrast values obtained during our experiments were all high, demonstrating the chemically amplified nature of the resist system. The best and most reproducible results, in terms of sensitivity and contrast, were obtained upon developing the resist with an aqueous solution of triethanolamine. A typical sensitivity and contrast curve obtained using this developing medium is shown in Figure 4. As shown by the sensitivity curve, exposure of the resist followed by baking at 130 °C for 8 min and development in an aqueous solution of triethanolamine affords a negative tone image with a sensitivity of 13.5 mJ/cm^2 with excellent contrast. Changing the developing medium used to remove the unexposed areas of the film to dilute AZ312MIF (10 V/V%) commercial developer did result in an increase in sensitivity to 10 mJ/cm^2 or less under some circumstances; however, some swelling was encountered during imaging experiments. These findings suggest that it may be possible to further increase the sensitivity and enhance the imaging characteristics of these resist films through the use of other basic developing media. The ability of polymer **1** to undergo a base-catalyzed decarboxylation process and function as a negative tone imaging material is best demonstrated through imaging experiments. Figure 5 shows a scanning electron micrograph for a relief image of a resist containing polymer **1** and photobase generator **8** after development with aqueous triethanolamine.

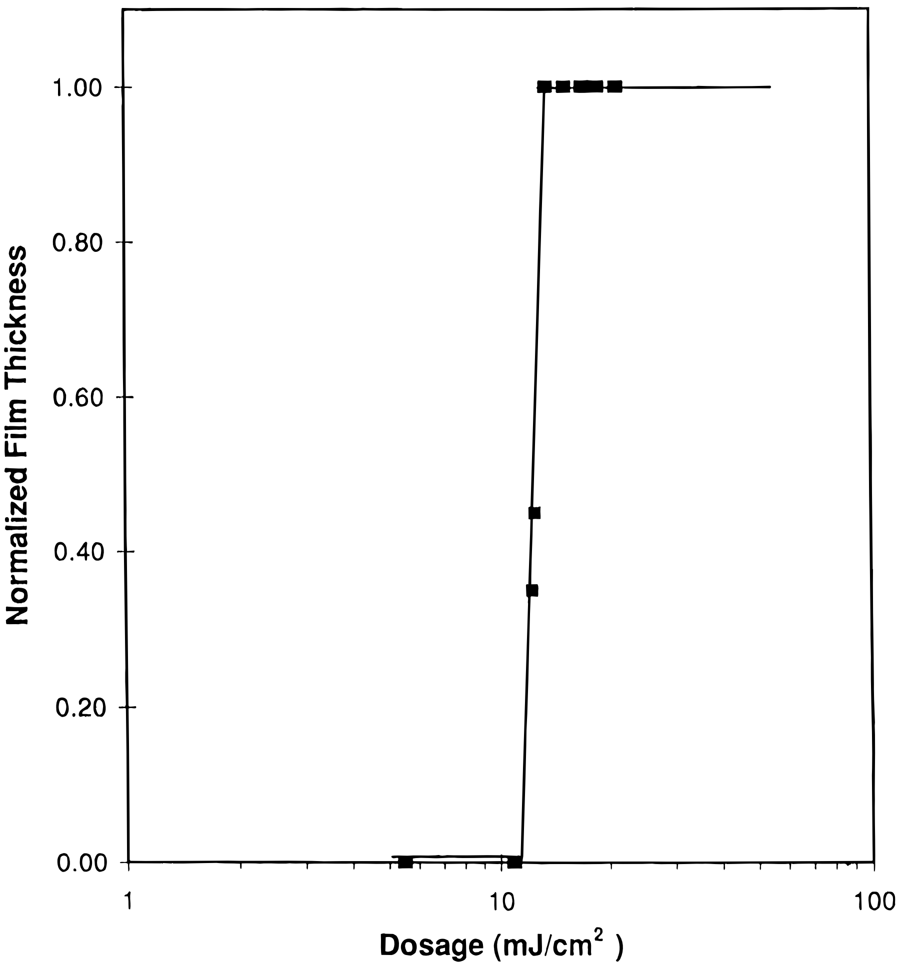

Figure 4. Sensitivity curve for a resist containing 90 wt % polymer **1** and 10 wt % photoamine generator **8**. Exposure to 254 nm irradiation was followed by baking at 130 °C for 8 min and development in aqueous triethanolamine (1.06 g/L) for 30 s.

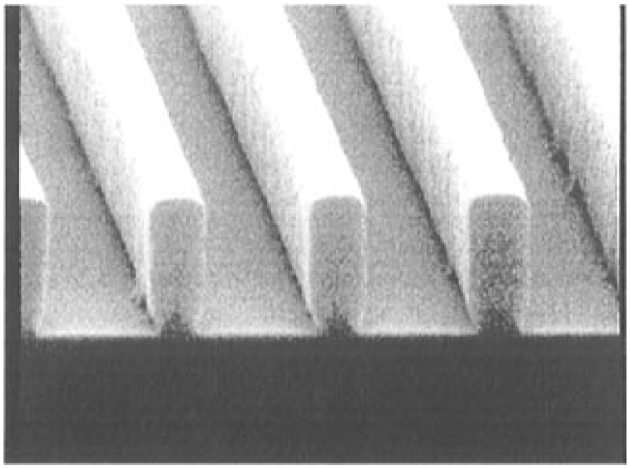

Figure 5. SEM of wet developed negative-tone image showing 0.5 μm wide features.

Image Reversal and Dry Development. The presence of carboxylic acid groups within the functional polymer and the removal of these moieties during the imaging step offers the possibility of employing a dry development process to reverse the tone of the obtained image. The silylation of carboxylic acid groups has been used previously[18] for the dry development processing of resist materials. A similar procedure was applied to the exposed films containing polymer **1** to demonstrate the versatility of the base-catalyzed decarboxylation process used for this material. The carboxylic acid moieties in the unexposed regions of the resist film can be converted to the corresponding silyl esters upon treatment with a silylating agent such as dimethylamino trimethylsilane. Incorporation of the silyl groups into the unexposed areas of the film provides a barrier to O_2-reactive ion etch (O_2-RIE) as these groups are transformed into silicon dioxide. Prior decarboxylation within the exposed areas of the film does not allow such a barrier to be formed, and these areas of the film are subsequently etched down to the substrate to provide a positive tone image.

The silylation reaction is highly critical to the image reversal process because the percentage of silicon introduced into the material must be high enough to afford a large differential rate of etching between the exposed and unexposed areas of the resist film. Incorporation of too little silicon into the film would not provide sufficient contrast between imaged areas and lead to degradation of the generated image. Monitoring of the gas-phase silylation of a 1 μm film of polymer **1** using IR spectroscopy shows that conversion of the acid group to the trimethylsilyl ester is quantitative. This is shown by the complete disappearance of the O−H band of the carboxylic acid (2500−3500 cm^{-1}) and the appearance of bands at 1253 and 845 cm^{-1} attributed to the CH_3−

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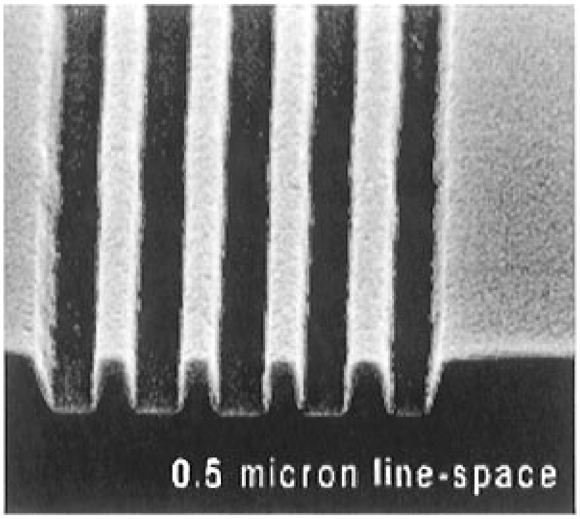

Figure 6. SEM of dry developed positive-tone image showing 0.5 μm wide features.

Si vibration.[19] Results from Rutherford backscattering (RBS) experiments[19] also indicate that silicon was incorporated into the unexposed areas of the resist film with a selectivity of 10:1 (unexposed:exposed) and that silylation of the carboxylic acid units proceeded throughout the whole thickness of the film. These silyl ester groups are stable for about 1 day if kept in a dry atmosphere of nitrogen; however, they readily decompose in less than 1 h when exposed to air. Interestingly, the hydrolysis of the silyl ester groups upon contact with air does not proceed with complete loss of the silicon group from the polymer film. Rather, a large proportion of the incorporated silicon remains in the unexposed areas of the film after hydrolysis or even after exposure to vacuum. IR analysis of the films left in air shows the reappearance of the absorbance bands associated with the carboxylic acid; however, the bands attributed to the silyl group do not disappear but rather show a reduction in intensity. Data from the RBS experiments also indicate that silicon is retained in the silylated areas of the film after hydrolysis of the ester moiety. It was found that silylated films exposed to air for 1 h retained more than 80% of the silicon content found in a film that was carefully transferred to an evacuated dry desiccator immediately after gas-phase silylation. While the exact mechanism and identity of the nonvolatile silicon species derived from the ester hydrolysis have not been ascertained, dry development to provide image reversal in this system was clearly successful. Figure 6 shows a 0.5 μm line-space image which was projection printed and then dry developed using a resist formulated with carboxylic acid polymer **1** and photobase generator **8**.

Experimental Section

Instrumentation. Reported boiling points are uncorrected. IR spectra were obtained on KBr disks and recorded on a Nicolet IR/44 spectrophotometer. A Nicolet 9430 spectrophotometer was used to obtain ultraviolet spectra. ^{1}H and ^{13}C NMR spectra were recorded on solutions in $CDCl_3$, on an IBM-Bruker AF300 (300 Mhz) spectrometer using the solvent proton signal or the solvent carbon signal as an internal standard. Size exclusion chromatography was performed on a liquid chromatograph consisting of a Waters 510 pump, a U6K injector (Waters), a Viscotek 110 differential viscometer and a differential refractometer−refractoMonitor (Milton Roy) with the detectors being connected in parallel. Four 5 μm PL gel columns connected in series in order of increasing pore size (100, 500, and 1000 Å, and mixed bed C) were used with THF as the mobile phase at 40 °C. The molecular weight data are relative to polystyrene standards. Differential scanning calorimetry was performed using a Mettler DSC 30 low-temperature cell coupled to a TC10A TA processor. Thermogravimetric analysis was performed on a Mettler TG50 thermobalance with a heating rate of 20 °C/min while under N_2. Microanalysis were performed by M.H.W. Laboratories, Phoenix, AZ. Chemicals were obtained from Alrich, Fluka, or TCI.

Resist film thickness was measured with a Tencor Alpha-Step 200 surface profiler. Deep-UV exposures were performed by contact printing using an Oriel 87301 exposure system comprising of a medium-pressure mercury lamp with a shutter system and an exposure timer. Photon flux was measured using an Optical Associates Inc. 354 exposure monitor. The output of the mercury lamp was filtered through a 254 nm narrow bandwidth interference filter from Oriel Corp. Varying dosages of light for deep-UV sensitivity measurement were obtained with a Series 1 Multidensity resolution target, Ditric Optics Inc. The amine photogenerator, bis[[(2-nitrobenzyl)-oxy]carbonyl]hexane-1,6-diamine (**8**) was prepared according to the previously published procedure.[6]

Synthesis of *p*-Vinylbenzyl Cyanide (4). A solution of sodium cyanide (19.0 g, 388 mmol) in water was added dropwise to a solution of *p*-vinylbenzyl chloride (**3**, 40.0 g, 263 mmol) in ethanol (50 mL). After the addition, the reaction mixture was heated to reflux for 5.5 h, cooled, and filtered to remove the sodium chloride that formed during the reaction. The filtered salt was washed with a small portion of ethanol and discarded. The ethanol in the filtrate was removed by simple distillation and the remaining solution was cooled and extracted with diethyl ether. The combined extracts were washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was first distilled under vacuum (1.5 mmHg, 90−120 °C) and then further fractionally distilled (1.7 mmHg, 108−111 °C) to afford **4** (24 g, 70%). ^{1}H NMR ($CDCl_3$) δ (ppm) 3.72 (s, 2H), 5.25 (d, 1H), 5.73 (d, 1H), 6.70 (dd, 1H), 7.26−7.46 (AA′BB′, 4H). IR (cm^{-1}) 2251 (CN), 1632, 991, 914 (C=C).

Synthesis of 2-Cyano-2-(*p*-vinylphenyl)butanoic Acid (5). To a one-necked round-bottom flask, equipped with a condenser, was added a solution of sodium hydroxide (10.2 g, 255 mmol in 20 mL of water), ethyl bromide (13.8 g, 127 mmol), *p*-vinylbenzyl cyanide (**4**, 10.0 g, 70 mmol) and benzyltrimethylammonium chloride (0.2 g, 0.88 mmol). The mixture was stirred at room temperature for 24 h and another portion of ethyl bromide (14.0 g, 128 mmol) was added. The mixture was stirred for an additional 30 h until all the *p*-vinylbenzyl cyanide was consumed. A portion of diethyl ether (30 mL) was added, and the organic layer was separated and washed with ice-cooled dilute HCl (8%) followed by water. The ether solution was dried over anhydrous $MgSO_4$ and concentrated at reduced pressure to afford a mixture of monoethylated (86%) and diethylated (14%) product. The crude mixture was used in the next reaction without further purification.

To a solution of diisopropylamine (12.6 g, 125 mmol) in THF (50 mL) at −78 °C was added, under nitrogen, a solution of *n*-BuLi (1.6 M in hexanes, 78 mL, 125 mmol). The solution was stirred at −78 °C for 2 h and a solution of 2-(*p*-vinylphenyl)butyronitrile (86% pure, 12.4 g, 62 mmol) in THF (50 mL) was added dropwise. After addition, the reaction mixture was stirred at −78 °C for 3 h and poured onto granulated dry ice (300 g). The slurry was kept under nitrogen and warmed slowly until almost all the dry ice was consumed. The mixture was then quenched with diluted HCl (8%) and extracted twice with diethyl ether. The combined ethereal extracts were washed with water and extracted with dilute KOH (5%) twice. The combined basic extracts were neutral-

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[19] Willson, C. G.; Cameron, J. F.; MacDonald, S. A.; Niesert, C.-P.; Fréchet, J. M. J.; Leung, M. K.; Ackman, A., *Proc. SPIE* **1993**, *1925*, 354.

ized and extracted with diethyl ether, dried over anhydrous sodium sulfate and concentrated at reduced pressure to provide a pale yellow solid (9.5 g, 73%). The crude product was recrystallized from a mixture of dichlormethane and hexanes to afford 7.8 g (60%) of **5**. ^{1}H NMR (CDCl$_3$) δ (ppm) 1.06−1.11 (t, J = 7.3 Hz, 3H), 2.16−2.23 (m, 1H), 2.36−2.47 (m, 1H), 5.29−5.33 (d, J = 11.4 Hz, 1H), 5.75−5.81 (d, J = 17.6 Hz, 1H), 6.65−6.74 (dd, J_1 = 17.6 Hz, J_2 = 11.4 Hz, 1H), 7.53−7.40 (AA′BB′, 4H), 10.2 (br s, 1H). ^{13}C NMR (CDCl$_3$) δ (ppm) 9.74, 30.9, 54.9, 115.6, 117.5, 126.6, 126.9, 132.5, 135.6, 138.6, 172.9. IR (cm^{-1}) 2400−3400 (COOH), 2245 (CN), 1726 (C=O), 1631, 1001, 912. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.38; H, 6.05; N, 6.43.

Synthesis of *tert*-Butyl 2-Cyano-2-(*p*-vinylphenyl)butyrate (6). To an ice-cooled solution of 2-cyano-2-(*p*-vinylphenyl)butanoic acid (**5**, 3.0 g, 14 mmol) in benzene (10 mL) was added oxalyl chloride (5.3 g, 42 mmol) followed by 5 drops of *N*,*N*-dimethylformamide. The mixture was stirred at room temperature for 4 h and then concentrated at reduced pressure. To an ice-cooled solution of the crude acid chloride redissolved in CH_2Cl_2 (10 mL) was added pyridine (3.2 g, 42 mmol) in CH_2Cl_2 (10 mL) and 2-methyl-2-propanol (5.2 g, 70 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature for 6 h and then washed sequentially with dilute HCl (1%), saturated K_2CO_3, and saturated NaCl solutions and finally dried over anhydrous sodium sulfate. Concentration at reduced pressure and purification of the crude product by flash chromatography on silica gel, eluting with EtOAc−hexanes (1:9) afforded **6** (2.6 g, 70%). ^{1}H NMR (CDCl$_3$) δ (ppm) 1.07−1.13 (t, J = 7.4 Hz, 3H), 1.42 (s, 9H), 2.02−2.04 (m, 1H), 2.31−2.43 (m, 1H), 5.28−5.31 (d, J = 10.5 Hz, 1H), 5.74−5.80 (d, J = 17.5 Hz, 1H), 6.65−6.75 (dd, J_1 = 10.9 Hz, J_2 = 17.5 Hz, 1H), 7.35−7.49 (AA′BB′, 4H). ^{13}C NMR (CDCl$_3$) δ (ppm) 9.86, 27.6, 31.4, 55.7, 84.2, 115.1, 118.6, 126.3, 126.8, 134.3, 135.9, 137.9, 166.4. IR (cm^{-1}) 2220 (CN), 1740 (C=O), 1252, 1153, 991, 915.

Free Radical Polymerization of *tert*-Butyl 2-Cyano-2-(*p*-vinylphenyl)butyrate. A solution of *tert*-butyl 2-cyano-2-(*p*-vinylphenyl)butyrate (**6**, 2.54 g, 9.04 mmol) and 2,2′-azobisisobutyronitrile (AIBN, 31 mg, 0.18 mmol) in toluene was heated at 73−78 °C for 18 h. The crude polymer was precipitated into hexanes, redissolved in chloroform and reprecipitated into methanol to afford **7** (1.83 g, 74%). $M_n = 1.78 \times 10^4$, $M_w = 5.05 \times 10^4$, PDI = 2.82 . ^{1}H NMR (CDCl$_3$) δ (ppm) 0.8−1.7 (15H), 1.92−2.2 (1H), 2.2−2.45 (1H), 6.2−6.6 (2H), 7.0−7.4 (2H). ^{13}C NMR (CDCl$_3$) δ (ppm) 10.2, 27.8, 31.5, 40.3, 42−46, 55.6, 84.2, 118.8, 126.1, 127.8, 133.3, 145.1, 166.5. IR (cm^{-1}) 2243 (CN), 1749 (C=O), 1252, 1158, 840.

Synthesis of Poly(2-cyano-2-(*p*-vinylphenyl)butanoic acid) (1). Poly(*tert*-butyl 2-cyano-2-(*p*-vinylphenyl)butyrate) (**7**, 0.95 g) was added to a solution of trifluoroacetic acid in dichloromethane (60%), and the resulting mixture stirred at room temperature for 5.5 h. Concentration of the solution at reduced pressure provided a slightly yellow solid which was redissolved in acetone and reprecipitated twice into pentane. The resulting solid was dried under vacuum to afford poly(2-cyano-2-(*p*-vinylphenyl)butanoic acid) (**1**, 0.73 g, 96%). ^{1}H NMR (CDCl$_3$) δ (ppm) 0.9−1.9 (6H), 1.9−2.3 (1H), 2.3−2.6 (1H), 6.1−6.8 (2H), 7.1−7.5 (2H). ^{13}C NMR (CDCl$_3$) δ (ppm) 10.4, 32.4, 41.6, 42−45, 56.2, 120.2, 127.3, 129.4, 134.4, 146.9, 170.4. IR (cm^{-1}) 2400−3600 (COOH), 2248 (CN), 1753 (C=O), 1220, 830, 789.

Resist Formulation and Processing. Poly(2-cyano-2-(*p*-vinylphenyl)butanoic acid) (**1**, 20 wt %) and bis[[(2-nitrobenzyl)oxy]carbonyl]hexane-1,6-diamine (**8**, 2 wt %) were dissolved in diglyme (78 wt %) and filtered through a 0.45 μm filter. The formulation was spin-coated onto silicon wafers and baked at 110 °C for 2 min to afford 1.0−1.1 μm thick films. Contrast curves for the sensitivity measurements were obtained by exposure to 254 nm irradiation through a multitransmission mask (Ditric Optics Inc.) followed by baking at 125−130 °C for 5−14 min and development in either dilute AZ312MIF developer (0.54 M aqueous solution of tetramethylammonium hydroxide, Shipley) or an aqueous solution of triethanolamine.

Acknowledgment. Financial support of this research by the Office of Naval Research is acknowledged with thanks.

CM970220K