Design of New Positive-Tone Photoresists Based on the Acid-Catalyzed Hydrolysis of Phenylmethanediol Diesters

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A series of novel phenylmethanediol diesters have been designed for use as dissolution inhibitors of phenolic resins in alkaline solution. The rates of triflic acid-catalyzed hydrolyses of these *gem* diesters to carboxylic acids in DMSO have been measured and correlated with their structural features. New three-component positive-tone photoresists consisting of these dissolution inhibitors, a photochemical generator of acid, and poly(4-hydroxystyrene) have been prepared and tested successfully. A 20 wt % loading of the additive effectively retards the dissolution of the phenolic resin in aqueous base developer. Following exposure to radiation and the application of heat, the photogenerated acid catalyzes the decomposition of the additive to afford two molecules of a carboxylic acid that act as dissolution promoters for the polymer. The reaction temperature has a drastic influence on the dissolution properties of the resist coatings. Optimization of the processing conditions can be facilitated by ^{1}H NMR analyses of processed resist materials. The resists have demonstrated high sensitivities with both deep-UV (<1 mJ/cm^2) and electron-beam radiation (ca. 1.7 μC/cm^2).

Introduction

Since their introduction in the 1960s, nonvolak/diazonaphthoquinone- (DNQ) based resists have been the most widely used positive-tone photoresists in the manufacturing of semiconductor devices. They may be developed in aqueous base without swelling, leading to high resolution while also providing excellent dry etch resistance.[1] However, the demand for ever-decreasing feature size in transistor elements has pushed the novolak/DNQ resists to their limits in terms of attainable resolution (ca. 0.35 μm) with conventional exposure techniques.[2] Further improvement in imaging resolution may be achieved using shorter wavelength radiation, e.g., deep-UV (190–280 nm), electron-beam, X-ray, and ion-beam, that are not applicable to current DNQ-based resists.[3] Among these new technologies, deep-UV imaging is believed to have the best potential for implementation in large scale production in the coming decade.[4] Therefore, there is a need and demand for new deep-UV imaging materials that possess high sensitivity.

One approach to improving sensitivity involves the concept of chemical amplification involving the photogeneration within the resist of species that catalyze many subsequent chemical events. The overall quantum efficiency of such reactions is effectively much higher than that for initial catalyst formation. The classical example is the acid-catalyzed deprotection of poly([((*tert*-butyloxy)carbonyl)oxy]styrene).[5,6] Over the past decade, a large number of new resists have been designed based on this concept.[2,7–19] Among these new designs, the principle of dissolution inhibition is still one

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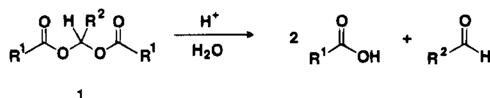
Scheme 1



1

a: $R^1 = (C_6H_5)_2CH$, $R^2 = H$

b: $R^1 = CH_3CH_2$, $R^2 = 4\text{-}CH_3C_6H_4$

c: $R^1 = C_6H_5$, $R^2 = 4\text{-}CH_3C_6H_4$

d: $R^1 = C_6H_5CH_2$, $R^2 = C_6H_5$

e: $R^1 = (C_6H_5)_2CH$, $R^2 = C_6H_5$

f: $R^1 = (C_6H_5)_2CH$, $R^2 = 4\text{-}AcOC_6H_4$

g: $R^1 = 2,4,6\text{-}(CH_3)_3C_6H_2$, $R^2 = C_6H_5$

h: $R^1 = CH_3$, $R^2 = C_6H_5$

i: $R^1 = CH_3$, $R^2 = 4\text{-}CH_3C_6H_4$

j: $R^1 = CH_3$, $R^2 = 4\text{-}CH_3OC_6H_4$

k: $R^1 = CH_3$, $R^2 = 4\text{-}ClC_6H_4$

l: $R^1 = CH_3$, $R^2 = 4\text{-}NO_2C_6H_4$

of the most widely studied for positive-tone resists. A masked phenol[15-17] or protected carboxylic acid[18,19] is mixed with a phenolic resin, resulting in a drastic decrease in the dissolution rate of the polymer in aqueous hydroxide solutions. A phototriggered acid-catalyzed deprotection reaction is then used to free the phenol or the carboxylic acid that has much higher solubility in basic solutions than their masked analogs. As a result, the dissolution inhibitor is effectively converted into a dissolution promoter in the radiation-exposed areas of the resist material allowing the development of positive tone images.

Because carboxylic acids are more acidic than phenols, the carboxylic acid additives are more soluble in the aqueous base developer than the phenolic additives. Therefore, for the same extent of deprotection of the dissolution inhibitor, one can expect a larger difference in the solubilities of the radiation-exposed and unexposed resists when a carboxylic acid derivative is used as the dissolution inhibitor. In the literature, only simple esters have been studied as dissolution inhibitors for photoresist applications.[18,19] In this report, the use of the more reactive *gem* diesters **1a**–**g** (Scheme 1) to modify the dissolution rate of poly(4-hydroxystyrene) in aqueous hydroxide developer is investigated. In addition to their inherently higher reactivity when compared to simple esters, *gem* diesters also produce *two* molecules of carboxylic acid by hydrolysis instead of one for the more conventional carboxylic acid-based dissolution inhibitors (Scheme 1). These two advantages have the potential to translate into a significant performance benefit as the increased lability of the diesters and the increased solubility of their decomposition byproduct both contribute to improvements in resist sensitivity.

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Experimental Section

Instrumentation. ^1H NMR spectra were recorded on a Bruker WM-300 300 MHz spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer at 75 MHz with the solvent carbon signal as standard. Infrared spectra were obtained on a Nicolet FTIR/44 spectrometer. A Hewlett-Packard 8452A diode array UV–visible spectrophotometer was used to obtain ultraviolet spectra.

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. Sensitivities reported are accurate to ±0.1 mJ/cm^2. E-beam exposures of the resist films were conducted with a Cambridge Instruments Electron Beam Microfabricator 10.5/CS operating at 20 kV. Scanning electron micrographs are recorded on a Cambridge Instruments Stereoscan 200 microscope.

Materials. Poly(4-hydroxystyrene) was obtained from IBM Corp.: T_g 160 °C; M_w 31 000; M_n 12 100 (universal calibration with in-line Viscotek viscosity detector). A 1.0 μm thick film has a UV absorbance of 0.41 at 254 nm. AZ312MIF developer, 0.54 N aqueous tetramethylammonium hydroxide solution, was obtained from Hoechst Celanese. The onium salt, triphenylsulfonium, hexafluoroantimonate, was provided by the General Electric Corp. The acid anhydrides were synthesized from the corresponding carboxylic acids using DCC in diethyl ether.[20]

Methanediol Bis(diphenyl acetate) (1a). Diester **1a** was prepared from diphenylacetic acid and dibromomethane using the procedure of Shaw and Kunerth.[21] The crude product was recrystallized from THF–hexane mixture to yield **1a** (64%) as a white crystalline solid: mp 93.5–94.0 °C; ^1H NMR ($CDCl_3$) δ 5.00 (s, CH_2, 2H), 5.85 (s, CH, 2H), 7.22–7.28 (m, ArH, 20H); ^1H NMR ($CDCl_3$) δ 56.6, 79.9, 127.4, 128.5, 128.6, 137.7, 171.0; IR (KBr) 3060, 3033, 1746, 1496, 1452, 1117, 992, 703 cm^{-1}. Anal. Calcd for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54. Found: C, 80.00; H, 5.65.

General Procedure for Syntheses of Phenylmethanediol Diesters 1b–g.[22] The acid anhydride (1.93 mmol) and the aldehyde (1.93 mmol) were dissolved in CCl_4 (1.3 mL) under an argon atmosphere. Phosphorus trichloride (0.193 mmol) was added and the mixture was stirred at 55 °C for 2–10 h. The progress of the reaction was monitored by periodic withdrawal of sample and analysis by ^1H NMR. When no further change was observed in the composition of the reaction mixture, heating was stopped and chloroform (20 mL) added. The solution was washed with water (3 × 7 mL), dried ($MgSO_4$), and evaporated to dryness. The crude product was purified by flash chromatography followed by distillation or recrystallization.

(4-Methylphenyl)methanediol Dipropionate (1b). Compound **1b** was obtained as a clear oil (23%): bp$_{0.15}$ 110 °C; ^1H NMR ($CDCl_3$) δ 1.14 (t, CH_3, 6H), 2.36 (s, CH_3, 3H), 2.38 (dq, CH_2, 4H), 7.20 (d, ArH, 2H), 7.40 (d, ArH, 2H), 7.66 (s, CH, 1H); ^{13}C NMR ($CDCl_3$) δ 8.7, 21.2, 27.4, 89.6, 126.5, 129.2,

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132.6, 139.6, 172.3; IR (KBr) 2985, 1762, 1463, 1180, 818 cm^{-1}; UV (ethanol) λ_{max} 218 (400), 228 (400), 256 nm (400).

(4-Methylphenyl)methanediol Dibenzoate (1c). Compound **1c** was obtained as a white crystalline solid (47%): mp 79.5–80.0 °C ($CHCl_3$–hexane); ^1H NMR ($CDCl_3$) δ 2.38 (s, CH_3, 3H), 7.26 (d, ArH, 2H), 7.43 (t, ArH, 4H), 7.56 (t, ArH, 2H), 7.60 (d, ArH, 2H), 8.08 (m, ArH, 4H), 8.17 (s, CH, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 90.7, 126.7, 128.4, 129.2, 130.0, 132.8, 133.5, 139.8, 164.4; IR (KBr) 1740, 1724, 1277, 1059, 708 cm^{-1}; UV (ethanol) λ_{max} 244 nm (17 100). Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.17; H, 5.19.

Phenylmethanediol Bis(phenyl acetate) (1d). Compound **1d** was obtained as a white crystalline solid (51%): mp 47.5–48.0 °C ($CHCl_3$–hexane); ^1H NMR ($CDCl_3$) δ 3.66 (s, CH_2, 4H), 7.20–7.40 (m, ArH, 15H), 7.70 (s, CH, 1H); ^{13}C NMR ($CDCl_3$) δ 40.9, 90.2, 126.6, 127.2, 128.5, 128.6, 129.3, 129.7, 133.1, 135.1, 169.4; IR (KBr) 1758, 1735, 1143, 954, 698 cm^{-1}; UV (ethanol) λ_{max} 218 (700), 232 nm (700), 258 nm (500). Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.78; H, 5.63.

Phenylmethanediol Bis(diphenyl acetate) (1e). Compound **1e** was obtained as a white crystalline solid (20%): 79.0–79.5 °C (Et_2O–hexane); ^1H NMR ($CDCl_3$) δ 5.02 (s, CH, 2H), 7.10–7.40 (m, ArH, 25H), 7.85 (s, CH, 1H); ^{13}C NMR ($CDCl_3$) δ 56.8, 90.5, 126.6, 127.3, 127.3, 128.5, 128.6, 128.7, 129.7, 137.9, 170.2; IR (KBr) 3063, 3032, 1761, 1497, 1455, 1119, 957, 698 cm^{-1}; UV (ethanol) λ_{max} 234 nm (2700), 260 nm (1300). Anal. Calcd for $C_{35}H_{28}O_4$: C, 82.01; H, 5.51. Found: C, 82.05; H, 5.58.

(4-Acetyloxyphenyl)methanediol Bis(diphenyl acetate) (1f). Compound **1f** was obtained as a white crystalline solid (38%): mp 112.0–112.5 °C ($CHCl_3$–hexane); ^1H NMR ($CDCl_3$) δ 2.29 (s, CH_3, 3H), 5.01 (s, CH, 2H), 7.02 (d, ArH, 2H), 7.15–7.30 (m, ArH, 20H), 7.32 (d, ArH, 2H), 7.84 (s, CH, 1H); ^{13}C NMR ($CDCl_3$) δ 21.1, 56.8, 89.9, 121.7, 127.3, 128.0, 128.6, 128.7, 132.4, 137.8, 151.5, 169.1, 170.2; IR (KBr) 3063, 3031, 1761, 1497, 1195, 966, 701 cm^{-1}; UV (ethanol) λ_{max} 244 nm (1300), 254 nm (1300), 260 nm (1400). Anal. Calcd for $C_{37}H_{30}O_6$: C, 77.88; H, 5.30. Found: C, 77.84; H, 5.37.

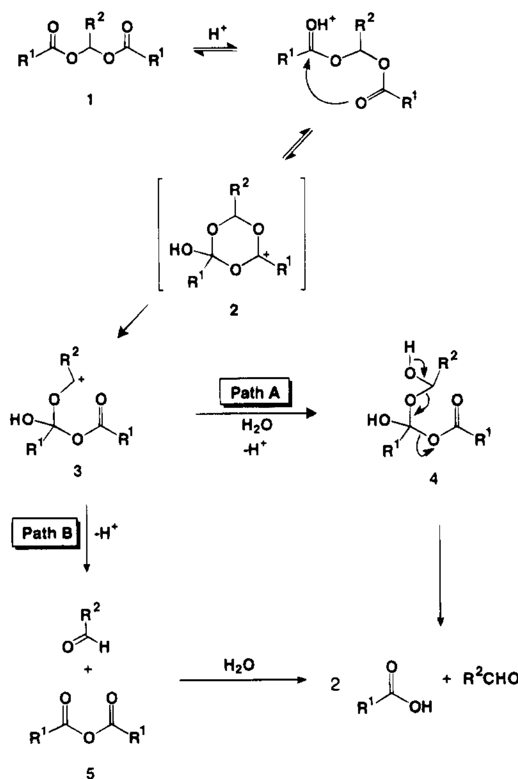
Phenylmethanediol Bis(2,4,6-trimethyl benzoate) (1g). Compound **1g** was obtained as a white crystalline solid (57%): mp 105.0–105.5 °C (hexane); ^1H NMR ($CDCl_3$) δ 2.24 (s, CH_3, 12H), 2.26 (s, CH_3, 6H), 6.83 (s, ArH, 4H), 7.41 (m, ArH, 3H), 7.64 (m, ArH, 2H), 8.16 (s, CH, 1H); ^{13}C NMR ($CDCl_3$) δ 19.8, 21.1, 90.7, 127.1, 128.5, 128.6, 129.6, 129.9, 135.3, 135.7, 139.8, 167.8; IR (KBr) 2923, 1749, 1727, 1613, 1274, 1253, 1049, 697 cm^{-1}; UV (ethanol) λ_{max} 250 nm (7900). Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 78.03; H, 6.76.

Measurement of Hydrolysis Rate in Solution. A stock solution of triflic acid was made up by adding triflic acid (1.2 μL, 0.0136 mmol) to DMSO-d_6 (2.3 mL). The phenylmethanediol diester compound (0.009 77 mmol) was dissolved in a mixture of DMSO-d_6 (0.45 mL) and H_2O (0.0140 mmol). A measured volume (0.05 mL) of the triflic acid stock solution was then added and the resulting solution mixed thoroughly before transferred into a NMR tube. The NMR tube was immersed in an oil bath maintained at 110 ± 1 °C and ^1H NMR spectra measured periodically.

Resist Formulation and Processing. Poly(4-hydroxystyrene) (0.214 g, 75.4 wt %), the phenylmethanediol diester (0.0575 g, 20.2 wt %) and triphenylsulfonium hexafluoroantimonate (0.0125 g, 4.4 wt %) were dissolved in propylene glycol monomethyl ether acetate (1.2 g) and filtered through a 0.45 μm filter. Spin-coating onto silicon wafers at 3600 rpm for 30 s followed by heating at 90 °C for 3 min affords 1.0 ± 0.05 μm films. All samples, unless otherwise stated, were heated at 100 °C for 90 s following the radiation exposure; these postexposure bake conditions were experimentally determined to afford the best results and higher temperatures may cause excessive evaporation of the carboxylic acids that are released during the process. Solvent development of the resists was done by dipping the wafer in a beaker of rapidly stirring solution of 30% aqueous AZ312MIF.

^1H NMR Analyses of Resist Films. The resist solution was spin-coated onto a 2 in. silicon wafer and heated at 90 °C for 3 min to give 1.0 ± 0.05 μm films. Following exposure to a known dose of deep-UV radiation and postexposure baking, the resist films were dissolved in deuterated acetone and the ^1H NMR spectra recorded.

Scheme 2



Results and Discussion

Despite their use as a protecting group for aldehydes,[23] the diesters of methanediols have not been studied as extensively as the more classical acetal protecting groups. The chemistry of phenylmethanediol diacetates is the most thoroughly described of this family of compounds. Phenylmethanediol diacetates are typically prepared by reaction of acetic anhydride with para-substituted benzaldehydes in the presence of Lewis acid catalysts.[22–24] Both acid-[25] and base-catalyzed[26] hydrolysis reactions have been reported in the literature for some of these compounds. There are also scattered examples of syntheses based on nucleophilic substitution reactions between carboxylic acid salts and alkyl dihalides.[21,27]

Acid-Catalyzed Hydrolysis of Phenylmethanediol Diesters in Solution. Gregory has investigated the hydrolysis of a series of para-substituted phenylmethanediol diacetates, **1h–l** (Scheme 1), in dilute HCl.[25] The correlation of the hydrolysis reaction rates with the Hammett aromatic substituent constants (σ^+) of the phenyl substituents establishes that the reaction proceeds by an alkyl scission pathway (Scheme 2). The entropies of activation obtained are consistent with the

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Table 1. ^{1}H NMR Kinetics Data for Triflic Acid Catalyzed Hydrolysis of Phenylmethanediol Diesters in Aqueous DMSO at 110 °C

compound	k, mol^{-1} dm^3 min^{-1}	$t_{1/2}{}^a$ min
1a	0.002 39	33 000 (estimated)
1b	1.456	54
1c	0.336	240
1d	0.169	700
1e	0.053	2200
1f	0.079	1500
1g	0.239	500

^{a} Reaction time for 50% conversion.

formation of the cyclic transition state **2**, in which a protonated acetoxy group acts as a Lewis acid in assisting the loss of the second acetoxy group. On the basis of these results, Gregory proposed a $A_{Al}1$ (unimolecular acid-catalyzed alkyl−oxygen fission) mechanism as shown in Scheme 2.

The rate determining step of the acid-catalyzed hydrolysis reaction is the formation of the open-chained carbocation **3**. The rate equation is

$$-\mathrm{d}[\mathbf{1}]_t/\mathrm{d}t = k[\mathbf{1}]_t[\mathrm{H}^+]$$

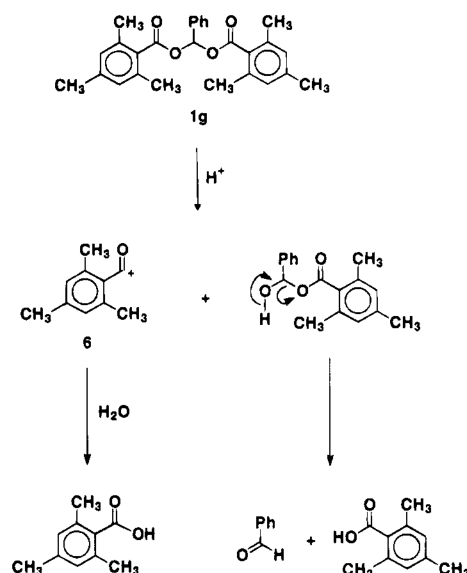
$$\Longrightarrow \quad \ln([\mathbf{1}]_0/[\mathbf{1}]_t) = k[\mathrm{H}^+]t$$

where k is the hydrolysis reaction rate constant; t is the reaction time elapsed; $[\mathbf{1}]_0$ is the initial concentration of compound **1**; $[\mathbf{1}]_t$ is the concentration of compound **1** at reaction time t. Thus, the reaction rate is expected to be independent of the amount of water in the system. A plot of $\ln([\mathbf{1}]_0/[\mathbf{1}]_t)$ vs reaction time (t) will be linear since the concentration of proton, which is a catalyst, should be constant; and the slope of this line is proportional to the rate constant, k, of the acid-catalyzed hydrolysis reaction.

A total of seven diol diesters, **1a−g** (Scheme 1), were prepared and the rates of acid-catalyzed hydrolysis in aqueous DMSO solutions at 110 °C were measured using ^{1}H NMR spectroscopy. Control experiments have shown that no reaction can be detected at room temperature. Therefore, withdrawal of samples from the oil bath immediately prior to ^{1}H NMR analyses should not introduce any error to the measurements. In all cases, good linear plots are obtained from the measured kinetic data. The calculated rate constants, k, and the half-lives of the reactions, $t_{1/2}$, are listed in Table 1. No reaction is observed in control experiments performed without triflic acid, confirming the acid-catalyzed nature of the reaction. The reaction rate is unaffected by varying the amount of water in the reaction mixture. Therefore, as predicted, water does not participate in the rate-determining step of the reaction.

The calculated rate constants of the acid-catalyzed hydrolysis reaction for compounds **1a−g** are consistent with the mechanism proposed by Gregory.[25] A comparison of compounds **1a**, **1e**, and **1f** shows that the stabilizing power of substituent R^2 (see Scheme 1) toward a positive charge increases within this series. The increase in stability of the derived carbocationic intermediate **3** is paralleled by an increase in the hydrolysis reaction rate constant as seen in the results obtained for compounds **1a**, **1e**, and **1f**. In addition, the reaction rate plummets as the size of the carboxylic acid component of the molecule increases (see **1b−c** and **1d−e**), this can be rationalized by considering the proposed cyclic transition state **2**, formation of which would be disfavored by the presence of bulky substituents in the molecule.

Scheme 3



In compound **1g**, the presence of the two methyl groups at the 2- and 6-positions relative to the carbonyl group is expected to inhibit the cyclization process to form **2** as depicted in the proposed $A_{Al}1$ mechanism (Scheme 2). It is believed that the hydrolysis reaction of **1g** proceeds instead via an $A_{Ac}1$ (unimolecular acid-catalyzed acyl−oxygen fission) mechanism in which the protonated ester decomposes into an acylium ion **6** (Scheme 3).[28] Further evidence that the acid-catalyzed hydrolysis of **1g** follows an $A_{Ac}1$ mechanism is obtained in the study of the corresponding resist material.

Preparation of Positive Tone Resists with Compounds 1a−g as Dissolution Inhibitors. Positive tone resists **A−G** are prepared by mixing the *gem*-diol diesters **1a−g**, triphenylsulfonium hexafluoroantimonate, and the phenolic resin. With the exceptions of **1c** and **1g**, all the diol diesters have negligible absorbance at 254 nm, making them ideal for deep-UV imaging. Despite its undesirable high dissolution rate in aqueous basic developer solutions, poly(4-hydroxystyrene) is used, instead of novolak, because of its superior transparency in the deep-UV region as well as its higher glass transition temperature that facilitate both the use of low-exposure dosages and of high temperatures for resist processing. However, the commercial sample of poly(4-hydroxystyrene) used in these experiments is not the best grade achievable in terms of UV transparency and glass transition temperature.

^{1}H NMR Analyses of the Radiation-Exposed Resist Films. Upon exposure to radiation, the photoactive compound, triphenylsulfonium hexafluoroantimonate, decomposes to release the super acid, hexafluoroantimonic acid, in the resist film. This photochemical process occurs readily at room temperature while the acid-catalyzed hydrolysis of compounds **1a−g** occurs only at elevated temperatures. Therefore, after expo-

(28) Bender, M. L.; Ladenheim, H.; Chen, M. C. *J. Am. Chem. Soc.* **1961**, *83*, 123. Bender, M. L.; Chen, M. C. *J. Am. Chem. Soc.* **1963**, *85*, 37.

Table 2. ¹H NMR Analyses of the Compositions of Radiation-Exposed Resist Films after Postexposure Baking

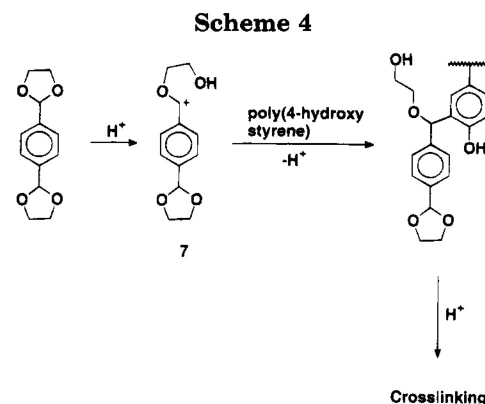
resist[a]	process	starting material remaining, %	acid detected, %	acid evaporated,[b] %	alkylated polymer, %	aldehyde detected, %
A	5.0 mJ/cm², 100 °C (5 min)	100	0	0	0	0
B	1.0 mJ/cm², 100 °C (5 min)	8	0	92	0	35
C	2.5 mJ/cm², 100 °C (5 min)	5	36	59	0	47
D	5.0 mJ/cm², 100 °C (5 min)	2	41	57	0	0
	5.0 mJ/cm², 80 °C (5 min)	2	44	54	0	5
	5.0 mJ/cm², 80 °C (30 s)	2	66	32	0	13
	1.5 mJ/cm², 100 °C (45 s)	2	55	43	0	6
E	5.0 mJ/cm², 100 °C (90 s)	3	86	11	0	2
	1.5 mJ/cm², 100 °C (45 s)	20	70	10	0	8
F	1.4 mJ/cm², 100 °C (90 s)	3	82	15	0	31
G	1.4 mJ/cm², 100 °C (90 s)	14	67	19	19	10
	2.0 mJ/cm², 70 °C (1 min)	20	73	7	8	27

[a] Resist **A** contains additive **1a**, resist **B** contains additive **1b**, similar terminology applies to the other resists. [b] Calculated by difference.

sure to radiation, the resist samples have to be heated to an appropriate temperature (postexposure bake) to provide the energy that is required for the acid-catalyzed hydrolysis reactions to proceed. In addition, the application of heat enables the removal of one of the reaction products, the aldehyde, by evaporation. Since most of the aldehydes that are liberated (e.g., benzaldehyde, tolualdehyde) have limited solubilities in aqueous base and might act as weak dissolution inhibitors, their removal by evaporation during the postexposure bake is beneficial. The acid-catalyzed hydrolysis of **1f** generates 4-acetoxybenzaldehyde that has a boiling point of 270 °C, which is too high to allow removal by evaporation at the typical post exposure bake temperature of 100 °C. Nevertheless, because 4-formylphenolate is a good leaving group, it is possible that 4-acetoxybenzaldehyde might instead be readily hydrolyzed during the aqueous base development to afford base-soluble 4-hydroxybenzaldehyde.

The proper choice of processing temperature is very critical to the performance of the resist. An excessively high temperature might cause thermal side reactions in the phenolic resin that would reduce overall sensitivity. To facilitate the choice of the optimum processing temperature for each individual resist formulation, ¹H NMR spectroscopy was used to analyze the chemical composition of the processed materials. Instead of developing with basic developer solutions, the radiation exposed and postbaked resist samples were dissolved in deuterated solvents and the ¹H NMR spectra recorded. This allows accurate monitoring of the extent of hydrolysis as well as the amount of residual aldehyde (Table 2). With the exception of resist **A**, exposure to 1−5 mJ/cm² of 254 nm radiation, followed by the postexposure bake leads to near quantitative breakup of the diol diesters, as indicated by the very small amounts of unreacted starting materials left. Postbaking temperatures of 80−100 °C are sufficient to remove most of the benzaldehyde generated in resists **D**, **E**, and **G** but only lead to partial evaporation of tolualdehyde (resists **B**, **C**) and 4-acetoxybenzaldehyde (resist **F**). On the other hand, according to entries for resists **C** and **D**, approximately 40−60% of the benzoic acid and phenylacetic acid released by hydrolysis are lost from the film, despite their high boiling points that exceed the postbaking temperatures by more than 150 °C. This demonstrates the high efficiency of evaporation of compounds from thin films. Results obtained with resist **D** also show that while changes in exposure dosage, heating temperature, and duration have little effect on the extent of the hydrolysis reaction, they have a dramatic influence on the loss of acids and aldehydes from the thin films.

Scheme 4



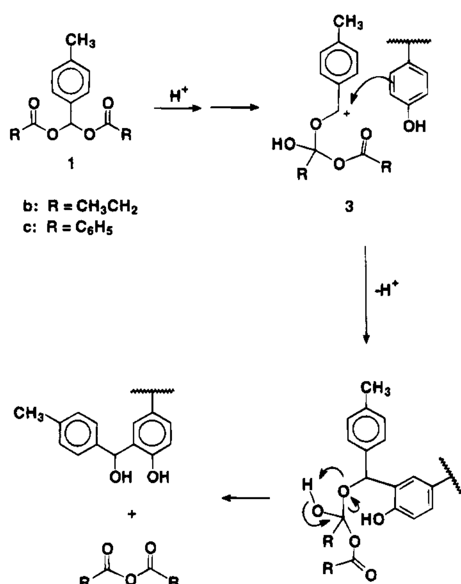
Schaedeli et al. have reported an acid-catalyzed crosslinking reaction of poly(4-hydroxystyrene) with 1,3-dioxolyl acetal (Scheme 4).[29] The reaction involves the formation of a carbocationic intermediate **7**, that undergoes an electrophilic aromatic substitution reaction with the phenolic polymer. Potentially, a similar electrophilic aromatic substitution reaction could also occur with poly(4-hydroxystyrene) and the carbocationic intermediate **3** shown in Scheme 2. For compounds **1b** and **1c**, this would result in the binding of a tolyl group to the polymer (Scheme 5) that would in turn be indicated by broad methyl resonances in the ¹H NMR spectra of the processed resist material. However, this is not observed in the corresponding ¹H NMR spectra implying that the electrophilic aromatic substitution reaction does not occur to a significant extent. The carbocationic center in intermediate **3** may be too sterically crowded for the approach of the polymer chains.

According to reaction path B in Scheme 2, decomposition of carbocation **3** might afford acid anhydride **5** that, under the conditions of the reaction, would be expected to react with the phenolic moiety of the polymer to form an ester. In resists **B**−**F**, no evidence can be found in the ¹H NMR spectra for the formation of any phenolic ester. This suggests that path A is the predominant reaction pathway for the carbocationic intermediate **3**.

A small amount of 4-hydroxybenzaldehyde, presumably formed from acid-catalyzed ester hydrolysis of the

(29) Schaedeli, U.; Holzwarth, H.; Muenzel, N. *Polym. Eng. Sci.* **1992**, *20*, 1523.

Scheme 5



4-acetoxybenzaldehyde liberated in the cleavage of the diester, was detected in the reaction of compound **1f**. Furthermore, **1f** can potentially undergo an acid-catalyzed Fries rearrangement[30] or a photo-Fries rearrangement[31] in which the acetyl group migrates to the ortho position liberating a free phenol. However, no trace of the possible reaction products, e.g., (3-acetyl-4-hydroxyphenyl)methanediol bis(diphenyl acetate) or 3-acetyl-4-hydroxybenzaldehyde, could be found in the irradiated and postbaked samples.

The ^{1}H NMR spectra for resist **G** are shown in Figure 1. The two broad peaks at 2.44 and 6.98 ppm (Figure 1b) are attributed to 2,4,6-trimethylbenzoyl groups attached to poly(4-hydroxystyrene). As mentioned earlier, the hydrolysis of **1g** proceeds via an $A_{Ac}1$ mechanism in which the protonated ester decomposes into an acylium ion **6**. This highly reactive acylium ion **6** can either react with water to give 2,4,6-trimethylbenzoic acid (**8**) or with the phenolic matrix to form phenyl ester **9** and substituted hydroxybenzophenone **10** (Scheme 6). The use of a lower processing temperature of 70 °C effectively reduces the formation of **9** and **10** by one-half, without drastically slowing down the hydrolysis reaction (Table 2). This optimizes the formation of the dissolution promoter, while reducing the generation of undesirable polymeric alkylation side products.

2,4,6-Trimethylbenzoic acid and its esters are known to undergo acid-catalyzed decarboxylation reactions to afford trimethylbenzene.[32] Analysis of the ^{1}H NMR integration data for resist **G** reveals that there is little change in the total of trimethylbenzoyl groups in the resist film before and after the irradiation and heating processes. The total number of protons attributed to the trimethylbenzoyl groups of **1g** are accounted for by the integration of the trimethylbenzoyl groups of **8**, **9**, **10**, and unreacted **1g**. This suggests that the decarboxylation reaction that affords trimethylbenzene does not occur to any significant extent.

Dissolution Properties of the Resist Coatings. While acetals are remarkably stable to base hydrolysis,

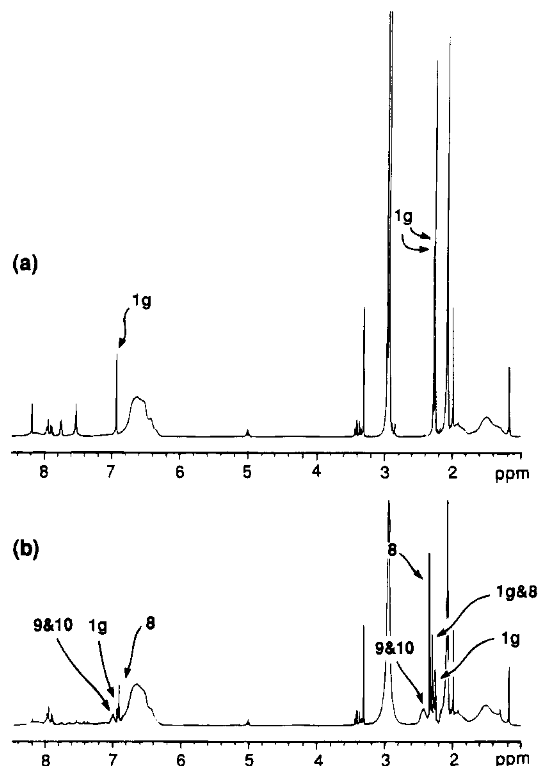
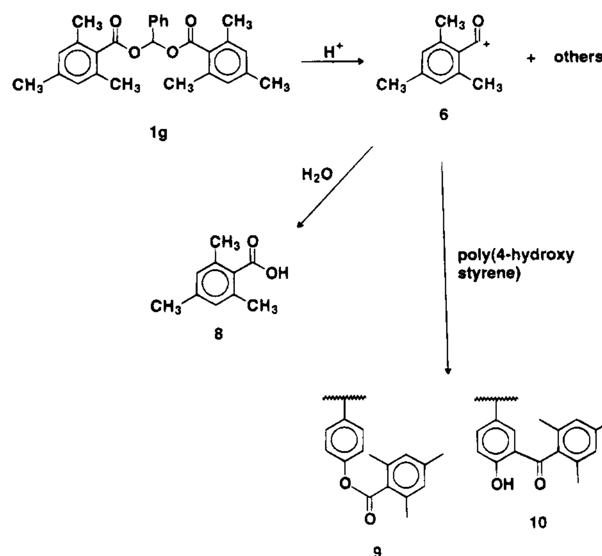


Figure 1. ^{1}H NMR spectra of resist **G**: (a) baked at 90 °C for 3 min, then at 100 °C for 90 s without intermediate exposure to UV light; (b) baked at 90 °C for 3 min, exposed to 1.4 mJ/cm^2 of 254 nm radiation, then postexposure baked at 100 °C for 90 s.

Scheme 6



several *gem*-diol diesters have been reported to be readily hydrolyzed in aqueous basic solution.[23,26] In particular, 1,1-ethanediol diacetate and dipropionate are hydrolyzed 4 orders of magnitude faster in 0.05 M aqueous sodium carbonate solution than in 0.05 M aqueous hydrochloric acid solution at 25 °C.[26] However, as shown by the dissolution rates of the unexposed resists in aqueous basic developer solution (Table 3), compounds **1a–g** are quite effective dissolution inhibitors of poly(4-hydroxystyrene) in tetramethylammonium hydroxide solution. Under identical conditions, a mixture of poly(4-hydroxystyrene) and triphenylsulfonium hexafluoroantimonate used in proportions similar to

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(31) Bellus, D.; Hrdlovic, P. *Chem. Rev.* **1967**, *67*, 599.
(32) Keumi, T.; Morita, T.; Ozawa, Y.; Kitajima, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 599.

Table 3. Dissolution Characteristics of Resists A–G in 30% Aqueous AZ312MIF Aqueous Base Developer at 20 °C

resist	additive	process	hydrolysis products	dissolution rate, nm/s	
				i[a]	ii[b]
A	**1a**	2 mJ/cm^2, 100 °C (5 min)	no reaction	3	3
B	**1b**	2 mJ/cm^2, 100 °C (5 min)	tolualdehyde (bp 204 °C) propionic acid (bp 141 °C)	7	7
C	**1c**	2 mJ/cm^2, 100 °C (5 min)	tolualdehyde (bp 204 °C) benzoic acid (bp 249 °C)	3	23
D	**1d**	(i) 2 mJ/cm^2, 80 °C (5 min)	benzaldehyde (bp 178 °C)	5	29
		(ii) 2 mJ/cm^2, 100 °C (5 min)	phenylacetic acid (bp 265 °C)	5	15
E	**1e**	(i) 2 mJ/cm^2, 80 °C (3 min)	benzaldehyde (bp 178 °C)	3	82
		(ii) 2 mJ/cm^2, 100 °C (90 s)	diphenylacetic acid (mp 148 °C)	3	79
F	**1f**	1.4 mJ/cm^2, 100 °C (90 s)	4-acetyloxybenzaldehyde (bp 270 °C) diphenylacetic acid (mp 148 °C)	2	44
G	**1g**	(i) 2 mJ/cm^2, 100 °C (90 s)	benzaldehyde (bp 178 °C)	3	3
		(ii) 2 mJ/cm^2, 70 °C (1 min)	2,4,6-trimethylbenzoic acid (mp 154 °C)	3	98
M	none[c]	2 mJ/cm^2, 100 °C (5 min)		15	13

[a] Before irradiation and baking processes. [b] After irradiation and baking processes. [c] Poly(4-hydroxystyrene) with 4.4 wt % triphenylsulfonium hexafluoroantimonate.

those used in resists **A**–**G** has a dissolution rate of 15 nm/s. This implies that the diesters have sufficient stabilities under the resist development conditions to be used in practical resist systems. The differences in dissolution rates among the resists formulated with compounds **1a**–**g** seem to be directly related to the hydrophobicities as well as the sizes of the molecules that, in turn, might affect their efficiencies in blocking the hydrophilic diffusion channels in the phenolic polymer matrix.[33]

Because the processed resist films have a much higher content of carboxylic acids than aldehydes, increases in resist dissolution rates are anticipated. The results shown in Table 3 confirm that upon exposure to 2.0 mJ/cm^2 of radiation at 254 nm followed by postbaking at a suitable temperature, significant increases in resist dissolution rates are observed with additives **1c**–**g**. Figure 2 shows the dissolution curves for resist **E**. The changes in dissolution rates are consistent with the changes in compositions of the resist films that result from the radiation and thermal processes (Table 2). For instance, no dissolution enhancement is observed in the case of **B** owing to the loss of the volatile propionic acid by evaporation during the postbaking process. The dissolution rates of processed samples of resist **G** are highly dependent on the postbaking conditions. Postbaking at 100 °C affords samples with much lower solubilities than those heated to 70 °C. This is readily explained by the formation of a larger amount of polymer-bound side products **9** and **10** at the higher postbaking temperature (Table 2). Alkylated structures **9** and **10** are expected to be much less soluble than poly(4-hydroxystyrene) or 2,4,6-trimethylbenzoic acid in the developer solution. Hattori et al. have reported that poly(3,5-dimethyl-4-hydroxy)styrene has a dissolution rate 100 times lower than that of poly(4-hydroxystyrene) of similar molecular weight in tetramethylammonium hydroxide solution.[34] Therefore, it is not surprising to observe that a seemingly small increase in the amounts of **9** and **10** in processed resists **G**, from 8% to 19%, actually has a tremendous effect on the solubility of the resists.

Sensitivity of the Resists. Resists **C** through **G** exhibit high sensitivities when exposed to deep-UV

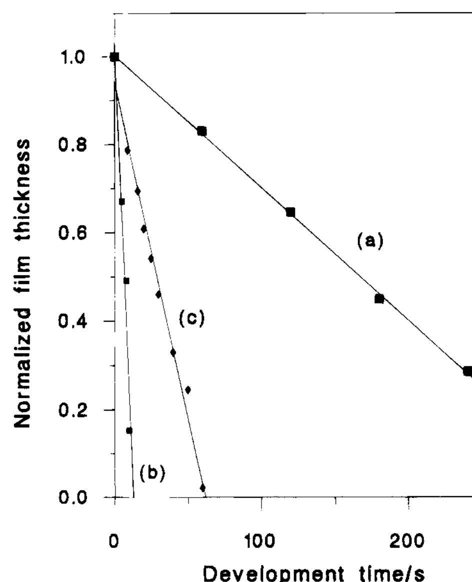

Figure 2. Dissolution curves of resist **E** in 30% aqueous AZ312MIF developer at 20 °C: (a) baked at 90 °C for 3 min, then at 100 °C for 90 s without intermediate exposure to UV light; (b) baked at 90 °C for 3 min, exposed to 2.0 mJ/cm^2 of 254 nm radiation, then postexposure baked at 100 °C for 90 s; (c) mixture of poly(4-hydroxystyrene) and triphenylsulfonium hexafluoroantimonate, baked at 90 °C for 3 min, then at 100 °C for 90 s without intermediate exposure to UV light.

irradiation and heated to appropriate postexposure bake temperatures (Table 4). The results obtained for resist **G** demonstrate the influence of the processing temperature on resist performance. No image can be obtained when the postexposure bake is done at 100 °C because the increased production of alkylated polymer structures **9** and **10** decreases the solubility of the exposed areas to the extent that there is no solubility difference between the exposed and unexposed regions. The unexposed areas of resists **C** and **D** suffer significant thinning due to the insufficient difference between the dissolution rates of the radiation-exposed and unexposed resists. The slight thinning observed in resists **E**–**G** is largely the result of resist shrinking during the postbaking process, rather than the simple dissolution of unexposed material in the developer.

With e-beam exposure, resist **E** exhibits a high sensitivity of 1.7 μC/cm^2 and a contrast of 12. A scanning electron micrograph of an image featuring 0.4 μm lines and spaces printed using e-beam exposure is

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(34) Hattori, T.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Iwayanagi, T. *Jpn. J. Appl. Phys.* **1991**, *30*, 3125.

Table 4. Deep-UV Sensitivities of Resists A–G with Aqueous Base Development

resist	additive	UV absorbance at 254 nm[a]	postbaking conditions	sensitivity, mJ/cm^2	contrast	film thickness l_0[b], μm
A	**1a**	0.54	100 °C (5 min)	*c*		
B	**1b**	0.55	100 °C (5 min)	*c*		
C	**1c**	0.97	100 °C (5 min)	2.3	2.1	0.78
D	**1d**	0.52	(i) 100 °C (5 min)	*d*		
			(ii) 80 °C (5 min)	0.9	1.3	0.72
			(iii) 80 °C (30 s)	1.4	1.3	0.72
E	**1e**	0.52	(i) 100 °C (90 s)	1.4	3.0	0.93
			(ii) 80 °C (3 min)	1.4	5.4	0.95
F	**1f**	0.52	100 °C (90 s)	1.3	4.7	0.89
G	**1g**	0.90	(i) 100 °C (90 s)	*c*		
			(ii) 70 °C (1 min)	1.4	2.1	0.91
			(ii) 80 °C (3 min)	1.4	5.4	0.95
L	none[e]	0.51	100 °C (90 s)	*c*		

[a] Thin film of 1 μm thickness. [b] l_0 is the thickness of unexposed resist after solvent development. [c] No image observed even after exposure to 10.0 mJ/cm^2. [d] Incomplete clearance even with dose of 10.0 mJ/cm^2. [e] Poly(4-hydroxystyrene) with 4.4 wt % triphenylsulfonium hexafluoroantimonate.

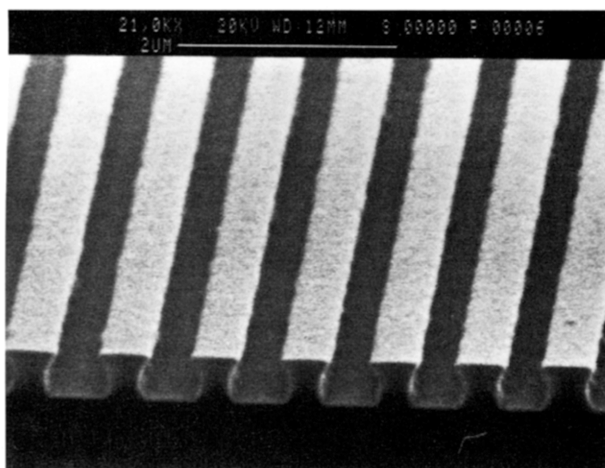

Figure 3. Scanning electron micrograph of image with 0.4 μm lines and spaces printed in resist **E** with electron beam radiation.

shown in Figure 3. Similar results are expected for the e-beam exposure of the other resists.

We have successfully demonstrated the use of poly(4-hydroxystyrene) as the polymer resin for a positive tone resist through modification of its dissolution behavior with compounds **1e–g**. Since poly(4-hydroxystyrene) has an exceedingly high dissolution rate in aqueous base developer, there are very few reports in the literature on the use of small molecule additives to modify its dissolution properties. The problem of excessive loss of film thickness during solvent development, commonly experienced in poly(4-hydroxystyrene)-based positive-tone resists[35] has been overcome using additives **1e–g**. Pawlowski and co-workers have shown that poly(aminals) but not low molecular weight aminals also have excellent dissolution inhibition properties on poly(4-hydroxystyrene).[36]

We are currently investigating the use of (4-hydroxyphenyl)methanediol bis(diphenyl acetate), a compound that is expected to possess an even higher reactivity in the acid-catalyzed hydrolysis reaction.

Conclusions

Novel phenylmethanediol *gem* diesters **1b–g** have been prepared for use as dissolution inhibitors of poly(4-hydroxystyrene) in aqueous basic solutions. The rates of their acid-catalyzed hydrolyses are related to the stabilities of the derived carbocationic intermediates and the sizes of the substituents. These compounds are very effective in inhibiting the dissolution of poly(4-hydroxystyrene). Upon irradiation and subsequent post-exposure bake, compounds **1b–g** are decomposed by the photogenerated acid to free carboxylic acids. This greatly increases the dissolution rates of the resist matrix forming the positive image. High sensitivities have been obtained with both deep-UV and electron beam radiation demonstrating that practical positive tone resists based on the chemistry of gem diesters can be formulated. Detailed analyses of the compositions of the processed resists have been made with ^{1}H NMR spectroscopy. These analyses have provided valuable information for a thorough understanding of the dissolution behavior of these resists. The processing temperature influences the extents of the hydrolyses of compounds **1b–g** and the evaporation of the reaction products, both affecting the resulting solubilities of the resist material. Therefore, temperature can be used as a tool to regulate sensitivity.

Acknowledgment. Financial support of this research by Semiconductor Research Corp. is acknowledged with thanks. This work was performed in part at the National Nanofabrication Facility which is supported by the National Science Foundation under Grant ECS-8619049, Cornell University, and industrial affiliates.

(35) (a) Ito, H. *Proc. SPIE* **1988**, *920*, 33. (b) Pawlowski, G.; Sauer, T.; Dammel, R.; Gordon, D. J.; Hinsberg, W.; McKean, D.; Lindley, C. R.; Merrem, H. J.; Röschert, H.; Vicari, R.; Willson, C. G. *Proc. SPIE* **1990**, *1262*, 391.

(36) Pawlowski, G.; Przybilla, K. J.; Spiess, W.; Wengenroth, H.; Röschert, H. *J. Photopolym. Sci. Technol.* **1992**, *5*, 55.