A Water-Castable, Water-Developable Chemically Amplified Negative-Tone Resist

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This paper describes an "environmentally friendly", water-castable, water-developable photoresist system. The chemically amplified negative-tone resist system consists of three water-soluble components: a polymer, poly(methyl acrylamidoglycolate methyl ether), [poly(MAGME)]; a photoacid generator, (2,4-dihydroxyphenyl)dimethylsulfonium triflate, and a cross-linker, 1,4-butanediol. In the three-component resist system, the acid generated by photolysis of the photoacid generator catalyzes the cross-linking of poly(MAGME) in the exposed regions during postexposure baking, thus rendering the exposed regions insoluble in water. Negative-tone relief images are obtained by developing with pure water. The resist is able to resolve 1 μm line/space features (1:1 aspect ratio) with a deep-UV exposure dose of 100 mJ/cm^2 (dose to print). The resist can be used to generate etched copper relief images on printed circuit boards using aqueous sodium persulfate as the etchant. The mechanism of cross-linking has been investigated by model compound studies using ^{13}C NMR.

Introduction

Current resist materials employ organic compounds as casting solvents and, in some cases, as developers. The use of organic solvents in the lithographic processes represents an environmental health and safety concern. Moreover, the disposal of the organic solvents is a source of mounting cost for manufacturers of semiconductor devices. A typical resist formulation consists of approximately 70 wt % of organic solvent. Most of that solvent is lost to the air plenum during the coating and baking processes. Still more organic waste is generated in the edge bead removal and back side rinse steps. The traditional casting solvents for resist formulations, such as glycol ethers and glycol ether acetates, are a source of health and safety concerns. The health and environmental hazards and the waste disposal cost associated with the use of these organic solvents have inspired this work directed toward minimizing the environmental impact of lithographic processing.

There are two possible ways to minimize the environmental impact of organic solvents in resist processing. One is to eliminate the casting solvents altogether by depositing resist films on substrates from vapor or solid phases and carrying out dry development.[1] The other is to replace the organic solvents with water. We have chosen to pursue the latter approach, which necessitates the development of a completely new class of resist materials. Previous work on water-soluble resist systems has produced both positive- and negative-tone resist materials. This work employed design principles involving radiation-induced water solubility switching through photochemical rearrangement,[2] photochemically induced deprotection,[3] and/or cross-linking.[4−6]

Taylor et al.[2,7] developed a water-castable, water-developable resist based on photochemical rearrangement of *N*-(1-pyridinio)amidates attached to water-soluble acrylic polymers. Exposure of the water-soluble polymer to 366 nm UV light resulted in a photochemical rearrangement of the *N*-(1-pyridinio)amidates to less polar *N*-acyldiazepine photoproducts, thus rendering the polymer insoluble in water. Development with water gave negative tone images with a resolution of 2.5 μm. They also demonstrated that the images could serve as an etch mask for copper. Shirai et al.[3] synthesized copolymers of 4-(9-fluorenylideneiminooxysulfonyl)-styrene. Photolysis of the −O−N= bond of the 9-fluorenylideneiminooxysulfonyl group led to formation of a

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more polar, sulfonic acid, thus enhancing water solubility. Therefore, positive-tone resists could be formulated from these polymers. However, the resist had be to formulated with and spin coated from organic solvents because the unexposed polymer is not soluble in water. Ichimura[4] reported that substitution of a very small fraction (<3 mol %) of styrylpyridinium or quinolinium groups on poly(vinyl alcohol) resulted in water-soluble negative-tone resists. The pendant styrylpyridinium or quinolinium groups functioned as cross-linking sites. However, no imaging experiments were reported. All of the single-component resists described above suffer from low sensitivity due to either a low concentration of the photoactive group in the resist or the low quantum efficiency of the photochemical reactions.

Morishita[6] and co-workers have recently reported a new water-soluble photoresist consisting of a polymeric azide sensitizer and poly(acrylamide-*co*-diacetone acrylamide) for use in the "black matrix process" for color picture tube fabrication. This new resist is reported to have high sensitivity, but no information is given regarding the resolution of the resist.

One way to improve resist sensitivity is to incorporate "chemical amplification".[8] In systems that incorporate chemical amplification, the primary photochemical event generates a substance that serves to catalyze a cascade of subsequent reactions that change the solubility of the resist. The most popular chemical amplification resist designs employ photochemically generated acid to catalyze deprotection or cross-linking reactions. In this way, the effective quantum efficiency and therefore the sensitivity is "amplified" through the catalytic function of the photochemically generated acid.

Early work by Hult et al.[5] led to a chemically amplified, water-soluble resist involved synthesis of acrylamide-based water-soluble homopolymers and copolymers. Negative-tone images were generated by an acid-catalyzed self-condensation cross-linking in these polymers at relatively low exposure doses. Development of the resist with water was demonstrated, but the resist was formulated in an organic solvent, cyclohexanone. Moreover, the resolution of the resist was reportedly limited to 2 μm, presumably due to swelling.

The purpose of this work is to develop a resist system that can be cast from and developed with *pure water.* We have auditioned a variety of systems, but here we report a chemically amplified resist system consisting of three water-soluble components; an acrylamide type polymer, poly(methyl acrylamidoglycolate methyl ether), poly(MAGME); a photoacid generator (PAG), (2,4-dihydroxyphenyl)dimethylsulfonium triflate; and a cross-linker, 1,4-butanediol (Scheme 1). This design is inspired by the earlier work of Hult and co-workers.[5]

The new resist has a gel dose of 30 mJ/cm^2 at 248 nm and resolves 1 μm features at 1:1 aspect ratio. Additionally, this resist was used to generate etched copper relief images on printed circuit board inner plane substrates. The cross-linking mechanism responsible for the function of the resist has been investigated by model compound studies. These studies show that acid catalyzed cross-linking of poly(MAGME) with 1,4-butanediol may proceed both via transesterification and transetherification of the aminal (transaminalization) at low temperatures, and also via alcoholysis of the amide at high temperatures.

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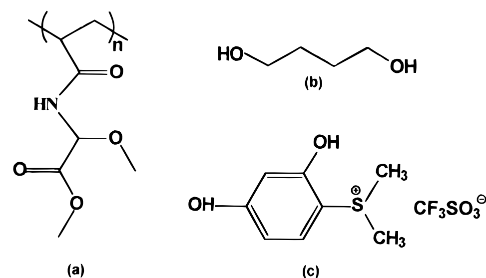
Scheme 1. Components of Water-Soluble Poly(MAGME) Resist: (a) Polymer Matrix, (b) Cross-Linker, and (c) Photoacid Generator



Experimental Section

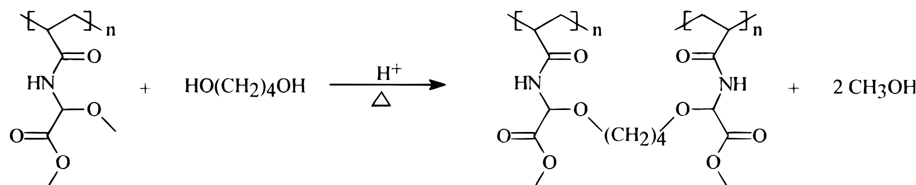
Methyl acrylamidoglycolate methyl ether (MAGME) monomer was obtained from American Cyanamid. It was used as received for polymerization but recrystallized from xylene for NMR studies. 2,2′-Azobisisobutyronitrile (AIBN) was obtained from Kodak. All other chemicals were purchased from Aldrich and used without further purification.

The photoacid generator, (2,4-dihydroxyphenyl)dimethylsulfonium triflate, was prepared by a two-step synthesis. Resorcinol (10.0 g, 90.8 mmol) was dissolved in 45 mL of methanol in a 250 mL three-necked round-bottom flask. Dimethyl sulfoxide (3.55 g, 90.8 mmol) was added and the solution was cooled to 0 °C. Anhydrous HCl was slowly bubbled through the solution until a solid product formed. The precipitate was collected, washed with diethyl ether, and dried under vacuum to afford the sulfonium chloride salt as a white powder (6.3 g, 67%): mp = 145−146 °C. A 10% (w/w) aqueous solution of this material (6.3 g, 30.5 mmol) was prepared, to which sodium triflate (5.3 g, 30.5 mmol) was added. The solution was allowed to stir for 1 h and then extracted three times with ethyl acetate. The combined organics were washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure yielded 7.0 g (71%) of a white powder: mp = 129−131 °C; ^{1}H NMR (ppm, acetone-d_6) δ 3.45 (s, 6H, 2 CH_3), 6.68 (d, 1H, ArH), 6.78 (d, 1H, ArH), 7.69 (d, 1H, ArH), 9.67 (s, 1H, OH), 10.45 (s, 1H, OH); ^{13}C NMR (ppm, acetone-d_6) δ 27 (CH_3), 99 (CH), 105 (CH), 110 (C−S(CH_3)$_2$), 134 (CH), 161 (COH), 165 (COH), 206 (CF_3). Anal. Calcd for $C_9H_{11}F_3O_5S_2$: C, 33.75; H, 3.46. Found: C, 33.75; H, 3.60.

Poly(MAGME) was prepared by solution free-radical polymerization of MAGME monomer using AIBN as the initiator.[5] Carbon tetrabromide was used as a chain-transfer agent to control molecular weight. A typical polymerization procedure is as follows: To a 250 mL three-neck round-bottom flask fitted with a condenser, an addition funnel and a magnetic stirrer, was added a mixture of 15 mL of toluene and 10 mL of *n*-butanol. The flask was immersed in an oil bath and heated to 80 °C. A solution of 7.0 g of MAGME, 0.03 g of AIBN, and 0.03 g of CBr_4 in a mixture of 45 mL of toluene and 30 mL of *n*-butanol was added slowly. The resulting solution was stirred at 80 °C for 4 h. under N_2. The mixture was then added to 100 mL of cold diethyl ether with rapid stirring. The precipitate was filtered and dried in vacuo to constant weight to provide 5.2 g (yield 74.5%) of white polymer.

^{13}C NMR spectra of the polymer and products of the model reactions were recorded on a GE QE300 spectrometer at 75 MHz using the solvent carbon signal as reference. Chloroform-*d* and DMSO-d_6 were used as solvents. Differential scanning calorimetry measurements were conducted on a Perkin-Elmer Thermal Analysis System 7 under a nitrogen atmosphere at a heating rate of 10 °C/min. The glass transi-

Scheme 2. Acid-Catalyzed Cross-Linking of Poly(MAGME) via Transacetalization



tion temperature was taken as the midpoint of the transition. UV−vis spectra were measured on approximately 1 μm thick resist films coated on quartz disks using a Cary 1E UV−visible spectrophotometer. UV−vis spectra were recorded after post-application baking (PAB) the resist films at 90 °C for 1 min, exposing, and postexposure baking (PEB) at 110 °C for 4 min. Resist film thickness was determined on a Tencor profilometer.

The molecular weight and molecular weight distribution of the polymers were determined using a Viscotek GPC equipped with light-scattering, refractive index, and viscosity detectors to provide universal calibration. The separation was achieved using a set of three cross-linked polystyrene columns, a linear mix, a 500 Å and a 100 Å column, all 5 mm, from American Polymer Standards. THF was used as the eluent. Silicon wafers were procured from Nova Electronic Materials, Inc.

The resist was formulated in deionized water with 20−25 wt % polymer, 10−15 wt % PAG, and 8 wt % 1,4-butanediol as a cross-linker. Unless otherwise specified, the percentage of PAG and cross-linker is relative to the polymer. The solution was filtered through a series of 0.8, 0.5, and 0.2 μm Teflon syringe filters. Prior to resist coating, the silicon wafers were flooded with hexamethyldisilazane (HMDS) for 40 s. The HMDS was spun off, and the filtered resist solution was then spin-coated at 2250−2750 rpm on 4 in. silicon wafers. The formulations provided excellent, striation-free coatings. The film was then post-apply baked (PAB) at 75−90 °C for 1 or 2 min on a hot plate. The resist film was then exposed through a 254 nm band-pass filter (Acton Research Corp.) using a JBA Model LS65 1 kW deep UV exposure system. Postexposure bake (PEB) at 100−110 °C for 1−5 min was followed by spray developing with pure deionized water for 30 s at room temperature.

Patterning of the poly(MAGME) resist was carried on a GCA XLS 7200 stepper (numerical aperture = 0.48, coherence = 0.55), coupled with a MTI Flexfab hot plate track and an MTI Flexfab spin-coating track. One micron thick films on bare silicon were post-apply baked at 90 °C for 1 min, exposed at 248 nm with an open frame reticle to determine the best dose, and then with a dose-focus matrix to obtain images. The exposed resist was postexposure baked at 110 °C for 1 min and then developed by rinsing with deionized water for 30 s. SEM photographs were obtained with Amray 1830FE field emission SEM operating at 5 kV. Samples were coated with a thin layer of gold prior to examination.

A series of experiments was carried out with the goal of demonstrating the utility of the new resist for patterning of copper on the inner planes of circuit board substrates. The surface of the copper was treated to improve adhesion. It was first cleaned with Kleen King (Bon Ami, Co.) copper cleaner, rinsed with water, and dried. The substrate was then flooded with a 2 wt % solution of benzotriazole in 2-propanol at room temperature for 1 min. and rinsed with 2-propanol to wash away excess benzotriazole. The resist was then applied by spin coating. The resist films thus prepared were imaged using a procedure similar to that described for silicon wafers, with the following exceptions: (1) the cross-linker concentration was increased to 15 wt % to improve resistance to the etchant, and (2) the baking time was extended by a factor of 5 because of differences in heat-transfer characteristics of the FR-4 epoxy−glass substrate materials and silicon. The resist image was transferred into the copper substrate by etching with an aqueous sodium persulfate solution (4 g/L) at room temperature.

Table 1. Results of Free Radical Polymerization of MAGME

sample	temp (°C)	AIBN (wt %)	CBr_4 (wt %)	yield (%)	M_n	M_w/M_n	T_g (°C)[a]
1[b]	80	0.02	0	64	*c*	*c*	79.3
2	70	0.02	0	67	*c*	*c*	~110
3	80	0.02	0	77	11200	1.50	77.0
4	80	0.04	0	77	8500	1.70	68.1
5	80	0.43	0	61	10600	1.61	57.4
6	70	0.43	0.43	85	6350	1.86	67.8
7	80	0.43	0.43	74	7680	1.71	67.7
8	80	0.43	0.43	87	7820	1.75	68.0

[a] As determined by DSC. [b] The monomer to solvent ratio in this sample was 2.75 times that of the other runs. [c] Insoluble in THF.

Results and Discussion

Control of Molecular Weight of poly(MAGME). Free radical polymerization of acrylamide monomers has been shown to give rise to polymers with very high molecular weights, often in the millions of daltons.[9] The molecular weight of poly(MAGME) must be properly controlled to give films with thickness about 1 μm at a reasonable spin speed of ~2500 rpm.

The molecular weight of the product derived from solution free radical polymerization can be controlled by the addition of a chain-transfer agent, and/or by variation of monomer and initiator concentrations. A study was conducted using a well-known chain-transfer agent, CBr_4. The concentrations of initiator AIBN and monomer were varied to establish control of the molecular weight of poly(MAGME). The results of this study are summarized in Table 1.

As can be seen from Table 1, without a chain-transfer agent, resulting polymers may be of molecular weight so high that they are not soluble. Reproducible molecular weights were not easily attainable. By use of the chain-transfer agent, we were able to reproducibly synthesize polymers with a molecular weight in the range of 6000−8000 daltons, which we have found appropriate for use in the resist studies.

Resist Formulation and Processing. The chemically amplified resist was formulated by dissolving the three components, poly(MAGME), (2,4-dihydroxyphenyl)dimethylsulfonium triflate; and 1,4-butanediol, in deionized water. The acid-catalyzed cross-linking of poly(MAGME) occurs through acid-catalyzed reaction with 1,4-butanediol and could, in principle, proceed by transesterification, transaminalization, alcoholysis of the amide, or any combination of all three reactions. The cross-linking reaction via transaminalization is depicted in Scheme 2. It has been reported that poly(MAGME) can also be cross-linked by an acid-catalyzed self-condensation.[5,10]

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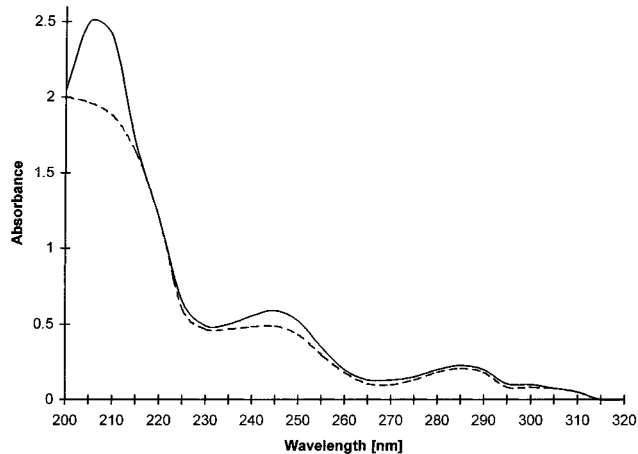


Figure 1. UV−vis spectra of the poly(MAGME) resist (15% PAG, 8% diol) before (—) and after (− − −) DUV exposure. Spectra have been normalized to absorbance per 1 μm.

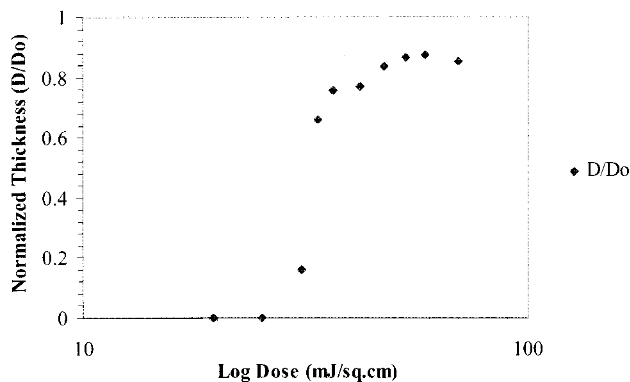


Figure 2. Sensitivity curve of poly(MAGME) resist. The resist contains 8 wt % 1,4-butanediol and 15 wt % PAG. PAB at 90 °C for 1 min, PEB at 110 °C for 2 min.

Cross-linking of the poly(MAGME) base polymer leads to an increase in its molecular weight and a corresponding decrease in solubility. Consequently, negative-tone relief images are obtained by development with water. 1,4-Butanediol concentrations from 4 to 15 wt % gave good lithographic performance under various PEB conditions: from 100 °C for 5 min to 110 °C for 1 min. These results indicate that the resist has a wide process latitude.

Figure 1 shows absorbance spectra of the water-soluble poly(MAGME) resist before and after DUV exposure. Like most acid-catalyzed DUV resist materials, the water-soluble resist does not bleach upon irradiation. The sensitivity curve, shown in Figure 2, is an indication of the effect of exposure dose on resulting film thickness after PEB and development. The normalized thickness is determined by calculating the ratio of the film thickness after development for each given dose to the thickness of the film prior to exposure. The nominal thickness of the samples used in the analysis was 1.0 μm. This resist formulation contains 8 wt % 1,4-butanediol and 15 wt % PAG. The film was baked (PAB) at 90 °C for 1 min and PEB at 110 °C for 2 min. Under these conditions, this resist formulation has a gel dose (the lowest dose at which any of the film is rendered insoluble in developer) of about 30 mJ/cm^2 and a contrast (the slope of the sensitivity curve at its steepest) of 4.

Imaging on Silicon Wafers. Figure 3 shows SEM photographs of poly(MAGME) resist that was post-apply baked at 90 °C for 1 min, exposed to 248 nm at a dose of 100 mJ/cm^2, and postexposure baked at 110 °C for 1 min. The images were obtained by spray development with deionized water. 1.0 μm line/space features were resolved. The 0.75 μm features are resolved, but the lines are larger than the spaces due to overexposure and/or swelling. Swelling is more evident in the 0.5 μm features. Work is underway in this group to develop water-soluble resist systems that develop without resolution loss due to swelling.

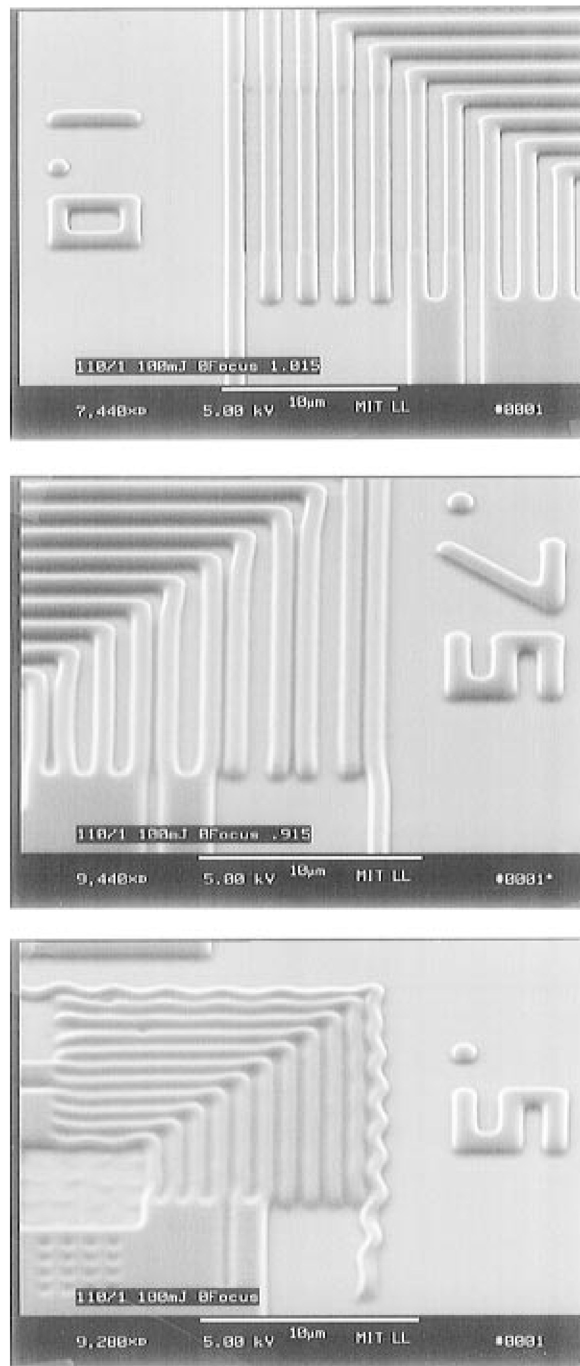
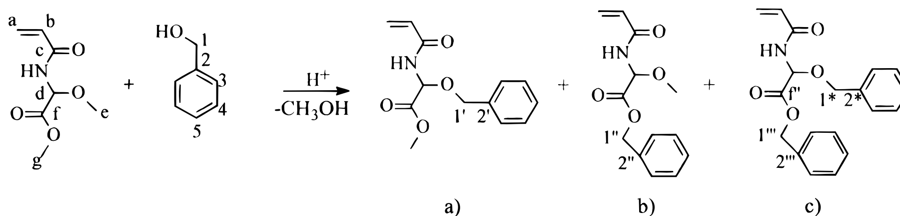


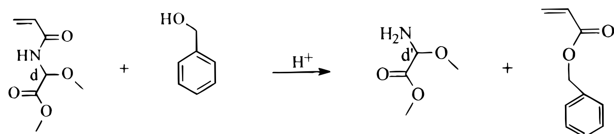
Figure 3. SEM photographs of poly(MAGME) resist for (a) 1.0, (b) 0.75, and (c) 0.5 μm line/space features.

Imaging Printed Circuit Boards. First attempts to image copper on FR-4 printed circuit board substrates using the new resist and $CuCl_2-H_2O_2$ did not yield satisfactory results. The reason appeared to be 2-fold: First, the adhesion of the resist to the copper substrate was poor. Second, the exposed regions did not provide

Scheme 3. Possible Cross-Linking Mechanisms of MAGME by an Alcohol: (a) Transacetalization, (b) Transesterification, and (c) Both Transacetalization and Transesterification



Scheme 4. Products Formed from a Transamidation Reaction



sufficient etch resistance. To improve the adhesion, the copper substrate was first cleaned and then treated with an adhesion promoter, benzotriazole. To enhance etch resistance, the cross-linking density was increased by increasing the concentration of the cross-linker, 1,4-butanediol, from 8 to 15 wt %, raising the postexposure temperature from 100 to 125 °C and using a milder copper etchant, sodium persulfate solution. These changes provided excellent copper relief images on printed circuit board inner planes.

Cross-Linking Mechanism. The water-soluble poly(MAGME) resist system functions through acid-catalyzed cross-linking of poly(MAGME) with 1,4-butanediol. However, the details of the cross-linking mechanism are not well understood. Three reactive functional groups are present in poly(MAGME), ester, aminal, and amide groups. Any or all of these could participate in the cross-linking reaction (Schemes 3 and 4). Hult et al.[5] suggested that cross-linking by self-condensation involves transaminalization. Lucas[10] indicated that cross-linking of MAGME acrylic copolymers by multifunctional amines involves transesterification. Lucas[10] also suggested a temperature-dependent cross-linking mechanism involving the ester moiety at ambient temperature and the methoxymethylamide group at elevated temperatures (≥100 °C).

A series of ^{13}C NMR experiments was conducted on model compounds in an attempt to elucidate the cross-linking mechanism of poly(MAGME). MAGME monomer was used as the model for poly(MAGME) and benzyl alcohol as the model alcohol. Benzyl alcohol was chosen because the chemical shift of its methylene group is well resolved from those of MAGME. The reactions of MAGME monomer with benzyl alcohol under *p*-toluenesulfonic acid catalysis in deuterated chloroform or DMSO were monitored at 60 and 130 °C.

Figure 4 shows the ^{13}C NMR spectrum of a mixture of MAGME, benzyl alcohol, and a catalytic amount of *p*-toluenesulfonic acid in deuterated chloroform before heating. The peak assignments are based on the labeling system defined in Scheme 3. Two peaks in the spectrum are of particular interest, the benzyl alcohol absorbances at 63.1 ppm (1) and 142.6 ppm (2), respectively. It was reasoned that any reaction of benzyl alcohol with MAGME would cause a detectable change in the chemical shift of these peaks. ^{13}C NMR spectra of the mixture that was heated at 60 °C for 3 and 15 h

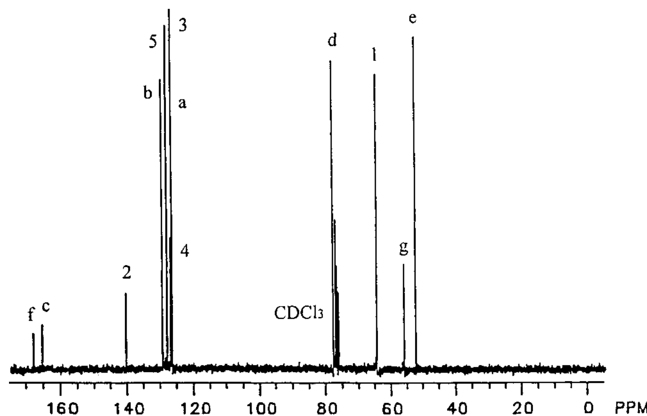
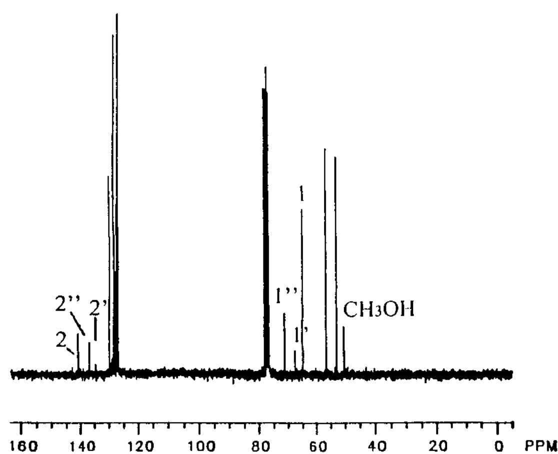


Figure 4. ^{13}C NMR spectrum of a mixture of MAGME, benzyl alcohol, and a catalytic amount of *p*-toluenesulfonic acid in deuterated chloroform before heating. See Scheme 3 for assignment of resonances.



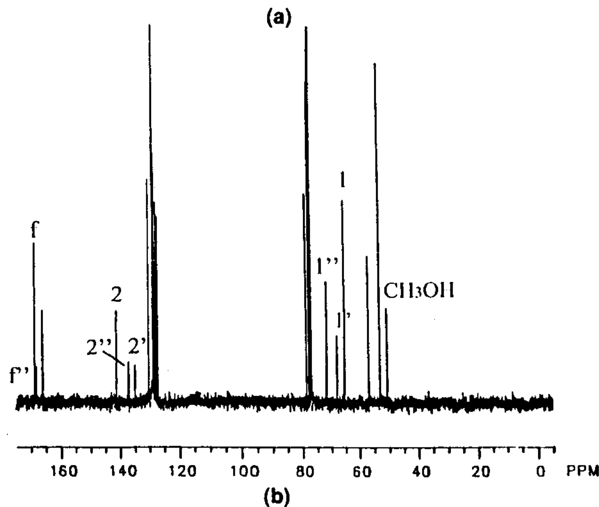


Figure 5. ^{13}C NMR spectra of products of the model reactions heated at 60 °C for 3 h (a) and 15 h (b). The appearance of resonances associated with transaminalization and transesterification are evident in both spectra. See Scheme 3 for assignment of resonances.

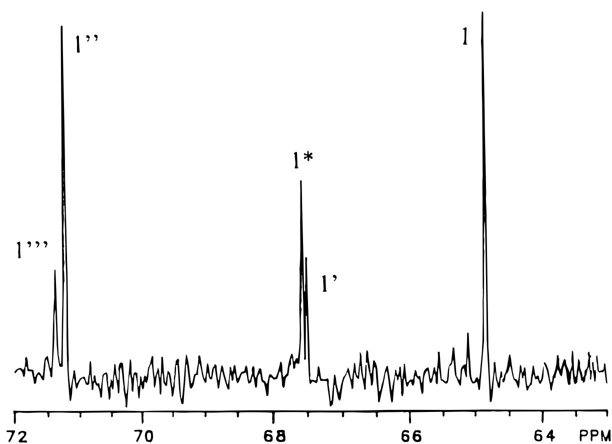


Figure 6. Expanded area of the ^{13}C NMR spectra of Figure 5b. Note that the benzylic carbon resonances of the two esters are resolved. See Scheme 3 for peak assignments.

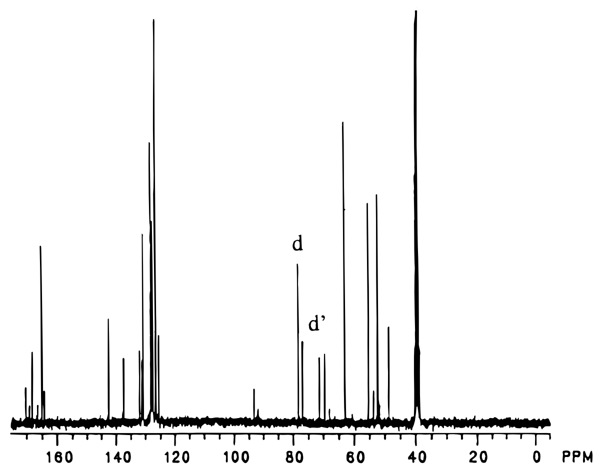


Figure 7. ^{13}C NMR spectra of the mixture in DMSO heated to 130 °C for 2 h. New resonances associated with alcoholysis of the amide are evident in the spectrum. See Scheme 3 for peak assignments.

are shown in Figure 5a,b, respectively. Heating at 60 °C for 3 h results in five new peaks in the NMR spectrum, a methanol peak at 50.2 ppm, two new benzyl methylene peaks and two new tertiary carbon peaks as shown in Figure 5. These changes are consistent with reactions in which both transaminalization and transesterification occur. From the relative intensities of the peaks, it appears that transesterification occurs more readily than transaminalization.

Further heating causes an increase in the intensities of the new peaks and a decrease in the intensity of the methoxy peaks of MAGME (Figure 5b). A more careful examination of the NMR spectrum (Figure 6) reveals that the benzylic resonances labeled 1′, 1″, and the carbonyl resonances in the region of 170 ppm are actually "doublets". This suggests double benzyl substitution (as shown in Scheme 3c). To summarize, model compound studies lead to the proposal that at 60 °C the cross-linking of poly(MAGME) by acid-catalyzed reaction with a diol proceeds via both transaminalization and transesterification reactions.

Heating the reaction mixture in DMSO at 130 °C gave results similar to those at 60 °C (Figure 7) except that a new peak at around 80 ppm was observed. This new peak can be attributed to a product formed from alcoholysis of the amide (Scheme 4). The increased temperature necessary (130 vs 60 °C) for the proposed alcoholysis of the amide functionality is consistent with the higher activation energy expected for such a transformation. The experiments with model compounds show evidence for three different reactions of MAGME monomer and alcohol under acidic conditions in solution. Therefore, we propose that acid-catalyzed cross-linking of poly(MAGME) by an alcohol may proceed via both transaminalization and transesterification reactions at lower temperatures and also via alcoholysis of the amide functionality at higher temperatures.

Conclusions

A chemically amplified, negative-tone, water-soluble resist system has been developed. The resist system consists of three water-soluble components, a polymer, poly(methyl acrylamidoglycolate methyl ether) [poly(MAGME)]; a photoacid generator, (2,4-dihydroxyphenyl) dimethylsulfonium triflate; and a cross-linker, 1,4-butanediol. Poly(MAGME) has been synthesized with molecular weights suitable for resist processing by solution free radical polymerization. The water soluble resist is able to resolve 1 μm line/space features on silicon substrates by projection printing at 248 nm (NA = 0.48) with an exposure dose of 100 mJ/cm^2. With appropriate modifications to the formulation and processing conditions, the photoresist can be used to generate etched relief copper images on printed circuit boards using aqueous sodium persulfate solution as the etchant. ^{13}C NMR was employed to characterize the products of acid-catalyzed reaction of a model compound with an alcohol to investigate the mechanism of cross-linking. On the basis of on the results of these studies, it is proposed that the acid-catalyzed cross-linking of the poly(MAGME) with 1,4-butanediol proceeds via transesterification and transaminalization reactions at low temperatures and also via alcoholysis of the amide at high temperatures.

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