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Design of Photoresists with Reduced Environmental Impact. 1. Water-Soluble Resists Based on Photo-Cross-Linking of Poly(vinyl alcohol)

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The feasibility of a chemically amplified fully water-soluble negative-tone resist based upon the cross-linking of a poly(vinyl alcohol) (PVA) matrix resin has been demonstrated. Two-component resists incorporating PVA and (2,4-dihydroxyphenyl)dimethylsulfonium triflate as a water-soluble photoacid generator were formulated in deionized water and spin-coated onto bare silicon wafers. Negative-tone images were obtained upon irradiation at 254 nm, postbaking, and subsequent development in pure water. The two-component resist suffered from swelling during development, but improved performance was obtained through the addition of a cross-linking agent, hexamethoxymethylmelamine (HMMM). The resulting three-component, water-soluble resist was able to resolve micron-sized images using a 248 nm stepper, at a dose of ca. 200 mJ/cm^2. Model studies conducted using ^{13}C NMR monitoring with 2,4-pentanediol as a model for PVA showed that under acidic catalysis HMMM reacts to form active electrophilic species that add to the diol, affording ether linkages with concomitant liberation of methanol.

Introduction

An increasing need for organic-solvent-free alternatives to the resist materials in use for the production of circuit boards, flat-panel displays, television screens, and semiconductor devices has led us to investigate photoresists spin-coated from and developed in only pure water.[1,2] Commercially available photoresist formulations used today are generally coated from organic solvents such as 1-methoxy-2-propyl acetate, also known as propylene glycol methyl ether acetate or PGMEA, and developed in solutions of aqueous base, primarily 0.26 N tetramethylammmonium hydroxide. The solvents used most commonly in the coating and the washing of wafers are typically volatile and flammable, while the strongly alkaline developer solutions are corrosive, contributing to potential environmental problems within the fabrication facility and adding to the cost of wafer processing. In addition to these problems, the use of solvents and aqueous base developers generates two separate waste streams, each with an associated cost of disposal. The use of pure water instead of organic or alkaline solvents would undoubtedly be not only environmentally desirable but it could also greatly simplify the imaging process, since pure water is already used in microprocessing facilities.

Various approaches to environmentally improved photoresist materials have been reported in the literature.[3−7] While spin-coated from organic solvents, a few of the reported materials, including both negative-[3] and positive-tone[4] designs, can be developed in pure water, removing the need for aqueous base developing solu-

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tions.[3,4] Several approaches to completely water-processable, low sensitivity, negative-tone resists have been described. These usually involve photochemically active pendant groups that cross-link[5,6] or rearrange[7] upon irradiation to afford a water-insoluble product. In one instance, polymers containing pendant pyridinium ylides produced nonswelling negative-tone images upon development in water.[7] The initially water-soluble resist undergoes photochemical rearrangement upon irradiation at 350 nm (near-UV) to afford water-insoluble *N*-acyldiazepine-containing polymers. Although these resists were said to possess improved image quality over conventional negative-tone resists, their ultimate resolution was not described. While all of these materials are spin-coated from and developed only in pure water, meeting our criteria for water-soluble photoresists, the performance of these resists is limited by low quantum yields.[3−7] We have now obtained improved performance through the incorporation of water-soluble photoactive catalysts into completely water-processable chemically amplified[8] resists.

Chemical amplification, first conceived by Fréchet, Willson, and Ito,[8] refers to the incorporation of a photoactive catalyst such as a photoacid generator (PAG)[9] into the resist film. The catalyst is liberated through the action of light and goes on to catalyze a cascade of solubility-modifying reactions within the irradiated regions of the film.[8] Chemically amplified resists are typically more sensitive than their nonamplified counterparts, since the action of every incident photon is amply enhanced. In addition to improving resist sensitivity, PAGs have also greatly increased the diversity of chemistries available to photoresist designers.[8]

Photoacid generators have been used to improve the sensitivities of environmentally enhanced resist materials.[1,2,10,11] Several imaging systems that incorporate standard chemical amplification catalysts into films spin-coated from organic solvents but developed in pure water have been reported, affording both negative-[10] or positive-tone[11] images. While these solvent-borne systems clearly do not meet the criterion of water solubility, they avoid the need for base-containing developer solutions. Truly water-processable resist materials incorporating chemical amplification have been spurred by reports of water-soluble photoacid generators.[1,2,12] One negative-tone imaging system, based upon the acid-catalyzed cross-linking of poly(methyl methoxy[(1-oxo-2-propenyl)amino]acetate), also known as poly(methyl acrylamidoglycolate methyl ether) or poly(MAGME), was investigated by our research groups.[2] This system had earlier been studied by Hult et al.,[10a] but it had to be spin-coated from organic solvents due to the water insolubilizing effect of the PAG used in its formulation. Three reactive functional groups are present in poly(MAGME), ester, aminal, and amide groups, all of which may participate in cross-linking. Our earlier studies on model compounds have indicated that transaminalization and transesterification reactions dominate at lower temperatures, while alcoholysis of the amide also occurs at higher temperatures. One-micron negative-tone line and space patterns were obtained after exposure to deep-UV and development in pure water.[2] Vekselman and Darling have also reported a class of water-soluble chemically amplified resist materials.[13]

One water-soluble polymer of interest to us for use in a new family of water-soluble resists was poly(vinyl alcohol) (PVA), by virtue of its water solubility, commercial availability, and low cost. PVA is prepared via the hydrolysis of poly(vinyl acetate). Partial hydrolysis of poly(vinyl acetate), with 80−90% cleavage of the ester groups, affords water-soluble commercial grade PVA. Due to extreme levels of hydrogen-bonding, the completely hydrolyzed polymer is insoluble in water.[14]

Poly(vinyl alcohol) has been investigated as a component for several water-borne coating materials. Negative-tone imaging materials based upon PVA functionalized with cross-linkable pendant groups have been reported.[5] In these materials, chromophores such as styrylthiazolium, -pyridinium or -quinolinium groups are attached to the PVA backbone through cyclic acetal moieties. Irradiation at the appropriate λ_{max} led to cross-linking via [2 + 2] cycloaddition reactions. Negative-tone images were obtained upon development in water, although no data was given on the resolution attainable with these systems.

Poly(vinyl alcohol) is widely used in the production of the phosphor raster of television screens and other devices.[15] To create the images needed for these devices, photosensitive films containing PVA, ammonium dichromate, and a phosphor are spin-coated as aqueous slurries. Broad spectrum UV lamps are used as illumination sources. The phosphor is inactive in the imaging process, but the ammonium dichromate acts as the photoactive site, absorbing near 360 nm. The mechanism of imaging in these materials has been elucidated,[16] proceeding through a complex series of oxidation reactions. During irradiation, Cr(VI) species are ultimately reduced to Cr(III), breaking PVA chains and cross-linking the newly formed chain ends in the process. Model studies using 2,4-pentanediol have shown that 3-penten-2-one is produced through oxidation by ammonium dichromate. In a first step, oxidation to a

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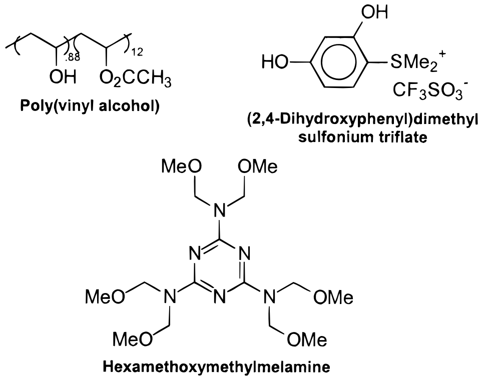
Scheme 1



ketone occurs through the formation of unstable chromium esters, followed by the ready dehydration of an adjacent alcohol to give an unsaturated ketone. In PVA, such unsaturated sites are open to attack by Cr(V) to yield glycol units that are subsequently cleaved by ammonium dichromate to afford two carboxylic acid chain ends. Cr(III) species can interact with as many as three of these acidic sites to form cross-linking complexes.

It is possible to make imageable PVA films without the incorporation of chromium or other undesirable toxic metals. We have investigated water-based two- and three-component imaging materials (Scheme 1) incorporating PVA, a water-soluble photoacid generator [(2,4-dihydroxyphenyl)dimethylsulfonium triflate],[2,12a] and hexamethoxymethylmelamine (HMMM) as an environmentally enhanced alternative to traditional solvent-cast[8] or metal-containing[15] photoresist materials.

Experimental Section

Materials. Poly(vinyl alcohol) (87−89% hydrolyzed with an average M_w of 13 000−23 000), *p*-toluenesulfonic acid monohydrate, and 2,4-pentanediol were obtained from Aldrich and used as received. Hexamethoxymethylmelamine (Pfaltz and Bauer) was used as received. (2,4-Dihydroxyphenyl)dimethylsulfonium triflate was prepared as previously described.[2,12a]

Instruments and Equipment. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DRX500 spectrometer. Shifts for ^{13}C NMR spectra are reported in ppm relative to TMS. A Hewlett-Packard 8452A diode array spectrophotometer was used to obtain UV spectra of films spin-coated on quartz wafers.

Resist Formulation and Processing. Resists were formulated in deionized water with ca. 15 wt % solids, the solids comprising 15−20 wt % PVA, 10−20 wt % PAG, and 0−20 wt % HMMM (see Scheme 1). Specific resist compositions are described in Tables 1 and 2. Solution viscosities were varied through the addition of more water as needed to achieve 0.7 μm film thickness after coating at 3000 rpm and a postapply bake (PAB) step. Resist solutions were filtered through 0.45 μm Gelman GHP Acrodisc filters. Prior to coating, silicon wafers either were cleaned with “piranha” [a mixture of 70% concentrated H_2SO_4, 30% H_2O_2 (30% in water)] at 120 °C for 10 min followed by 5 min in boiling ultrapure water or were allowed to form thick oxide layers through thermal treatment. No priming treatment was used, as this was found to have an adverse effect on adhesion. The resist samples were spin-coated onto silicon or quartz wafers, with a usual film thickness of 0.7 μm. All formulations were found to give excellent films. Coating was performed either on a Headway spinner or on an MTI Flexifab automated coating track. Hard contact PAB steps of 3 min at 120 °C were used. Film thickness measurements were performed using either a Tencor Alphastep 200 profilometer or a Prometrix SM300 film thickness mapper. Cauchy parameters for the Prometrix were determined using a Woollam variable angle scanning ellipsometer.

Table 1. Deep-UV Sensitivity and Contrast of Resists Containing PVA and PAG

PAG (wt %)	PEB temp (°C)	sensitivity[a,b] (*mJ/cm*^{2})	γ[c]
10	100	275	4.0
10	110	250	5.3
10	120	200	2.6
10	130	180	3.1
20	100	200	2.8
20	110	160	2.8
20	120	120	5.6
20	130	110	2.4

[a] PEB of 2 min in all cases. [b] Irradiated at 254 nm and developed in pure water. [c] Contrast determined from the slopes of the sensitivity curves.

Table 2. Deep-UV Sensitivity and Contrast of Three-Component PVA Resists

PAG (wt %)	HMMM (wt %)	PEB temp (°C)	sensitivity[a,b] (mJ/cm^2)	γ[c]
10	10	100	130	7.6
10	10	110	120	7.6
10	10	120	110	3.1
10	10	130	105	5.2
10	20	100	110	7.6
10	20	110	105	5.8
10	20	120	100	10.8
10	20	130	100	5.6
20	10	100	90	10.0
20	10	110	85	10.0
20	10	120	85	5.2
20	10	130	80	0.8
20	20	100	80	7.1
20	20	110	80	7.1
20	20	120	75	1.7
20	20	130	*d*	*d*

[a] PEB of 2 min in all cases. [b] Irradiated at 254 nm and developed in pure water. [c] Contrast determined from the slope of the sensitivity curves. [d] Films were thermally cross-linked during PAB.

Initial imaging experiments were carried out using an Oriel 68811 power supply coupled to an Oriel deep-UV illumination system fitted with a 500 W HgXe lamp and an exposure timer. Photon flux was measured using an Oriel Merlin radiometer equipped with a silicon detector head. The output of the mercury lamp was filtered through a 254 nm narrow bandwidth filter from Oriel Corporation. A hard contact postexposure bake (PEB) step of 2 min at 100−130 °C was used prior to development by two 10-s dips in pure water at ambient temperature.

Final patterning experiments were carried out on an Integrated Solutions XLS 248 nm stepper with 0.53 lens NA. The illuminator type was conventional with 0.74 σ. All exposures were performed with a 4× binary mask. Hard contact postexposure bakes for 2 min at 110 °C on the MTI Flexifab track were used prior to a development step consisting of two 10-s dips in puddles of deionized water at ambient temperature.

Etch data was gathered on a LAM TCP 9400 prototype etcher, with 300 W power and 150 sccm HBr, 50 sccm Cl_2 gas mix for 60 s, and directly compared to films of commercially available resists APEX-E and SPR510L. Scanning electron microscopy (SEM) was performed with a Leo 1550 operating at 3 kV. Samples were coated with 15 Å of Au/Pd prior to examination.

Results and Discussion

Two-Component PVA Resists. A chemically amplified resist was formulated by dissolving ca. 15 wt % of

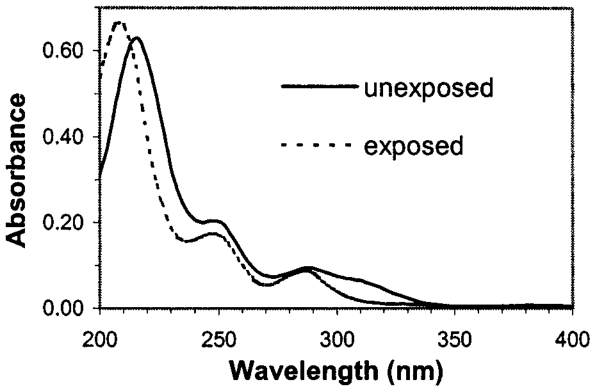
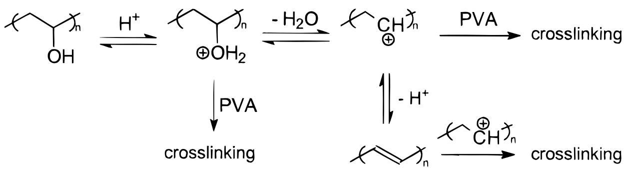


Figure 1. UV–visible spectra of 0.7 μm PVA films containing 10% PAG, before and after 425 mJ/cm^2 at 254 nm.

Scheme 2



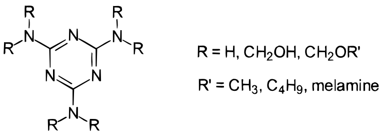
87–89% hydrolyzed PVA and the water-soluble PAG, (2,4-dihydroxyphenyl) dimethylsulfonium triflate, in deionized water. Images are obtained through acid-catalyzed cross-linking reactions, which may proceed through a number of different pathways, as illustrated in Scheme 2.

Resist solutions containing either 10 or 20 wt % PAG were prepared (Table 1). Spin coating onto bare silicon wafers gave good films with no striations. The solid content of the solutions (ca. 15 wt %) was adjusted to give 0.7 μm films when spin-coated at 3000 rpm with a PAB step of 2 min at 120 °C. Films were irradiated at 254 nm and a PEB step of 2 min at temperatures ranging from 100 to 130 °C was used. Negative-tone images were obtained after two 10 s dips in deionized water. The results of these experiments are summarized in Table 1. A wide range of contrasts and sensitivities were obtained, depending upon the conditions chosen. The best sensitivities were obtained with higher loadings of PAG and with higher PEB temperature (130 °C). However, the films were found to cross-link thermally when the PEB temperature was above 130 °C.

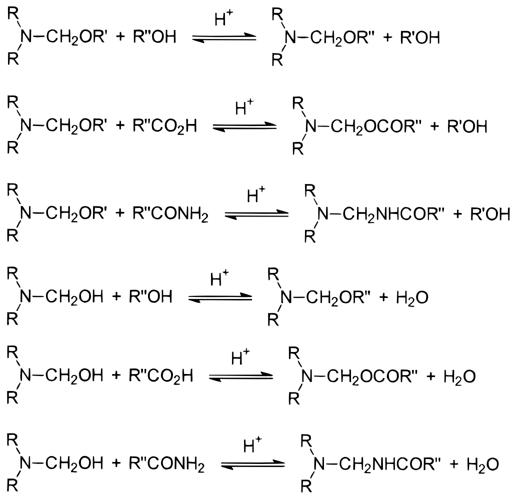
A 0.7 μm film of the water-soluble resist containing 10% PAG was spin-coated onto a quartz wafer and its optical properties were investigated. The absorbance spectra of this film before and after exposure to 425 mJ/cm^2 at 254 nm are shown in Figure 1. Small changes between the two spectra are due to the photochemical changes in the PAG upon exposure to deep-UV light. Since PVA is essentially transparent at 254 nm, the absorbance of the film can be controlled by regulating the content of PAG.

Resolution testing showed that 2.5 μm features, the largest available on the stepper mask, could not be fully resolved. Development in pure water led to badly swollen features under a variety of processing conditions. However, it was possible to print 4 μm lines using simple contact printing.

Scheme 3



Scheme 4



Three-Component PVA Resists. In an attempt to improve image quality, varying amounts of a water-soluble cross-linking agent, hexamethoxymethylmelamine (HMMM), were added to the solutions of PVA and PAG in deionized water. The more commonly utilized melamines (Scheme 3) include the melamine–formaldehyde resins (R = H, CH_2OH, or CH_2OR' where $R' = CH_3$, C_4H_9 or melamine), hexamethylolmelamine ($R = CH_2OH$), hexabutoxymethylmelamine ($R = CH_2OR'$ where $R' = C_4H_9$), and HMMM ($R = CH_2OR'$ where $R' = CH_3$).

Melamines have been used extensively as cross-linking agents in thermoset coatings[17–19] as well as in negative-tone photoresists.[20] Cross-linking occurs through their reaction with the matrix resin (Scheme 4)[18] and with themselves; the specific reaction pathway depends on the melamine chosen and the conditions used. Matrix resins that typically contain either alcoholic, amide, or carboxylic moieties react thermally or catalytically with the melamines to form insoluble network structures. Melamine–formaldehyde resins, prepared through the condensation of formaldehyde with melamine, contain some or all of the functional groups depicted in Scheme 3, making the study of their curing chemistries difficult, although several reports have been published.[18]

Several aqueous formulations of PVA with 10 to 20 wt % PAG and 10 to 20 wt % HMMM were prepared (Table 2) and tested. Spin-coating onto bare silicon

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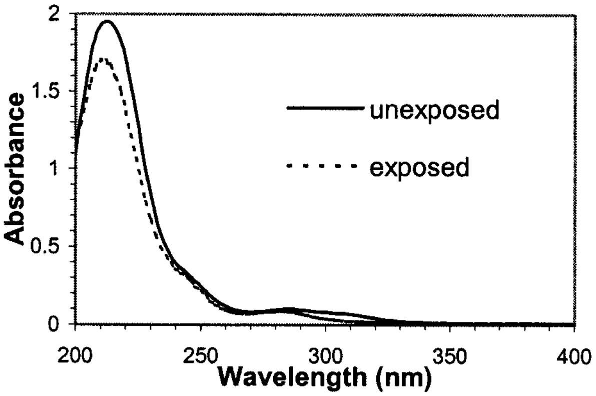


Figure 2. UV–visible spectra of 0.7 μm PVA films containing 10% PAG and 20% HMMM, before and after 425 mJ/cm^2 at 254 nm.

wafers gave good films with no striations. The viscosity of the resist solutions was adjusted by varying the solids content (ca. 15 wt %) to obtain 0.7 μm films upon coating at 3000 rpm with a PAB of 2 min at 120 °C. Irradiation at 254 nm was followed by a PEB of 2 min at temperatures ranging from 100 to 130 °C. Negative-tone images were obtained after two 10-s dips in deionized water. The results of these experiments are summarized in Table 2. A wide range of contrasts and sensitivities were obtained, depending upon the conditions chosen.

As may be seen in Table 2, the sensitivities of the three-component resists were improved over those of the two-component systems. Increased amounts of both PAG and HMMM afforded the best sensitivities, as did the use of higher PEB temperatures. However, baking above 110 °C generally had a negative effect upon the contrast, and films containing 20 wt % of both the PAG and HMMM were found to cross-link thermally at 130 °C.

Films (0.7 μm) were spin-coated onto quartz wafers and their UV absorbance was investigated. The absorbance spectra of one film containing 10% PAG and 10% HMMM before and after exposure to 425 mJ/cm^2 at 254 nm are shown in Figure 2. As expected, little change is evident in these spectra.

Mechanism of Cross-Linking and Model Studies. The water-soluble PVA resist system functions through acid-catalyzed cross-linking reactions between PVA and HMMM, and possibly also the water-soluble PAG, since it contains potentially reactive phenolic sites. HMMM is frequently chosen for use in model studies,[19] as it contains essentially only methoxymethylamino groups, allowing cross-linking to occur through only the first three pathways of Scheme 4. In the absence of acidic catalysts, the reactivity of matrix resins with HMMM has been determined to be $RCO_2H \gg RCONH_2 > ROH$, with alcohol-containing polymers exhibiting negligible reactivity with HMMM. However, the incorporation of a strongly acidic catalyst increases the reactivity of all three functional groups with HMMM, with the order of reactivity changing to $ROH > RCONH_2 > RCO_2H$.[19b]

To investigate the chemistry that occurs in the resist film, a series of model experiments was carried out. The acid-catalyzed chemistry of melamines is fairly well-understood, occurring through the formation of stabilized carbocationic species with concomitant release of methanol. These active carbocationic sites can then react with nucleophiles, as illustrated in Scheme 5.[19] The PAG used in our PVA resists may also be directly involved in the cross-linking reaction, since its phenolic functionalities are quite acidic (pH = 3.4 in 0.1 M aqueous solution), and we found that increased PAG content improved the sensitivity of our materials.

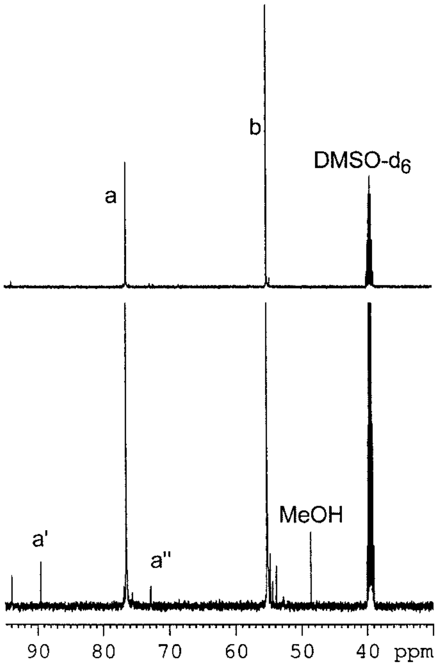
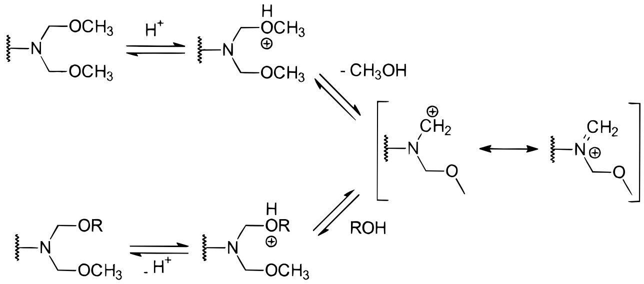
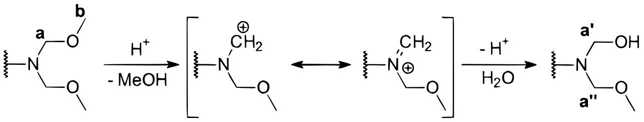


Figure 3. ^{13}C NMR spectra of HMMM with a catalytic amount of PTSA in DMSO-d_6 before and after heating at 80 °C for 8 h. See Scheme 6 for assignment of resonances.

Scheme 5



Scheme 6



A series of ^{13}C NMR experiments was conducted on model compounds in an attempt to elucidate the mechanism of cross-linking in this family of resist materials. 2,4-Pentanediol was chosen as a model for PVA. Its solutions with HMMM, the PAG and *p*-toluenesulfonic acid (PTSA) in DMSO-d_6 were monitored before and after heating at 80 °C for 8 h.

Figure 3 shows a ^{13}C NMR spectrum of a mixture of HMMM with a catalytic amount of PTSA in DMSO-d_6 before and after heating for 8 h at 80 °C. The peak assignments are based on the labeling system defined in Scheme 6. The peak at 48.6 ppm indicates the presence of methanol formed by acid-catalyzed decomposition of HMMM. A new peak is also seen at 89.5 ppm,

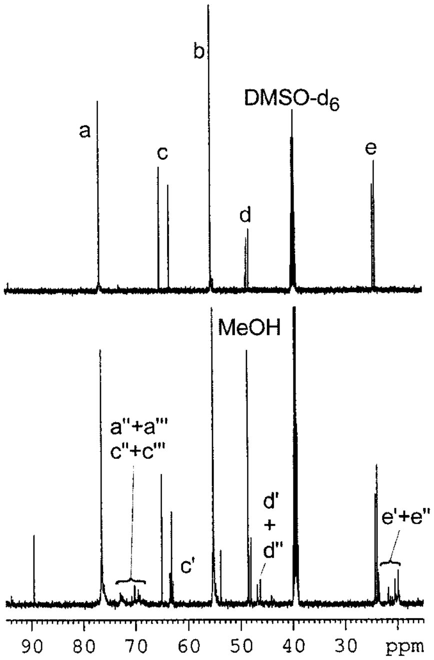
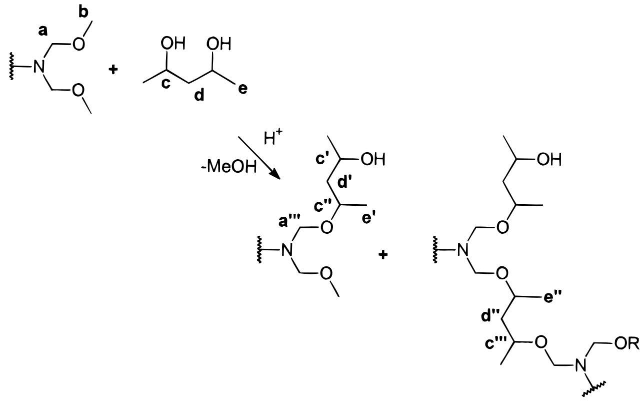


Figure 4. ^{13}C NMR spectra of a 1:1 molar mixture of HMMM and 2,4-pentanediol in DMSO-d_6, with a catalytic amount of PTSA before and after heating at 80 °C for 8 h. See Scheme 7 for assignment of resonances.

Scheme 7



probably from a new NCH_2OH group (a′) (Scheme 6) arising from reaction of water with carbocationic sites.

Figure 4 shows a ^{13}C NMR spectrum of a 1:1 molar mixture of HMMM and 2,4-pentanediol with a catalytic amount of PTSA in DMSO-d_6 before and after heating for 8 h at 80 °C. The peak assignments are based on the labeling system defined in Scheme 7. Note that the 2,4-pentanediol was a mixture of isomers and has twice the expected number of peaks in its spectrum. Again, methanol released by HMMM is seen at 48.6 ppm. In addition, new CH_3 peaks from 20 to 23 ppm correlate to species of type e′ and e″ (Scheme 7), while new CH_2 peaks at 46.3 and 46.8 ppm correlate to species of type d′ and d″ (Scheme 7). A new pair of CH peaks at 63.0 and 63.5 ppm likely arise from species of type c′, and a variety of new peaks from 68 to 73 ppm are due to new species labeled a″, a‴, c″, and c‴ in Scheme 7. These assignments support previously published mechanistic data on the cross-linking chemistry of the melamine–alcohol systems.[19a]

The reaction mechanism between HMMM and alcoholic moieties previously studied by Meijer[19a] was found to proceed through an S_N1 mechanism, as outlined in Scheme 5. Initial protonation at an oxygen atom, followed by liberation of an alcohol, affords a delocalized carbocationic moiety stabilized by the lone pair on the adjacent nitrogen atom. This highly electrophilic moiety is able to react with any available nucleophile, such as the hydroxyl functional groups present on the matrix resin. Due to the reversible nature of the reactions, evaporation of methanol from the film is crucial to the successful formation of a highly cross-linked network.

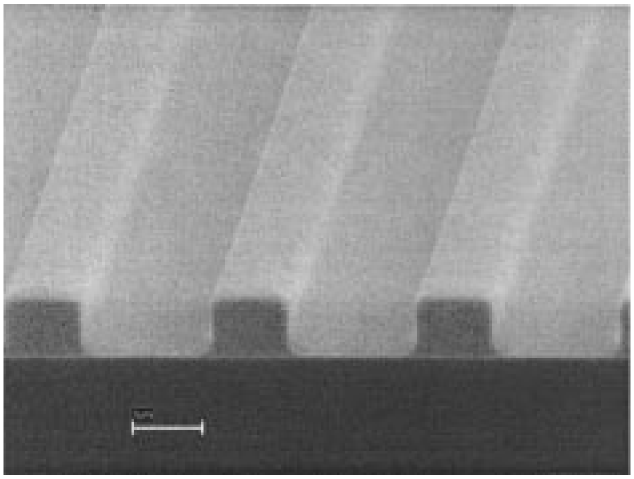


Figure 5. SEM cross sectional image of 1.5 μm negative-tone line and space patterns of PVA resist containing 10 wt % PAG and 10 wt % HMMM.

Control experiments found no reaction between the PAG and the diol, or between HMMM and the PAG, even after heating at 80 °C for 8 h with a catalytic amount of PTSA in DMSO-d_6. Thus it is likely that improvements in sensitivity linked to increased content of PAG in both two- and three-component PVA resists are due solely to the increased acidity of the film as irradiation releases more acid. The phenolic moieties of this PAG are quite acidic and may contribute to the cross-linking reactions that occur under strongly acidic catalysis, especially at high bake temperatures.

Imaging on Silicon Wafers. Figure 5 shows a cross sectional SEM image of a three-component PVA resist formulated with 10 wt % PAG and HMMM, after a PAB of 2 min at 120 °C, 396 mJ/cm^2 at 248 nm, and 2 min at 110 °C. Figure 6 shows a SEM image of a three-component PVA resist formulated with 20 wt % PAG and 20 wt % HMMM after a PAB of 2 min at 120 °C, 236 mJ/cm^2 at 248 nm, and 2 min at 110 °C. In both cases, coating and development were performed with pure water.

While the resist containing the higher amounts of PAG and cross-linker was more sensitive, better image quality was obtained using only 10 wt % of both the PAG and the cross-linker. The three-component resists containing higher levels of PAG and HMMM also afford good images, although cross sectional investigation of features shows more undercutting in this case, probably due to the higher absorbance of the films at 248 nm. It was possible to resolve 1.5 μm line and space patterns with both 10 and 20 wt % loadings of PAG and HMMM. Isolated lines were resolved down to 1.2 μm while swelling problems were encountered with features below this size.

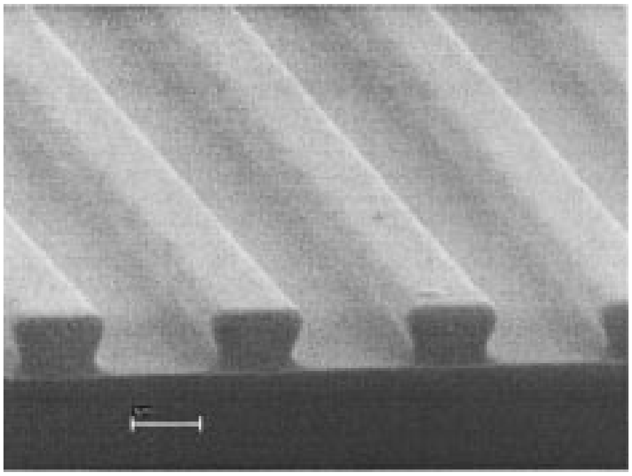


Figure 6. SEM cross sectional image of 1.5 μm negative-tone line and space patterns of PVA resist containing 20 wt % PAG and 20 wt % HMMM.

Table 3. Etching of a PVA Film Containing 20% HMMM and 10% PAG

thickness (Å)		rate (Å/min)			rate vs	
starting	final		SPR510L	APEX-E	SPR510L	APEX
8663	6471	2192	702	842	3.12	2.60

Etch Testing. A film of PVA containing 20% HMMM and 10% PAG was etched in a Lam TCP 9100 prototype etcher. Exposure to 50 sccm of Cl_2 and 150 sccm of HBr in a Lam TCP 9100 prototype etcher for 60 s at 300 W gave the results shown in Table 3. Control experiments under identical conditions showed that SPR510L was etched at 702 Å/min and that APEX-E was etched at 842 Å/min. The PVA film was found to etch at 2192 Å/min. These results are not unexpected, as the poly(vinyl alcohol) matrix is acyclic and free of aromatic rings and therefore is expected to possess little etch resistance.[21] The lack of etch resistance of these photopolymer systems may make them attractive for potential adaptation to antireflective coatings.[22]

Conclusions

This work has demonstrated the feasibility of completely water-soluble chemically amplified photoresist materials.[1,2,13] Resists based on the acid-catalyzed cross-linking of poly(vinyl alcohol) with or without additional cross-linkers such as hexamethoxymethylmelamine were found to give good low-resolution images.

The resolution of this family of resists was limited to about 1 μm, because of the cross-linking process involved in insolubilization. Cross-linking generally does not lead to a large change in polarity, leading to swelling problems when the cross-linked areas of the film retain affinity for the developing medium.[23] Swelling could be avoided if larger changes in polarity were achieved during the imaging process. Many of the previously described solvent-based deep-UV resist have utilized phenolic matrixes, which are amenable to development in aqueous base via an ionization pathway.[8] Unlike these phenolic materials, our water-soluble resists do not have the option of development via formation of ionic species, as they are spin-coated from and developed solely in water.

While these materials may not have the resolution capability needed for cutting-edge microcircuitry, they are still quite useful for other lower resolution applications. Phosphor raster screens for televisions, circuit boards, and CCD displays are some applications which could benefit from the use of an inexpensive, water-soluble, water-processable resist material.

Finally, and as pointed out by a referee, it should be emphasized that truly environmentally friendly resists would only be obtained if the polymer matrix itself as well as the photoactive compounds and cross-linkers were biodegradable and nontoxic. This is not the case for the materials described in this study.

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