

Chemically Amplified, Positive Tone, Cross-Linkable Thick-Film Polymer

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ABSTRACT: A new class of positive tone, permanent materials has been demonstrated, which are chemically amplified (CA), aqueous-developable, and cross-linkable. The intended purpose is a patterning and cross-linking method to create high sensitivity permanent dielectrics for microelectronic devices and packages. The photochemistry is based on traditional CA, acid-catalyzed deprotection of a protected organic functionality to yield an aqueous base soluble group such as a carboxylic acid or alcohol. This CA chemistry produces high contrast and high photo-speed patterning, which is especially valuable for thick-film applications where high UV exposure doses are required for non-CA materials. The photospeed is about an order of magnitude faster than commercial materials at a similar thickness. Subsequent to patterning, the remaining films or features can be cross-linked by a variety of chemical mechanisms. The working photo-patterning and cross-linking mechanisms are demonstrated on a random copolymer of tert-butyl methacrylate (TBMA) and 2-hydroxyethyl methacrylate (HEMA). The optical contrast (at 248 nm) was found to be 12.7 and the sensitivity, D_{100} , was calculated to be 50.2 mJ/cm^2 in a $9.07\text{-}\mu\text{m}$ -thick film. Undeveloped regions were cross-linked after patterning. The esterification reaction is much slower than the TBMA deprotection, so that the cross-linking reaction does not interfere with the photopatterning. Cross-linking was also evident by the change in thin film stress 6.2 to 17.9 MPa during a thermal cure. Other polymers for Fischer esterification are discussed with their advantages and disadvantages along with other cross-linking chemistries. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 759–765, 2013

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INTRODUCTION

Permanent polymeric thin films are used in many electronic packaging applications on printed circuit boards, chip package substrates such as ball grid arrays, and on-chip as interlayer dielectrics, stress relief layers, and redistribution layers.^{1–3} In these applications, it is required for the materials to be mechanically sound, temperature resistant, and to have low water permeability.^{1,4,5} These properties are required in order to fabricate highly reliable packages that will not degrade during processing or use. Additionally, these films should have a low dielectric constant so that dense connections can be made between devices without capacitive losses.

Polymers can generally provide these electrical, mechanical, and chemical properties with the added benefit of easy and low-cost processing. Some polymer dielectrics are photo-definable, which reduces the number and severity of the steps required to etch vias through the dielectric films. Positive tone materials are more suitable for interlayer dielectric applications than negative tone materials, because positive tone materials use mostly opa-

que masks, making photolithography less sensitive to particulates and increasing yield. Additionally, the ability to develop the latent image in an aqueous solution (e.g., aqueous base) reduces the need for environmentally harmful organic solvents.

A desirable combination of attributes for thick film, permanent dielectrics is to have positive tone imaging, aqueous development, and high optical sensitivity and contrast. However, common diazonaphthoquinone (DNQ)-containing, positive tone materials have low sensitivity and photospeed as a result of the low quantum efficiency of DNQ.⁶ DNQ also has a high absorption coefficient making exposure of thick films difficult. Fortunately, the absorption coefficient of the DNQ photoproduct, indene carboxylic acid, is less than DNQ, providing a photo-bleaching effect. However, thick films still require doses in the order of 100 to 1000 mJ/cm^2 .^{7,8}

Chemically amplified (CA) mechanisms are a route to improving the photospeed compared to DNQ-based systems. The most popular positive tone CA systems are made possible by an acid-catalyzed deprotection of a pendent functional group to cause a

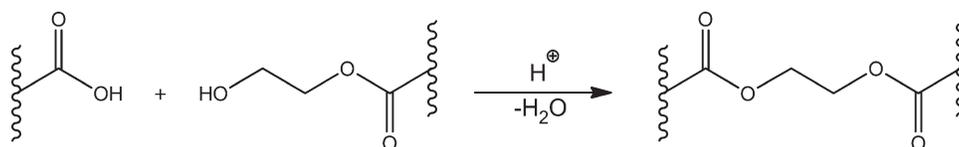


Figure 1. Acid-catalyzed Fischer esterification.

developer solubility switch, making the exposed regions soluble in aqueous base developer.^{9,10} The addition and exposure of a small amount of a photoacid generator (PAG) can result in multiple deprotection reactions. The most common CA systems involve the deprotection of a tert-butoxycarbonyl (TBOC) or a tert-butyl ester (TBE) moiety to produce an alcohol or a carboxylic acid, respectively. The resulting deprotected groups are soluble in aqueous base developer, whereas the unexposed regions remain insoluble. The high optical sensitivity of these mixtures enables thick film, positive tone polymer films with good lithographic properties.

In order to obtain good mechanical and electrical properties in a permanent dielectric, it is often necessary to cross-link the polymer film. Problems can arise with cross-linking in CA chemistries because many cross-linking mechanisms are acid catalyzed. For example, epoxy cross-linkers readily ring open in the presence of an acid and react with alcohols and carboxylic acids to form base-insoluble ethers and esters at low temperature, respectively.^{11,12} Exposure and baking of a positive tone CA film with multifunctional epoxy additives would cause the deprotection and immediate cross-linking of the exposed regions, leaving the exposed regions insoluble in the base developer.

In this article, the chemical functionalities and mechanism to enable positive tone, aqueous-developable, CA, cross-linkable dielectrics are disclosed. The experimental results demonstrating the CA, aqueous development uses a model polymer backbone. While this backbone is not suitable for use as a permanent dielectric, it nevertheless serves the purpose during this phase of the research to show that CA photo-definability is possible. The cross-linking mechanism disclosed is compatible with the traditional CA solubility switching mechanism. Also, the cross-linking mechanism does not interfere with the acid-activated deprotection and subsequent development of polymers with pendent TBOC, TBE, or other protected functionalities. The cross-linking is enabled by the inclusion of an alcohol and a carboxylic

acid as organic pendent groups on a polymer backbone. These functionalities can be on the original polymer or can be produced via the acid-catalyzed deprotection. After the exposed portions of the film are removed by an aqueous base solution, the film can be cross-linked via the Fischer esterification of an alcohol and carboxylic acid, as shown in Figure 1. This cross-linking mechanism does not interfere with the photo-patterning, because the esterification reaction is slow compared to the deprotection of the polymer at normal processing temperatures. The final cure should involve the continuous removal of water from the film since it is a product of the esterification. This can be done under an inert atmosphere at low temperatures or under normal atmospheric conditions at higher temperature (> 100°C).

The patternability and subsequent cross-linking of this system are demonstrated in this work on a random copolymer of tert-butyl methacrylate (TBMA) and 2-hydroxyethyl methacrylate (HEMA), shown in Figure 2. Unexposed films are insoluble in aqueous base. Incorporation of a PAG into the formulation and exposure to 248-nm radiation causes the aqueous base solubility switch. Films are effectively patterned at exposure doses characteristic of CA systems and then cross-linked during an extended cure at an elevated temperature. Other possible CA systems with varying organic pendent functionalities and small molecule additives are discussed with their advantages and disadvantages.

EXPERIMENTAL

Characterization Equipment

¹H-NMR spectra were recorded on a Varian Mercury Vx 400 MHz instrument. Spectra were recorded in CDCl₃ and the protonated solvent peak at 7.26 ppm was used as an internal standard. Molecular weight measurements were made by gel permeation chromatography (GPC), using a Waters 2690 separation module and a 2410 differential refractive index detector. These were connected to Waters Styragel columns (HP 1, HP 3, and HP 4), and THF was used as an eluent and solvent. Molecular weights were compared to polystyrene standards. Glass

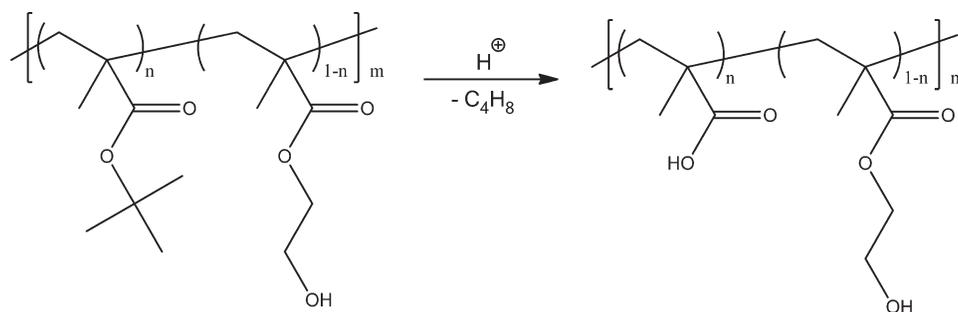


Figure 2. Acid-catalyzed deprotection of poly(TBMA-co-HEMA).

transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) with a TA Instruments DSC Q20 equipped with a Q-series DSC pressure cell. Measurements were taken under an unpressurized, nitrogen atmosphere. DSC samples were heated to 160°C at a rate of 10°C/min and then cooled to 60°C to remove the thermal history. Samples were again heated to 160°C at a rate of 10°C/min for T_g measurements. Thermogravimetric analysis (TGA) was done with a TA Instruments TGA Q50. TGA samples were heated at 5°C/min to a final temperature of 500°C. Scanning electron microscopy (SEM) was performed on a Zeiss Ultra 60 SEM. Samples for SEM were coated with 18–20 nm of palladium using a Hummer 6 Sputterer to prevent charging during analysis.

Synthesis of Poly(TBMA-co-HEMA)

TBMA and HEMA monomers were purchased from TCI America and Alfa Aesar, respectively, and were filtered through alumina before use to remove inhibitors. Azobisisobutyronitrile (AIBN) was purchased from Sigma Aldrich. A 100-mL round bottom flask was loaded with THF (25.5 mL), TBMA (5 g, 35.2 mmol), HEMA (2.29 g, 17.6 mmol), AIBN (31.9 mg, 0.194 mmol), and a stir bar. The flask was purged with dry nitrogen gas for 30 min, and the clear solution was stirred at 60°C for 23 h. The polymer was precipitated in H₂O (700 mL) from THF and collected on filter paper. The polymer was then precipitated in hexanes (750 mL) from THF, collected on filter paper, and dried *in vacuo* at 50 °C to yield a white powder in good yield (6.13 g, 83.8%).

Preparation of Thin Films

Formulations were made containing 20–35 wt % poly(TBMA-co-HEMA) in propylene glycol monomethyl ether acetate (PGMEA) and various loadings of Rhodorsil FABA PAG (provided by Promerus LLC). Films were cast by spin coating on a CEE 100CB spinner at a speed of 1500–2500 rpm onto untreated <100> silicon wafers. Thin films (< 5 μm) were baked after spin coating at 100°C for 1 min to remove residual solvent. Thicker films were baked after spin coating at 100°C for 2 min.

Lithographic Property Measurements

UV exposures were performed with an Oriel Instruments flood exposure source with a 1000 W Hg(Xe) broadband lamp filtered to 248 nm. A postexposure bake was performed at various temperatures and times to catalyze the deprotection reaction in exposed regions. The films were then developed in MF-319, a 0.26 N tetramethylammonium hydroxide (TMAH) developer. Contrast and sensitivity were measured by exposing 9- to 10-μm-thick films through a variable density optical mask (Optoline International). Thickness measurements were made with a Veeco Dektak 3 profilometer, and the thickness was plotted against the logarithmic exposure dose. The contrast (γ) is defined as the slope of this curve, which was fitted in a linear least squares method nearest to D_{100} (minimum dose at which 100% of film develops).¹³ Films were cured in a tube furnace under a N₂ atmosphere at 120°C for 10 hours.

Stress Measurements

Wafer curvature was measured with a Flexus Tencor Thin Film Stress Measurement System, Model F2320, equipped with a He-

Ne laser. Deflection measurements were recorded over the middle 80 mm of a 100 mm Si wafer with 670 and 750 nm laser irradiations. The wavelength with the highest reflected intensity was used to prevent errors due to destructive interference. The thin film stress (σ) was calculated using Stoney's equation:

$$\sigma = \left(\frac{E}{1-\nu} \right) \frac{h^2}{6Rt},$$

where $E/1-\nu$ is the biaxial elastic modulus of the substrate, h is the substrate thickness, R is the effective radius of curvature of the substrate, and t is the film thickness. R is calculated by

$$\frac{1}{R} = \frac{1}{R_2} - \frac{1}{R_1}$$

where R_1 is the radius of curvature of the bare substrate and R_2 is the new radius of curvature after film deposition.

RESULTS AND DISCUSSION

Poly(TBMA-co-HEMA)

A TBMA;HEMA random copolymer was synthesized for use in a CA, aqueous-developable, cross-linkable system. The polymethacrylate backbone was chosen as a model backbone for exploring the CA patterning and cross-linking reactions. It is not suitable as a permanent dielectric material. However, the same patterning and cross-linking reactions described here are being transposed onto polymer backbones that qualify as permanent dielectrics. The polymer composition was found to be 68.7 : 31.3 TBMA : HEMA via ¹H-NMR peak integration. This composition was found to be insoluble in 0.26 N TMAH. The polymer was characterized by GPC to have a M_n of 54,400 g/mol, M_w of 151,100 g/mol, and a polydispersity of 2.78. This polydispersity is characteristic of free radical polymerization reactions.¹⁴ The T_g of the poly(TBMA-co-HEMA) copolymer was found to be 123°C as measured by DSC (Figure 3). This T_g is adequate for film processing as it is above the postexposure bake temperature at 100–110°C for the acid-catalyzed deprotection of TBMA. Reflow of the exposed films could degrade the spatial distribution of the photo-acid and degrade the lithographic critical dimensions. The TGA of the neat polymer revealed two decomposition temperatures. The first decomposition temperature (T_{d1}) at 214.2°C corresponds to the deprotection of the TBMA group. The mass percent decrease at T_{d1} was measured to be 28.1%, which agrees well with the theoretical value of 27.9% for the loss of isobutylene at this polymer composition. A second decomposition temperature (T_{d2}) was observed at 378.7°C because of backbone degradation. TGA measurements were also performed on PAG-loaded formulations after spin coating, postapply bake, and blanket exposure. The presence of a photoacid causes a shift in T_{d1} to a lower temperature, 71.8°C, as shown in Figure 4.

Contamination of the spin-cast film by ambient organic base in the atmosphere can interfere with the CA mechanism of positive tone resists. Trace amounts of base in the atmosphere can absorb at the solid/air interface and neutralize the acid photoproduct.^{15,16} The atmospheric base can have a profound effect because of the catalytic nature of the deprotection reaction.

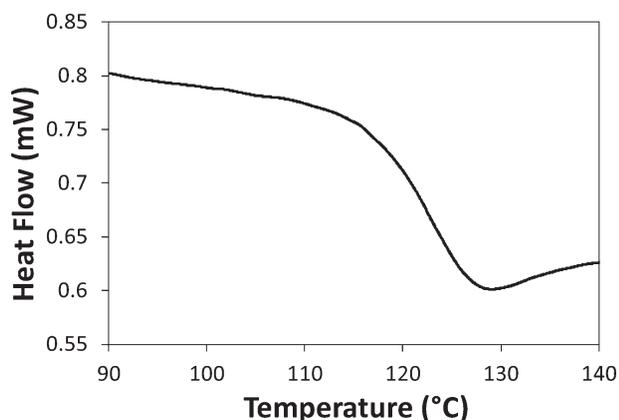


Figure 3. DSC analysis of poly(TBMA-co-HEMA).

A base-insoluble surface layer was observed on patterned films in the exposed regions because of organic base contamination in the ambient air, even though some carbon filtering of the air was implemented. The surface layer was easily removed by mechanical agitation of the film in the developer. This contamination can be further reduced by additional filtration of the air through activated carbon and limiting the exhaust of volatile bases into the air.

The contrast and sensitivity for two formulations of poly(TBMA-co-HEMA) were evaluated. Formulation A contained 1 part per hundred parts resin (pphr), mass basis, Rhodorsil FABA PAG, and Formulation B contained 3 pphr Rhodorsil FABA PAG, as listed in Table I. The contrast curves for these formulations are shown in Figure 5. In both cases, an insoluble layer was seen at doses above the conventional D_{100} value, and the thickness of this layer decreased with higher dose. It is hypothesized that this layer is due to organic base adsorbed at the wafer surface. It was also observed that pre-rinsing the wafer in an acid solution can have a significant effect on the thickness of this layer. The processing of this technique has not been optimized. Formulation A was found to have a thick film contrast of 12.7 and a D_{100} of 50.2 mJ/cm². These are good values for positive tone, thick film formulations. In Formulation B, the

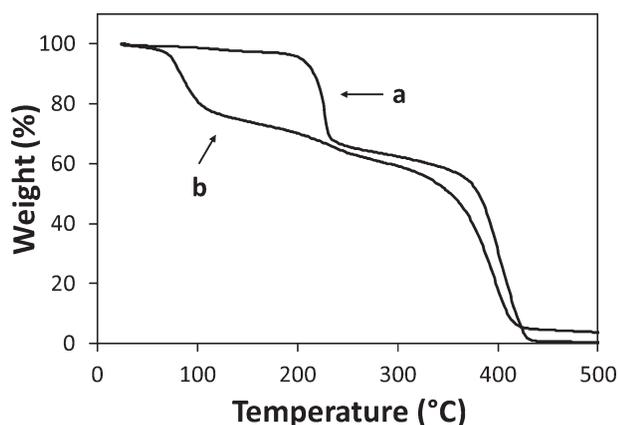


Figure 4. TGA of (a) neat poly(TBMA-co-HEMA) and (b) poly(TBMA-co-HEMA) with PAG, exposed.

Table I. Contrast Experiment Conditions

Formulation	A	B
PAG loading (pphr)	1	3
Thickness (μm)	9.07	9.87
PEB time (s)	120	120
Developing time (s)	120	150

increased PAG loading caused the contrast to decrease to 5.1 and the D_{100} to decrease to 31.2 mJ/cm². The decrease in contrast is not desirable and can be attributed to higher acid diffusion into the unexposed regions or to the higher absorption coefficient of the film. The increase in sensitivity, however, is a favorable trait of Formulation B. Figure 6 shows a SEM image of the patterned trenches in a Formulation A film. In Figure 6, the half-pitch of the trenches from bottom-to-top are 16, 12.5, and 10 μm . It can be seen that the high contrast of Formulation A produces a vertical sidewall profile.

The lithographic properties for other positive tone, thick film, permanent dielectrics are presented in Table II. The CA system presented here has a much smaller D_{100} value than photo-patternable polyimide or benzocyclobutene dielectrics because of the reuse of the photogenerated acid catalyst. The DNQ-based dielectrics are less efficient, because each photon can produce at

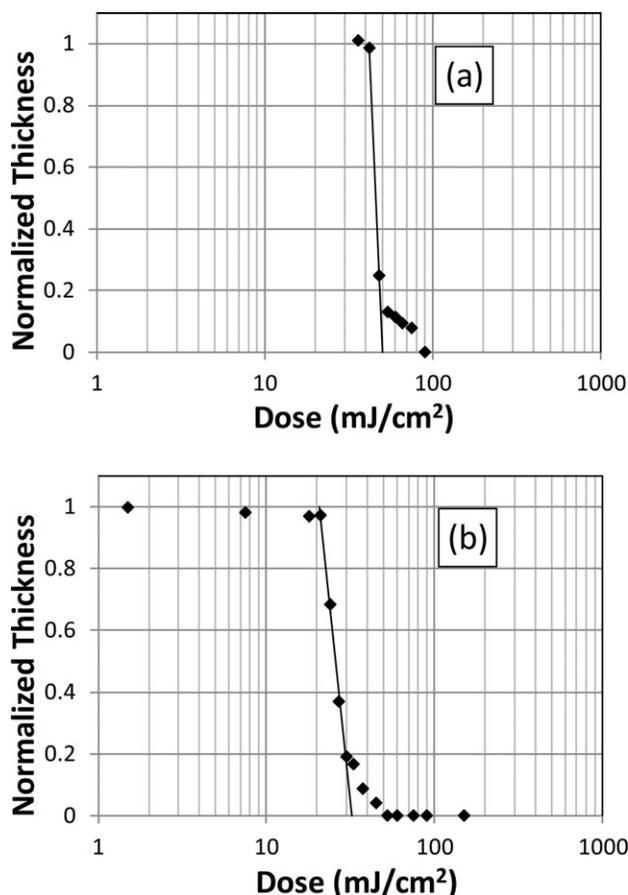


Figure 5. Contrast curves for (a) Formulation A and (b) Formulation B.

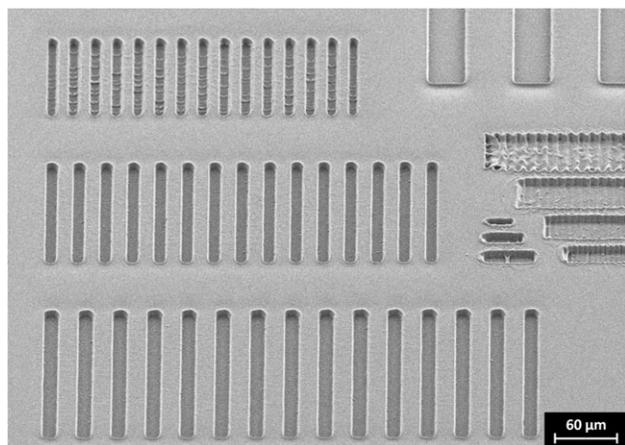


Figure 6. Developed trenches in film of Formulation A.

most one chemical reaction. In addition, the absorption coefficient of DNQ makes exposure of thick films difficult because the light intensity decreases exponentially with depth into the film. This also causes the contrast of these dielectrics to degrade with film thickness. The high exposure doses for DNQ-based dielectrics results in regions that are partially exposed, containing both DNQ and indene carboxylic acid.⁸ These regions have partial solubility in TMAH. Low loadings of the photoactive compound are necessary in the poly(TBMA-*co*-HEMA) system so that radiation can penetrate the entire depth of the film resulting in a reasonable exposure dose.

The chemical amplification mechanism can be demonstrated by comparing the number of chemical reactions to the number of photons absorbed. Assuming a density of 1.0 g/cm³, a 9.8- μ m-thick film of Formulation A contains approximately 4.8×10^{-6} mol of the TBMA moiety and 9.7×10^{-10} mol of PAG per square centimeter. A dose of 50.2 mJ/cm² of 248-nm radiation has a maximum incident dose of 1.04×10^{-7} mol of protons per square centimeter. This means that less than one photon is required for every 46.3 TBMA moieties at these processing conditions. Although it is not expected that 100% of TBMA groups need to be deprotected for aqueous base solubility, the number of deprotections caused by a noncatalytic photoreaction would be insufficient to cause the observed photopatterning. This shows that the solubility-switching reaction must be CA in nature.

Cross-Linking of Poly(TBMA-*co*-HEMA)

After developing, the patterned films were given a blanket exposure of 1000 mJ/cm² of 248-nm irradiation to activate the PAG

Table II. Lithographic Property Comparison of Poly(TBMA-*co*-HEMA) to Reported Positive Tone, Permanent Dielectrics

Dielectric	Film thickness (μ m)	D_{100} (mJ/cm ²)	Contrast
Polyimide ²¹	7.5	350	1.2
Benzocyclobutene ⁵	16.4	810	1.02
Formulation A	9.07	50.2	12.7
Formulation B	9.87	31.2	5.1

in the undeveloped portions of film. This dose was chosen to ensure that all of the PAG is activated, however, a much smaller dose would suffice. The film was then cured at 120°C for 10 hours in a nitrogen atmosphere to carry out the Fischer esterification reaction. These conditions were chosen to ensure full cross-linking of the film and continuous removal of water. After curing, the films were insoluble in 0.26 N TMAH, which is a good indication that the carboxylic acid and alcohol functionalities on the base polymer underwent the acid-catalyzed Fischer esterification reaction. Films coated at thicknesses greater than $\sim 4 \mu$ m would crack during the cure step. This could be because of the large volume change during cross-linking or to a mismatch between the coefficients of thermal expansion for the film and the substrate. Films thinner than 4 μ m were crack-free and had good film quality after curing. The mechanical properties and volume change of the film could be tuned by varying the polymer backbone or monomer ratio.

Cross-linking was confirmed by measuring the film stress before and after a thermal cure. A formulation of poly(TBMA-*co*-HEMA) with 5 pphr PAG was coated to a thickness of 3.94 μ m, baked at 100°C for 60 s, and given an exposure dose of 1000 mJ/cm² of 248-nm irradiation. A postexposure bake of 110°C for 60 s caused the film thickness to decrease to 3.01 μ m. The stress of the coated wafer was calculated to be 6.2 MPa. The sample was then cured at 120°C for 10 h under ambient atmosphere. The thickness after cure was measured to be 2.77 μ m. The final stress was calculated to be 17.9 MPa. The large increase in stress during the cure is a result of film cross-linking. A separate sample was processed under the same conditions as far as the postexposure bake is considered. After this, the sample was developed in 0.26 N TMAH to verify that these processing conditions did not result in cross-linking prior to the cure.

Polymers for Esterification Cross-Linking

Poly(methylmethacrylate) is used in this article as a model polymer backbone to investigate photo-definability and cross-linking. More appropriate backbones are available for use as a permanent dielectric. Polystyrene or polynorbornene may be suitable alternatives for a thermally stable polymer backbone with good mechanical and electrical properties. Several cross-linking options exist to create a stable, permanent dielectric after patterning that do not interfere with the CA patterning process. It is desirable to have the films be initially insoluble in aqueous base in the unexposed form, followed by a reaction leading to a solubility switch when exposed to UV radiation. Prior to curing, it is desirable to have both carboxylic acid and alcohol functionalities present, at least one on the base polymer.

Table III. Possible Monomer Functionalities

	Monomer 1	Monomer 2
Polymer 1	TBE	Alcohol
Polymer 2	Carboxylic acid	TBOC
Polymer 3	TBE	TBOC

Three example copolymers for this function are shown in Table III.

Polymer 1 is the system already described in this article, having an alcohol functionality (HEMA) pendent to the base polymer and a pendent carboxylic acid functionality. The carboxylic acid can be produced via the thermal deprotection of TBE on TBMA. This system was chosen because the volume change during deprotection is likely to be small. The deprotection of the TBE produces isobutylene, whereas the deprotection of the TBOC produces both isobutylene and carbon dioxide. Polymer 2 would be attractive if a lower temperature or shorter deprotection time was needed as the TBOC deprotection occurs more readily than that of the TBE.¹⁷ However, having pendent carboxylic acids moieties on the base polymer would likely increase the uptake of aqueous base in unexposed regions, similar to other positive tone systems that contain a pendent carboxylic acid.⁸ This could lead to a higher degree of swelling and could distort the spatial resolution of the patterned film. Polymer 3 would likely have less uptake of aqueous base in the unexposed regions because of the lack of an acidic proton. Polymer 3 would also likely have the best contrast of the three polymers in Table III because of the largest change in solubility between the unexposed and exposed states. Additionally, a 1 : 1 ratio of the two monomers would decrease the number of unreacted monomers in the film after cross-linking. This would improve the material properties and the dielectric constant. However, since each monomer would have to undergo a deprotection reaction, the volume change for Polymer 3 would be the largest.

Another option would be a terpolymer of any of the three polymers listed in Table III with an additional unreactive monomer to improve the dielectric constant. A saturated hydrocarbon pendent group would serve this purpose. With this terpolymer, there would be more room to adjust the monomer ratios to achieve full cross-linking of the alcohol and carboxylic acid moieties while maintaining control of solubility and patternability. Finally, small molecule cross-linkers could be added to the formulation. Depending on the base polymer, these could be multifunctional alcohols or multifunctional carboxylic acids. This would allow for partial cross-linking of the unexposed films and lessen the volume change because of the deprotection reaction. For example, if the Polymer 2 formulation contained a small amount of glycol additives, a low temperature cure could be done to cross-link some of the carboxylic acid groups with the glycol additives. Subsequent deprotection of the TBOC moieties by exposure and baking would produce more alcohol groups, and a final cure would be done to complete the cross-linking reaction.

Alternate Cross-Linking Mechanisms

The cross-linking mechanism needs to be carefully selected so that it is not catalyzed during creation of the latent image. In the example shown here for the positive tone, CA, aqueous-developable dielectric, a slower acid-catalyzed cross-linking reaction was used than the acid-catalyzed deprotection. If a fast cross-linking reaction were acid catalyzed, then the latent image would be insoluble in aqueous base. A variety of mechanisms other than esterification are possible. The addition of unsaturated pendent groups on the base polymer would allow for

cross-linking via a free radical polymerization mechanism. The conditions of the curing would be subject to the radical initiator activation. For example, cross-linking could be initiated at a specific temperature after patterning by selection of a thermally generated free radical initiator. Photogenerated free radical initiators are also available. If these types of initiators were chosen so that they absorb at wavelengths different from the PAG exposure wavelength, a photo-induced cross-linking of the film could be performed. This could allow for positive tone patterning of the film at one wavelength followed by negative tone cross-linking at a different wavelength.

Another possible method to cross-link the carboxylic acid or alcohol moieties would be to include an α -diazoketone that is stable under acidic conditions. α -diazoketone compounds can be added as small molecules to the polymer mixture or can be pendent to the base polymer. Exposure to elevated temperatures or radiation can cause the liberation of nitrogen gas from the α -diazoketone, after which the functional group can undergo the Wolff rearrangement to form a reactive ketene.^{18,19} The ketene product could readily react with both carboxylic acids and alcohols to form acid anhydrides and esters, respectively.²⁰ A readily available α -diazoketone that may serve this purpose is DNQ, used in many positive tone photoresists. Unfortunately, DNQ is highly absorbing at ultraviolet wavelengths and would hinder the patternability of the films. For this purpose, the PAG and the α -diazoketone moiety should not absorb strongly at the same wavelengths.

SUMMARY AND CONCLUSION

A mechanism and the functional groups to enable a working, positive tone, CA, aqueous-developable dielectric have been presented. The base polymer used to study the photo-patterning and cross-linking reactions was poly(TBMA-co-HEMA). The patternability is based on exposure of PAG followed by the acid-catalyzed deprotection of TMBA and development in TMAH. After deprotection of the remaining areas, carboxylic acid and alcohol moieties are present as pendent to the polymer. These are cross-linked via a slow Fischer esterification reaction during a long cure at an elevated temperature of 120°C. A formulation of poly(TBMA-co-HEMA) with 1 pphr of PAG had a contrast of 12.7 and a D_{100} of 50.2 mJ/cm². Cross-linking produced a film that was insoluble in aqueous base. The stress of a poly(TBMA-co-HEMA) film containing 5 pphr PAG changed from 6.2 to 17.9 MPa during a thermal cure, indicating film cross-linking. Many variations based on the Fischer esterification cross-linking are also presented. These include a variety of different copolymers and terpolymers as well as formulations with small molecule cross-linkers. Other cross-linking schemes that retain CA patternability are identified. Efforts to demonstrate the same patterning and cross-linking reactions on a permanent dielectric backbone are underway.

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