

## ANTI-REFLECTIVE COATINGS USING VINYL ETHER CROSSLINKERS

## FEDERALLY SPONSORED RESEARCH/DEVELOPMENT PROGRAM

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5 DASG60-01-C-0047 awarded by the U.S. Army Space and Missile Defense Command.  
The United States government has certain rights in the invention.

## BACKGROUND OF THE INVENTION

## Related Applications

10 This application claims the priority benefit of a provisional application entitled  
ANTI-REFLECTIVE COATING USING VINYL ETHER CROSSLINKERS, Serial  
No. 60/566,329, filed April 29, 2004, incorporated by reference herein.

## Field of the Invention

15 The present invention is concerned with novel wet developable anti-reflective  
coating compositions and methods of using the same.

## Description of the Prior Art

20 As feature sizes shrink to less than 110 nm, new and more advanced materials  
will be needed to achieve the goals set by the semiconductor industry. Improvements  
in both photoresists and bottom anti-reflective coatings are needed to achieve high-  
resolution lithography targets. For example, resist thickness loss that occurs during the  
bottom anti-reflective coating and substrate etch steps becomes a critical issue because  
new resists are much thinner than older generation materials. While resist thickness is  
25 being reduced, bottom anti-reflective coating thickness is not expected to decrease at  
the same rate, which further complicates the problem of resist loss. A solution to this  
problem is to eliminate the bottom anti-reflective coating etch step by using a wet-  
developable bottom anti-reflective coating.

30 Wet-developable bottom anti-reflective coatings have typically utilized a  
polyamic acid soluble in alkaline media as a polymer binder, thus allowing the bottom  
anti-reflective coating to be removed when the resist is developed. These traditional  
wet-developable bottom anti-reflective coatings are rendered insoluble in resist solvents  
taking advantage of a thermally driven amic acid-to-imide conversion. This process

works well, however, it has two limitations: (1) the bake temperature window can be narrow (less than 10°C) where the bottom anti-reflective coating remains insoluble in organic solvents but soluble in alkaline developer; and (2) the wet-develop process is isotropic, meaning the bottom anti-reflective coating is removed vertically at the same rate as horizontally, which leads to undercutting of the resist lines. While this is not a problem with larger geometries (greater than 0.2 micron), it can easily lead to line lifting and line collapse at smaller line sizes.

#### SUMMARY OF THE INVENTION

The present invention overcomes the problems of prior art wet developable anti-reflective coatings by providing new wet developable compositions that are useful in the manufacture of microelectronic devices.

In more detail, the inventive compositions comprise a compound selected from the group consisting of polymers, oligomers, and mixtures thereof dissolved or dispersed in a solvent system. The compound is preferably present in the composition at a level of from about 0.5-10% by weight, preferably from about 0.5-5% by weight, and even more preferably from about 1-4% by weight, based upon the total weight of all ingredients in the composition taken as 100% by weight.

If the compound is a polymer, it is preferred that the average molecular weight be from about 1,000-100,000 Daltons, and more preferably from about 1,000-25,000 Daltons. Preferred polymers include those selected from the group consisting of aliphatic polymers, acrylates, methacrylates, polyesters, polycarbonates, novolaks, polyamic acids, and mixtures thereof.

If the compound is an oligomer, it is preferred that the molecular weight be from about 500-3,000 Daltons, and more preferably from about 500-1,500 Daltons. Preferred oligomers include substituted and unsubstituted acrylates, methacrylates, novolaks, isocyanurates, glycidyl ethers, and mixtures thereof.

Regardless of whether the compound is an oligomer or polymer, and regardless of the structure of the polymer backbone or oligomer core, it is preferred that the compound comprise an acid functional group. The acid group is preferably present in the compound at a level of at least about 5% by weight, preferably from about 5-90%

by weight, and even more preferably from about 5-50% by weight, based upon the total weight of the compound taken as 100% by weight. Preferred acid groups are groups other than phenolics, such as carboxylic acids (-COOH).

Unlike prior art compositions, the acid group is preferably not protected by a protective group. That is, at least about 95%, preferably at least about 98%, and preferably about 100% of the acid groups are free of protective groups. A protective group is a group that prevents the acid from being reactive.

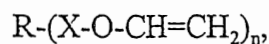
Because protective groups are not necessary with the present invention, it is also preferred that the compound is not acid-sensitive. An acid-sensitive polymer or oligomer is one that contains protective groups that are removed, decomposed, or otherwise converted in the presence of an acid.

In another embodiment, a combination of protected acid groups and unprotected acid groups could be utilized. In these embodiments, the molar ratio of protected acid groups to unprotected acid groups is from about 1:3 to about 3:1, and more preferably from about 1:2 to about 1:1.

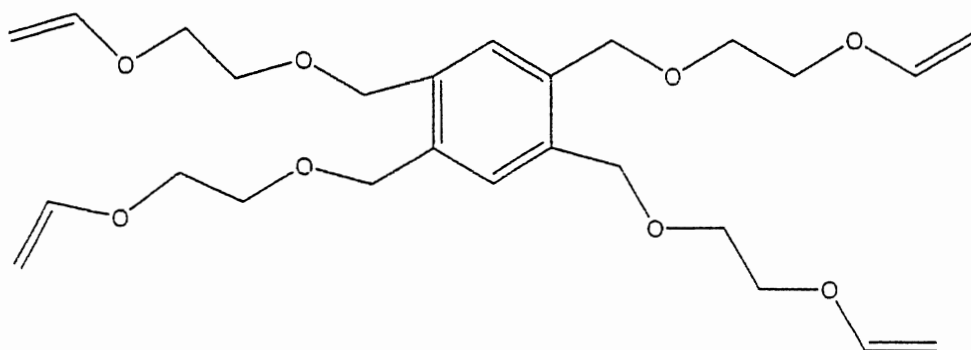
It is also preferred that the inventive compositions comprise a chromophore (light attenuating compound or moiety). The chromophore can be bonded with the compound (either to a functional group on the compound or directly to the polymer backbone or oligomer core), or the chromophore can simply be physically mixed in the composition. The chromophore should be present in the composition at a level of from about 5-50% by weight, and preferably from about 20-40% by weight, based upon the total weight of the compound taken as 100% by weight. The chromophore is selected based upon the wavelength at which the compositions will be processed. For example, at wavelengths of 248 nm, preferred chromophores include naphthalenes (e.g., naphthoic acid methacrylate, 3,7-dihydroxynaphthoic acid), heterocyclic chromophores, carbazoles, anthracenes (e.g., 9-anthracene methyl methacrylate, 9-anthracenecarboxylic acid), and functional moieties of the foregoing. At wavelengths of 193 nm, preferred chromophores include substituted and unsubstituted phenyls, heterocyclic chromophores (e.g., furan rings, thiophene rings), and functional moieties of the foregoing. The preferred inventive compositions will also include a crosslinker.

Preferred crosslinkers are vinyl ether crosslinkers. It is preferred that the vinyl ether crosslinkers be multi-functional, and more preferably tri- and tetra-functional.

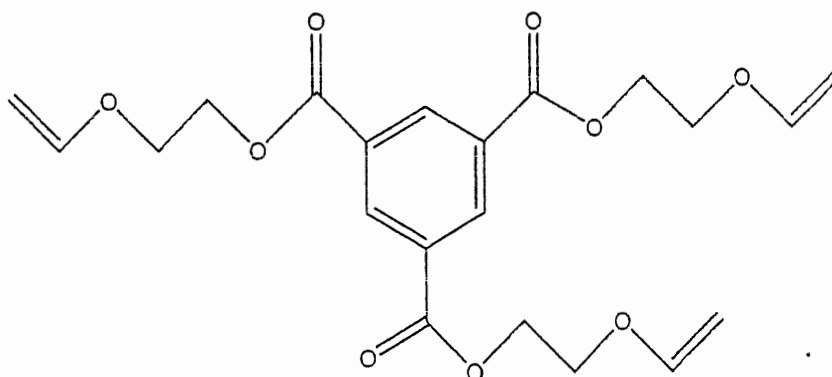
Preferred vinyl ether crosslinkers have the formula



where R is selected from the group consisting of aryls (preferably C<sub>6</sub>-C<sub>12</sub>) and alkyls (preferably C<sub>1</sub>-C<sub>18</sub>, and more preferably C<sub>1</sub>-C<sub>10</sub>), each X is individually selected from the group consisting of: alkyls (preferably C<sub>1</sub>-C<sub>18</sub>, and more preferably C<sub>1</sub>-C<sub>10</sub>); alkoxys (preferably C<sub>1</sub>-C<sub>18</sub>, and more preferably C<sub>1</sub>-C<sub>10</sub>); carboxys; and combinations of two or more of the foregoing, and n is 2-6. The most preferred vinyl ether crosslinkers include those selected from the group consisting of ethylene glycol vinyl ether, trimethylolpropane trivinyl ether, 1,4-cyclohexane dimethanol divinyl ether, and mixtures thereof. Another preferred vinyl ether crosslinker has a formula selected from the group consisting of



and



The preferred compositions also contain a catalyst. The preferred catalyst is an acid generator, and particularly a photoacid generator ("PAG," both ionic and/or non-ionic). Any PAG that produces an acid in the presence of light is suitable. Preferred PAGs include onium salts (e.g., triphenyl sulfonium perfluorosulfonates such as triphenyl sulfonium nonaflate and triphenyl sulfonium triflate), oxime-sulfonates (e.g., those sold under the name CGI<sup>®</sup> by CIBA), and triazines (e.g., TAZ108<sup>®</sup> available from Midori Kagaku Company).

The compositions preferably comprise from about 0.1-10% by weight of catalyst, and more preferably from about 1-5% by weight of catalyst, based upon the total weight of the polymer and oligomer solids in the composition taken as 100% by weight.

It will be appreciated that a number of other optional ingredients can be included in the compositions as well. Typical optional ingredients include surfactants, amine bases, and adhesion promoters.

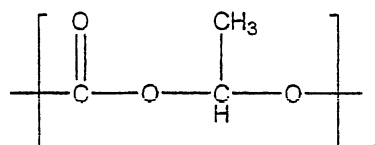
Regardless of the embodiment, the anti-reflective compositions are formed by simply dispersing or dissolving the polymers, oligomers, or mixtures thereof in a suitable solvent system, preferably at ambient conditions and for a sufficient amount of time to form a substantially homogeneous dispersion. The other ingredients (e.g., crosslinker, PAG) are preferably dispersed or dissolved in the solvent system along with the compound.

Preferred solvent systems include a solvent selected from the group consisting of propylene glycol methyl ether acetate (PGMEA), propylene glycol methyl ether (PGME), propylene glycol *n*-propyl ether (PnP), ethyl lactate, and mixtures thereof. Preferably, the solvent system has a boiling point of from about 50-250°C, and more preferably from about 100-175°C. The solvent system should be utilized at a level of from about 80-99% by weight, and preferably from about 95-99% by weight, based upon the total weight of the composition taken as 100% by weight.

The method of applying the compositions to a substrate (such as a microelectronic substrate) simply comprises applying a quantity of a composition hereof to the substrate surface by any known application method (including spin-coating). The substrate can be any conventional circuit substrate, and suitable substrates can be planar

or can include topography (e.g., contact or via holes, trenches). Exemplary substrates include silicon, aluminum, tungsten, tungsten silicide, gallium arsenide, germanium, tantalum, tantalum nitride, SiGe, low k dielectric layers, dielectric layers (e.g., silicon oxide), and ion implant layers.

After the desired coverage is achieved, the resulting layer should be heated to a temperature of from about 100-250°C, and preferably from about 120-200°C, to induce crosslinking of the compound in the layer. In embodiments where the polymer or oligomer includes a carboxylic acid group, and the crosslinker is a vinyl ether crosslinker, the crosslinked polymers or oligomers will comprise acetal linkages having the formula



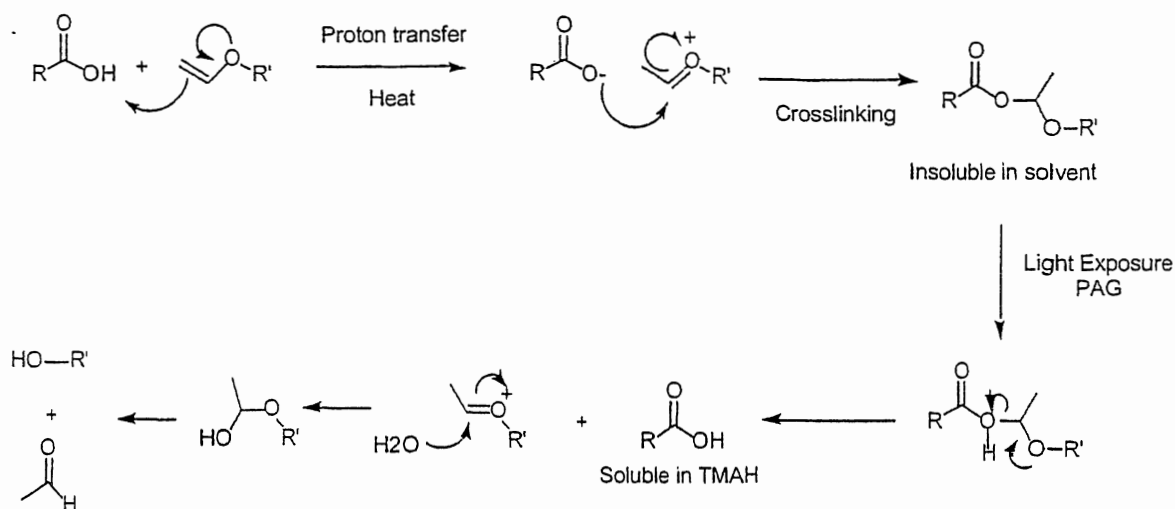
The crosslinked layer will be sufficiently crosslinked that it will be substantially insoluble in typical photoresist solvents. Thus, when subjected to a stripping test, the inventive coating layers will have a percent stripping of less than about 5%, preferably less than about 1%, and even more preferably about 0%. The stripping test involves first determining the thickness (by taking the average of measurements at five different locations) of a cured layer. This is the average initial film thickness. Next, a solvent (e.g., ethyl lactate) is puddled onto the cured film for about 10 seconds, followed by spin drying at about 2,000-3,500 rpm for about 20-30 seconds to remove the solvent. The thickness is measured again at five different points on the wafer using ellipsometry, and the average of these measurements is determined. This is the average final film thickness.

The amount of stripping is the difference between the initial and final average film thicknesses. The percent stripping is:

5                      
$$\% \text{ stripping} = \left( \frac{\text{amount of stripping}}{\text{initial average film thickness}} \right) \times 100 .$$

10                      The crosslinked layers will also have superior light absorbance. The n value of this cured anti-reflective layer or coating will be at least about 1.3, and preferably from about 1.4-2.0, while the k value will be least about 0.1, and preferably from about 0.2-0.8, at the wavelength of use (e.g., 157 nm, 193 nm, 248 nm, 365 nm). The OD of the cured layers will be at least about 5/ $\mu$ m, preferably from about 5-15/ $\mu$ m, and even more preferably from about 10-15  $\mu$ m, at the wavelength of use (e.g., 157 nm, 193 nm, 248 nm, 365 nm).

15                      After the layers are cured, further steps can be carried out as necessary for the particular manufacturing process. For example, a photoresist can be applied to the cured layer and subsequently patterned by exposure to light of the appropriate wavelength followed by development of the exposed photoresist. Advantageously, as the photoresist is exposed to light, so is the inventive coating. Upon exposure to light,  
20                      an acid is generated from the PAG, and this acid "decrosslinks" the compound in the layer. That is, the acid breaks the bond that was formed between the compound and the crosslinker upon thermal crosslinking. When a carboxylic acid is the acid group on the polymer or oligomer, decrosslinking results in the formation of the same polymer or oligomer originally present in the composition as well as an alcohol and an  
25                      acetylaldehyde. This reaction is demonstrated in the scheme below (where R represents the polymer backbone or oligomer core, and R' represents the remainder of the vinyl ether crosslinker).

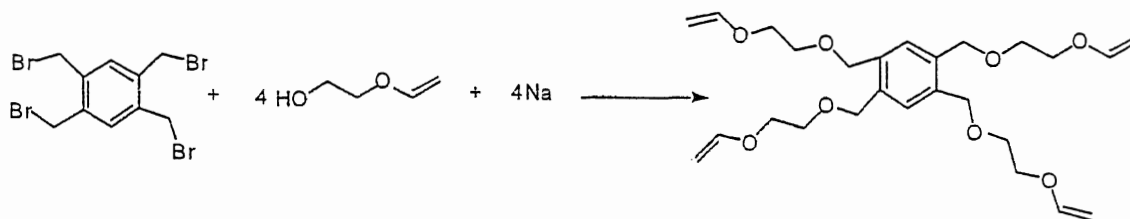


It will be appreciated that after this decrosslinking has occurred, the inventive coatings are rendered wet developable. That is, the cured compositions that have been exposed to light can be substantially (and preferable completely) removed with conventional aqueous developers such as tetramethyl ammonium hydroxide and KOH developers. Some of these developers are commercialized under the names PD523AD (available from JSR Micro), MF-319 (available from Shipley, Massachusetts), and NMD3 (available from TOK, Japan) developers. At least about 95%, preferably at least about 99%, and even more preferably 100% of the inventive coatings will be removed by a base developer such as tetramethyl ammonium hydroxide and/or KOH developers. This high percent solubility in commercially-available developers after light exposure is a significant advantage over the prior art as this shortens the manufacturing process and makes it less costly.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples set forth preferred methods in accordance with the invention. It is to be understood, however, that these examples are provided by way of illustration and nothing therein should be taken as a limitation upon the overall scope of the invention.

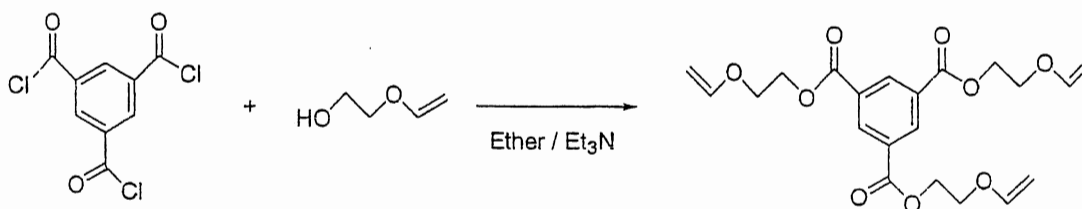
## MATERIALS AND METHODS

1. *In-house Preparation of Tetrafunctional Vinyl Ether Crosslinker*

|       |        |       |      |        |
|-------|--------|-------|------|--------|
| FW:   | 449.79 | 88.11 | 23   | 478.55 |
| gr:   | 3.6976 | 2.9   | 0.8  |        |
| mmol: | 8.22   | 32.9  | 34.8 |        |

The reaction was carried out under  $N_2$  in a 250-ml, 3-neck, round bottom flask. The Na cube was rinsed with hexane prior to use to remove mineral oil, placed quickly in a vial for weighing, and then transferred to the flask, which contained 50 ml THF. An alcohol solution in THF (20 ml) was added dropwise through an addition funnel (about 15 minutes), and then heated to reflux until all of the Na was dissolved (about 30 minutes). The solution was light yellow and homogeneous. Tetrabromo durene dissolved in THF (15 ml) was added to the reaction flask dropwise (about 30 minutes), and allowed to reflux overnight. Upon addition, the mixture became heterogenous (NaBr precipitates).

After cooling, the salts were filtered and rinsed with THF. The THF was removed in a rotary evaporator, and the remaining oil was redissolved in  $CHCl_3$  (25 ml). The chloroform solution was washed with water (2x25 ml), and then with brine (saturated NaCl, 25 ml). The organic layer was dried by passing it over a bed of silica gel. The solvent was removed. The product was left under vacuum for further drying.

2. *In-house Preparation of Trifunctional Vinyl Ether Crosslinker*

Ethylene glycol vinyl ether (6 grams) and triethyl amine (7.5 ml) were mixed in ether (40 ml) and treated dropwise with a solution of trimesic acid chloride (6 grams) in ether (40%). After addition, the mixture was heated to reflux for 1.5 hours. Residual salts were removed by filtration, and the ether solution was washed with 10% NaOH (2 x 25 ml), washed with water (25 ml), and then dried over anhydrous magnesium sulfate. After removal of the solvent under pressure, light yellow oil was collected (69% yield).

## EXAMPLE 1

## Polymer Composition Without Acid Sensitive Groups

A homopolymer of methacryloyloxy ethyl phthalate (28.9 mmol, obtained from Aldrich) and 2,2'-azobisisobutyronitrile ("AIBN," 0.58 mmol radical initiator, obtained from Aldrich) were mixed in 50 ml tetrahydrofuran ("THF," obtained from Aldrich) under a nitrogen atmosphere and heated to reflux for 15 hours. The reaction was allowed to cool, concentrated to about 25 ml, and then precipitated into 200 ml hexane. After filtration and drying, about 8 grams of the remaining white powder were collected. The polymer molecular weight ("Mw") was measured by using polystyrene standards and gel permeation chromatography ("GPC") and was determined to be 68,400.

A 193-nm bottom anti-reflective coating was prepared as follows: A 3% solids formulation containing ethyl lactate ("EL," obtained from General Chemical), the polymer prepared above, 28% by weight Vectomer 5015 (a vinyl ether crosslinker

obtained from Aldrich), and 4% by weight triphenyl sulfonium nonaflate (a PAG, obtained from Aldrich) was prepared and filtered through 0.1-micron endpoint filter. The crosslinker and PAG amounts were based on the weight of the polymer.

The above formulation was spin coated at 1,500 rpm on a silicon substrate and then baked at 160°C. The films were rinsed with EL to determine resistance to the resist solvent, exposed to light for 2 seconds, heated in a post-exposure bake ("PEB") at 130°C, and immersed in developer (tetramethylammonium hydroxide or "TMAH," sold under the name PD523AD, obtained from JSR Micro) for 60 seconds to decrosslink and remove the bottom anti-reflective coating. Table 1 below shows that the bottom anti-reflective coating had good solvent resistance, and that it could only be removed by an alkaline developer *after* exposure. This example shows that a polymer having an acid-sensitive group is not required for the crosslinking/decrosslinking process.

Table 1

| Initial Thickness (Å) | Thickness After 20 sec. EL Rinse (Å) | % Loss | Thickness After Development (No Exposure) (Å) | % Loss | Thickness After Exposure, PEB <sup>a</sup> , and Development (Å) | % Loss |
|-----------------------|--------------------------------------|--------|-----------------------------------------------|--------|------------------------------------------------------------------|--------|
| 619                   | 590                                  | 4.7    | 712                                           | 0      | 65                                                               | 90     |

<sup>a</sup> Post-exposure bake

## EXAMPLE 2

### Bottom Anti-Reflective Coating Containing

### Chromophore, Acid, and Dissolution Enhancer

Methacrylic acid ("MAA," 31.2 mmol, obtained from Aldrich), tert-butyl methacrylate ("tBMA," 26.0 mmol, obtained from Aldrich), 9-anthracene methyl methacrylate ("9-AMMA," 14.5 mmol, obtained from St-Jean Photochemicals Inc.), and AIBN (1.4 mmol) were mixed in 60 ml THF under nitrogen atmosphere and heated to reflux for 19 hours. The reaction was allowed to cool, was concentrated to about 35 ml, and was then precipitated into 150 ml hexane. After filtration and drying, about 10 grams of a light yellow powder were collected. The polymer Mw, measured by using polystyrene standards and GPC, was determined to be 23,800.

A 3% solids formulation containing the polymer, PGME (obtained from General Chemical), PGMEA (obtained from General Chemical), 10% tetrafunctional vinyl ether crosslinker prepared in-house as described above, and 4% triphenyl sulfonium triflate (a PAG obtained from Aldrich) was prepared and filtered through a 0.1-micron endpoint filter. The crosslinker and PAG amounts were based on polymer weight. The above formulation was spin coated at 1,500 rpm onto a silicon substrate and then baked at 160°C. The optical constants at 248 nm were measured using a variable angle spectroscopic ellipsometer ("VASE") and were determined to be  $k = 0.42$  and  $n = 1.4589$ . The film was rinsed with EL to test resistance to a resist solvent. After a rinse and spin dry cycle, no change in film thickness occurred. The cured film was immersed in 0.26 N TMAH solution, and no thickness loss occurred. However, after the film was exposed to light from a mercury-xenon lamp for 2 seconds and underwent a subsequent post-exposure bake at 130°C for 90 seconds, the film became soluble in developer.

### EXAMPLE 3

#### Control of Optical Properties by Polymer Composition

Several polymers were prepared using the procedure in Example 2 and using varying amounts of chromophore (9-AMMA) in order to demonstrate control of the optical properties of the bottom anti-reflective coating while maintaining dissolution properties. A 3% solids formulation containing PGME, PGMEA, 10% tetrafunctional vinyl ether crosslinker prepared in-house as described above, and 4% triphenyl sulfonium triflate PAG was prepared and filtered through a 0.1-micron endpoint filter.

Table 2 shows that by increasing chromophore loading in the polymer, optical density, and substrate reflectivity can be controlled.

Table 2

| 9-AMMA<br>(Mole %) <sup>a</sup> | k value | n value | OD/ $\mu\text{m}$ | 1st Minimum<br>Thickness ( $\text{\AA}$ ) | Reflectivity at 1st<br>Minimum Thickness (%) |
|---------------------------------|---------|---------|-------------------|-------------------------------------------|----------------------------------------------|
| 10                              | 0.27    | 1.52    | 6.1               | 660                                       | 2.6                                          |
| 20                              | 0.42    | 1.459   | 10.8              | 660                                       | 0.08                                         |
| 30                              | 0.54    | 1.462   | 13.3              | 620                                       | 0.87                                         |

<sup>a</sup> based upon total moles of solids in composition

## EXAMPLE 4

## Comparative Example with Phenolic Polymer

A comparative example was prepared to demonstrate that vinyl ether crosslinking with a phenolic resin does not provide sufficient crosslinking density to prevent stripping by photoresist solvent.

In this procedure, 0.5 grams of polyhydroxystyrene ("PHS," obtained from DuPont), 0.02 grams of a triazine PAG (TAZ107, obtained from Midori Kagaku Company), 8.5 grams of EL, and various amounts of triscarboxyphenyl trivinyl ether prepared in-house were mixed and filtered through a 0.1-micron endpoint filter. Two additional formulations were also prepared in which 9-anthracene carboxylic acid ("9-ACA," a chromophore obtained from Aldrich) were added to the composition to form a bottom anti-reflective coating for 248-nm lithography. Films were spin coated onto silicon substrates and then baked at varying temperatures up to 205°C. Table 3 shows the results obtained. In all cases, the bottom anti-reflective coating stripped completely when rinsed with EL.

Table 3

| Polymer | Crosslinker:PHS Ratio | Bake Temperature (°C) | PAG    | Chromophore | EL Stripping (% change in film thickness) |
|---------|-----------------------|-----------------------|--------|-------------|-------------------------------------------|
| PHS     | 2:1                   | 150, 205              | TAZ107 | --          | 100                                       |
| PHS     | 4:1                   | 150, 205              | TAZ107 | --          | 100                                       |
| PHS     | 2:1                   | 100-205 <sup>a</sup>  | TAZ107 | 9-ACA       | 100                                       |
| PHS     | 4:1                   | 100-205               | TAZ107 | 9-ACA       | 100                                       |

<sup>a</sup> tests were carried out at 10-degree intervals through this temperature range.

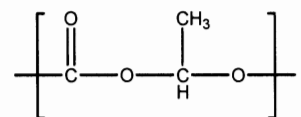
**We claim:**

1. A method of forming a microelectronic structure, said method comprising the steps of:

providing a substrate having a surface;

applying a composition to said surface, said composition comprising compounds dissolved or dispersed in a solvent system, said compounds being selected from the group consisting of polymers, oligomers, and mixtures thereof, and said compound comprising respective acid groups other than phenolic groups, and having protected acid groups and unprotected acid groups, wherein the molar ratio of protected acid groups to unprotected acid groups is from about 1:3 to about 3:1, wherein said acid groups include carboxylic acid groups;

crosslinking the compounds in said composition to yield crosslinked compounds comprising linkages having the formula



forming a photoresist layer on said composition; and

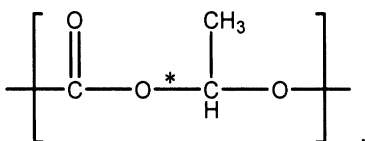
exposing said composition to light so as to decrosslink said crosslinked compounds.

2. The method of claim 1, wherein said crosslinking step comprises thermally crosslinking said compounds.

3. The method of claim 1, wherein said crosslinking step yields a layer of composition that is substantially insoluble in photoresist solvents.

4. The method of claim 1, where said exposing step yields a layer of composition that is substantially soluble in photoresist developers.

5. The method of claim 1, wherein said exposing step results in the breaking of the bond (\*) of the linkage having the formula



6. The method of claim 1, wherein said substrate is a microelectronic substrate.

7. The method of claim 6, wherein said substrate is selected from the group consisting of silicon, aluminum, tungsten, tungsten silicide, gallium arsenide, germanium, tantalum, tantalum nitride, SiGe, ion implant layers, low k dielectric layers, and dielectric layers.

8. The method of claim 1, wherein:  
said substrate further comprises structure defining a hole, said structure including sidewalls and a bottom wall; and  
said applying step comprises applying the composition to at least a portion of said hole sidewalls and bottom wall.

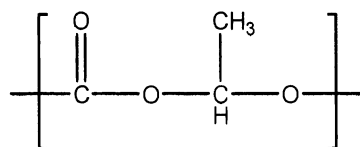
9. The method of claim 1, wherein said substrate comprises an ion implant layer, and said applying step comprises forming a layer of said composition adjacent said ion implant layer.

10. A method of forming a microelectronic structure, said method comprising the steps of:

providing a substrate having a surface;

applying a composition to said surface, said composition comprising compounds dissolved or dispersed in a solvent system, said compounds being selected from the group consisting of polymers, oligomers, and mixtures thereof, wherein said polymers are selected from the group consisting of aliphatic polymers, acrylates, methacrylates, polyesters, polycarbonates, novolaks, polyamic acids, and mixtures thereof, and said oligomers are selected from the group consisting of acrylates, methacrylates, novolaks, isocyanurates, glycidyl ethers, and mixtures thereof, said compounds comprising respective acid groups other than phenolic groups, wherein said acid groups include carboxylic acid groups and at least about 95% of said carboxylic acid groups are free of protective groups;

crosslinking the compounds in said composition, to yield crosslinked compounds comprising linkages having the formula



forming a photoresist layer on said composition; and

exposing said composition to light so as to decrosslink said crosslinked compounds.