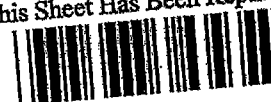


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02/02/1996POLYIMIDE PATTERNINGBackground of the Invention

5 This invention relates to a method of making a polyimide pattern on a substrate and to the resulting article. In particular, it relates to the inclusion of a photosensitive system in a polyamic acid solution deposited on a substrate from which a polyimide pattern is made.

10 Polyimides are used in the semiconductor industry for many application, such as dielectric coatings on silicon chips. In some applications, it is necessary to form a pattern of a polyimide coating on a substrate. One method by which this can be accomplished is to prepare a solution in an organic solvent of a polyamic acid, apply the solution to the substrate, and evaporate the solvent. A positive photoresist
15 is applied over the solid coating and the photoresist is exposed to UV light through a mask. The exposed portions of the photoresist and those portions of the polyamic acid coating underneath are removed using an aqueous base developer. After the remaining photoresist is removed in an
20 organic solvent, the polyamic acid is cured to form a polyimide coating. (See, for example, U.S. Patent No. 5,393,864, herein incorporated by reference.)

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While this process works well, the removal of portions of the polyamic acid coating can result in severely sloped sidewalls, i.e., polyamic acid can be removed in the isotropic direction that is not directly under the photoresist that was exposed to UV light. Severe isotropic developing can create problems such as poor resolution or patterns that have severely sloped sidewalls.

Summary of the Invention

I have discovered that the isotropic developing of the polyamic acid coating patterns can be reduced if a photosensitive system that becomes more soluble in the aqueous base developer when exposed to UV light is mixed in with the polyamic acid. The UV light passes through the photoresist layer and renders the exposed portions of the polyamic acid coating more soluble in the developer. When UV-exposed photosensitizer in the polyamic acid coating is removed using the developer, the exposed portion of the coating dissolves more readily. This controls the development time and the sidewall slope.

Brief Description of the Drawings

Figure 1 is a scanning electron micrograph (SEM) of the developed film made in Example 1.

Figure 2 is a graph showing the UV absorbance of five samples made in Example 2 at various UV wavelengths.

Figures 3 and 4 are photographs explained in Example 3 that show the degree of sidewall slope of polyimide coatings. In Figure 3, no photosensitizer was used and in Figure 4, 10 wt% photosensitizer was used.

5

Description of the Preferred Embodiments

In the first step of the process of this invention, a solution is prepared of a polyamic acid in an organic solvent. The polyamic acid is the reaction product of a dianhydride and a diamine. Generally, stoichiometric quantities of diamine and dianhydride are used to obtain the highest molecular weight polyamic acid, but the equivalent ratio of dianhydride to diamine can range from 1:2 to 2:1. Examples of suitable dianhydrides include:

10

1,2,5,6-naphthalene tetracarboxylic dianhydride;

15

1,4,5,8-naphthalene tetracarboxylic dianhydride;

2,3,6,7-naphthalene tetracarboxylic dianhydride;

2-(3',4'-dicarboxyphenyl) 5,6-dicarboxybenzimidazole
dianhydride;

2-(3',4'-dicarboxyphenyl) 5,6-dicarboxybenzoxazole
dianhydride;

20

2-(3',4'-dicarboxyphenyl) 5,6-dicarboxybenzothiazole
dianhydride;

2,2',3,3'-benzophenone tetracarboxylic dianhydride;

2,3,3',4'-benzophenone tetracarboxylic dianhydride;



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- 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA);
2,2',3,3'-biphenyl tetracarboxylic dianhydride;
2,3,3',4'-biphenyl tetracarboxylic dianhydride;
3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA);
5 bicyclo-[2,2,2]-octen-(7)-2,3,5,6-tetracarboxylic-2,3,5,6-
dianhydride;
thio-diphthalic anhydride;
bis (3,4-dicarboxyphenyl) sulfone dianhydride;
bis (3,4-dicarboxyphenyl) sulfoxide dianhydride;
10 bis (3,4-dicarboxyphenyl oxadiazole-1,3,4) paraphenylene
dianhydride;
bis (3,4-dicarboxyphenyl) 2,5-oxadiazole 1,3,4-dianhydride;
bis 2,5-(3',4'-dicarboxydiphenylether) 1,3,4-oxadiazole
dianhydride;
15 bis (3,4-dicarboxyphenyl) ether dianhydride or oxydiphthalic
anhydride (ODPA);
bis (3,4-dicarboxyphenyl) thioether dianhydride;
bisphenol A dianhydride;
bisphenol S dianhydride;
20 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride
or 5,5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]
bis-1,3-isobenzofurandione) (6FDA);
hydroquinone bisether dianhydride;
bis (3,4-dicarboxyphenyl) methane dianhydride;
25 cyclopentadienyl tetracarboxylic acid dianhydride;



cyclopentane tetracarboxylic dianhydride;
ethylene tetracarboxylic acid dianhydride;
perylene 3,4,9,10-tetracarboxylic dianhydride;
pyromellitic dianhydride (PMDA);
5 tetrahydrofuran tetracarboxylic dianhydride; and
resorcinol dianhydride.

The preferred dianhydrides are PMDA, BPDA, BTDA, and ODA
or mixtures thereof, as these dianhydrides are readily
available and give a polyimide having better thermal,
10 mechanical, and adhesive properties.

The dianhydrides can be used in their tetraacid form or
as mono, di, tri, or quatra esters of the tetra acid, but the
dianhydride form is preferred because it is more reactive.
Aromatic dianhydrides are especially preferred as they give
15 superior properties.

The diamine used in preparing the polyamic acid is also
preferably aromatic. Examples of aromatic diamines include:

m-phenylenediamine (m-PDA);
p-phenylenediamine (p-PDA);
20 2,4-(TDA), 2,5- and 2,6-diaminotoluene;
p- and m-xylenediamine;
4,4'-diaminobiphenyl;
4,4'-diaminodiphenyl ether or 4,4'-oxydianiline; (ODA)
3,4'-oxydianiline;



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- 4,4'-diaminobenzophenone;
- 3,3', 3,4', or 4,4-diaminophenyl sulfone or m,m-, m,p- or
p,p- sulfone dianiline;
- 4,4'-diaminodiphenyl sulfide;
- 5 3,3' or 4,4'-diaminodiphenylmethane or m,m- or p,p-methylene
dianiline;
- 3,3'-dimethylbenzidine;
- 4,4'-isopropylidenedianiline;
- 1,4-bis(p-aminophenoxy)benzene;
- 10 1,3-bis(p-aminophenoxy)benzene;
- 4,4'-bis(4-aminophenoxy)biphenyl;
- 1,3-bis(3-aminophenoxy)benzene (APB);
- 2,4-diamine-5-chlorotoluene;
- 2,4-diamine-6-chlorotoluene;
- 15 2,2-bis-(4[4-aminophenoxy]phenyl propane (BAPP);
- trifluoromethyl-2,4-diaminobenzene;
- trifluoromethyl-3,5-diaminobenzene;
- 2,2'-bis(4-aminophenyl)-hexafluoropropane;
- 2,2-bis(4-phenoxy aniline) isopropylidene;
- 20 2,4,6-trimethyl-1,3-diaminobenzene;
- 4,4'-diamino-2,2'-trifluoromethyl diphenyloxide;
- 3,3'-diamino-5,5'-trifluoromethyl diphenyloxide;
- 4,4'-trifluoromethyl-2,2'-diamino biphenyl;
- 2,4,6-trimethyl-1,3-diaminobenzene;
- 25 diaminoanthraquinone;

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4,4'-oxybis[2-trifluoromethyl)benzeneamine] (1,2,4-OBABTF);

4,4'-oxybis[(3-trifluoromethyl)benzeneamine];

4,4'-thiobis[(2-trifluoromethyl)benzeneamine];

4,4'-thiobis[(3-trifluoromethyl)benzeneamine];

5 4,4'-sulfoxylbis[(2-trifluoromethyl)benzeneamine];

4,4'-sulfoxylbis[(3-trifluoromethyl)benzeneamine];

4,4'-ketobis[(2-trifluoromethyl)benzeneamine];

4,4'-[(2,2,2-trifluoromethyl-1-(trifluoromethyl)-
ethylidene)bis(3-trifluoromethyl)benzeneamine];

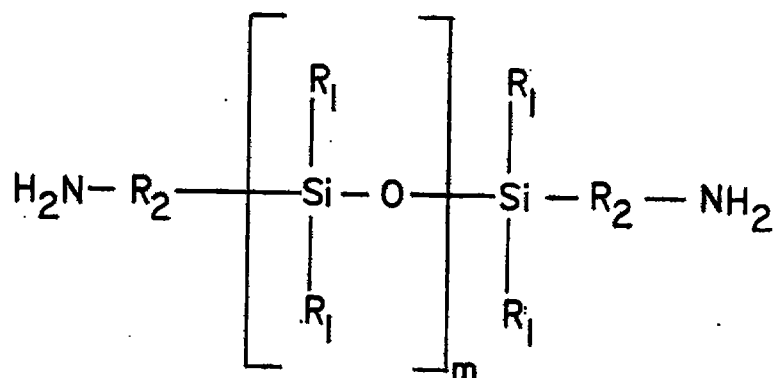
10 4,4'-dimethylsilylbis[(3-trifluoromethyl)benzeneamine].

The preferred aromatic diamines are ODA, p-PDA, m-PDA, APB, and BAPP, due to the excellent properties of polyimides made from them.

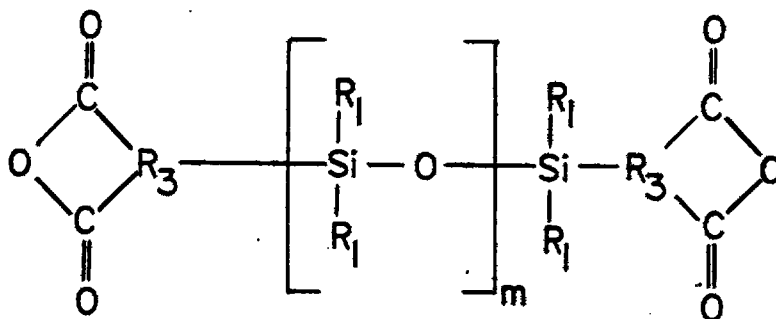
15 A polyimidesiloxane can be prepared by using a mixture of a diamine that does not contain siloxane groups with a diamine that contains siloxane groups. Alternatively, a dianhydride that contains siloxane groups can be used to replace a portion of a dianhydride that does not contain siloxane groups. For example, a polyimidesiloxane can be made from about 1 to about
20 80 wt% siloxane-containing monomers and about 20 to about 99 wt% monomers that do not contain siloxane. Siloxane-containing polyimides are preferred because they have lower moisture absorption and better adhesion to substrates, and they preferably are made from about 1 to about 30 wt%
25 siloxane-containing monomers and about 70 to about 99 wt% monomers that do not contain siloxane.



The siloxane-containing compounds may be either aromatic or non-aromatic, but non-aromatic compounds are preferred as they are more readily available. Examples of siloxane diamines that can be used include compounds having the formula



- 5 Examples of siloxane dianhydrides that can be used include compounds having the formula

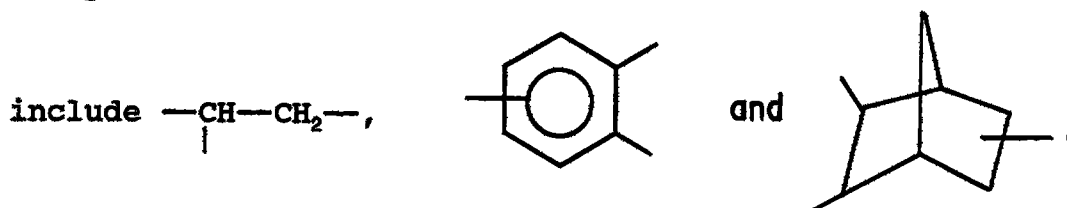


wherein R_1 and R_2 , and R_3 are mono, di, and triradicals, respectively, each independently selected from a substituted or unsubstituted 1 to 12 carbon atom aliphatic group or a substituted or unsubstituted 6 to 10 carbon atom aromatic



group, and m is 1 to 200 and is preferably 1 to 12. (Siloxane diamines are herein denoted by the notation " G_n ".) Examples of monoradicals include $-\text{CH}_3$, $-\text{CF}_3$, $-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_n\text{CF}_3$, $-\text{C}_6\text{H}_5$, $-\text{CF}_2-\text{CHF}-\text{CF}_3$, and $-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3$.

5 Examples of diradicals include $-(\text{CH}_2)_n-$, $-(\text{CF}_2)_n-$, $-(\text{CH}_2)_n(\text{CF}_2)_n-$, and $-\text{C}_6\text{H}_4-$, where each n can be 1 to 10. Examples of triradicals

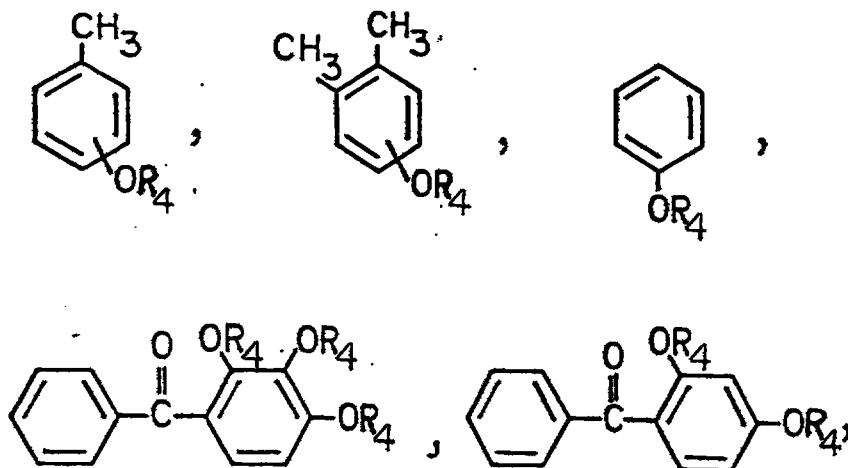


The monomers react at room temperature in a solvent to form a solution of the polyamic acid. The solvent must, of course, dissolve the polyamic acid. Suitable solvents depend upon the particular composition of the polyamic acid that is to be made and dissolved, but may include N-methylpyrrolidinone (NMP), diglyme, triglyme, cyclohexanone, cyclopentanone, dimethylacetamide, and mixtures of these solvents. The solvent preferably has a boiling point between 130 and 210°C as lower boiling solvents may evaporate too readily from the film and higher boiling solvents may be too difficult to remove from the film. The solution of the polyamic acid in the solvent can be any percent solids desired, but it is preferably about 5 to about 30 wt% solids as more dilute solutions mean more solvent to evaporate and more concentrated solutions are too viscous.

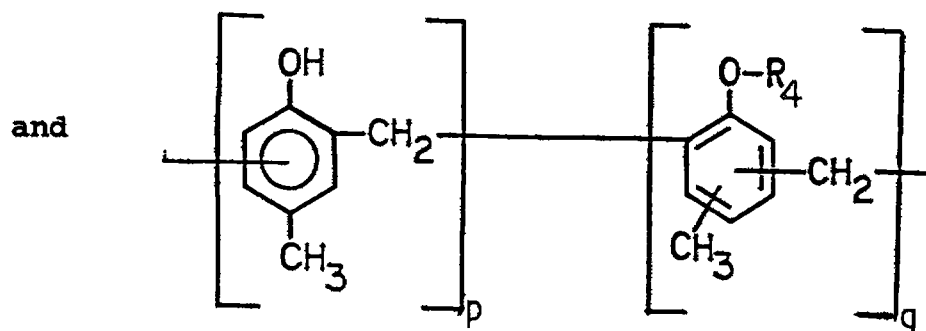
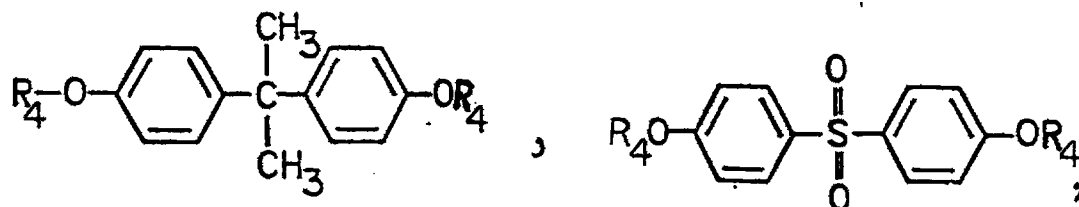
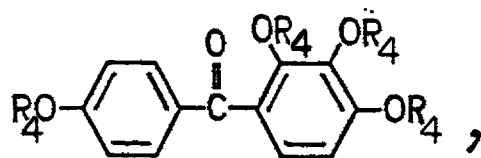


The polyamic acid can be up to about 40% imidized and it is preferably about 20 to about 40% imidized. A greater degree of imidization makes the polyamic acid too insoluble and less can make it too soluble during subsequent removal to form a pattern. Partial imidization can be accomplished by heating the solution of polyamic acid to about 100 to about 160°C for about 5 minutes to about 2 hours.

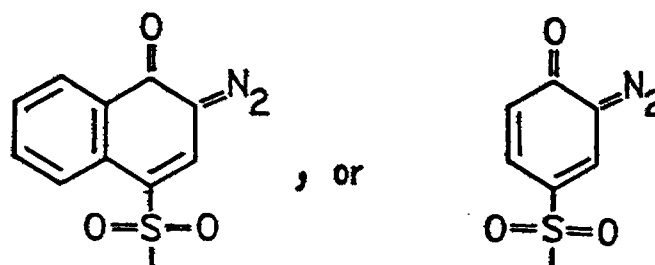
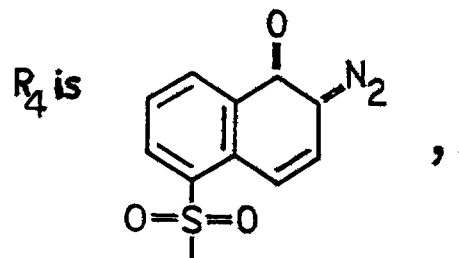
The solution of the polyamic acid must contain about 1 to about 10 wt%, based on polyamic acid weight, of a photosensitive system that becomes more soluble in the developer when exposed to actinic light. The photosensitive system may be, for example, a photosensitizer or a dissolution inhibitor and a photoactive compound. Photosensitizers that can be used can be found in European Patent 478321 A1 invented by M. Oba et al., p. 68-82, herein incorporated by reference. Examples of such photosensitizers include derivatives of 1,2 naphthoquinone (2)-diazido-4-sulfonate, 1,2 naphthoquinone (2)-diazido-5-sulfonate and azide compounds. The following are examples of positive photosensitizers:



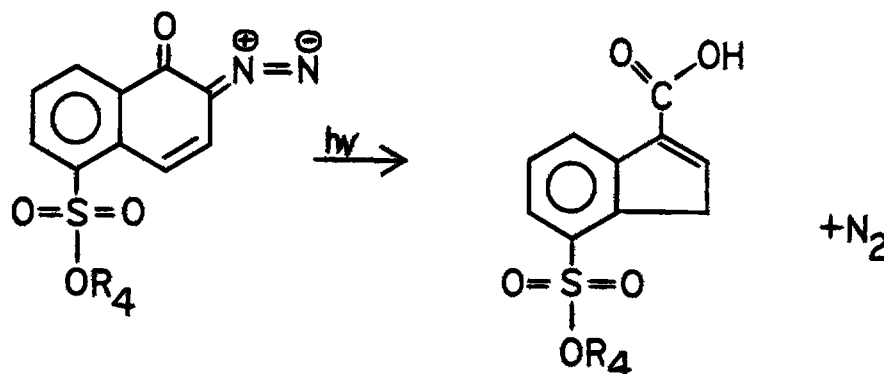
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where p is 1 to 100, q is 1 to 100, and



In general, when these photosensitizers are exposed to actinic or ultraviolet light, nitrogen is removed and the double bonded oxygen group is converted into the more water soluble carboxylic acid group. A preferred example of a positive photosensitizer is a derivative of 1,2-naphthoquinone-(2)-diazido-5-sulfonate which undergoes the following photoreaction by UV exposure:

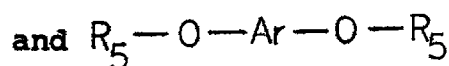
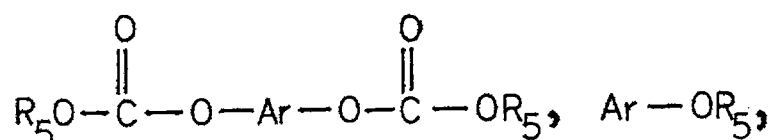
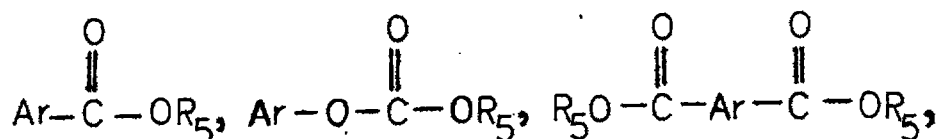


The preferred photosensitizer is 2,1,4 or 2,1,5-diazonaphthoquinone sulfonic esters. While this photosensitizer does not react with the partially imidized polyamic acid, it is initially insoluble in alkali water and its hydrophobicity prevents the partially imidized polyamic acid from dissolving in alkali water. However, when it is exposed to light it becomes soluble in the aqueous base developer and permits the dissolution of partially imidized polyamic acid with which it is in contact.

A photosensitive system of the partially imidized polyamic acid can also be prepared from dissolution inhibitors

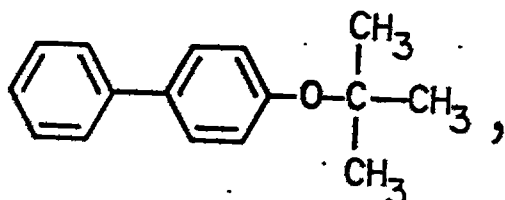


and photoactive compounds. The dissolution inhibitors contain an acid labile blocking group, such as t-butyl ester or a t-butyl carbonate. The photoactive compounds should generate a strong acid by UV irradiation and the strong protonic acid can deblock the acid labile groups during a subsequent postbake process. A positive image can be obtained by developing with aqueous base. The dissolution inhibitors are as follows:

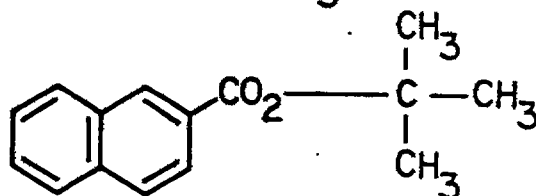
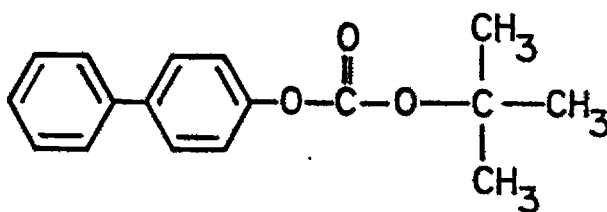


where Ar is aromatic or cycloaliphatic and R_5 is H or $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$.

Examples of dissolution inhibitors include:



and



Examples of the photoactive compounds, which can produce a strong acid by UV exposure, include derivatives of 1,2-naphthoquinone-(2)-diazide-4-sulfonate, diaryl iodium salts, p-nitrobenzyl-9,10-diethoxyanthracene sulfonate, etc.

5 In the next step of the process of this invention, the solution of partially imidized polyamic acid containing the photosensitizer is applied to a substrate, forming a coating on the substrate. Suitable substrates include, for example, silicon wafers, copper, aluminum, silicon dioxide, and silicon
10 nitride. The formation of the coating on the substrate can be accomplished by using a doctor blade, spin coating, or other means.

Solvent is then evaporated from the coating to form a solid coating. Evaporation of the solvent can be accomplished
15 by heating on a hot plate or in an oven below the decomposition temperature of the photosensitizer. For example, if the solvent is N-methylpyrrolidone, heating can be at 100 to 150°C. Heating at this stage should remove most of the solvent but should result in very little imidization of
20 the polyamic acid and very little decomposition of the photosensitizer.

In the next step, a layer of a positive photoresist is applied over the solid polyamic acid coating. The application of the positive photoresist can be accomplished by techniques



well-known in the art, such as the use of a doctor blade or spin coating from solution and evaporation of the solvent. The photoresist should be sensitive to the same wavelength of light that the photosensitizer is sensitive to. Any type of positive photoresist can be used for this purpose. Suitable photoresists are commercially available products and can be purchased from Hoechst Celanese Corp., Olin Corp., Shipley Co., Tokyo Ohka Co., etc. The preferred photoresists are G-line or I-line sensitive and respond to UV light from 360 to 450 nm.

The layer of positive photoresist should be thick enough to protect the coating of polyamic acid beneath it during the dissolution step, but should be thin enough so that actinic light can pass through it into the polyamic acid coating beneath it. A thickness of about 0.5 to about 2 microns is usually suitable.

In the next step, the positive photoresist is exposed to a pattern of actinic or UV light for a time and intensity sufficient to pass through the layer of photoresist into the polyamic acid coating and activate the photosensitizer in the polyamic acid coating. A pattern of light can be formed using a mask, which can be applied using techniques well-known in the art. The UV light renders those portions of the photoresist layer and the polyamic acid coating that are exposed to the light more soluble in the developer.



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The exposed portions of the layer of photoresist are removed using a developer appropriate for the particular photoresist selected. The exposed portions of the polyamic acid coating are then removed by dissolution in the same developer. A preferred aqueous developer is water containing 0.1 to 0.5 normal base. Preferably, the base is organic because inorganic bases, such as potassium hydroxide or sodium hydroxide, can leave behind low concentrations of sodium or potassium ions, which can adversely affect the dielectric properties of the resulting polyimide coating. Quaternary ammonium salts, such as tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, tetrapropyl ammonium hydroxide, or tetrabutyl ammonium hydroxide, are preferred. Contact with the developer should be about 10 seconds to about 5 minutes, and preferably about 30 seconds to about 2 minutes, as longer times may attack unexposed areas and shorter times may leave exposed polyamic acid unremoved.

The remaining unexposed photoresist layer is then removed using an appropriate solvent. Finally, the polyamic acid coating remaining on the substrate is imidized, which can be accomplished by heating in stages, such as at 150°C for 30 minutes followed by heating at 250°C to 350°C for 1 to 2 hours.

The following examples further illustrate this invention.

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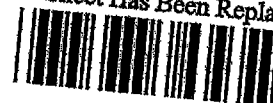
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Example 1

To a 500 ml 3-necked flask equipped with a mechanical stirrer, a Dean-Stark trap, a reflux condenser, and a thermometer was added 1188 ml dry NMP, followed by stirring
5 20.97 g (0.194 mole) p-PDA and 1.45 g (0.006 mole) diaminopropyl terminated dimethyl siloxane oligomer having an average repeat unit of 1 (G_1). After dissolving the diamines completely, 58.84 g (0.2 mole) BPDA was added at room temperature and the polymerization was run overnight. For the
10 partial imidization, 264 ml toluene was added and mixed homogeneously. The temperature was raised to 145°C and the mixture was refluxed for 5 minutes then cooled in an ice bath. The resin was precipitated in deionized water, filtered, washed in fresh deionized water or methanol again, and
15 filtered. The filtered resin was dried at room temperature under a hood with slow air flow. The imidization measured by acid titration was 32.5%. The size of molecules in DMAC measured by gel phase chromatography (GPC) with polystyrene references was 6084 g/mole (M_n), 15780 g/mole (M_w), and 2.3
20 polydispersity.

Example 2

The dry resin of Example 1 was dissolved in NMP at 28.6 wt% and the solution was filtered through a 5 μ m filter. A



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positive photosensitizer, ester of 1,2-naphthoquinone-(2)-
diazide-5-sulfonic acid with p-cresol, (sold by Toyo Gosei
Kogyo Co. as "PC-5"), 0.57 g, was added to the 10 g filtered
solution and mixed for complete dissolution. The formulated
5 solution was spin-coated on a silicon wafer at 2500 rpm for 40
seconds and soft-baked at 120°C for 15 minutes in a convection
oven. A positive photoresist, sold by Shipley Co. as Shipley
Microposit®1813 photoresist, was spin-coated onto the soft-
baked wafer, then soft-baked again on a hot plate at 100°C for
10 5 minutes. The coating was exposed to UV light through a mask
for 3 seconds using a 350 watt mercury-xenon lamp. The UV
exposed wafer was developed for 30 seconds in tetramethyl
ammonium hydroxide (TMAH) developer, Shipley MF-312 CD-27.

After developing and drying the wafer, the photoresist
15 was washed in ethyl acetate. The developed film was baked at
80, 150, 250, and 350°C for 30 minutes at each temperature.
The pattern thickness was 5 μ m and the SEM picture with a
sharp profile pattern is shown in Figure 1.

Example 3

20 The dry resin of Example 1 was dissolved in NMP at a
concentration of 28.5%. After this solution had been filtered
through a 5 μ m filter, samples 1 to 5 were prepared with 0, 5,
10, 15, and 20 wt% "PC-5" photosensitizer. The solutions were
spin-coated on silicon wafers at 2000 rpm for 40 seconds and



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the coated wafers were soft-baked at 120°C for 15 minutes in a convection oven. The positive photoresist, Shipley Microposit®1813, was spin-coated on the soft-baked wafers at 2500 rpm for 40 seconds and then soft-baked again on a hot plate at 100°C for 5 minutes. The wafers were exposed to UV light through a mask for 1 to 4 seconds with a 350 watt Hg-Xe lamp. UV spectra of the spin-coated films on quartz disks are shown in Figure 2, where the ordinate is absorbance and the abscissa is wavelength in nm. The UV exposed wafers were developed in Shipley MF-312 CD-27 for about 20 seconds (but only about 15 seconds for the control, where no photosensitizer was used). After developing and drying of wafers, the photoresist on the precursors of polyimides was washed in acetone. When the remaining films were cured at 90, 150, 250, and 350°C for 30 minutes at each temperature, the final cured films were about 8 to 10 μ m thick. From a comparison of SEM pictures of patterns obtained from the above samples (see Figures 3 and 4), it was established that the addition of the photosensitizer produced sharp edges, especially at the bottom layer of patterns. There is much more isotropic developing in Figure 3, where no photosensitizer was used, than in Figure 4, where 10 wt% photosensitizer was used, even though the pattern in Figure 4 was exposed to the developer for about 5 seconds longer.

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Example 4

To a 100 ml 3-necked flask with a mechanical stirrer, 55 g dry NMP was added, followed by 4.3 g (0.0213 mole) ODA and 0.16 g (0.00066 mole) G₁. After dissolving the diamines completely by stirring, 4 g (0.018 mole) PMDA and 1.18 g (0.00366 mole) BTDA were added and polymerized with stirring overnight at room temperature. One sample was used as prepared and another sample was formulated with 5% positive photosensitizer PC-5. Two solutions were spin-coated on silicon wafers at 1200 rpm for 40 seconds and soft-baked at 120°C for 5 minutes in a convection oven. Then a positive photoresist, Shipley 1813, was spin-coated at 2000 rpm for 40 seconds and soft-baked at 100°C for 3 minutes on a hot plate. The wafers were exposed to UV light through a mask for 1 to 4 seconds from a 350 watt Hg-Xe light source. The pure polyamic acid sample was developed for 10 to 18 seconds in TMAH developer and the profile of patterns had more severely sloped sidewalls than in Examples 2 and 3. The 5 wt% PC-5 sample was developed in TMAH developer for 30 to 52 seconds.





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WE CLAIM:

- 1 1. A method of making a polyimide pattern on a substrate
2 comprising
3 (A) preparing a solution in an organic solvent of a
4 polyamic acid and about 1 to about 10 wt% of a
5 photosensitive system that becomes more soluble in
6 an aqueous base developer when exposed to actinic
7 light;
8 (B) forming a coating of said solution on a substrate;
9 (C) evaporating solvent from said coating;
10 (D) applying a positive photoresist over said coating;
11 (E) exposing said positive photoresist and said coating
12 to a pattern of actinic light;
13 (F) removing the exposed portions of said photoresist;
14 (G) removing exposed portions of said coating by
15 dissolution in an aqueous base developer;
16 (H) removing remaining photoresist; and
17 (I) imidizing polyamic acid coating remaining on said
18 substrate.

2. A method according to Claim 1 wherein said substrate is
a silicon wafer.

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3. A method according to Claim 1 wherein said photosensitive system is 2,1,4 or 2,1,5-diazo naphthoquinone sulfonic esters.
4. A method according to Claim 1 wherein said positive photoresist is sensitive to UV light having a wavelength from about 360 to about 450 nm.
5. A method according to Claim 3 wherein said aqueous base developer is about 0.1 to about 0.5 normal aqueous solution of an organic base.
6. A method according to Claim 5 wherein said organic base is a quaternary ammonium salt.
7. A method according to Claim 5 wherein said quaternary ammonium salt is tetramethylammonium hydroxide.
8. A method according to Claim 1 wherein said polyamic acid is about 20 to about 40% imidized.

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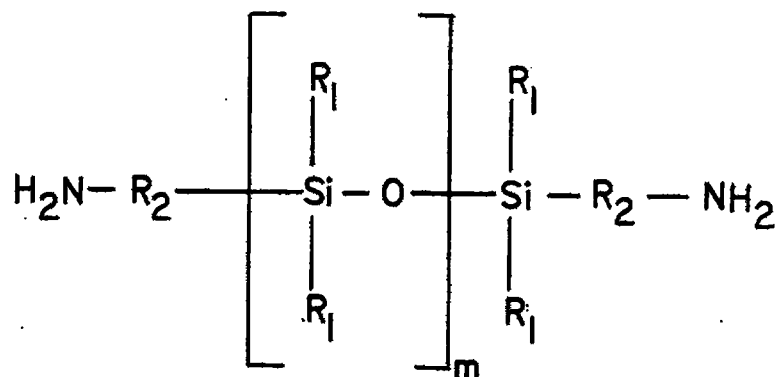




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1 9. A method according to Claim 1 wherein said polyamic acid
2 is the reaction product of an aromatic dianhydride and
3 diamine, where about 70 to about 99 wt% of said diamine
4 is aromatic diamine that does not contain siloxane groups
5 and about 1 to about 30 wt% of said diamine is diamine
6 that contains siloxane groups.

1 10. A method according to Claim 9 wherein said dianhydride is
2 selected from the group consisting of oxydiphthalic
3 anhydride, 3,3'4,4'-bisphenyl tetracarboxylic
4 dianhydride, 3,3'4,4'-benzophenone tetracarboxylic
5 dianhydride, 2,2-bis(3,4-
6 dicarboxyphenyl)hexafluoropropane dianhydride, and
7 pyromellitic dianhydride, said aromatic diamine is
8 selected from the group consisting of 4,4'-oxydianiline,
9 m-phenylene diamine, p-phenylene diamine, 1,3-bis(3-
10 aminophenoxy)benzene, and 2,2-bis(4-[4-
11 aminophenoxy]phenyl)propane, and said diamine that
12 contains siloxane groups has the formula



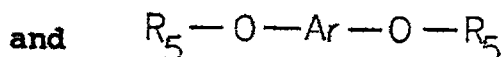
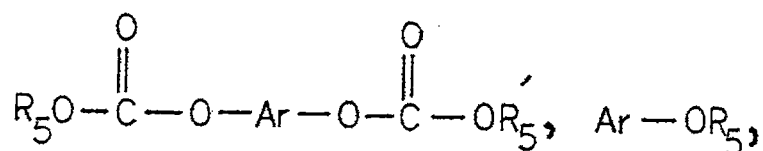
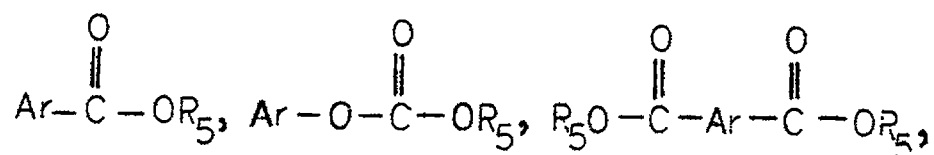


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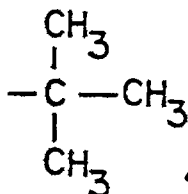
13 where R and R₁ are mono and diradicals, respectively,
14 each independently selected from a substituted or
15 unsubstituted 1 to 12 carbon atom aliphatic group or a
16 substituted or unsubstituted 6 to 10 carbon atom aromatic
17 group and m is 1 to 200.

11. A method according to Claim 1 wherein said photosensitive system is a mixture of dissolution inhibitors and photosensitive compounds.

12. A method according to Claim 11 wherein said dissolution inhibitor is selected from the group consisting of



where Ar is aromatic or cycloaliphatic and R₅ is H or



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13. A method according to Claim 11 wherein said photoactive compound is selected from the group consisting of derivatives of 1,2-naphthoquinone-(2)-diazide-4-sulfonate, diaryl iodium salts, p-nitrobenzyl-9,10-diethoxyanthracene sulfonate.

14. An article made according to the method of Claim 1.

1 15. In a process for making a polyimide pattern on a
2 substrate wherein a positive photoresist is applied to a
3 coating of a polyamic acid on a substrate, the
4 photoresist is exposed to a pattern of actinic light, and
5 the exposed portions of the photoresist and the polyamic
6 acid coating therebeneath are removed, an improvement
7 which makes the sidewall of the pattern more vertical
8 comprising mixing into said polyamic acid about 1 to
9 about 10 wt% of a photosensitive system that becomes more
10 soluble in aqueous base when exposed to actinic light and
11 removing said therebeneath polyamic acid coating using an
12 aqueous medium.

16. A method according to Claim 15 wherein said substrate is a silicon wafer.

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17. A method according to Claim 15 wherein said photosensitive system is 2,1,4 or 2,1,5-diazo naphthoquinone sulfonic esters.

1 18. A method of making a polyimidesiloxane pattern on a
2 substrate comprising

3 (A) preparing a solution in an organic solvent of

4 (1) about 1 to about 10 wt% of a photosensitizer
5 that becomes more soluble in water after
6 exposure to ultraviolet light; and

7 (2) a polyamic acid that is the 1:2 to 2:1 molar
8 reaction product of

9 (a) aromatic dianhydride; and

10 (b) diamine, where said diamine is about 70
11 to about 99 wt% aromatic diamine that
12 does not contain siloxane groups and
13 about 1 to about 30 wt% of a diamine that
14 does contain siloxane groups;

15 (B) heating said solution to imidize about 20 to about
16 40% of the amic acid groups in said polyamic acid;

17 (C) forming a coating of said solution on a substrate;

18 (D) heating said coating to evaporate organic solvent
19 therefrom and solidify said coating;

20 (E) applying a layer of a positive photoresist to said
21 solidified coating;

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- 22 (F) exposing said layer of positive photoresist and said
23 underlying coating to a pattern of ultraviolet
24 light;
25 (G) removing those portions of said positive photoresist
26 that were exposed to ultraviolet light, thereby
27 exposing the polyamic acid coating thereunder;
28 (H) removing said exposed polyamic acid coating using an
29 aqueous developer;
30 (I) removing photoresist layer that remains on said
31 polyamic acid coating; and
32 (J) heating polyamic acid coating that remains on said
33 substrate to a temperature sufficient to form
34 polyimidesiloxane.
19. A method according to Claim 18 wherein said substrate is
a silicon wafer.
20. A method according to Claim 18 wherein said aqueous
developer is about 0.1 to about 0.5 normal
tetramethylammonium hydroxide.

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