

Process for Producing a Heat Resistant Relief Structure

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Field of Invention

[0002] The present invention relates to the process for preparing heat-resistant relief structures using a bilayer imaging system suitable for forming a pattern under exposure to radiation with the wavelength below 250 nm.

Background of the Invention

[0003] Polymers that provide high temperature resistance, such as polyimides, are well known in microelectronic applications. Some of the uses include protective layers, insulating layers, interlevel dielectrics, and antireflective layers. In some cases, the polyimide may be coated from a solution of polyimide, but are generally coated as a polyimide precursor, such as a polyamic acid or polyamic ester, and subsequently converted to polyimides by known techniques, such as exposure to high temperatures. Frequently in the early steps of patterning applications, the properties of the polyimide precursors are more useful than the fully imidized polyimide. In the later stages, the properties of the fully imidized polyimide usually are more desired.

[0004] Preparation of polyimide patterns may use a photosensitive polyimide precursor or employ a bilayer approach where the polyimide precursor is not photosensitive. A method of patterning non-photosensitive polyimide films was described in US Patent No. 3,700,497, incorporated by reference. According to this method, a film of polyamic acid was formed on the surface of a substrate. Then, a layer of a diazonaphthoquinone/novolak type photoresist was formed on the top of

the film of polyamic acid, followed by patternwise exposure using ultraviolet light. The exposed areas of photoresist and the layer of polyamic acid underneath it were etched away in a dilute organic or inorganic base developer. The remaining photoresist was removed using acetone and the film of polyamic acid was cured at
5 temperatures higher than 250°C, creating a patterned polyimide layer to remain as part of the device structure.

[0005] The pattern profile obtained from this type of process depends on the ability to control the dissolution rate of the polyimide precursor, the thickness of the
10 polyimide precursor, and strength and type of developer employed for the photoresist and for the polyimide precursor layers. Significant undercut of the photoresist layer can occur with high dissolution rates of the polyamic acid in the developer. This property has been utilized in preparing lift off structures from thin, sacrificial, polyimide precursor layers, which may be partially imidized, as disclosed
15 in US Patent Nos. 5,360,697 and US 5,017,459.

[0006] The dissolution rate of the polyimide precursor is a function of its chemical structure and the degree of imidization. The chemical structure of the polyimide precursor, which will subsequently form the polyimide with the properties
20 desired for the application, may have a low dissolution rate. The polyimide precursor may be partially imidized to control dissolution rate as in US Patent No. 4,113,550. These factors may lead to development being a two-step process. First the photoresist layer is developed with one developer and then the polyimide precursor layer is developed with another developer, frequently of a different type.
25 Two-step development processes of polyimide precursor bilayer systems are described, for example, in US Patent Nos. 4,039,371, US 4,411,735, US 5,374,503, US 4,113,550 and US 5,470,693. Typical developers employed for the polyimide precursor layer are based on amines, tetramethyl ammonium hydroxide (TMAH) in alcohol, or a mixture of tetramethyl ammonium hydroxide, water, and N-methyl
30 pyrrolidone. US Patent No. 4,039,370 discloses a developer based on tetramethyl

ammonium hydroxide, water, and either acetic, tartaric or oxalic acid. US Patent No. 6,221,567 discloses a development process with multiple developer/rinse steps.

[0007] At the present time many semiconductor production facilities use 248 nm exposure tools and chemically amplified photoresists. Some facilities only maintain exposure equipment with one wavelength light. Therefore, it is desirable to have the ability to prepare patterned polyimide using 248 nm or 193 nm light. The prior art cited above is silent on the use of Deep UV exposure (<250 nm light) to prepare polyimide patterns of thickness >200 nm for applications such as dielectric coatings and buffer coat in which the polyimide film is retained in the semiconductor device.

[0008] US Patent No. 5,372,914 discloses the use of a chemically amplified photoresist over a protective layer of a polyimide precursor cured to polyimide using an e-beam exposure. The photoresist development step did not develop the polyimide. US Patent No. 6,054,254 discloses the use of 248 nm exposure in the patterning of a chemically amplified photoresist over a thin layer (200 nm) of partially imidized polyamic acid operating as an antireflective coating. Antireflective coatings of this type are removed in subsequent processing. The polyimide precursor profiles undercut the photoresist layer and were deemed unsuitable for the application. US Patent No. 6,458,508 discloses the use of a thin barrier layer of acid containing polymers as an underlayer to protect chemically amplified photoresists from basic contaminants during processing. Typical thicknesses were a few hundred angstroms.

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[0009] Solvents employed for polyimide precursors are typically polar solvents. Dimethyl acetamide and N-methyl pyrrolidone (NMP) are the most commonly used solvents for polyimide precursors for bilayer applications. However, it has been established that nitrogen-containing solvents such as NMP have detrimental effects on the performance of chemically amplified 248 and 193

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nm photoresists. (U.S. Patent No. 6,277,546; see also "Influence of Polymer Properties On Airborne Chemical Contamination of Chemically Amplified Resists", W. D. Hinsberg, S. A. MacDonald, N. J. Clecak, C. D. Snyder, and H. Ito, SPIE vol. 1925, pp. 43-52, 1993). As a result, the use of NMP-containing compositions is prohibited in many semiconductor fabrication facilities where such chemically amplified photoresists are used. NMP is difficult to remove from the polyimide precursor film because of its high boiling point and the relatively low temperature softbakes employed with the polyimide precursor film to prevent imidization. US Patent No. 5,667,922 disclosed that a process employing a water rinse step after formation of a polyamic acid film resulted in better-defined polyimide patterns because of NMP removal by the water rinse.

[0010] The use of alternate, but weaker, polar solvents such as *gamma*-butyrolactone is more acceptable to the industry. However, many polyimide precursor compositions with desirable cured properties are not soluble in *gamma*-butyrolactone.

[0011] The invention described herein discloses a process for making high temperature resistant patterns using a bilayer system exposed at wavelengths <250 nm and using a polyimide precursor composition for the bottom layer formulated in a non-NMP solvent.

Summary of the Invention

[0012] The present invention provides a process of producing high temperature resistant patterns using a bilayer imaging system at wavelength below 250 nm. The bottom layer of the bilayer system is cast from a formulation comprising polyamic acid and *gamma*-butyrolactone (GBL). The top layer is formed by coating a Deep UV photoresist over the bottom layer. The present invention also relates to the articles of manufacture obtained by this process.

**Detailed Description of the Invention
And Preferred Embodiments**

[0013] Non-photosensitive polyimide precursor compositions comprising
5 polyamic acids can be used to form high temperature relief patterns when used in
combination with a photosensitive composition. A film of the non-photosensitive
polyimide precursor composition is formed on a substrate and then overcoated with
the photosensitive composition. The photosensitive composition is patterned and
developed to provide an image. An image in the underlying non-photosensitive
10 polyimide precursor composition is developed concurrent with the image formation in
the photosensitive composition or in a subsequent step. The present invention
relates to a process of making a heat-resistant relief structures comprising the steps
of:

- (a) providing a substrate;
 - 15 (b) in a first coating step, coating the substrate with a composition comprising a
polyamic acid and *gamma*-butyrolactone to form a layer of polyamic acid
having a thickness of at least about 0.5 μm ;
 - (c) baking the layer of polyamic acid at a temperature or temperatures below 140
°C;
 - 20 (d) in a second coating step, coating a layer of a Deep UV photoresist over the
layer of polyamic acid to form a bilayer coating;
 - (e) exposing the bilayer coating to radiation < 250 nm
 - (f) developing the bilayer coating with one or more aqueous tetramethyl
ammonium hydroxide developers;
 - 25 (g) removing the remaining Deep UV photoresist layer; and
 - (h) curing the polyamic acid layer at a temperature at least about 200 °C to
produce a polyimide structure
- wherein the polyamic acid is soluble in aqueous tetramethyl ammonium and
insoluble in a solvent used with the photoresist.

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[0014] Substrates suitable for use in this invention include, but are not limited

to, silicon, aluminum, copper, chromium, nickel, gold, ferrous metals, aluminum/copper alloys, polymeric resins, silicon dioxide, doped silicon dioxide, silicone resins, silicon nitride, silicon arsenide, gallium arsenide, indium phosphide, indium selenide, indium-tin oxide, tantalum, polysilicon, inorganic glasses, and
5 ceramics that have been spin coated with a stress buffer coating composition. The preferred substrates are thermally grown silicon oxide/silicon wafers such as those employed in the production of microprocessors, memories, and other miniaturized integrated circuit components. The most preferred substrates are silicon wafers on which all of the processes necessary to fabricate functional semiconductor devices
10 have been completed.

[0015] To ensure proper adhesion of the polyamic acid composition to the substrate the substrate may be optionally treated with an (external) adhesion promoter before the first coating step or the polyamic acid composition may employ
15 an internal adhesion promoter. Any suitable method of treatment of the substrate with adhesion promoter known to those skilled in the art may be employed. Examples include treatment of the substrate with adhesion promoter vapors, solutions or at 100% concentration. The time and temperature of treatment will depend on the particular substrate, adhesion promoter, and method, which may
20 employ elevated temperatures. Any suitable external adhesion promoter may be employed. Classes of suitable external adhesion promoters include but are not limited to vinylalkoxysilanes, methacryloxyalkoxyisilanes, mercaptoalkoxysilanes, aminoalkoxysilanes, epoxyalkoxysilanes and glycidoxyalkoxysilanes. Aminosilanes and glycidoxysilanes are more preferred. Primary aminoalkoxysilanes are more
25 preferred. Examples of suitable external adhesion promoters include, but are not limited to *gamma*-aminopropyltrimethoxy-silane, *gamma*-glycidoxypropylmethyldimethoxysilane, *gamma*-glycidoxypropylmethyldiethoxysilane, *gamma*-mercaptopropylmethyldimethoxysilane, 3-methacryloxypropyldimethoxymethylsilane, and 3-methacryloxypropyltrimethoxysilane.
30 *gamma*-Aminopropyltrimethoxysilane is more preferred. Additional suitable

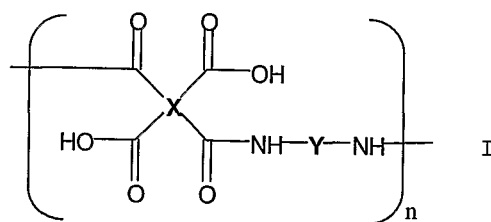
adhesion promoters are described in "Silane Coupling Agent" Edwin P. Plueddemann, 1982 Plenum Press, New York.

[0016] Any suitable means of coating the polyamic acid layer may be employed. Coating of the polyamic acid formulation of the present invention on a substrate is preferably done by spin coating process. During the spin coating process, the silicon wafer or other substrate is placed on a vacuum chuck and spun at a high speed (e.g. 500 – 3,000 rpm) after or while a stress buffer composition is centrally dispersed onto the top surface of the wafer. The spin coating process parameters such as spin speed, spin time, and the like may be varied according to desired use.

[0017] The polyamic acid formulation used in the present invention comprises one or more polyamic acids and *gamma*-butyrolactone.

[0018] To be suitable for this invention, the non-photosensitive polyimide precursor composition should have several specific characteristics. It should be soluble enough in GBL to form coatings of the desired thickness. The non-photosensitive polyimide should be insoluble in the solvent used for the photosensitive composition (e.g., PGMEA resistant) to avoid intermixing of the photosensitive composition and non-photosensitive polyimide precursor composition. The term solvent resistant is defined to be a dissolution rate of the polyamic acid film of less than about 600 angstroms/min. Additionally, the non-photosensitive polyimide precursor composition should not become cracked or crazed during the preparation of the photosensitive composition layer. The non-photosensitive polyimide precursor composition should also be soluble in the aqueous tetramethyl ammonium hydroxide developer.

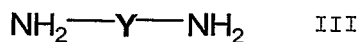
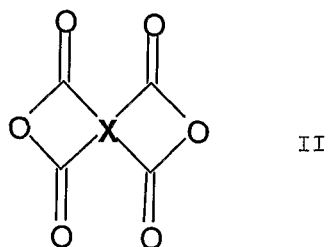
[0019] Polyamic acids having the Formula (I) are generally suitable for use in this invention where n is an integer ranging from about 5 to about 200.



- 5 A preferred range for n is from about 25 to about 175. A more preferred range for n is from about 50 to about 150.

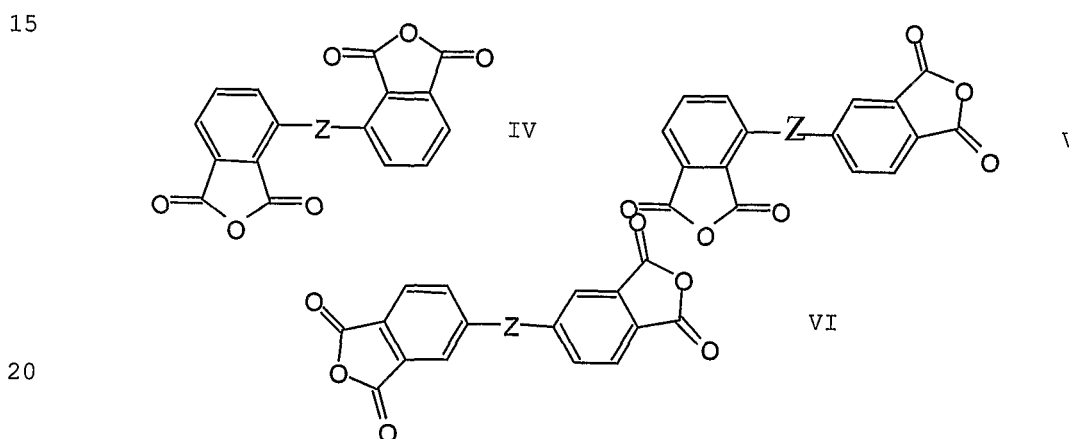
[0020] Polyamic acids of Formula I may be prepared by reacting monomers of Formula II with monomers of Formula III

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- 15 where X and Y can independently be aromatic or aliphatic moieties with or without heteroatoms or by other methods known to those skilled in the art. Monomers of Formula II can be a single dianhydride or a mixture of two or more dianhydrides, provided that the final polymer is soluble in *gamma*-butyrolactone. Examples of suitable dianhydrides of Formula II include, but are not limited to the to 3,3',4,4'-
 20 biphenyltetracarboxylic acid dianhydride, 3,3',4,4' diphenylsulfidetetracarboxylic acid dianhydride, 3,3',4,4'-diphenylsulfonetetracarboxylic acid dianhydride, 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride, 3,3',4,4'-diphenylmethanetetracarboxylic acid dianhydride, 2,2',3,3' -diphenylmethanetetracarboxylic acid dianhydride, 2,3,3',4'-biphenyltetracarboxylic
 25 acid dianhydride, 2,3,3',4'-benzophenonetetracarboxylic acid dianhydride, dianhydrides of oxydiphthalic acids, particularly 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride (4,4'-oxydiphthalic acid dianhydride),

2,3,6,7-naphthalenetetracarboxylic acid dianhydride, 1,4,5,7-naphthalenetetracarboxylic acid dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 1,3-diphenylhexafluoropropane-
 5 3,3,4,4-tetracarboxylic acid dianhydride, 1,4,5,6-naphthalenetetracarboxylic dianhydride, 2,2',3,3'-diphenyltetracarboxylic acid dianhydride, 3,4,9,10-perylenetetracarboxylic acid dianhydride, 1,2,4,5 naphthalenetetracarboxylic acid dianhydride, 1,4,5,8-naphthalenetetracarboxylic acid dianhydride, 1,8,9,10-phenanthrenetetracarboxylic acid dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane
 10 dianhydride, 1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride, 1,2,3,4-benzenetetracarboxylic acid dianhydride and 1,2,4,5-benzenetetracarboxylic acid dianhydride (pyromellitic dianhydride, PMDA). In a preferred embodiment, the dianhydride of Formula II comprises a compound selected from the group consisting of compounds described by the structures (IV - VI):



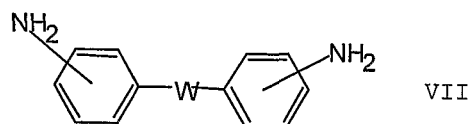
where Z = -O-, -S-, -C(CF₃)₂-, -CH₂-, -SO₂-, -NHCO- or -Si(R')₂- (R' is a linear, branched or cyclic alkyl group containing from 1 to 8 carbon atoms). In another preferred embodiment, the dianhydride of Formula II comprises a mixture of two or
 25 more compounds of the Formulae IV, V, and VI. In another preferred embodiment Z in Formulae IV, V, and VI is -O-. In a more preferred embodiment at least 80% of the total amount of dianhydride of Formula II comprises dianhydrides described by Formulae IV, V, and VI where Z = -O-.

[0021] In the most preferred embodiments, the dianhydride of Formula II is 3,3',4,4'-diphenyloxidetetra-carboxylic acid dianhydride (4,4'-oxydiphthalic acid dianhydride, ODPDA) or mixture of 95-85% of ODPDA and 5-15% of another dianhydride of Formula II.

[0022] Diamine monomers of Formula III can be a single diamine or a mixture of two or more diamines provided that the final polymer is soluble in GBL. Examples of diamine monomers of Formula III include but are not limited to 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI), *m*-phenylenediamine, *p*-phenylenediamine, 2,2'-bis(trifluoromethyl)-4,4'-diamino-1,1'-biphenyl, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 2,4-tolylenediamine, 3,3'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ketone, 3,3'-diaminodiphenyl ketone, 3,4'-diaminodiphenyl ketone, 1,3-bis(4-aminophenoxy) benzene, 1,3-bis(3-aminophenoxy) benzene, 1,4-bis(γ -aminopropyl)tetramethyldisiloxane, 2,3,5,6-tetramethyl-*p*-phenylenediamine, *m*-xylylenediamine, *p*-xylylenediamine, methylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, 2,5-dimethylhexamethylenediamine, 3-methoxyhexamethylenediamine, heptamethylenediamine, 2,5-dimethylheptamethylenediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, octamethylenediamine, nonamethylenediamine, 2,5-dimethylnonamethylenediamine, decamethylenediamine, ethylenediamine, propylenediamine, 2,2-dimethylpropylenediamine, 1,10-diamino-1,10-dimethyldecane, 2,11-diaminododecane, 1,12-diaminooctadecane, 2,17-diaminoeicosane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, bis(4-aminocyclohexyl)methane, bis(3-aminonorbornyl)methane, 3,3'-diaminodiphenylethane, 4,4'-diaminodiphenylethane, and 4,4'-diaminodiphenyl sulfide,

2,6-diaminopyridine, 2,5-diaminopyridine, 2,6-diamino-4-trifluoromethylpyridine, 2,5-diamino-1,3,4-oxadiazole, 1,4-diaminocyclohexane, piperazine, 4,4'-methylenedianiline, 4,4'-methylene-bis(o-chloroaniline), 4,4'-methylene-bis(3-methylaniline), 4,4'-methylene-bis(2-ethylaniline), 4,4'-methylene-bis(2-methoxyaniline), 4,4'-oxy-dianiline, 4,4'-oxy-bis-(2-methoxyaniline), 4,4'-oxy-bis-(2-chloroaniline), 4,4'-thio-dianiline, 4,4'-thio-bis-(2-methylaniline), 4,4'-thio-bis-(2-methoxyaniline), 4,4'-thio-bis-(2-chloroaniline), 3,3'-sulfonyl-dianiline, and 3,3'-sulfonyl-dianiline. In a preferred embodiment, diamine monomers of Formula III comprise at least one compound having the structure VII

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where W = -O-, -S-, -C(CF₃)₂-, -CH₂-, -SO₂-, -NHCO- or -Si(R')₂- (R' is a linear branched or cyclic alkyl group containing from 1 to 8 carbon atoms)

[0023] A diamine described by Formula VII where W is -O- is a preferred diamine. In a more preferred embodiment this diamine comprises more than 80% of the total amount of diamine III. The most preferred embodiment of monomer III is 4,4'-diaminodiphenyl ether (also known as oxydianiline and ODA).

[0024] A preferred polyamic acid polymer of Formula I comprises a polymer synthesized from a dianhydride or dianhydrides of Formula IV, V or VI and a diamine or diamines of Formula VII. A more preferred polyamic acid polymer comprises a polyamic acid polymer synthesized from a dianhydride or dianhydrides of Formulae IV, V or VI where Z = -O- and a diamine or diamines of Formula VII where W = -O-. Examples of preferred polymers of the present invention are polyamic acid polymers synthesized from 4,4'-diaminodiphenyl ether and 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride (4,4'-oxydiphthalic acid dianhydride, ODPA) and a polyamic acid polymer synthesized from 4,4'-diaminodiphenyl ether

and a mixture of 95-85% of ODPa and 5-15% of another dianhydride of Formula II.

[0025] The ratio of diamine to dianhydride units in the polyamic acid polymer of Formula I can vary from about 0.9 to about 1.1. A preferred polyamic acid
5 polymer diamine to dianhydride unit ratio is from about 0.9 to about 1.

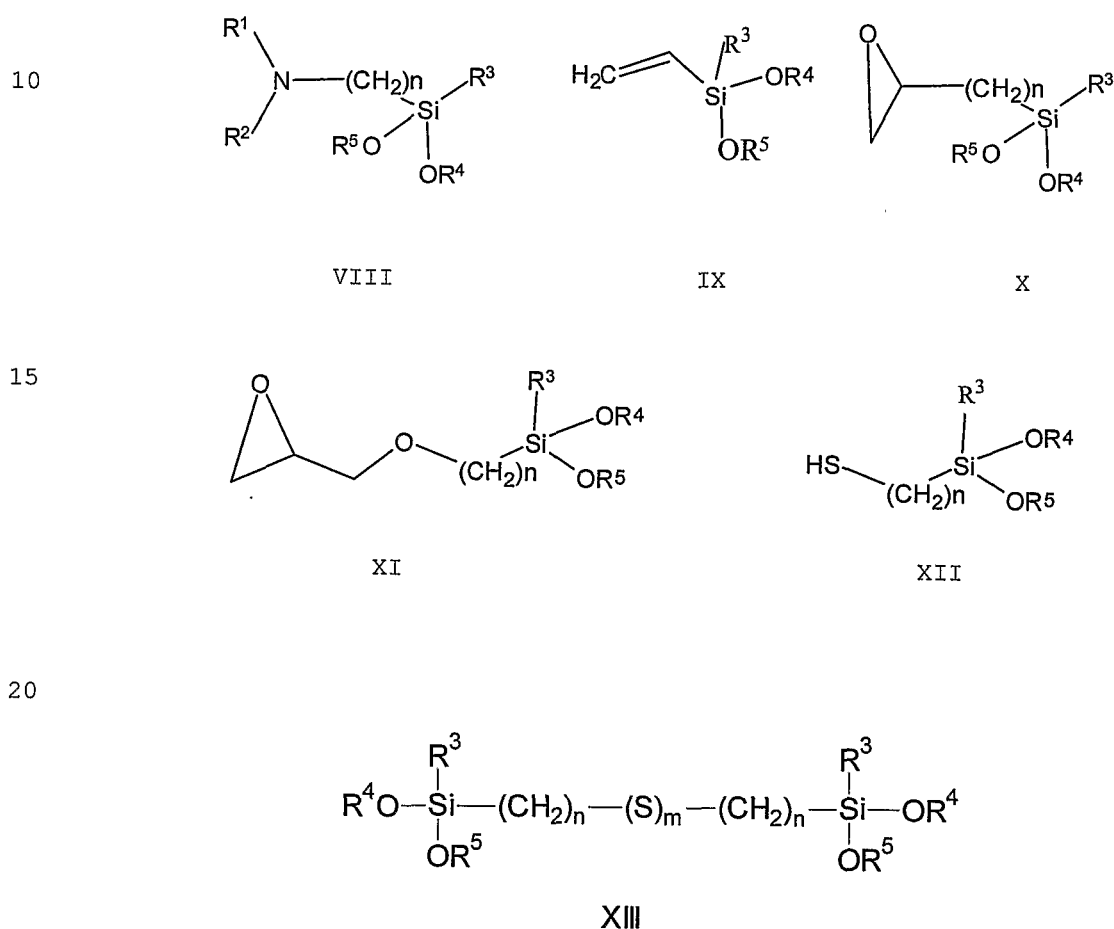
[0026] The % of polyamic acid polymer of Formula I in the composition may vary depending on the thickness desired, the molecular weight of the polymer of Formula I, and the viscosity of the coating solvent. A preferred concentration of
10 polyamic acid polymer of Formula I in the composition is from about 8% to about 25 % by weight. A more preferred concentration is from about 12% to about 22 % by weight. The most preferred concentration is from about 16% to about 21% by weight.

[0027] The composition used in the present invention also comprises *gamma*-butyrolactone as a solvent. The amount of *gamma*-butyrolactone is between about 92% and about 74 %. A cosolvent may also be employed. The cosolvent may be employed up to about 20% of the total amount of solvent used. Examples of cosolvents include but are not limited to other lactones, such as *gamma*-
20 valerolactone, *gamma*-caprolactone, and *delta*-valerolactone, and ketones such as 2-hexanone, 3-hexanone, 2-heptanone, 3-heptanone, 4-methyl -2-pentanone. Suitable cosolvents should have a boiling point between about 110 °C and about 230 °C.

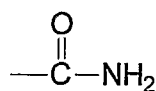
[0028] The formulation may also contain various additives such as adhesion promoters, dyes, co-solvents and dissolution modifiers. The amount of each non-adhesion promoter additive in the formulation, if used, is from about 0.02 to about 2% of the formulation by weight. A preferred amount of each non-adhesion promoter additive, if used, is from about 0.05 to about 1.5% and a more preferred
30 amount is from about 0.1 to about 1% of the formulation by weight. The amount of

adhesion promoter in the formulation is from about 0.05 to about 2% by weight of the formulation. A preferred amount of adhesion promoter is from about 0.15 to about 1% by weight and a more preferred amount is from about 0.2 to about 0.6% by weight of the formulation. Any suitable adhesion promoter may be used.

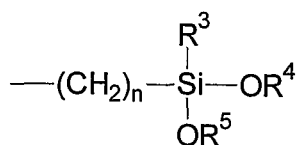
- 5 Preferred formulations contain a least one adhesion promoter selected from the group consisting of compounds described by Formulae VIII – XIII



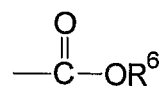
where R¹ is H, C₁–C₁₀ linear, cyclic or branched alkyl, phenyl or halophenyl or alkyl substituted phenyl. R² is C₁–C₁₀ linear, cyclic or branched alkyl, phenyl, halophenyl or alkyl substituted phenyl or one of the following moieties XIV or XV or XVI



XIV

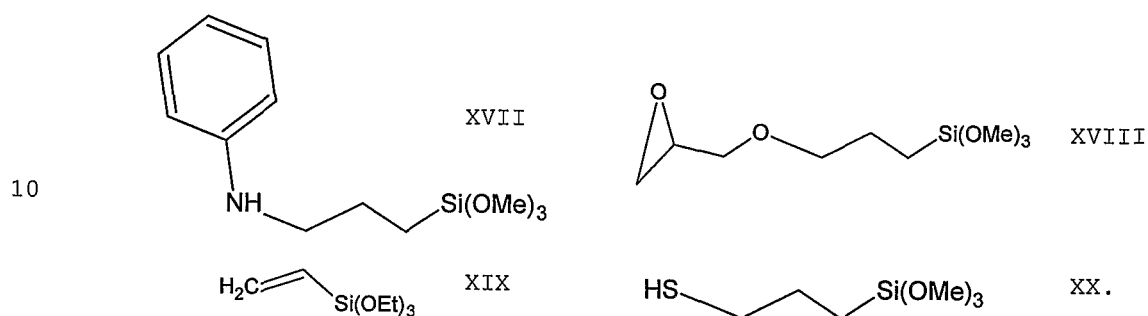


XV



XVI

where R³ is C₁–C₄ linear or branched alkyl or C₁–C₄ linear or branched alkoxy group, R⁴, R⁵, and R⁶ are independently C₁–C₄ linear or branched alkyl group and n is an integer from 1 to about 5. Preferred adhesion promoters are those described by Formulae VIII, IX, XI, and XII. Specific examples of preferred adhesion promoters include but are not limited to those of Formulae XVII, XVIII, XIX, and XX.



[0029] After the first coating step, the coated substrate is baked. The baking may take place at one temperature or multiple temperatures. Baking may take place on a hot plate or in various types of ovens known to those skilled in the art. Suitable ovens include ovens with thermal heating, vacuum ovens with thermal heating, and infrared ovens or infrared track modules. Typical times employed for baking will depend on the chosen baking means and the desired time and temperature and will be known to those skilled in the art. A preferred method of baking is on a hot plate. When baking on a hot plate, typical times range from about 0.5 minute to about 5 minutes at temperatures typically between about 80-130 °C. Lower bake temperatures and/or times increase the amount of residual solvent in the polyamic acid film, which may cause problems such as intermixing when the Deep UV

photoresist is coated. Higher temperatures and times can cause imidization of the polyamic acid, resulting in lower dissolution in the developer during lithography. The degree of imidization which occurs during this bake may depend on the specific chemical structure and physical properties of the polyamic acid employed. For the purposes of this invention, no or minimal imidization is desired. A preferred baking temperature range is from about 100 °C to less than about 140 °C. Another preferred baking temperature range is from about 90 °C to about 125 °C. Yet another preferred baking temperature range is from about 100 °C to less than about 130 °C. Another preferred baking temperature range is from about 110 °C to about 120 °C. Other suitable temperature ranges are from about 120 °C to less than 140 °C or from about 120 °C to less than 130 °C. Another preferred baking temperature range is from about 110 °C to about 135 °C

[0030] The thickness of the polyamic acid layer may be from about 0.5 μm to about 50 μm. A preferred thickness range is from about 2 μm to about 40 μm. A more preferred thickness range is from about 4 μm to about 20 μm.

[0031] In the second coating step, a layer of Deep UV photoresist is coated over the film of polyamic acid. For the purposes of this disclosure, Deep UV photoresist means any photoresist imageable using radiation < 250 nm and > 100 nm. Any suitable means of coating may be employed. A preferred method of coating of the Deep UV photoresist is spin coating. Any suitable application techniques and spin rates may be used and are known to those skilled in the art.

[0032] The Deep UV photoresists useful for this invention are photosensitive compositions that image at wavelength below 250 nm. In a preferred embodiment, the Deep UV photoresists are chemically amplified photoresists and may be positive or negative acting.

[0033] Positive acting Deep UV photoresists comprise a polymer, one or more

photoacid generators (PAGs) and a solvent. Representative Deep UV photoresists suitable for this invention may be found in US Patent Nos. 4,491,628, US 5,679,495, US 6,379,861, US 6,329,125, and US 5,206,317, which are incorporated herein by reference. Additional additives to the Deep UV photoresists such as bases, dyes, 5 adhesion promoters, or dissolution inhibitors may also be employed. Examples of suitable polymers for chemically amplified photoresists contain a polymer with alkali solubilizing group blocked by an acid sensitive group. Examples of suitable alkali solubilizing groups include, but are not limited to, carboxylic acids, phenols, hydroxyimides, hydroxymethylimides and fluorinated alcohols. Examples of suitable 10 blocking groups include, but are not limited to, alkyl groups containing tertiary carbons, and α alkoxy alkyls, and arylisopropyl groups. Examples of suitable blocked alkali solubilizing groups include, but are not limited to, *t*-butyl esters, *alpha* alkoxy esters, *t*-butoxyphenyl, *t*-butoxyimido, and *t*-butoxymethylimido. Examples of blocked alkali solubilizing groups can be found in US Patent Nos. 5,468,589, US 15 4,491,628, US 5,679,495, US 6,379,861, US 6,329,125, and US 5,206,317.

[0034] In addition to the polymer, chemically amplified photoresists suitable for this invention will also comprise photoacid generators. Any suitable photoacid generator compound may be employed in the radiation sensitive photoresist 20 compositions. Examples of suitable photoacid generators include, but are not limited to, iodonium and sulfonium salts of carboxylic or sulfonic acids, oxime sulfonates; and nitrobenzyl esters of carboxylic or sulfonic acids.

[0035] Preferred photoacid generators are those generating sulfonic or sulfinic 25 acids. Suitable classes of photoacid generators generating sulfonic or sulfinic acids include, but are not limited to, sulfonium or iodonium salts, oximidosulfonates, bisulfonyldiazomethane compounds, and nitrobenzylsulfonate esters. Suitable photoacid generator compounds are disclosed, for example, in U.S. Patent Nos. 5,558,978 and US 5,468,589, which are incorporated herein by reference. 30 Particularly preferred are di-aryl or di-alkyl iodonium salts of strong acids or triaryl,

diarylalkyl, dialkylaryl, or trialkyl substituted sulfonium salts of sulfonic acids.

[0036] Suitable examples of photoacid generators are triphenylsulfonium bromide, triphenylsulfonium chloride, triphenylsulfonium iodide, triphenylsulfonium
5 hexafluorophosphate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium trifluoromethanesulfonate, diphenylethylsulfonium chloride, phenacyldimethylsulfonium chloride, phenacyltetrahydrothiophenium chloride, 4-nitrophenacyltetrahydro-thiophenium chloride, and 4-hydroxy-2-methylphenylhexahydrothiopyrylium chloride.

10

[0037] Additional examples of suitable photoacid generators for use in this invention include triphenylsulfonium perfluorooctanesulfonate, triphenylsulfonium perfluorobutane-sulfonate, methylphenyldiphenylsulfonium perfluorooctane-sulfonate, methylphenyl-diphenylsulfonium perfluorooctanesulfonate, 4-n-butoxy-
15 phenyldiphenylsulfonium perfluorobutanesulfonate, 2,4,6-trimethylphenyldiphenyl-sulfonium perfluorobutanesulfonate, 2,4,6-trimethylphenyldiphenylsulfonium benzenesulfonate, 2,4,6-trimethylphenyldiphenylsulfonium 2,4,6-triisopropyl-benzenesulfonate, phenylthiophenyl-diphenylsulfonium 4-dodecylbenzensulfonic acid, tris(-t-butylphenyl)sulfonium perfluorooctanesulfonate, tris(-t-
20 butylphenyl)sulfonium perfluorobutanesulfonate, tris(-t-butylphenyl)sulfonium 2,4,6-triisopropylbenzenesulfonate, tris(-t-butylphenyl)sulfonium benzenesulfonate, and phenylthiophenyldiphenylsulfonium perfluorooctanesulfonate.

[0038] Examples of suitable iodonium salts for use in this invention include,
25 but are not limited to, diphenyl iodonium perfluorobutanesulfonate, bis-(t-butylphenyl)iodonium perfluoro-butanesulfonate, bis-(t-butylphenyl)iodonium perfluorooctanesulfonate, diphenyl iodonium perfluorooctanesulfonate, bis-(t-butylphenyl)iodonium benzenesulfonate, bis-(t-butylphenyl)iodonium 2,4,6-triisopropylbenzenesulfonate, and diphenyliodonium 4-methoxybenzensulfonate.

30

[0039] Further examples of suitable photoacid generators for use in this invention are bis(p-toluenesulfonyl)diazomethane, methylsulfonyl p-toluenesulfonyldiazomethane, 1-cyclo-hexylsulfonyl-1-(1,1-dimethylethylsulfonyl)diazomethane, bis(1,1-dimethylethyl-sulfonyl)diazomethane, 5 bis(1-methylethylsulfonyl)diazomethane, bis(cyclohexyl-sulfonyl)diazomethane, 1-p-toluenesulfonyl-1-cyclohexylcarbonyldiazomethane, 2-methyl-2-(p-toluenesulfonyl)propiophenone, 2-methanesulfonyl-2-methyl-(4-methylthio-propiophenone, 2,4-methyl-2-(p-toluenesulfonyl)pent-3-one, 1-diazo-1-methylsulfonyl-4-phenyl-2-butanone, 2-(cyclohexylcarbonyl-2-(p-toluenesulfonyl)propane, 1-cyclohexyl-sulfonyl-1-cyclohexylcarbonyldiazomethane, 1-diazo-1-cyclohexylsulfonyl-3,3-dimethyl-2-butanone, 1-diazo-1-(1,1-dimethylethylsulfonyl)-3,3-dimethyl-2-butanone, 1-acetyl-1-(1-methylethylsulfonyl)diazomethane, 1-diazo-1-(p-toluenesulfonyl)-3,3-dimethyl-2-butanone, 1-diazo-1-benzenesulfonyl-3,3-dimethyl-2-butanone, 1-diazo-1-(p-toluenesulfonyl)-3-methyl-2-butanone, cyclohexyl 2-diazo-2-(p-toluenesulfonyl)acetate, tert-butyl 2-diazo-2-benzenesulfonylacetate, isopropyl-2-diazo-2-methanesulfonylacetate, cyclohexyl 2-diazo-2-benzenesulfonylacetate, tert-butyl-2-diazo-2-(p-toluenesulfonyl)acetate, 2-nitrobenzyl p-toluenesulfonate, 2,6-dinitrobenzyl p-toluenesulfonate, and 2,4-dinitrobenzyl p-trifluoromethylbenzene-sulfonate. 20 sulfonate.

[0040] The photoacid generator compound is typically employed in the amounts of about 0.0001 to 20% by weight of polymer solids and more preferably about 1% to 10% by weight of polymer solids. Preferred photoacid generators are 25 sulfonium salts. The photoacid generator may be used alone or in combination with one or more photoacid generators. The percentage of each photoacid generator in photoacid generator mixtures is between about 10% to about 90% of the total photoacid generator mixture.

30 **[0041]** Negative acting chemically amplified Deep UV photoresists typically

comprise an alkali soluble polymer, a photoacid generator, a crosslinker, and a solvent. Examples of suitable polymers are polymers or copolymers having hydroxystyrene monomer units. Suitable photoacid generators are similar to those described above for positive acting Deep UV photoresists. Any suitable cross-
5 linking agent may be used. Examples of suitable crosslinking agents include as methylolated and/or methylolated and etherified melamines, methylolated and/or methylolated and etherified guanamines and compounds containing at least two hydroxymethylphenyl groups. Examples of suitable negative acting chemically amplified Deep UV photoresists can be found in US Patent Nos. 6,406,829, US
10 6,399,275, US 6,245,930, US 6,130,270, and US 6,048,666.

[0042] The choice of solvent for the Deep UV photoresist and the concentration thereof depends principally on the type of functionalities incorporated in the acid labile polymer, the photoacid generator, and the coating method. The
15 solvent should be inert, should dissolve all the components in the photoresist, should not undergo any chemical reaction with the components and should be removable by drying after coating. Suitable solvents for the photoresist composition may include ketones, ethers and esters, such as methyl ethyl ketone, methyl isobutyl ketone, 2-heptanone, cyclopentanone, cyclohexanone, 2-methoxy-1-propylene
20 acetate, 2-ethoxyethyl acetate, 1-methoxy-2-propyl acetate, 1,2-dimethoxy ethane, ethyl acetate, cellosolve acetate, propylene glycol monoethyl ether acetate, methyl pyruvate, ethyl pyruvate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, 1,4-dioxane, diethylene glycol dimethyl ether, and the like and the mixture thereof. More preferred solvents are propylene glycol monoethyl ether acetate, 2-heptanone,
25 cyclohexanone, 2-ethoxyethyl acetate or mixture thereof. The most preferred solvent is propylene glycol monoethyl ether acetate.

[0043] Base additives may be added to the Deep UV photoresist. One purpose of the base additive is to scavenge protons present in the photoresist prior
30 to being irradiated by the actinic radiation. The base prevents attack and cleavage

of the acid labile groups by the undesirable acids, thereby increasing the performance and stability of the photoresist. A second purpose of the base additive is to control photoacid diffusion to control and improve resolution. The percentage of base in the composition should be significantly lower than the photoacid generator
5 because it would not be desirable for the base to interfere with the cleavage of the acid labile groups after the photoresist composition is irradiated. A preferred range of the base compounds, when present, is from about 3% to about 50% by weight of the photoacid generator compound. Examples of useful bases include but are not limited to alkyl amines, cyclic amine, or salts of hydroxide ions. Suitable examples
10 of base additives are 2-methylimidazole, triisopropylamine, 4-dimethylaminopyridine, 4,4'-diaminodiphenyl ether, 2,4,5-triphenylimidazole, tetrabutyl ammonium hydroxide and 1,5-diazobicyclo[4.3.0]non-5-ene.

[0044] After the second coating step, the coated substrate is baked. Baking
15 may take place on a hot plate or in various types of ovens known to those skilled in the art. Suitable ovens include ovens with thermal heating, vacuum ovens with thermal heating, and infrared ovens or infrared track modules. Typical times employed for baking will depend on the chosen baking means and the desired time and temperature and will be known to those skilled in the art. A preferred method of
20 baking is on a hot plate. When baking on a hot plate, typical times range from about 0.5 minute to about 5 minutes at temperatures typically between about 80 °C to about 140 °C. Optimum bake parameters may vary depending on the Deep UV photoresist and solvent employed. Bake conditions should be employed which will minimize decomposition of Deep UV photoresist and minimize imidization of the
25 polyamic acid.

[0045] The thickness of the Deep UV photoresist can be from about 0.1 μm to about 3 μm . A preferred thickness range is from about 0.5 μm to about 2.5 μm . A more preferred thickness range is from about 1 μm to about 2 μm .

30

[0046] Subsequently, the resulting bilayer system is exposed to actinic rays

through a mask having a desired pattern. The wavelength of the actinic radiation should be less than 250 nm. Preferred wavelengths include 248 nm, 193 nm and 157 nm because these are exposure wavelengths of lasers used in the industry exposure systems. A more preferred wavelength is 248 nm.

5

[0047] Following exposure to actinic radiation, it is advantageous to heat the coated substrate in an optional step to a temperature from between about 70° C and to about 140 °C. This process step is commonly referred to in the art as post exposure baking and is carried out to ensure enough acid catalyzed deblocking has occurred to differentially dissolve the more soluble portion of the photoresist coating. A preferred post exposure temperature range is from about 80 °C to about 120 °C. The duration of the post exposure bake step is for a short period of time, typically from about several seconds to about several minutes when carried out on a hot plate. Other suitable baking means may be employed with the baking times being chosen to be appropriate for the method.

[0048] The bilayer film is developed using an aqueous tetramethyl ammonium hydroxide developer to obtain a relief pattern. The developer may contain an appropriate amount of a surfactant or other additives, but should not contain any cosolvents. Development can be carried out by means of immersion, spray, puddling, or other similar developing methods known to those skilled in the art with or without agitation. Development may take place in several steps in which sequential treatments with developer occur. Multiple rinse steps with deionized water may be employed as well. Variations in tetramethyl ammonium hydroxide concentrations in the developer may be employed in different steps. Following the last developer treatment, the bilayer relief pattern is then rinsed using deionized water. An optional drying step may be employed using any suitable drying means. Examples of suitable drying means include spin drying, baking on a hot plate or an oven and is usually for a short duration of time.

30

[0049] After the development (or the optional drying step, if employed), the top photoresist layer is removed by dissolving it in an appropriate solvent in a process called "stripping". The stripping solvent should dissolve the photoresist layer but should not dissolve the bottom layer of polyamic acid. Suitable stripping
5 solvents may include ketones, ethers and esters, such as methyl ethyl ketone, methyl isobutyl ketone, 2-heptanone, cyclopentanone, cyclohexanone, 2-methoxy-1-propylene acetate, 2-ethoxyethyl acetate, 1-methoxy-2-propyl acetate, 1,2-dimethoxy ethane, ethyl acetate, cellosolve acetate, propylene glycol monoethyl ether acetate, methyl pyruvate, ethyl pyruvate, methyl 3-methoxypropionate, ethyl 3-
10 methoxypropionate, 1,4-dioxane, diethylene glycol dimethyl ether, and mixtures thereof. Preferred solvents are propylene glycol monoethyl ether acetate, 2-heptanone, cyclohexanone, 2-ethoxyethyl acetate or mixtures thereof. The most preferred solvent is propylene glycol monoethyl ether acetate. The stripping process may be done by immersing the bilayer coated substrate having relief structures into
15 the stripping solvent or, preferably, by spraying the stripping solvent over the bilayer relief structures while slowly rotating the substrate on a chuck. Subsequently, the substrate, now having only a polyamic acid relief structure coated on it, may be rinsed with fresh stripping solvent and dried by suitable drying means.

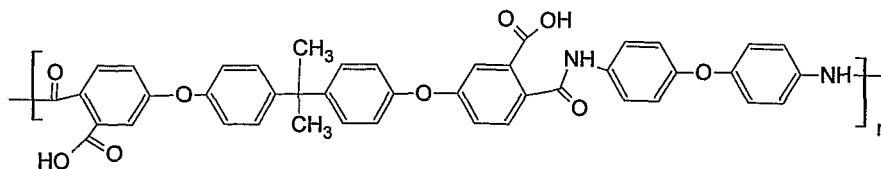
[0050] The polyamic acid is then cured to polyimide by baking the substrate
20 with the polyamic acid relief structure at or above the glass transition temperature, T_g , of the polyamic acid polymer to obtain the high heat resistant polyimide. The temperature employed may vary depending on the particular polyimide and the substrate employed. The curing temperature may range from about 200 °C to about 500 °C. A preferred range is from about 250 °C to about 450 °C. A more preferred
25 range is from about 300 °C to about 450 °C. The cure may be accomplished using a hot plate, a heated diffusion tube, or oven and may take place at a single temperature, or several temperatures, or be ramped up over a broad temperature range. The cure time will depend on the particular heating means employed, but will typically be from about 30 minutes to 60 minutes. The atmosphere in which the
30 bake takes place may be in an inert gas, such as nitrogen, or in air.

[0051] The application of the said polyimide films in semiconductor industry include, but are not limited to, stress relieve coatings for packaged semiconductors, alpha particle barrier films, interlevel dielectrics, insulating films and patterned engineering plastic layers. The examples of articles of commerce made using the disclosed formulation and method include, but not limited to memory devices, such as DRAMs, logic devices, such as microprocessors or microcontrollers, plating stencils, etc.

[0052] The following examples are provided to illustrate the principles and practice of the present invention more clearly. It should be understood that the present invention is not limited to the examples described.

[0053] Comparative Example 1

Preparation of Bisphenol A dianhydride (BPADA) / oxydianiline (ODA) polyamic acid



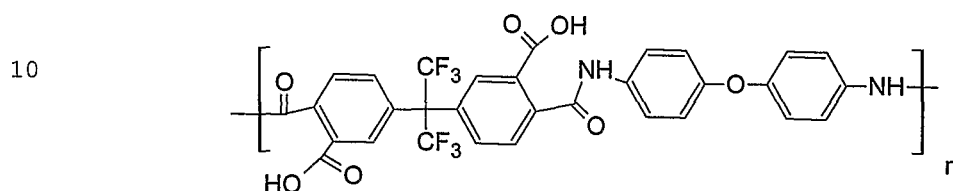
A 500 mL, three neck, round bottom flask was equipped with a mechanical stirrer, temperature controller and nitrogen inlet. 199 g of *gamma*-butyrolactone was added to this reaction flask followed by addition of 26.03 g (50 mmole) of bis-phenol A dianhydride (BPADA). The reaction mixture was stirred at room temperature for 15 minutes and then at 50 -51°C until bis-phenol A dianhydride was fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. In this case no precipitate was formed. 9.81 g (49 mmole) of oxydianiline was added portion wise within an hour in 3g portions. 3.2 g *gamma*-butyrolactone was added to rinse the oxydianiline container into the reaction flask. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction

mixture was allowed to stir at this temperature for 24 hours. The kinematic viscosity of the final product was 1350 cSt. The polymer was found to be insoluble in 0.262 N aqueous tetramethyl ammonium hydroxide.

5 [0054]

Comparative Example 2

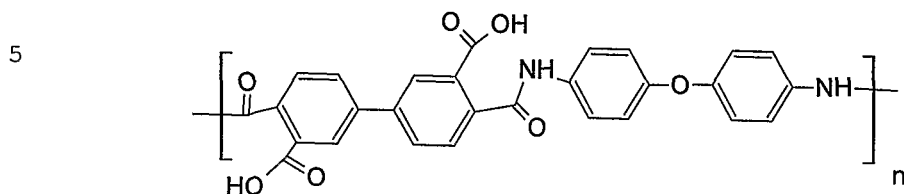
Preparation of 2,2'-Bis-(3,4-Dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) / oxydianiline (ODA) polyamic acid



A 500 mL, three neck, round bottom flask was equipped with a mechanical stirrer, temperature controller and nitrogen inlet. 230.54 g of gamma-butyrolactone was added to this reaction flask followed by addition of 44.42 g (100 mmole) of 6FDA. The reaction mixture was stirred at room temperature for 15 minutes and then at 50 –51 °C until 6FDA was fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. In this case no precipitate was formed. 19.62 g (98 mmole) of oxydianiline was added portion wise within an hour in 3g portions. 12.81 g gamma-butyrolactone was added to rinse the oxydianiline container into the reaction flask. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this temperature for 24 hours. The viscosity of the final product was 4480 cSt. The solution was diluted with 75 g of gamma-butyrolactone to achieve the final solution with a kinematic viscosity of 1029 cSt. This polymer was found not to be PGMEA resistant

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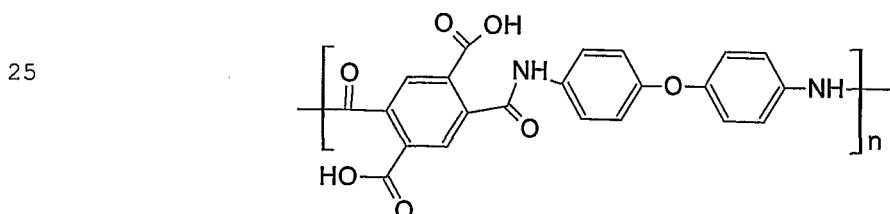
[0055]

Comparative Example 3**Preparation of 3,3',4,4'-biphenyltetracarboxylic dianhydride(S-BPDA)/oxydianiline (ODA) polyamic acid**

A 500 mL, three neck, round bottom flask was equipped with a mechanical
 10 stirrer, temperature controller and nitrogen inlet. 176.54 g of *gamma*-butyrolactone
 was added to this reaction flask followed by addition of 29.42 g (100 mmole) of S-
 BPDA. The resulting slurry was stirred at room temperature for 15 minutes and then
 at 50 –51 °C. The slurry did not dissolve. The reaction slurry was cooled to 15 °C.
 19.62 g (98 mmole) of oxydianiline was added portion wise within an hour in 3 g
 15 portions. 59 g *gamma*-butyrolactone was added to rinse the oxydianiline into the
 reaction flask. The reaction temperature was kept at 15 °C for another 15 minutes
 and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this
 temperature for 24 hours. The heavy viscous slurry did not dissolve. The reaction
 was discarded.

20

[0056]

Comparative Example 4**Preparation of pyromellitic dianhydride (PMDA) / oxydianiline (ODA) polyamic acid**

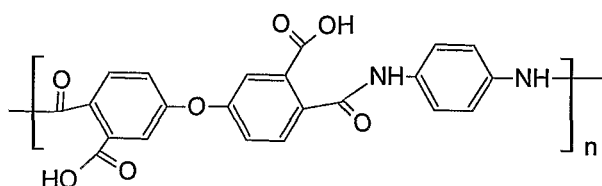
A 500 mL, three neck, round bottom flask was equipped with a mechanical
 30 stirrer, temperature controller and nitrogen inlet. 200.00 g of *gamma*-butyrolactone

was added to this reaction flask followed by addition of 21.8 g (100 mmole) of PMDA. The resulting slurry was stirred at room temperature for 15 minutes and then at 50 –51 °C. The slurry did not dissolve. The reaction slurry was cooled to 15 °C. 19.62 g (98 mmole) of oxydianiline was added portion wise within an hour in 3 g portions. 17.5 g *gamma*-butyrolactone was added to rinse the oxydianiline into the reaction flask. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this temperature for 24 hours. The heavy viscous slurry did not dissolve. The reaction was discarded.

[0057]

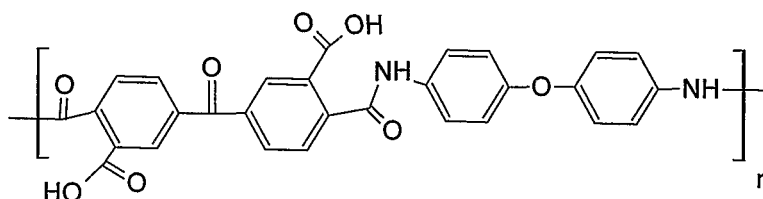
Comparative Example 5

**Preparation of 4,4'-oxydiphthalic dianhydride (ODPA) / 1,4 Phenylenediamine
Polyamic acid**



A 500 mL, three neck, round bottom flask was equipped with a mechanical stirrer, temperature controller and nitrogen inlet. 224.75 g of *gamma*-butyrolactone was added to this reaction flask followed by addition of 46.53 g (150 mmole) of 4,4'-oxydiphthalic dianhydride (ODPA). The ODPA charging funnel was rinsed 12.5 g of *gamma*-butyrolactone. The reaction mixture was stirred at room temperature for 15 minutes and then at 73 –75 °C until 4,4'-oxydiphthalic dianhydride was fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. The 4,4'-oxydiphthalic dianhydride was partially precipitated. 15.90 g (147 mmole) of 1,4-Phenylenediamine was added portion wise within an hour. 12.5 g *gamma*-butyrolactone was added to rinse the oxydianiline container. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this temperature for 24 hours. The reaction produced black tarry solid and was discarded.

[0058]

Comparative Example 6**Preparation of 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) / 4,4'-oxydianiline (ODA) polyamic acid**

10 A 500 mL, three neck, round bottom flask was equipped with a mechanical stirrer, temperature controller and nitrogen inlet. 186.60 g of *gamma*-butyrolactone was added to this reaction flask followed by addition of 32.20 g (100 mmole) of BTDA. The BTDA charging funnel was rinsed using 10.40 g of *gamma*-butyrolactone. The reaction mixture was stirred at room temperature for 15 minutes

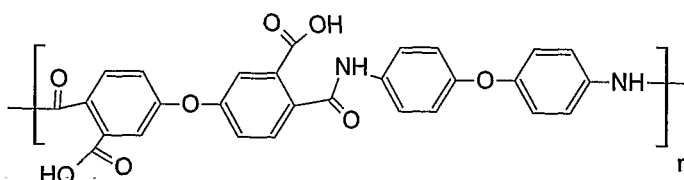
15 and then at 95-100 °C until BTDA was fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. 19.624 g (98 mole) of ODA was added portion wise within an hour. 10.4 g *gamma*-butyrolactone was added to rinse the oxydianiline container. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to

20 stir at this temperature for 24 hours. The reaction produced turbid solution. The reaction mixture was discarded.

[0059]

Example 1

25 **Preparation of 4,4'-oxydiphthalic dianhydride (ODPA) / oxydianiline (ODA) polyamic acid**



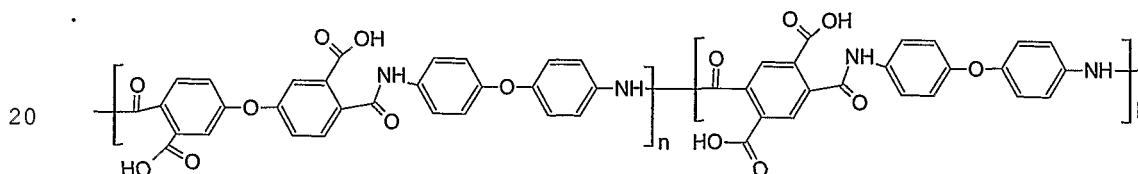
A 500 mL, three neck, round bottom flask was equipped with a mechanical

stirrer, temperature controller and nitrogen inlet. 270 g of *gamma*-butyrolactone was added to this reaction flask followed by addition of 31.022 g (100 mmole) of 4,4'-oxydiphthalic dianhydride (ODPA). The ODPA charging funnel was rinsed with 15g of *gamma*-butyrolactone. The reaction mixture was stirred at room temperature for 15 minutes and then at 73 –75 °C until 4,4'-oxydiphthalic dianhydride was fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. The 4,4'-oxydiphthalic dianhydride was partially precipitated. 19.62 g (98 mmole) of oxydianiline was added portion wise within an hour. 13.3 g *gamma*-butyrolactone was added to rinse the oxydianiline container. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this temperature for 24 hours. The reaction was complete as evidenced by the absence of anhydride peak (1800 cm⁻¹) from IR spectrum of the solution. The kinematic viscosity of the final product was 1384 cSt.

15 [0060]

Example 2

Preparation of 4,4'-oxydiphthalic dianhydride (ODPA)-pyromellitic dianhydride (PMDA) / oxydianiline (ODA) polyamic acid



A 500 mL, three neck, round bottom flask was equipped with a mechanical stirrer, temperature controller and nitrogen inlet. 234.9 g of *gamma*-butyrolactone was added to this reaction flask followed by addition of 27.92 g (90 mmole) of 4,4'-oxydiphthalic dianhydride (ODPA) and 2.18 g (10 mmole) of pyromellitic dianhydride (PMDA). The ODPA/PMDA charging funnel was rinsed with 13.05 g of *gamma*-butyrolactone. The reaction mixture was stirred at room temperature for 15 minutes and then at 70 –72 °C until the dianhydrides were fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. The solids partially precipitated. 19.62 g (98 mmole) of oxydianiline was added portion wise within an hour in 3 g portions.

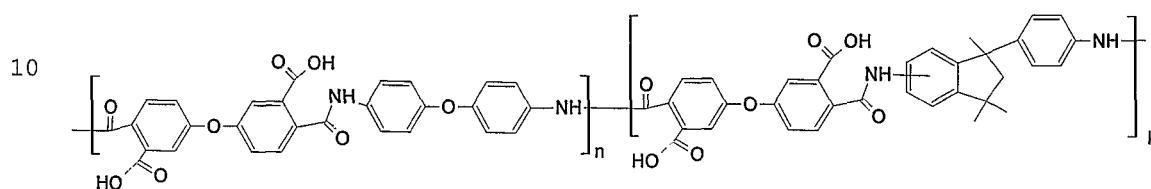
13.3 g *gamma*-butyrolactone was added to rinse the oxydianiline container into the reaction flask. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this temperature for 24 hours. The kinematic viscosity of the final product was 472 cSt.

5

[0061]

Example 3

Preparation of 4,4'-oxydiphthalic dianhydride (ODPA)/ 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)/ oxydianiline (ODA) polyamic acid

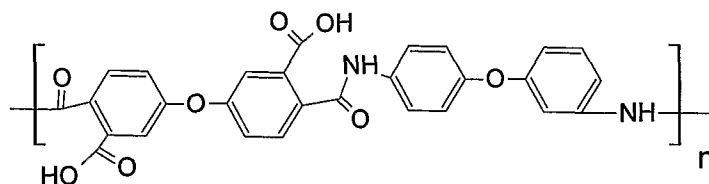


A 500 mL, three neck, round bottom flask was equipped with a mechanical
 15 stirrer, temperature controller and nitrogen inlet. 187 g of *gamma*-butyrolactone was added to this reaction flask followed by addition of 31.022 g (100 mmole) of ODPA. The reaction mixture was stirred at room temperature for 15 minutes and then at 50 –51 °C until ODPA was fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. The 4,4'-oxydiphthalic dianhydride was partially precipitated. 15.7
 20 g (78.4 mmole) of oxydianiline was added portion wise within an hour in 3 g portions, followed by 5.22 g (19.6 mmole) of DAPI in 3 g portions as well. 12.81 g *gamma*-butyrolactone was added to rinse the oxydianiline and DAPI container into the reaction flask. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this
 25 temperature for 24 hours. The kinematic viscosity of the final product was 4186 cSt. The solution was diluted with 48 g of *gamma*-butyrolactone to achieve the final solution with a kinematic viscosity of 1120 cSt.

[0062]

Example 4

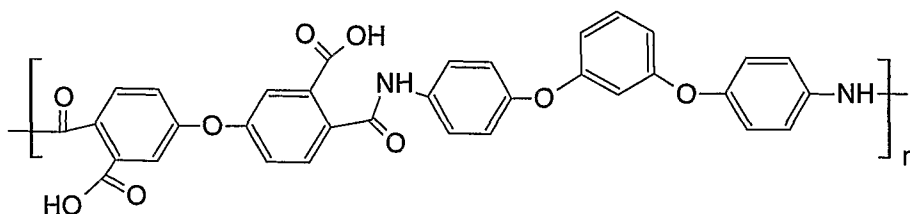
30 **Preparation of 4,4'-oxydiphthalic dianhydride (ODPA) / 4,3'-oxydianiline**

polyamic acid

5

A 500 mL, three neck, round bottom flask was equipped with a mechanical stirrer, temperature controller and nitrogen inlet. 181.00 g of *gamma*-butyrolactone was added to this reaction flask followed by addition of 31.022 g (100 mmole) of 4,4'-oxydipthalic dianhydride (ODPA). The ODPA charging funnel was rinsed using 10 g of *gamma*-butyrolactone. The reaction mixture was stirred at room temperature for 15 minutes and then at 73 –75 °C until 4,4'-oxydipthalic dianhydride was fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. The 4,4'-oxydipthalic dianhydride was partially precipitated. 19.22 g (96 mmole) of 4,3'-oxydianiline was added portion wise within an hour. 8 g *gamma*-butyrolactone was added to rinse the oxydianiline container. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this temperature for 24 hours. The reaction was complete as evidenced by the absence of anhydride peak (1800 cm⁻¹) from IR spectrum of the solution. The kinematic viscosity of the final product was 1075 cSt.

20

[0063]**Example 5.****Preparation of 4,4'-oxydipthalic dianhydride (ODPA) / 1,3-bis(4-aminophenoxy)benzene (TPE-R) polyamic acid**

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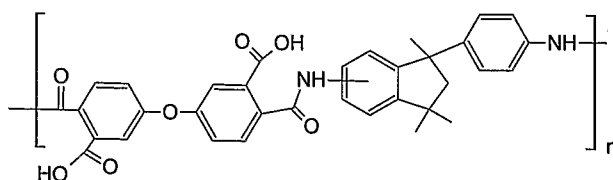
A 500 mL, three neck, round bottom flask was equipped with a mechanical stirrer, temperature controller and nitrogen inlet. 214.83 g of *gamma*-butyrolactone

30

was added to this reaction flask followed by addition of 31.022 g (100 mmole) of 4,4'-oxydiphthalic dianhydride (ODPA). The ODPA charging funnel was rinsed with 11.93 g of *gamma*-butyrolactone. The reaction mixture was stirred at room temperature for 15 minutes and then at 70 -72°C until 4,4'-oxydiphthalic dianhydride was fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. The 4,4'-oxydiphthalic dianhydride was partially precipitated. 28.65 g (98 mmole) of 1,3-bis(4-aminophenoxy)benzene (TPE-R) was added portion wise within an hour (in 3 g portions). 15.63 g *gamma*-butyrolactone was added to rinse the 1,3-bis(4-aminophenoxy)benzene (TPE-R) container into the reaction mixture. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this temperature for 24 hours. The kinematic viscosity of the final product was 1356 cSt.

[0064]**Example 6.**

Preparation of 4,4'-oxydiphthalic dianhydride (ODPA) / 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) polyamic acid



A 500 mL, three neck, round bottom flask was equipped with a mechanical stirrer, temperature controller and nitrogen inlet. 270 g of *gamma*-butyrolactone was added to this reaction flask followed by addition of 31.022 g (100 mmole) of 4,4'-oxydiphthalic dianhydride (ODPA). The ODPA charging funnel was rinsed with 15g of *gamma*-butyrolactone into the reaction flask. The reaction mixture was stirred at room temperature for 15 minutes and then at 70 -72 °C until 4,4'-oxydiphthalic dianhydride was fully dissolved. The clear, pale yellow reaction solution was cooled to 15 °C. The 4,4'-oxydiphthalic dianhydride was partially precipitated. 26.11g (98 mmole) of DAPI was added portion wise within an hour in 3 g portions. 14.94g *gamma*-butyrolactone was added to rinse the DAPI container into the reaction

mixture. The reaction temperature was kept at 15 °C for another 15 minutes and then slowly increased to 40 °C. The reaction mixture was allowed to stir at this temperature for 24 hours. The kinematic viscosity of the final product was 390 cSt.

5 [0065]

Example 7**Dissolution rate study of polyamic acids in 0.262 N aqueous tetramethyl ammonium hydroxide (TMAH) solution**

The solutions of appropriate polyamic acids prepared in Examples 1-6, and Comparative Example 2 were filtered through 1 µm Teflon filter membrane. These
10 solutions were spin coated onto a silicon wafer, which was cleaned by O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. The coated wafer was baked at 120 °C for 3 minutes. The thickness of the polyamic acid films thus obtained was 3 - 4 µm. The wafers were submerged into 0.262 N aqueous TMAH solution. The time needed for the polyamic acid film to dissolve was
15 recorded from which the dissolution rate was calculated (see Table 1).

[0066]

Example 8**Dissolution rate study of polyamic acids in propylene glycol methyl ether acetate (PGMEA)**

The solutions of polyamic acids prepared in Examples 1-6, and Comparative
20 Example 2 were filtered through 1 µm Teflon filter membrane. These solutions were spin coated onto a silicon wafer, which was cleaned by O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. The coated wafer was baked at 120 °C for 3 minutes. The thickness of the polyamic acid films thus obtained was
25 3 - 4 µm. Then, about 20 mL of propylene glycol ethyl ether acetate (PGMEA) was poured on the top of the wafers forming a puddle covering almost all surface of the wafer. After about 1 min the PGMEA was poured off and the films on the wafers were examined for damage (creases) and film thickness loss. Films that exhibited any signs of damage or/and film thickness loss more than 600 angstroms were
30 designated as having bad PGMEA resistance. The results are in Table 1.

Table 1

Example	Polyamic acid	Dissolution rate	Resistance to PGMEA
1	ODPA/ODA	30 $\mu\text{m}/\text{min}$	Good
2	ODPA/PMDA/ODA	15 $\mu\text{m}/\text{min}$	Good
3	ODPA/DAPI/ODA	24 $\mu\text{m}/\text{min}$	Good
4	ODPA/4,3'ODA	56 $\mu\text{m}/\text{min}$	Good
5	ODPA/TPE-R	5 $\mu\text{m}/\text{min}$	Good
6	ODPA/DAPI	0.4 $\mu\text{m}/\text{min}$	NA
Comparative 2	6FDA/ODA	36 $\mu\text{m}/\text{min}$	Bad

[0067]**Example 9****5 Infrared (IR) study of ODPA/ODA polyamic acid baked at different temperature**

100g of ODPA/ODA polyamic acid solution in GBL (16 wt %), prepared in the way similar to the one described in Example 1, were diluted with 60 g of GBL. The solution was spin coated onto double polished silicon wafers, which were cleaned by

10 O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. The coated wafers were subjected to different softbakes, 100 °C, 120 °C, 140 °C, 160 °C and 180°C, for 3 minutes. The thickness of the polyamic acid films thus obtained was 0.5-0.6 μm . The coated wafers, thus obtained, were examined by IR for presence of imide peak at $\sim 1800\text{-}1850\text{ cm}^{-1}$. The results are summarized in

15 Table 2.

[0068]**Example 10****Dissolution rate measurements of ODPA/ODA polyamic acid baked at different temperatures**

20 ODPA/ODA polyamic acid solution in GBL (16 wt %), prepared in the way similar to the one described in Example 1 was spin coated onto silicon wafers, which

were cleaned by O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. The coated wafers were subjected to different softbakes, 100 °C, 120 °C, 140 °C, 160 °C and 180 °C, for 3 minutes. The thickness of the polyamic acid films thus obtained was 3-3.5 μm. The wafers were submerged into 0.262 N aqueous TMAH solution. The time needed for the polyamic acid film to dissolve was recorded from which the dissolution rate was calculated. The data is summarized in Table 2.

Table 2. IR and dissolution rate study of ODPA/ODA polyamic acid films baked at different temperatures.

Bake temperature	Imide peak (~1750-1800 cm ⁻¹)	Dissolution rate (μm/min)
100°C	None	25 μm/min
120°C	None	23 μm/min
140°C	Weak	9 μm/min
160°C	Strong	< 0.5 μm/min
180°C	Strong	< 0.5 μm/min

[0069]

Examples 11a-18a, Comparative 8a - 11a

Stability Testing of Polyamic Acid Solutions Containing Adhesion Promoter

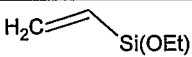
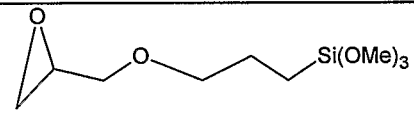
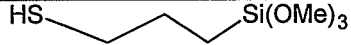
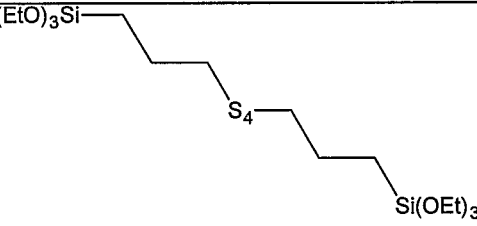
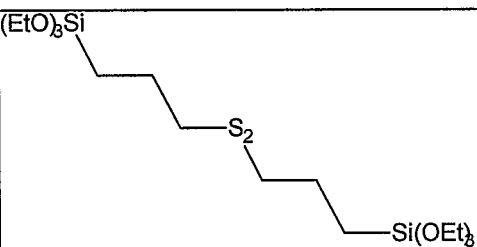
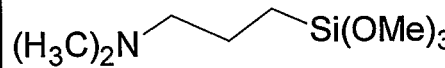
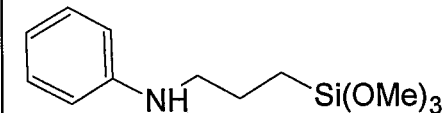
The stability of a series of polyamic acid solutions containing various adhesion promoters (products of OSI Specialties of Greenwich, CT) was tested. Each formulation consisted of 2.4g of a 10% solution of adhesion promoter in GBL added to 50g of the 4,4'-oxydiphthalic dianhydride (ODPA)/ oxydianiline (ODA) polyamic acid solution prepared in Example 1. The solutions were mixed for 24 hours at room temperature and examined for gelation. Results are summarized in Table 3. Those solutions not showing signs of gelation were also filtered through a 1 μm filter to confirm the lack of gelation.

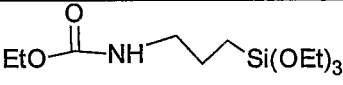
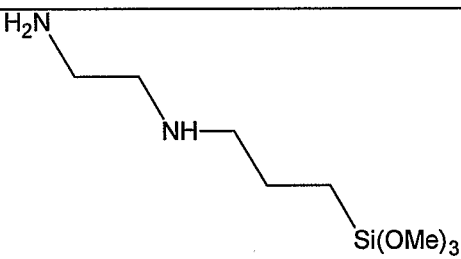
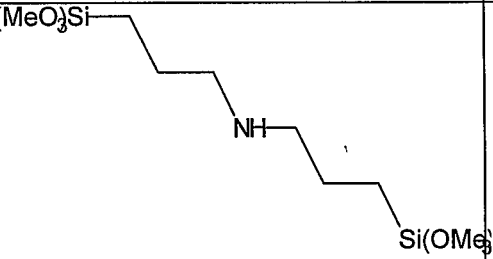
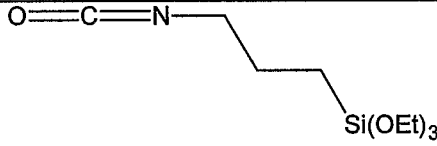
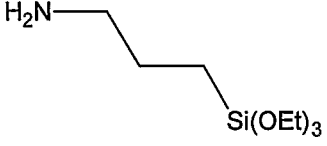
[0070]

Examples 11b-13b, 16b-18b**Adhesion test of Polyamic Acid Solutions Containing Adhesion Promoter according to ASTM D-3359-83.**

5 1 part of an adhesion promoters listed in the Table 1 was dissolved in 3 parts of *gamma*-butyrolactone. This solution was added drop-wise to 208 parts of 4,4'-oxydiphthalic dianhydride (ODPA) / oxydianiline (ODA) polyamic acid solution of Example 1. The mixture was stirred for 24 hours and a clear solution was obtained. A silicon wafer was cleaned by O₂ plasma in Mercator Life Systems apparatus (500
10 watts, 0.3-0.5 torr) for 10 min. This solution was spin coated onto above mentioned silicon wafer. The coated wafer was baked at 120 °C for 3 minutes. The thickness of the film of polyamic acid thus obtained was 7 - 8 μm. A 2 μm film of Deep UV photoresist GKR-4401 (commercially available from Arch Chemicals) was prepared by coating over the polyamic acid layer by spin coating and baking at 110 °C for 90
15 seconds. The wafers were then exposed patternwise using a broadband mercury lamp light for 108.2 seconds (the lamp output was 1000 mJ/cm² @ 400nm during the exposure time) with Karl Suss MA-56 broadband exposure tool. A ten by ten grid of 2 mm squares was thus created. The exposed wafer was then baked at 110 °C for 60 seconds. Then, the wafer was developed in 0.262 N aqueous
20 tetramethylammonium hydroxide using puddle development (2 puddles, 50 seconds each). The remaining photoresist was removed using an atomized spray of photoresist stripper RER 600, which is commercially available from Arch Chemicals, during a 30 second treatment while spinning at 2000 revolutions per minute. The wafer was then spun at 3000 revolutions per minute until it was dried. The patterned
25 layer of polyamic acid was imidized under N₂ atmosphere at 350 °C for 1 hour. The product was then placed in a pressure cooker pot and was exposed to saturated steam at 121 °C for 100 hrs. Then, the adhesion of the film to the wafers was tested using a tape peel test using 3M tape #720 as described in ASTM D-3359-83.
If no squares of the grid were peeled off, then the formulation passed the test.
30 The results are summarized in Table 3.

Table 3: Results of stability and adhesion tests of non-photosensitive polyamic acid compositions containing adhesion promoters.

Example #	Adhesion promoter structure	Formulation stability (a)	Adhesion (b)
11		stable	Pass
12		stable	pass
13		stable	Pass
14		stable	NT
15		stable	NT
16		Stable	pass
17		stable	Pass

18		Stable	pass
Comparative Example 8		Gelled; unstable	NT
Comparative Example 9		Gelled; unstable	NT
Comparative Example 10		gelled	NT
Comparative Example 11		Gelled; unstable	NT

NT = not tested

[0071]**Lithographic Example 1**

Lithographic evaluation of 4,4'-oxydiphthalic dianhydride (ODPA)/oxydianiline (ODA) polyamic acid in Deep UV bilayer process

5

A silicon wafer was cleaned by O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. This wafer was primed with external adhesion promoter *gamma*-aminopropyl triethoxy silane by dispensing 1-3 mL of 1%

(wt) solution of gamma-aminopropyl triethoxy silane in ethanol on the wafer and spin-drying the wafer at 4 000 rpm for 45 sec. The 4,4'-oxydiphthalic dianhydride (ODPA) / oxydianiline (ODA) polyamic acid prepared in Example 1 was spin coated on the primed silicon wafer. The coated wafer was baked at 120 °C for 3 minutes.

5 The thickness of the film of polyamic acid thus obtained was 7.7 μm. A 2 μm film of Deep UV photoresist GKR-4401 (commercially available from Arch Chemicals) was prepared by coating over the polyamic acid layer by spin coating and baking at 110 °C for 90 seconds. The coated silicon wafer was then exposed pattern-wise with a KrF excimer laser beam (248 nm) in a Canon FPA-3000 EX6 stepper through a

10 photo mask containing a line/space pattern using graduated exposures in different locations. The exposed film was baked for 90 seconds at 85 °C. Then, the wafer was developed in 0.262 N aqueous TMAH using puddle development (2 puddles, 50 seconds each). The remaining photoresist was removed using an atomized spray of photoresist stripper RER 600, which is commercially available from Arch Chemicals,

15 during a 30 second treatment while spinning at 2000 rpm. The patterned layer of polyamic acid was imidized under N₂ atmosphere at 350 °C for 1 hour. The resulting patterned polyimide film had 15-25 μm features well resolved.

[0072]**Lithographic Example 2**

20 **Lithographic evaluation of 4,4'-oxydiphthalic dianhydride (ODPA) / oxydianiline (ODA) polyamic acid along with adhesion promoter in Deep UV bilayer process**

1 part of N-phenyl-*gamma*-aminopropyltrimethoxysilane was dissolved in 3 parts of *gamma*-butyrolactone. This solution was added drop-wise to 208 parts of

25 4,4'-oxydiphthalic dianhydride (ODPA) / oxydianiline (ODA) polyamic acid solution of Example 1. The mixture was stirred for 24 hours and a clear solution was obtained. A silicon wafer was cleaned by O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. This solution was spin coated onto the cleaned silicon wafer. The coated wafer was baked at 120 °C for 3 minutes. The thickness

30 of the film of polyamic acid thus obtained was 7 - 8 μm. A 2 μm film of Deep UV

photoresist GKR-4401 (commercially available from Arch Chemicals) was prepared by coating over the polyamic acid layer by spin coating and baking at 110 °C for 90 seconds. The wafers were then exposed using a broadband mercury lamp light for 108.2 seconds (the lamp output was 1000 mJ/cm² @ 400nm during the exposure
5 time) with Karl Suss MA-56 broadband exposure tool. The exposed wafer was then baked at 110 °C for 60 seconds. Then, the pattern was developed in 0.262 N aqueous TMAH using puddle development (2 puddles, 50 seconds each). The remaining photoresist was removed using an atomized spray of photoresist stripper RER 600, which is commercially available from Arch Chemicals, during a 30 second
10 treatment while spinning at 2000 revolutions per minute. The wafer was then spun at 3 000 revolutions per minute until it was dried. The patterned layer of polyamic acid was imidized under N₂ atmosphere at 350 °C for 1 hour. The product was then placed in a pressure cooker pot and passed the tape peel test after 500 hours.

15 [0073]

Lithographic Example 3**Lithographic evaluation of 4,4'-oxydiphthalic dianhydride (ODPA)/oxydianiline (ODA) polyamic acid in Deep UV bilayer process without adhesion promoter**

A silicon wafer was cleaned by O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. 4,4'-oxydiphthalic dianhydride (ODPA) / oxydianiline (ODA) polyamic acid solution of Example 1 was spin coated onto above mentioned silicon wafer. The coated wafer was baked at 120 °C for 3 minutes. The thickness of the film of polyamic acid thus obtained was 7 - 8 μm. A 2
25 μm film of Deep UV photoresist GKR-4401 (commercially available from Arch Chemicals) was prepared by coating over the polyamic acid layer by spin coating and baking at 110 °C for 90 seconds. The wafers were then exposed using a broadband mercury lamp light for 108.2 seconds (the lamp output 1000 mJ/cm² @ 400nm during the exposure time) with Karl Suss MA-56 broadband exposure tool.
30 The exposed wafer was then baked at 110 °C for 60 seconds. Then, the wafer was

developed in 0.262 N aqueous TMAH using puddle development (2 puddles, 50 seconds each). The remaining photoresist was removed using an atomized spray of photoresist stripper RER 600, which is commercially available from Arch Chemicals, during a 30 second treatment while spinning at 2000 revolutions per minute. The wafer was then spun at 3000 revolutions per minute until it was dried. The patterned layer of polyamic acid was imidized under N₂ atmosphere at 350 °C for 1 hour. The product was then placed in a pressure cooker pot and failed the tape peel test in less than 100 hours.

10 [0074]

Lithographic Example 4**Lithographic evaluation of 4,4'-oxydiphthalic dianhydride (ODPA) / oxydianiline (ODA) polyamic acid with internal adhesion promoter in Deep UV bilayer process**

1 part of N-phenyl-*gamma*-aminopropyltrimethoxysilane was dissolved in 182 parts of 18.3 % (wt) 4,4'-oxydiphthalic dianhydride (ODPA) / oxydianiline (ODA) polyamic acid solution prepared as described in the Example 1. A silicon wafer was cleaned by O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. This solution was spin coated onto above mentioned silicon wafer. The coated wafer was baked at 120 °C for 3 minutes. The thickness of the film of polyamic acid thus obtained was 7.9 μm. A 2 μm film of Deep UV photoresist GKR-4401 (commercially available from Arch Chemicals) was prepared by coating over the polyamic acid layer by spin coating and baking at 110 °C for 90 seconds. The coated silicon wafer was then exposed pattern-wise with a KrF excimer laser beam (248 nm) in a Canon FPA-3000 EX6 stepper through a photo mask containing a line/space pattern using graduated exposures in different locations. The exposed wafer was then baked at 85 °C for 90 seconds. Then, the wafer was developed in 0.262 N aqueous TMAH using puddle development (2 puddles, 50 seconds each). The remaining photoresist was removed using an atomized spray of photoresist stripper RER 600, which is commercially available from Arch Chemicals, during a 30 second treatment while spinning at 2000 revolutions per minutes. The patterned

layer of polyamic acid was imidized under N₂ atmosphere at 350 °C for 1 hour. The resulting patterned polyimide film had 15-25 μm features well resolved.

[0075] Lithographic Example 5

5

Lithographic evaluation of 4,4'-oxydiphthalic dianhydride (ODPA) / 1,3-bis(4-aminophenoxy)benzene (TPE-R) polyamic acid in Deep UV bilayer process

A silicon wafer was cleaned by O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. This wafer was primed with external adhesion promoter *gamma*-aminopropyl triethoxy silane by dispensing 1-3 mL of 1% (wt) solution of *gamma*-aminopropyl triethoxy silane in ethanol on the wafer and spin-drying the wafer at 4000 revolutions per minutes for 45 sec. The 4,4'-oxydiphthalic dianhydride (ODPA) / 1,3-bis(4-aminophenoxy)benzene (TPE-R) polyamic acid prepared in Example 2 was spin coated on the primed silicon wafer. The coated wafer was baked at 130 °C for 3 minutes. The thickness of the film of polyamic acid thus obtained was 8.37 μm. A 2 μm film of Deep UV photoresist GKR-4401 (commercially available from Arch Chemicals) was prepared by coating over the polyamic acid layer by spin coating and baking at 120 °C for 90 seconds. The coated silicon wafer was then exposed pattern-wise with a KrF excimer laser beam (248 nm) in a Canon FPA-3000 EX6 stepper through a photo mask containing a line/space pattern using graduated exposures in different locations. The exposed film was baked for 90 seconds at 85 °C. Then, the wafer was developed in 0.262 N aqueous TMAH using puddle development for 60 sec. The remaining photoresist was removed using an atomized spray of photoresist stripper RER 600, which is commercially available from Arch Chemicals, during a 30 second treatment while spinning at 2000 revolutions per minutes. The patterned layer of polyamic acid was imidized under N₂ atmosphere at 350 °C for 1 hour. Examination under electron scanning microscope revealed a thick residue in the exposed areas.

30

[0076]

Comparative Lithographic Example 1**Lithographic evaluation of Bisphenol A dianhydride (BPADA)/oxydianiline (ODA) polyamic acid in Deep UV bilayer process**

5 A silicon wafer was cleaned by O₂ plasma in Mercator Life Systems apparatus (500 watts, 0.3-0.5 torr) for 10 min. This wafer was primed with external adhesion promoter gamma-aminopropyl triethoxy silane by dispensing 1-3 mL of 1% (wt) solution of gamma-aminopropyl triethoxy silane in ethanol on the wafer and spin-drying the wafer at 4000 rpm for 45 sec. The Bisphenol A dianhydride
10 (BPADA) / oxydianiline (ODA) polyamic acid solution obtained in Comparative Example 1 was spin coated on a silicon wafer. The coated wafer was baked at 120 °C for 3 minutes. The thickness of the film of polyamic acid thus obtained was 7.7 μm. A 2 μm film of Deep UV photoresist GKR-4401 (commercially available from Arch Chemicals) was formed on the top of the polyamic acid layer by spin coating
15 and baking at 110 °C for 90 seconds. The coated silicon wafer was then exposed pattern-wise with a KrF excimer laser beam (248 nm) in a Canon FPA-3000 EX6 stepper through a photo mask containing a line/space pattern using graduated exposures in different locations. The exposed film was baked for 90 seconds at 85 °C. Then, the wafer was developed in 0.262 N aqueous TMAH using puddle
20 development (2 puddles, 50 seconds each). The remaining photoresist was removed using an atomized spray of photoresist stripper RER 600, which is commercially available from Arch Chemicals, during a 30 second treatment while spinning at 2000 rpm. It was found that the polyamic acid of Comparative Example 1 is not soluble in 0.262 N aqueous TMAH developer and no pattern was formed on
25 the bottom layer.

[0077]

Lithographic Example 6

Lithographic evaluation of 4,4'-oxydiphthalic anhydride (ODPA)/ 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)/ oxydianiline (ODA) polyamic acid in Deep UV bilayer process

1 part of vinyl triethoxysilane was dissolved in 3 parts of gamma-butyrolactone. This solution was added drop-wise to 208 parts of the ODPA / DAPI / ODA polyamic acid prepared in Example 3. The mixture was stirred for 24 hours and a clear solution was obtained.

[0078] The solution containing the ODPA / DAPI / ODA polyamic acid prepared above was spin coated on a silicon wafer. The coated wafer was baked at 130 °C for 3 minutes. An approximately 2 μm thick film of Deep UV photoresist GKR-4401 (commercially available from Arch Chemicals) was prepared by coating over the polyamic acid layer by spin coating at 2500 rpm for 30 seconds and baking at 110 °C for 90 seconds. Coating defects interfered with obtaining exact film thickness measurements. The coated silicon wafer was then exposed pattern-wise with a KrF excimer laser beam (248 nm) in a Canon FPA-3000 EX6 stepper through a photo mask containing a line/space pattern to an exposure dose of 95 mJ/cm² and baked for 90 seconds at 85 °C. Then, the pattern was developed in 0.262 N aqueous TMAH using puddle development for 60 sec. The remaining photoresist was removed using an atomized spray of photoresist stripper RER 600, which is commercially available from Arch Chemicals, during a 60 second treatment while spinning at 2000 revolutions per minutes. The patterned layer of polyamic acid was imidized under N₂ atmosphere at 350 °C for 1 hour. The resulting patterned polyimide film had 50 μm features well resolved.

[0079]

Lithographic Example 7

Lithographic evaluation of oxydiphthalic anhydride (ODPA) / 4,3'-oxydianiline polyamic acid in Deep UV bilayer process

1 part of *gamma*-glycidoxypyrroltrimethoxysilane was dissolved in 3 parts of
5 gamma-butyrolactone. This solution was added drop-wise to 208 parts of the oxydiphthalic anhydride (ODPA) / 4,3'-oxydianiline polyamic acid prepared in Example 4. The mixture was stirred for 24 hours and a clear solution was obtained.

[0080] The solution containing the oxydiphthalic dianhydride (ODPA) / 4,3'-
10 oxydianiline polyamic acid prepared above was spin coated on a silicon wafer. The coated wafer was baked at 130 °C for 3 minutes. The thickness of the film of polyamic acid thus obtained was about 12.1 μm. An approximately 2 μm thick film of Deep UV photoresist GKR-4401 (commercially available from Arch Chemicals) was prepared by coating over the polyamic acid layer by spin coating at 2500 rpm
15 for 30 sec and baking at 110 °C for 90 seconds. The coated silicon wafer was then exposed pattern-wise with a KrF excimer laser beam (248 nm) in a Canon FPA-3000 EX6 stepper through a photo mask containing a line/space pattern to a dose of 95 mJ/cm² and baked for 90 seconds at 85 °C. Then, the pattern was developed in 0.262 N aqueous TMAH using puddle development for 60 seconds. The
20 development process was repeated 4 times. The remaining photoresist was removed using an atomized spray of photoresist stripper RER 600, which is commercially available from Arch Chemicals, during a 60 second treatment while spinning at 2000 revolutions per minutes. The patterned layer of polyamic acid was imidized under N₂ atmosphere at 350 °C for 1 hour. The resulting patterned
25 polyimide film had 50 μm features well resolved.

[0081] While the invention has been described herein with reference to the specific embodiments thereof, it will be appreciated that changes, modification and
30 variations can be made without departing from the spirit and scope of the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes,

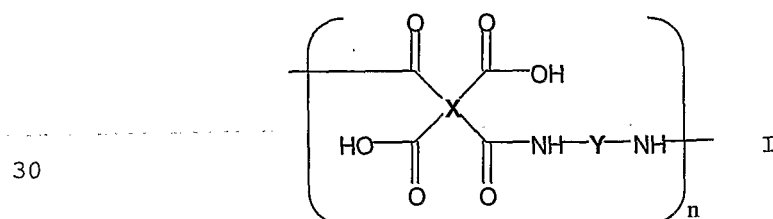
modification and variations that fall with the spirit and scope of the appended claims.

We claim:

1. A process for producing a heat resistant relief structure on a substrate, the process comprising the steps of:

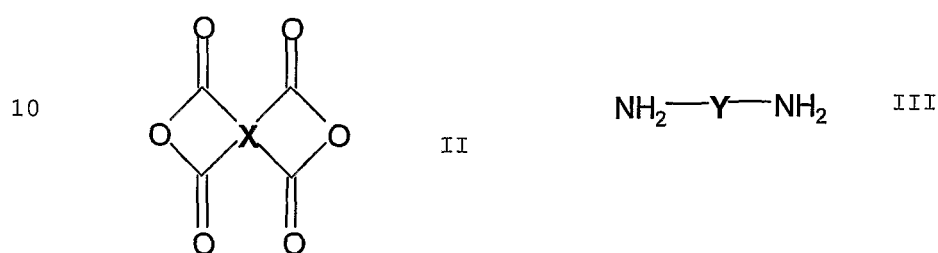
5 (a) providing a substrate;
 (b) in a first coating step, coating the substrate with a composition comprising a polyamic acid and *gamma*-butyrolactone to form a layer of polyamic acid having a thickness of at least about 0.5 μm ;
 (c) baking the layer of polyamic acid at a temperature or temperatures
 10 below 140 °C;
 (d) in a second coating step, coating a layer of a photoresist over the layer of polyamic acid to form a bilayer coating;
 (e) exposing the bilayer coating to radiation < 250 nm
 (f) developing the bilayer coating with one or more aqueous tetramethyl
 15 ammonium hydroxide developers;
 (g) removing the remaining photoresist layer; and
 (h) curing the polyamic acid layer at a temperature at least about 200°C to produce a polyimide structure
 wherein the polyamic acid is soluble in aqueous tetramethyl
 20 ammonium hydroxide and insoluble in a solvent used with the photoresist.

2. A process according to claim 1 wherein the polyamic acid is selected from
 25 the group consisting of polyamic acids of the Formula I



where n is an integer ranging from about 25 to about 175 wherein X and Y are independently selected from aromatic and aliphatic moieties which may contain heteroatoms.

3. A process according to claim 2 wherein the polyamic acid of Formula I is one prepared by reacting at least one dianhydride monomer of Formula II with at least one diamine monomer of Formula III



15 and wherein the dianhydride monomer is selected from the group consisting of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride, 3,3',4,4'-diphenylsulfidetetracarboxylic acid dianhydride, 3,3',4,4'-diphenylsulfonetetracarboxylic acid dianhydride, 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride, 3,3',4,4'-diphenylmethanetetracarboxylic acid dianhydride, 2,2',3,3' -diphenylmethanetetracarboxylic acid dianhydride, 2,3,3',4'-biphenyltetracarboxylic acid dianhydride, 2,3,3',4'-benzophenonetetracarboxylic acid dianhydride, 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride, 2,3,6,7-naphthalenetetracarboxylic acid dianhydride, 1,4,5,7-naphthalenetetracarboxylic acid dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 1,3-diphenylhexafluoropropane-3,3,4,4-tetracarboxylic acid dianhydride, 1,4,5,6-naphthalenetetracarboxylic dianhydride, 2,2',3,3'-diphenyltetracarboxylic acid dianhydride, 3,4,9,10-perylenetetracarboxylic acid dianhydride, 1,2,4,5 naphthalenetetracarboxylic acid dianhydride,

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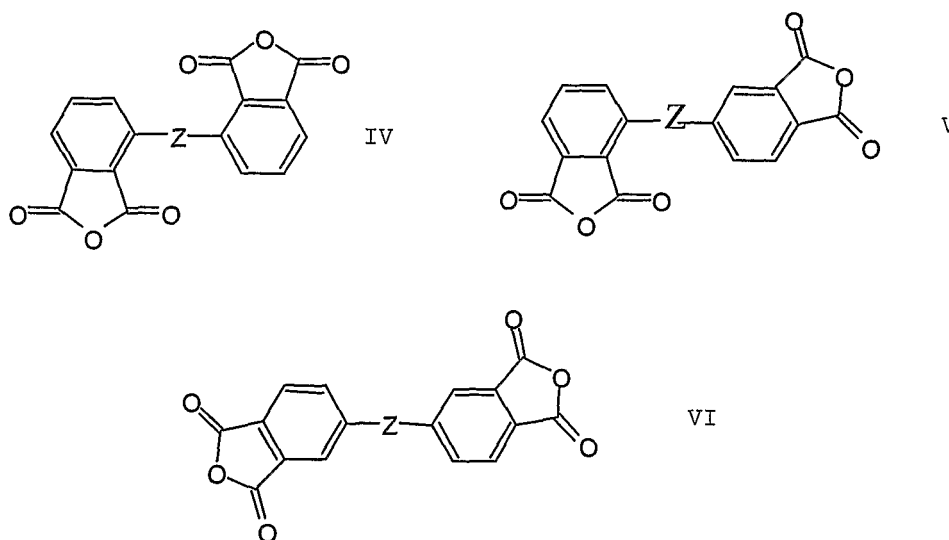
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1,4,5,8-naphthalenetetracarboxylic acid dianhydride, 1,8,9,10-phenanthrenetetracarboxylic acid dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, 1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride, 1,2,3,4-benzenetetracarboxylic acid dianhydride and 1,2,4,5-benzenetetracarboxylic acid dianhydride, and the diamine monomer is selected from the group consisting of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane, *m*-phenylenediamine, *p*-phenylenediamine, 2,2'-bis(trifluoromethyl)-4,4'-diamino-1,1'-biphenyl, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 2,4-tolylenediamine, 3,3'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ketone, 3,3'-diaminodiphenyl ketone, 3,4'-diaminodiphenyl ketone, 1,3-bis (4-aminophenoxy) benzene, 1,3-bis(3-amino-phenoxy) benzene, 1,4-bis (γ -aminopropyl)tetramethyldisiloxane, 2,3,5,6-tetramethyl-*p*-phenylenediamine, *m*-xylylenediamine, *p*-xylylenediamine, methylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, 2,5-dimethylhexamethylenediamine, 3-methoxyhexamethylenediamine, heptamethylenediamine, 2,5-dimethylheptamethylenediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, octamethylenediamine, nonamethylenediamine, 2,5-dimethylnonamethylenediamine, decamethylenediamine, ethylenediamine, propylenediamine, 2,2-dimethylpropylenediamine, 1,10-diamino-1,10-dimethyldecane, 2,11-diaminododecane, 1,12-diaminooctadecane, 2,17-diaminoeicosane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, bis(4-aminocyclohexyl)methane, bis(3-aminonorbornyl)methane, 3,3'-diaminodiphenylethane, 4,4'-diaminodiphenylethane, and 4,4'-diaminodiphenyl sulfide, 2,6-diaminopyridine, 2,5-diaminopyridine, 2,6-diamino-4-trifluoromethylpyridine, 2,5-diamino-1,3,4-oxadiazole, 1,4-

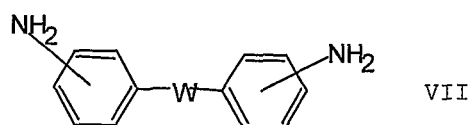
diaminocyclohexane, piperazine, 4,4'-methylenedianiline, 4,4'-methylene-bis(o-chloroaniline), 4,4'-methylene-bis(3-methylaniline), 4,4'-methylene-bis(2-ethylaniline), 4,4'-methylene-bis(2-methoxyaniline), 4,4'-oxy-dianiline, 4,4'-oxy-bis-(2-methoxyaniline), 4,4'-oxy-bis-(2-chloroaniline), 4,4'-thio-dianiline, 4,4'-thio-bis-(2-methylaniline), 4,4'-thio-bis-(2-methoxyaniline), 4,4'-thio-bis-(2-chloroaniline), 3,3'-sulfonyl-dianiline, and 3,3'-sulfonyl-dianiline.

4. A process according to claim 3 wherein the dianhydride monomer is selected from the group consisting of a compound selected from the group consisting of compounds described by the structures IV to VI:



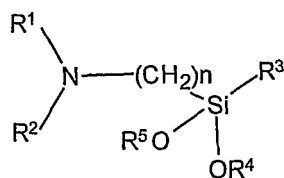
where Z= is selected from the group consisting of -O-, -S-, -C(CF₃)₂-, -CH₂-, -SO₂-, -NHCO- or -Si(R')₂- where R' is a linear, branched or cyclic alkyl group containing from 1 to 8 carbon atoms.

5. A process according to claim 4 wherein the diamine monomer is at least one compound having the structure VII

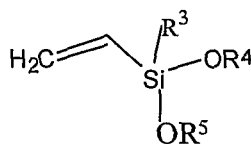


where W= is selected from the group consisting of -O-, -S-, -C(CF₃)₂-, -CH₂-, -SO₂-, -NHCO- and -Si(R')₂- where R' is a linear branched or cyclic alkyl group containing from 1 to 8 carbon atoms.

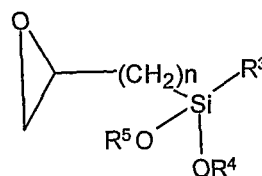
- 6, A process according to claim 5 wherein Z is -O- and W is -O-.
7. A process according to claim 3 wherein the polyamic acid is a polyamic acid selected from the group consisting of those from a polyamic acid from 4,4'-diaminodiphenyl ether and 3,3',4,4'- diphenyloxidetetra carboxylic acid dianhydride, a polyamic acid polymer from 4,4'-diaminodiphenyl ether and a mixture of 95-85% of 3,3',4,4'- diphenyloxidetetra carboxylic acid dianhydride and 5-15% of another dianhydride of Formula II.
8. A process according to claim 1 wherein the polyamic acid containing composition also contains an adhesion promoter.
9. A process according to claim 8 wherein the adhesion promoter is selected from the group consisting of compounds of Formulae VIII to XIII



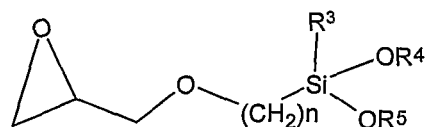
VIII



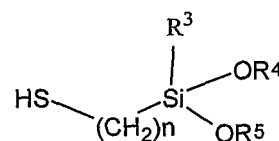
IX



X

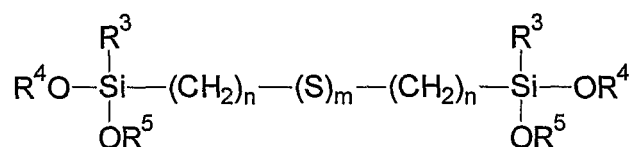


XI



XII

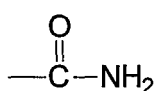
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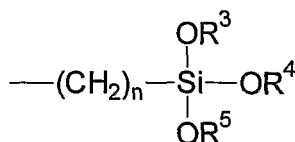
XIII

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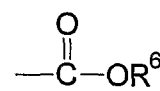
wherein R^1 is selected from the group consisting of H, $C_1 - C_{10}$ linear, cyclic or branched alkyl, phenyl, halophenyl and alkyl substituted phenyl, R^2 is selected from the group consisting of $C_1 - C_{10}$ linear, cyclic or branched alkyl, phenyl, halophenyl and alkyl substituted phenyl or one of the following moieties XIV or XV or XVI



XIV



XV



XVI

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where R^3 is selected from the group consisting of a $C_1 - C_4$ linear or branched alkyl and $C_1 - C_4$ linear or branched alkoxy group; R^4 , R^5 and R^6 are independently a $C_1 - C_4$ linear or branched alkyl group, m is an integer from 1 to about 4, and n is an integer from 1 to about 5.

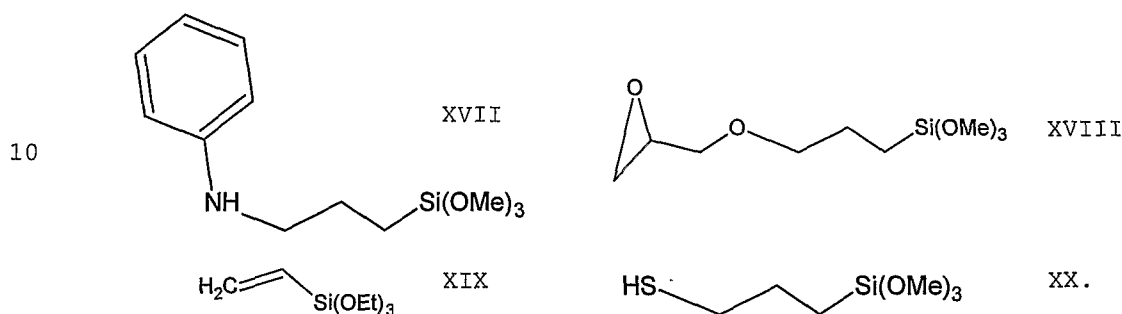
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10. A process according to claim 9 wherein the adhesion promoter is one selected from those of the Formulae VIII, IX, XI and XII.

11. A process according to claim 9 wherein the adhesion promoter is one of

Formula VIII wherein R^1 and R^2 are both independently C_1 – C_{10} linear, cyclic or branched alkyl or one of R^1 and R^2 is phenyl.

12. A process according to claim 9 wherein the adhesion promoter is selected from the group consisting of those of Formulae XVII, XVIII, XIX and XX



13. A process according to claim 8 wherein the adhesion promoter comprises from about 0.05% to about 1.5% by weight of the composition.
14. A process according to claim 8 wherein the polyamic acid is a polyamic acid selected from the group consisting of those from a polyamic acid from 4,4'-diaminodiphenyl ether and 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride, a polyamic acid polymer from 4,4'-diaminodiphenyl ether and a mixture of 95-85% of 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride and 5-15% of another dianhydride of Formula II.
15. A heat resistant relief structure on a substrate produced by the process of claim 1.