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(54) **PHOTOSENSITIVE POLYIMIDE COMPOSITIONS**

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(57) **ABSTRACT**

A photosensitive resin composition comprising a pre-imidized aromatic polyimide, which when coated on a silicon wafer, has a light transmittance at a wavelength of 365 nm of at least 1% and imparts low residual stress after cure. The composition can be patterned through I-line exposure followed by development with organic or alkaline solutions, and can be cured at relatively mild temperature to yield low-stress polyimide patterns. Electronic components having the polyimide patterns have high reliability.

PHOTOSENSITIVE POLYIMIDE COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application in a continuation-in-part of U.S. application Ser. No. 11/248,803 filed Oct. 12, 2005, the entire contents of which is incorporated herein by reference thereto for all permissible purposes.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a photosensitive polyimide resin composition, to a method of using the composition for patterning, and to electronic components made using the photosensitive resin composition.

[0004] 2. Description of Related Art

[0005] In the semiconductor industry, organic substances with good heat resistance such as polyimide resins and the like have been used as interlayer insulating materials, because of their good characteristics, in place of conventional inorganic materials. Circuit patterning of semiconductor integrated circuits and printed circuits with polyimides requires many complicated steps of, for example, forming a resist film on the surface of a substrate, removing the unnecessary part of the film through selective exposure and etching at predetermined sites, and rinsing the polyimide surface of the thus-processed substrate. It is therefore desired to develop heat-resistant polyimide-based photosensitive materials for use as photoresists that can be directly used as insulating layers after having been patterned through exposure and development.

[0006] Heat-resistant photosensitive materials have been proposed. Above all, photosensitive heterocyclic polymers such as aromatic polyimides are specifically noted, because their heat resistance is good and impurities (e.g., water, solvents, photosensitive groups of the polymer, photoinitiators, sensitizers, etc.) can be removed if desired.

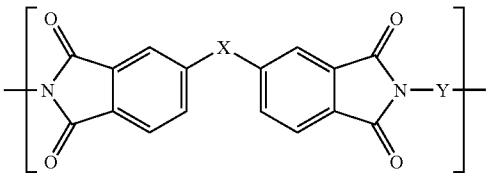
[0007] Photolithographic methods to for patterned polyimide structures are known as in U.S. Pat. No. 6,329,110. This method requires a cure step to imidize the polyimide precursor pattern.

[0008] Polyimides containing photocrosslinkable groups pendant to the polymer chain are known as in U.S. Pat. No. 6,342,333. This method also requires a cure step to imidize the polyimide precursor pattern.

[0009] An undesirable consequence of processing polyimide and polybenzoxazole intermediates is that high cure temperatures must be employed to fully cyclodehydrate the intermediates. Generally, there is no known process whereby polyimide resins could be used in traditional spin-coating and photo-development. It is more desirable to use a photodefinable recipe that does not require high cure temperatures. In this regard, a polyimide that is soluble in the fully imidized form is desired. In this case a temperature necessary to evaporate the spin coating solvent is all that is necessary to form a polyimide coating.

SUMMARY OF THE INVENTION

[0010] A composition comprising a polyimide component represented by a polyimide having a repeat unit represented the formula



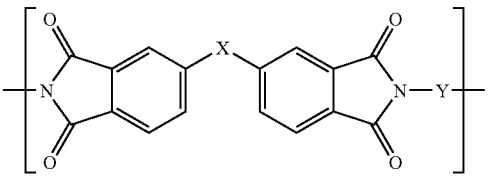
[0011] wherein X can be equal to SO_2 or $C(CF_3)_2$, $C(CF_3)$phenyl, $C(CF_3)CF_2CF_3$, or $C(CF_2CF_3)$phenyl, and combinations thereof, and

[0012] wherein Y is derived from a hydroxyl- or carboxyl-containing diamine, for example a diamine selected from the group consisting of, 2,2'-bis(3-amino-4-hydroxyphenyl-)hexafluoropropane (6F-AP), 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), 2,4-diaminophenol, 2,3-diaminophenol, 3,3'-diamino-4,4'-dihydroxy-biphenyl and 2,2'-bis(3-amino-3-hydroxyphenyl)hexafluoropropane, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, methylene-bis-anthranilic acid and mixtures thereof wherein a percentage of the total hydroxyl or carboxyl groups of the diamine component from between and including any two of the following numbers, 0, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 98 and 100 mole percent have been derivatized to contain an ethylenically unsaturated moiety capable of crosslinking is useful in photolithographic processes to produce electronic devices, and/or wherein at least a portion of the hydroxyl or carboxyl groups of the diamine component have been derivatized to contain an o-quinonediazidosulfonyl moiety.

[0013] The invention includes in one embodiment solvent-soluble polyimide resins including polyimide resins formed from materials known in the art except that the diamine component is selected to provide at least one hydroxyl moiety, for example between 1 and 6 hydroxyl moieties, typically 1, 2, 3, or 4 hydroxyl moieties, which are optionally further derivatized with an acrylate moiety, for example by reacting with acroyl chloride. In the above-description, a carboxylate moiety provides a hydroxyl moiety. The invention includes in another embodiment solvent-soluble polyimide resins including polyimide resins formed from materials known in the art except that a sufficient amount of the diamine component is selected to provide a sufficient number of hydroxyl moieties so that the polyimide material can be solubilized in solvent. Such solubilized polyimide materials can be used in spin-coating substrates in for exaple photolithographic steps to form an integrated circuit substrate.

DETAILED DESCRIPTION

[0014] Generally, the polyimide component of the present invention can be represented by the general formula:



where X can be equal to SO_2 or $C(CF_3)_2$, $C(CF_3)$phenyl, $C(CF_3)CF_2CF_3$, $C(CF_2CF_3)$phenyl (and combinations thereof); and where Y is derived from a diamine component. In one embodiment, the X component can be any X component known in the art. The Y component is a diamine, and the Y component diamines can include any diamine components known in the art, can include both diamine components which do not provide hydroxyl moieties as well as diamine components which do provide hydroxyl moieties, so long as there are a sufficient number of Y components providing hydroxyl moieties so that the. More advantageously, the hydroxyl moieties are able to be derivatized with for example acrylate moieties.

[0015] In a first embodiment Y is derived from a diamine component comprising a hydroxyl- or carboxyl-containing diamine selected from the group consisting of, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-AP), 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), 2,4-diaminophenol, 2,3-diaminophenol, 3,3'-diamino-4,4'-dihydroxy-biphenyl and 2,2'-bis(3-amino-3-hydroxyphenyl)hexafluoropropane, methylene-bis-anthranilic acid and mixtures thereof. The Y component may also be for example 2,2'-bis(3-amino-4-hydroxyphenyl-)hexafluoropropane, alone or in combination with any of the above.

[0016] A preferred Y component has the amines and at least one hydroxyl moiety attached to a benzene ring. In one embodiment, the hydroxyl groups are attached to benzene rings, thereby (if there is one hydroxyl moiety per ring) forming phenol moieties. An example having one hydroxy moiety is 2,4-diaminophenol. More than one phenol ring can be used, as in for example 3,3'-dihydroxy-4,4'-diaminobiphenyl. We believe that, in one embodiment, more than one hydroxyl moiety can be attached to a benzene ring, for example when the Y component is 3',5-diaminobiphenyl-3, 4,4'-triol or 4,6-diaminobenzene-1,3-diol. Other useful components will be known to one of skill in the art having the benefit of this disclosure. One of skill in the art having the benefit of this disclosure would know that the Y component can be derived from any of the above compounds. One of skill in the art having the benefit of this disclosure would know that the Y component can be derived from mixtures of compounds, though generally only one Y component is incorporated into the polyimide material between any to X components.

[0017] In a second embodiment two or more diamine components are used wherein a first Y is derived from a hydroxyl- or carboxyl-containing diamine component of a diamine, for example selected from the group consisting of, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-AP), 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), 2,4-diaminophenol, 2,3-diaminophenol, 3,3'-diamino-4,4'-dihydroxy-biphenyl and 2,2'-bis(3-amino-3-hydroxyphenyl-)hexafluoropropane, methylene-bis-anthranilic acid and mixtures thereof, and a second Y can be a known Y component which may not contribute a hydroxide moiety, e.g., 3,4'-diaminodiphenyl ether (3,4'-ODA), 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl (TFMB), 3,3',5,5'-tetramethylbenzidine, 2,3,5,6-tetramethyl-1,4-phenylenediamine, 3,3'-diaminodiphenyl sulfone, 3,3'dimethylbenzidine, 3,3'-bis(trifluoromethyl)benzidine, 2,2'-bis-(p-aminophenyl-)hexafluoropropane, bis(trifluoromethoxy)benzidine (TFMOB), 2,2'-bis(pentafluoroethoxy)benzidine (TFEOB), 2,2'-trifluoromethyl-4,4'-oxydianiline (OBABTF), 2-phenyl-2-trifluoromethyl-bis(p-aminophenyl)methane, 2-phenyl-2-trifluoromethyl-bis(m-aminophenyl)methane, 2,2'-bis(2-heptafluoroisopropoxy-tetrafluoroethoxy)benzidine (DFPOB), 2,2-bis(m-aminophenyl)hexafluoropropane (6-FmDA), 2,2-bis(3-amino-4-methylphenyl)hexafluoropropane, 3,6-bis(trifluoromethyl)-1,4-diaminobenzene (2TFMPDA), 1-(3,5-diaminophenyl)-2,2-bis(trifluoromethyl)-3,3,4,4,5,5,5-heptafluoropentane, 3,5-diaminobenzotrifluoride (3,5-DABTF), 3,5-diamino-5-(pentafluoroethyl-)benzene, 3,5-diamino-5-(heptafluoropropyl)benzene, 2,2'-dimethylbenzidine (DMBZ), 2,2',6,6'-tetramethylbenzidine (TMBZ), 3,6-diamino-9,9-bis(trifluoromethyl)xanthene (6FCDAM), 3,6-diamino-9-trifluoromethyl-9-phenylxanthene (3FCDAM), 3,6-diamino-9,9-diphenyl xanthene. The various diamines can be used alone or in combination with one another, but at least some of the diamines must contain an hydroxyl moiety, for example one or two hydroxyl moieties, and advantageously the amount of diamines that contain an hydroxyl moiety that are incorporated into a polyimide are sufficient so that the polyimide can be solubilized to an extent sufficient for forming a layer by for example spin coating the substrate with the solubilized polyimide. In such a case, after the solvents have been removed, a polyimide film can be formed, without having to undergo a high temperature conversion.

[0018] In this second embodiment the first Y which is derived from a hydroxyl- or carboxyl-containing diamine component comprises from between and including any two of the numbers 0.001, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 98 and 100 mole percent of the total diamine component and the second Y comprises from 100, 98, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 2, and 0.001 mole percent. It can be readily determined by one of ordinary skill in the art having benefit of this disclosure without undue experimentation how much of the various Y components must contain at least one hydroxyl moiety to provide the required solubility. Generally speaking regarding this second embodiment the present inventors found that if less than about 2 mole percent (of the total diamine component) comprises hydroxyl- or carboxyl-containing diamines which are derivatized as described herein, the functionalized polyimide that is formed may not sufficiently photoactive on its own and may require the presence of a photo initiator. In addition, if more than about 75 mole percent of the diamine component is a phenolic containing diamine which is not derivatized, the polyimide may be highly susceptible to unwanted water absorption. However, if the hydroxyl- or

carboxyl-containing diamines are derivatized as described herein then there is no upper limit to the mole percent of that diamine.

Preparation of the Polyimide

[0019] The polyimides of the invention are prepared by reacting a suitable dianhydride (or mixture of suitable dianhydrides, or the corresponding diacid-diester, diacid halide ester, or tetracarboxylic acid thereof) with one or more selected diamines. The mole ratio of dianhydride component to diamine component is preferably from between 0.9 to 1.1. Preferably, a slight molar excess of dianhydrides can be used at mole ratio of about 1.01 to 1.02. End capping agents, such as phthalic anhydride, can be added to control chain length of the polyimide.

[0020] Some dianhydrides found to be useful in the practice of the present invention, i.e., to prepare the polyimide component, can be 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA), 2,2-bis(3,4-dicarboxyphenyl)1,1,1,3,3,3-hexafluoropropane dianhydride (6-FDA), 1-phenyl-1,1-bis(3,4-dicarboxyphenyl)-2,2,2-trifluoroethane dianhydride, 1,1,1,3,3,4,4,4-octylfluoro-2,2-bis(3,4-dicarboxyphenyl)butane dianhydride, 1-phenyl-2,2,3,3,3-pentafluoro-1,1-bis(3,4-dicarboxylphenyl)propane dianhydride, 4,4'-oxydiphthalic anhydride (ODPA), 2,2'-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2'-bis(3,4-dicarboxyphenyl)-2-phenylethane dianhydride, 2,3,6,7-tetracarboxy-9-trifluoromethyl-9-phenylxanthene dianhydride (3FCDA), 2,3,6,7-tetracarboxy-9,9-bis(trifluoromethyl)xanthene dianhydride (6FCDA), 2,3,6,7-tetracarboxy-9-methyl-9-trifluoromethylxanthene dianhydride (MTXDA), 2,3,6,7-tetracarboxy-9-phenyl-9-methylxanthene dianhydride (MPXDA), 2,3,6,7-tetracarboxy-9,9-dimethylxanthene dianhydride (NMXDA) and combinations thereof. These dianhydrides can be used alone or in combination with one another.

Solvents

[0021] In the practice of the present invention an organic solvent is selected that can easily dissolve the polyimide component and which can be evaporated off (later in processing) at a relatively low operating temperature. The polyimide component can typically be in the 'polyimide state' (i.e., as opposed to the polymer being in the polyamic acid, or other polyimide precursor state). As such, a lower processing temperature can be achieved (in order to dry the composition of solvent) provided that certain solvents disclosed herein are chosen to allow the polyimide of the present invention to possess sufficient solubility and resistance to moisture sorption, particularly during a screen-printing process.

[0022] Solvents known to be useful in accordance with the practice of the present invention include organic liquids having both (i.) a Hanson polar solubility parameter between and including any two of the following numbers 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9 and 3.0, and (ii) a normal boiling point ranging from between and including any two of the following numbers 210, 220, 230, 240, 250 and 260° C. In one embodiment of the present invention, a useful solvent is selected from one or more dibasic acid ester solvents including, but not limited to, DuPont DBE® solvents including dimethyl succinate, dimethyl glutarate and dimethyl adipate. Other useful solvents include propyleneglycol diacetate (PGDA), Dowanol® PPh, butyl carbitol acetate, carbitol acetate and mixtures of these. Cosolvents may be added provided that the composition is still soluble, performance in film-casting or screen-printing is not adversely affected, and lifetime storage is also not adversely affected.

[0023] Other solvents useful in the compositions and methods of the invention include those solvents known to be useful in spin-casting operations in lithography, including but not limited to aprotic polar solvents, including, for example, N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, hexamethylphosphoramide, tetramethylene sulfone, .gamma.-butyrolactone, methyl ethyl ketone etc. The solvent may also be cyclohexanone, cyclopentanone, or the like. One or more of these solvents may be used either singly or in combination.

[0024] Another advantage to using the solvents disclosed in the present invention is that in certain embodiments, very little, if any, precipitation of the polyimide is observed when handling a photosensitive composition. Also, the use of a polyamic acid solution may be avoided. Instead of using a polyamic acid, which can be thermally imidized to the polyimide later during processing, an already formed polyimide is used. This allows for lower curing temperatures to be used, temperatures not necessary to convert, to near completion, a polyamic acid to a polyimide. In short, the resulting solutions can be directly incorporated into a liquid or paste composition for coating, casting and screen-printing applications without having to cure the polyimide.

[0025] Polyimides in general are insoluble. The few polyimides that are soluble are only soluble in select polar organic solvents. But, many polar organic solvents act like a sponge and absorb water from the ambient environment. Often, the relative humidity of an atmosphere is sufficiently high enough that water absorption into the composition is significant. The water in the composition and in the polyimide solutions can cause the polyimide to precipitate, which essentially renders the composition unusable for most purposes. The composition must be discarded, and the wafer may be damaged in attempts to remove intractable coating.

Imidization

[0026] The polyimides of the present invention can be made by thermal and chemical imidization using a different solvent as otherwise described herein. The polyimide component can be removed from the solvent by precipitation in a non-solvent such as methanol, then re-dissolved in a solvent disclosed earlier herein. Using a thermal method, the dianhydride can be added to a solution of the diamine in any of the following polar solvents, m-cresol, 2-pyrrolidone, N-methylpyrrolidone (NMP), N-ethylpyrrolidone, N-vinylpyrrolidone), N,N'-dimethyl-N,N'-propylene urea (DMPU), cyclohexylpyrrolidone (CHP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and γ-butyrolactone (BLO). The reaction temperature for preparation of the polyamic acid or polyamic acid ester is typically between 25° C. and 40° C. Alternatively, the dianhydrides were dissolved in one of these solvents, and the diamines were added to the dianhydride solution.

[0027] After the polyamic acid (or polyamic acid ester) is produced, the temperature of the reaction solution is then

raised considerably to complete the dehydration ring closure. The temperatures used to complete the ring closure are typically from 150° C. to 200° C. A high temperature is used is to assure converting the polyamic acid into a polyimide. Optionally, a co-solvent can be used help remove the water produced during imidization (e.g., toluene, xylene and other aromatic hydrocarbons).

[0028] The chemical method includes the use of a chemical imidizing agent, which is used to catalyze the dehydration, or ring closing. Chemical imidization agents such as acetic anhydride and β-picoline can be used. The reaction solvent is not particularly limited so long as it is capable of dissolving the polyamic acid and polyimide. The resulting polyimide is then precipitated. This can be performed by adding the polyimide to a non-solvent. These non-solvents can be methanol, ethanol, or water. The solid is washed several times with the non-solvent, and the precipitate is oven dried.

Transmittance

[0029] The aromatic polyimide for use in the invention is preferably one in which the light transmission at a wavelength of 365 nm through a film made from the precursor and having a thickness of 10 μm is at least 1%, more preferably at least 5%, even more preferably at least 10%. If the light transmittance is smaller than 1%, photosensitive resin compositions capable of being patterned into high-resolution patterns having a good profile are difficult to obtain. Especially preferably, the light transmittance falls between 10% and 80%. The polyimide film can be formed by applying a solution of the polyimide in a solvent onto a substrate followed by drying. The light transmittance at a wavelength of 365 nm through the polyimide film can be measured with a spectrophotometer.

Residual Stress

[0030] Also preferably, the aromatic polyimide of the invention forms a polyimide film and when deposited on a silicon wafer, has a residual stress of no more than 25 MPa. If the residual stress is larger than 25 MPa, the polyimide films formed are defective in that, when they are formed on silicon wafers or when they are used in silicon chips, the silicon wafers warp and the residual stress inside the silicon chips is large. More preferably, the residual stress according to the present invention falls between 0 and 20 MPa. The residual stress of the polyimide film is measured at room temperature (25° C.), for example, with a thin film stress meter.

Derivatization

[0031] Polyimides of the present invention can be made to be photocrosslinkable by copolymerizing one or more aromatic diamines containing one or more phenolic hydrogens. Some of the preferred examples include aromatic diamines such as 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), and 2,2'-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (6F-AP). It is also possible to produce polyimides that contain latent carboxylic acid groups by copolymerizing diamines such as methylene-bis-anthranilic acid. After cyclodehydration of the poly(amic acid), preferably by the thermal or chemical conversion methods described above, the resulting polyimide contains residual phenolic groups and/or carboxyl acid groups, the concentration of which is defined by the amount of phenolic-containing diamine or carboxyl-containing diamine respectively used during the synthetic process. Methylene-bis-anthranilic acid is more amenable to preparing an aqueous developable photosensitive polyimide, although hydrophilic carboxylic acid functionality will remain present in the cured composition.

[0032] In one embodiment of the invention the latent phenolic functionality can be derivatized with one or more compounds containing unsaturated moieties, acryloyl chloride or methacryloyl chloride for example, which can react with the phenolic group to generate an ester linkage, thereby covalently bonding the unsaturated group to the polyimide backbone. Alternatively the latent phenolic functionality can be esterified by transesterification with one or more compounds containing unsaturated moieties, methyl methacrylate or methyl acrylate for example. Any unsaturated moiety containing an ethylenically unsaturated carbon-carbon bond is suitable for use in the compounds of the invention. This resulting polymer can then be formulated with a suitable photopackage that, when exposed to g-line or I-line radiation, will generate free radicals capable of reacting the unsaturated group to generate crosslinks between polyimide chains, thus forming an insoluble network. Typical of negative-acting systems, the irradiated areas are rendered insoluble to organic developers commonly used in the industry.

[0033] Alternatively, the phenolic or carboxylic acid containing diamine can be derivatized so the crosslinking functionality is incorporated prior to the polymerization reaction which forms the poly(amic acid) and resulting polyimide. In another embodiment, the unsaturation is incorporated by chemically imidizing the phenolic-containing poly(amic acid) with methacrylic anhydride as the dehydrating agent, since is has been shown that the phenolic functionality is predominately methacrylated when chemically converted with acetic anhydride. Or, the acetylated phenolic groups resulting from chemical conversion can be trans-esterified with acrylic or methacrylic acid, or another carboxylic acid containing the desired alkyl chain length, ether linkage, glycol linkage, or other structural and functional molecular designs desired to introduce unsaturation into the polyimide backbone.

[0034] In some embodiments a portion of the hydroxyl or carboxyl groups are functionalized, such as for example a percentage from between and including any two of the following numbers 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 95, and 98.

End Cap Derivatization

[0035] In addition to pendant unsaturated functionality afforded by the above description, it is also possible to incorporate unsaturated functionality by reacting the amine terminated polyimide chain, for example, with acryloyl chloride, methacryloyl chloride or other derivatizing agents that are reactive with the terminal nitrogen, and which contain an ethylenically unsaturated carbon-carbon bond. This method is more useful if the polyimide is of lower molecular weight, thus allowing for higher concentrations of chain ends and ultimately higher concentrations of photoactive chain terminations. However, it is not desirable to lower the polyimide molecular weight to the point of sacrificing substantially the mechanical properties of the final product.

[0036] In some embodiments a portion of the end caps are functionalized, such as for example a percentage from

between and including any two of the following numbers 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 95, and 98.

Optional Additional Components

[0037] Although the polyimides prepared by the above methods are inherently photosensitive, additional photosensitive compounds can optionally be added to the formulation. In fact it is possible to use a non-photosensitive polyimide in combination with the formulations below to generate a photosensitive compositions. In many embodiments of the present invention, the compositions further comprise additional components. These components can be catalysts, adhesion promoters, flame retardant additives, photo-initiators and the like. These components can be used to render the compositions reactive to thermal and/or radiant energy thereby making the compositions useful in a variety of photoimagable packaging applications.

[0038] To obtain a photosensitive composition, photo monomers, a photo initiator, and a sensitizer are added to the polyimide solution. Ethylenically unsaturated photo monomers suitable for use in the invention include a mixture of at least one amine (meth)acrylate, or amine methacrylamide, and a non-amine-containing (meth)acrylate compound. Useful amine (meth)acrylate and amine methacrylamide compounds include N-methylamino-bis-(ethyl methacrylate), dimethylaminopropyl methacrylamide, dimethylaminoethyl methacrylate, acrylated amine oligomer, and combinations thereof. Useful non-amine containing (meth)acrylate compounds include polyethylene glycol (200) diacrylate, 1,6, hexanediol diacrylate, 1,6-hexanediol dimethacrylate, triethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,10-decanediol diacrylate, 1,12-dodecanediol diacrylate, oxyethylated phenol acrylate, and combinations thereof. Particularly suitable amine di(meth)acrylates include an acrylated amine oligomer, sold under the tradename EBECRYL 7100, available from UCB Chemicals Corporation of Smyrna, Ga., and N-methyldiethanolamine dimethacrylate, available from Sartomer Company of Exton, Pa. Amine (meth)acrylates catalyze the conversion of polyamic acids to polyimides, which lowers the cure temperature and provides a higher percentage of conversion of polyamic acid to polyimide. The amount of amine (meth)acrylates used should be kept to a minimum to avoid lowering adhesion with sulfuric acid testing. Other particularly suitable di(meth)acrylates include hexanediol dimethacrylate, available from Sartomer Company under the product codes SR239 and SR259, which products are polyethylene glycol 200 diacrylates.

[0039] The amine (meth)acrylate photo monomers form a salt with the carboxylic acid on the methylene-bis-anthanilic acid, which renders the photo monomer compatible with the polyamic acid (binder). If the photo monomer used lacks an amine functionality, a suitable amount of amine (meth)acrylate is added to the photo monomer mixture.

[0040] The photopolymer must be able to withstand aqueous carbonate development. In this regard, the use of di(meth)acrylates renders the photosensitive composition less susceptible to attack by a developer agent. The amount of di(meth)acrylate used influences the flexibility after cure, i.e., lower amounts improve flexibility.

[0041] Suitable photo initiators for use in the invention are known in the art and include benzophenone, Michler's ketone, ethyl Michler's ketone, p-dialkylaminobenzoate alkyl esters, thioxanthones, isopropyl thioxanthone, hexaarylbiimidizoles, benzoin dialkyl ethers, 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone, 2-(o-chlorophenyl)-4,5-bis (m-methoxyphenyl)-imidazole dimer; 1,1'-biimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl-(Bis(2-o-chlorophenyl-4,5-diphenylimidazole)), 1H-imidazole, 2,5-bis(o-chlorophenyl)-4-[3,4-dimethoxyphenyl] dimer, and combinations thereof.

[0042] Suitable sensitizers for use in the invention include bis-p-diethylamino-benzophenone, ethyl Michler's ketone; isopropylthioxanthone, coumarins, including 2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-11-oxo-1H,5H,11H-(1)benzopyrano[5,7,8-ij]quinolizine-10-carboxylic acid ethyl ester, bis(p-dialkylaminobenzylidene) ketones, arylidene aryl ketones, N-alkylindolylidene alkanones, N-alkylbenzothiazolylidene alkanones, methylene blue, and combinations thereof.

[0043] A suitable combination of photo initiator and sensitizer is 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl-(Bis(2-o-chlorophenyl-4,5-diphenylimidazole)) and ethyl Michler's ketone (EMK). The amount of EMK may be adjusted to obtain optimum light penetration through the coating.

[0044] An adhesion promoter may also be optionally added to the composition to improve adhesion to the substrate. Suitable adhesion promoters include: 3-mercapto-1H-1,2,4-triazole, 5-amino-1,3,4-thiadiazole-2-thiol, 2-mercaptobenzimidazole 2-(2'-hydroxy-5-methacrylyloxyethylphenyl)-2H-benzotriazole, polybenzimidazole, and combinations thereof. Of the above, 3-mercapto-1H,2,4-triazole not only adheres well to copper, but can increase photo speed.

Positive Working Polyimides

[0045] The polyimides in the present invention can also be derivitized to create positive working systems. In this present embodiment, the phenolic finctionality present on the polyimide can be derivitized to create a polyimide that will generate polar groups upon irradiation. Members of the diazoquinone family provide this functionality, 2-diazo-1-naphthol-5-sulfonyl chloride; 1,2-benzoquinone-2-diazido-4-sulfonyl chloride; 1,2-naphthoquinone-2-diazido-5-sulfonyl chloride; and 1,2-naphthoquinone-2-diazido-4-sulfonyl chloride for example, when reacted with the hydroxyl group to create a polyimide that will generate polar groups upon irradiation. The increased polarity of the matrix provides a mechanism for solvent selectivity during development of exposed features. One skilled in the art will recognize other derivatization agents that will provide this functionality.

[0046] The o-quinonediazidosulfonyl chlorides include, for example, 1,2-benzoquinone-2-diazido-4-sulfonyl chloride, 1,2-naphthoquinone-2-diazido-5-sulfonyl chloride, 1,2-naphthoquinone-2-diazido-4-sulfonyl chloride, etc.

Lithographic Processes

[0047] In another embodiment any of the polyimide compositions of the invention, are useful in lithographic processes by performing in sequence

[0048] 1. applying the polyimide compound in organic solution to a substrate, such as by spin coating

[0049] 2. evaporating at least a portion of the organic solvent

[0050] 3. exposing the polyimide to radiation, such as for example I-line radiation through a mask

[0051] 4. developing the exposed image to form a patterned polyimide structure

[0052] 5. typically, but not always a heating step to evaporate volatiles from the patterned polyimide structure is performed. This heating step differs from a cure step of prior art processes during which the imidization reaction occurs.

[0053] The patterned polyimide structure thus formed is heat resistant, and is well-suited for surface-protecting films, dielectric films, interlayer insulting films, and other applications needed in microelectronics.

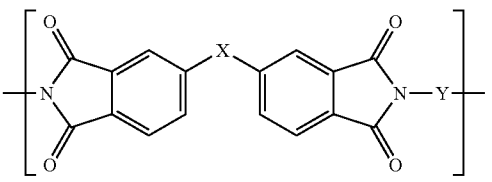
[0054] In one prophetic example, a polyimide in which X is $C(CF_3)_2$, a first Y is 6F-AP, and a second Y is TFMB is prepared and imidized by the methods as herein described. The polyimide thus formed is combined with a photo initiator, for example isopropyl thioxanthone, and dissolved in methyl ethyl ketone. The mixture is useful in the lithographic process described above.

[0055] In another prophetic example, a polyimide in which X is $C(CF_3)_2$, and Y is 6F-AP is prepared and imidized by the methods as herein described. The polyimide thus formed is derivatized with methyl methacryloyl chloride such that about 94% of the hydroxyl groups are functionalized with a methyl methacrylate moiety. The derivatized polyimide is dissolved in methyl ethyl ketone. The mixture is useful in the lithographic process described above.

What is claimed is:

1. A composition comprising a polyimide component and an organic solvent,

wherein the polyimide component is represented by a polyimide having a repeat unit represented the formula;



where X can be equal to SO_2 or $C(CF_3)_2$, $C(CF_3)$phenyl, $C(CF_3)CF_2CF_3$, or $C(CF_2CF_3)$phenyl, and combinations thereof, and

wherein the Y component Y is derived from one or more diamines, wherein at least a portion of the Y component is derived from a hydroxyl- or carboxyl-containing diamine compound,

wherein a percentage of the total hydroxyl or carboxyl groups of the diamine component from between and including any two of the following numbers, 0, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 98 and 100 mole percent have been derivatized to contain an ethylenically unsaturated moiety capable of crosslinking.

2. The composition of claim 1 wherein Y is derived from a hydroxyl- or carboxyl-containing diamine compound selected from the group consisting of, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-AP), 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), 2,4-diaminophenol, 2,3-diaminophenol, 3,3'-diamino-4,4'-dihydroxy-biphenyl and 2,2'-bis(3-amino-3-hydroxyphenyl)hexafluoropropane, methylene-bis-anthranilic acid and mixtures thereof.

3. The composition of claim 1 wherein at least a portion of the Y is derived from a hydroxyl- or carboxyl-containing diamine compound selected from the group consisting of, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-AP), 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), 2,4-diaminophenol, 2,3-diaminophenol, 3,3'-diamino-4,4'-dihydroxy-biphenyl and 2,2'-bis(3-amino-4-hydroxyphenyl-)hexafluoropropane, methylene-bis-anthranilic acid and mixtures thereof.

4. The composition of claim 1 wherein the Y components provide at least one half mole of hydroxyl or carboxyl moieties per mole of diamine compounds.

5. The composition of claim 1 wherein the Y components provide at least one mole of hydroxyl or carboxyl moieties per mole of diamine compounds.

6. The composition of claim 1 wherein the polyimide compound is solvent soluble and spin-coatable onto a substrate.

7. The composition of claim 1 wherein the polyimide compound is solvent soluble and spin-coatable onto a substrate to form a polyimide film, wherein the maximum temperature the substrate is exposed to during this process is less than 100° C.

8. The composition of claim 1 further comprising a polyimide component in which X can be equal to SO_2 or $C(CF_3)_2$, $C(CF_3)$phenyl, $C(CF_3)CF_2CF_3$, or $C(CF_2CF_3)$phenyl, and combinations thereof, and Y is selected from the group consisting of 3,4'-diaminodiphenyl ether (3,4'-ODA), 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl (TFMB), 3,3',5,5'-tetramethylbenzidine, 2,3,5,6-tetramethyl-1,4-phenylenediamine, 3,3'-diaminodiphenyl sulfone, 3,3'dimethylbenzidine, 3,3'-bis(trifluoromethyl)benzidine, 2,2'-bis-(p-aminophenyl)hexafluoropropane, bis(trifluoromethoxy)benzidine (TFMOB), 2,2'-bis(pentafluoroethoxy)benzidine (TFEOB), 2,2'-trifluoromethyl-4,4'-oxydianiline (OBABTF), 2-phenyl-2-trifluoromethyl-bis(p-aminophenyl)methane, 2-phenyl-2-trifluoromethyl-bis(m-aminophenyl)methane, 2,2'-bis(2-heptafluoroisopropoxy-tetrafluoroethoxy)benzidine (DFPOB), 2,2-bis(m-aminophenyl)hexafluoropropane (6-FmDA), 2,2-bis(3-amino-4-methylphenyl)hexafluoropropane, 3,6-bis(trifluoromethyl)-1,4-diaminobenzene (2TFMPDA), 1-(3,5-diaminophenyl)-2,2-bis(trifluoromethyl)-3,3,4,4,5,5,5-heptafluoropentane, 3,5-diaminobenzotrifluoride (3,5-DABTF), 3,5-diamino-5-(pentafluoroethyl-)benzene, 3,5-diamino-5-(heptafluoropropyl)benzene, 2,2'-dimethylbenzidine (DMBZ), 2,2',6,6'-tetramethylbenzidine (TMBZ), 3,6-diamino-9,9-bis(trifluoromethyl)xanthene (6FCDAM), 3,6-diamino-9-trifluoromethyl-9-phenylxanthene (3FCDAM), 3,6-diamino-9,9-diphenyl xanthene and mixtures thereof.

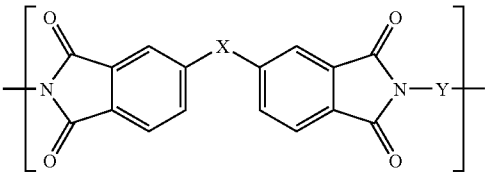
9. The composition of claim 1 wherein at least a portion of the hydroxyl or carboxyl groups of the diamine component have been derivatized to contain an o-quinonediazidosulfonyl moiety.

10. The composition of claim 1 wherein at least a portion of the hydroxyl or carboxyl groups of the diamine component have been derivatized to contain an ethylenically unsaturated moiety capable of crosslinking.

11. The composition of claim 1 wherein the polyimide material has an end and wherein the end of the polyimide chain has been derivatized to contain an ethylenically unsaturated moiety capable of crosslinking.

12. A composition comprising a polyimide component and an organic solvent,

wherein the polyimide component is represented by a polyimide having a repeat unit represented the formula;



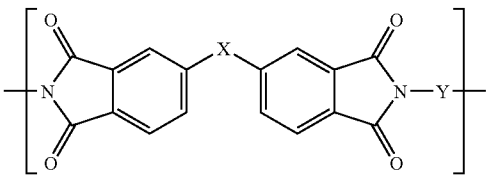
where X can be equal to SO_2 or $C(CF_3)_2$, $C(CF_3)$phenyl, $C(CF_3)CF_2CF_3$, or $C(CF_2CF_3)$phenyl, and combinations thereof, and

wherein Y is derived from a hydroxyl- or carboxyl-containing diamine component of a diamine selected from the group consisting of, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-AP), 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), 2,4-diaminophenol, 2,3-diaminophenol, 3,3'-diamino-4,4'-dihydroxybiphenyl and 2,2'-bis(3-amino-3-hydroxyphenyl)hexafluoropropane, methylene-bis-anthranilic acid and mixtures thereof

wherein a percentage of the total hydroxyl or carboxyl groups of the diamine component from between and including any two of the following numbers, 0, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 98 and 100 mole percent have been derivatized to contain an o-quinonediazidosulfonyl moiety.

13. A composition comprising a polyimide component and an organic solvent.

wherein the polyimide component is represented by a polyimide having a repeat unit represented the formula;



where X can be equal to SO_2 or $C(CF_3)_2$, $C(CF_3)$phenyl, $C(CF_3)CF_2CF_3$, or $C(CF_2CF_3)$phenyl, and combinations thereof, and

wherein Y is derived from a hydroxyl- or carboxyl-containing diamine component of a diamine selected from the group consisting of, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-AP), 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), 2,4-diaminophenol, 2,3-diaminophenol, 3,3'-diamino-4,4'-dihydroxybiphenyl and 2,2'-bis(3-amino-3-hydroxyphenyl)hexafluoropropane, methylene-bis-anthranilic acid and mixtures thereof

wherein the end of the polyimide chain has been derivatized to contain an ethylenically unsaturated moiety capable of crosslinking.

14. A process comprising

(a) applying the composition of claim 1 to a substrate;

(b) evaporating at least a portion of the organic solvent to form a polyimide film;

(c) exposing the polyimide film to radiation through a mask;

(d) and developing the exposed image to form a patterned polyimide structure.

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