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(54) Title: POLYURETHANE UREA POLISHING PAD

(57) **Abstract:** The present invention relates to an article for altering a surface of a workpiece, or a polishing pad having a window. In particular, the polishing pad includes a polyurethane urea material wherein the polyurethane urea material contains cells which are at least partially filled with gas. The polyurethane urea material can be prepared by combining polyisocyanate and/or polyurethane prepolymer, hydroxyl-containing material, amine-containing material and blowing agent. The polishing pad according to the present invention is useful for polishing articles, and is especially useful for chemical mechanical polishing or planarization of microelectronic and optical electronic devices such as but not limited to semiconductor wafers. The window of the polishing pad is at least partially transparent and thus, can be particularly useful with polishing or planarizing tools that are equipped with through-the-platen wafer metrology.



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POLYURETHANE UREA POLISHING PAD

[0001] The present invention relates to an article for altering a surface of a workpiece. In particular, the present invention is directed to a polishing pad having a window. More particularly, the polishing layer of the pad can include a polyurethane urea material wherein cells at least partially filled with gas are substantially uniformly distributed throughout at least a portion of the material and/or pad. The polyurethane urea material can be prepared by combining polyisocyanate and/or polyurethane prepolymer, hydroxyl-containing material, amine-containing material and blowing agent. The polishing pad according to the present invention is useful for polishing articles, and is especially useful for chemical mechanical polishing or planarization of microelectronic and optical electronic devices such as but not limited to semiconductor wafers. The window of the polishing pad is at least partially transparent and thus, can be particularly useful with polishing or planarizing tools that are equipped with through-the-platen wafer metrology.

[0002] The polishing or planarization of a rough surface of an article such as a microelectronic device, to a substantially smooth surface generally involves rubbing the rough surface with the work surface of a polishing pad using a controlled and repetitive motion. A polishing fluid can be interposed between the rough surface of the article that is to be polished and the work surface of the polishing pad.

[0003] The fabrication of a microelectronic device can comprise the formation of a plurality of integrated circuits on a semiconductor substrate. The composition of the substrate can include silicon or gallium arsenide. The integrated circuits generally can be formed by a series of process steps in which patterned layers of materials, such as conductive, insulating and semi-conducting materials, are formed on the substrate. In order to maximize the density of integrated circuits per wafer, it is desirable to have a planar polished substrate at various stages throughout the production process. As such, production of a microelectronic device typically involves at least one polishing

step and can often involve a plurality of polishing steps, which can result in the use of more than one polishing pad.

[0004] The polishing step can include rotating the polishing pad and the semiconductor substrate against each other in the presence of a polishing fluid. The polishing fluid can be mildly alkaline and can optionally contain an abrasive particulate material such as but not limited to particulate cerium oxide, particulate alumina, or particulate silica. The polishing fluid can facilitate the removal and transport of abraded material off and away from the rough surface of the article.

[0005] Polishing pad characteristics such as pore volume and pore size can vary from pad-to-pad and throughout the operating lifetime of a particular pad. Variations in the polishing characteristics of the pads can result in inadequately polished and planarized substrates which can be unsuitable for fabricating semiconductor wafers. Thus, it is desirable to develop a polishing pad that exhibits reduced pad-to-pad variation in polishing and planarization characteristics. It is further desirable to develop a polishing pad that exhibits reduced variations in polishing and planarization characteristics throughout the operating lifetime of the pad.

[0006] Planarizing tools having the ability to measure the progress of the planarization process while the wafer is held in the tool and in contact with the pad are known in the art. Measuring the progress of planarizing a microelectronic device during the planarizing process can be referred to in the art as "in-situ metrology". United States Patents 5,964,643 and 6,159,073, and European Patent 1,108,501 describe polishing or planarizing tools and in-situ metrology systems. In general, in-situ metrology can include directing a beam of light through an at least partially transparent window located in the platen of the tool; the beam of light can be reflected off the surface of the wafer, back through the platen window, and into a detector. The polishing pad can include a window that is at least partially transparent to the wavelengths used in the metrology system, and essentially aligned with the platen window.

[0007] Thus, it is desirable to develop a polishing pad

that comprises a window area useful for in-situ metrology. It is further desirable that the window provides suitable transparency throughout the operating life of the pad.

[0008] One disadvantage with known pads having windows which are coplanar with the polishing surface, can include wearing of the window portion at a slower rate than the pad surface. A further disadvantage with known pads having a coplanar window can include scratching of the window as a result of its contact with abrasive particles in the slurry during the polishing or planarization process. A scratched window can generally reduce the transparency of the window and can cause an attenuation of the metrology signal.

[0009] For the purposes of this specification, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0010] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0011] The present invention includes a pad adapted to polish a microelectronic substrate. The pad includes a polyurethane urea-containing polishing layer. The polishing layer can include at least partially gas-filled cells, at least a portion of the at least partially gas-filled cells can be formed by an in-situ reaction.

The polishing layer has an opening formed therein. The pad of the present invention includes a second layer wherein at least a portion of the second layer can include an at least partially transparent window. The polishing layer is at least partially connected to the second layer, and the opening in the polishing layer is at least partially aligned with the window of the second layer.

[0012] The present invention includes a polishing pad having a window. The polishing pad can include a first layer and a second layer. The second layer can be at least partially connected to the first layer. The term "connected to" means to link together or place in relationship either directly, or indirectly by one or more intervening materials. The first layer can function as the work surface or the polishing layer of the pad. The polishing layer can at least partially interact with the substrate to be polished and the polishing slurry. In a non-limiting embodiment, at least a portion of the second layer of the pad can comprise a window which is at least partially transparent to wavelengths used by the metrology instrumentation of polishing tools. In a non-limiting embodiment, the polishing pad of the present invention can include a sub-pad layer at least partially connected to the second layer. In a non-limiting embodiment, the cells can be substantially uniformly distributed throughout the material and/or polishing layer.

[0013] In alternate non-limiting embodiments, the polyurethane urea of the present invention can be prepared by combining a polyisocyanate with hydroxyl-containing material, amine-containing material and blowing agent; or by reacting a two-component composition comprising combining polyisocyanate and hydroxyl-containing material to form a polyurethane prepolymer, and then reacting the prepolymer with amine-containing material and blowing agent; or by combining polyisocyanate and/or polyurethane prepolymer, optional hydroxyl-containing material, amine-containing material and blowing agent.

[0014] In alternate non-limiting embodiments, the amount of polyisocyanate, hydroxyl-containing material and amine-containing material can be selected such that the equivalent ratio of (NCO +

NCS): (NH + OH) can be greater than 0.95, or at least 1.0, or at least 1.05, or less than 1.3, or less than 1.2, or less than 1.1.

[0015] Polyisocyanates useful in the preparation of the polyurethane urea of the present invention are numerous and widely varied. Suitable polyisocyanates can include but are not limited to polymeric and C₂-C₂₀ linear, branched, cyclic and aromatic polyisocyanates. Non-limiting examples can include polyisocyanates having backbone linkages chosen from urethane linkages (-NH-C(O)-O-).

[0016] The molecular weight of the polyisocyanate can vary widely. In alternate non-limiting embodiments, the number average molecular weight (Mn) can be at least 100 grams/mole, or at least 150 grams/mole, or less than 15,000 grams/mole, or less than 5000 grams/mole. The number average molecular weight can be determined using known methods. The number average molecular weight values recited herein and the claims were determined by gel permeation chromatography (GPC) using polystyrene standards.

[0017] Non-limiting examples of suitable polyisocyanates can include but are not limited to polyisocyanates having at least two isocyanate groups.

[0018] Non-limiting examples of polyisocyanates can include but are not limited to aliphatic polyisocyanates, cycloaliphatic polyisocyanates wherein one or more of the isocyanato groups are attached directly to the cycloaliphatic ring, cycloaliphatic polyisocyanates wherein one or more of the isocyanato groups are not attached directly to the cycloaliphatic ring, aromatic polyisocyanates wherein one or more of the isocyanato groups are attached directly to the aromatic ring, and aromatic polyisocyanates wherein one or more of the isocyanato groups are not attached directly to the aromatic ring.

[0019] In a non-limiting embodiment of the present invention, the polyisocyanate can include but is not limited to aliphatic or cycloaliphatic diisocyanates, aromatic diisocyanates, cyclic dimers and cyclic trimers thereof, and mixtures thereof. Non-limiting examples of suitable polyisocyanates can include but are not limited to Desmodur N 3300A (hexamethylene diisocyanate trimer) which is commercially available from Bayer; Desmodur N 3400

(60% hexamethylene diisocyanate dimer and 40% hexamethylene diisocyanate trimer).

[0020] In a non-limiting embodiment, the polyisocyanate can include dicyclohexylmethane diisocyanate and isomeric mixtures thereof. As used herein and the claims, the term "isomeric mixtures" refers to a mixture of the cis-cis, trans-trans, and cis-trans isomers of the polyisocyanate. Non-limiting examples of isomeric mixtures for use in the present invention can include the trans-trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate), hereinafter referred to as "PICM" (para-isocyanato cyclohexylmethane), the cis-trans isomer of PICM, the cis-cis isomer of PICM, and mixtures thereof.

[0021] In one non-limiting embodiment, the PICM used in this invention can be prepared by phosgenating the 4,4'-methylenebis(cyclohexyl amine) (PACM) by procedures well known in the art such as the procedures disclosed in United States Patents 2,644,007 and 2,680,127 which are incorporated herein by reference. The PACM isomer mixtures, upon phosgenation, can produce PICM in a liquid phase, a partially liquid phase, or a solid phase at room temperature. The PACM isomer mixtures can be obtained by the hydrogenation of methylenedianiline and/or by fractional crystallization of PACM isomer mixtures in the presence of water and alcohols such as methanol and ethanol.

[0022] In a non-limiting embodiment, the isomeric mixture can contain from 10-100 percent of the trans,trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate) (PICM).

[0023] In a non-limiting embodiment, the polyisocyanate can include 2,4-tolylene diisocyanate; 2,6-tolylene diisocyanate and mixtures of these isomers ("TDI").

[0024] Additional aliphatic and cycloaliphatic diisocyanates that can be used in alternate non-limiting embodiments of the present invention include 3-isocyanato-methyl-3,5,5-trimethyl cyclohexyl-isocyanate ("IPDI") which is commercially available from Arco Chemical, and meta-tetramethylxylene diisocyanate (1,3-bis(1-isocyanato-1-methylethyl)-benzene) which is commercially available from Cytec Industries Inc. under the tradename TMXDI.RTM. (Meta) Aliphatic Isocyanate.

[0025] As used herein and the claims, the terms aliphatic and cycloaliphatic diisocyanates refer to 6 to 100 carbon atoms linked in a straight chain or cyclized having two diisocyanate reactive end groups. In a non-limiting embodiment of the present invention, the aliphatic and cycloaliphatic diisocyanates for use in the present invention can include TMXDI and compounds of the formula $R-(NCO)_2$ wherein R represents an aliphatic group or a cycloaliphatic group.

[0026] Further non-limiting examples of suitable polyisocyanates can include but are not limited to aliphatic polyisocyanates; ethylenically unsaturated polyisocyanates; alicyclic polyisocyanates; aromatic polyisocyanates wherein the isocyanate groups are not bonded directly to the aromatic ring, e.g., α,α' -xylene diisocyanate; aromatic polyisocyanates wherein the isocyanate groups are bonded directly to the aromatic ring, e.g., benzene diisocyanate; halogenated, alkylated, alkoxyated, nitrated, carbodiimide-modified, urea-modified and biuret-modified derivatives of polyisocyanates thereof; and dimerized and trimerized products of polyisocyanates thereof.

[0027] Further non-limiting examples of aliphatic polyisocyanates can include ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, nonamethylene diisocyanate, 2,2'-dimethylpentane diisocyanate, 2,2,4-trimethylhexane diisocyanate, decamethylene diisocyanate, 2,4,4,-trimethylhexamethylene diisocyanate, 1,6,11-undecanetriisocyanate, 1,3,6-hexamethylene triisocyanate, 1,8-diisocyanato-4-(isocyanatomethyl)octane, 2,5,7-trimethyl-1,8-diisocyanato-5-(isocyanatomethyl)octane, bis(isocyanatoethyl)-carbonate, bis(isocyanatoethyl)ether, 2-isocyanatopropyl-2,6-diisocyanatohexanoate, lysinediisocyanate methyl ester and lysinetriisocyanate methyl ester.

[0028] Examples of ethylenically unsaturated polyisocyanates can include but are not limited to butene diisocyanate and 1,3-butadiene-1,4-diisocyanate. Alicyclic polyisocyanates can include but are not limited to isophorone diisocyanate, cyclohexane diisocyanate, methylcyclohexane

diisocyanate, bis(isocyanatomethyl) cyclohexane, bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane and 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane.

[0029] Examples of aromatic polyisocyanates wherein the isocyanate groups are not bonded directly to the aromatic ring can include but are not limited to bis(isocyanatoethyl)benzene, $\alpha,\alpha,\alpha',\alpha'$ -tetramethylxylene diisocyanate, 1,3-bis(1-isocyanato-1-methylethyl)benzene, bis(isocyanatobutyl)benzene, bis(isocyanatomethyl)naphthalene, bis(isocyanatomethyl)diphenyl ether, bis(isocyanatoethyl) phthalate, mesitylene triisocyanate and 2,5-di(isocyanatomethyl)furan. Aromatic polyisocyanates having isocyanate groups bonded directly to the aromatic ring can include but are not limited to phenylene diisocyanate, ethylphenylene diisocyanate, isopropylphenylene diisocyanate, dimethylphenylene diisocyanate, diethylphenylene diisocyanate, diisopropylphenylene diisocyanate, trimethylbenzene triisocyanate, benzene triisocyanate, naphthalene diisocyanate, methylnaphthalene diisocyanate, biphenyl diisocyanate, ortho-toluidine diisocyanate, ortho-tolylidine diisocyanate, ortho-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, bis(3-methyl-4-isocyanatophenyl)methane, bis(isocyanatophenyl)ethylene, 3,3'-dimethoxy-biphenyl-4,4'-diisocyanate, triphenylmethane triisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, naphthalene triisocyanate, diphenylmethane-2,4,4'-triisocyanate, 4-methyldiphenylmethane-3,5,2',4',6'-pentaaisocyanate, diphenylether diisocyanate, bis(isocyanatophenylether)ethyleneglycol, bis(isocyanatophenylether)-1,3-propyleneglycol, benzophenone

diisocyanate, carbazole diisocyanate, ethylcarbazole diisocyanate and dichlorocarbazole diisocyanate.

[0030] In alternate non-limiting embodiments of the present invention, polyisothiocyanate or a combination of polyisocyanate and polyisothiocyanate can be used in place of polyisocyanate. In these alternate non-limiting embodiments, isothiocyanate can have at least two isothiocyanate groups.

[0031] In a non-limiting embodiment of the present invention, the polyisocyanate for use in the present invention can include polyurethane prepolymer.

[0032] In a non-limiting embodiment, polyisocyanate can be reacted with hydroxyl-containing material to form polyurethane prepolymer, and said prepolymer can be reacted with amine-containing material and blowing agent to produce the polyurethane urea of the present invention. In another non-limiting embodiment, polyisocyanate and polyurethane prepolymer can be reacted with hydroxyl-containing material, amine-containing material and blowing agent. In a further non-limiting embodiment, polyisocyanate and polyurethane prepolymer can be reacted with amine-containing material and blowing agent.

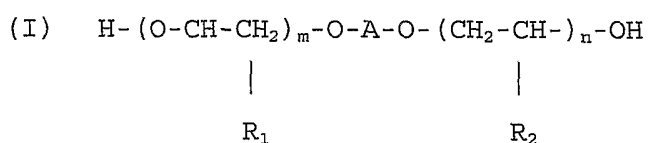
[0033] Hydroxyl-containing materials are varied and known in the art. Non-limiting examples can include but are not limited to polyols; sulfur-containing materials such as but not limited to hydroxyl functional polysulfides, and SH-containing materials such as but not limited to polythiols; and materials having both hydroxyl and thiol functional groups.

[0034] Suitable hydroxyl-containing materials for use in the present invention can include a wide variety of materials known in the art. Non-limiting examples can include but are not limited to polyether polyols, polyester polyols, polycaprolactone polyols, polycarbonate polyols, and mixtures thereof.

[0035] Polyether polyols and methods for their preparation are known to one skilled in the art. Many polyether polyols of various types and molecular weight are commercially available from various manufacturers. Non-limiting examples of polyether polyols can include but are not limited to polyoxyalkylene polyols, and polyalkoxylated polyols. Polyoxyalkylene polyols can be prepared in

accordance with known methods. In a non-limiting embodiment, a polyoxyalkylene polyol can be prepared by condensing an alkylene oxide, or a mixture of alkylene oxides, using acid- or base-catalyzed addition with a polyhydric initiator or a mixture of polyhydric initiators, such as but not limited to ethylene glycol, propylene glycol, glycerol, and sorbitol. Non-limiting examples of alkylene oxides can include ethylene oxide, propylene oxide, butylene oxide, amylene oxide, aralkylene oxides, such as but not limited to styrene oxide, mixtures of ethylene oxide and propylene oxide. In a further non-limiting embodiment, polyoxyalkylene polyols can be prepared with mixtures of alkylene oxide using random or step-wise oxyalkylation. Non-limiting examples of such polyoxyalkylene polyols include polyoxyethylene, such as but not limited to polyethylene glycol, polyoxypropylene, such as but not limited to polypropylene glycol.

[0036] In a non-limiting embodiment, polyalkoxylated polyols can be represented by the following general formula:



wherein m and n can each be a positive integer, the sum of m and n being from 5 to 70; R₁ and R₂ are each hydrogen, methyl or ethyl; and A is a divalent linking group such as a straight or branched chain alkylene which can contain from 1 to 8 carbon atoms, phenylene, and C₁ to C₉ alkyl-substituted phenylene. The chosen values of m and n can, in combination with the chosen divalent linking group, determine the molecular weight of the polyol.

[0037] Polyalkoxylated polyols can be prepared by methods that are known in the art. In a non-limiting embodiment, a polyol such as 4,4'-isopropylidenediphenol can be reacted with an oxirane-containing material such as but not limited to ethylene oxide, propylene oxide and butylene oxide, to form what is commonly referred to as an ethoxylated, propoxylated or butoxylated polyol having hydroxy functionality. Non-limiting examples of polyols suitable for use in preparing polyalkoxylated polyols can include

those polyols described in United States Patent 6,187,444 B1 at column 10, lines 1-20, which disclosure is incorporated herein by reference.

[0038] As used herein and the claims, the term "polyether polyols" can include the generally known poly(oxytetramethylene) diols prepared by the polymerization of tetrahydrofuran in the presence of Lewis acid catalysts such as but not limited to boron trifluoride, tin (IV) chloride and sulfonyl chloride. In a non-limiting embodiment, the polyether polyol can include TerathaneTM polyether glycol which is commercially available from DuPont. Also included are the polyethers prepared by the copolymerization of cyclic ethers such as but not limited to ethylene oxide, propylene oxide, trimethylene oxide, and tetrahydrofuran with aliphatic diols such as but not limited to ethylene glycol, 1,3-butanediol, 1,4-butanediol, diethylene glycol, dipropylene glycol, 1,2-propylene glycol and 1,3-propylene glycol. Compatible mixtures of polyether polyols can also be used. As used herein, "compatible" means that the polyols are mutually soluble in each other so as to form a single phase.

[0039] A variety of polyester polyols known in the art can be used in the present invention. Suitable polyester polyols can include but are not limited to polyester glycols. Polyester glycols for use in the present invention can include the esterification products of one or more dicarboxylic acids having from four to ten carbon atoms, such as but not limited to adipic, succinic or sebacic acids, with one or more low molecular weight glycols having from two to ten carbon atoms, such as but not limited to ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol and 1,10-decanediol. Esterification procedures for producing polyester polyols is described, for example, in the article D.M. Young, F. Hostettler et al., "Polyesters from Lactone," Union Carbide F-40, p. 147.

[0040] In a non-limiting embodiment, the polyol for use in the present invention can include polycaprolactone polyols. Suitable polycaprolactone polyols are varied and known in the art. In a non-limiting embodiment, polycaprolactone polyols can be prepared by condensing caprolactone in the presence of difunctional

active hydrogen compounds such as but not limited to water or low molecular weight glycols as recited herein. Non-limiting examples of suitable polycaprolactone polyols can include commercially available materials designated as the CAPA series from Solvay Chemical which includes but is not limited to CAPA 2047A, and the TONE™ series from Dow Chemical such as but not limited to TONE 0201.

[0041] Polycarbonate polyols for use in the present invention are varied and known to one skilled in the art. Suitable polycarbonate polyols can include those commercially available (such as but not limited to Ravecarb™ 107 from Enichem S.p.A.). In a non-limiting embodiment, the polycarbonate polyol can be produced by reacting an organic glycol such as a diol, described hereinafter and in connection with the glycol component of the polyurethane or polyurethane urea, and a dialkyl carbonate, such as described in United States Patent 4,160,853. In a non-limiting embodiment, the polyol can include polyhexamethyl carbonate such as $\text{HO}-(\text{CH}_2)_6-[\text{O}-\text{C}(\text{O})-\text{O}-(\text{CH}_2)_6]_n-\text{OH}$, wherein n is an integer from 4 to 24, or from 4 to 10, or from 5 to 7.

[0042] In a non-limiting embodiment, the glycol material can comprise low molecular weight polyols such as polyols having a number average molecular weight of less than 500 grams/mole, and compatible mixtures thereof. As used herein, the term "compatible" means that the glycols are mutually soluble in each other so as to form a single phase. Non-limiting examples of these polyols can include but are not limited to low molecular weight diols and triols. In a further non-limiting embodiment, the amount of triol chosen can be such to avoid a high degree of cross-linking in the polyurethane or polyurethane urea. In alternate non-limiting embodiments, the organic glycol can contain from 2 to 16, or from 2 to 6, or from 2 to 10, carbon atoms. Non-limiting examples of such glycols can include but are not limited to ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, 1,2-, 1,3- and 1,4-butanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-methyl-1,3-pentanediol, 1,3- 2,4- and 1,5-pentanediol, 2,5- and 1,6-hexanediol, 2,4-heptanediol, 2-ethyl-1,3-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol,

1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, 1,2-bis(hydroxyethyl)-cyclohexane, glycerin, tetramethylolmethane, pentaerythritol, trimethylolethane and trimethylolpropane; and isomers thereof.

[0043] In alternate non-limiting embodiments, the hydroxyl-containing material can have a molecular weight of at least 200 grams/mole, or at least 1000 grams/mole, or at least 2000 grams/mole. In alternate non-limiting embodiments, the hydroxyl-containing material can have a number average molecular weight of less than 10,000 grams/mole, or less than 15,000 grams/mole, or less than 20,000 grams/mole, or less than 32,000 grams/mole.

[0044] In a non-limiting embodiment, the hydroxyl-containing material for use in the present invention can include teresters produced from at least one low molecular weight dicarboxylic acid, such as adipic acid.

[0045] In a non-limiting embodiment, the hydroxyl-containing material can comprise block polymers including blocks of ethylene oxide-propylene oxide and/or ethylene oxide-butylene oxide. In a non-limiting embodiment, the hydroxyl-containing material can comprise a block polymer of the following chemical formula:



wherein R can represent hydrogen or C₁-C₆ alkyl; Y_n can represent C₀-C₆ hydrocarbon; n can be an integer from 0 to 6; a, b, and c can each be an integer from 0 to 300, wherein a, b and c are chosen such that the number average molecular weight of the material does not exceed 32,000 grams/mole.

[0046] In further alternate non-limiting embodiments, hydroxyl-containing materials such as but not limited to Pluronic.RTM R, Pluronic.RTM, Tetronic.RTM R and Tetronic.RTM Block Copolymer Surfactants, which are commercially available from BASF, can be used as the hydroxyl-containing material in the present invention.

[0047] Further, non-limiting examples of suitable polyols for use in the present invention can include straight or branched chain alkane polyols, such as but not limited to 1,2-ethanediol,

1,3-propanediol, 1,2-propanediol, 1,4-butanediol, 1,3-butanediol, glycerol, neopentyl glycol, trimethylolethane, trimethylolpropane, di-trimethylolpropane, erythritol, pentaerythritol and di-pentaerythritol; polyalkylene glycols, such as but not limited to diethylene glycol, dipropylene glycol and higher polyalkylene glycols such as but not limited to polyethylene glycols which can have number average molecular weights of from 200 grams/mole to 2,000 grams/mole; cyclic alkane polyols, such as but not limited to cyclopentanediol, cyclohexanediol, cyclohexanetriol, cyclohexanedimethanol, hydroxypropylcyclohexanol and cyclohexanediethanol; aromatic polyols, such as but not limited to dihydroxybenzene, benzenetriol, hydroxybenzyl alcohol and dihydroxytoluene; bisphenols, such as, 4,4'-isopropylidenediphenol; 4,4'-oxybisphenol, 4,4'-dihydroxybenzophenone, 4,4'-thiobisphenol, phenolphthalein, bis(4-hydroxyphenyl)methane, 4,4'-(1,2-ethenediyl)bisphenol and 4,4'-sulfonylbisphenol; halogenated bisphenols, such as but not limited to 4,4'-isopropylidenebis(2,6-dibromophenol), 4,4'-isopropylidenebis(2,6-dichlorophenol) and 4,4'-isopropylidenebis(2,3,5,6-tetrachlorophenol); alkoxyated bisphenols, such as but not limited to alkoxyated 4,4'-isopropylidenediphenol which can have from 1 to 70 alkoxy groups, for example, ethoxy, propoxy, α -butoxy and β -butoxy groups; and biscyclohexanols, which can be prepared by hydrogenating the corresponding bisphenols, such as but not limited to 4,4'-isopropylidene-biscyclohexanol, 4,4'-oxybiscyclohexanol, 4,4'-thiobiscyclohexanol and bis(4-hydroxycyclohexanol)methane; polyurethane or polyurethane urea polyols, polyester polyols, polyether polyols, poly vinyl alcohols, polymers containing hydroxy functional acrylates, polymers containing hydroxy functional methacrylates, and polymers containing allyl alcohols.

[0048] In a non-limiting embodiment, the polyol can be chosen from multifunctional polyols, including but not limited to trimethylolpropane, ethoxylated trimethylolpropane, pentaerythritol.

[0049] In alternate non-limiting embodiments, the polyurethane prepolymer can have a number average molecular weight (Mn) of less than 50,000 grams/mole, or less than 20,000 grams/mole, or less than 10,000 grams/mole. The Mn can be determined using a

variety of known methods. In a non-limiting embodiment, the Mn can be determined by gel permeation chromatography (GPC) using polystyrene standards.

[0050] In alternate non-limiting embodiments, the hydroxyl-containing material for use in the present invention can be chosen from polyether glycols and polyester glycols having a number average molecular weight of at least 200 grams/mole, or at least 300 grams/mole, or at least 750 grams/mole; or no greater than 1,500 grams/mole, or no greater than 2,500 grams/mole, or no greater than 4,000 grams/mole.

[0051] In a further non-limiting embodiment, polyether glycols for use in the present invention can include but are not limited to polytetramethylene ether glycol.

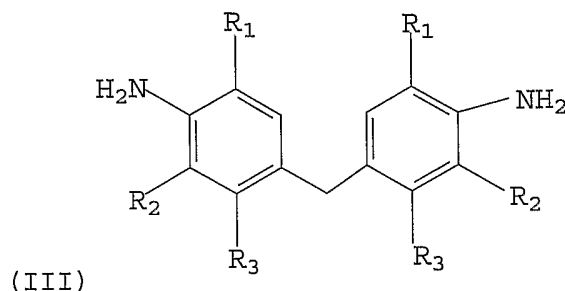
[0052] In a non-limiting embodiment, the hydroxyl-containing material can include both hydroxyl and thiol groups, such as but not limited to 2-mercaptoethanol, 3-mercapto-1,2-propanediol, glycerin bis(2-mercaptoacetate) and 1-hydroxy-4-mercaptocyclohexane.

[0053] In general, polyurethanes and polyurethane prepolymers can be polymerized using a variety of techniques known in the art. In a non-limiting embodiment of the present invention, the polymerization process can include the use of an amine-containing material for curing.

[0054] Amine-containing curing agents for use in the present invention are numerous and widely varied. Non-limiting examples of suitable amine-containing curing agents can include but are not limited to aliphatic polyamines, cycloaliphatic polyamines, aromatic polyamines and mixtures thereof. In alternate non-limiting embodiments, the amine-containing curing agent can be a polyamine having at least two functional groups independently chosen from primary amine ($-NH_2$), secondary amine ($-NH-$) and combinations thereof. In a further non-limiting embodiment, the amine-containing curing agent can have at least two primary amine groups. In another non-limiting embodiment, the amine-containing curing agent can comprise a mixture of a polyamine and at least one material selected from a polythiol and polyol. Non-limiting examples of suitable polythiols and polyols include those previously recited herein. In still another non-limiting embodiment, the amine-containing curing

agent can be a sulfur-containing amine-containing curing agent. A non-limiting example of a sulfur-containing amine-containing curing agent can include Ethacure 300 which is commercially available from Albemarle Corporation.

[0055] Suitable amine-containing curing agents for use in the present invention can include but are not limited to materials having the following chemical formula:



wherein R_1 and R_2 can each be independently chosen from methyl, ethyl, propyl, and isopropyl groups, and R_3 can be chosen from hydrogen and chlorine. Non-limiting examples of amine-containing curing agents for use in the present invention include the following compounds, manufactured by Lonza Ltd. (Basel, Switzerland):

LONZACURE.RTM. M-DIPA: $R_1 = C_3H_7$; $R_2 = C_3H_7$; $R_3 = H$

LONZACURE.RTM. M-DMA: $R_1 = CH_3$; $R_2 = CH_3$; $R_3 = H$

LONZACURE.RTM. M-MEA: $R_1 = CH_3$; $R_2 = C_2H_5$; $R_3 = H$

LONZACURE.RTM. M-DEA: $R_1 = C_2H_5$; $R_2 = C_2H_5$; $R_3 = H$

LONZACURE.RTM. M-MIPA: $R_1 = CH_3$; $R_2 = C_3H_7$; $R_3 = H$

LONZACURE.RTM. M-CDEA: $R_1 = C_2H_5$; $R_2 = C_2H_5$; $R_3 = Cl$

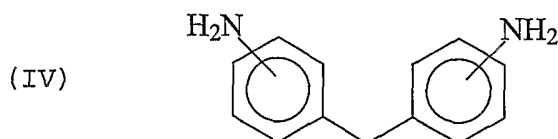
wherein R_1 , R_2 and R_3 correspond to the aforementioned chemical formula.

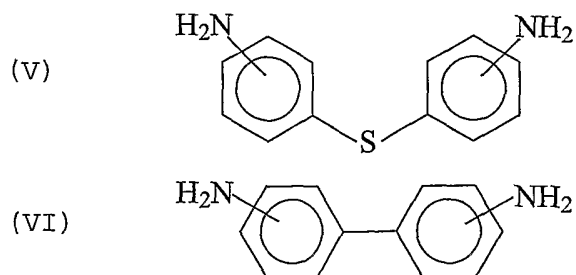
[0056] In a non-limiting embodiment, the amine-containing curing agent can include but is not limited to a diamine curing agent such as 4,4'-methylenebis(3-chloro-2,6-diethylaniline), (Lonzacure.RTM. M-CDEA), which is available in the United States from Air Products and Chemical, Inc. (Allentown, Pa.). In alternate non-limiting embodiments, the amine-containing curing agent for use in the present invention can include 2,4-diamino-3,5-diethyl-toluene, 2,6-diamino-3,5-diethyl-toluene and mixtures thereof (collectively "diethyltoluenediamine" or "DETDA"), which is commercially

available from Albemarle Corporation under the trade name Ethacure 100; dimethylthiotoluenediamine (DMTDA), which is commercially available from Albemarle Corporation under the trade name Ethacure 300; 4,4'-methylene-bis-(2-chloroaniline) which is commercially available from Kingyorker Chemicals under the trade name MOCA. DETDA can be a liquid at room temperature with a viscosity of 156 cPs at 25°C. DETDA can be isomeric, with the 2,4-isomer range being from 75 to 81 percent while the 2,6-isomer range can be from 18 to 24 percent.

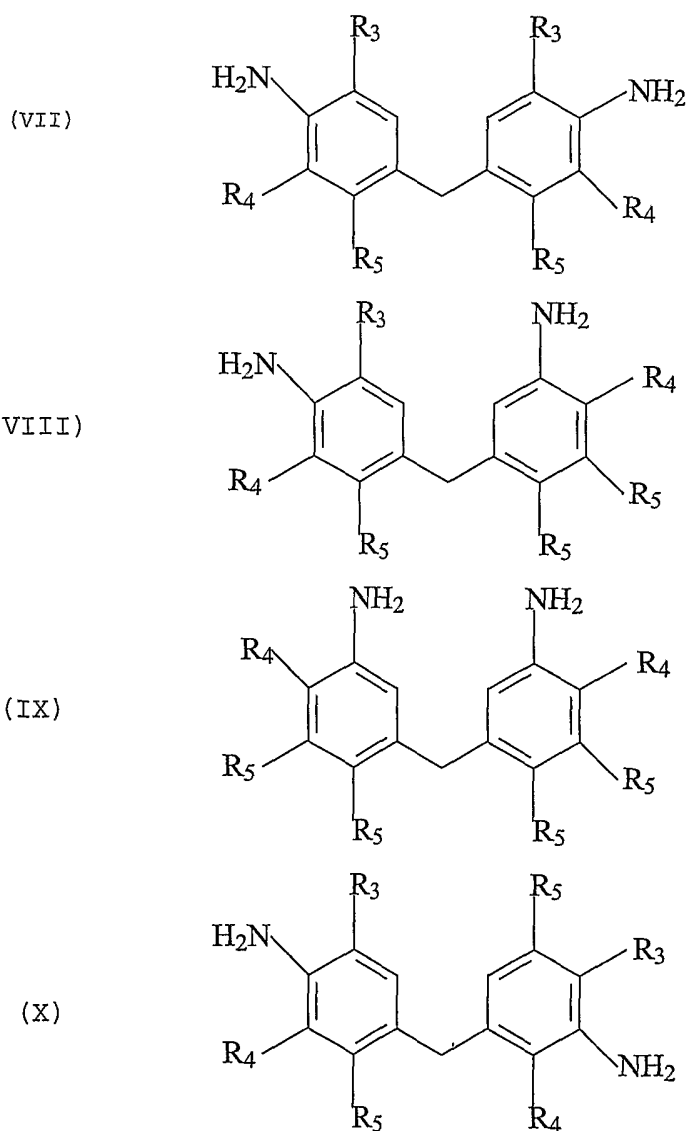
[0057] Non-limiting examples of amine-containing curing agents can include ethyleneamines. Suitable ethyleneamines can include but are not limited to ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), piperazine, morpholine, substituted morpholine, piperidine, substituted piperidine, diethylenediamine (DEDA), and 2-amino-1-ethylpiperazine. In alternate non-limiting embodiments, the amine-containing curing agent can be chosen from one or more isomers of C₁-C₃ dialkyl toluediamine, such as but not limited to 3,5-dimethyl-2,4-toluediamine, 3,5-dimethyl-2,6-toluediamine, 3,5-diethyl-2,4-toluediamine, 3,5-diethyl-2,6-toluediamine, 3,5-diisopropyl-2,4-toluediamine, 3,5-diisopropyl-2,6-toluediamine, and mixtures thereof. In alternate non-limiting embodiments, the amine-containing curing agent can be methylene dianiline or trimethyleneglycol di(para-aminobenzoate).

[0058] In alternate non-limiting embodiments of the present invention, the amine-containing curing agent can include one of the following general structures:

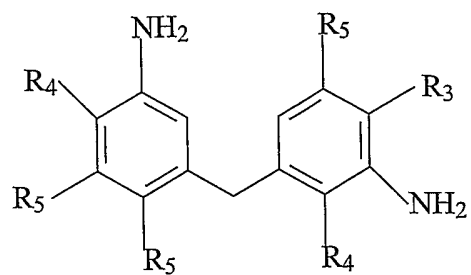




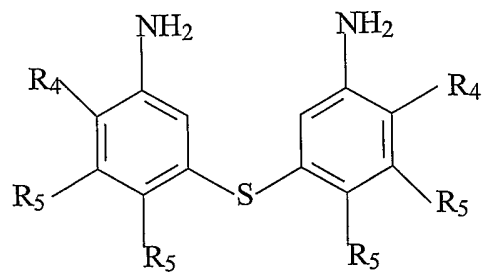
[0059] In further alternate non-limiting embodiments, the amine-containing curing agent can include one or more methylene bis anilines which can be represented by the general formulas VII-XI, one or more aniline sulfides which can be represented by the general formulas XII-XVI, and/or one or more bianilines which can be represented by the general formulas XVII-XX,



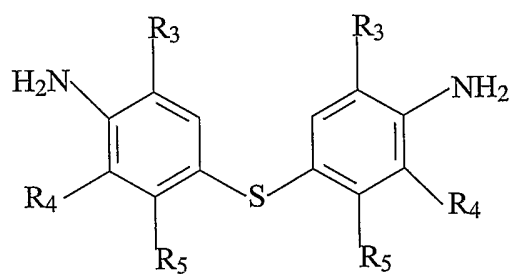
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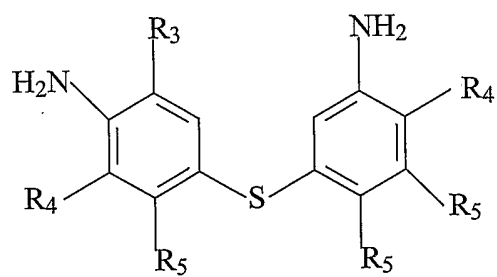
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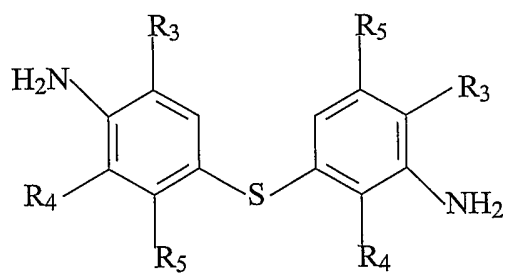
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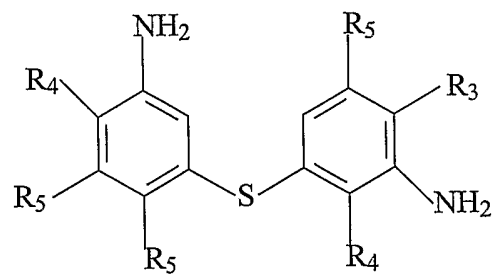
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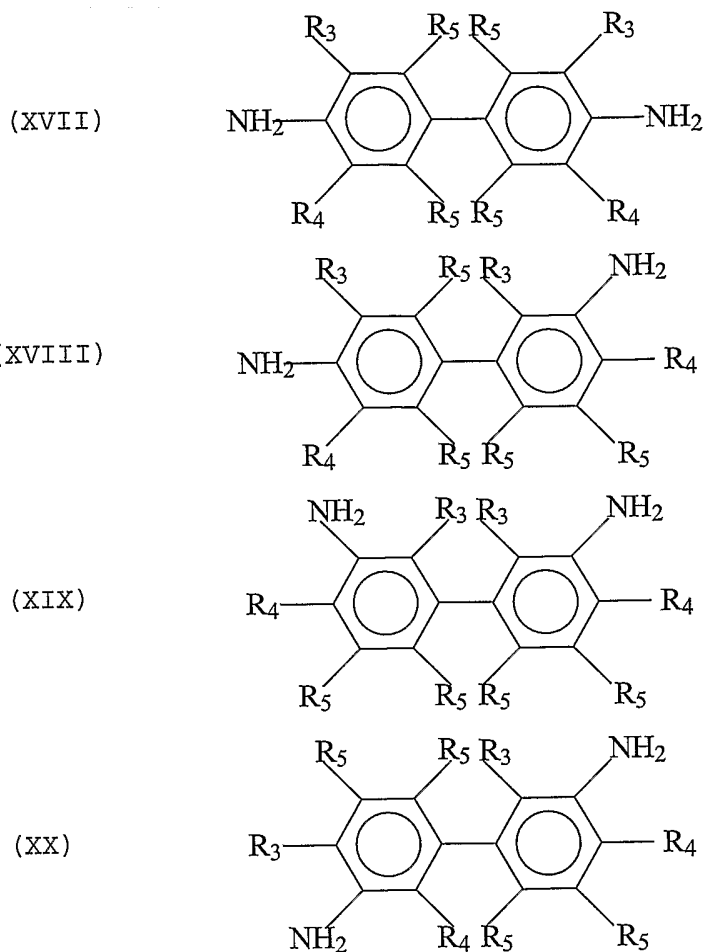


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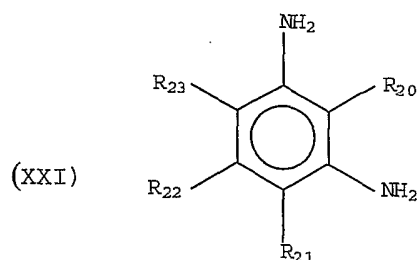
(XVI)





wherein R_3 and R_4 can each independently represent C_1 to C_3 alkyl, and R_5 can be chosen from hydrogen and halogen, such as but not limited to chlorine and bromine. The diamine represented by general formula VII can be described generally as a 4,4'-methylene-bis (dialkylaniline). Suitable non-limiting examples of diamines which can be represented by general formula XII include but are not limited to 4,4'-methylene-bis(2,6-dimethylaniline), 4,4'-methylene-bis(2,6-diethylaniline), 4,4'-methylene-bis(2-ethyl-6-methylaniline), 4,4'-methylene-bis(2,6-diisopropylaniline), 4,4'-methylene-bis(2-isopropyl-6-methylaniline) and 4,4'-methylene-bis(2,6-diethyl-3-chloroaniline).

[0060] In a further non-limiting embodiment, the amine-containing curing agent can include materials which can be represented by the following general structure (XXI):



where R₂₀, R₂₁, R₂₂, and R₂₃ can be independently chosen from H, C₁ to C₃ alkyl, CH₃-S- and halogen, such as but not limited to chlorine or bromine. In a non-limiting embodiment of the present invention, the amine-containing curing agent which can be represented by general Formula XXI can include diethyl toluene diamine (DETDA) wherein R₂₃ is methyl, R₂₀ and R₂₁ are each ethyl and R₂₂ is hydrogen. In a further non-limiting embodiment, the amine-containing curing agent can include 4,4'-methylenedianiline.

[0061] In alternate non-limiting embodiments, the amine-containing material and blowing agent can be mixed with the polyisocyanate and hydroxyl-containing materials using a variety of methods and equipment, such as but not limited to an impeller or extruder. In a non-limiting embodiment, the mixing equipment can include a mechanical stirrer operating at low pressure such as less than 20 bar. In another non-limiting embodiment, the components can be mixed by impingement mixing wherein the components are injected at high velocity and pressure into a mixing chamber, and the components are then mixed in the chamber by kinetic energy. In this embodiment, the components are typically injected at a velocity of from 100 to 200 meters per second, and a pressure of from 20 to 3000 bar.

[0062] In alternate non-limiting embodiments, polyurethane prepolymer and optionally polyisocyanate can be contained in a first feed of a mixing unit, the amine-containing agent and optionally hydroxyl-containing material in a second feed and the blowing agent in a third feed; or the second feed can include both the amine-containing material and the blowing agent, and optionally hydroxyl-containing material.

[0063] In another non-limiting embodiment, the polyurethane

urea can be prepared by a one-pot process by combining polyisocyanate and/or polyurethane prepolymer, hydroxyl-containing material, amine-containing material and blowing agent.

[0064] In a non-limiting embodiment of the present invention, a mixing unit having three feeds can be used in combining the polyisocyanate and/or polyurethane prepolymer, hydroxyl-containing material, amine-containing material and blowing agent. The ingredients can be added into the feeds using a variety of configurations. In alternate non-limiting embodiments, the first feed of a mixing unit can contain polyisocyanate and/or polyurethane prepolymer and the second feed can contain hydroxyl-containing material, amine-curing agent and blowing agent; or the second feed can contain hydroxyl-containing material and amine-containing material, and a third feed can contain blowing agent; or the second feed can contain amine-containing material, and the third feed can contain hydroxyl-containing material and blowing agent; or the second feed can contain hydroxyl-containing material, and the third feed can contain amine-containing material and blowing agent. In further non-limiting embodiments, wherein polyurethane prepolymer is present in a first feed, the presence of hydroxyl-containing material in another feed is optional.

[0065] A blowing agent can be used in the present invention to form cells at least partially filled with gas within the polyurethane urea material. In a non-limiting embodiment, the cells are substantially uniformly distributed throughout the polyurethane urea material. The size of the cells can vary widely. In alternate non-limiting embodiments, a cell can be from at least 1 micron, or at least 20 microns, or at least 30 microns, or at least 40 microns; to less than 1000 microns, or less than 500 microns or less than 100 microns.

[0066] In a non-limiting embodiment, the blowing agent can be water. The water can react in-situ with isocyanate (NCO) to produce carbon dioxide. In a further non-limiting embodiment, one or more auxiliary blowing agents can be used in combination with the blowing agent. Suitable auxiliary blowing agents for use in the present invention can vary widely and can include substances which can be substantially volatile at the reaction temperature. The

auxiliary blowing agent can be selected from those known in the art. Non-limiting examples can include but are not limited to acetone, ethyl acetate, halogen substituted alkanes such as methylene chloride, chloroform, ethylidene chloride, vinylidene chloride, monofluorotrichloromethane, chlorodifluoromethane, dichlorodifluoromethane, dichloromonofluoromethane, butane, pentane, cyclopentane hexane, heptane, and diethylether.

[0067] The amount of blowing agent used in the present invention can vary. In alternate non-limiting embodiments, the blowing agent can be present in an amount such that a selected or desired density and/or pore volume of the polishing pad can be achieved. In alternate non-limiting embodiments, the density can be from 0.50 to 1.10 g/cc; the pore volume can be from 5% to 55% based on volume of polyurethane urea material. Density can be measured using a variety of methods known to one of ordinary skill in the art. The density values recited herein are determined in accordance with ASTM 1622-88. Pore volume can also be measured using a variety of methods known to a skilled artisan. The pore volume values recited herein are determined in accordance with ASTM D 4284-88, using an Autopore III mercury porosimeter manufactured by Micromeritics. In a further non-limiting embodiment, the amount of blowing agent can be from 0 to 5% by weight of the reaction mixture.

[0068] In a non-limiting embodiment, the amine-containing material can contain at least a small concentration of residual moisture or water sufficient to act as the blowing agent.

[0069] In another non-limiting embodiment, a urethane-forming catalyst and/or blowing catalyst can be used in the present invention to enhance the reaction of the polyurethane urea-forming materials, and/or accelerate the reaction with blowing agent. In a further non-limiting embodiment, one or more materials can be used wherein each material can exhibit characteristics of a urethane-forming and blowing catalyst.

[0070] Suitable urethane-forming catalysts can vary widely, for example, suitable urethane-forming catalysts can include those catalysts that are known in the art to be useful for the formation of urethane by reaction of the NCO and OH-containing materials. Non-limiting examples of suitable catalysts can be chosen from the

group of Lewis bases, Lewis acids and insertion catalysts as described in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, 1992, Volume A21, pp. 673 to 674. In a non-limiting embodiment, the catalyst can be a stannous salt of an organic acid, such as but not limited to stannous octoate, dibutyl tin dilaurate, dibutyl tin diacetate, dibutyl tin mercaptide, dibutyl tin dimaleate, dimethyl tin diacetate, dimethyl tin dilaurate, and mixtures thereof. In alternate non-limiting embodiments, the catalyst can be zinc octoate, bismuth, or ferric acetylacetonate.

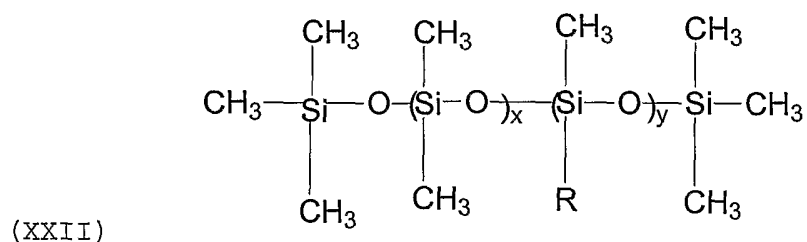
[0071] Non-limiting examples of suitable blowing catalysts can include tertiary amines such as but not limited to 1,4-diazabicyclo[2.2.2]octane, bis-2-dimethyl aminoethyl ether, pentamethyldiethylene triamine, triethylamine, triisopropylamine, N-methylmorpholine and N,N-dimethylbenzylamine. Such suitable tertiary amines are disclosed in United States Patent 5,693,738 at column 10, lines 6-38, the disclosure of which is incorporated herein by reference. Tertiary amine catalysts may also include those containing hydroxyl functionality such as N,N-dimethylethanolamine, 2-(2-dimethylaminoethoxy-)ethanol, N,N,N'-trimethyl-N'-hydroxyethyl-bisaminoether, N,N-(dimethyl)-N,N'-diisopropanol-1,3-propanediamine, and N,N-bis-(3-dimethylaminopropyl)-N-isopropanolamine.

[0072] In a non-limiting embodiment the catalyst can be chosen from phosphines, tertiary ammonium salts and tertiary amines, such as but not limited to tributyl phosphine, triethylamine; triisopropylamine and N,N-dimethylbenzylamine. Additional non-limiting examples of suitable tertiary amines are disclosed in United States Patent 5,693,738 at column 10 lines 6 through 38, the disclosure of which is incorporated herein by reference.

[0073] In another non-limiting embodiment, a surfactant can be present during polymerization. Surfactants can influence the formation and stabilization of the at least partially gas-filled cells. In a non-limiting embodiment, the surfactant can be selected such that it has high surface activity for nucleation and stabilization of the cells. In another non-limiting embodiment, the surfactant can be selected such that it has good emulsifying abilities for a blowing agent. Suitable surfactants for use in the

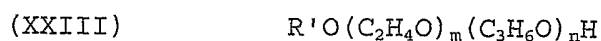
present invention are wide and varied. In a non-limiting embodiment, a silicone surfactant can be used. The silicone surfactant can be selected from siloxane-polyoxyalkylene copolymer surfactants. Non-limiting examples of such surfactants can include but are not limited to polydimethylsiloxane-polyoxyalkylene block copolymers which are available from GE Silicons Incorporated under the designations Niasx RTM. Silicone L-1800, L-5420 and L-5340; Dow Corning Corporation under the designations DC-193, DC-5357 and DC-5315; and Goldschmidt Chemical Corporation under the designations B-8404 and B-8407.

[0074] In a further non-limiting embodiment, the siloxane-polyoxyalkylene copolymer surfactant can be represented by the following general formula,



wherein x is a number from 1 to 150, y is a number of from 1 to 50, the ratio of x:y is from 10:1 to 1:1 and R is an alkyl alkoxyate. With reference to the general formula I, x can be from 10 to 50, or from 10 to 42, or from 13 to 42; and y can be from 2 to 20, or from 5 to 20, or from 7 to 20, or from 7 to 10. The ratio of x:y can be between 2.4 and 6.8.

[0075] R can be an alkyl alkoxyate which can be represented by the following general formula XXIII,



wherein R' is an alkylene group containing from 3 to 6 carbon atoms, m is a number of from 5 to 200, and n is a number of from 0 to 20, or from 2 to 18. The molecular weight of R is in the range of from 400 to 4000, and the molecular weight of the surfactant represented by general formula XXII can be from 6,000 to 50,000.

[0076] The siloxane-polyoxyalkylene copolymer surfactant can be prepared as described in United States Patent 5,691,392, column 3, line 25 through column 4, line 18, which is incorporated herein by reference.

[0077] The amount of surfactant useful in the present invention can vary widely. In alternate non-limiting embodiments, the amount is such that the surfactant is from 0.001% to 10%, or 0.01% to 1%, or from 0.05% to 0.5% by weight of the reaction mixture.

[0078] In another non-limiting embodiment, a nucleating agent can be used during polymerization in preparing the polyurethane urea of the present invention. Suitable nucleating agents for use in the present invention can include materials which enhance the generation of relatively small substantially uniform cells. The nucleating agent can be selected from those known in the art. Non-limiting examples can include but are not limited to relatively small size polymer particles such as but not limited to polypropylene, polyethylene, polystyrene, polyurethane, polyester, and polyacrylates. The amount of nucleating agent used can vary widely. In general, the nucleating agent can be used in an amount which is effective to generate said cells. In alternate non-limiting embodiments, the nucleating agent can be present in an amount of from 0.01% to 1.00%, or from 0.05% to 0.5%, by weight of the reaction mixture.

[0079] In a non-limiting embodiment, feeds containing polyisocyanate and/or polyurethane prepolymer, hydroxyl-containing material, amine-containing material, blowing agent and any optional additives can be directed into a mixing unit. Optional additives can include a wide variety of additives known to one having ordinary skill in the art. Non-limiting examples can include but are not limited to antioxidants, hindered amine UV stabilizers, UV absorbers, plasticizers, internal mold release agents, dyes and pigments. In further alternate non-limiting embodiments, any or all of the feeds can be heated to reduce the viscosity of the feeds and/or the resulting mixture. The reaction mixture exiting the mixing unit then can be poured into an open cavity to form a polishing pad. In a non-limiting embodiment, the cavity can be

controlled to a temperature of from 22°C to 150°C, or from 60°C to 110°C.

[0080] The polishing pad of the present invention can have one or more work surfaces, wherein "work surface" as used herein and the claims refers to a surface of the pad that can come into contact with the surface of the article that is to be polished and a polishing slurry. In a non-limiting embodiment, the article to be polished can be a silicon wafer. In further non-limiting embodiments, the work surface of the polishing layer can have surface features such as but not limited to channels, grooves, perforations and combinations thereof.

[0081] Surface features can be incorporated into the work surface of the polishing layer by means that are known to those of ordinary skill in the art. In a non-limiting embodiment, the work surface can be mechanically modified, for example, by abrading or cutting. In another non-limiting embodiment, surface features can be incorporated into the work surface during the molding process, for example, by providing at least one interior surface of the mold with raised features that can be imprinted into the work surface during its formation. Surface features can be distributed in the form of random or uniform patterns across the work surface. Non-limiting examples of surface feature patterns can include but are not limited to spirals, circles, squares, cross-hatches and waffle-like patterns.

[0082] In a non-limiting embodiment, the polyurethane urea can comprise an abrasive particulate material. The abrasive particulate material can be distributed substantially uniformly or non-uniformly throughout the polyurethane urea. In alternate non-limiting embodiments, the abrasive particulate material can be present in an amount of less than 70 percent by weight, or at least 5 percent by weight, or from 5 percent to 65 percent by weight, based on the total weight of the polishing pad.

[0083] In alternate non-limiting embodiments, the abrasive particulate material can be in the form of individual particles, aggregates of individual particles, or a combination of individual particles and aggregates. In further alternate non-limiting embodiments, the shape of the abrasive particulate material can

include but is not limited to spheres, rods, triangles, pyramids, cones, regular cubes, irregular cubes, and mixtures and/or combinations thereof.

[0084] In general, the average particle size of the Abrasive particulate material can vary widely. In alternate non-limiting embodiments, the average particle size can be at least 0.001 micron, or at least 0.01 micron, or at least 0.1 micron. In further alternate non-limiting embodiments, the average particle size of the abrasive particulate material can be less than 50 microns, or less than 10 microns, or less than 1 micron. In a non-limiting embodiment, the average particle size of the abrasive particulate material can be measured along the longest dimension of the particle.

[0085] Non-limiting examples of suitable abrasive particulate materials for use in the present invention can include aluminum oxide, such as but not limited to gamma alumina, fused aluminum oxide, heat treated aluminum oxide, white fused aluminum oxide, and sol gel derived alumina; silicon carbide, such as but not limited to green silicon carbide and black silicon carbide; titanium diboride; boron carbide; silicon nitride; tungsten carbide; titanium carbide; diamond; boron nitride, such as but not limited to cubic boron nitride and hexagonal boron nitride; garnet; fused alumina zirconia; silica, such as but not limited to fumed silica; iron oxide; cromia; ceria; zirconia; titania; tin oxide; manganese oxide; and mixtures thereof. In a further non-limiting embodiment, the abrasive particulate material can be chosen from aluminum oxide, silica, cerium oxide, zirconia and mixtures thereof.

[0086] In a non-limiting embodiment, the abrasive particulate material used in the present invention can have a surface modifier thereon. Non-limiting examples of suitable surface modifiers can include surfactants, coupling agents and mixtures thereof. In a non-limiting embodiment, surfactants can be used to improve the dispersibility of the abrasive particles in the polyurethane urea. In another non-limiting embodiment, coupling agents can be used to enhance binding of the abrasive particles to the matrix of the polyurethane urea. In further non-limiting embodiments, the surface modifier can be present in an amount of

less than 25 percent by weight, or from 0.5 to 10 percent by weight, based on the total weight of the abrasive particulate material and surface modifier.

[0087] Non-limiting examples of suitable surfactants for use as surface modifiers in the present invention can include anionic, cationic, amphoteric and nonionic surfactants, such as but not limited to metal alkoxides, polalkylene oxides, salts of long chain fatty carboxylic acids. Non-limiting examples of suitable coupling agents for use in the present invention can include silanes, such as but not limited to organosilanes, titanates and zircoaluminates. In a non-limiting embodiment, the coupling agent can include SILQUEST Silanes A-174 and A-1230, which are commercially available from Witco Corporation.

[0088] In a further non-limiting embodiment, the thickness of the polishing layer can vary from 0.5 mm to 5 mm.

[0089] In a non-limiting embodiment, the polishing layer can have a density of from 0.5 grams per cubic centimeter (g/cc) to 1.1 g/cc as measured by ASTM 1622-88. In another non-limiting embodiment, the polishing layer can have a Shore A Hardness value of at least 80, or from 85 to 98, and Shore D Hardness value of at least 35, or 85 or less, or from 45 to 80, as determined in accordance with ASTM D 2240.

[0090] While not intending to be bound by any theory, it is believed that when in use, while polishing or planarizing the surface of a silicon wafer, the porosity of the work surface of the polishing layer can remain substantially constant. As the work surface of the polishing pad is worn away during, for example a polishing or pad conditioning process, new surface pores are formed as those embedded pores residing proximately below the work surface are exposed. Further, as the work surface of the polishing pad is worn away during the polishing process, the gas contained within the at least partially gas-filled cells can be exposed. The gas can be released into the work environment and the remaining void(s) can be at least partially filled with polishing slurry.

[0091] The polishing pad of the present invention includes a second layer at least partially connected to the polishing layer. The second layer can include a variety of materials known in the

art. The second layer can be selected from substantially non-volume compressible polymers and metallic films and foils. As used herein and the claims, "substantially non-volume compressible" means that the volume can be reduced by less than 1% when a load of 20 psi is applied.

[0092] Non-limiting examples of substantially non-volume compressible polymers can include polyolefins, such as but not limited to low density polyethylene, high density polyethylene, ultra-high molecular weight polyethylene and polypropylene; polyvinylchloride; cellulose-based polymers, such as but not limited to cellulose acetate and cellulose butyrate; acrylics; polyesters and co-polyesters, such as but not limited to PET and PETG; polycarbonate; polyamides, such as but not limited to nylon 6/6 and nylon 6/12; and high performance plastics, such as but not limited to polyetheretherketone, polyphenylene oxide, polysulfone, polyimide, and polyetherimide; and mixtures thereof.

[0093] Non-limiting examples of metallic films can include but are not limited to aluminum, copper, brass, nickel, stainless steel, and combinations thereof.

[0094] The thickness of the second layer can vary. In alternate non-limiting embodiments, the second layer can have a thickness of at least 0.0005, or at least 0.0010; or 0.0650 inches or less, or 0.0030 inches or less.

[0095] In a non-limiting embodiment, the second layer can be flexible to enhance or increase the uniformity of contact between the polishing pad and the surface of the substrate being polished. A consideration in selecting the material for the second layer can be the capability of a material to provide compliant support to the work surface of the polishing pad such that the polishing pad substantially conforms to the macroscopic contour or long-term surface of the device being polished. A material having said capability can be desirable for use as the second layer in the present invention.

[0096] The flexibility of the second layer can vary. The flexibility can be determined using a variety of conventional techniques known in the art. As used herein and the claims the term "flexibility" (F) refers to the inverse relationship of the second

layer thickness cubed (t^3) and the flexural modulus of the second layer material (E), i.e. $F = 1/t^3E$. In alternate non-limiting embodiments, the flexibility of the second layer can be at least $0.5 \text{ in}^{-1}\text{lb}^{-1}$; or at least $100 \text{ in}^{-1}\text{lb}^{-1}$; or from $1 \text{ in}^{-1}\text{lb}^{-1}$ to $100 \text{ in}^{-1}\text{lb}^{-1}$.

[0097] In a non-limiting embodiment, the second layer can have a compressibility which allows the polishing pad to substantially conform to the surface of the article to be polished. The surface of a microelectronic substrate, such as a semiconductor wafer, can have a "wave" contour as a result of the manufacturing process. It is contemplated that if the polishing pad cannot adequately conform to the "wave" contour of the substrate surface, the uniformity of the polishing performance can be degraded. For example, if the pad substantially conforms the ends of the "wave", but cannot substantially conform and contact the middle portion of the "wave", only the ends of the "wave" can be polished or planarized and the middle portion can remain substantially unpolished or unplanarized.

[0098] The compressibility of the second layer can vary. The term "compressibility" refers to the percent volume compressibility measurement when a load of 20 psi is applied. In alternate non-limiting embodiments, the percent volume compressibility of the second layer can be at least one percent; or three percent or less; or from one to three percent. The percent volume compressibility can be determined using a variety of conventional methods known in the art.

[0099] In a non-limiting embodiment, the second layer is substantially non-volume compressible.

[00100] In another non-limiting embodiment, the second layer can distribute the compressive forces experienced by the polishing pad over a larger area of a sub-pad layer.

[00101] In a non-limiting embodiment, the polishing pad of the present invention can be used without a sub-pad layer. The polishing pad without a sub-pad layer can be placed directly on the platen of a motorized polishing tool, machine, or apparatus. In a further non-limiting embodiment, the polishing pad can be included in a polishing pad assembly, wherein a backing layer can be adhered

to the back surface of the polishing pad. In a non-limiting embodiment, a polishing pad assembly can comprise:

- (a) a polishing pad having a work surface and a back surface;
- (b) a backing layer having an upper surface and a lower surface; and
- (c) an adhesive means interposed between and in contact with at least a portion of the back surface of said polishing pad and at least a portion of the upper surface of said backing layer.

[00102] In a non-limiting embodiment, the backing sheet of the polishing pad assembly can be rigid or flexible, and can support or stabilize or cushion the polishing pad during polishing operations. The backing sheet can be fabricated from materials that are known to the skilled artisan. In alternate non-limiting embodiments, the backing sheet can be fabricated from organic polymeric materials, such as but not limited to polyesters, such as polyethylene terephthalate sheet, and polyolefins, such as polyethylene sheet and polypropylene sheet.

[00103] In another non-limiting embodiment, the backing sheet of the polishing pad assembly of the present invention can be a release sheet, which can be peeled away from the adhesive means, thereby allowing the pad to be adhered to another surface, for example, the platen of a polishing apparatus, by means of the exposed adhesive means. In general, release sheets are known to those of ordinary skill in art. In a non-limiting embodiment, the release sheet can be fabricated from paper or organic polymeric materials, such as but not limited to polyethylene terephthalate sheet, polyolefins, for example, polyethylene sheet and polypropylene sheet, and fluorinated polyolefins, for example, polytetrafluoroethylene. In a further non-limiting embodiment, the upper surface of the release sheet can comprise a release coating thereon that can be in contact with the adhesive means. Release coatings are well known to the skilled artisan. Non-limiting examples of release coatings can include fluorinated polymers and silicones.

[00104] The adhesive can be chosen from a wide variety of adhesive materials known in the art. A suitable adhesive for use in the present invention can provide sufficient peel resistance such

that the pad layers essentially remain in place during use. Further, the adhesive can be selected to sufficiently withstand shear stresses which are present during the polishing or planarization process and moreover, can sufficiently resist chemical and moisture degradation during use. The adhesive can be applied using conventional techniques known to the skilled artisan. In a non-limiting embodiment, the adhesive can be applied to a lower surface of the polishing pad and/or an upper surface of the second layer which are parallel facing to one another.

[00105] Non-limiting examples of suitable adhesive means can include but not limited to contact adhesives, pressure sensitive adhesives, structural adhesives, hot melt adhesives, thermoplastic adhesives, and curable adhesives, such as thermosetting adhesives. Non-limiting examples of structural adhesives can be chosen from polyurethane adhesives, and epoxy resin adhesives; such as those based on the diglycidyl ether of bisphenol A. Non-limiting examples of pressure sensitive adhesives can include an elastomeric polymer and a tackifying resin.

[00106] The elastomeric polymer can be chosen from natural rubber, butyl rubber, chlorinated rubber, polyisobutylene, poly(vinyl alkyl ethers), alkyd adhesives, acrylics such as those based on copolymers of 2-ethylhexyl acrylate and acrylic acid, block copolymers such as styrene-butadiene-styrene, and mixtures thereof. In a non-limiting embodiment, a pressure sensitive adhesive can be applied to a substrate using an organic solvent such as toluene or hexane, or from a water-based emulsion or from a melt. As used herein, "hot melt adhesive" refers to an adhesive comprised of a nonvolatile thermoplastic material that can be heated to a melt, then applied to a substrate as a liquid. Non-limiting examples of hot melt adhesives can be chosen from ethylene-vinyl acetate copolymers, styrene-butadiene copolymers, ethylene-ethyl acrylate copolymers, polyesters, polyamides such as those formed from the reaction of a diamine and a dimer acid, and polyurethanes.

[00107] In a non-limiting embodiment, the adhesive layer can be applied to the back surface of the polishing pad and/or the upper surface of the backing sheet, prior to pressing the polishing pad and backing sheet together.

[00108] In alternate non-limiting embodiments, the adhesive means of the polishing pad assembly can be selected from an adhesive assembly or an adhesive layer.

[00109] In further non-limiting embodiment, the adhesive assembly can comprise an adhesive support sheet interposed between an upper adhesive layer and a lower adhesive layer. The upper adhesive layer of the adhesive assembly can be in contact with the back surface of the polishing pad, and the lower adhesive layer can be in contact with the upper surface of the backing sheet. Non-limiting examples of adhesive support sheets can be fabricated from an organic polymeric material, such as but not limited to polyesters, for example, polyethylene terephthalate sheet, and polyolefins, for example, polyethylene sheet and polypropylene sheet. In a further non-limiting embodiment, the upper and lower adhesive layers of the adhesive assembly can be chosen from those adhesives as recited previously herein with regard to the adhesive layer. In a non-limiting embodiment, the upper and lower adhesive layers can each be contact adhesives. In a further non-limiting embodiment, the adhesive assembly can be a two-sided or double-coated tape, such as but not limited to double-coated film tapes, which can be commercially obtained from 3M, Industrial Tape and Specialties Division.

[00110] At least a portion of the polishing pad of the present invention includes an at least partially transparent window. In a non-limiting embodiment of the present invention, the polishing layer can comprise an opening. In a further non-limiting embodiment, at least a portion of the second layer can comprise a window which is at least partially transparent to wavelengths used by the metrology instrumentation of the planarizing equipment. The opening in the polishing layer can at least partially align with the window in the second layer. The size, shape, and positioning of the opening in the polishing layer and/or the window in the second layer can be dependent upon the metrology instrumentation and polishing apparatus being employed to polish and/or planarize the pad. The opening in the polishing layer can be produced by a variety of conventional methods known in the art. In alternate non-limiting embodiments, the opening can be made by punching, die cutting, laser

cutting or water jet cutting. In a further non-limiting embodiment, the opening can be formed when molding the polishing layer. In an alternate non-limiting embodiment, the opening can be die cut into the polishing layer using an NAEF Model B die press fitted with dies of suitable size and shape, which are commercially available from MS Instruments Company, Stony Brook, NY.

[00111] In a non-limiting embodiment, the opening in the polishing layer can be produced prior to stacking together and/or at least partially connecting the polishing layer with the second layer.

[00112] At least a portion of the second layer can comprise an at least partially transparent window. In a non-limiting embodiment, the second layer can comprise an at least partially transparent material. In another non-limiting embodiment, the second layer can comprise a substantially non-transparent material; an opening can be cut into the second layer to remove a portion of the second layer; an at least partially transparent material can be inserted into the opening in the second layer. The opening can be made using a variety of methods previously described herein. In a non-limiting example, the second layer can include a metal foil; an opening can be cut into the metal foil to remove a portion of the metal foil; a piece of polyester can be cut into a size and shape that substantially corresponds to the opening; the polyester can be fitted into the opening in the metal foil to form an at least partially transparent window.

[00113] In a non-limiting embodiment, the second layer can comprise an adhesive assembly. The adhesive assembly can include interposing a middle layer between an upper adhesive layer and a lower adhesive layer. In a non-limiting embodiment, the upper adhesive layer of the adhesive assembly can be at least partially connected to the lower surface of the polishing layer. In a non-limiting embodiment, the lower adhesive layer of the adhesive assembly can be at least partially connected to the platen of the polishing tool. In another non-limiting embodiment, the lower adhesive layer of the adhesive assembly can be at least partially connected to the upper surface of a sub-pad layer. The middle layer of the adhesive assembly can be selected from the aforementioned

suitable materials for the second layer of the polishing pad. The upper and lower adhesive layers of the adhesive assembly can be selected from the non-limiting examples of adhesives previously mentioned herein. In a non-limiting embodiment, the upper and lower adhesive layers each can be contact adhesives. The adhesive assembly can be referred to in the art as two-sided or double-coated tape. Non-limiting examples of commercially available adhesive assemblies include those from 3M, Industrial Tape and Specialties Division.

[00114] In a further non-limiting embodiment, at least a portion of the adhesive layer can be removed from the second layer of the adhesive assembly exposing at least a portion of the at least partially transparent middle layer of the adhesive assembly, thereby forming an at least partially transparent window in the second layer. In alternate non-limiting embodiments, the removal of the adhesive can be performed prior to stacking the layers or after the layers are stacked. The removal process can include a variety of methods known to the skilled artisan, including but not limited to dissolution of the adhesive in solvent or aqueous detergent solution, or physically stripping the adhesive from the second layer. In a non-limiting embodiment, physically stripping the adhesive can include contacting the adhesive with a material to which the adhesive substantially adheres, and then pulling the material from the second layer, whereby the adhesive is removed with the material.

[00115] In a further non-limiting embodiment, the window of the second layer can be recessed below the surface of the pad by a distance equal to the thickness of the polishing layer of the pad. In another non-limiting embodiment, the pad can include a coating on at least a portion of a side of the window of the second layer. The coating can be at least partially applied with an adhesive in place or following removal of the adhesive. The coating can be at least partially applied prior to stacking the layers or after the layers have been stacked. The coating can provide any one of the following properties, for example: improved transparency of the window area, improved abrasion resistance, improved puncture resistance.

[00116] In a non-limiting embodiment, the coating can

include a resin film, or a cast-in-place resin coating. Non-limiting examples of suitable resin films for use in the present invention can include the materials described above for the second layer. In alternative non-limiting embodiments, the resin film chosen for the coating can be the same material or different material as that comprising the second pad layer. The resin film can be at least partially adhered to the window area of the second layer by any means known to the skilled artisan, such as the adhesive methods and materials listed above for pad stack adhesives. In a non-limiting embodiment, the coating can be a layer of resin film that can be the same as the material used for the second layer. The coating can be at least partially applied after assembly of the pad stack. The coating can be at least partially applied to both the top and bottom surfaces of the window area of the second layer, and the adhesive can be at least partially adhered using a contact adhesive used as the stack adhesive.

[00117] In a non-limiting embodiment, the coating can be a cast-in-place resin coating, which can be applied as a liquid, as a solvent solution, dispersion, or aqueous latex, as a melt, or as a blend of resin precursors that can react to form the coating. The application of the liquid can be accomplished by a variety of known methods, including spraying, padding, and pouring. Non-limiting examples of suitable materials for the coating include thermoplastic acrylic resins, thermoset acrylic resins, such as hydroxyl-functional acrylic latexes crosslinked with urea-formaldehyde or melamine-formaldehyde resins, hydroxyl-functional acrylic resins crosslinked with epoxy resins, or carboxyfunctional acrylic latexes crosslinked with carbodiimides or polyimines or epoxy resins; urethane systems, such as hydroxyfunctional acrylic resin crosslinked with polyisocyanate, moisture-cured isocyanate-terminated resins; carbamate-functional acrylic resins crosslinked with melamine-formaldehyde resins; epoxy resins, such as polyamide resin crosslinked with bisphenol A epoxy resins, phenolic resins crosslinked with bisphenol A epoxy resins; polyester resins, such as hydroxyl-terminated polyesters crosslinked with melamine-formaldehyde resins or with polyisocyanates or with epoxy crosslinkers.

[00118] In a non-limiting embodiment, the coating can be an aqueous acrylic latex, which can be applied following stacking of the pad assembly. The coating can be at least partially applied to the top and bottom surfaces of the window area of the second layer. Application of the coating can be performed following removal of an adhesive from the window area.

[00119] In another non-limiting embodiment, the polishing pad of the present invention can include a sub-pad layer. The sub-pad layer can be at least partially connected to the second layer, and the second layer can be at least partially connected to the polishing layer. In a non-limiting embodiment, the second and/or sub-pad layers can be at least partially connected by an adhesive means. Suitable adhesive means can include those previously described herein. In a further non-limiting embodiment, a sub-pad layer can be used to increase the uniformity of contact between the polishing pad and the surface of the substrate which is being polished. The sub-pad layer can be made of a compressible material capable of imparting substantially even pressure to the work surface of the polishing pad. Non-limiting examples of sub-pad layers can include but are not limited to polyurethane or polyurethane urea impregnated felt, and foam sheet made of natural rubber, synthetic rubber, thermoplastic elastomer; or combinations thereof.

[00120] In alternate non-limiting embodiments, the material of the sub-pad layer can be foamed or blown to produce a porous structure. The porous structure can be open cell, closed cell, or combinations thereof.

[00121] Non-limiting examples of synthetic rubbers can include neoprene rubber, silicone rubber, chloroprene rubber, ethylene-propylene rubber, butyl rubber, polybutadiene rubber, polyisoprene rubber, EPDM polymers, styrene-butadiene copolymers, copolymers of ethylene and ethyl vinyl acetate, neoprene/vinyl nitrile rubber, neoprene/EPDM/SBR rubber, and combinations thereof. Non-limiting examples of thermoplastic elastomers can include polyurethanes such as those based on polyethers and polyesters, and copolymers thereof. Non-limiting examples of foam sheet can include polyurethane foam sheet and polyolefin foam sheets, such as but not

limited to those which are commercially available from Rogers Corporation, Woodstock, CT.

[00122] In a further non-limiting embodiment, the sub-pad layer can include non-woven or woven fiber mat, and combinations thereof; such as but not limited to polyolefin, polyester, polyamide, or acrylic fibers, which have been impregnated with a resin. The fibers can be staple or substantially continuous in the fiber mat. Non-limiting examples can include but are not limited to non-woven fabric impregnated with polyurethane, such as polyurethane impregnated felt. A non-limiting example of a commercially available non-woven sub-pad layer can be Suba™ IV, from Rodel, Inc. Newark DE.

[00123] The thickness of the sub-pad layer can vary widely. In general, the sub-pad layer thickness should be such that the stacked pad is not too thick. A stacked pad which is too thick can be difficult to place on and take off of the planarization equipment. Thus, in a non-limiting embodiment, the thickness of the sub-pad layer can be from 0.2 to 2 mm.

[00124] In a non-limiting embodiment, the polishing pad of the present invention can comprise a sub-pad layer, and the sub-pad layer can function as the bottom layer of the pad which can be attached to the platen of the polishing tool.

[00125] In a non-limiting embodiment, the sub-pad layer can be substantially nonporous and substantially impermeable to polishing slurry. As used herein and the claims, the term "substantially nonporous" means generally impervious to the passage of liquid, gas, and bacteria. On a macroscopic scale, a substantially nonporous material exhibits few if any pores. As used herein and the claims, the term "porous" means having pore(s) and the term "pore(s)" refers to minute opening(s) through which matter passes.

[00126] In another non-limiting embodiment, a three-layer stacked pad can be constructed by at least partially connecting the polishing layer to the second layer and at least partially connecting the second layer to a sub-pad layer. In a further non-limiting embodiment, a 22.0" diameter SUBA IV subpad commercially available from Rodel, Incorporated can comprise the sub-pad layer.

An opening can be cut into the polishing layer, second layer and sub-pad layer as described previously herein. In a further non-limiting embodiment, the opening can be rectangular in shape, having dimensions of 0.5" x 2.0", being positioned with the long axis radially oriented and centered 4" from the center of the pad. A window can be formed in the second layer as previously described herein. In alternate non-limiting embodiments, the opening can be cut into the SUBA IV pad prior to at least partially connecting it to the second layer, or the opening can be cut following at least partially connecting the polishing layer, second layer and sub-pad layer.

[00127] In another non-limiting embodiment, the window can be formed in the polishing layer and second layer assembly as previously described herein, and the sub-pad layer containing an opening then can be at least partially connected to the second layer such that the opening in the sub-pad layer is at least partially aligned with the opening in the polishing pad and window in the second layer. An opening can be cut into the sub-pad prior to or after at least partially connecting the sub-pad to the polishing pad and second layer assembly. In alternate non-limiting embodiments, the opening can be produced by any suitable means known in the art, such as those previously identified relative to the opening in the polishing layer. Further, as previously identified, the size, shape and position of the opening can be dependent upon the metrology instrumentation and polishing apparatus employed.

[00128] In another non-limiting embodiment, the polishing pad of the present invention can comprise a polishing layer, a second layer, and a sub-pad layer. The polishing and sub-pad layers can each comprise an opening. The openings in these two layers can be at least partially aligned with one another. At least a portion of the second layer can include an at least partially transparent window. The window can be at least partially coated on both sides with contact adhesive, and the layers can be pressed together to form a stacked pad assembly. The adhesive can then be physically stripped from the top and bottom surface of the window area of the second layer using a material to which the adhesive substantially adheres. A non-limiting example of a material to which the adhesive

substantially adheres is Teslin® SP-1000, a synthetic sheet material which is commercially available from PPG Industries, Inc, Pittsburgh, PA.

[00129] In a non-limiting embodiment, the polishing pad of the present invention can be used in combination with polishing slurries which are known in the art. Non-limiting examples of suitable slurries for use with the pad of the present invention, include but are not limited to the slurries disclosed in United States Patent Application having Serial Numbers 09/882,548 and 09/882, 549, which were both filed on June 14, 2001 and are pending. In a non-limiting embodiment, the polishing slurry can be interposed between the polishing pad and the substrate to be polished. The polishing or planarizing process can include moving the polishing pad relative to the substrate being polished. A variety of polishing slurries are known in the art. Non-limiting examples of suitable slurries for use in the present invention include slurries comprising abrasive particles. Abrasives that can be used in the slurries include particulate cerium oxide, particulate alumina, particulate silica and the like. Examples of commercial slurries for use in the polishing of semiconductor substrates include but are not limited to ILD1200 and ILD1300 available from Rodel, Inc. Newark DE and Semi-Sperse AM100 and Semi-Sperse 12 available from Cabot Microelectronics Materials Division.

[00130] The window pad of the present invention can be used with a variety of polishing equipment known in the art. In a non-limiting embodiment, a Mirra polisher, produced by Applied Materials Inc, Santa Clara CA, can be used wherein the shape of the opening is a rectangle, having a size 0.5" x 2", being positioned with the long axis radially oriented and centered 4" from the center of the pad. The platen for the Mirra polisher is 20" in diameter. A pad for use with this polisher can comprise a circle of a 20-inch diameter having a window located in the area as described.

[00131] In a further non-limiting embodiment, a Teres polisher commercially available from Lam Research Corporation, Fremont, CA, can be employed. This polisher uses a continuous belt instead of a circular platen. The pad for this polisher can be a continuous belt of 12" width and 93.25" circumference, which has a

window area suitably sized and positioned to align with the metrology window of the Teres polisher can be such that it can be at least partially aligned with the at least partially transparent window in the second layer.

[00132] The polishing pad of the present invention can have shapes chosen from but not limited to circles, ellipses, squares, rectangles and triangles. In a non-limiting embodiment, the polishing pad can be in the form of a continuous belt. The polishing pad according to the present invention can have a wide range of sizes and thicknesses. In a non-limiting embodiment, a circular polishing pad can have a diameter ranging from 3.8 cm to 137 cm.

[00133] The present invention is more particularly described in the following examples, which are intended to be illustrative only, since numerous modifications and variations therein will be apparent to those skilled in the art. Unless otherwise specified, all parts and all percentages are by weight.

EXAMPLE

Example 1

[00134] 36.00 kilograms of Airthane PHP-75D polyurethane prepolymer, 1.26 kilograms of Desmodur N 3300A and 0.19 kilograms of Niox L-1800 surfactant were charged into the first tank of a Baule' three-component low pressure dispensing machine and held at 140°F with 15 PSI of nitrogen pressure. This tank was mixed with low agitation. A curative mixture was prepared by melting 35.5 kilograms of Lonzacure MCDEA at a temperature of 210°F then 5.5 kilograms of Versalink P-250 were added with stirring. Next, 0.21 kilograms of Niox L1800 added and stirred until uniformly mixed. This curative mixture was then charged into the second tank and held at 210°F with 40 psi of nitrogen pressure and mixed with low agitation. Then a mixture of 219 grams Versalink P-650, 60 grams of DABCO BL-19 catalyst and 21 grams of deionized water were charged into the third tank at ambient temperature and pressure. The fluids of the first, second and third tanks were fed into a mixer, by constant delivery pumps, at a weight ratio of 242 grams from the first tank : 100 grams from the second tank : 1.80 grams from the

third tank. The fluids were mixed under high agitation and dispensed into an open circular mold having a diameter of 31 inches and a thickness of 0.090 inches which had been preheated to 160°F. The open mold was placed in an oven at 160°F for 15 minutes. After this time, the product was removed from the mold. Curing was continued for 18 hours at 230°F. The product was then allowed to cool to ambient temperature. A circular pad having a 20" diameter was cut from the molded part. The pad was then cut to a thickness of 0.090 inches and the upper and lower surfaces of the pad were made parallel using a milling machine. Concentric circular grooves 0.020" wide x 0.030" deep with a pitch of 0.060" were machined into the work surface. A window opening was then cut in the pad. The shape of the opening was rectangular, having dimensions of 0.5" x 2.0", being positioned with the long axis radially oriented and centered 4" from the center of the pad. A layer of double-coated film tape with release liner was then applied to the surface of the disk which was not grooved such that the rectangular opening in the first layer was substantially spanned by the tape. The film tape was commercially obtained from 3M as High Performance Double Coated Tape type 9500PC.

[00135] A stacked pad was constructed by mounting the polishing pad assembly on a third layer of subpad with opening. The subpad consisted of a polyurethane foam disk having a diameter of 20" which was die cut from a sheet of PORON FH 48 available from Rogers Corporation, Woodstock, CT,, having a thickness of 1.5 millimeters and a density of 0.48 g/cm³. Another double-coated film tape with release liner was commercially obtained from Adhesives Research, Inc. under the trade name ARclad 90334 was applied to one surface of the polyurethane foam. A window opening was then cut into the 20" diameter foam pad and ARclad 90334 tape with release liner. The shape of the opening was rectangular, having dimensions of 0.5" x 2.0", being positioned with the long axis radially oriented and centered 4" from the center of the pad. Next, the release liner of 3M 9500PC on the polishing pad assembly was removed, exposing the adhesive. The polishing pad assembly was then firmly bonded, with this adhesive, to the polyurethane foam side of the subpad. Care was taken during mounting so that the window

opening in the subpad was aligned with the pad window. The three-layer stack assembly was then passed through a calendar roll set. The adhesive on the upper and lower sides of the second layer in the window area was removed by contacting it with a ½"x2" rectangular piece of Teslin SP-1000, commercially available from PPG Industries, Incorporated. This was accomplished by pressing the piece by hand to ensure good contact between the adhesive and the Teslin SP-1000, then peeling away the Teslin SP-1000. The adhesive selectively adhered to the Teslin SP-1000, leaving the substantially clear film of the window free of adhesive. The resulting pad stack had a transparent rectangular window having a size of ½"x2". The remaining release liner on the subpad can be removed to permit attachment to a commercial planarizing apparatus.

In the claims:

1. A pad adapted to polish a microelectronic substrate, said pad comprising:
 - a. a polyurethane urea-containing polishing layer, said polishing layer comprising at least partially gas-filled cells, at least a portion of said at least partially gas-filled cells formed by an in-situ reaction, wherein an opening is formed in said polishing layer; and
 - b. a second layer wherein at least a portion of said second layer comprises an at least partially transparent window, wherein said polishing layer is at least partially connected to said second layer, and said opening in said polishing layer is at least partially aligned with said window of said second layer.
2. A pad adapted to polish a microelectronic substrate, said pad comprising:
 - a. a polyurethane urea-containing polishing layer, said polishing layer comprising at least partially gas-filled cells, said polishing layer formed by reaction of polyurethane prepolymer with amine-containing material and blowing agent, wherein an opening is formed in said polishing layer; and
 - b. a second layer wherein at least a portion of said second layer comprises an at least partially transparent window, wherein said polishing layer is at least partially connected to said second layer, and said opening in said polishing layer at least partially aligns with said window of said second layer.
3. A pad adapted to polish a microelectronic substrate, said pad comprising:
 - a. a polyurethane urea-containing polishing layer, said polishing layer comprising at least partially gas-filled cells, said polishing layer formed by reaction of polyisocyanate with hydroxyl-containing material, amine-containing material and blowing agent, wherein an opening is formed in said polishing layer; and

- b. a second layer wherein at least a portion of said second layer comprises an at least partially transparent window, wherein said polishing layer is at least partially connected to said second layer, and said opening in said polishing layer at least partially aligns with said window of said second layer.
4. A pad adapted to polish a microelectronic substrate, said pad comprising:
- a. a polyurethane urea-containing polishing layer, said polishing layer comprising at least partially gas-filled cells, said polishing layer formed by reaction of polyisocyanate and polyurethane prepolymer, amine-containing material, blowing agent, and optionally hydroxyl-containing material, wherein an opening is formed in said polishing layer; and
- b. a second layer wherein at least a portion of said second layer comprises an at least partially transparent window, wherein said polishing layer is at least partially connected to said second layer, and said opening in said polishing layer at least partially aligns with said window of said second layer.
5. The pad of claim 1, wherein said polishing layer is formed by reaction of hydroxyl-containing material, amine-containing material, blowing agent and at least one material selected from the group consisting of polyisocyanate, polyurethane prepolymer and mixtures thereof.
6. The pad of claim 1, wherein gas in at least a portion of said at least partially gas-filled cells is exposed when at least a portion of a work surface of said pad is at least partially worn away when said work surface is in contact with a substrate to be polished.
7. The pad of claim 3 wherein said polyisocyanate has at least two isocyanate functional groups.
8. The pad of claim 3 wherein said polyisocyanate is selected from the group consisting of polymeric and C₂-C₂₀ linear, branched, cyclic and aromatic polyisocyanates.

9. The pad of claim 2 wherein said hydroxyl-containing material is selected from the group consisting of polyether polyols, polyester polyols, polycaprolactone polyols, polycarbonate polyols, and mixtures thereof.
10. The pad of claim 2, wherein said amine-containing material is selected from the group consisting of aliphatic polyamines, cycloaliphatic polyamines, aromatic polyamines and mixtures thereof.
11. The pad of claim 2, wherein said amine-containing material comprises a polyamine and at least one material selected from the group consisting of polythiol and polyol.
12. The pad of claim 2, wherein said amine-containing material further comprises sulfur.
13. The pad of claim 2, further comprising at least one material selected from urethane catalyst, blowing catalyst, surfactant, and nucleating agent.
14. The pad of claim 1 wherein said pad has a work surface and said surface comprises at least one feature selected from the group consisting of channels, grooves and perforations.
15. The pad of claim 1 wherein said polyurethane urea comprises abrasive particulate material.
16. The pad of claim 15 wherein said abrasive particulate material is distributed substantially uniformly throughout said polyurethane urea.
17. The pad of claim 15 wherein said abrasive particulate material is present in an amount of from 5% by weight to less than 70% by weight based on the total weight of the pad.
18. The pad of claim 15 wherein said abrasive particulate material has an average particle size of from 0.001 micron to less than 50 microns.
19. The pad of claim 15 wherein said abrasive particulate material is silica.
20. The pad of claim 1 wherein said second layer is selected from polyolefins, cellulose-based polymers, acrylics, polyesters and co-polyesters, polycarbonates, polyamides, plastics, and combinations thereof.

21. The pad of claim 1 wherein said second layer is selected from substantially non-compressible polymers, metallic films and foils, and combinations thereof.
22. The pad of claim 1 further comprising a sub-pad layer having an opening formed therein, said sub-pad layer at least partially connected to said second layer, and wherein said opening in said sub-pad layer at least partially aligns with said window of said second layer and said opening in said polishing layer.
23. The pad of claim 22 wherein said sub-pad layer is chosen from non-woven fiber mat, woven fiber mat, or combinations thereof.
24. The pad of claim 22 wherein said sub-pad layer is chosen from polyurethane impregnated felt, polyurethane urea impregnated felt, or combinations thereof.
25. The pad of claim 22 wherein said sub-pad layer is selected from foam sheet containing natural rubbers, synthetic rubbers, thermoplastic elastomers or combinations thereof.
26. A method of preparing a pad adapted to polish microelectronic substrates, comprising:
 - a. forming a polyurethane urea-containing polishing layer wherein said polyurethane urea comprises at least partially gas-filled cells, and wherein at least a portion of said at least partially gas-filled cells is formed by an in-situ reaction;
 - b. forming an opening in said polishing layer;
 - c. forming a second layer which comprises an at least partially transparent window;
 - d. at least partially aligning said opening in said polishing layer and said window of said second layer; and
 - e. at least partially connecting said polishing layer and said second layer.
27. The method of claim 26 wherein said polishing layer is formed by combining polyisocyanate with hydroxyl-containing material, amine-containing material and blowing agent to produce polyurethane urea wherein at least a portion of said urea contains at least partially gas-filled cells.

28. The method of claim 26 wherein said polishing layer is formed by combining polyisocyanate with hydroxyl-containing material to form polyurethane prepolymer; and combining said polyurethane prepolymer with amine-containing material and blowing agent to form polyurethane urea wherein at least a portion of said urea contains at least partially gas-filled cells.
29. The method of claim 27 wherein said polishing layer is formed by combining polyisocyanate and polyurethane prepolymer with hydroxyl-containing, amine-containing material and blowing agent to form polyurethane urea wherein at least a portion of said urea contains at least partially gas-filled cells.
30. The method of claim 27 wherein ingredients are combined at a pressure of less than 20 bar.
31. The method of claim 28 wherein ingredients are combined at a pressure of at least 20 bar.
32. The method of claim 26 wherein said at least partially gas-filled cells comprise carbon dioxide.
33. The method of claim 26 wherein said at least partially gas-filled cells have an average size of from at least 1 micron to less than 100 microns.
34. The method of claim 26 wherein said substantially gas-filled cells are substantially uniformly distributed throughout said polyurethane urea.
35. The method of claim 27 wherein said blowing agent comprises water.
36. The method of claim 28 wherein said blowing agent is water.
37. The method of claim 27 further comprising adding an auxiliary blowing agent.
38. The method of claim 28 further comprising combining said polyurethane prepolymer with an auxiliary blowing agent.
39. The method of claim 37 wherein said auxiliary blowing agent is selected from the group consisting of acetone, ethyl acetate, and halogen-substituted alkanes.

40. The method of claim 38 wherein said auxiliary blowing agent is selected from the group consisting of acetone, ethyl acetate, and halogen-substituted alkanes.
41. The method of claim 26 further comprising:
- a. forming a sub-pad layer wherein an opening is formed therein;
 - b. at least partially aligning said opening in said sub-pad layer with said window of said second layer and said opening in said polishing layer; and
 - c. at least partially connecting said sub-pad layer and said second layer.
42. A pad assembly comprising:
- a. a polishing layer comprising polyurethane urea wherein at least a portion of said polyurethane urea comprises at least partially gas-filled cells wherein at least a portion of said cells are formed by an in-situ reaction, said polishing layer having a work surface and a back surface;
 - b. a backing sheet having an upper surface and a lower surface; and
 - c. an adhesive means interposed between and at least partially connecting said back surface of said polishing layer and an upper surface of said backing sheet, at least a portion of said adhesive means being at least partially transparent,
- wherein an opening is formed in each of said polishing layer and said backing sheet, and wherein said openings in each polishing layer and backing sheet are at least partially aligned with said transparent portion of said adhesive means, and wherein said polishing layer is at least partially connected to said adhesive means and said adhesive means is at least partially connected to said backing sheet.
43. The pad assembly of claim 42 wherein said polyurethane urea is formed by combining hydroxyl-containing material, amine-containing material, blowing agent and at least one material selected from the group consisting of polyisocyanate, polyurethane prepolymer and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/021176

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B24B37/04 B24D3/32 B32B5/20 C09J9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B24B B24D B32B C09J B29B B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 306 163 A (JSR CORPORATION) 2 May 2003 (2003-05-02) paragraphs '0156! - '0158!; claims 1-10; figures 1-28	1-43
Y	US 6 387 312 B1 (ROBERTS JOHN V. H ET AL) 14 May 2002 (2002-05-14) column 1, line 12 - line 38; claims 1-5 column 4, line 18 - line 62	1-43
Y	US 2004/021243 A1 (SHIH WEN-CHANG ET AL) 5 February 2004 (2004-02-05) paragraphs '0008!, '0017! - '0026!; claims 1-34; examples 1-3	1-43

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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