CLEANING LEAD-FRAMES TO IMPROVE WIREBONDING PROCESS

This application claims the priority to U.S. provisional application 61/478,582 filed April 25, 2011, incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0001] The present invention is directed to a method for cleaning metal surfaces on semiconductor chips and leadframes to improve the wirebonding process. In particular, the present invention is directed to a method involving exposing the metal surfaces to aqueous-based cleaning solutions to remove metal oxides, contamination, and other residues from the metal surfaces on the chips and leadframes.

[0002] During the production of semiconductor devices, leadframes are traditionally used as a cost-effective way to mount and process a plurality of semiconductor dies or chips concurrently. Each leadframe typically has a plurality of die pads for mounting the chips. The leadframe also acts as a means to electrically connect the chip to external devices via leads of the leadframe. Bonding wires are connected to electrical contacts found on the chip and said leads of the leadframe in a process known as wire bonding. The bond pads are typically composed of Al but they can also be Cu. The other ends of the wires are attached to the contact leads (can be Ag, Au, etc.) on the leadframe.

[0003] A typical conventional process for manufacturing a die package, in relevant part, is depicted in FIG. 1. First, at step 10, a die is cut or sawn from the wafer on which it has been formed. After the die has been cut from the wafer, the back side of the die is firmly attached to a carrier or leadframe in a die bonding or die attach step 12. Typically, in the die bonding step 12, the die is attached to the leadframe using an organic adhesive, such as an epoxy and then cured by baking. Once the epoxy has cured, in step 14 the die is bonded to the leadframe.

[0004] The above-described process of connecting the metal wires to the bond pads and contacts is called "wirebonding." One problem that can occur during wirebonding is that the metal wires do not stick to the bond pads and/or the contacts. Poor adhesion between the wires and the bond pads/contacts can have several causes such as, for

example, the metal surfaces are oxidized; and there is contamination on the metal surfaces. Poor adhesion between the metal wires and the bond pads/contacts can directly or indirectly cause process failures by such mechanisms as NSOP (No stick on pads), NSOL (Non stick on leads), short tails, lifted ball defects, poor intermetallic compound uniformity, bond pad cratering, voiding, etc. These not only lead to inefficient bonding processes, but can also cause poor device reliability. To improve the adhesion, the metal surfaces need to be cleaned before wirebonding.

[0005] In the past, before the wire bonding step 14, the front side of the die is cleaned by, for example, subjecting the leadframe and attached die to an argon plasma. This argon plasma process, however, has several drawbacks. For example, an argon plasma process does not completely clean residues and particulates on Cu and Al bond pads. Also, the argon plasma process does not efficiently remove copper or aluminum oxide from bond pads. As a final example, the argon plasma process does not efficiently remove other contaminants such as fluorine from Al bond pads, without causing damage to the treated components. Accordingly, there is a need for a method of cleaning the metal surfaces involved in the wirebonding process such as, for example, wires, bond pads, and leadframe contacts that does not suffer from the above-mentioned drawbacks.

BRIEF SUMMARY OF THE INVENTION

[0006] The present invention satisfies this need by providing a method of processing a leadframe assembly to remove undesired material therefrom or to prepare a surface of the leadframe assembly for subsequent bonding wherein a leadframe assembly comprises one or more of the following parts or components: leadframe, dies, dies having bond pads thereon, contacts, contact leads, and wires, the method comprising the step of contacting at least a portion of the leadframe assembly or parts of the leadframe assembly with a composition comprising water and at least one acid or at least one salt. The composition used in the contacting step may comprise from 0.003 to about 25% by weight of one or more carboxylic acids.

[0007] A method of processing a leadframe assembly or substrates comprising a leadframe and at least one of one or more of the following list of parts or components: dies, bond pads, die-attach materials, mold compounds, contacts, and wires, the method comprising the steps of: contacting the leadframe assembly (semiconductor substrate) or a portion thereof with a composition comprising, consisting essentially of or consisting of: an acid buffer solution having an acid selected from a carboxylic acid or a polybasic acid and a salt (for example an ammonium salt) of the acid in a molar ratio of acid to salt (for

example ammonium salt) ranging from 10:1 to 1:10; and optionally an organic polar solvent that may be miscible in all proportions in water; and optionally a fluoride, and water, wherein in some embodiments the composition has a pH ranging from about 3 to about 7, and wherein the leadframe may comprise aluminum metal on at least one surface; and the method may comprise the additional step of drying the semiconductor substrate.

[0008] In another aspect, the present invention provides a method of processing a semiconductor substrate or leadframe assembly or substrate to remove undesired material therefrom or to prepare a surface of the leadframe assembly or substrate for subsequent bonding wherein the leadframe assembly comprises a leadframe comprising at least one of one or more of the following list of components: die, bond pad, die-attach material, mold compound, contact, and wire, the method comprising the steps of: contacting the leadframe or portion of the leadframe with a composition comprising, consisting essentially of or consisting of: about 0.005 to about 16% by weight of at least one carboxylic acid, salt thereof or mixture thereof or an amine group-containing carboxylic acid, salt thereof or mixture thereof; about 0.003 to about 4% by weight of at least one hydroxyl carboxylic acid, salt thereof or mixture thereof or an amine group-containing hydroxyl carboxylic acid, salt thereof or mixture thereof; and the remainder being substantially water, and having a pH of about 1 to about 4, wherein the semiconductor substrate comprises copper metal on at least one surface; and drying the semiconductor substrate. In some embodiments, the dicarboxylic acids are preferred.

[0009] In yet another aspect, the present invention provides a method of processing a leadframe assembly comprising a leadframe, said method comprising: attaching one or more individual dies to a leadframe comprising contact leads to form an assembly having exposed (for example, aluminum, copper, Ni , Pd, Au, Ag, and Mg) metal surfaces; contacting the leadframe assembly with a composition comprising, consisting essentially of or consisting of: an acid buffer solution having an acid selected from a carboxylic acid or a polybasic acid and a salt (for example, an ammonium salt) of the acid in a molar ratio of acid to salt (for example, ammonium salt) ranging from 10:1 to 1:10; and optionally an organic polar solvent (that is miscible in all proportions in water); and optionally a fluoride, and water, wherein the composition may have a pH ranging from about 3 to about 7; drying the substrate; performing a wirebonding step comprising attaching wires between bond pads on the dies and the contact leads on the leadframe

to form a die and leadframe assembly; and forming a mold over the a die and leadframe assembly to form a packaged circuit.

[0010] In still yet another aspect, the present invention provides a method of processing a microelectronic device substrate comprising a leadframe, said method comprising: attaching individual dies to a leadframe comprising contact leads to form a substrate having exposed aluminum metal surfaces; contacting the semiconductor substrate with a composition comprising, consisting essentially of or consisting of: about 0.005 to about 16% by weight of at least one dicarboxylic acid, salt thereof or mixture thereof; about 0.003 to about 4% by weight of at least one hydroxyl carboxylic acid, salt thereof or mixture thereof or an amine group-containing acid, salt thereof or mixture thereof; and the remainder being substantially water, and having a pH of about 1 to about 4; drying the substrate; performing a wirebonding step comprising attaching wires between bond pads on the dies and the contact leads on the leadframe to form a die and leadframe assembly; and forming a mold over the a die and leadframe assembly to form a packaged circuit.

[0011] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims. All weight % described herein are based on the total weight of the composition unless otherwise specified. "Consisting essentially of" means that the composition may contain unclaimed components as long as those unclaimed components when added to an otherwise identical claimed cleaning composition do not materially impact the removal of metal oxide from the bond pads of the leadframe assemblies when used in the same cleaning process. The removal of metal oxide from the leadframe assembly is preferably about 2 Å/min or greater. The above oxide removal rate is not intended to indicate a limitation of the leadframe cleaning process. For instance, in a batch cleaning process one could immerse many leadframes into a cleaning bath containing the cleaning solutions described herein that give an oxide removal rate of 1-2 Å/min for long periods of time, e.g. 100 minutes, and still obtain a clean leadframe.

[0012] This invention further provides leadframe cleaning compositions useful in the methods described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The foregoing summary, as well as the following detailed description of preferred embodiments of the invention, will be better understood when read in

conjunction with the appended drawings. For the purpose of illustrating the invention, there is shown in the drawings embodiments that are presently preferred. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

[0014] FIG. 1 is a block diagram illustrating the conventional steps involved in the preparation of an integrated circuit device;

[0015] FIG. 2 is a block diagram illustrating the steps of a method of the present invention;

[0016] FIG. 3 is a graph illustrating the aluminum surface treatment performance of an embodiment of the present invention;

[0017] FIG. 4 is a graph illustrating the performance of an embodiment of the present invention;

[0018] FIG. 5 is a graph illustrating the performance of an embodiment of the present invention;

[0019] FIG. 6 is a graph illustrating the performance in terms of copper oxide removal and re-growth for an embodiment of the present invention; and

[0020] FIG. 7 is a graph illustrating the performance in terms of copper oxide removal and re-growth for an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The present invention relates to compositions for processing of microelectronic device substrates and packages, including compositions useful for the preparation of metal surfaces during the process of connecting metal wires from bond pads to leadframes during a wirebonding process. The term "leadframe" may be used; however it is not meant to be limiting and includes all types of semiconductor packaging substrates, such as, plated or unplated BGA and organic substrates and leadframes. The present invention also relates to methods of processing a leadframe assembly or semiconductor substrate to remove undesired material therefrom or to prepare a surface of the leadframe assembly or semiconductor substrate for subsequent bonding. The term "leadframe assembly" or "leadframe substrate" may be used to mean; however it is not meant to be limiting, any type of leadframe that has at least one or more dies bonded thereto and may also comprise other components that are part of, attached to, e.g. bonded or soldered, thereto.

[0022] For ease of reference, "microelectronic device" corresponds to semiconductor substrates and packages, flat panel displays, and microelectromechanical systems (MEMS), manufactured for use in microelectronic, integrated circuit, or computer chip applications. It is to be understood that the term "microelectronic device" is not meant to be limiting in any way and includes any substrate that will eventually become a microelectronic device or microelectronic assembly. Preferably, the microelectronic device comprises a leadframe assembly or semiconductor substrate.

[0023] As used herein "carboxylic acid" means (unless otherwise defined or apparent from the context) mono-, di- or poly- carboxylic acid, including amine group containing mono-, di- or poly- carboxylic acids, salts thereof or mixtures thereof, including hydroxy group containing mono-, di- or poly- carboxylic acids, salts thereof or mixtures thereof and/or other group-containing mono-, di- or poly- carboxylic acids.

[0024] As used herein, the term "semiconductor substrate" includes any substrate or partly formed package that will eventually become a microelectronic device or microelectronic assembly. Preferably, the semiconductor substrate comprises a leadframe assembly comprising a die attached to a leadframe.

[0025] As used herein, "about" is intended to correspond to ±5% of the stated value.

[0026] As used herein, "suitability" for cleaning contaminants from a microelectronic device having said contaminants (including metal oxides) thereon corresponds to at least partial removal of said residue/contaminants from the microelectronic device, more specifically the leadframe assembly or parts of the leadframe assembly, for example, the die or bond pads on the die. Preferably, at least 90% of the residue/contaminants is removed from the microelectronic device, more specifically the leadframe assembly or parts of the leadframe assembly, for example, the die or bond pads on the die, using the compositions and methods of the invention, more preferably, at least 99% of the residue/contaminants is removed.

[0027] It has become popular to fabricate integrated circuits using copper or aluminum interconnect metallization technology due to the advantages in electrical performance and cost. In order to prevent intermetallic phases, the ICs are provided with copper or aluminum pads. Typically, wire bonding of the IC with the chip carrier or leadframe is performed using gold and copper wire materials, although aluminum and silver have also been used. Bonding these wires to different pad materials produces different

metallurgical systems. Recently there has been a trend to move from gold to copper wire mainly motivated by reasons of significantly lower cost.

[0028] Unfortunately, both copper and aluminum oxidize very quickly, making it more difficult to achieve a reliable wire bond. Thus, to ensure bondability and reliability of the wire bond, one of the critical conditions is that the bonding surface should be free or substantially free of any contaminants, which includes oxides. Typically multiple circuits are formed on a single wafer at one place and then the wafers are transported to another place where the die are cut from the wafer and packaged. Since considerable time may pass between the wafer fabrication and the packaging processes, oxidation of the copper or aluminum bond pads on the dies can occur during such time. Accordingly, the present invention provides for effectively cleaning the copper and aluminum pads of an integrated circuit after fabrication of the circuit on a wafer, but before the die have been encapsulated or completely packaged.

[0029] Referring now to FIG. 2, a method of preparing a semiconductor wafer having a plurality of integrated circuits formed thereon. The integrated circuits may have bond pads formed of copper or aluminum. Methods of forming circuits with such pads on a silicon wafer are known and a detailed discussion thereof is not required for an understanding of the present invention. It is understood that the processes of the present invention are performed after an integrated circuit(s) has been formed on the wafer. Generally, this is after all layers have been applied to the wafer and the wafer has been rinsed in deionized water and the back of the wafer has been ground to remove unnecessary material. Later, the wafer is processed at a test/assembly/packaging facility where testing of each chip or die is performed when still as a wafer; at this step known as Wafer Level test, the good die are identified. The wafer is then diced or singulated by a dicing process. Each resulting chip or die that has been determined to pass the wafer level test ("known good die") may be attached to a leadframe by a die attach process step or steps, including applying epoxy, solder paste or other adhesive material to a leadframe and/or surface which may be the back surface of a die or dies and attaching the die or dies to the leadframe. The leadframe may have solder bumps or stud bumps or similar attachment parts formed thereon to receive the die and onto which the epoxy, solder paste or other adhesive material is applied or received. Typically, leadframes, which can be in the form of strips or continuous tapes/reels, contain many attached die that will later be formed into packages. If an epoxy is applied, the leadframe or substrate may then be epoxy-cured in a high temperature process to ensure proper adhesion of

the die to the substrate. If a solder paste is used, it will be followed by a soldering step. Subsequently, wires are connected between the bond pads on the die and the contacts on the leadframe. These leadframes or leadframe assemblies will (later) be singulated to form individual packages that will be molded and encapsulated. The present invention is directed to the cleaning performed on the leadframe assembly that may occur after the high temperature epoxy cure or other die attaching steps, and before wire bonding, and provides for removing oxides and other contaminants from the metal bond pads and leadframe or substrate contacts and surface.

[0030] Referring now to FIG. 2, a method of preparing a semiconductor wafer having a plurality of integrated circuits formed thereon is shown. The integrated circuits may have bond pads formed of copper or aluminum. Methods of forming circuits with such pads on a silicon wafer are known and a detailed discussion thereof is not required for an understanding of the present invention. It is understood that the processes of the present invention are performed after an integrated circuit(s) has been formed on the wafer. Generally, this is after all layers have been applied to the wafer and the wafer has been rinsed in deionized water and the back of the wafer has been ground to remove unnecessary material, and further, preferably after testing of each chip or die has been performed. Typically, after testing and before dicing is performed, the wafer is cleaned again using solvents such as deionized water, isopropyl alcohol, acetone, and methanol. The present invention is directed to the cleaning performed after the wafer typically has undergone testing, dicing, and either before or after the formation of the leadframe assembly and provides for removing oxides from the metal bond pads, and then attaching the leadwires to the bond pads. After those steps, may follow the step of molding a packing over the leadframe assembly typically under vacuum. Although not shown in Fig. 2, the method of this invention includes a method in which the cleaning step occurs just before or just before the formation of the leadframe assembly, followed by the formation of the leadframe assembly (that is, attachment of the die(s) to the leadframe) followed by the attachment of the leadwires to the bond pads.

[0031] More specifically, beginning at step 20, which is divided into step 20A and step 20B, the wafer and particularly the metal bond pads of each die are contacted with a cleaning composition, as shown either of two cleaning compositions, Composition A or Composition B, each of which will be described in more detail below. (The method in Figure 2 could have been shown with a single cleaning step.) Preferably, the cleaning step of the method of the present invention comprises contacting the leadframe

assembly or at least a portion of the leadframe assembly, such as the dies or bond pads on the dies that may be already attached to the leadframe, with either Composition A (preferably for Al-containing substrates) or Composition B (preferably for Al-containing or Cu-containing substrates). The at least a portion of the leadframe assembly is preferably dipped or immersed in a bath comprising the composition at room or elevated temperature for a time period of from between about 1 minute to about 40 minutes, preferably from about 5 minutes to about 30 minutes, and more preferably from about 20 to about 30 minutes.

[0032] The composition used to clean the bond pads of the leadframe assembly comprises an aqueous solution comprising an acid or a salt or a mixture of acid and salt. The composition used to clean the bond pads of the leadframe assembly comprises an aqueous solution comprising an acid, preferably one or more carboxylic acids or polybasic acids. The composition may comprise water and from about 0.003% by weight to about 25% by weight of one or more acids. Some embodiments of the composition may have a pH from 1 to 7. In some embodiments, the composition comprises an acid buffer solution; the acid being part of the acid buffer solution. In other embodiments, the composition comprises one or more carboxylic acids. The composition may comprise one or more acids, and/or one or more solvents and/or one or more fluorides (also referred to as fluoride containing compounds) and/or one or more additives. The additives may comprise surfactants and/or corrosion inhibitors. For example, some embodiments of compositions useful in the method of this invention comprise citric acid and optionally surfactant. Some embodiments of the composition may comprise in addition to one or more acids, 0% or 30% by weight to 90% by weight of an organic polar solvent; 0.0005% by weight to 20% by weight of a fluoride; 0.5% by weight to 40% by weight water; up to 15% by weight of an optional corrosion inhibitor and/or surfactant. Examples of some compositions useful in the method of this invention comprise water, acetic acid or citric acid, ammonium fluoride and dimethylacetamide and optionally propylene glycol and optionally corrosion inhibitor.

[0033] Composition A will be used to refer to those compositions useful in the method of this invention for cleaning leadframe assemblies that comprise an acid buffer solution. Composition B will be referred to those compositions useful in the method of this invention for cleaning leadframe assemblies that do not comprise an acid buffer solution.

Composition A

[0034] In one embodiment of the present invention, the cleaning composition is Composition A. Composition A is a cleaning composition comprising an acid buffer solution and water and may also comprise a polar solvent (that is preferably miscible in all proportions in water), and/or a fluoride. In certain embodiments, the composition is adjusted to a pH ranging from about 3 to about 7 and optionally includes a corrosion inhibitor and/or other additives. Some embodiments of composition A may be corrosion inhibitor-free, and/or additive-free and/or surfactant-free and/or solvent free. The acid that is part of the acid buffer solution preferably comprises a carboxylic acid and/or a polybasic acid.

[0035] Preferably, Composition A is comprised of an acid buffer solution in an amount necessary to obtain a composition with a pH ranging from 3 to 7; 0% by weight to 90% by weight or 30 % by weight to 90 % by weight of an organic polar solvent that is miscible in all proportions in water; 0.001% by weight to 20% by weight of a fluoride; 0.5% by weight to 40% by weight water; and up to 15% by weight of a corrosion inhibitor (and/or other additives). In alternative embodiments, the composition may comprise up to 90% by weight or greater than 90% by weight water.

[0036] As mentioned previously, Composition A described herein includes an acid buffer solution. The acid buffer solution, when added to the compositions disclosed herein, provides a buffered composition with a pH adjusted to minimize corrosion of sensitive metals such as aluminum, copper, titanium, etc. The acid buffer solution is added in an amount that is necessary to obtain the desired pH range for the composition. The term "acid buffer solution" as used herein, is a solution that resists changes in pH as a result of small additions of acids or bases to the composition. The addition of the acid buffer solutions to the compositions disclosed herein prevents pH swings due to dilution with water or contamination by bases or acids.

[0037] The molar ratio of acid to its conjugate base in the acid buffer solution to provide such a buffering effect within the composition ranges from 10:1 to 1:10, or substantially 1:1, or 1:1, where substantially means ± 2% by weight of the equimolar concentration. Buffers are typically thought of as weak acids and the widest buffering range against either an acid or a base is about one pH unit on either side of the pk_a of the weak acid group. Setting the pH for the buffer may be accomplished by having a molar ratio of acid to base ranging from 10:1 to 1:10 or substantially 1:1 of the acid and conjugate base for the acid (or in certain embodiments a protonated base) with the appropriate pk_a for the desired pH range.

[0038] In addition, certain salts having a pKa less than about 6 when dissolved in water may be used with or without the acid when dissolved in water to make the cleaning compositions.

[0039] In certain preferred embodiments, the acid buffer solution contains an ammonium salt of a carboxylic acid or a polybasic acid, such as, phosphoric acid. Exemplary acid buffer solutions may include acetic acid/acetate salts (e.g., ammonium salt, amine salts, etc.), benzoic acid/benzoate salts (e.g., ammonium salt, amine salts, etc.), and phenolic acid/phenolate salts (e.g., ammonium salt, amine salts, etc.). An example of an ammonium salt is an ammonium salt of acetic acid or phosphoric acid. In one embodiment, the acid buffer solution is an aqueous solution of ammonium acetate and acetic acid. In yet another embodiment, the acid buffer solution is benzoic acid and ammonium benzoate.

[0040] The composition may comprise from 0.003 to 30 % by weight or from 0.5 to 25 % by weight or from 0.5 to 20 % by weight or from 0.5 to 15 % by weight acid, that is the acid used in the buffer. In certain embodiments, the acid buffer solution may contain a weak acid such as trihydroxybenzene, dihydroxybenzene, and/or salicylhydroxamic acid. In these embodiments, the amount of weak acid added may range from 0.003 to 30 % by weight or from 0.5 to 25 % by weight or from 0.5 to 20 % by weight or from 0.5 to 3% by weight. The amount of conjugate base is a function of the amount of acid added to the composition to provide a buffering solution to the composition.

[0041] Although the pH of the composition according to the present invention may be from 1 to 11, in certain embodiments, a pH ranging from about 3 to about 9, or ranging from about 3 to about 7, or ranging from about 3 to about 6 will allow most sensitive metals to passivate with minimum corrosion. Preferably, the pH range is from about 3 to about 7.

[0042] One or more organic polar solvents that may be added to the compositions disclosed herein are those solvents that are miscible in water. These solvents may be used alone or in any combination. The one or more solvents in the compositions may be present therein comprise from about 0% by weight to about 90% by weight, or 30% by weight to about 90% by weight, or from about 30% by weight to about 70% by weight and may be organic polar solvent that is miscible in all proportions in water. Examples of organic polar solvents include, but are not limited to, dimethylacetamide (DMAC), monoethanolamine, n-methylethanolamine, formamide, n-methyl formamide, gamma-butyrolactone, N-methylpyrrolidone, and the like. Still further solvents include dihydric

and polyhydric alcohols such as diols and polyols such as (C_2– C_{20}) alkane diols and (C_3– C_{20}) alkane triols, cyclic alcohols and substituted alcohols. Other solvents include ureas, such as dimethyl urea, tetramethyl urea and the like. Particular examples of these organic polar solvents are propylene glycol, tetrahydrofurfuryl alcohol (THFA), diacetone alcohol and 1, 4-cyclohexanedimethanol. Preferred solvents include one or more of: dimethylacetamide, dimethyl urea, propylene glycol used alone or in combination with eachother or other solvents.

[0043] In certain embodiments, the organic polar solvent may be one or more glycol ethers. The glycol ethers are typically water miscible and may include glycol mono(C_1–C_6)alkyl ethers and glycol di(C_1– C_6)alkyl ethers, such as but not limited to, (C_1–C_{20})alkane diols, (C_1– C_6)alkyl ethers, and (C_1– C_{20})alkane diol di(C_1– C_6)alkyl ethers. Examples of glycol ethers are ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monoisopropyl ether, diethylene glycol monobutyl ether, diethylene glycol monoisobutyl ether, diethylene glycol monobenzyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, triethylene glycol monomethyl ether, triethylene glycol dimethyl ether, polyethylene glycol monomethyl ether, diethylene glycol methyl ethyl ether, triethylene glycol methyl ethyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol monobutyl ether, propylene glycol monopropyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monoisopropyl ether, dipropylene monobutyl ether, dipropylene glycol diisopropyl ether, tripropylene glycol monomethyl ether, 1-methoxy-2-butanol, 2-methoxy-1-butanol, 2-methoxy-2-methylbutanol, 1,1-dimethoxyethane and 2-(2-butoxyethoxy) ethanol. More typical examples of glycol ethers are propylene glycol monomethyl ether, propylene glycol monopropyl ether, tri(propylene glycol) monomethyl ether and 2-(2-butoxyethoxy) ethanol. One example is dipropylene glycol monomethyl ether used alone or in combination with other solvents in the compositions used in this invention.

[0044] Fluoride is preferably present in the compositions of Composition A described herein. Fluorides, also referred to as fluoride-containing compounds include those of the general formula $R_1R_2R_3R_4NF$ where R_1, R_2, R_3, and R_4 are independently hydrogen, an alcohol group, an alkoxy group, an alkyl group or mixtures thereof. Examples of such

compounds are ammonium fluoride (NH4F), tetramethyl ammonium fluoride, tetraethyl ammonium fluoride, tetrabutyl ammonium fluoride and choline fluoride. Still further examples of fluoride-containing compounds include fluoroboric acid, and hydrofluoric acid. The fluoride is preferably present in amounts of from 0.0005 or 0.001% by weight to 20% by weight or from 0.1% by weight to 10% by weight. Ammonium fluoride is preferred. In these embodiments, ammonium fluoride may be available commercially as a 40% aqueous solution.

[0045] Water is present as an element of the compositions of the present invention and used in the method of the present invention. It can be present coincidentally as a component of other elements of the invention such as an aqueous ammonium fluoride solution or an aqueous acid buffer solution, or it can be added separately. Preferably, water is present in amounts of from 0.5% by weight to 40% by weight. In certain embodiments, the presence of water may improve the solubility of ammonium fluoride in the compositions of the present invention and aids in the removal of contaminants.

[0046] Corrosion inhibitors, in an amount of up to 20% by weight, can be added to compositions of the present invention. Preferably, the inhibitor concentration is from about 0.5% by weight to 8% by weight. Any corrosion inhibitor known in the art for similar applications, such as those disclosed in U.S. Pat. No. 5,417,877 which are incorporated herein by reference may be used. In certain embodiments, it has been found that inhibitor compositions with a pKa greater than 6 do not function as well as inhibitor compositions having a pKa of less than about 6 in systems with a pH range of about 3 to about 6. Therefore, preferred inhibitor compositions are those having a pKa of about 6 or less. For lower pH cleaning solutions a pKa less than about 4 may be preferred. Corrosion inhibitors may be an organic acid, an organic acid salt, a phenol, a triazole, or a hydroxylamine. Examples of preferred inhibitor compositions include anthranilic acid, salicylic acid, gallic acid, benzoic acid, isophthalic acid, maleic acid, fumaric acid, D,L-malic acid, malonic acid, phthalic acid, maleic anhydride, phthalic anhydride, carboxybenzotriazole, diethyl hydroxylamine and the lactic acid and citric acid salts thereof, and the like. Further examples of corrosion inhibitors that may be used include catechol, tert-butyl catechol, pyrogallol, and esters of gallic acid, or catechol, salicylic acid, pyrogallol, and esters of gallic acid.

[0047] The composition may also include one or more of the following optional additives: surfactants, chelating agents, chemical modifiers, dyes, biocides, and other additives. The additive(s) may be added to the extent that they do not adversely affect

the pH range of the composition. Some examples of representative additives include acetylenic alcohols and derivatives thereof, acetylenic diols (non-ionic alkoxylated and/or self-emulsifiable acetylenic diol surfactants) and derivatives thereof, alcohols, quaternary amines and di-amines, amides (including aprotic solvents such as dimethyl formamide and dimethyl acetamide), alkyl alkanolamines (such as diethanolethylamine), and chelating agents such as beta-diketones, beta-ketoimines, carboxylic acids, mallic acid and tartaric acid based esters and diesters and derivatives thereof, and tertiary amines, diamines and triamines. Also included herein are the surfactants that are described below for Composition B at the amounts described for the surfactants and other additives. In certain embodiments, the carboxylic acid that may be added to the composition in the acid buffer solution may also serve as a chelating agent.

[0048] Formulations suitable for use as Composition A in the present invention are disclosed in U.S. Patent No. 6,828,289 and U.S. Patent No. 7,361,631, the disclosures of which are incorporated herein by reference in their entireties.

Composition B

[0049] Composition B will refer to those compositions useful in the method of this invention to clean leadframe assemblies that comprise one or more acids, but do not comprise an acid buffer solution.

[0050] Composition B is a fluoride-free or a fluoride containing aqueous composition. The term "fluoride-free" refers to at least substantially fluoride-free (e.g. containing no more than about 100 ppb of fluoride). Composition B may comprise about 0.003 to about 25% by weight acid, preferably one or more carboxylic acids and water (in an aqueous solution). In some embodiments the composition may comprise about 0.003 to about 25% by weight acid, water, and up to 20% by weight of one or more surfactants and/or one or more corrosion inhibitors. In some embodiments, the surfactant comprises one or more sulfonic acid surfactants.

[0051] In some embodiments, composition B may comprise 0.005 to about 16% by weight of at least one carboxylic acid, salt thereof or mixture thereof, which may be an amine group-containing carboxylic acid, salt thereof or mixture thereof; and/or about 0.003 to about 4% by weight of at least one hydroxyl carboxylic acid, salt thereof or mixture thereof or an amine group-containing carboxylic acid, salt thereof or mixture thereof, and the remainder being substantially water, and having a pH of about 1 to about 4.

[0052] In other embodiments, composition B may comprise 0.005 to about 16% by weight of at least one dicarboxylic acid, salt thereof or mixture thereof, about 0.003 to about 4% by weight of at least one hydroxy carboxylic acid, salt thereof or mixture thereof; or an amine group-containing carboxylic acid, salt thereof or mixture thereof, and the remainder being substantially water, and having a pH of about 1 to about 4.

[0053] Typical carboxylic acids include dicarboxylic acids, including those having two to six carbon atoms, and include oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid and fumaric acid. The preferred acid is citric acid. Suitable salts include the alkali metal and ammonium salts. A mixture comprising citric acid and oxalic acid and optionally malonic acid may be employed in Composition B. Examples of amine group containing dicarboxylic acids include glutamic acid and aspartic acid.

[0054] Examples of hydroxycarboxylic acids includes malic acid, tartaric acid and citric acid.

The preferred hydroxycarboxylic acid is citric acid. Suitable salts include alkali metal, and ammonium salts.

[0055] A preferred salt of a hydrocarboxylic acid is ammonium citrate.

[0056] The amine-containing carboxylic acid may be glycine, valine, alanine, phenylalanine, and the like.

[0057] Preferred mono-carboxylic acids include formic, acetic and propionic acids.

[0058] In certain embodiments, composition B may further comprise one or more solvents, preferably organic solvents or organic polar solvents, preferably that are miscible in water. These solvents may be used alone or in combination. All the solvents that were previously described as useful in Composition A are useful in any composition of this invention. The preferred solvents for use in Composition B are, although not limited to, dimethylacetamide (DMAC), monoethanolamine, n-methylethanolamine, formamide, n-methyl formamide, gamma-butyrolactone, N-methylpyrrolidone, and the like, dihydric and polyhydric alcohols such as diols and polyols such as (C_2– C_{20}) alkane diols and (C_3– C_{20}) alkane triols, cyclic alcohols and substituted alcohols urea, such as dimethyl urea, tetramethyl urea and the like. Particular examples of these organic polar solvents are propylene glycol, tetrahydrofurfuryl alcohol (THFA), diacetone alcohol and 1, 4-cyclohexanedimethanol and propylene glycol monomethyl ether. The solvent if present is preferably present in amounts of from 0 % by weight to 60 % by weight, or from 0 % by weight to 40 % by weight, or from 10 % by weight to 40 % by weight.

[0059] Composition B may further comprise one or more fluorides (that is fluoride containing compounds) described above for composition A. Examples of such compounds are ammonium fluoride, tetramethyl ammonium fluoride, tetraethyl ammonium fluoride, tetrabutyl ammonium fluoride and choline fluoride. Still further examples of fluoride-containing compounds include hydrofluoric acid. The fluoride-containing compound, if present, is preferably present in amounts of from 0.0005% by weight to 20% by weight or 0.001% by weight to 20 % by weight or from 0.1% by weight to 10% by weight or from 0.001% by weight to 5% by weight or from 0.001% by weight to 2% by weight. Ammonium fluoride is preferred. In some embodiments, ammonium fluoride may be available commercially as a 40% aqueous solution. In compositions comprising fluoride, it is preferred that organic solvent is also present therein, although there are also embodiments of Composition B that have fluoride and no organic solvent, and other embodiments having organic solvent and no fluoride present therein.

[0060] In addition to water, preferably deionized water, Composition B can include one or more of the following optional additives: surfactants, biocides, corrosion inhibitors, chelating agents, chemical modifiers, dyes, and other additives. One example of an additive includes up to about 0.002% by weight of the active portion of a biocide. A typical biocide is Kathan. Kathan comprises:

1.2% 5-chloro-2-methyl-4-isothiazolin-3-one
0.4% 2-methyl-4-isothiazolin-3-one
1.1% $MgCl_2$
1.75% $Mg(NO_3)_2$
0.16% copper nitrate trihydrate

water 95.85%. This biocide may be used in any composition of this invention.

[0061] The additive(s) may be added to the extent that they do not adversely affect the desired pH range of the composition. Some examples of representative additives include surfactants such as acetylenic alcohols and derivatives thereof, acetylenic diols (non-ionic alkoxylated and/or self-emulsifiable acetylenic diol surfactants) and derivatives thereof, sulfonic acid surfactants, such as linear alkylbenzenesulfonates (LAS), straight chain fatty acids and/or salts thereof, coconut oil fatty acid derivatives, tall oil acid derivatives, sarcosides, aceylated polypeptides, secondary alkylbenzenesulfonate, lignin sulfonates, N-acyl-n-alkyltaurates, fatty alcohol sulfates (FAS), petroleum sulfonates, secondary alkanesulfonates (SAS), paraffin sulfonates, fatty alcohol ether sulfates (FAES), α-Olefin sulfonates, sulfosuccinate esters, alkylnapthalenesulfonates,

isethionates, sulfuric acid esters, sulfated linear primary alcohols, sulfated polyoxyethylenated straight chain alcohols, sulfated triglyceride oils, phosphoric and polyphosphoric acid esters and perfluorinated anionics and mixtures thereof of these and any of the surfactants disclosed herein and other known surfactants, alcohols, quaternary amines and di-amines, amides (including aprotic solvents such as dimethyl formamide and dimethyl acetamide), alkyl alkanolamines (such as diethanolethylamine), and chelating agents such as beta-diketones, beta-ketoimines, carboxylic acids, mallic acid and tartaric acid based esters and diesters and derivatives thereof, and tertiary amines, diamines and triamines. In certain embodiments, the carboxylic acid that may be added to the composition may also serve as a chelating agent. Additives may be available commercially in relatively pure form or as diluted components in water or other solvents. SAS-10 for example is available as a 10 wt% concentration of SAS in water. Additives may also include the corrosion inhibitors and preferred corrosion inhibitors described earlier for Composition A; however, in certain embodiments, the inhibitor compositions with a pKa greater than about 4 do not function as well as inhibitor compositions having a pKa of less than about 4 in systems with a pH range of about 1 to about 4. The total amount of additives, if present, is typically from about 0.001 to about 10, or from about 0.005 to about 5, or from about 0.01 to about 1 weight %. The preferred additives are one or more surfactants and/or corrosion inhibitors. In embodiments that comprise carboxylic acids, surfactant and water, the preferred surfactants are one or more sulfonic acid surfactants.

[0062] One preferred embodiment comprises one or more acids, one or more fluorides, one or more organic solvents and one or more surfactants in the weight ranges defined herein for Composition B. Other preferred embodiments are compositions comprising one or more acids, one or more fluorides, one or more organic solvents and one or more corrosion inhibitors in the weight ranges defined herein for Composition B. Other compositions comprise water and acid and each of the fluorides, solvents and additives are optional components.

[0063] Composition B typically comprises greater than 35 wt % water. In embodiments without solvent, Composition B typically comprises greater than about 50, or greater than about 75, or greater than about 90, or greater than about 95.5, or greater than about 98 wt % water. When Composition B comprises one or more solvents, composition B typically comprises from 35 to 95 wt% water or from 40 to 90 wt% water or 45 to 85 wt% water.

[0064] The carboxylic or dicarboxylic acid and/or salt is typically present in amounts of about 0.005 to about 16 weight %, more typically about 0.1 to about 3 weight % and preferably about 0.3 to about 0.5 weight %. When mixtures of acids are used, examples being a mixture of oxalic and malonic acids, or citric acid and oxalic acid, each one is typically present in amounts of about 0.003 to about 8 weight %, more typically about 0.05 to about 1.5 weight % and preferably about 0.1 to about 0.3 weight %.

[0065] The hydroxycarboxylic acid, if present in the composition, is typically present in the composition at amounts of about 0.003% to about 8% by weight, more typically about 0.05 to about 1.5 weight % and preferably about 0.1% to about 0.3% by weight.

[0066] When employed, the amino-group containing acid such as glycine, if present in the composition, is typically employed in amounts of about 0.003 to about 4% by weight, more typically about 0.005 to about 1.5 weight % and preferably about 0.005 to about 0.05% by weight.

[0067] Although the pH of the composition according to the present invention may be from 1 to 11, it is preferred that, for Composition B, the pH preferably is from about 1 to about 4 and more preferably about 1 to about 3, a particular example being about 2. The pH is typically measured using pH paper or suitable pH reference electrode. It has been discovered according to the present invention that the pH is important in achieving objectives of the present invention. In particular, the compositions are capable of removing metallic and non-metallic particulate oxides, as well as silicon dioxide; metal ion contaminants such as K, Ca, Ti, Cr, Mn, Fe, Ni, Cu and Zn; various sulfur and chloride impurities adsorbed on the various surface materials present on the die or substrate.

[0068] A further feature of the present invention is that the composition even in concentrated form is relatively stable. For instance, concentrates of the composition comprising about 0.1 to about 16% by weight and preferably about 6% to about 10% by weight of the dicarboxylic acid, about 0.05% to about 8% by weight, and preferably about 3% to about 5% by weight of the dihydroxy carboxylic acid or amino acid and the remainder being substantially water can be provided and transported to the end user, the user can then dilute it such as about a 19:1 dilution by weight at the process tool for convenience and for economical reasons.

[0069] Formulations suitable for use as Composition B in the present invention are disclosed in U.S. Patent No. 6,627,546 and U.S. Patent No. 7,524,801, the disclosures of which are incorporated herein by reference in their entireties.

[0070] The cleaning process according to the present invention leaves the metal surfaces cleaner and, thus, provides for better adhesion between the metal wires and the bond pads on the dies and leadframe contacts.

[0071] Referring back to FIG. 2, after expositing (contacting) the substrate or a portion of the leadframe cleaning assembly to the cleaning compositions in either step 20A or 20B, the substrate is dried and the wirebonding step 14 is performed. The substrate may be actively or passively dried using either ambient or warm air that may be moved relative to the leadframe assemblies, for example by a commercial blow dryer or by moving the leadframe assemblies. Alternatively, the substrate may be dried using compressed air or a gas, such as nitrogen. The drying time may vary from a few seconds to a few minutes. However, it is preferred that the substrate is not exposed to ambient air for an extended period of time because that would allow the metal pads to oxidize.

[0072] A rinsing step with deionized water may be performed after the cleaning step and before the drying step.

[0073] Once the wirebonding is complete, the substrate is molded at step 16. Preferably, the substrate is vacuum packed at step 16. The vacuum packing may be performed using generally known commercially available vacuum packing equipment. Preferably the substrate is packed in a shock proof container made of a non-reactive material.

[0074] As is apparent, the present invention provides methods for preparing die with metal pads such that when the die on the wafers are ready to be packaged, the metal pads have less oxidation and other contaminants and thus wire bonding of the pads yields more reliable bonds. The present invention further provides a method of preparing a die with metal bond pads during the die packaging process that reduces oxidation and other contaminants on the metal bond pads so that wire bonding of the pads yields more reliable bonds. As will be appreciated, the present invention is directed to preparing metal bond pads, such as, for example, copper and aluminum pads, for wire bonding. The present invention is not limited to using copper wires for the wire bonding, as other wires could be used, such as gold or aluminum. Further, although the present invention has been performed using ball bonding, it is not limited to ball bonding, and may be practiced with wedge bonding.

[0075] Although the present invention has been principally described in connection with cleaning semiconductor substrates, the cleaning compositions of the invention can be employed to clean any substrate that includes organic and inorganic residues.

EXAMPLES

[0076] The following examples illustrate that cleaning solutions A1, A2, B1 and B2 will remove the metal oxides on the bond pads and contacts. These cleaning solutions will also remove contamination, fluorine, and other residues on the bond pads and contacts. These cleaning solutions will leave the metal surfaces in a cleaner state so the metal wires will have good adhesion during wirebonding. Cleaning solutions A1 and A2, which correspond to Composition A above, will remove metal oxides from Al bond pads. Cleaning solutions B1 and B2, which correspond to Composition B above, will remove metal oxides from Cu bond pads. The compositions evaluated are as follows:

[0077] Cleaning Solution A1: Dimethylacetamide (57.5%); DI Water (13.9%); Ammonium Acetate (15.6%); Acetic Acid (12.0%); Ammonium Fluoride (1.0%).

[0078] Cleaning Solution A2: N-Methy-2-Pyrrolidone (63.9%); DI Water (30.0%); Ammonium Acetate (2.6%); Acetic Acid (2.0%); Ammonium Fluoride (0.50%); Carboxy Benzotriazole (1.0%).

[0079] Cleaning Solution B1: DI Water (98.333%); Citric Acid (0.667%); Malonic Acid (0.333%); Oxalic Acid (0.667%).

[0080] Cleaning Solution B2: DI Water (98.27%); Citric Acid (0.667%); Malonic Acid (0.333%); Oxalic Acid (0.667%); SAS-10 (0.063%).

[0081] The process for cleaning leadframes (which have attached die) in cleaning solutions A1, A2, B1, and B2 is as follows. The cleaning solutions are applied to the leadframes after the die attach cure step and before the wirebonding step. The cleaning solutions are applied to the leadframes in any of these ways: 1) immersing the leadframes into a tank of the cleaning solution 2) spraying the cleaning solution onto the leadframes. The optimal temperature of the cleaning solutions ranges from 25°C to 50°C. The optimal time of exposure to the cleaning solutions ranges from 5 minutes to 30 minutes. After exposure to the cleaning solutions, the leadframes are rinsed with deionized water. The optimal temperature of the DI water rinse is 25°C (room temperature). The optimal time for the DI water rinse ranges from 30 seconds to 3 minutes. After rinsing the leadframes in DI water they are dried. Once the leadframes have been dried they can go to the wirebonding step.

Ability of Composition A to Remove Al Oxide

[0082] Shown below is data that was collected using X-Ray Photoelectron Spectroscopy (XPS). This data was collected on Al bond pads on die on a whole wafer. Prior to exposure to cleaning solution A, the thickness of the Al oxide layer on the Al bond pad was about 70-85 Å. After exposure to cleaning solutions A1 and A2 the thickness of the Al oxide decreased to about 30-40 Å which is the typical thickness of the native oxide layer that naturally forms on an Al surface. This data indicates that cleaning solutions A1 and A2 removed the Al oxide and then the native layer of Al oxide grew back. The net decrease in Al oxide thickness after exposure to cleaning solutions A1 and A2 is large and will improve the adhesion between the metal wires and the Al bond pads during wirebonding.

Table 1: XPS Data for Al Oxide Thickness / Patterned Al Bond Pad Wafers

Stripper	Time (minutes)	Al Oxide Thickness (Å)	
		Before Processing	After Processing
Cleaning Solution A1 @ 25°C	5	69	30
	30	71	32
Cleaning Solution A2 @ 25°C	5	87	34
	30	73	42

Process conditions: cleaning solution → DI water, 25°C, 30 seconds → N_2 blow dry

[0083] Referring to FIG. 3, additional data is presented showing cleaning solution A1 removing Al oxide. This data was collected using Auger depth profiling. Before exposure to cleaning solution A1, oxygen exists in the Al metal down to a depth of about 100 Å. Accordingly, this is a measurement of the thickness of the Al oxide layer. After exposure to cleaning solution A1 the oxygen only penetrates into the Al down to a depth of about 35 Å. The Al oxide thickness has been substantially decreased. And this is after letting the exposed Al bond pad sit in air for 3 days. Additional data is also shown after letting the Al bond pads sit in air for 14 days. Again, the depth of penetration of the oxygen level is much less than before exposure to cleaning solution A1.

Ability of Composition A to Remove Fluorine On Al Bond Pads

[0084] Another contaminant on Al bond pads that can cause poor adhesion is embedded fluorine (F). F can get on the Al bond pad, for example, during the plasma etch process used to etch through the passivation layer and open up the Al bond pad. The plasma is typically CF_4 based so the F from the plasma can get on the Al surface. F can react with moisture in the air to cause corrosion on the Al bond pads. This corrosion will continue to occur as long as the F is still on the Al. So removing this F will minimize

the corrosion that occurs as the Al bond pads sit in air. If less corrosion occurs then the Al surface will be cleaner and the metal wires will have better adhesion to the bond pads. FIGS. 4 and 5 show the ability of cleaning solution A1 to remove F from an Al bond pad.

Composition A Protects the Underlying Al

[0085] Cleaning solutions A1 and A2 are very effective in removing the Al oxide but they also need to have a very small etch rate on the underlying Al metal. If they remove the Al oxide and severely etch the underlying Al metal then the wirebonding performance may not improve. The data in Table 2 below shows that cleaning solutions A1 and A2 have very low etch rates on Al.

Table 2: Al Etch Rates

Product	Temperature (°C)	Al Etch Rate (Å/min)
Cleaning Solution A1	25	6
Cleaning Solution A2	25	4

Ability of Composition B to Remove Cu Oxide and Minimize the Re-growth Rate

[0086] The data illustrated by FIGS. 6 and 7 was collected using ellipsometry. The initial thickness of Cu oxide on a blanket wafer of Cu was measured prior to exposure to the cleaning solutions. The data shows this initial thickness of Cu oxide (shown in the graphs at time = -1 day) was about 25-30 Å thick. After exposure to cleaning solutions B1 and B2 the thickness of the Cu oxide decreased to about 5-10 Å. This data indicates that cleaning solutions B1 and B2 removed most of the Cu oxide. Cu will naturally passivate and form a native oxide layer. The thickness of the Cu oxide layer was re-measured every couple of days out to 14 days. During these 14 days the Cu wafer was exposed to ambient air. The data shows that the re-growth of Cu oxide over the 14 days is slow. So cleaning solutions B1 and B2 not only remove the Cu oxide, they minimize the re-growth rate of the Cu oxide.

Composition B Protects the Underlying Cu

[0087] Cleaning solutions B1 and B2 are very effective in removing the Cu oxide but they also need to have a very small etch rate on the underlying Cu metal. If they remove the Cu oxide and severely etch the underlying Cu metal then the wirebonding performance may not improve. The data in Table 3 below shows that cleaning solutions B1 and B2 have very low etch rates on Cu.

Table 3: Cu Etch Rates

Product	Temperature (°C)	Cu Etch Rate (Å/min)
Cleaning Solution B1	25	1
Cleaning Solution B2	25	1

Additional examples of Cleaning Solution A

[0088] The following experiments were carried out using beakers with stir bars to simulate the leadframe cleaning process.

[0089] Cleaning Solution **A1** (disclosed above) was prepared as follows: To a one liter HDPE poly-bottle was added 575 gm of dimethylacetamide (DMAc), 139 gm of de-ionized water (DIW), 156 gm of ammonium acetate, 120 gm of acetic acid, and 10 gm of ammonium fluoride. The bottle was capped and shaken. A sample of Cleaning Solution A1 was diluted with DIW to make a 5% solution and the solution pH was measured to be 4.9.

[0090] The Al or Al2O3 wafers tested in this experiment were blanket wafers. The wafer immersion in the beaker was set up to last 90 minutes.

[0091] Al(0.5% Cu) metal on titanium nitride (TiN) substrate with a resistivity of 338.24 ohms-Å/Sq was obtained from SVMI and had nominally 8000Å thickness of Al. During storage the Al substrate can grow up to 150Å of an oxide layer. Prior to etch rate determinations the Al substrate was therefore pretreated by immersing a 2"x2" piece of Al into an aqueous solution of 42.5 wt% H_3PO_4 in de-ionized water for 2 minutes at 25°C. After immersing for 2 minutes, the Al piece was rinsed for 3 minutes with de-ionized water, dried with a N_2 gun for 30 seconds, and the Al film thickness was then measured. Al pieces pretreated in this way were used immediately in etch rate measurements performed.

[0092] The Al or Al2O3 removal tests were conducted as follows. Each 2"x2" piece of Al or Al2O3 substrate was immersed into 330 ml of the Cleaning Solution **A1** in a 500 ml glass beaker and the solution stirred on a stir plate at 300 rpm. The temperature was recorded to be 25°C. Thickness measurements in Å were made in triplicate after times 0, 20, 40, 60, and 90 minutes.

[0093] Al thickness measurements were made using a ResMap Four Point probe. The film thickness versus time data was then regressed. For cleaning solution A1 an etch rate was determined for Al to be 1.8 Å/min.

[0094] Ellipsometry tests were carried out to measure the Al2O3 oxide thickness using a FilmTek SCI ellipsometer. The film thickness versus time data was then regressed. For cleaning solution A1 an etch rate was determined for Al2O3 to be 10.1 Å/min.

[0095] Additional cleaning solutions **A94B, A94E, A97E, A97F, and A97G** were prepared as for **A1** but with varying concentrations of components. In these solutions DI water accounts for the balance of the composition to make 100 wt%. These solution compositions, their pH measurements and their etch rate results are summarized in Table I. These etch rates for Al and Al2O3 show that varying relative etch rates of Al and Al2O3 can be obtained by varying component concentrations. The A1 solution shows an Al2O3 etch rate higher than Al etch rate.

Table I.

Component (wt%)	A94B	A97E	A97F	A94E	A97G	A1
DMAC	0	30	50	0	50	57.6
NH4F	0.005	0.005	0.005	0.005	0.005	1
Acetic acid	12	12	12	24.8	24.8	12
ammonium (NH4) acetate	15.6	15.6	15.6	2.8	2.8	15.6
pH(neat)	4.86	5.22	6.47	3.41	4.91	4.9 (5% dilution)
Al etch rate @ 25°C (Å/min)	14	6	2.6	25	9	1.8
Al2O3 etch rate @ 25°C (Å/min)	1	1.2	0.9	2	2	10.1

[0096] Cleaning solution A**96G was** prepared as for Cleaning Solution **A1** but with propylene glycol (PG) replacing DMAC. The composition, its pH measurement and the etch rate results are summarized and compared with Cleaning Solution A1 in Table II.

Table II.

Component (wt%)	A1	A96G
DMAC	57.6	0
PG	0	57.6
NH4F	1	1
Acetic acid	12	12
NH4 acetate	15.6	15.6
pH	4.9	5.5
Al etch rate @ 25°C (Å/min)	1.8	1
Al2O3 etch rate @ 25°C (Å/min)	10.1	4.2

[0097] Cleaning solutions A**94A, A94D, A96A and A96B** were prepared as for **A1** but with PG replacing DMAC. In these solutions DI water accounts for the balance of the composition to make 100 wt%. The composition, its pH measurement and the etch rate results are summarized in Table III. The examples show that the relative etch rates of Al and Al2O3 can be modified by modifying the components and buffer concentrations to achieve the desired cleaning performance.

Table III.

Component (wt%)	A94A	A96A	A94D	A96B
PG	0	30	0	30
NH4F	0.0017	0.005	0.0017	0.005
Acetic acid	12	12	24.8	24.8
NH4 acetate	15.6	15.6	2.8	2.8
pH(neat)	4.89	5.01	3.40	3.49
Al etch rate @ 25°C (Å/min)	3.7	4.3	8	10
Al2O3 etch rate @ 25°C (Å/min)	0.6	0.8	1	2.1

[0098] Cleaning solutions A**96E** and A**96F** were prepared as for A1 but with PG replacing DMAC. In these solutions DI water accounts for the balance of the composition to make 100 wt%. The composition, its pH measurement and the etch rate results are summarized and compared with A**96A and A97E** in Table IV. Since an aqueous-based formulation at lower solvent concentration may sometimes be preferable, a lower solvent

amount was used. The best cleaning for a particular application will be afforded by the relative amount of solvent versus water, amount of fluoride and the solution pH. The solvent type will further allow fine tuning of the cleaning results.

Table IV.

Component (wt%)	A96A	A96F	A96E	A97E
DMAc	0	0	0	30
PG	30	30	30	0
NH4F	0.005	0.10	1	1
Acetic acid	12	12	12	12
NH4 acetate	15.6	15.6	15.6	15.6
pH(neat)	5.01	5.35	5.37	5.22
Al etch rate @ 25°C (Å/min)	4	75	11	6
Al2O3 etch rate @ 25°C (Å/min)	0.8	10	6	1.2

[0099] Cleaning solutions A**96C, A96D,** A**97B, and A97D** were prepared as for A1 but with dimethyl urea (DMU) solvent and showing the effect of adding dipropyleneglycol monomethylether (DPM) co-solvent to PG. In these solutions DI water accounts for the balance of the composition to make 100 wt%. The composition, its pH measurement and the etch rate results are summarized and compared with A**96A and A96B** in Table V.

Table V.

Component (wt%)	A97D	A96A	A96C	A97B	A96B	A96D
DMU	30	0	0	30	0	0
PG	0	30	30	0	30	30
DPM	0	0	20	0	0	20
NH4F	0.005	0.005	0.005	0.005	0.005	0.005
Acetic acid	12	12	12	24.8	24.8	24.8
NH4 acetate	15.6	15.6	15.6	2.8	2.8	2.8
pH(neat)	5.37	5.01	5.48	3.41	3.49	3.96
Al etch rate @ 25°C (Å/min)	6	4.3	2.3	11	10	6
Al2O3 etch rate @ 25°C (Å/min)	-0.7 (SWELLING)	0.8	0.7	1.4	2	2

Additional Examples of Cleaning Solution B

[00100] Cleaning solutions B**91A, B92A,** B**92D, B92E and B92F** were prepared and tested as for A1 but using the matrix of components shown in Table VI. In these solutions DI water accounts for the balance of the composition to make 100 wt%. Using a 0.45 wt% citric acid and 0.0017 wt% NH4F plus water matrix, etch rates were determined for 0, 10, 30, and 40 wt% PG formulations.

Table VI.

Component (wt%)	B91A	B92A	B92D	B92F	B92E
Citric acid	0.45	0.45	0.45	0.45	0.45
PG	0	10	30	40	30
NH4F	0.0017	0.0017	0.0017	0.0017	0.005
pH	2.36	2.33	2.54	2.53	2.52
Al etch rate @ 25°C (Å/min)	31	17	8	6.6	29
Al2O3 etch rate @ 25°C (Å/min)	4.6	3.7	3	2.5	7

[00101] Cleaning solutions B**92F, B92H,** B**92I, and B92J** were prepared and tested as for A1 but using the matrix of components shown in Table VII. In these solutions DI water accounts for the balance of the composition to make 100 wt%.

Table VII.

Component (wt%)	B92F	B92H	B92I	B92J
Citric acid	0.45	0.45	0.45	0.45
PG	40	30	40	30
NH4F	0.0017	0.001	0.001	0.001
Catechol	0	0	0	2.84
pH	2.53	2.47	2.51	2.48
Al etch rate @ 25°C (Å/min)	6.6	4.0	2.9	3.2
Al etch rate @ **40°C** (Å/min)	17.3	14.4	6.6	11.5
Al2O3 etch rate @ 25°C (Å/min)	2.5	1.7	1.5	1.8
Al2O3 etch rate @ **40°C** (Å/min)	9.5	6.2	4.2	6.0

[00102] Additional tests were performed using other corrosion inhibitor molecules for B1 cleaning solutions in **B100A, B100B, B100C, B100D and B101A**. Citric acid was 0.45 wt% absolute.

			Etch Rate at 25°C (Å/min)		Comments
Additive (0.5 wt%)	PG (wt%)	NH4F (wt%)	Al	Al2O3	
NONE	30	0.005	29	7	**B92E**
Dodecyl gallate	30	0.005	N.D.	N.D	**B100A**; pH initially 2.57 adjusted to 4.5 with KOH. Solids remained.
Propyl gallate	30	0.005	24	8	**B100B**; pH = 2.42; Solution very cloudy.
Salicylic acid	30	0.005	13	2	**B100C**; pH initially 2.28 adjusted to 4.5 with KOH. Very small amount of solids remained. Used supernatant.
AKYPO LF surfactant*	30	0.005	25	8	**B100D**; pH = 2.39; Solution very cloudy.
NONE	40	0.0017	7	2.5	**B92F**; pH = 2.53
HEDTA**	40	0.0017	6	2	**B101A**; pH = 2.58.

* AKYPO LF surfactant is a glycol ether carboxylic acid surfactant

**HEDTA is a hydroxyethylenediamine triacetic acid

[00103] The foregoing examples and description of the preferred embodiments should be taken as illustrating, rather than as limiting the present invention as defined by the claims. As will be readily appreciated, numerous variations and combinations of the features and components in the compositions set forth above can be utilized without departing from the present invention as set forth in the claims. Such variations are not regarded as a departure from the spirit and scope of the invention, and all such variations are intended to be included within the scope of the following claims. All of the components described herein may be combined in any of the ranges disclosed. The Composition A and B components are interchangeable in either of those compositions in the ranges described for either. All comprising language includes consisting essentially of and consisting of.

CLAIMS

1. A method of processing a leadframe assembly to remove undesired material therefrom or to prepare a surface of the leadframe assembly for subsequent bonding wherein a leadframe assembly comprises one or more of the following parts: leadframe, dies, dies having bond pads thereon, contacts, contact leads, and wires, the method comprising the steps of:

attaching one or more dies having bond pads thereon to a leadframe to form a leadframe assembly, said leadframe comprising contact leads having exposed metal surfaces;

contacting said bond pads and said contact leads with a composition comprising water and from 0.003 to about 25% by weight of one or more carboxylic acids, salt thereof or mixture thereof to remove metal oxides from said bond pads and said contact leads;

drying the leadframe assembly; and

performing a wirebonding step comprising attaching wires between the bond pads on the one or more dies and the contact leads on the leadframe.

2. The method of claim 1 further comprising the step of forming a mold over the leadframe assembly to form a packaged circuit after said performing step.

3. The method of any one of the preceding claims wherein said composition used in said contacting step has a pH from about 1 to about 7.

4. The method of any one of the preceding claims wherein said composition used in said contacting step comprises an acid buffer solution, said acid of said acid buffer solution selected from a carboxylic acid or a polybasic acid and said acid buffer solution further comprising a salt of the acid in a molar ratio of acid to salt ranging from 10:1 to 1:10.

5. The method of claim 4 further wherein said acid buffer solution in said composition used in said contacting step comprises at least one of: acetic acid/acetate salts, benzoic acid/benzoate salts, and phenolic acid/phenolate salts.

6. The method of any one of the preceding claims wherein said composition used in said contacting step comprises about 0.003 to about 4% by weight of at least one hydroxyl carboxylic acid, salt thereof or mixture thereof or an amine group-containing carboxylic acid, salt thereof or mixture thereof.

7. The method of any one of the preceding claims wherein said composition used in the contacting step comprises one or more carboxylic acids, salts or mixtures thereof selected from the group consisting of citric acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid and fumaric acid, and salts thereof or mixtures thereof.

8. The method of any one of the preceding claims wherein said composition used in the contacting step comprises citric acid.

9. The method of any one of the preceding claims wherein the composition used in said contacting step comprises:

about 0.005 to about 16% by weight of at least one carboxylic acid, salt thereof or mixture thereof;

about 0.003 to about 4% by weight of at least one hydroxyl carboxylic acid, salt thereof or mixture thereof or an amine group-containing acid, salt thereof or mixture thereof; and the remainder being substantially water.

10. The method of any one of the preceding claims wherein said composition used in the contacting step comprises two or more carboxylic acids, salts or mixtures thereof selected from the group consisting of citric acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid and fumaric acid, and salts thereof or mixtures thereof and further comprises one or more solvents, one or more fluorides, and optionally one or more surfactants.

11. The method of any one of the preceding claims wherein said composition used in said contacting step comprises fluoride selected from the group consisting of compounds of the general formula $R_1R_2R_3R_4NF$ where R_1, R_2, R_3, and R_4 are independently hydrogen, an alcohol group, an alkoxy group, an alkyl group or mixtures thereof.

12. The method of any one of the preceding claims wherein said composition used in said contacting step further comprises one or more components selected from the group consisting of organic polar solvent, fluoride, surfactant and corrosion inhibitor.

13. The method of any one of the preceding claims wherein said composition used in said contacting step further comprises organic polar solvent and fluoride.

14. The method of any one of the preceding claims wherein said composition used in said contacting step further comprises a solvent selected from the group consisting of dimethylacetamide (DMAC), monoethanolamine, n-methylethanolamine, formamide, n-methyl formamide, gamma-butyrolactone, N-methylpyrrolidone, dihydric alcohols, polyhydric alcohols, diols and polyols such as (C_2– C_{20}) alkane diols and (C_3– C_{20}) alkane triols, cyclic alcohols and substituted alcohols and glycols, a glycol ether, tetrahydrofurfuryl alcohol (THFA), diacetone alcohol, 1, 4-cyclohexanedimethanol, and ureas and mixtures thereof.

15. The method of any one of the preceding claims wherein said composition used in said contacting step further comprises 30% by weight to 90% by weight of an organic polar solvent; 0.0005% by weight to 20% by weight of a fluoride; 0.5% by weight to 40% by weight water; up to 15% by weight of an optional corrosion inhibitor.

16. The method of any one of the preceding claims wherein said composition used in said contacting step has a pH ranging from 3 to 7; and said composition comprises 30% by weight to 90% by weight of said organic polar solvent; 0.001% by weight to 20% by weight of said fluoride; up to 15% by weight of an optional surfactant, and further wherein said water is present from 0.5% by weight to 40% by weight.

17. The method of any one of the preceding claims wherein said composition used in the contacting step comprises an ammonium salt.

18. The method of any one of the preceding claims wherein said composition used in the contacting step comprises propylene glycol or dimethylacetamide or mixtures thereof.

19. The method of any one of the preceding claims wherein said composition used in the contacting step further comprises one or more surfactants.

20. The method of any one of the preceding claims wherein said composition used in said contacting step comprises:

about 0.1 to about 3% by weight of at least one dicarboxylic acid, salt thereof or mixture thereof;

about 0.05 to about 1.5% by weight of at least one hydroxyl carboxylic acid, salt thereof or mixture thereof;

and the remainder being substantially water, and said composition having a pH of about 1 to about 4.