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TITLE OF THE INVENTION:

REMOVAL OF SURFACE OXIDES BY ELECTRON ATTACHMENT FOR WAFER BUMPING APPLICATIONS

BACKGROUND OF THE INVENTION

[0001] The present invention relates generally to fluxless processes for removing metal oxides from the surface of a substrate. More specifically, the invention relates to a method for the fluxless reflow of solders on a substrate surface, particularly for wafer bumping applications.

[0002] Wafer bumping is a process used to make thick metal bumps on the chip bond pads for inner lead bonding. The bumps are commonly made by depositing a solder on the pads and then reflowing (referred to herein as a first reflow) to conduct alloying and to change the shape of the solder bump from a mushroom-shape into a hemispherical-shape. The chip with the first-reflowed bumps is "flipped" to correspond to the footprint of the solder wettable terminals on the substrate and then subjected to a second reflow to form solder joints. These solder joints are referred to herein as inner lead bonds.

High-melting point solders (e.g., $> 300^{\circ}\text{C}$) are normally used in the wafer bumping process because it allows for subsequent assembly steps such as outer lead bonding to proceed using lower-melting point solders (e.g., $< 230^{\circ}\text{C}$) without disruption of the inner lead bonds.

[0003] The shape of the solder bumps after the first reflow is critical. For example, a large bump height is preferable for better bonding and higher fatigue resistance. Further, the bumps formed should preferably be substantially uniform to ensure planarity.

Substantially uniform solder bumps having relatively larger bump heights is believed to be associated with an oxide-free bump surface during the first reflow. Currently, there



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are two major approaches of removing solder oxides during first reflow of the solder bumped wafer. One approach is fluxless soldering using pure hydrogen at a reflow temperature of 400 to 450°C. The major challenge of this approach is the flammable nature of the pure hydrogen, which largely limits the application of this approach. The

5 second approach is applying organic fluxes over the deposited solder bumps, or within a solder paste mixture that has been printed onto the wafer to form the bumps, and reflowing the bumps in an inert environment so that the fluxes can effectively remove initial oxides on the solder surface. However, this approach has its drawbacks. Small voids may form in the solder bumps due to flux decomposition. These voids may not
10 only degrade the electrical and mechanical properties of the formed solder bonds but also destroy the co-planarity of the solder bumped wafer and affect the subsequent chip bonding process. The decomposed flux volatiles can also contaminant the reflow furnace which can increase the maintenance cost. In addition, flux residues are oftentimes left upon the wafer which can cause corrosion and degrade the performance
15 of the assembly.

[0004] To remove the flux residues from the reflow processes described above, a post cleaning process may be adopted using chlorofluorocarbons (CFCs) as cleaning agents.

However, post-cleaning adds an additional process step and increases the

manufacturing processing time. Further, the use of chlorofluorocarbons (CFCs) as

20 cleaning agents is banned due to the potential damage to the earth's protective ozone layer. Although no-clean fluxes have been developed by using a small amount of activators to reduce residues, there is a trade-off between the gain and loss in the amount of flux residues and the activity of the fluxes. Therefore, a catalytic method to assist generating highly reactive H_2 radicals, and thus reducing the effective ranges of
25 hydrogen concentration and processing temperature for reducing surface oxides, has been sought by the industry.

[0005] Fluxless (dry) soldering has been performed in the prior art using several techniques. One technique is to employ lasers to ablate or heat metal oxides to their vaporization temperatures. Such processes are typically performed under inert or reducing atmospheres to prevent re-oxidation by the released contaminants. However, the melting or boiling points of the oxide and base metal can be similar and it may not be desirable to melt or vaporize the base metal. Therefore, such laser processes are difficult to implement. Lasers are typically expensive and inefficient to operate and require a direct line of sight to the oxide layer. These factors limit the usefulness of laser techniques for most soldering applications.

[0006] Surface oxides can be chemically reduced (e.g., to H_2O) through exposure to reactive gases (e.g., H_2) at elevated temperatures. A mixture containing 5% or greater reducing gas in an inert carrier (e.g., N_2) is typically used. The reaction products (e.g., H_2O) are then released from the surface by desorption at the elevated temperature and carried away in the gas flow field. Typical process temperatures exceed $350^{\circ}C$.

However, this process can be slow and ineffective, even at elevated temperatures.

[0007] The speed and effectiveness of the reduction process can be increased using more active reducing species. Such active species can be produced using conventional plasma techniques. Gas plasmas at audio, radio, or microwave frequencies can be used to produce reactive radicals for surface de-oxidation. In such processes, high intensity electromagnetic radiation is used to ionize and dissociate H_2 , O_2 , SF_6 , or other species, including fluorine-containing compounds, into highly reactive radicals. Surface treatment can be performed at temperatures below $300^{\circ}C$. However, in order to obtain optimum conditions for plasma formation, such processes are typically performed under vacuum conditions. Vacuum operations require expensive equipment and must be performed as a slow, batch process rather than a faster, continuous process. Also, plasmas are typically dispersed diffusely within the process chamber and are difficult to direct at a

specific substrate area. Therefore, the reactive species cannot be efficiently utilized in the process. Plasmas can also cause damage to process chambers through a sputtering process, and can produce an accumulation of space charge on dielectric surfaces, leading to possible microcircuit damage. Microwaves themselves can also
5 cause microcircuit damage, and substrate temperature may be difficult to control during treatment. Plasmas can also release potentially dangerous ultraviolet light. Such processes also require expensive electrical equipment and consume considerable power, thereby reducing their overall cost effectiveness.

[0008] U. S. Pat. No. 5,409,543 discloses a process for producing a reactive hydrogen
10 species (i.e., atomic hydrogen) using a hot filament to thermally dissociate molecular hydrogen in a vacuum condition. The energized hydrogen chemically reduces the substrate surface. The temperature of the hot filament may range from 500°C to 2200°C. Electrically biased grids are used to deflect or capture excess free electrons emitted from the hot filament. The reactive species or atomic hydrogen is produced from mixtures
15 containing 2% to 100% hydrogen in an inert carrier gas.

[0009] U.S. Pat. No. 6,203,637 discloses a process for activating hydrogen using the discharge from a thermionic cathode. Electrons emitted from the thermionic cathode create a gas phase discharge, which generates active species. The emission process is performed in a separate or remote chamber containing a heated filament. Ions and
20 activated neutrals flow into the treatment chamber to chemically reduce the oxidized metal surface. However, such hot cathode processes require vacuum conditions for optimum effectiveness and filament life. Vacuum operations require expensive equipment, which must be incorporated into soldering conveyor belt systems, thereby reducing their overall cost effectiveness.

[0010] Potier, et al., "Fluxless Soldering Under Activated Atmosphere at Ambient
25 Pressure", Surface Mount International Conference, 1995, San Jose, CA, and U.S. Pat.

Nos. 6,146,503, 6,089,445, 6,021,940, 6,007,637, 5,941,448, 5,858,312 and 5,722,581 describe processes for producing activated H₂ (or other reducing gases, such as CH₄ or NH₃) using electrical discharge. The reducing gas is generally present at "percent levels" in an inert carrier gas (N₂). The discharge is produced using an alternating voltage source of "several kilovolts". Electrons emitted from electrodes in a remote chamber produce excited or unstable species that are substantially free of electrically charged species, which are then flowed to the substrate. The resulting processes reduce oxides on the base metal to be soldered at temperatures near 150°C. However, such remote discharge chambers require significant equipment costs and are not easily retrofitted to existing soldering conveyor belt systems. In addition, these processes are typically employed for pre-treating the metal surface before soldering rather than removing solder oxides.

[0011] U.S. Pat. No. 5,433,820 describes a surface treatment process using electrical discharge or plasma at atmospheric pressure from a high voltage (1 kV to 50 kV) electrode. The electrode is placed in the proximity of the substrate rather than in a remote chamber. The free electrons emitted from the electrodes produce reactive hydrogen radicals --a plasma containing atomic hydrogen-- which then pass through openings in a dielectric shield placed over the oxidized substrate. The dielectric shield concentrates the active hydrogen onto those specific surface locations requiring de-oxidation. However, such dielectric shields can accumulate surface charge that may alter the electric field and inhibit precise process control. The described process is only used to flux base metal surfaces.

[0012] Accordingly, there is a need in the art to provide an economical and efficient process for fluxless reflow of solder bumped wafer under relatively low temperatures to reduce thermal energy. There is a further need in the art to provide a process and apparatus for fluxless reflow under near ambient or atmospheric pressure conditions to

avoid the expense of purchasing and maintaining vacuum equipment. Additionally, there is a need in the art to provide a fluxless reflow process using a non-flammable gas environment.

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BRIEF SUMMARY OF THE INVENTION

[0013] The present invention satisfies some, if not all, of the needs of the art by providing a method for removing metal oxides from the surface of a substrate without the use of a flux. Specifically, in one aspect of the present invention, there is provided a method for removing metal oxides from the surface of a substrate to be treated

10 comprising: providing the substrate which is proximal to a first electrode; providing a second electrode that is proximal to the first electrode and the substrate wherein at least a portion of the treating surface is exposed to the second electrode and wherein the first and the second electrodes and the substrate reside within a target area; passing a gas mixture comprising a reducing gas through the target area; supplying energy to at least
15 one of the first or the second electrodes to generate electrons within the target area wherein at least a portion of the electrons attach to at least a portion of the reducing gas thereby forming a negatively charged reducing gas; and contacting the substrate with the negatively charged reducing gas to reduce the metal oxides on the treating surface of the substrate.

20 **[0014]** In yet another aspect of the present invention, there is provided a method for removing metal oxides from the surface of a substrate comprising a plurality of solder bumps, the method comprising: providing the substrate which is connected to a first electrode as a target assembly; providing a second electrode adjacent to said target assembly wherein at least a portion of the surface comprising the plurality of solder
25 bumps is exposed to the second electrode; providing a gas mixture comprising a reducing gas and a carrier gas between the first and second electrodes; supplying

voltage between the first and second electrodes to generate electrons wherein at least a portion of the electrons attach to at least a portion of the reducing gas thereby forming a negatively charged reducing gas; contacting the target assembly with the negatively charged reducing gas wherein the negatively charged reducing gas reduces the metal oxides on the surface of the substrate; and removing at least a portion of the electrons accumulated on the surface of the substrate.

[0015] In a further aspect of the present invention, there is provided a method comprising: providing the substrate which is connected to a first electrode; providing a second electrode that is proximal to the first electrode and the substrate wherein the second electrode has a negative bias in electric potential relative to the first electrode and wherein at least a portion of the surface comprising the plurality of solder bumps is exposed to the second electrode; passing a gas mixture comprising hydrogen and nitrogen between the first and the second electrodes; supplying voltage between the first and the second electrodes to generate electrons from the second electrode wherein at least a portion of the electrons attach to the hydrogen and form negatively charged hydrogen ions and wherein the temperature of the second electrode ranges from 100 to 1500°C; contacting the substrate with the negatively charged hydrogen ions to reduce the metal oxides on the surface of the substrate; and removing at least a portion of the electrons accumulated on the surface of the substrate.

[0016] In a still further aspect of the present invention there is provided a method comprising: providing the substrate which is connected to a first electrode within a heating chamber; providing a second electrode that is proximal to the first electrode and the substrate wherein the second electrode has a negative bias in electric potential relative to the first electrode and wherein at least a portion of the surface comprising the plurality of solder bumps is exposed to the second electrode; passing a gas mixture comprising from 0.1% to 4 % by volume hydrogen and from 1% to 99.9% by volume

nitrogen between the first and the second electrodes wherein the pressure of the gas mixture ranges from 10 to 20 psia; supplying voltage between the first and the second electrodes to generate electrons from the second electrode wherein at least a portion of the electrons attach to the hydrogen and form negatively charged hydrogen ions;

- 5 contacting the substrate with the negatively charged hydrogen ions to reduce the metal oxides on the surface of the substrate; and changing the polarity of the second electrode to a positive bias in electrical potential to remove at least a portion of the electrons from the surface of the substrate.

[0017] These and other aspects of the invention will become apparent from the
10 following detailed description.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0018] Figures 1a and 1b illustrate a voltage pulse on a emission and a base electrode, respectively.

- 15 [0019] Figures 2a through 2i is a schematic illustration of various electrode geometries suitable for emission and/or retrieval of electrons.

[0020] Figure 3 provides an example of one embodiment of the electrode suitable for emission and/or retrieval of electrons employing a plurality of tips.

- [0021] Figure 4 provides an example of one embodiment of the electrode suitable for
20 emission and/or retrieval of electrons having a segmented assembly.

[0022] Figure 5 provides an example of one embodiment of the present invention illustrating removal of surface metal oxides in a wafer bumping application.

- [0023] Figure 6 illustrates a particular embodiment of the present invention for
25 removing negatively charged ions on the substrate surface by changing the electrode polarity during the reflow of wafer bumps.

[0024] Figures 7a and 7b illustrates the transportation of the charged species between two electrodes when the polarity of the two electrodes is changed.

[0025] Figure 8 provides an illustration of a particular embodiment of the present invention for removing electrons on the surface of a substrate by employing an additional
5 electrode with a positive bias relative to the base electrode.

[0026] Figures 9a through 9e provide various illustrations of particular embodiments of the present invention employing movement of at least one electrode with respect to the substrate.

[0027] Figures 10a and 10b provide an illustration of an unidirectional voltage pulse
10 and a bi-directional voltage pulse, respectively.

DETAILED DESCRIPTION OF THE INVENTION

[0028] The present invention relates to a method for the removal of metal oxides from a substrate surface by exposure to negatively charged ions. The negatively charged
15 ions react and reduce the surface metal oxides. The present invention can be employed by modifying traditional reflow and soldering equipments such as, for example, the reflow machine used for reflow of solder bumped wafer. The present invention can also be applied to other processes wherein the removal of the surface metal oxides from a substrate is desired such as, but not limited to, metal plating (i.e., the solder plating of
20 portions of printed circuit boards or metal surfaces to make them more amenable to subsequent soldering), reflow and wave soldering for outer lead bonding, surface cleaning, brazing, welding, and removing surface oxides of metals, such as copper oxide, formed during silicon wafer processing. The removal of metal oxides using the method and apparatus of the present invention is equally applicable to the
25 aforementioned processes or any other process desirous of removing oxides without the need for organic fluxes.

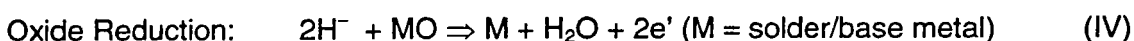
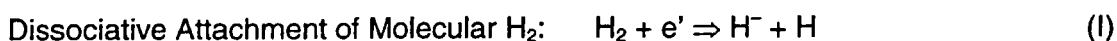
[0029] The term "substrate" as used herein generally relates to a material such as silicon, silicon coated with silicon dioxide, aluminum-aluminum oxide, gallium arsenide, ceramic, quartz, copper, glass, epoxy, or any material suitable for use within an electronic device. In certain embodiments, the substrate is an electrically insulated or semi-conductive substrate having solder disposed thereupon. Exemplary solder compositions include, but are not limited to, a fluxless tin-silver, a fluxless tin-silver-copper, a fluxless tin-lead, or a fluxless tin-copper. However, the method of the present invention is suitable for a variety of different substrates and solder compositions. In a certain preferred embodiment, the substrate is a silicon wafer having a plurality of solder bumps disposed thereupon.

[0030] While not wishing to be bound by theory, it is believed that when an energy source such as a direct current voltage source is applied between at least two electrodes, electrons are generated from one of the two electrodes having a negative electrical bias relative to the other electrode (referred to herein as an "emission electrode") and/or the gas phase between the two electrodes. The generated electrons drift toward the other electrode, which is grounded or has a positive electrical bias (referred to herein as a "base electrode"), along the electric field. The substrate having a plurality of solder bumps upon its surface is placed within the area defined by the base and the emission electrodes (referred to herein as the "target area") with the solder-bumped surface or treating area exposed to the emission electrode. In certain embodiments, the substrate may be connected to the base electrode forming a target assembly. A gas mixture comprising a reducing gas and optionally a carrier gas is passed through the electric field generated by the electrodes. During the electron drift, part of the reducing gas forms negative ions by electron attachment which then drift to the target assembly, i.e., the base electrode and substrate surface. On the substrate surface, negatively charged ions can thus reduce the existing metal oxides without the

need for traditional fluxes. Further, the adsorption of the active species on the surface to be treated can be promoted due to the drifting of the negatively charged ions along the electric field.

[0031] In embodiments wherein the reducing gas comprises hydrogen, it is believed

5 that the method of the present invention occurs as follows:



10 In these embodiments, the activation energy of metal oxide reduction using the electron attachment method of the present invention is lower than methods that use molecular hydrogen because the formation of atomic hydrogen ions with electron attachment eliminates the energy associated with bond breaking of molecular hydrogen.

[0032] In certain embodiments, energy is supplied to at least one of the electrodes,

15 preferably the emission electrode, sufficient to cause the emission electrode to generate electrons. The energy source is preferably an electric energy or voltage source, such as an AC or DC source. Other energy sources, such as an electromagnetic energy source, a thermal energy source, or a photo energy source may also be used alone, or in combinations with any of the aforementioned energy sources. In certain embodiments of
20 the present invention, the emission electrode is connected to a first voltage level and the base electrode is connected to a second voltage level. The difference in the voltage levels creates a bias in electrical potential. One of the first or the second voltage levels may be zero indicating that either of the two electrodes can be grounded.

[0033] To produce negatively charged ions by electron attachment, a large quantity of

25 electrons needs to be generated. In this connection, the electrons can be generated by

a variety of ways such as, but not limited to, cathode emission, gas discharge, or combinations thereof. Among these electron generation methods, the selection of the method depends mainly on the efficiency and the energy level of the electrons generated. For embodiments wherein the reducing gas is hydrogen, electrons having an energy level approaching 4 eV is preferred. In these embodiments, such low energy level electrons are preferably generated by cathode emission rather than gas discharge. The generated electrons may then drift from the emission electrode toward the base electrode which creates a space charge. The space charge provides the electron source for generating the negatively charged hydrogen ions by electron attachment when hydrogen passes through the at least two electrodes or within the target area.

[0034] For embodiments involving electron generation through cathode emission, these embodiments may include: field emission (referred to herein as cold emission), thermal emission (referred to herein as hot emission), thermal-field emission, photoemission, and electron or ion beam emission.

[0035] Field emission involves applying an electric field with a negative bias on the emission electrode relative to the base electrode that is sufficiently high in intensity to overcome an energy barrier for electrons to be generated from the surface of the emission electrode. In certain preferred embodiments, a DC voltage is applied between the two electrodes that ranges from 0.1 to 50kV, preferably ranging from 2 to 30kV. In these embodiments, the distance between the electrodes may range from 0.1 to 30 cm, preferably from 0.5 to 5 cm.

[0036] Thermal emission, on the other hand, involves using a high temperature to energize electrons in the emission electrode and separate the electrons from the metallic bond in the material of the emission electrode. In certain preferred embodiments, the temperature of the emission electrode may range from 800 to 3500°C, preferably from 800 to 1500°C. The emission electrode may be brought to and/or maintained at a high

temperature by a variety of methods such as, but not limited to, directly heating by passing AC or DC through the electrode; indirect heating such as contacting the cathode surface with an electrically insulated hot surface heated by a heating element, IR radiation, or combinations thereof.

5 **[0037]** Thermal-field emission is a hybrid of field emission and thermal emission methods for electron generation in which both an electric field and a high temperature are applied. Therefore, thermal-field emission may require a lesser electric field and a lower electrode temperature for generating the same quantity of electrons as compared with pure field emission and pure thermal emission. Thermal-field emission can
10 minimize difficulties encountered with pure field emission, such as the tendency of degradation in electron emission by contamination on the emission surface, and a high restriction on the planarity and uniformity of the emission surface. Further, thermal-field emission may also avoid problems related to thermal emission such as a high potential of chemical reaction between the emission electrode and the gas phase. In
15 embodiments wherein the thermal-field emission is used for electron generation, the temperature of the emission electrode can range from ambient to 3500°C, or more preferably from 150 to 1500°C. In these embodiments, the electric voltage can range from 0.01 to 30 KV, or more preferably from 0.1 to 10 KV.

[0038] In certain preferred embodiments, the thermal emission or thermal-field
20 emission method is used for electron generation. In these embodiments, a high temperature emission electrode used in either of these methods may also act as a heat source for the gas mixture that is passed through the electric field generated by the two electrodes, so that the thermal energy required for heating the gas for a subsequent reflow process step can be reduced.

25 **[0039]** In certain embodiments of the present invention, the electron generation is accomplished via a combination of cathode emission and corona discharge methods. In

these embodiments, an energy source such as a DC voltage is applied between the two electrodes and electrons may be generated from both the emission electrode (cold or hot) and the gas phase (corona discharge) near the emission electrode. The corona discharge is preferably minimized in order to increase the efficiency of forming negatively charged ions by electron attachment and increase the lifetime of the emission electrode.

[0040] In embodiments wherein the cathode emission mechanism is used for electron emission, the voltage applied across the two electrodes may be constant or pulsed. The frequency of the voltage pulse ranges from 0 to 100 kHz. Figures 1a and 1b provide an illustration of a voltage pulse on an emission electrode and a base electrode,

respectively. In these embodiments, it is believed that a pulsed voltage, such as that shown in Figures 1a and 1b, is preferable to constant voltage to improve the amount of electron generation and to reduce the tendency of gas phase discharge.

[0041] For embodiments involving electron generation through gas discharge, these embodiments may include thermal discharge, photo-discharge, and various avalanche discharge, including glow discharge, arc discharge, spark discharge, and corona discharge. In these embodiments, electrons are generated by gas phase ionization.

The gas phase is a gas mixture comprising the reducing gas and an inert gas. In certain embodiments of gas phase ionization, a voltage source is applied between two

electrodes and electrons may be generated from the inert gas within the gas mixture

between the two electrodes that then drift toward the positively biased electrode such as the base electrode. During this electron drift, some of these electrons may attach on the reducing gas molecules and form negatively charged ions by electron attachment. In addition, some positive ions are also created in the inert gas that then drift toward the negatively biased electrode such as the emission electrode and are neutralized at the electrode surface.

[0042] As mentioned previously, electrons can be generated from an emission

electrode when it has a negative bias relative to a base electrode. Referring to Figures

2a through 2i, the emission electrode may have a variety of geometries, such as, for

example, a thin wire 2a, a rod with a sharpened tip 2b, a rod with several sharpened tips

5 or comb 2c, a screen or wire mesh 2d, a loose coil, an array of combs 2f, a bundle of thin wires or filament 2g, a rod with sharp tips protruding from its surface 2h, or a plate with a

knurled surface 2i. Additional geometries may include combinations of the above

geometries such as plates or rods with surface protrusions, rods wrapped with wire

windings or filament, coils of thin wires, etc. A plurality of electrodes may be employed

10 that may be arranged in a parallel series or in an intersecting grid. Still further

geometries may include a "wagon wheel" geometry wherein a plurality of electrodes is

arranged in a radial fashion such as in "spokes" of a wheel. In certain embodiments,

such as embodiments wherein field emission is involved, the cathode is preferably made of geometries having a large surface curvature, such as a plurality of sharp tips to

15 maximize the electric field near the electrode surface such as the geometry depicted in

Figure 3. As Figure 3 illustrates, electrode 1 has a series of thin wires 2 that reside

within grooves on the electrode surface along with a plurality of tips 3 emanating from its surface.

[0043] The electrode material that acts as an emission electrode is preferably

20 comprised of a conductive material with relatively low electron-emission energy or work function. The material preferably also has a high melting point and relatively high

stability under processing conditions. Examples of suitable materials include metals, alloys, semiconductors, and oxides coated or deposited onto conductive substrates.

Further examples include, but are not limited to, tungsten, graphite, high temperature

25 alloys such as nickel chromium alloys, and metal oxides such as BaO and Al₂O₃ that are deposited onto a conductive substrate.

[0044] The electrode that acts as a base electrode is comprised of a conductive material such as a metal or any of the other materials described therein. The base electrode can have a variety of different geometries depending upon the application.

[0045] In certain embodiments of the present invention involving thermal-field

5 emission, the emission electrode may comprise a segmented assembly such as the electrode depicted in Figure 4. In this regard, the core 10 of the emission electrode may be made of a metal with a high electrical resistance. A plurality of tips 11 emanate from core 10. Tips 11 may be made of a conductive material with relatively low electron emission energy or work function such as any of the materials disclosed herein. The
10 core may be heated by directly passing an AC or a DC current (not shown) through core 10. The thermal conduction will transfer the heat from the core to tips 11. The hot core 10 and the plurality of tips 11 are enclosed within an enclosure 12 which is then inserted into a support frame thereby forming a segmented assembly as shown. Tips 11 are exposed outside the enclosure 12. Enclosure 12 is composed of an insulating material.
15 The segmented assembly allows for the thermal expansion of the core during operation. In this arrangement, electrons can be generated from hot tips 11 by applying a negative voltage bias on the emission electrode relative to the base electrode .

[0046] In another preferred embodiment of the present invention involving thermal-field emission, indirect heating can raise the temperature of the emission electrode. This may

20 be accomplished by using a heating cartridge as the core of the emission electrode. The surface of the heating cartridge may be comprised of an electrically conductive material such as a metal that is electrically insulated from the heating element inside the cartridge. To promote electron emission, a plurality of distributed emission tips can be mounted on the surface of the heating cartridge. The cartridge can be heated by
25 passing an AC or DC current through the heating element inside the cartridge. Electrons can be generated from the distributed tips of the cartridge by applying a negative voltage

bias on the surface of the cartridge relative to a second electrode. For creating the voltage bias in this arrangement, the second electrode can be grounded so that the cartridge may be negatively biased or, alternatively, the cartridge can be grounded so that the second electrode may be positively biased. In some embodiments, the latter

case may be preferable for eliminating a potential interference between two electric circuits, e.g., one circuit may be the AC or DC current along the heating element, and the another circuit may be the high voltage bias between the surface of the cartridge and the second electrode. In these embodiments, the hot cartridge electrode may also act as a heat source for the gas mixture to achieve the required temperatures for the reflow

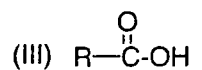
process step.

[0047] As mentioned previously, a gas mixture comprising a reducing gas is passed through the electric field generated by the at least two electrodes. The reducing gas contained within the gas mixture may fall within one or more of the following categories:

1) an intrinsically reductant gas, 2) a gas capable of generating active species which

form gaseous oxides upon reaction of the active species with the metal oxide, or 3) a gas capable of generating active species which form liquid or aqueous oxides upon reaction of the active species with the metal oxide.

[0048] The first category of gases, or an intrinsically reductant gas, includes any gas that thermodynamically acts as a reductant to the oxides to be removed. Examples of intrinsically reductant gases include H_2 , CO , SiH_4 , Si_2H_6 , formic acid, alcohols such as, for example, methanol, ethanol, etc., and some acidic vapors having the following formula (III):



In formula (III), substituent R may be an alkyl group, substituted alkyl group, an aryl, or

substituted aryl group. The term "alkyl" as used herein includes straight chain, branched,

or cyclic alkyl groups, preferably containing from 1 to 20 carbon atoms, or more preferably from 1 to 10 carbon atoms. This applies also to alkyl moieties contained in other groups such as haloalkyl, alkaryl, or aralkyl. The term "substituted alkyl" applies to alkyl moieties that have substituents that include heteroatoms such as O, N, S, or

5 halogen atoms; OCH₃; OR (R=alkyl C₁₋₁₀ or aryl C₆₋₁₀); alkyl C₁₋₁₀ or aryl C₆₋₁₀; NO₂; SO₃R (R=alkyl C₁₋₁₀ or aryl C₆₋₁₀); or NR₂ (R=H, alkyl C₁₋₁₀ or aryl C₆₋₁₀). The term "halogen" as used herein includes fluorine, chlorine, bromine, and iodine. The term "aryl" as used herein includes six to twelve member carbon rings having aromatic character. The term "substituted aryl" as used herein includes aryl rings having substituents that include
10 heteroatoms such as O, N, S, or halogen atoms; OCH₃; OR (R=alkyl C₁₋₁₀ or aryl C₆₋₁₀); alkyl C₁₋₁₀ or aryl C₆₋₁₀; NO₂; SO₃R (R=alkyl C₁₋₁₀ or aryl C₆₋₁₀); or NR₂ (R=H, alkyl C₁₋₁₀ or aryl C₆₋₁₀). In certain preferred embodiments, the gas mixture contains hydrogen.

[0049] The second category of reducing gas includes any gas that is not an intrinsically reductive but can generate active species, such as, for example, H, C, S, H', C', and S',
15 by dissociative attachment of electron on the gas molecules and form gaseous oxides by reaction of the active species with the metal oxides to be removed. Examples of this type of gas include: NH₃, H₂S, C₁ to C₁₀ hydrocarbons such as but not limited to CH₄, C₂H₄, acidic vapors having the formula (III), and organic vapors having the following formula (IV):



In formulas (III) and (IV), substituent R may be an alkyl group, substituted alkyl group, an aryl, or substituted aryl group.

[0050] The third category of reducing gas includes any gas that is not an intrinsically reductive but can form active species, such as, for example, F, Cl, F', and Cl', by
25 dissociative attachment of electron on the gas molecules and form liquid or aqueous

oxides by reaction of the active species with the metal oxides. Examples of this type of gas include fluorine and chlorine containing gases, such as CF_4 , SF_6 , CF_2Cl_2 , HCl , BF_3 , WF_6 , UF_6 , SiF_3 , NF_3 , CClF_3 , and HF .

[0051] Besides including one or more of the above categories of reducing gases, the

5 gas mixture may further contain one or more carrier gases. The carrier gas may be used, for example, to dilute the reducing gas or provide collision stabilization. The carrier gas used in the gas mixture may be any gas with an electron affinity less than that of the reducing gas or gases within the gas mixture. In certain preferred embodiments, the carrier gas is an inert gas. Examples of suitable inert gases include, but are not

10 limited to, N_2 , Ar, He, Ne, Kr, Xe, and Rn.

[0052] In certain preferred embodiments, the gas mixture comprises hydrogen as the reducing gas and nitrogen as the carrier gas due to its relatively lower cost and the

environmental friendliness of the exhaust gas release. In these embodiments, the gas mixture comprises from 0.1 to 100% by volume, preferably 1 to 50% by volume, or more
15 preferably from 0.1 to 4% by volume of hydrogen. Amounts of hydrogen lower than 4% are preferred, which makes gas mixture non-flammable.

[0053] In certain embodiments, the gas mixture is passed through the field generated by the at least two electrodes at a temperature ranging from ambient to 450°C , more preferably ranging from 100 to 350°C . The pressure of the gas mixture is preferably

20 ambient atmospheric pressure, i.e., the existing pressure of the area of the process. No special pressure, such as vacuum, may be required. In embodiments where the gas mixture is pressurized, the pressure may range from 10 to 20 psia, preferably from 14 to 16 psia.

[0054] The substrate surface in which the oxides are to be removed is preferably

25 located between the emission electrode and the base electrode with the surface facing the emission electrode. In certain preferred embodiments of the present invention, the

substrate may be connected to the base electrode to provide a target assembly and facing the emission electrode. In these embodiments, the distance between the emission electrode and the top surface of the wafer/or target assembly may range from 0.1 to 30 cm, preferably from 0.5 to 5 cm.

5 **[0055]** Figure 5 provides an illustration of the process used for a wafer bumping application wherein the substrate is silicon wafer 20. Referring to Figure 5, a second electrode 24 is located above a wafer 20, and the wafer 20 comprising a plurality of solder bumps (not shown) is placed upon a first electrode 22 to form a target assembly. At least a portion of the surface of wafer 20 containing the plurality of solder bumps is
10 exposed to second electrode 24. While the wafer 20 is shown as being placed upon first electrode 22, it is envisioned that the wafer 20 can be placed anywhere between electrodes 22 and 24. A pulsed voltage 25 is applied across the first electrode 22 and the second electrode 24 to generate an electric field. A gas mixture 26 containing hydrogen and nitrogen is passed through the electric field. Low energy electrons 28 are
15 generated within the electric field which drift towards the first electrode 22 and wafer 20 disposed thereupon. In addition, a portion of the hydrogen within gas mixture 26 forms hydrogen ions 30 by electron attachment which also drift towards the first electrode 22 and wafer 20 disposed thereupon. The drift of negatively charged hydrogen ions 30 and electrons 28 towards the electrode 22 with wafer 20 disposed thereupon promotes
20 adsorption of ions 30 onto the surface of wafer 20 and fosters de-oxidation of the wafer surface (referred to herein as surface de-oxidation).

[0056] Depending upon the conductivity of the substrate, some of the electrons that are generated as a reaction byproduct from surface de-oxidation can accumulate on the substrate surface. In addition, a portion of the free electrons can directly adsorb on the
25 substrate due to the drifting along the electric field. This electron build-up on the substrate surface may prevent additional adsorption of the negatively charged ions as

well as adversely affect the equilibrium of the surface de-oxidation. To make the surface de-oxidation process more efficient, the electrons on the substrate surface need to be periodically removed.

[0057] One method to remove the electrons on the substrate surface may be to change the polarity of both of the electrodes relative to each other. During the polarity change, the voltage level on each electrode may not necessarily be the same. In one embodiment, the polarity change can be achieved by applying a bi-directional voltage pulse between at least two electrodes such as that shown in Fig. 10b. Figure 6 provides an example of a polarity change wherein an electrode may generate electrons in one phase of the voltage pulse (i.e., a negative bias) and retrieve electrons in another phase of the voltage pulse (i.e., a positive bias). In Fig. 6, electrode 110 is used as both the electron emission and electron retrieving electrode and electrode 120 is used as a base electrode. This arrangement allows the efficiency of surface de-oxidation to be maximized. Electrode 110 containing a plurality of sharp tips 101 is located above wafer 103. Electrode 110 is heated by connecting to an AC power source 104. Another electrode 120 is located underneath wafer 103. The change in polarity of electrodes 110 and 120 can be obtained, for example, by a bi-directional pulsed DC power 105. An example of bi-directional voltage pulse is illustrated in Figure 10b. When electrode 110 is negatively biased, at least a portion of the electrons generated from tips 101 attach to at least a portion of the reducing gas and newly created reducing gas ions drift towards wafer 103. When the polarity is reversed, electrons are released from the surface of wafer 103 and retrieved back at tips 101. Figures 7a and 7b illustrate the transportation of the charged species during each cycle of the voltage pulse. The frequency of changing the polarity of the two electrodes can range from 0 to 100 kHz.

[0058] In an alternative embodiment, excess electrons on the substrate surface may be removed by employing one or more additional electrodes. Figure 8 provides such

example wherein a wafer is the substrate. Referring to Figure 8, wafer 200 is disposed upon a grounded base electrode 201. Two electrodes, electrode 202 having a negative voltage bias relative to base electrode 201 and electrode 203 having a positive voltage bias relative to base electrode 201 are installed above the wafer surface 200. In this arrangement, electrons are continually generated from electrode 202 and retrieved at electrode 203. In one particular embodiment, the polarity of electrode 202 and electrode 203 may be periodically changed from a positive to a negative voltage bias, and vice versa, relative to the base electrode 201.

[0059] In yet another embodiment, electrons or residual surface charge may be removed from the substrate surface by employing a neutralizer after surface de-oxidation. If left untreated, residual charge contamination can cause electrostatic discharge damage to sensitive electronic components. In these embodiments, flowing a high purity gas such as N₂ through a commercially available neutralizer device and then across the substrate surface can neutralize the residual charge on the wafer surface.

The positive ions present in the gas will neutralize any residual electrons and provide an electrically neutral surface. Suitable charge neutralizer devices may, for example, consist of Kr-85 radioactive sources that produce equal densities of positive and negative ions in the gas. While positive and negative ions are produced in the gas as it flows through the wafer, the net charge of the gas stream is zero.

[0060] In certain embodiments, the substrate or target assembly may be moved with respect to the electrode that acts as an emission electrode. In this regard, the emission electrode may be in a fixed position and the substrate may be moved, the emission electrode may be moved and the substrate may be in a fixed position, or both the emission electrode and the substrate are moved. The movement may be vertical, horizontal, rotational, or along an arc. In these embodiments, surface de-oxidation may then occur within a localized area of the substrate surface.

[0061] For the following Figures 9a through 9e, the substrate is a silicon wafer that is disposed upon a base electrode, which is grounded. At least portion of the wafer surface comprising a plurality of solder bumps (not shown) is exposed to a second electrode that acts as both an emitting and a retrieving electrode (i.e., changing polarity, for example, from a negative to a positive bias in electrical potential). Figure 9a shows a silicon wafer 300 moved rotationally under a heated linear electrode 302 to which is applied a bi-directionally pulsed voltage relative to the base electrode 304 that may be cycled in a frequency range from 0 to 100KHz thereby generating an ion area shown as 306. A motor located outside the processing chamber (not shown) rotates the wafer. Such rotation is frequently accomplished in semiconductor processing without significant contamination of the wafer surface. Contamination may be avoided by employing high cleanliness, rotational feed-throughs and control of flow patterns. Figure 9b shows a silicon wafer 310 moved linearly under a heated linear electrode 312 to which is applied a bi-directionally pulsed voltage relative to the base electrode 314 thereby generating an ion area shown as 316. This arrangement may be suitable for applications wherein a conveyor belt is used to move wafers through tubular bumping furnaces such as, for example, printed circuit boards through reflow furnaces. Figure 9c shows a silicon wafer 320 moved rotationally under a pair of heated linear emission electrodes 324 and 326: the base electrode 322 has a steady positive bias and the emission electrodes 324 and 326 has a steady negative bias relative to the base electrode 322 so that electrons can be generated to and be retrieved back from the wafer surface thereby generating an ion area shown as 328. A motor located outside the processing chamber (not shown) rotates the wafer. Figure 9d shows a silicon wafer 330 moved linearly under a heated pair of linear electrodes 334 and 336 that are held at steady and opposite polarities relative to the base electrode 332 to conduct electron emission and retrieving separately thereby generating an ion area shown as 338. Lastly, Figure 9e employs a relatively smaller electrode 344 located on the end of a pivoting arm 346. The polarity of the electrode 344 is frequently altered relative to the base electrode 342 thereby generating an ion area shown as 348. The arm is swung over a rotating wafer 340, in for example an arc-like motion, to affect complete and uniform treatment of the entire wafer surface.

[0062] The method of the present invention can be used in several areas of the microelectronics manufacturing in addition to the reflow of a solder bumped wafer such as, for example, surface cleaning, metal plating, brazing, welding, and reflow and wave soldering for outer lead bonding. An example of reflow and wave soldering apparatuses that are suitable for the method of present invention is in Figs. 1-3 provided in pending U.S. application 09/949,580 which assigned to the assignee of the present invention and is incorporated herein by reference in its entirety. In one particular embodiment, the method of the present invention can be used to reduce surface oxides of metals, such as copper oxide, formed during silicon wafer processing or thin film de-oxidation. Such oxides may form as a result of the various wet processing steps, such as chemical mechanical planarization, that are used to form micro-electronic devices on the wafers. These surface oxides reduce device yield and device reliability. The present invention allows surface oxides to be removed in a fully dry, environmentally friendly manner that does not require the use of aqueous reducing agents. Further, since the present invention is performed at relatively low temperatures, it does not significantly affect the thermal budget of the device during processing. Higher temperatures, by contrast, tend to reduce device yield and reliability by causing diffusion of dopants and oxides thereby reducing device performance. Since the method of the present invention can be performed on a single wafer, the method can be integrated with other single wafer processes, thereby providing better compatibility with other fabrication steps.

[0063] The method and apparatus of the present invention are particularly suitable for applications of wafer bumping and thin film de-oxidation. The conveniences of using the present invention for wafer bumping and thin film de-oxidation are numerous. First, compared to typical reflow soldering processes for outer lead bonding, wafer bumping and thin film de-oxidation are both single-face treatment. In this connection, the space above the surface to be deoxidized can be as small as 1 cm, thereby resulting in an

efficient process for both ion generation and transportation. Second, the processing temperatures for reflow in wafer bumping are significantly higher than that of typical reflow soldering processes. The higher temperatures promote the formation of the negatively charged ions by electron attachment. Third, in wafer bumping and thin film de-oxidation processes, the solder bumps and thin films are completely exposed thereby minimizing any "shadow" effect during surface de-oxidation. Further, compared to other soldering processes whereby the solder has to wet and spread over the component surface, the deposited solder bumps on the wafer need only exhibit solder ball formation upon first reflow.

- 10 **[0064]** The invention will be illustrated in more detail with reference to the following examples, but it should be understood that the present invention is not deemed to be limited thereto.

Example 1

- 15 **[0065]** A first experiment was conducted by using a lab-scale furnace. The sample used was a fluxless tin-lead solder preform (melting point 183°C) on a grounded copper plate (anode), which was loaded inside a furnace and heated up to 250°C under a gas flow of 5% H₂ in N₂. When the sample temperature was at equilibrium, a DC voltage was applied between the negative electrode (cathode) and the grounded sample (anode) and
- 20 gradually increased to about -2kV with a current of 0.3mA. The distance between the two electrodes was about 1cm. The pressure was ambient, atmospheric pressure. It was found that the solder was indeed very well wetted on the copper surface. Without applying an electric voltage, a good wetting of a fluxless solder on a copper surface can never be achieved at such low temperature, even in pure H₂, because the effective
- 25 temperature for pure H₂ to remove tin-oxides on a tin-based solder is above 350°C.

Therefore, this result confirms that the electron-attachment method is effective in promoting H₂ fluxless soldering.

Example 2

5 **[0066]** Several cathode materials were investigated for electron-attachment assisted hydrogen fluxless soldering by using the field emission mechanism using the same set-up as Example 1. The results of the investigation is provided in Table I.

10 **[0067]** As Table I illustrates, the best result was obtained by using a Ni/Cr cathode, which provided the highest fluxing efficiency and thus resulted in the shortest wetting time. It is believed that the Ni/Cr cathode generates a relatively larger quantity of electrons and has suitable energy level of the electrons compared to other cathode materials.

Table I: Effect of Cathode Material on Wetting Time at 250°C and 20% H₂

Material of Cathode Rod with a Sharp Tip (1/16" dia.)	Time to Complete Wetting
Brass	1 min 55 sec
Copper	1 min 44 sec
Nickel Chromium	39 sec
Aluminum	1 min 28 sec
Stainless Steel	1 min
Tungsten	1 min 54 sec

15

Example 3

[0068] The present example was conducted to investigate the effectiveness of the thermal-field emission method for generating electrons. A 3mm diameter graphite rod, having a number of 1mm long machined tips protruding from its surface, acted as the cathode and had a geometry similar to that depicted in Figure 2i . Each of the protruding machined tips had a tip angle of 25 degrees. The graphite rod was heated up in a gas mixture of 5% H_2 and 95% N_2 to about 400 to 500°C by resistive heating using an AC power source. A DC voltage source of 5KV was applied between the graphite cathode and a copper plate that acted as an anode having a 1.5 cm gap therebetween. All the tips on the graphite rod were illuminated thereby indicating that electrons could uniformly be generated from the distributed tips on the graphite rod. Without heating of the graphite rod, there would be either no electron emission from the cathode, or arcing between one of the tips and the anode plate. This demonstrates that the combination of using a cathode having multiple tips and elevated temperatures, i.e., a thermal-field emission method, is effective for obtaining uniform electron emission from an integrated emitting system.

Example 4

[0069] The present example was conducted using a 0.04" diameter nickel-chromium alloy heating wire clamped horizontally between two machined Al_2O_3 refractory plates such as the electrode illustrated in Figure 4. A series of five nickel-chromium alloy emitting wires, each with a sharp tip (12.5 degree) on one end of the wire, protruded perpendicularly from the nickel-chromium heating wire and were vertically positioned between two refractory plates. The nickel-chromium heating wire and tips were heated up in a gas mixture of 5% H_2 and 95% N_2 to about 870°C using an AC power source. A DC voltage of 2.6KV was applied between the cathode and a copper plate that acted as

the anode having a 6 mm gap between the two electrodes. All five tips were illuminated and the total emission current reached 2.4 mA. Without heating of the wire, there would be either no electron emission from the cathode, or arcing between one of the tips and the anode plate. Like example 3, example 4 demonstrates that thermal-assisted field
5 emission provides uniform electron emission. Further, because of the higher temperature of the emission electrode, it also increases the quantity of the electron emission at a given electric potential.

Example 5

10 **[0070]** The present example was conducted to demonstrate the effect of a voltage pulse between two electrodes on cathode emission. A single-tip nickel-chromium alloy wire was used as the emission electrode and a grounded copper plate acted as a base electrode. The copper plate was located 3mm below the tip of the emission electrode. A tin/lead solder preform was disposed upon the copper plate. The nickel-chromium wire,
15 preform, and copper plate were maintained in a furnace at ambient temperature in a gas mixture of 4% H_2 and the remainder N_2 . A pulsed uni-directional voltage of various frequencies and amplitudes was applied between the two electrodes. In this connection, the electric potential of the emission electrode was varied from negative to zero relative to the grounded base electrode thereby allowing electrons to be generated
20 from the tip electrode. The results are provided in Table II.

[0071] The results in Table II indicate that greater quantities of electrons are generated from the emission electrode when a voltage pulse of higher pulsing frequency and amplitude is applied .

Table II: Uni-Directional Voltage Pulse

Pulsing Frequency (Hz)	0	250	500	1000	2500
Emission Current at 3.4 kV	0	0.3	0.4	0.5	0.6
Pulsing Amplitude (mA)					
Emission Current at 1.0 kV	0	0.1	0.1	0.2	0.2
Pulsing Amplitude (mA)					

Example 6

[0072] The present example was conducted to demonstrate surface discharge by

5 altering the polarity of the two electrodes using the same set-up as example 5.

[0073] A bi-directional voltage pulse with a total pulsing amplitude of 3.4 kV (e.g. from +1.7 kV to -1.7 kV) was applied between the two electrodes. During the bi-directional voltage pulse, the polarity of the two electrodes was changed. In other words, the tip of the emission electrode was varied from a positive to a negative electrical bias relative to the grounded base electrode thereby allowing electrons to be generated from and

10 retrieved to the tip electrode.

[0074] Table III provides the leakage current from the base electrode for each frequency of the polarity change. As Table III illustrates, the higher the frequency of the polarity change, the lower the charge build up will be by observing the leakage current

15 passing through the copper base electrode.

Table III: Bi-Directional Voltage Pulse

Pulsing Frequency (Hz)	250	500	1000	2500
Leakage Current (mA)	0.00069	0.00054	0.00015	0.00015

Example 7

[0075] The present example was conducted to demonstrate remote surface discharge by employing an additional electrode. A 90 Pb/10Sn solder preform having a melting point of 305°C was set on a small piece of a copper substrate that was set on an electrically insulated wafer. A grounded copper plate was placed underneath the wafer and acted as a base electrode. Two single-tip nickel-chromium wires, one with a negative voltage and one with a positive voltage, were installed 1 cm above the base electrode with the solder preform. The distance between the two single-tip electrodes was 1.5 cm. The arrangement was heated within a gas mixture containing 4% H₂ in N₂ from room temperature to a given reflow temperature above the melting point of the solder. When the reflow temperature reached equilibrium, electron attachment was started by applying the positive and the negative voltages to the two single-tip electrodes and the time required for the solder preform to form a spherical ball was recorded. The formation of a spherical solder ball indicated an oxide-free solder surface. As shown in Table IV, the surface de-oxidation is quite efficient at a range of temperature from 310 to 330°C, which is only 5 to 15°C above the melting point of the solder.

Table IV

Isotherm Reflow Temperature (°C)	310	320	330
Ball formation Time (seconds)	20, 18, 20, 24	17, 13, 16	14, 12
Average Ball Formation Time (seconds)	20.5	15.3	13

[0076] While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS

1. A method of removing metal oxides from a treating surface of a substrate, the method comprising:

providing the substrate which is proximal to a first electrode;

providing a second electrode that is proximal to the first electrode and the substrate wherein at least a portion of the treating surface is exposed to the second electrode and wherein the first and the second electrodes and the substrate reside within a target area;

passing a gas mixture comprising a reducing gas through the target area;

supplying energy between the first and second electrodes to generate electrons within the target area wherein at least a portion of the electrons attach to at least a portion of the reducing gas thereby forming a negatively charged reducing gas, wherein the energy comprises a pulsed direct current voltage; and

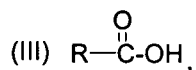
contacting the treating surface with the negatively charged reducing gas to reduce the metal oxides on the treating surface of the substrate, wherein the method is performed in the absence of a vacuum.

2. The method of claim 1 further comprising removing at least a portion of the electrons that accumulates on the treating surface of the substrate.

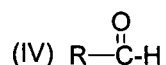
3. The method of claim 2 wherein the removing step comprises changing a polarity of the first and the second electrodes.

4. The method of claim 3 wherein a frequency of the polarity change ranges from 0 to 100 kHz.

5. The method of claim 2 wherein the removing step comprises providing a third electrode proximal to the first electrode, the second electrode, and the substrate wherein the third electrode has a positive bias in electric potential relative to the first and second electrodes.
6. The method of claim 2 wherein the removing step comprises passing a high purity gas through a neutralizer to provide an ionized neutral gas and contacting the treating surface with the ionized neutral gas.
7. The method of claim 1 wherein the reducing gas is a gas selected from the group consisting of H₂, CO, SiH₄, Si₂H₆, CF₄, SF₆, CF₂Cl₂, HCl, BF₃, WF₆, UF₆, SiF₃, NF₃, CClF₃, HF, NH₃, H₂S, straight, branched or cyclic C₁ to C₁₀ hydrocarbons, formic acid, alcohols, acidic vapors having the following formula (III):



organic vapors having the following formula (IV),



and mixtures thereof, wherein substituent R in formula (III) and formula (IV) is an alkyl group, a substituted alkyl group, an aryl group, or a substituted aryl group.

8. The method of claim 1 wherein the reducing gas is H₂.
9. The method of claim 7 wherein the gas mixture comprises 0.1 to 100% by volume of hydrogen.
10. The method of claim 9 wherein said gas mixture is 0.1 to 4% by volume of hydrogen.

11. The method of claim 1 wherein the gas mixture further comprises a carrier gas.
12. The method of claim 11 wherein the carrier gas comprises at least one gas selected from the group consisting of nitrogen, helium, argon, neon, xenon, krypton, radon, or mixtures thereof.
13. The method of claim 11 wherein the carrier gas has an electron affinity that is less than the electron affinity of the reducing gas.
14. The method of claim 1 wherein the substrate is at a temperature ranging from 0 to 450°C.
15. The method of claim 14 wherein the substrate is at a temperature ranging from 100 to 350°C.
16. The method of claim 1 wherein the distance between the treating surface and the second electrode ranges from 0.1 to 30 cm.
17. The method of claim 16 wherein the distance between the treating surface and the second electrode ranges from 0.5 to 5 cm.
18. The method of claim 1 wherein the first electrode is grounded.
19. The method of claim 1 wherein the second electrode is grounded.

20. The method of claim 1 wherein the method is used in at least one process selected from the group consisting of reflow soldering, wave soldering, wafer bumping, metal plating, brazing, welding, surface cleaning, thin film de-oxidation, or mixtures thereof.
21. The method of claim 1 wherein the electrons are generated in the supplying step by at least one additional method selected from the group consisting of cathode emission, gas discharge, and combinations thereof.
22. The method of claim 21 wherein the electrons are generated by a cathode emission method selected from the group consisting of field emission, thermal emission, thermal-field emission, photoemission, and electron beam emission.
23. The method of claim 22 wherein the electrons are generated by thermal-field emission.
24. A method of removing metal oxides from a surface of a substrate comprising a plurality of solder bumps, the method comprising:
- providing the substrate which is connected to a first electrode as a target assembly;
 - providing a second electrode adjacent to said target assembly wherein at least a portion of the surface comprising the plurality of solder bumps is exposed to the second electrode;
 - providing a gas mixture comprising a reducing gas and a carrier gas between the first and second electrodes;
 - supplying a pulsed direct current voltage between the first and second electrodes to generate electrons wherein at least a portion of the electrons attach to at least a portion of the reducing gas thereby forming a negatively charged reducing gas;

contacting the target assembly with the negatively charged reducing gas wherein the negatively charged reducing gas reduces the metal oxides on the surface of the substrate; and

removing at least a portion of the electrons accumulated on the surface of the substrate by changing a polarity of the first and second electrodes.

25. The method of claim 24 wherein a frequency of the polarity change ranges from 0 to 100 kHz.

26. The method of claim 24 wherein the temperature of the second electrode ranges from 25 to 3500°C.

27. The method of claim 26 wherein the temperature of the second electrode ranges from 150 to 1500°C.

28. The method of claim 24 wherein the second electrode is moved.

29. The method of claim 28 wherein the target assembly is moved.

30. The method of claim 24 wherein the target assembly is moved.

31. The method of claim 24 wherein the voltage ranges from 0.01 to 50 kV.

32. The method of claim 31 wherein the voltage ranges from 0.1 to 30 kV.

33. The method of claim 24 wherein the voltage pulse is uni-directional.

34. The method of claim 24 wherein the voltage pulse is bi-directional.
35. The method of claim 24 wherein the distance between the substrate and the second electrode ranges from 0.1 to 30 cm.
36. The method of claim 35 wherein the distance between the substrate and the second electrode ranges from 0.5 to 5 cm.
37. A method of removing metal oxides from the surface of a substrate comprising a plurality of solder bumps, the method comprising:
- providing the substrate which is connected to a first electrode;
 - providing a second electrode that is proximal to the first electrode and the substrate wherein the second electrode has a negative bias in electric potential relative to the first electrode and wherein at least a portion of the surface comprising the plurality of solder bumps is exposed to the second electrode;
 - passing a gas mixture comprising hydrogen and nitrogen between the first and the second electrodes;
 - supplying a pulsed direct current voltage between the first and the second electrodes to generate electrons from the second electrode wherein at least a portion of the electrons attach to the hydrogen to form negatively charged hydrogen ions and wherein the temperature of the second electrode ranges from 100 to 1500°C;
 - contacting the substrate with the negatively charged hydrogen ions to reduce the metal oxides on the surface of the substrate; and
 - removing at least a portion of the electrons accumulated on the surface of the substrate by changing polarity of the first and second electrodes.

38. The method of claim 37 further comprising heating the plurality of solder bumps to a temperature sufficient for the solder bumps to wet at least a portion of the surface of the substrate.
39. The method of claim 38 wherein at least a portion of the voltage in the supplying step is used for the heating step.
40. The method of claim 37 wherein the voltage pulse is unidirectional.
41. The method of claim 37 wherein the voltage pulse is bi-directional.
42. The method of claim 37 wherein the gas mixture comprises 0.1 to 4 % by volume hydrogen.
43. The method of claim 37 wherein a geometry of the second electrode is at least one selected from the group consisting of a thin wire, a rod with a sharpened tip, a comb, a screen, a loose coil, an array of combs, a bundle of thin wires, a rod with sharp tips protruding from its surface, a plate with a knurled surface, a wagon wheel, or mixtures thereof.
44. The method of claim 37 wherein the second electrode is a segmented assembly.
45. The method of claim 37 wherein the second electrode is composed of at least one material selected from the group consisting of brass, stainless steel, copper, nickel chromium, aluminum, tungsten, graphite, metal oxides deposited on a metal substrate, or mixtures thereof.

46. The method of claim 37 wherein the pressure of the gas mixture ranges from 10 to 20 psia.

47. The method of claim 37 wherein the second electrode is heated by at least one method selected from the group consisting of direct heating, indirect heating, infrared radiation heating, or combinations thereof.

48. A method of removing metal oxides from the surface of a substrate comprising a plurality of solder bumps, the method comprising:

- providing the substrate which is connected to a first electrode within a heating chamber;
- providing a second electrode that is proximal to the first electrode and the substrate wherein the second electrode has a negative bias in electric potential relative to the first electrode and wherein at least a portion of the surface comprising the plurality of solder bumps is exposed to the second electrode;
- passing a gas mixture comprising from 0.1% to 4% by volume hydrogen and from 1% to 99.9% by volume nitrogen between the first and the second electrodes wherein the pressure of the gas mixture ranges from 10 to 20 psia;
- supplying voltage between the first and the second electrodes to generate electrons from the second electrode wherein at least a portion of the electrons attach to the hydrogen to form negatively charged hydrogen ions;
- contacting the substrate with the negatively charged hydrogen ions to reduce the metal oxides on the surface of the substrate; and
- changing polarity of the second electrode to a positive bias in electric potential to remove at least a portion of the electrons from the surface of the substrate.

49. The method of claim 21 wherein the electrons are generated by gas discharge.
50. The method of claim 49 wherein the electrons are generated by a gas discharge method selected from thermal discharge, photo-discharge, avalanche discharge, and combinations thereof.
51. The method of claim 37 wherein the second electrode is composed of a semiconductor.
52. The method of claim 37 wherein the first electrode is composed of a semiconductor.
53. The method of claim 1 wherein the method is used in at least one process comprising wafer bumping.
54. The method of claim 21 wherein the electrons are generated by the cathode emission method comprising thermal-field emission.
55. The method of claim 37 wherein a geometry of the second electrode comprises a rod with a sharpened tip.
56. The method of claim 37 wherein a material for the second electrode comprises nickel chromium.
57. The method of claim 37 wherein the second electrode is heated by at least one method comprising direct heating.

58. The method of claim 21 wherein the electrons are generated by the gas discharge method comprising avalanche discharge.

59. A method of removing copper oxide from a treating surface of a substrate, the method comprising:

providing a substrate which is proximal to an anode, the substrate comprising a treating surface comprising copper oxide;

providing a cathode that is proximal to the anode and the substrate wherein at least a portion of the treating surface is exposed to the cathode and wherein the anode and the cathode and the substrate reside within a target area, wherein the cathode has a shape defined by a plate having protruding tips;

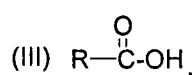
passing a gas mixture comprising a reducing gas through the target area;

supplying a pulsed direct current voltage between the anode and the cathode to generate electrons within the target area, wherein at least a portion of the electrons attach to at least a portion of the reducing gas thereby forming a negatively charged reducing gas;

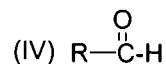
contacting the treating surface with the negatively charged reducing gas to reduce the metal oxides on the treating surface of the substrate; and

changing polarity of the second electrode to a positive bias in electric potential to remove at least a portion of the electrons from the surface of the substrate.

60. The method of claim 59 wherein the reducing gas is a gas selected from the group consisting of H₂, CO, SiH₄, Si₂H₆, CF₄, SF₆, CF₂Cl₂, HCl, BF₃, WF₆, UF₆, SiF₃, NF₃, CClF₃, HF, NH₃, H₂S, straight, branched or cyclic C₁ to C₁₀ hydrocarbons, formic acid, alcohols, acidic vapors having the following formula (III):



organic vapors having the following formula (IV),



and mixtures thereof, wherein substituent R in formula (III) and formula (IV) is an alkyl group, a substituted alkyl group, an aryl group, or a substituted aryl group.

61. The method of claim 59 wherein the reducing gas comprises H₂.
62. The method of claim 59 wherein the cathode comprises a nickel chromium alloy.
63. The method of claim 59 wherein the pressure of the gas mixture ranges from 10 to 100 psia.
64. The method of claim 59 wherein the voltage ranges from 0.1 to 30 kV.
65. The method of claim 59 wherein the substrate is at a temperature ranging from 100 to 350°C.
66. The method of claim 59 wherein the voltage is pulsed at a frequency between 0 and 20 KHz to prevent arcing.
67. The method of claim 59 wherein the method is a thin-film de-oxidation method.
68. A method of removing a thin film of copper oxide from a treating surface of a substrate, the method comprising:
providing a substrate which is proximal to an anode, the substrate comprising a treating surface comprising a thin film of copper oxide;

providing a cathode that is proximal to the anode and the substrate wherein at least a portion of the treating surface is exposed to the cathode and wherein the anode and the cathode and the substrate reside within a target area, wherein the cathode comprises a nickel chromium alloy and has a shape defined by a plate having protruding tips;

passing a gas mixture at a pressure of between 10 and 100 psia through the target area, the gas mixture comprising a reducing gas, the reducing gas comprising a mixture of H_2N_2 , wherein the mixture is from 0.1 to 100% by volume of H_2 ;

supplying a pulsed direct current voltage between the anode and the cathode to generate electrons within the target area, wherein the voltage is supplied in a range of from 0.1 to 30 kV and is pulsed at a frequency between 0 and 20 KHz, and wherein at least a portion of the electrons attach to at least a portion of the reducing gas thereby forming a negatively charged reducing gas;

contacting the treating surface with the negatively charged reducing gas to reduce the metal oxides on the treating surface of the substrate;

removing at least a portion of the electrons that accumulates on the treating surface of the substrate by changing polarity of the first and second electrodes,

wherein the substrate is at a temperature ranging from 100 to 350°C.