



POST-CMP CLEANING OF SEMICONDUCTOR WAFER SURFACES USING A COMBINATION OF AQUEOUS AND CRYOGENIC CLEANING TECHNIQUES

FIELD OF THE INVENTION

5 The present invention relates to the field of cleaning contaminants from post-chemical mechanical polishing of semiconductor materials and, in particular, to the removal of contaminants after chemical mechanical polishing of metals and dielectric films using a combination of aqueous-based and cryogenic enhanced (ACE) cleaning technologies.

BACKGROUND OF THE INVENTION

10 Chemical mechanical polishing (CMP) is used for the global planarization of metals and dielectric films in the process of fabrication for silicon based devices, optics fabrication, and compound semiconductor-based device fabrication. The CMP process involves holding and rotating a thin, flat substrate of the semiconductor material against a wetted polishing pad under controlled pressure and temperature in the presence of chemicals known as slurries. The slurry contains particles such as Ceria, alumina, or fumed or colloidal silica, along with surfactants, etchants, and other additives as appropriate to the CMP process. Following the CMP process, contaminants consisting of particles from the polishing slurry, chemicals added to the slurry, and reaction by-products of the polishing slurry are left behind on the wafer surface. These contaminants must be removed prior to any further steps in the IC fabrication process to avoid degradation of device reliability and introduction of defects into the device. Many particles of these contaminants are smaller than 0.3 μm .

25 Conventional cleaning techniques used to remove post-CMP contaminants, such as aqueous chemical cleaning processes in combination with megasonics and brushing, are inadequate to remove these smaller sized contaminants. Conventional wet techniques use fluid flow over the wafer surface to remove contaminants and, as such, their efficiency is limited by the thickness of the boundary layer created by the fluid flow. A particle smaller than the boundary layer is shielded from the physical drag force of the fluid and therefore remains on the wafer surface. The Van der Waals force on sub-0.3 μm slurry particles is such that ionic double layer repulsion, brought about by the similarity of the zeta potential of particles and surfaces in wet cleaning, is not sufficient to adequately clean the wafer



of particles and surfaces in wet cleaning, is not sufficient to adequately clean the wafer surface. As such, the fluid flow does not remove these smaller sized contaminants. Additional adhesion, due to chemical and hydrogen bonding, further complicates the cleaning capabilities of wet cleaning techniques and significantly reduces the efficiency of these processes for removing smaller sized contaminants.

Megasonics may be used in conjunction with these conventional wet techniques to significantly reduce the boundary layer thickness. The boundary layer may be decreased in thickness to 0.5 μm at 1 MHz. However, it is still not sufficient to efficiently remove these small sub-0.3 μm sized particles of which post-CMP slurry is composed. As such, these contaminants remain on the wafer surface.

The use of low k dielectric films such as carbon-doped oxides or organic films in dual damascene integration has added a further challenge to the post-CMP cleaning in which only aqueous-based chemistries are used. These films as well as CMP stop layers, such as silicon carbide, silicon nitride, and silicon oxynitride, are very hydrophobic and hence cannot be cleaned with water-based wet cleaning.

As such, there is a need for a cleaning technique which is able to remove post-CMP contaminants which are sub-0.3 μm particles from the surface of semiconductor wafers or other metals or dielectric films, especially when the surface from which particle removal is done is hydrophobic.

SUMMARY OF THE INVENTION

The present invention provides for a new and improved method of cleaning semiconductor surfaces as well as the surfaces of metals, dielectric films particularly hydrophobic low k dielectric films, and CMP etch stop films to remove post-CMP contaminants.

The present invention also provides for a process for the removal of post-chemical mechanical polishing (CMP) contaminants from the surface of semiconductors, metals, dielectric films particularly hydrophobic low k dielectric films, and CMP etch stop films where such contaminants are 0.3 μm in size or smaller.

The ACE cleaning process of the present invention comprises a unique combination of aqueous and cryogenic cleaning to remove these small contaminant particles from the surface of the semiconductor, metal, or film. At its broadest, the present invention comprises a process for cleaning such surfaces to remove contaminant particles

wherein the process includes the steps of providing a surface which has undergone chemical-mechanical polishing (CMP), cleaning the surface with an aqueous-based cleaning process, at least partially drying the surface, and, shortly thereafter, cleaning the surface with a CO₂ cryogenic cleaning process. Using this process, contaminant particles including small sub-0.3 μm particles as well as sub-0.1 μm particles are removed from the surface. The present invention also removes such contaminants from surfaces which are hydrophobic and hence difficult to clean with aqueous-based cleaning techniques alone.

BRIEF DESCRIPTION OF FIGURES

Figure 1 is a flow chart outlining the general steps of the prior art as well as the process of the present invention.

Figure 2 is a flow chart outlining the general apparatus used in CO₂ cryogenic cleaning.

DETAILED DESCRIPTION

A flow chart showing the general steps of the ACE cleaning process is provided in Figure 1. The ACE cleaning process comprises the steps of cleaning the surface having CMP contaminants with an aqueous-based cleaning solution, optionally using megasonics and/or brushing, removing the bulk water from the surface, and cleaning the surface with a CO₂ cryogenic cleaning process. The step of aqueous cleaning preferably occurs prior to the step of cryogenic cleaning to obtain the best results.

Standard wet (aqueous) cleaning processes are well known in the industry and these may be used. An example of such a process is described in U.S. Patent No. 5,922,136 which issued to patent on July 13, 1999. As a general example, the wet cleaning process consists broadly of the steps of rinsing the semiconductor wafer surface with deionized water, using one or more aqueous-based or solvent-based cleaners, and re-rinsing the surface with deionized water. These steps may be repeated where more than one aqueous or solvent based cleaner is used and rinsing would occur between each use of cleaner. The wet based cleaning comprises the use of deionized (DI) water which may also include cleaning agents. Further, the wet based cleaning process may incorporate megasonics and/or brush scrubbing to further remove contaminant particles.

After wet cleaning, the bulk water is removed from the wafer surface and it then undergoes cryogenic cleaning. Preferably, the cryogenic cleaning occurs shortly after the

wet cleaning to reduce the possibility of particle adhesion. Standard cryogenic cleaning processes are well known in the industry and may be incorporated into the ACE cleaning process. An example of these techniques is described in U.S. Patent No. 5,853,962 issued December 29, 1998 to Eco-Snow Systems Inc. The cryogenic cleaning process
5 incorporated into the ACE cleaning process may also include newer forms of cryogenic cleaning utilizing liquid and/or vapour assistance.

As an example of CO₂ cryogenic cleaning, liquid CO₂ under pressure (for example, at 850 psi and 25°C) is expanded through a specially designed nozzle. The rapid expansion of the liquid causes the pressure and temperature to drop resulting in the formation of solid
10 CO₂ snow particles entrained in a gaseous CO₂ stream. The stream of solid and gaseous CO₂ is directed at the wafer surface removing the contaminants. Particulate contaminants are removed by momentum transfer by the cryogenic particles overcoming the force of adhesion of the contaminant particles on the wafer surface. Thin films of organic
15 contaminants are removed by the dissolution of the film in liquid CO₂ formed at the interface of the cryogenic particles and the wafer surface due to the pressure on the particles.

The ACE cleaning process may be applied to semiconductor wafers and wafer surfaces but is not limited to silicon based materials only. CMP is used in the fabrication of not only silicon based devices but also in optics fabrication, and compound
20 semiconductor-based device fabrication. The ACE cleaning process may also be used to remove contaminants from metal surfaces and dielectric films which have undergone CMP. Whenever the terms "wafer" or "wafer surface" are used herein, it is intended that these other materials may also be used and that the process of the present invention may be applied to them in a similar manner.

The ACE cleaning process incorporates cleaning techniques known in the semiconductor industry. Wet or aqueous cleaning is a well known method for cleaning semiconductor wafer surfaces. Its use is standard in the industry. However, it has heretofore been unknown to use CO₂ cryogenic cleaning for cleaning semiconductor
25 wafers to remove post-CMP contaminants and in particular to remove sub 0.3 µm, or even sub-0.1 µm, contaminants particles from wafer surfaces. It has also been unknown to use a combination of aqueous-based cleaning followed by CO₂ cryogenic cleaning to
30 remove such post-CMP contaminant particles from wafer surfaces. The combination of aqueous-based cleaning and CO₂ cryogenic cleaning allows for all of the post-CMP

contaminants to be removed including the smaller sized particles. Wet or aqueous based cleaning is not sufficient to remove all of the contaminants, particularly the smaller-sized particles, and is not efficient in removing the contaminants where the particles must be removed from hydrophobic surfaces. Cryogenic cleaning by itself will also not remove all
5 CMP contaminants. Additives used in CMP include surfactants and corrosion inhibitors which are organic in nature. These additives will not be removed with cryogenic cleaning and will impede the particle removal by cryogenic cleaning if left on the wafer surface. It has therefore been surprisingly found that cryogenic cleaning along with wet cleaning is suitable and desirable for use in the semiconductor industry to remove post-CMP
10 contaminants from wafer surfaces and, when used in combination with wet cleaning, provides for the enhanced removal of these small sub-0.3 μm contaminants from the wafer surface, especially hard to clean hydrophobic surfaces, than that obtained through the use of wet cleaning alone.

Each of the wet and cryogenic cleaning processes may incorporate steps well-
15 known in their respective art. They have not however, prior to this, been used in combination to remove contaminants from wafer surfaces and cryogenic cleaning has not been used in the semiconductor industry to remove post-CMP contaminants. CO_2 cryogenic cleaning does not depend on the wetting of the wafer surface but, rather, on momentum transfer. Hence, it is able to remove CMP contaminants even from
20 hydrophobic low k dielectric films. This, therefore, enables the copper-low k integration scheme to be extended to further technology nodes from those in which it is traditionally used.

The ACE cleaning process combines aqueous-based and cryogenic cleaning technologies to overcome the major problems faced with the use of aqueous-based
25 cleaning technologies alone: the limitation of the boundary layer in effectively removing sub-0.3 μm particles, or even sub-0.1 μm particles, from the wafer surface, and cleaning hydrophobic surfaces. The cryogenic cleaning process works by momentum transfer wherein the cryogenic particles arriving at high velocities on the wafer surface are able to overcome the force of adhesion of the contaminant particles by their impact. Once the
30 particles have overcome their force of adhesion, the drag force due to the gaseous CO_2 flow removes the particles completely off the surface. Thus, the cleaning does not depend on wetting the surface and hence is not limited by the hydrophobic/hydrophilic properties of the surface or a film deposited on it.

During cryogenic cleaning, there is also a boundary layer formed due to the flow of the CO₂ gas over the wafer surface. However, the boundary layer manifests itself differently since the major mechanism of particle removal in cryogenic cleaning is momentum transfer as compared to hydrodynamic drag in wet cleaning. The CO₂ cryogenic particles have to cross this boundary layer to arrive at the wafer surface. During their passage through this layer, the velocity of the cryogenic particles decreases due to the drag force on them. The decrease in velocity of the cryogenic particles is measured in terms of its relaxation time. The relaxation time is the time in which the velocity of the cryogenic particles decreases to 36% of their initial velocity and is given by the following expression:

$$\tau = (2 r^2 \rho_p C_c) / 9 \eta$$

where r is the radius of the cryogenic particle, ρ_p is the cryogenic particle density, C_c is the Cunningham slip correction factor, and η is the viscosity of the medium. This equation shows that if the viscosity of the medium is high, the relaxation time constant is low implying that the cryogenic particles experience a greater drag force crossing the boundary layer, resulting in faster decrease of their velocity and momentum arriving at the wafer surface. It also shows that larger particles can arrive at the wafer surface with greater velocity and momentum to overcome the force of adhesion of the contaminant particles on the wafer surface. An example calculation shows that to remove 0.1 μm contaminant particles held by Van der Waals forces to a wafer surface, cryogenic particles larger than 1.2 μm in diameter must arrive at the wafer surface with a velocity greater than 14 m/s. This velocity is achievable with typical aggressive nozzles such as an EcoSnowTM cleaning tool. The smallest cryogenic particle that can cross a 50 μm thick boundary with a velocity of at least 14 m/s is 0.2 μm . Hence, this example shows that the boundary layer is not a limiting factor for removal of small size particles since the entire size distribution of cryogenic particles required to remove the small contaminant particles can cross the boundary layer created by the CO₂ gas flow over the wafer surface.

EXAMPLES

Wet Cleaning Process

To remove the post-CMP contaminants from a semiconductor wafer in a conventional wet cleaning process, the wafer is placed in a flowing water bath and rinsed for up to one minute with deionized water. Aqueous-based cleaners are then applied to the wafer for up to approximately two minutes to clean it. After this step, the wafer is rinsed again in a flowing water bath with deionized water for approximately one minute. It is then dried in a spin rinse dryer at approximately 1500 rpm for approximately three minutes.

Alternatively, the step of cleaning with aqueous- or solvent-based cleaners may occur in several steps with a deionized water rinse between each step. Solvents include any of those solvents generally used in the industry to clean contaminants from wafer surfaces. These include but are not limited to SC1, which is a combination of ammonium hydroxide, hydrogen peroxide, and water generally mixed at a ratio in the range of from 0.2:1:5 to 1:1:5; a solution of 0.5%-2% by volume ammonium hydroxide in water; dilute hydrofluoric acid in deionized water of concentration 0.2 to 1.0%; chelating agents suitable for use in post-CMP cleaning; oxidizing agents such as hydrogen peroxide; and surfactants to reduce the surface tension. Solvents are chosen depending upon the contaminants to be removed.

During the cleaning step, the use of megasonics and/or brush scrubbing with PVA brushes is common. These techniques are well known in the industry and these well known methods may be used. A brief description of these steps follows as examples of usable processes, however, any known or standard technique may be used as well.

Megasonics and Brushing Techniques

For megasonic cleaning, either batch cleaning or single wafer cleaning processes may be used. In megasonic cleaning tanks using a batch process, the wafers are placed vertically in the tank with the megasonic transducer at the bottom of the tank. In a single wafer cleaning system, the wafer is placed horizontally and a megasonic wand moved in a sweeping motion over the wafer surface. The megasonic transducer or wand operates at a frequency of about 800 kHz to about 1.3 MHz. The vibrations of the megasonic transducer or wand results in the formation of acoustic waves caused by wave attenuation in a viscous

medium. These waves result in streaming flows and the formation of small cavitation bubbles, both of which aid in the removal of particles from the wafer surface.

In brush scrubbing, a PVA brush is used. The brush is comprised of a soft sponge-like material and is highly compressible. It rotates across the wafer surface with cleaning liquids simultaneously being directed through its core. The brush does not come in contact with the wafer surface. Instead, it hydroplanes over it, dislodging the contaminant particles by hydrodynamic drag forces as the liquid is both compressed and pushed along by the brush. It is therefore important that the wafer surface be hydrophilic so that the brush hydroplanes over the wafer surface and does not touch it. Once the contaminant particles are dislodged, they remain suspended in the liquid until they are removed from the wafer surface by the fluid flow.

Drying the Surface

After wet cleaning, the bulk water is removed from the wafer surface and it then undergoes cryogenic cleaning. The bulk water may be removed by dipping the wafer in alcohol to displace the water or spraying it with alcohol while spinning the wafer. If desired, the surface may be completely dried.

Cryogenic Cleaning Process

Preferably, the cryogenic cleaning occurs shortly after the wet cleaning to reduce the possibility of particle adhesion. Preferably, the cryogenic cleaning will occur within 24 hours or less after wet cleaning. Standard cryogenic cleaning processes are well known in the industry and may be incorporated into the ACE cleaning process. An example of these techniques is described in U.S. Patent No. 5,853,962 issued December 29, 1998 to Eco-Snow Systems Inc.

As an example of such a process, the typical cleaning system is shown in Figure 2. The cleaning container 12 provides an ultra clean, enclosed or sealed cleaning zone. Within this cleaning zone is the wafer 1 held on a platen 2 by vacuum. The platen with wafer is kept at a controlled temperature of up to 100°C. Liquid CO₂, from a cylinder at room temperature and 850 psi, is first passed through a sintered in-line filter 4 to filter out very small particles from the liquid stream to render the carbon dioxide as pure as possible and reduce contaminants in the stream. The liquid CO₂ is then made to expand through a small aperture nozzle, preferably of from 0.05" to 0.15" in diameter. The rapid expansion

of the liquid causes the temperature to drop resulting in the formation of solid CO₂ snow particles entrained in a gaseous CO₂ stream flowing at a rate of approximately 1-3 cubic feet per minute. The stream of solid and gaseous CO₂ is directed at the wafer surface at an angle of about 30 to about 60 degrees, preferably at an angle of about 45 degrees. The nozzle is preferably positioned at a distance of approximately 0.375" to 0.5" measured along the line of sight of the nozzle to the wafer. During the cleaning process, the platen 2 moves back and forth on track 9 in the y direction while the arm of the cleaning nozzle moves linearly on the track 10 in the x direction. This results in a rastered cleaning pattern on the wafer surface of which the step size and scan rate can be pre-set as desired. The humidity in the cleaning chamber is preferably maintained as low as possible, for example <-40°C dew point. The low humidity is present to prevent the condensation and freezing of water on the wafer surface from the atmosphere during the cleaning process which would increase the force of adhesion between the contaminant particles and the wafer surface by forming crystalline bridges between them. The low humidity can be maintained by the flow of nitrogen or clean dry air. As well, throughout the cleaning process, it is important that the electrostatic charge in the cleaning chamber be neutralized. This is done by the bipolar corona ionization bar 5. The system also has a polonium nozzle mounted directly behind the CO₂ nozzle for enhancing the charge neutralization of the wafer which is mounted on an electrically ground platen. The electrostatic charge develops by triboelectrification due to the flow of CO₂ through the nozzle and across the wafer surface and is aided by the low humidity maintained in the cleaning chamber.

For particulate contaminants, the removal mechanism is primarily by momentum transfer of the CO₂ cryogenic particles to overcome the force of adhesion of the contaminant particles on the wafer surface. Once the particles are "loosened", the drag force of the gaseous CO₂ removes it from the surface of the wafer. The cleaning mechanism for organic film contaminants is by the formation of a thin layer of liquid CO₂ at the interface of the organic contaminant and the surface due to the impact pressure of the cryogenic CO₂ on the wafer surface. The liquid CO₂ can then dissolve the organic contaminants and carry it away from the wafer surface.

In a liquid-assisted cryogenic process, described in more detail in U.S. patent application number 60/369,853 filed April 5, 2002 and incorporated herein by reference, a liquid having a high vapour pressure, such as but not limited to isopropyl alcohol, ethanol, acetone, ethanol-acetone mixtures of 50%v/v, methanol, methyl formate, methyl iodide,

and ethyl bromide, is sprayed on the wafer surface either during the cryogenic cleaning or prior to it. The liquid may be sprayed on the surface either as a thin layer for particle removal or as a thicker film which, when pushed by the cryogenic spray, would introduce additional drag forces to remove the particles. The liquid may be sprayed using any
5 standard apparatus such as a Teflon misting nozzle used in wet benches for spraying deionized water on wafer surfaces. Additionally, a vapour of the liquid may be condensed on the wafer surface as in the vapour assisted cryogenic cleaning as described in U.S. patent application 60/369,852 filed April 5, 2002, incorporated herein by reference. The wafer is covered with the liquid preferably for up to ten minutes. It may be covered by one
10 layer of spraying of the liquid or the wafer may be repeatedly sprayed with layers to ensure that the wafer remains wetted. After this time period, the CO₂ cryogenic spray is initiated. Standard techniques are used such as those described above. The liquid reduces the force of adhesion of the particle contaminants on the wafer surface by reducing the Hamaker constant component of the intervening medium. Therefore, the CO₂ cryogenic
15 particles can easily dislodge the contaminants from the surface.

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CLAIMS:

1. A process for the removal of chemical-mechanical polishing (CMP) contaminants from the surface of a semiconductor wafer, metal, or film, comprising the steps of:
 - 5 a) Wet cleaning the surface with deionized water and/or an aqueous or solvent-based cleaner;
 - b) At least partially drying the surface; and
 - c) Cryogenically cleaning the surface with CO₂.
- 10 2. The process of claim 1 wherein the surface is partially dried by the removal of bulk water.
3. The process of claim 1 wherein the surface is substantially dried.
- 15 4. The process of claim 1 wherein step (a) comprises the steps of rinsing the surface with deionized water, cleaning the surface with an aqueous or solvent based cleaner, and rinsing the surface with deionized water.
5. The process of claim 4 wherein step (a) further comprises repeating the steps of
20 cleaning the surface with one or more aqueous or solvent-based cleaners and rinsing the surface with deionized water.
6. The process of claim 1 wherein step (a) comprises the step of buffing the surface with deionized water and/or an aqueous or solvent based cleaner.
- 25 7. The process of claim 1 wherein step (c) comprises the steps of expanding liquid CO₂ through a nozzle under pressure to result in the formation of solid CO₂ entrained in a gaseous CO₂ stream; and directing the CO₂ stream at the surface to remove contaminants.
- 30 8. The process of claim 2 wherein the bulk water is removed by dipping the surface in alcohol and slowly removing the surface from the alcohol or by spinning the surface while spraying alcohol on the surface.

9. The process of claim 7 wherein step (c) is preceded by spraying the surface with a liquid having a high vapour pressure; and allowing the liquid to remain on the surface for a desired period of time.
- 5 10. The process of claim 7 wherein step (c) is preceded by the steps of covering the surface with a vapour of a liquid to reduce the force of particle-surface adhesion; and allowing the vapour to remain on the surface for a desired period of time.
11. A process for the removal of contaminants having a size of 0.3 μm or smaller
10 from a surface of a semiconductor wafer, metal, or film, produced by post-chemical mechanical polishing of said semiconductor wafer, metal, or film, comprising the steps of:
- a) Wet cleaning the surface comprising cleaning the surface with deionized water, cleaning the surface with an aqueous-based cleaner in deionized water,
15 or buffing the surface with deionized water and/or aqueous cleaner;
 - b) At least partially drying the surface by removing bulk water; and
 - c) Cryogenically cleaning the surface with CO_2 comprising the steps of expanding liquid CO_2 through a nozzle under pressure to result in the formation of solid CO_2 entrained in a gaseous CO_2 stream, and directing the
20 CO_2 stream at the surface to remove contaminants.
12. The process of claim 11 wherein the surface is fully dried.
13. The process of claim 11 wherein step (a) comprises the steps of rinsing the surface
25 with deionized water, cleaning the surface with an aqueous-based cleaner, and re-rinsing the surface with deionized water.
14. The process of claim 11 wherein step (c) is preceded by the steps of spraying the surface with a liquid having a high vapour pressure; and allowing the liquid to
30 remain on the surface for a desired period of time.

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15. The process of claim 11 wherein step (c) is preceded by the steps of covering the surface with a vapour of a liquid having a high vapour pressure to reduce the force of particle-surface adhesion; and allowing the vapour to remain on the surface for a desired period of time.

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