METHODS AND APPARATUS FOR CLEANING SEMICONDUCTOR SUBSTRATES AFTER POLISHING OF COPPER FILM

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to methods and apparatus for processing and cleaning a substrate, and more specifically to methods and apparatus for cleaning semiconductor substrates after polishing of copper films.

2. Background Information

In the manufacture of advanced semiconductor devices, copper (Cu) is beginning to replace aluminum (Al) as the material for metallization. Cu has become desirable due to its lower resistivity and significantly improved electromigration lifetime, when compared to Al.

One process for Cu metallization uses a dual damascene approach. As illustrated in Figure 1a, a dielectric layer 110 is deposited above a substrate 100. Dielectric layer 120 may be made up of materials such as silicon dioxide. Vias and/or trenches 120 are then formed in the dielectric layer 110, as illustrated in Figure 1b. Vias/trenches 120 may be formed, for example, using dry etching techniques. Next, a thin layer of barrier material (barrier layer) 130, for example, tantalum (Ta), titanium (Ti), or titanium nitride (TiN) is deposited as illustrated in Figure 1c. After barrier layer 130 is deposited the vias/trenches 120 are filled with copper (Cu) layer 140, as illustrated in Figure 1d. Cu layer 140 may be deposited using well known deposition techniques, for example, chemical vapor deposition (CVD), physical vapor deposition (PVD), or electroplating. In order to isolate the copper interconnects, as illustrated in Figure 1e, the excess copper layer 140 and barrier layer 130 must be removed.

One method for removing the excess copper layer 140 and barrier layer 130 is polishing the surface of the substrate, for example, polishing using chemical mechanical polishing (CMP). In a CMP process, the semiconductor substrate is polished with a slurry containing abrasive particles, such as alumina particles, and an oxidant, such as hydrogen peroxide. In the CMP process, contaminants are introduced which include particles and/or metal contamination on the copper layer 150, dielectric surface 160, and in the dielectric subsurface 165.

Regardless of how the CMP process is performed, the surface of semiconductor substrate must be cleaned of contaminants. If not removed, these contaminants may affect device performance characteristics and may cause device failure to occur at faster rates than usual. Cleaning the semiconductor substrate after chemical mechanical polishing of copper may be necessary to remove such contaminants from the copper layer and dielectric layers.

One method for cleaning the semiconductor substrate after polishing of the copper layer is brush scrubbing. Brush scrubbing, whether single-sided or double-sided brush scrubbing, is the industry standard for cleaning oxide and tungsten CMP applications. However, there are several problems associated with applying brush scrubbing to post copper CMP cleaning.

One such problem is brush loading. During the CMP process, the top surface of the copper layer may be oxidized and forms copper oxide, for example copper oxide (Cu_2O or CuO) or copper hydroxide ($Cu(OH)_2$). In basic or neutral pH cleaning environments, the copper oxide or copper hydroxide does not dissolve and may be transferred to the brushes, thus loading the brushes. The contaminated (or loaded) brushes may then transfer the copper oxide or copper hydroxide contaminants to subsequently processed substrates during cleaning.

For tungsten and other oxide applications, brush loading could be curtailed by adding a dilute ammonium hydroxide (NH_4OH). In the presence of NH_4OH, part of the copper oxide may form $Cu(NH_3)^{2+}$ complex and may be dissolved; however, due to the high pH environment, the dilute ammonium hydroxide has been found to be insufficient to prevent brush loading of copper oxide. Additionally, it has been found that scrubbing with dilute ammonium hydroxide also causes etching of the copper layer and may cause serious surface roughening.

Brush loading may also occur when alumina particles are used in the copper CMP process. In neutral or inorganic acid (e.g. HCl) cleaning environments, there is an electrostatic attraction between alumina particles and the silicon dioxide surface which makes it difficult to remove the alumina particles from the surface of the dielectric material. Because of the electrostatic attractive force, the alumina particles may also adhere to the brush and cause another brush loading problem with similar effects to those discussed above.

Yet another problem caused by the CMP process is that the surface and subsurface of the dielectric layer may become contaminated during polishing with metal from the copper layer and barrier layer as well as other contaminants from the slurry. During the CMP process, contaminants, especially metal contaminants, may penetrate into the dielectric layer up to approximately 100 angstroms (Å) from the surface. Again, these contaminants may affect device performance characteristics and may cause device failure.

Thus, what is needed is a cleaning environment and methods for cleaning post copper CMP substrates that alleviate the problems of brush loading without affecting the quality of the copper and dielectric layers.

Furthermore, what is needed is a cleaning environment and methods for cleaning post copper CMP substrates that have the capability of removing surface and subsurface contaminants from the copper and dielectric layers.

SUMMARY OF THE INVENTION

A cleaning solution, methods and apparatus for cleaning semiconductor substrates after chemical mechanical polishing of copper films is described. The present invention includes a cleaning solution which combines deionized water, an organic compound, and a fluoride compound in an acidic pH environment for cleaning the surface of a semiconductor substrate after polishing a copper layer.

Additional features and benefits of the present invention will become apparent from the detailed description, figures, and claims set forth below.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is illustrated by way of example and not limitation in the accompanying figures in which:

Figure 1a illustrates a semiconductor substrate having a dielectric layer deposited thereon.

Figure 1b illustrates the semiconductor substrate of Figure 1a after vias and/or trenches are formed in the dielectric layer.

Figure 1c illustrates the semiconductor substrate of Figure 1b after a thin barrier layer has been deposited thereon.

Figure 1d illustrates the semiconductor substrate of Figure 1c after a layer of Copper material has been deposited thereon.

Figure 1e illustrates the semiconductor substrate of Figure 1d after chemical mechanical polishing of the excess copper layer and barrier layer.

Figure 2 illustrates one embodiment of a scrubber system.

Figure 3 illustrates a flowchart of one embodiment of the process of the present invention.

DETAILED DESCRIPTION

Methods and Apparatus for Cleaning Semiconductor Substrates After Polishing of Copper Film are disclosed. In the following description, numerous specific details are set forth such as specific materials, processes, parameters, dimensions, etc. in order to provide a thorough understanding of the present invention. It will be obvious, however, to one skilled in the art that these specific details need not be employed to practice the present invention. In other instances, well known materials or methods have not been described in detail in order to avoid unnecessarily obscuring the present invention.

The following description describes a cleaning solution, methods, and apparatus for cleaning a semiconductor substrate after the formation of copper interconnect(s) and chemical mechanical polishing (CMP)/planarization of that copper interconnect(s). It should be noted that the processes for formation of copper interconnects in semiconductor device fabrication are well known in the art and are therefore not described in detail herein.

It should also be noted that, although the term semiconductor substrate is used throughout this disclosure and claims the term semiconductor substrate is used to refer to a silicon semiconductor substrate or a part thereof, such as gallium arsenide, upon which device layers have been or are going to be formed. It should also be noted that the term substrate includes but is not limited to: fully processed, semi-processed, or unprocessed substrates with semiconductor materials thereon.

Additionally it should be noted that, although the present invention is described in conjunction with the scrubbing of a semiconductor substrate or wafer, it will be appreciated that any similarly shaped, i.e. generally flat substrate, may be processed by the methods and apparati of the present invention. Further, it will be appreciated that reference to a semiconductor substrate or wafer may include a bare or pure semiconductor substrate, with or without doping, a semiconductor substrate with epitaxial layers, a semiconductor substrate incorporating one or more device layers at any stage of processing, other types of substrates incorporating one or more semiconductor layers such as substrates having semiconductor on insulator (SIO) devices, or substrates for processing other apparati and devices such as flat panel displays, multichip modules, etc.

As described in the background of the invention after the copper interconnects on a semiconductor substrate have been planarized using CMP techniques, it is necessary to clean the semiconductor substrate and remove any contaminants from the surface and subsurface of the semiconductor substrate. One such technique for removing contaminants from the semiconductor substrate is scrubbing the semiconductor substrate (substrate).

As an example, and not by limitation, the present invention is described in conjunction with a scrubbing process, more specifically, a scrubbing process in which both sides of the wafer are scrubbed simultaneously. The scrubber may include a number of stations. Each of these stations represents one or more steps in the substrate cleaning process. Contaminated substrates are loaded at one end of the system and cleaned and dried substrates are unloaded from the other end of the system. Example of a systems of this type are the DSS-200™ Scrubber

and the Synergy™ Scrubber available from OnTrak Systems, Inc. of Milpitas, California.

Figure 2 represents a cross sectional view of a Synergy™ configuration (cleaning system). Usually, the contaminated substrates are delivered to the cleaning system after chemical mechanical planarization (CMP), from a wet bench, or from other processes resulting in contamination. At the start of the cleaning process contaminated substrates are loaded into a wafer cassette 280 (cassette) and the cassette 280 is then placed into the wet send indexer station 210. After cassette 280 is placed into wet send indexer station 210, the substrates are automatically removed from the cassette 280 and placed, one at a time, into the outside brush station 220.

In the outside brush station 220, a substrate is processed through a first scrub. During the first scrub, the cleaning solution may be applied to the substrate in several different ways. For example, in one embodiment the cleaning solution is sprayed onto the substrate. In another embodiment the cleaning solution is applied to the substrate through brushes 221. Yet another embodiment applies the cleaning solution by dripping the cleaning solution onto the substrate.

The scrubbed substrate is then automatically removed from the outside brush station 220 and placed into the inside brush station 230. In the inside brush station 230, the substrate is processed through a second scrub. In the inside brush station 230 the cleaning solution may be applied to the substrate in a similar manner as in outside brush station 220.

After the second scrub the substrate is then automatically removed from the inside brush station 230 and placed into the rinse, spin and dry station 240. Rinse, spin, and dry station 240 rinses, spins, and dries the substrate. At this point the wafer has been cleaned.

Once the rinse, spin, and dry steps have been completed the substrate is then transported from the rinse, spin, and dry station 240 to the output station 250 where the substrate will be placed into cassette 281. The transfer is usually carried out by a robotic arm which lifts the substrate out of the rinse, spin, and dry station 240 by its edges and places it into the cassette 281. The cassette is then transferred to storage or to another cleaning or processing system.

It will be clear to one of ordinary skill in the art that some of the steps in the cleaning system described above may occur in another order and/or with various solutions depending upon the substrate or substrate layer being cleaned. For example, different cleaning solutions, such as water, citric acid, ammonium hydroxide, ammonium citrate, and hydrofluoric acid solution (or mixtures of solutions) may be used in one of the brush stations. Also, other systems may include one brush station, or more than two brush stations. Moreover, other systems may omit one or more of the above stations/steps and may include additional processing stations, such as a CMP station.

It should be noted that while the following description illustrates the use of the present invention in a cleaning system in which both sides of the substrate are scrubbed simultaneously, the present invention may be used in other cleaning systems and processes. For example, a cleaning system in which only a single side of the substrate is scrubbed or a cleaning system in which the substrate is cleaned with chemical spray.

Figure 3 illustrates one embodiment of the process of the present invention. At step 310, the copper layer is planarized using chemical mechanical polishing. It should be noted that other techniques for planarization of the copper layer may be used and that it may still be desirable to clean the semiconductor substrate using the present

invention after such planarization in order to remove potential contaminants from the substrate surface and/or subsurface.

At step 320, the polished semiconductor substrate is then placed in a scrubber. The substrate is then scrubbed, at step 330, to remove the contaminants caused by the polishing process. During scrubbing, a cleaning solution is applied to the substrate in order to aid and/or effectuate the removal of the contaminants (step 340). This cleaning solution may be used in either outside brush station 220 or inside brush station 230, or both brush stations if necessary, of the scrubber in Figure 2.

In one embodiment, the present invention uses a cleaning solution that is made up of deionized water, an organic compound, and a fluoride compound, all of which are combined in an acidic pH environment for cleaning the surface of a semiconductor substrate after polishing a copper layer. The use of an acidic pH environment helps dissolve copper oxide and alleviates some of the problems of brush loading discussed in the background of the invention. It should be noted that it is desirable to keep the acidic pH environment within a pH level range of approximately 1-6. In one embodiment of the present invention, the acidic pH environment has a pH level in the range of approximately 2-4.

The use of an organic compound helps to change the electrostatic forces between the particles and surfaces of the brush and substrate in order to make them repulsive. Thus, the particles repel the brushes and the substrate and the substrate and brushes repel the particles providing favorable conditions for particle removal. The organic compound used may be an organic acid, the ammonium salt of an organic acid, or an anionic surfactant. Some examples of potential organic acids may be: citric acid, malic acid, malonic acid, succinic acid, or any combination of such organic acids.

It should be noted that it is desirable to dissolve the organic compound in deionized water (DIW) in a concentration range of approximately 100ppm to 2% by weight. In one embodiment of the present invention the organic compound is dissolved in DIW such that the concentration range is approximately 200ppm to 0.2% by weight.

The use of a fluoride compound helps to remove the contaminants from the surface and subsurface of the dielectric layer. The present invention incorporates the use of fluoride compounds such as hydrogen fluoride acid (HF) or ammonium fluoride (NH_4F) in the cleaning solution. HF or buffered HF (ammonium fluoride mixed with HF) etches silicon dioxide. Thus, during the scrubbing process the silicon dioxide layer is also etched. For example during the brush scrubbing process, typically between 10-100 Å of the oxide layer is removed, leaving clean, uncontaminated dielectric surface on the substrate.

It should be noted that it is desirable to dissolve the fluoride compound in deionized water (DIW) in a concentration range of approximately 0.1% to 5% by weight. In one embodiment of the present invention the fluoride compound is dissolved in DIW such that the concentration range is approximately 0.2% to 1% by weight.

The cleaning solution of the present invention is a mixture of chemicals in DIW containing a fluoride compound such as HF or NH_4F; an organic acid, an ammonium salt of an organic acid, or an anionic surfactant; in an acidic pH environment. It should be noted, however, that hydrochloric acid (HCl) may also be added to the solution to adjust pH and help dissolve copper oxide. It should also be noted that the chemicals of the present invention are pre-mixed in the same cleaning solution to simultaneously solve several problems related to post copper CMP cleaning using a brush scrubber. Cross contamination from

substrate to substrate and within the same substrate are therefore reduced substantially, or even prevented in this simple approach.

One example of the many different ways in formulating the cleaning solution is: 0.5% HF, 0.1% Citric Acid, and 0.4% NH_4OH by weight mixed in DIW. The pH level of the solution in this example is approximately 3. It should be noted however, that the present invention covers various formulations of the cleaning solution, and that each component in the solution may be replaced by different chemical that has similar properties. Thus, methods and apparatus for cleaning semiconductor substrates after polishing of copper film have been described. Although specific embodiments, including specific equipment, parameters, methods, and materials have been described, various modifications to the disclosed embodiments will be apparent to one of ordinary skill in the art upon reading this disclosure. Therefore, it is to be understood that such embodiments are merely illustrative of and not restrictive on the broad invention and that this invention is not limited to the specific embodiments shown and described.

CLAIMS

What is claimed is:

1. A cleaning solution for cleaning semiconductor substrates comprising:

a first amount of a deionized water;

a second amount of an organic acid;

a third amount of a fluoride compound;

wherein said deionized water, said organic acid, and said fluoride compound are combined in an acidic pH environment.

2. The cleaning solution as described in claim 1 wherein said acidic pH environment is a buffered acidic pH environment.

3. The cleaning solution as described in claim 1 wherein said acidic pH environment has a pH level in the range of approximately 1-6.

4. The cleaning solution as described in claim 1 wherein said acidic pH environment has a pH level in the range of approximately 2-4.

5. The cleaning solution as described in claim 1 wherein said second amount of organic acid is dissolved in said first amount of deionized water such that said second amount of organic acid has a concentration range of approximately 100ppm to 2% by weight.

6. The cleaning solution as described in claim 1 wherein said second amount of organic acid is dissolved in said first amount of deionized water such that said second amount of organic acid has a concentration range of approximately 200ppm to 0.2% by weight.

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7. The cleaning solution as described in claim 1 wherein said third amount of said fluoride compound is dissolved in said first amount of deionized water such that said third amount of said fluoride compound has a concentration range of approximately 0.1% to 5% by weight.

8. The cleaning solution as described in claim 1 wherein said third amount of said fluoride compound is dissolved in said first amount of deionized water such that said third amount of said fluoride compound has a concentration range of approximately 0.2% to 1% by weight.

9. The cleaning solution as described in claim 1 wherein said second amount of organic acid is selected from the group consisting of: citric acid, malic acid, malonic acid, succinic acid, and any combination thereof.

10. The cleaning solution as described in claim 1 wherein said third amount of said fluoride compound is selected from the group consisting of: hydrogen fluoride (HF), ammonium fluoride (NH_4F), buffered hydrogen fluoride (ammonium fluoride mixed with hydrogen fluoride), and any combination thereof.

11. A cleaning solution for cleaning semiconductor substrates comprising:

a first amount of a deionized water;

a second amount of an ammonium salt of an organic acid;

a third amount of a fluoride compound;

wherein said deionized water, said ammonium salt, and said fluoride compound are combined in an acidic pH environment.



12. The cleaning solution as described in claim 11 wherein said acidic pH environment is a buffered acidic pH environment.

13. The cleaning solution as described in claim 11 wherein said acidic pH environment has a pH level in the range of approximately 2-4.

14. The cleaning solution as described in claim 11 wherein said second amount of organic acid is dissolved in said first amount of deionized water such that said second amount of organic acid has a concentration range of approximately 200ppm to 0.2% by weight.

15. The cleaning solution as described in claim 11 wherein said third amount of said fluoride compound is dissolved in said first amount of deionized water such that said third amount of said fluoride compound has a concentration range of approximately 0.2% to 1% by weight.

16. The cleaning solution as described in claim 11 wherein said third amount of said fluoride compound is selected from the group consisting of: hydrogen fluoride, ammonium fluoride, buffered hydrogen fluoride, and any combination thereof.

17. A cleaning solution for cleaning semiconductor substrates comprising:

a first amount of a deionized water;

a second amount of an anionic surfactant;

a third amount of a fluoride compound;

wherein said deionized water, said anionic surfactant, and said fluoride compound are combined in an acidic pH environment.

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18. The cleaning solution as described in claim 17 wherein said acidic pH environment is a buffered acidic pH environment.

19. The cleaning solution as described in claim 17 wherein said acidic pH environment has a pH level in the range of approximately 2-4.

20. The cleaning solution as described in claim 17 wherein said second amount of organic acid is dissolved in said first amount of deionized water such that said second amount of organic acid has a concentration range of approximately 200ppm to 0.2% by weight.

21. The cleaning solution as described in claim 17 wherein said third amount of said fluoride compound is dissolved in said first amount of deionized water such that said third amount of said fluoride compound has a concentration range of approximately 0.2% to 1% by weight.

22. The cleaning solution as described in claim 17 wherein said third amount of said fluoride compound is selected from the group consisting of: hydrogen fluoride, ammonium fluoride, buffered hydrogen fluoride, and any combination thereof.

23. A method to remove contaminants from a semiconductor substrate comprising:

placing said semiconductor substrate having a polished copper layer in a scrubbing apparatus; and

scrubbing said semiconductor substrate in an acidic cleaning solution.



24. The method as described in claim 23 wherein said acidic cleaning solution comprises:

a first amount of a deionized water;

a second amount of an organic acid; and

a third amount of a fluoride compound.

25. The method as described in claim 23 wherein said acidic cleaning solution is a buffered acidic cleaning solution.

26. The method as described in claim 23 wherein said acidic cleaning solution has a pH level in the range of approximately 1-6.

27. The method as described in claim 23 wherein said acidic cleaning solution has a pH level in the range of approximately 2-4.

28. The method as described in claim 24 wherein said second amount of organic acid is dissolved in said first amount of deionized water such that said second amount of organic acid has a concentration range of approximately 100ppm to 2% by weight.

29. The method as described in claim 24 wherein said second amount of organic acid is dissolved in said first amount of deionized water such that said second amount of organic acid has a concentration range of approximately 200ppm to 0.2% by weight.

30. The method as described in claim 24 wherein said third amount of said fluoride compound is dissolved in said first amount of deionized water such that said third amount of said fluoride compound has a concentration range of approximately 0.1% to 5% by weight.

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31. The method as described in claim 24 wherein said third amount of said fluoride compound is dissolved in said first amount of deionized water such that said third amount of said fluoride compound has a concentration range of approximately 0.2% to 1% by weight.

32. The method as described in claim 24 wherein said second amount of organic acid is selected from the group consisting of: citric acid, malic acid, malonic acid, succinic acid, and any combination thereof.

33. The method as described in claim 24 wherein said third amount of said fluoride compound is selected from the group consisting of: hydrogen fluoride (HF), ammonium fluoride (NH_4F), buffered hydrogen fluoride (ammonium fluoride mixed with hydrogen fluoride), and any combination thereof.

34. The method as described in claim 23 wherein said acidic cleaning solution comprises:

a first amount of a deionized water;

a second amount of an ammonium salt; and

a third amount of a fluoride compound.

35. The method as described in claim 23 wherein said acidic cleaning solution comprises:

a first amount of a deionized water;

a second amount of an anionic surfactant; and

a third amount of a fluoride compound.

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36. A method to remove contaminants from a semiconductor substrate comprising:

placing said semiconductor substrate having a polished copper layer in a scrubbing apparatus; and

scrubbing said semiconductor substrate in an acidic cleaning solution, wherein said acidic cleaning solution comprises:

a first amount of a deionized water;

a second amount of an organic acid; and

a third amount of a fluoride compound.

37. The method as described in claim 36 wherein said acidic cleaning solution is a buffered acidic cleaning solution.

38. The method as described in claim 36 wherein said acidic cleaning solution has a pH level in the range of approximately 1-6.

39. The method as described in claim 36 wherein said acidic cleaning solution has a pH level in the range of approximately 2-4.

40. The method as described in claim 36 wherein said second amount of organic acid is dissolved in said first amount of deionized water such that said second amount of organic acid has a concentration range of approximately 100ppm to 2% by weight.

41. The method as described in claim 36 wherein said second amount of organic acid is dissolved in said first amount of deionized water such that said second amount of organic acid has a concentration range of approximately 200ppm to 0.2% by weight.

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42. The method as described in claim 36 wherein said third amount of said fluoride compound is dissolved in said first amount of deionized water such that said third amount of said fluoride compound has a concentration range of approximately 0.1% to 5% by weight.

43. The method as described in claim 36 wherein said third amount of said fluoride compound is dissolved in said first amount of deionized water such that said third amount of said fluoride compound has a concentration range of approximately 0.2% to 1% by weight.

44. The method as described in claim 36 wherein said second amount of organic acid is selected from the group consisting of: citric acid, malic acid, malonic acid, succinic acid, and any combination thereof.

45. The method as described in claim 36 wherein said third amount of said fluoride compound is selected from the group consisting of: hydrogen fluoride (HF), ammonium fluoride (NH_4F), buffered hydrogen fluoride (ammonium fluoride mixed with hydrogen fluoride), and any combination thereof.

46. A scrubber for processing a semiconductor substrate comprising:

an input to receive a semiconductor substrate having a polished copper layer

a brush assembly coupled to said input

a cleaning solution delivery system for delivering a cleaning solution comprising a deionized water, an organic acid, and a fluoride compound, wherein said cleaning solution delivery system delivers said cleaning solution premixed in an acidic pH environment to said semiconductor substrate having a polished copper layer.

47. A scrubber for processing a semiconductor substrate comprising:

an input to receive a semiconductor substrate having a polished copper layer

a brush assembly coupled to said input

a cleaning solution delivery system for delivering a cleaning solution comprising a deionized water, an ammonium salt, and a fluoride compound, wherein said cleaning solution delivery system delivers said cleaning solution premixed in an acidic pH environment to said semiconductor substrate having a polished copper layer.

48. A scrubber for processing a semiconductor substrate comprising:

an input to receive a semiconductor substrate having a polished copper layer

a brush assembly coupled to said input

a cleaning solution delivery system for delivering a cleaning solution comprising a deionized water, an anionic surfactant, and a fluoride compound, wherein said cleaning solution delivery system delivers said cleaning solution premixed in an acidic pH environmentto said semiconductor substrate having a polished copper layer.