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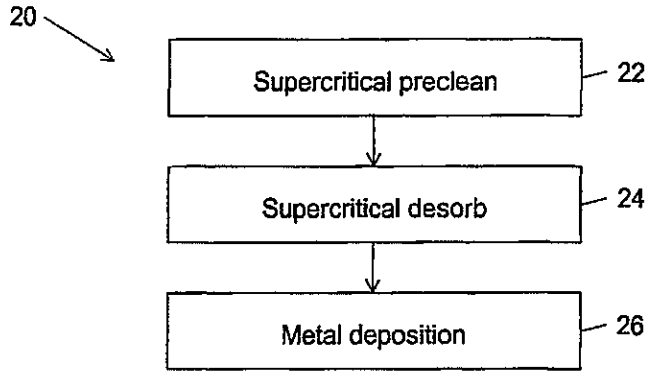
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(54) Title: METHOD OF DEPOSITING METAL FILM AND METAL DEPOSITION CLUSTER TOOL INCLUDING SUPERCRITICAL DRYING/CLEANING MODULE



(57) Abstract: A method of depositing a metal film on a substrate includes a supercritical preclean step, a supercritical desorb step, and a metal deposition step. Preferably, the preclean step comprises maintaining supercritical carbon dioxide and a chelating agent in contact with the substrate in order to remove an oxide layer from a metal surface of the substrate. More preferably, the preclean step comprises maintaining the supercritical carbon dioxide, the chelating agent, and an acid in contact with the substrate. Alternatively, the preclean step comprises maintaining the supercritical carbon dioxide and an amine in contact with the oxide layer. The desorb step comprises maintaining supercritical carbon dioxide in contact with the substrate in order to remove adsorbed material from the substrate. The metal deposition step then deposits the metal film on the substrate without exposing the substrate to an oxidizing material which oxidizes the metal surface of the precleaned substrate and without exposing the substrate to a nonvolatile adsorbing material which adsorbs to the substrate. An apparatus for depositing the metal film on a substrate includes a transfer module, a supercritical processing module, a vacuum module, and a metal deposition module. The supercritical processing module is coupled to the transfer module. The vacuum module couples the metal deposition module to the transfer module. In operation, the apparatus for depositing the metal film performs the supercritical preclean step, the supercritical desorb step, and the metal deposition step.

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METHOD OF DEPOSITING METAL FILM AND METAL DEPOSITION CLUSTER TOOL INCLUDING SUPERCRITICAL DRYING/CLEANING MODULE

RELATED APPLICATIONS

This application claims priority from U.S. Provisional Patent Application No. 60/199,580 filed on Apr. 25, 2000, which is incorporated by reference.

FIELD OF THE INVENTION

This invention relates to the field of deposition of films. More particularly, this invention relates to the field of deposition of films onto a substrate where a prior processing step includes desorbing or precleaning of the substrate.

BACKGROUND OF THE INVENTION

Deposition of a metal film in semiconductor processing often requires desorb and preclean steps prior to the deposition of the metal film. The desorb and preclean steps assure good adhesion of the metal film to a substrate and also provides better contact resistance between a substrate metal and the metal film.

In the prior art, the desorb step, the preclean step, and the deposition of the metal film take place within a cluster tool so that the substrate is not exposed to atmosphere between the desorb or preclean steps and the deposition of the metal film.

The desorb step of the prior art heats the substrate under vacuum in order to degas the substrate. By heating the substrate under vacuum, material adsorbed to the surface of the substrate or absorbed within the substrate are removed from the substrate. Typical process conditions include vacuum of 10^{-3} Torr or higher vacuum, and temperature within the range of 200 and 400 °C. Generally, higher temperatures are employed in order to minimize process times, which for the higher temperatures are generally within the range of 30 and 60 s.

The preclean step of the prior art exposes the substrate to ion bombardment in what is often referred to as a sputter-etch preclean. In the sputter-etch preclean, argon ions, hydrogen ions, helium ions, or some combination thereof, and electrons form a plasma, which bombards a surface of the substrate to sputter away a thin layer of material. Typically, in the semiconductor processing, an etching step precedes the deposition of the metal film. The etching step forms trenches and via holes in the substrate to an underlying metal layer. After the etching step, an oxide forms on an exposed surface of the underlying metal layer at the via holes due to exposure of the substrate to atmosphere. The sputter-etch preclean attempts to etch away the oxide and any remaining residue after ashing and wet cleaning. The sputter-etch preclean typically requires a vacuum of 10^{-3} Torr or higher vacuum.

A particular metal deposition process of the prior art deposits a barrier metal layer and a copper seed layer onto a semiconductor substrate forming contacts with an

underlying copper layer at the via holes. In the etching step, the via holes are formed through silicon dioxide and silicon nitride layers to the underlying copper layer. In another etching step of the prior art, the via holes are formed in low-k dielectric materials such as a polymer-based materials and fluorine or carbon containing oxides. After the etching step and before the deposition of the metal film, a plasma ashing step and a wet cleaning step substantially remove photoresist, photoresist residue, and etch residue leaving material adsorbed to the surface of the substrate and leaving a thin copper oxide layer on the underlying copper layer at the via holes. The desorb step of the prior art removes the material adsorbed to the surface of the substrate. The sputter-etch preclean removes the copper oxide layer within the via holes and removes an exposed layer of the substrate surrounding the via holes. The barrier metal is then deposited followed by the copper seed layer. Subsequently, an electroplating step deposits an additional copper layer on the copper seed layer.

The cluster tool of the prior art includes a handoff station, a front transfer module, a back transfer module, a degas module, a sputter-etch module, and a metal deposition module. The front transfer module includes a first robot. The back transfer module includes a second robot. The handoff station is coupled to the front transfer module by a first valve or loadlock. The degas module and the sputter-etch module are coupled to the front transfer module. The back transfer module is coupled to the front transfer module by a second valve or loadlock. The metal deposition module is coupled to the back transfer module. Often, the cluster tool includes two degas modules, two sputter-etch modules, and two or more metal deposition modules. In operation, the front and back transfer modules operate at vacuum. A second cluster tool for performing the desorb, preclean and metal deposition of the prior art includes a single transfer module, the degas module, the sputter-etch module, and the metal deposition module, where the degas module, the sputter-etch module, and the metal deposition module are coupled to the single transfer module.

Operation of the cluster tool begins with the first robot transferring a substrate from the handoff station to the degas module, where the desorb step takes place. The first robot then transfers the substrate to the sputter-etch module where the sputter-etch preclean takes place. The first robot then transfers the substrate to the second robot, which places the substrate in the metal deposition module. After the deposition of the metal film, the second robot then returns the substrate to the first robot, which returns the substrate to the handoff station.

Because the desorb step of the prior art operates at elevated temperatures, there is potential for temperature induced damage of the substrate. This concern is especially apt for polymer materials because future integrated circuits may employ the polymer materials as insulators due to their low dielectric constant properties.

In the preclean step, the plasma can cause plasma damage of the surface of the substrate. Also, it is well known that the sputter-etch preclean causes corner clipping

at edges of the trenches and at edges of the via holes creating facets. The corner clipping is especially detrimental to smaller dimension integrated circuits since the corner clipping reduces separation of adjacent lines leading to unacceptable electrical interference between the adjacent lines. Not only does the sputter-etch preclean cause physical damage of integrated circuits, it could also causes electrical damage.

Further, sputtering of the underlying metal layer in the trenches and the via holes can cause barreling as well as causing deposition of sputtered material on sidewalls of the trenches and the via holes. For example, sputter-etch preclean of the copper oxide layer within the via holes causes copper and copper oxide to deposit on the sidewalls of the via holes. Moreover, the sputter-etch preclean is inappropriate for precleaning polymer based materials due to expected damage caused by the physical bombardment in the sputter-etch preclean. Also, even if the sputter-etch preclean can be used, the hydrogen ions cannot be used when the polymer materials are exposed since the hydrogen will hydrate the polymer-based materials. Additionally, the sputter-etch preclean becomes less effective as an aspect ratio (depth divided by width) of the trenches and of the via holes increases.

Both the degas module and the sputter-etch module require high vacuum pumps and associated vacuum plumbing, which increases purchase and maintenance costs of the cluster tool. The sputter-etch module further increases the purchase and maintenance costs of the cluster tool because it relatively complex and requires frequent maintenance to ensure that it does not become a source of particulate contamination.

What is needed is a desorb method compatible with metal deposition that does not require excessive temperatures.

What is needed is a preclean method compatible with metal deposition that does not use a plasma.

What is needed is a desorb method compatible with low-k materials such as polymer materials, and fluorine or carbon containing oxides.

What is needed is a preclean method compatible with low-k materials such as polymer materials, and fluorine or carbon containing oxides.

What is needed is a desorb method compatible with metal deposition which is less expensive.

What is needed is a preclean method compatible with metal deposition which is less expensive.

SUMMARY OF THE INVENTION

According to one aspect of the present invention, there is provided a method of depositing a metal film on a substrate comprising the steps of maintaining supercritical carbon dioxide and a chelating agent in contact with the substrate to remove an oxide layer from a metal surface of the substrate, thereby forming a

precleaned substrate; and depositing the metal film on the precleaned substrate without exposing the precleaned substrate to a material which oxidizes the metal surface of the precleaned substrate.

According to another aspect of the present invention, there is provided a method of depositing a metal film on a substrate comprising the steps of maintaining supercritical carbon dioxide and an amine in contact with the substrate to remove an oxide layer from a metal surface of the substrate, thereby forming a precleaned substrate; and depositing the metal film on the precleaned substrate without exposing the precleaned substrate to a material which oxidizes the metal surface of the precleaned substrate.

According to yet another aspect of the present invention, there is provided a method of depositing a film on a substrate comprising the steps of maintaining supercritical carbon dioxide in contact with the substrate in a first processing chamber to remove a sorbate selected from the group consisting of an absorbate and an adsorbate from the substrate, thereby forming a desorbed substrate; transferring the desorbed substrate to a second processing chamber without exposing the desorbed substrate to a material which forms a nonvolatile sorbate; and depositing the film on the desorbed substrate.

According to one aspect of the present invention, there is provided a method of depositing a metal film on a substrate comprising the steps of maintaining supercritical carbon dioxide in contact with the substrate to remove a sorbate selected from the group consisting of an absorbate and an adsorbate from the substrate; maintaining the supercritical carbon dioxide and a chelating agent in contact with the substrate to remove an oxide layer from a metal surface of the substrate; and subsequently depositing the metal film on the substrate without exposing the substrate to a first material which forms a nonvolatile sorbate prior to depositing the metal film and without exposing the substrate to a second material which forms the oxide prior to depositing the metal film.

According to yet another aspect of the present invention, there is provided a method of depositing a metal film on a substrate comprising the steps of maintaining supercritical carbon dioxide, a chelating agent, and an acid in contact with the substrate such that the acid dissolves an oxide layer from a metal surface of the substrate and further such that the depositing the metal film on the precleaned substrate without exposing the precleaned substrate to a material which oxidizes the metal surface of the precleaned substrate.

According to one aspect of the present invention, there is provided an apparatus for depositing a metal film on a substrate comprising a transfer module; a supercritical processing module coupled to the transfer module; a metal deposition

module; a vacuum module coupling the metal deposition module to the transfer module; and means for transferring the substrate between the supercritical processing module and the metal deposition module.

According to another aspect of the present invention, there is provided an apparatus for depositing a metal film on a substrate comprising a transfer module comprising an entrance and a first robot; a supercritical processing module coupled to the transfer module; a metal deposition module; and a vacuum module coupling the metal deposition module to the transfer module, the vacuum chamber and a second robot, wherein the first robot and the second robot are configured to transfer the substrate between the supercritical processing module and the metal deposition module.

According to yet another aspect of the present invention, there is provided an apparatus comprising a front transfer module comprising one or more supercritical modules configured to treat a substrate with a supercritical solution; a back transfer module coupled to the front transfer module, the back transfer module comprising one or more deposition modules configured to deposit a layer of material onto the treated substrate; and means for transferring the substrate between the front transfer module and the back transfer module without exposing the substrate to the environment.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically illustrates the preferred method of the present invention.

FIG. 2 schematically illustrates an alternative method of the present invention.

FIG. 3 illustrates the preferred metal deposition cluster tool of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred method of the present invention is schematically illustrated in FIG. 1. The preferred method 20 deposits a metal film on a substrate. Preferably, the substrate is a semiconductor substrate having via holes through a dielectric material to an underlying metal layer. When the metal film is deposited on the semiconductor substrate, the metal film contacts the underlying metal layer at the via holes. More preferably, the semiconductor substrate includes via holes and trenches in a dual damascene structure. In the dual damascene structure, the metal layer also contacts the underlying metal layer at the via holes. Alternatively, the metal film is deposited on an alternative substrate where the metal film contacts an exposed metal surface on the alternative substrate.

The preferred method 20 comprises a supercritical preclean step 22, a supercritical desorb step 24, and a metal deposition step 26. In the supercritical preclean step 22, the substrate is maintained in a supercritical chamber and is preferably exposed to supercritical carbon dioxide and a chelating agent. The

chelating agent in conjunction with the supercritical carbon dioxide reacts with an oxide on the underlying metal layer to form chelates of the underlying metal. The supercritical carbon dioxide carries away the chelates. In the supercritical desorb step 24, the substrate is maintained within the supercritical chamber and exposed to supercritical carbon dioxide, which desorbs adsorbed materials or absorbed materials from the substrate.

More preferably, the supercritical preclean step 22 comprises maintaining an acid as well as the supercritical carbon dioxide and the chelating agent in contact with the substrate. The acid acts to dissolve the oxide while the chelating agent attaches to loose metal ions and carries away the loose metal ions.

Preferably, the chelating agent is selected from the group comprising 2,4-pentane-dione, 1,1,1,6,6,6-hexafluoro-2,4-pentanedione, 1,1,1-trifluoropentane-2,4-dione, 2,6-dimethylheptane-3,5-dione, 2,2,7-trimethyloctane-2,4-dione, 2,2,6,6-tetramethyl-heptane-3,5-dione, ethylenediamine diacetic acid (EDTA), and nitrilotriacetic acid (NTA).

Preferably, the acid is selected from the group comprising an organic acid or an inorganic acid depending upon the particular oxide that is being precleaned. Preferably, the organic acid is used for a preclean of copper oxide. More preferably, for the preclean of copper oxide, the organic acid is selected from the group comprising acetic acid, formic acid, oxalic acid and malonic acid; alpha hydroxy acids such as glycolic acid, citric acid, malic acid or lactic acid; or amino acids such as glycine, alanine, leucine, valine, glutamine or lysine.

Preferably, the inorganic acid is used for a preclean of aluminum oxide. More preferably, for the preclean of aluminum oxide, the inorganic acid is selected from the group comprising hydrofluoric acid and buffered hydrofluoric acid formulations such as ammonium fluoride and ammonium bifluoride.

Alternatively, in the preclean step 22, the chelating agent and the acid are replaced by an amine. The amine acts to dissolve the oxide and to carry away metal ions. Preferably, the amine is selected from the group comprising triethanolamine, 2-methylaminoethanol, pyridine, 2,2'-bipyridine, and pentamethyldiethylenetriamine.

In the supercritical preclean step 22, the supercritical chamber is preferably pressurized to an elevated pressure exceeding the critical pressure and the supercritical carbon dioxide and the chelating agent are flowed over the substrate. More preferably, the supercritical carbon dioxide, the chelating agent, and the acid are flowed over the substrate. Alternatively, the supercritical carbon dioxide and the amine are flowed over the substrate.

In order to achieve supercritical conditions within the supercritical chamber, temperature within the chamber must be maintained at or above a critical temperature, which is 30.5 °C. Following this, the pressure is cycled at least one and a half times

between the elevated pressure and a lower pressure. Preferably, the lower pressure is above the critical pressure.

The supercritical desorb step 24 is preferably part of the supercritical preclean step 22. Gases and liquids adsorbed to the substrate or absorbed within the substrate will desorb during the supercritical preclean step 22. Elevating the temperature within the chamber is anticipated to improve the supercritical desorb step 24. Alternatively, the supercritical desorb step 24 is performed as a separate step, either before or after the supercritical preclean step 22.

Preferably, during the supercritical preclean and desorb steps, 22 and 24, the temperature within the chamber is within the range of 31 and 100 °C. Alternatively, the temperature within the chamber is maintained below a temperature limit of the substrate.

The metal deposition step 26 comprises depositing the metal film on the substrate. Preferably, the substrate includes the via holes to the underlying metal layer. The metal deposition step 26 preferably deposits the metal film within the via holes so that the metal film contacts the underlying metal layer. Preferably, the metal deposition step 26 is a chemical vapor deposition (CVD) process. Alternatively, the metal deposition step 26 is a physical vapor deposition (PVD) process.

It is important that between the supercritical preclean, supercritical desorb, and metal deposition steps, 22, 24, and 26, the substrate is not exposed to atmosphere or other gases which will form a nonvolatile adsorbate on the substrate, which will not form a nonvolatile absorbate within the substrate, or which will react with the substrate. Forming a volatile adsorbate on the substrate is not detrimental because a brief exposure to vacuum at an end of the supercritical preclean step 22 or at the end of the supercritical desorb step 24 will cause the volatile adsorbate to quickly desorb from the substrate. Similarly, forming a volatile absorbate is not detrimental because the brief exposure to vacuum will cause the volatile absorbate to quickly desorb from the substrate. Preferably, the substrate is maintained in vacuum between the supercritical preclean, supercritical desorb, and metal deposition steps, 22, 24, and 26. Alternatively, the substrate is maintained in an inert gas environment between the supercritical preclean, supercritical desorb, and metal deposition steps, 22, 24, and 26, where the inert gas environment does not form the nonvolatile adsorbate nor the nonvolatile absorbate.

By using the supercritical preclean step 22 rather than a sputter-etch preclean step, plasma damage of the substrate is avoided. Further, using the supercritical preclean step 22 rather than the sputter-etch preclean step avoids corner clipping and facet creation at edges of trenches and of via holes, avoids barreling of the trenches and of the via holes, and avoids deposition of sputtered material onto sidewalls of the trenches and of the via holes. Additionally, using the supercritical preclean step 22 rather than the sputter-etch preclean step avoids electrical damage of an integrated

circuit that is fabricated on the substrate. Moreover, the supercritical preclean step 22 will cause less damage to polymer based dielectric materials than the sputter-etch preclean step.

Using the supercritical desorb step 24 rather than heating the substrate under vacuum to degas the substrate avoids use of excessive temperature in processing the substrate, which is especially important for the polymer based dielectric materials.

Depending on specific process requirements, either the supercritical preclean step 22 or the supercritical desorb step 24 may be unneeded. In a first alternative method of the present invention, the supercritical preclean step 22 and the metal deposition step 26 are performed but the supercritical desorb step 24 is not performed. In a second alternative method of the present invention the supercritical desorb step 24 and the metal deposition step 26 are performed but the supercritical preclean step 22 is not performed. In a third alternative method of the present invention, the metal deposition step 26 of the second alternative method is replaced by an alternative deposition step. In the alternative deposition step, a film other than the metal film is deposited on the substrate.

A fourth alternative method of the present invention is schematically illustrated in FIG. 2. The fourth alternative method 30 adds a supercritical residue removal step 32 to the preferred method 20. The supercritical residue removal step 32 removes residue remaining on the substrate following a preceding etching step. In the preceding etching step, photoresist masks portions of the substrate so that only unmasked portions of the substrate are etched. The etching step also etches the photoresist, which is sometimes etched to completion. Generally, following the etching step there is some remaining photoresist on the substrate and there is also etch residue and photoresist residue on the substrate. Thus, the residue remaining on the substrate following the etching step includes the photoresist residue, the etch residue, and possibly the remaining photoresist. The supercritical residue removal step 32 comprises exposing the substrate with the residue to the supercritical carbon dioxide and a solvent until the residue is removed from the substrate. The supercritical residue removal step 32 is the subject of U.S. Patent Application No. 09/697,227 filed on Oct. 25, 2000, which is incorporated by reference in its entirety.

The preferred metal deposition cluster tool of the present invention is illustrated in FIG. 3. The preferred metal deposition cluster tool 40 comprises a loader module 42, a front transfer module 44, a front transfer module robot 46, first through fourth supercritical modules, 48-51, a back transfer module 52, a back transfer module robot 54, and first through fourth metal deposition modules, 56-59. The loader module 42 comprises first and second loadlocks, 60 and 62, and a loader robot 64. The first and second loadlocks, 60 and 62, comprise an entrance for the front transfer module.

The loader module 42, the front transfer module robot 46, the first through fourth supercritical modules, 48-51, are coupled to the front transfer module. The back transfer module 52 is coupled to the front transfer module via a valve 66. The back transfer module robot 54 and the first through fourth metal deposition modules 56-59 are coupled to the back transfer module 52.

In operation, first and second front opening unit pods (FOUP's), 68 and 70, employing a standard mechanical interface (SMIF) concept couple with the loader module 42. Preferably, the first pod 68 initially contains semiconductor substrates 72 which were etched, ashed, and cleaned in a wet clean process. The loader robot 64 transfers a semiconductor substrate 72 from the first pod 68 to the first loadlock 60. The loadlock 60 closes and is pumped to vacuum. The loadlock 60 is then opened to the front transfer module 46, which is at vacuum. The front transfer module robot 46 transfers the semiconductor substrate 72 to the first supercritical module 48 where the supercritical preclean and desorb steps, 22 and 24 (FIG. 1), take place. Meanwhile, additional semiconductor substrates are loaded from the first pod through the first loadlock 60 to the second through third supercritical modules, 49-51. Alternatively, the FOUP's are replaced by SMIF pods, or open cassettes.

Once the supercritical preclean and desorb steps, 22 and 24, are complete, the semiconductor substrate 72 is transferred from the first supercritical module 48 to the back transfer module robot 52 through the valve 66. The back transfer module 52 also operates at vacuum. The back transfer module robot 54 then transfers the semiconductor substrate 72 to the first metal deposition module 56 where the metal deposition step 26 (FIG. 1) takes place. Meanwhile, the additional semiconductor substrates are transferred from the second through third supercritical modules, 49-51, to the second through third metal deposition modules, 57-59.

Once the metal deposition step 26 is complete, the semiconductor substrate 72 is transferred from the first metal deposition module 56 to the first transfer module robot 46 by the second transfer module robot 54. The first transfer module robot 46 then transfers the semiconductor substrate 72 to the first loadlock 60, which is pressurized to atmosphere. The semiconductor substrate 72 is then transferred by the loader module robot 46 to the first pod 68. Subsequently, the additional semiconductor substrates are transferred from the second through third metal deposition modules, 57-59, to the first pod 68. Later, more semiconductor substrates are processed from the second pod 70 and then returned to the second pod 70.

It will be readily apparent to one skilled in the art that more or less supercritical processing modules can be coupled to front transfer module 44. Further, it will be readily apparent to one skilled in the art that more or less metal deposition module can be coupled to the back transfer module 52. Moreover, it will be readily apparent to one skilled in the art that a single loadlock for the front transfer module 44 will suffice for the entrance to the front transfer module 44.

In a first alternative metal deposition cluster tool, the front transfer module 44 operates at atmospheric pressure and provides an inert gas environment for the semiconductor wafer. In the first alternative metal deposition cluster tool, third and fourth loadlocks couple the front transfer module 44 to the back transfer module 52. Also in the first alternative metal deposition cluster tool, an inert gas injection arrangement is coupled to the front transfer module.

In a second alternative metal deposition cluster tool, the first and second supercritical processing modules, 48 and 49, and the first and second metal deposition modules, 56 and 57, are coupled to a single transfer module. The first alternative metal deposition tool is less preferred than the preferred metal deposition tool 40 because the preferred metal deposition tool separates the supercritical processing modules from the metal deposition modules by arranging the modules about respective transfer modules. This allows for a cleaner metal deposition process The first alternative metal deposition tool is taught in U.S. Patent Application No. 09/704,641 filed on Nov. 1, 2000, which is incorporated by reference in its entirety.

It will be readily apparent to one skilled in the art that other various modifications may be made to the preferred embodiment without departing from the spirit and scope of the invention as defined by the appended claims.

CLAIMS

1. A method of depositing a metal film on a substrate comprising the steps of:

a. maintaining supercritical carbon dioxide and a chelating agent in contact with the substrate to remove an oxide layer from a metal surface of the substrate, thereby forming a precleaned substrate; and

b. depositing the metal film on the precleaned substrate without exposing the precleaned substrate to a material which oxidizes the metal surface of the precleaned substrate.

2. The method of claim 1 wherein the step of maintaining the supercritical carbon dioxide and the chelating agent in contact with the substrate further comprises maintaining an acid in contact with the substrate such that the acid dissolves the oxide layer.

3. The method of claim 2 wherein the acid is selected from the group consisting of an organic acid and an inorganic acid.

4. The method of claim 2 wherein the oxide layer comprises a copper oxide.

5. The method of claim 4 wherein the acid comprises an organic acid.

6. The method of claim 4 wherein the acid is selected from the group consisting of acetic acid, formic acid, oxalic acid, malonic acid, alpha hydroxy acid, glycolic acid, citric acid, malic acid, lactic acid, amino acid, glycine, alanine, leucine, valine, glutamine, and lysine.

7. The method of claim 2 wherein the oxide comprises an aluminum oxide.

8. The method of claim 7 wherein the acid comprises an inorganic acid.

9. The method of claim 7 wherein the acid is selected from the group consisting of hydrofluoric acid, buffered hydrofluoric acid, ammonium fluoride, and ammonium bifluoride.

10. The method of claim 1 further comprising the step of maintaining the supercritical carbon dioxide in contact with the substrate to desorb an adsorbate from the substrate prior to the step of depositing the metal film.

11. The method of claim 10 wherein the step of maintaining the supercritical carbon dioxide in contact with the substrate desorbs an absorbate from the substrate.

12. The method of claim 1 further comprising the step of maintaining the supercritical carbon dioxide and a solvent in contact with the substrate to remove a residue selected from the group consisting of a photoresist, a photoresist residue, and an etch residue from the substrate prior to the step of depositing the metal film.

13. The method of claim 1 wherein the chelating agent is selected from the group consisting of 2,4-pentanedione, 1,1,1,6,6,6-hexafluoro-2,4-pentanedione, 1,1,1-trifluoropentane-2,4-dione, 2,6-dimethylheptane-3, 5-dione, 2,2,7-trimethyloctane-2,4-dione, 2,2,6,6-tetramethylheptane-3,5-dione, ethylenediamine diacetic acid, and nitrilotriacetic acid.

14. A method of depositing a metal film on a substrate comprising the steps of:

a. maintaining supercritical carbon dioxide and an amine in contact with the substrate to remove an oxide layer from a metal surface of the substrate, thereby forming a precleaned substrate ; and

b. depositing the metal film on the precleaned substrate without exposing the precleaned substrate to a material which oxidizes the metal surface of the precleaned substrate.

15. The method of claim 14 wherein the amine is selected from the group consisting of triethanolamine, 2-methylaminoethanol, pyridine, 2,2'-bipyridine, and pentamethyldiethylenetriamine.

16. The method of claim 14 further comprising the step of maintaining the supercritical carbon dioxide in contact with the substrate to desorb an adsorbate from the substrate prior to the step of depositing the metal film.

17. The method of claim 16 wherein the step of maintaining the supercritical carbon dioxide in contact with the substrate desorbs an absorbate from the substrate.

18. The method of claim 14 further comprising the step of maintaining the supercritical carbon dioxide and a solvent in contact with the substrate to remove a residue selected from the group consisting of a photoresist, a photoresist residue, and an etch residue from the substrate prior to the step of depositing the metal film.

19. A method of depositing a film on a substrate comprising the steps of:

a. maintaining supercritical carbon dioxide in contact with the substrate in a first processing chamber to remove a sorbate selected from the group consisting of an absorbate and an adsorbate from the substrate, thereby forming a desorbed substrate;

b. transferring the desorbed substrate to a second processing chamber without exposing the desorbed substrate to a material which forms a nonvolatile sorbate; and

c. depositing the film on the desorbed substrate.

20. The method of claim 19 where in the film comprises a metal film.

21. The method of claim 20 further comprising the step of maintaining the supercritical carbon dioxide and a chelating agent in contact with the substrate to remove an oxide layer from a metal surface of the substrate prior to the step of depositing the metal film on the substrate.

22. The method of claim 21 wherein the step of maintaining the supercritical carbon dioxide and the chelating agent in contact with the substrate further comprises maintaining an acid in contact with the substrate such that the acid dissolves the oxide layer.

23. The method of claim 20 further comprising the step of maintaining the supercritical carbon dioxide and an amine in contact with the substrate to remove an oxide layer from a metal surface of the substrate prior to the step of depositing the metal film on the substrate.

24. The method of claim 20 further comprising the step of maintaining the supercritical carbon dioxide and a solvent in contact with the substrate to remove a residue selected from the group consisting of a photoresist, a photoresist residue, and an etch residue from the substrate prior to the step of depositing the metal film.

25. A method of depositing a metal film on a substrate comprising the steps of:

a. maintaining supercritical carbon dioxide in contact with the substrate to remove a sorbate selected from the group consisting of an absorbate and an adsorbate from the substrate;

b. maintaining the supercritical carbon dioxide and a chelating agent in contact with the substrate to remove an oxide layer from a metal surface of the substrate; and

c. subsequently depositing the metal film on the substrate without exposing the substrate to a first material which forms a nonvolatile sorbate prior to depositing the metal film and without exposing the substrate to a second material which forms the oxide prior to depositing the metal film.

26. The method of claim 25 wherein the step of maintaining the supercritical carbon dioxide and the chelating agent in contact with the substrate further comprises maintaining an acid in contact with the substrate such that the acid dissolves the oxide layer.

27. The method of claim 25 further comprising the step of maintaining the supercritical carbon dioxide and a solvent in contact with the substrate to remove a residue selected from the group consisting of a photoresist, a photoresist residue, and an etch residue from the substrate prior to the step of depositing the metal film.

28. A method of depositing a metal film on a substrate comprising the steps of:

a. maintaining supercritical carbon dioxide in contact with the substrate to remove a sorbate selected from the group consisting of an absorbate and an adsorbate from the substrate;

b. maintaining the supercritical carbon dioxide and an amine in contact with the substrate to remove an oxide layer from a metal surface of the substrate; and

c. subsequently depositing the metal film on the substrate without exposing the substrate to a first material which forms a nonvolatile sorbate prior to depositing the metal film and without exposing the substrate to a second material which forms the oxide prior to depositing the metal film.

29. The method of claim 28 further comprising the step of maintaining the supercritical carbon dioxide and a solvent in contact with the substrate to remove a residue selected from the group consisting of a photoresist, a photoresist residue, and an etch residue from the substrate prior to the step of depositing the metal film.

30. A method of depositing a metal film on a substrate comprising the steps of:

a. maintaining supercritical carbon dioxide, a chelating agent, and an acid in contact with the substrate such that the acid dissolves an oxide layer from a metal surface of the substrate and further such that the chelating agent carries away meal ions, thereby forming a precleaned substrate; and

b. depositing the metal film on the precleaned substrate without exposing the precleaned substrate to a material which oxidizes the metal surface of the precleaned substrate.

31. An apparatus for depositing a metal film on a substrate comprising:

a. a transfer module;

b. a supercritical processing module coupled to the transfer module;

c. a metal deposition module;

d. a vacuum module coupling the metal deposition module to the transfer module; and

e. means for transferring the substrate between the supercritical processing module and the metal deposition module.

32. The apparatus of claim 31 wherein the transfer module comprises an entrance and a first robot.

33. The apparatus of claim 32 wherein the entrance comprises a loadlock.

34. The apparatus of claim 33 further comprising an inert gas injection arrangement coupled to the transfer module such that in operation the transfer module provides an inert gas environment.

35. The apparatus of claim 33 further comprising a vacuum pump coupled to the transfer module such that in operation the transfer module operates at vacuum.

36. The apparatus of claim 32 wherein the vacuum module comprises a second robot.

37. The apparatus of claim 36 further comprising a valve, the valve coupling the transfer module to the vacuum module.

38. The apparatus of claim 37 further comprising a vacuum pump coupled to the vacuum module.

39. The apparatus of claim 36 further comprising a loadlock, the loadlock coupling the transfer module to the vacuum module.

40. The apparatus of claim 31 wherein the supercritical processing module comprises a pressure vessel.

41. An apparatus for depositing a metal film on a substrate comprising:

a. a transfer module comprising an entrance and a first robot;

b. a supercritical processing module coupled to the transfer module;

c. a metal deposition module; and

d. a vacuum module coupling the metal deposition module to the transfer module, the vacuum module comprising a vacuum chamber and a second robot,

wherein the first robot and the second robot are configured to transfer the substrate between the supercritical processing module and the metal deposition module.

42. An apparatus comprising:

a. a front transfer module comprising one or more supercritical modules configured to treat a substrate with a supercritical solution;

b. a back transfer module coupled to the front transfer module, the back transfer module comprising one or more deposition modules configured to deposit a layer of material onto the treated substrate; and

c. means for transferring the substrate between the front transfer module and the back transfer module without exposing the substrate to the environment.

43. The apparatus of claim 42, wherein the means for transferring the substrate between the first transfer module and the second transfer module comprises one or more transfer robots.

44. The apparatus of claim 42, further comprising a valve for isolating the substrate within the one of the front transfer module and the back transfer module.

45. The apparatus of claim 42, further comprising a loader module for introducing the substrate.

46. The apparatus of claim 45, wherein the loader module is coupled to the front transfer module.