

ETCHING FORMULATIONS FOR ISOTROPIC COPPER ETCHING

FIELD OF THE INVENTION

This invention pertains to methods for etching copper. More particularly, the invention pertains to methods for isotropically etching copper on semiconductor substrates.

BACKGROUND

Copper and copper alloys are widely used in the field of semiconductor fabrication as conducting materials. As a conductor, copper is often preferred to other metals, such as aluminum, due to its high electrical conductivity and good electromigration resistance properties. Because of these advantages, copper-filled lines and vias are now ubiquitously seen as conducting paths connecting elements of semiconductor devices, such as in integrated circuits.

Processing of copper during fabrication of semiconductor devices, however, presents a set of challenges. Because copper is not easily amenable to plasma etching, copper-containing devices typically need to be fabricated using damascene processing. In damascene processing, copper is deposited as an inlay on a substrate having a pattern of pre-formed recessed damascene features, such as vias and trenches. The pattern of recessed features is usually formed by photolithographic techniques. After the recessed features have been formed, copper is globally deposited onto the substrate such that it fills the recessed features and also forms an overburden layer over the field region, where the field region refers to the top plane of the substrate prior to copper deposition. Subsequently, the overburden is removed by a planarization technique such as chemical mechanical polishing (CMP), providing a planarized substrate having a pattern of copper-filled conductive paths.

While methods for efficient copper removal are desirable at various stages of semiconductor device fabrication, conventional wet copper etching techniques have not been widely introduced because they generally could not be successfully integrated into semiconductor device fabrication processes. One of significant drawbacks of conventional etching chemistries includes their anisotropic nature. Anisotropic etching leads to preferential etching of copper in one specific direction and/or preferential etching of one type of grain orientation and, consequently, leads to

roughening of copper surface, pitting, and grain boundary dependent non-uniform copper removal. This drawback, in many instances, cannot be tolerated in semiconductor fabrication where clean, smooth, and isotropic removal of copper is typically desired.

SUMMARY

The present invention addresses the problems identified above by providing formulations for isotropic copper etching and methods for removing copper isotropically with the use of isotropic etching formulations. These formulations can be used to remove copper at very high etch rates (e.g. at a rate of at least about 1,000 Å/minute) without causing substantial surface roughening. For example, in some embodiments, provided solutions are capable of removing 1,000 Å of copper without increasing surface roughness of etched copper surface (as judged by lack of decrease in surface reflectivity upon etching). In other embodiments, the surface roughness is increased only insignificantly (e.g., causing less than about 20% initial decrease of surface reflectivity per 1,000 Å of etched copper).

In one aspect, provided etching formulation includes an aqueous solution which comprises (a) a bidentate, tridentate, or quadridentate complexing agent selected from the group consisting of a diamine, a triamine, and a tetramine; and (b) an oxidizing agent. The solution has a pH of between about 5 and 12, more typically between about 6 and 10. The solution in some embodiments, may include other components, such as, for example, a pH adjustor.

Suitable oxidizers include, without limitation, peroxides, permanganates, persulfates and ozone solution. Hydrogen peroxide (H_2O_2) is a preferred oxidizer in many embodiments.

In some embodiments, the complexing agent used in the formulation is a diamine. Examples of suitable bidentate diamines include ethylenediamine (EDA, $H_2NCH_2CH_2NH_2$) and N-methylethylenediamine ($H_3CNHCH_2CH_2NH_2$).

In some embodiments, the complexing agent is a triamine, e.g., a tridentate triamine, - diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$).

In yet other embodiments, the complexing agent is a tetramine, such as tris (2-aminoethyl)amine ($\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$). The etching solution may include in some embodiments mixtures of polyamines, wherein the polyamines are selected from the group consisting of a diamine, a triamine, and a tetramine.

In one specific embodiment, the etching formulation includes ethylenediamine, hydrogen peroxide, and, optionally, a pH adjuster (e.g., sulfuric acid), and has a pH of between about 6 and 10.

In another aspect a method of etching copper-containing portions of a partially fabricated semiconductor substrate, is provided. The method can be used in a variety of processes. For example, it can be used to etch copper overburden, to make recesses in copper-filled vias, in etching-and-capping processes, etc. The method includes (a) receiving the partially fabricated semiconductor substrate comprising an exposed region of copper; and (b) etching copper on the substrate by contacting the substrate with a wet etching solution at a pH in a range of between about 5 and 12, wherein the solution comprises (i) a bidentate, tridentate, or quadridentate complexing agent selected from the group consisting of a diamine, a triamine and a tetramine; and (ii) an oxidizer. The etching solution can have a composition as described above and is, preferably capable of isotropically etching copper at high rates.

The etching solution can be delivered onto the substrate using a number of methods, which include immersing, spraying, spin on contact, contacting in a thin film reactor, etc. Spraying the solution onto the substrate is preferred in some embodiments.

These and other features and advantages of the invention will be described in more detail below, with reference to the associated drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A-1C present a schematic illustration of cross sections of a portion of a Damascene structure illustrating exemplary processes in which isotropic copper etching can be used.

Figure 2 is an experimental bar graph showing copper etch rates for different etch chemistries.

Figure 3 is an experimental plot illustrating dependence of the amount of etched copper on the spray etch time for an etching solution containing EDA and hydrogen peroxide.

Figure 4 is an experimental plot illustrating pH dependence of the copper etch rate for an etching solution containing EDA and hydrogen peroxide.

Figure 5 is an experimental plot illustrating dependence of the copper etch rate on hydrogen peroxide concentration for an etching solution containing EDA and hydrogen peroxide.

Figure 6 is an experimental plot illustrating dependence of the copper etch rate on EDA concentration for an etching solution containing EDA and hydrogen peroxide.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

As indicated, the present invention provides formulations and methods for isotropically etching copper. Provided formulations are particularly useful for etching copper on partially fabricated semiconductor substrates, such as for etching copper overburden, making recesses in copper-filled vias, etc.

“Copper” as used herein refers to copper metal and its alloys, as well as copper metal impregnated with organic compounds (such as levelers, accelerators and suppressors commonly used during copper electroplating). It is noted that provided formulations are also capable of etching other copper-containing materials, such as oxidized copper species, including but not limited to copper oxides and hydroxides.

“Semiconductor substrates” as used herein refer to substrates containing a semiconductor material (e.g., Si wafer or a die) at any stage during processing of such substrate. The semiconductor substrate may include a variety of materials (e.g., dielectrics and conductors) deposited thereon.

“Isotropic etching” refers to removal of copper at substantially similar rates in all directions and/or to removal of copper at substantially similar rates at all grain orientations. In some implementations, isotropic etching is characterized by little or no surface roughening of copper during etching. Surface roughening can be measured

by measuring surface reflectivity prior to etching and after a certain amount of copper (e.g., 1,000 Å) has been removed. In some embodiments, provided etching formulations are characterized by less than about 20% initial decrease in reflectivity per 1,000 Å of etched copper. In some embodiments, the initial decrease in reflectance is less than about 15%, such as less than about 10%, e.g., 5% or less.

Etching of copper can be accomplished isotropically with the use of particular compositions containing an oxidizing agent and a complexing agent. It was unexpectedly discovered that the nature of complexing agent is of particular importance when isotropic uniform etching without significant pitting or roughening is desired. Etching compositions that provide high etch rates (e.g., at least about 1,000 Å/minute, preferably at least about 2,000 Å/minute) in the pH range of between about 5-12, preferably between about 6 – 10 were developed. Significantly, in some embodiments etching occurs at substantially the same rates within the recessed features (or copper-filled lines) of different sizes. Further, different surfaces within the recessed features are etched at substantially the same rates, e.g., etching at the corners of the formed recessed features occurs at the same rate as etching at the feature bottoms. Etching with the described compositions also, in some embodiments, occurs uniformly across the wafer, with little etch rate variation between the central portions and the edges of the wafer.

In contrast, conventional copper etching compositions, e.g., etching compositions having low pH of less than about 5, commonly exhibit non-isotropic behavior, with etch rates within smaller features being substantially greater than etch rates within larger features. Further, high pitting and surface roughness are observed with the use of conventional etching compositions.

The unusual isotropic behavior of the etches described herein is attributed to the rate-limiting reaction occurring at the copper surface. Without being bound by a particular theory, it is possible that in the pH range of between about 6-12, copper oxide is being formed at the copper surface and is immediately solubilized and removed by the complexing agent of the copper etching composition. It is noted, that advantageously, in some embodiments, etching compositions described herein do not form a layer of copper oxide resident on copper surface, but instead afford a smooth oxide-free copper surface having high reflectivity (e.g., reflectivity greater than 120% (relative to Si surface) after 5,000 Å etch, and with reflectivity decrease of less than about 10% per 1,000 Å of etched copper). Thus, if any oxide is being formed during the etching reaction, it is immediately removed *in situ*, such that an additional oxide-removing operation is not required.

The etching is typically non-grain specific, e.g., it does not occur at substantially higher rates along any particular grain orientation or at grain boundaries, and therefore does not result in undesired faceting. The etch rate is feature size and pitch independent. Further, the described etching formulations can provide reduced pitting and surface roughness and afford smooth oxide-free surfaces having high reflectivity.

According to one embodiment the compositions include an oxidizing agent (e.g., a peroxide, a persulfate, a permanganate, an ozone solution, etc.) and a bidentate, tri-dentate or quadridentate complexing agent which is a diamine, a triamine, or a tetramine. Hydrogen peroxide is a preferred oxidizing agent in some embodiments, due to its high solubility and low cost.

The nature of complexing agent was found to be of particular importance. For example, simple unidentate ligands, such as ammonia, and large carboxylate-rich multidentate ligands, such as ethylene diamine tetraacetic acid (EDTA) were found to afford low etch rates and result in surface oxide formation. In some embodiments, provided wet etching solutions are substantially free from ligands having denticities greater than 4 (such as EDTA), and from ammonia and its salts.

Unexpectedly, bidentate, tridentate and quadridentate diamines, triamines, and tetramines, were found to afford excellent etch rates, isotropic behavior, low surface roughness, and no residual surface oxide. A variety of bidentate, tridentate and quadridentate amines can be used. These can be derivatized at nitrogen (e.g., can be N-alkyl substituted) or at other positions, or underivatized. Examples include ethylenediamine (EDA, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$), N-methylethylenediamine ($\text{CH}_3\text{NHCH}_2\text{CH}_2\text{NH}_2$), diethylenetriamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$), and tris(2-aminoethyl)amine ($\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$). Mixtures of bidentate, tridentate and quadridentate amines can be also used in the etching formulation.

Advantageously, provided etching compositions afford very high etch rates and lead to smooth metal surfaces having very high reflectivity. Further, in some embodiments, polyamines do not require any or significant quantities of potentially expensive basic pH adjusters to reach the desired pH. Examples of typical etching compositions comprising polyamines include compositions having a pH of between about 6 – 10, a polyamine (e.g., EDA) and H_2O_2 . In other embodiments, basic pH adjusters such as tetraalkylammonium hydroxides, may be added to the compositions. In some embodiments, etching compositions include acidic pH adjusters, such as sulfuric acid (H_2SO_4) to lower the pH. It is understood that at a pH above 5 (at which provided compositions operate) acidic pH adjusters will be predominantly present in

the etching solutions as salts. Therefore, for example, the term "etching solutions comprising sulfuric acid" is to be interpreted as a solution comprising the appropriate conjugate base of sulfuric acid for a requisite pH. A variety of acidic pH adjustors can be used for etching compositions. In some embodiments, it is preferable to exclude toxic or explosive pH adjustors, such as HClO_4 .

One typical exemplary etching composition is a composition which includes ethylenediamine, hydrogen peroxide and, optionally, sulfuric acid, wherein the pH of the composition is between about 6 and 10. While etching solutions generally may contain a variety of additional components (e.g., surfactants, corrosion inhibitors, etc.), in some embodiments the solutions consist essentially of water, a bidentate, tridentate or quadridentate complexing agent selected from the group consisting of diamines, triamines, and tetramines; an oxidizing agent, and, optionally, a pH adjustor.

Another advantageous feature of the present compositions is that etching can be rapidly quenched (i.e., the etching rate can be decreased) at high pH. For example, if etching needs to be stopped at a particular time in the process, a basic pH adjuster may be supplied into the system to increase the pH of the etchant to, e.g., greater than about 10-12. The etch rate for the described etching compositions decreases at high pH, and etching can be shut down at high pH by introduction of a suitable pH adjuster (e.g., an OH-containing adjustor). Suitable basic pH adjustors include tetraalkylammonium hydroxides, such as tetramethylammonium hydroxide (TMAH).

The provided etching formulations are aqueous solutions which are distinct from chemical mechanical polishing solutions or slurries in that they do not contain either abrasive particles and do not rely on mechanical abrasion of the surface with a pad during metal removal. Thus, for example, pads (either with abrasive in the solution, or abrasives held or fixed in the pad, or not in the pad or in the solution) are not necessary for provided etching methods, and etching can be accomplished simply by immersing the substrate into the etching solution, or spraying the solution onto the substrate. Spraying, in many embodiments, is the preferred method of delivering the etching composition onto the substrate. In one exemplary implementation, the etching solution is sprayed from a nozzle that creates a line of spray across the surface (so-called "fan-nozzle") onto a rotating substrate that is rotated (e.g., at a rate of between about 20-200 rpm) at ambient temperatures. Generally higher temperatures can be used to increase the etch rate. In some examples, apparatus for applying etching solution include those used for many EBR (edge bevel removal) or SRD (spin rinse drier) applications. An example of a suitable apparatus and methods for its use are

described further in US Patent No. 6,309,981 issued October 30, 2001 to Mayer et al., and in US Patent No. 6,586,342 issued July 1, 2003 to Mayer et al. Further, in some embodiments etching solution may be brought in contact with the substrate using spin on contact method or in a thin film reactor.

The described etching compositions can be used in a variety of contexts during semiconductor processing. For example, the compositions may be used for forming recesses in copper lines in the presence of exposed dielectric. Further, the described compositions can be used for selective etching of copper in the presence of diffusion barrier material (e.g., tantalum and/or tantalum nitride). In another example, etching compositions are delivered onto the substrate comprising copper overburden to partially or completely remove the overburden.

It is understood, that the use of compositions for isotropic etching described herein is not limited to the applications mentioned above, and can be employed in any application where isotropic etching of copper is desired. While the described compositions and methods are particularly advantageous for use during fabrication of semiconductor devices having copper-filled features with widths of less than about 400 nm, in a wide variety of applications beyond integrated circuit (IC) fabrication.

When used in semiconductor processing, the method of copper etching involves (a) providing a semiconductor substrate comprising a copper region; and (b) contacting the copper region with the etching composition described herein. In some embodiments, after an initial period of etching, the etching reaction is quenched (i.e., the rate of etching is decreased or reaction is stopped) by increasing the pH of the etching solution (e.g., by adding a basic pH adjustor).

Figures 1A-1C provide exemplary cross-sectional views of Damascene structures in which provided etching methods can be used. Figure 1A illustrates a structure comprising a substrate 101 (e.g., a dielectric) having an embedded copper-filled recessed feature 111. A layer of copper overburden 109 resides over the field region of the substrate. A thin conformal diffusion barrier layer 105 (e.g., tantalum and/or tantalum nitride) resides between copper regions 109 and 111 and the substrate region 101. In one embodiment, overburden 109 can be completely or partially etched by contacting the substrate with an isotropic wet etching solution provided herein. In some embodiments, a planarization operation, such as CMP or electroplanarization is performed before or after wet etching.

Figure 1B shows a substrate, obtained after removal of overburden. The diffusion barrier layer 105 is exposed in the field region and copper layer 111 is

exposed at the top of the copper-filled recessed feature. In some embodiments, isotropic etching solutions provided herein can be delivered onto the substrate to form a recess in the copper layer 111, selectively in the presence of diffusion barrier layer 105 (without etching the diffusion barrier layer) to arrive to the structure shown in Figure 1C which illustrates a recess formed in the top portion of copper-filled layer 111. Next, in some embodiments this recess may be filled with a cap (e.g., cobalt-containing cap) by, for example, electroless deposition. Such capped copper interconnects are desirable in some implementations, as they improve electromigration properties of interconnects.

It is understood that the use of isotropic etching compositions provided herein is not limited to the illustrative examples (e.g., etching-and-capping), discussed above. Provided isotropic compositions can be used in a variety of contexts in Damascene process flows (e.g., overburden etching in many contexts) and beyond. For example, provided etchants can be used to remove unwanted copper from edge region of the semiconductor substrate, or from the backside of the substrate.

Experimental details of provided etching compositions and methods are described in the following section.

EXPERIMENTAL

A comparison of ligands in copper etching compositions

A blanket coated copper film layer was first deposited and then was etched using a variety of wet etching compositions. The reflectivity measurements of copper surface were performed before and after etching at a wavelength of about 480 nm and are given in percent relative to silicon surface. The following aqueous solutions were tested for their ability to etch copper isotropically:

(a) Ethylenediamine (0.066M), H_2O_2 (1.06 M), pH 8.9, 20 °C

This solution exhibited a very high etch rate of 4600 Å/min, and also exhibited excellent isotropic behavior. Reflectivity of copper surface was 131% after etching (134 % prior to etching) per 6900 Å removed.

(b) Glycine (0.066M), H_2O_2 (1.06 M), pH 8.9, 20 °C.

This solution exhibits an etch rate of 1580 Å/min and isotropic behavior. The etch rate is lower than for EDA. Reflectivity of copper surface was 140% after etching (134 % prior to etching) per 1053 Å removed.

(c) Ammonium persulfate (0.066M), no hydrogen peroxide, pH 2.6, 20 °C.

This low pH (acidic) etching solution exhibits an etch rate of 1849 Å/min, however copper surface with high roughness was obtained after etching. Reflectivity of copper surface was only 61% after etching (134 % prior to etching) per 1849 Å removed. A matt finish was observed.

(d) Ammonium acetate (0.066M), H₂O₂ (1.06 M), pH 3.6, 20 °C.

This low pH etching solution exhibits an etch rate of 1163 Å/min, however a red/brown copper oxide surface film was obtained during and after etching. Reflectivity of copper surface was only 8.8% after etching (134 % prior to etching) per 1163 Å removed.

(e) Ammonium persulfate (0.066M), no hydrogen peroxide, pH 8.9, 20 °C.

This etching solution exhibits an etch rate of only 613 Å/min, however copper surface with red/brown oxide was obtained after etching. Reflectivity of copper surface was 52% after etching (134 % prior to etching) per 429 Å removed.

(f) Ammonium hydroxide (0.066M), H₂O₂ (1.06 M), pH 8.9, 20 °C.

This etching solution exhibits an etch rate of only 53 Å/min, however copper surface with red/brown oxide was obtained after etching. Reflectivity of copper surface was 68% after etching (134 % prior to etching) per 53 Å removed.

(g) EDTA (0.066M), H₂O₂ (1.06 M), pH 8.9, 20 °C.

This ethylenediaminetetraacetic acid (EDTA) containing etching solution exhibits an etch rate of only 5 Å/min. Reflectivity of copper surface was 135% after etching (134 % prior to etching) per 5 Å removed, indicating very little interaction with the surface (i.e. little metal removal or film formation).

(h) Citric acid (0.066M), H₂O₂ (1.06 M), pH 8.9, 20 °C.

This etching solution also exhibits no appreciable etching at all.

(i) Oxalic acid (0.066M), H₂O₂ (1.06 M), pH 8.9, 20 °C.

This etching solution also exhibits no appreciable etching at all.

(j) Ammonium acetate (0.066M), H_2O_2 (1.06 M), pH 9.6, 20 °C.

This etching solution exhibits an etch rate of 429 Å/min, however copper surface with red/brown oxide was obtained after etching. Reflectivity of copper surface was 13% after etching (134 % prior to etching) per 429 Å removed.

A bar graph illustrating dependence of etch rates on etching chemistry is shown in Figure 2.

It can be seen from the given examples that only EDA and glycine provide both high etching rates and isotropic behavior. Ammonium hydroxide and ammonium salts lead to formation of oxide deposits on copper surface and/or to high surface roughness. EDTA, citric and oxalic acids do not exhibit appreciable etch rates. EDA is superior to glycine as it provides substantially higher etching rates.

Etching solutions containing EDA and H_2O_2

A copper film was etched by spraying an etching solution containing EDA (4 g/L, 0.067 M), and H_2O_2 (120 g/L of 30% H_2O_2 , or about 1.9 M) onto the substrate. The pH of solution was 8.9; the temperature was 20 °C. Etch rate of about 4,600 Å/minute was observed. After 7,000 Å of copper were removed, the reflectivity was 122% (compared to 125% reflectivity prior to etching).

Figure 3 illustrates a dependence of the amount of etched copper on the spray etch time. It can be seen that about 9,000 Å were removed in about 120 seconds. The amount of etched copper linearly depends on the spray etch time.

In another experiment pH dependence of copper etch rate was studied. The plot of etch rate vs. pH dependence is shown in Figure 4. An etching solution containing 2 g/L (0.033 M) EDA and 30 g/L of 30% H_2O_2 (9 g/L, or 0.47M) was used. pH was adjusted with H_2SO_4 or TMAH depending on the need to increase or decrease the pH from the un-modified EDA/peroxide mixture value. It was observed that at pH values lower than 7, copper surface became rough and had a matt surface reflection, and had streaks or swirls, and was generally non-uniform in appearance. At high pH (above 11) the etch rates declined though the surface appeared relatively unaltered (reflective/smooth). It was found that the preferred pH for EDA etch was from about 7 to about 10.5, more typically from about 8.5 to 10.

Figure 5 illustrates etch rate dependence on the concentration of H_2O_2 for a solution containing EDA (0.067M) and H_2O_2 (10-40 g/L) at a fixed pH of 8.9. The etch rate is moderately increasing as the amount of H_2O_2 is increased.

Figure 6 illustrates etch rate dependence on the concentration of EDA for a solution containing EDA (0 – 8 g/L) and H_2O_2 (1 M) at pH 8.9. It can be seen that etch rate is strongly dependent on the concentration of EDA and increases in near linear fashion with increase in the EDA concentration.

Table 2 illustrates changes of reflectance (measure of isotropic behavior) for etching solutions containing EDA and hydrogen peroxide, wherein EDA concentrations ranged from 1 to 8 g/L, hydrogen peroxide concentrations ranged from about 10 to about 40 g/L and pH values ranged from 7 to 11.6. It can be seen that in all cases the reflectance value did not decrease by more than 15%.

Table 2. Copper surface roughness obtained after etching with different solutions comprising EDA.

EDA Concentration (g/L)	H ₂ O ₂ Concentration (g/L)	pH	% Change Reflectance/(1000Å)
1	39.6	8.9	11.1
2	9.9	7	5.4
2	9.9	8.1	3.9
2	9.9	8.9	2.8
2	9.9	10.3	14.4
2	9.9	11.6	14.2
4	9.9	8.9	1.4
4	19.8	8.9	0.67
4	39.6	8.9	0.34
8	39.6	8.9	2.8

Etching solutions with other complexing agents containing an aminogroup

A number of solutions containing different complexing agents were tested. pH was adjusted to 8.9 or 8.8 with TMAH or H_2SO_4 .

(a) N-methylethylenediamine (0.066M), H_2O_2 (1.00 M), pH 8.9, 20 °C.

This solution exhibits an appreciable etch rate of 1575 Å/min and isotropic behavior. Reflectivity of copper surface was 127% after etching (134 % prior to etching) per 1575 Å removed.

(b) Sarcosine (0.066M), H_2O_2 (1.00 M), pH 8.9, 20 °C.

This solution exhibits an etch rate of 11.5 Å/min.

(c) Taurine (0.066M), H₂O₂ (1.00 M), pH 8.9, 20 °C.

This solution exhibits an etch rate of 12 Å/min.

(d) Ethanolamine (0.066M), H₂O₂ (1.00 M), pH 8.9, 20 °C.

This solution does not exhibit appreciable etching.

CLAIMS

What is claimed is:

1. A wet etching formulation comprising an aqueous solution, the solution comprising:
 - (a) ethylenediamine ; and
 - (b) hydrogen peroxide , whereinthe pH of the etching solution is between about 7 and 10.5 and wherein said etching formulation is capable of isotropically etching copper, such that reflectivity of etched copper surface does not decrease by more than 15% per 1,000 Å of etched copper.
2. The wet etching formulation of claim 1, wherein said formulation is capable of etching copper at an etch rate of at least about 1,000 Å/minute.
3. The wet etching formulation of claim 1, wherein said formulation is capable of removing at least about 1,000 Å of copper from a substrate, without increasing surface roughness of an etched copper region.
4. The wet etching formulation of claim 1, wherein the formulation comprises a pH adjustor.
5. The wet etching formulation of claim 4, wherein the pH adjustor comprises sulfuric acid.
6. A method of isotropically etching copper-containing portions of a partially fabricated semiconductor substrate containing a copper region, the method comprising:
 - (a) receiving the partially fabricated semiconductor substrate comprising an exposed region of copper; and

(b) isotropically etching copper on the substrate by contacting the substrate with a wet etching solution at a pH in a range of between about 5 and 12, wherein the solution comprises (i) a bidentate, tridentate, or quadridentate complexing agent selected from the group consisting of a diamine, a triamine and a tetramine; and (ii) a peroxide, and wherein contacting the substrate is selected from the group consisting of spraying the etching solution onto the rotating substrate, spin on contact, and contacting the substrate with the etching solution in a thin film reactor.

7. The method of claim 6, wherein the wet etching solution further comprises a pH adjustor.
8. The method of claim 6, wherein the complexing agent comprises a diamine.
9. The method of claim 6, wherein the diamine is selected from the group consisting of ethylene diamine or N-methylethylenediamine.
10. The method of claim 6, wherein the wet etching solution comprises ethylenediamine and hydrogen peroxide.
11. The method of claim 10, wherein the wet etching solution further comprises a pH adjustor.
12. The method of claim 11, wherein the wet etching solution has a pH of between about 6 and 10.
13. The method of claim 6, wherein the complexing agent is selected from the group consisting of a triamine and a tetramine.
14. The method of claim 6, wherein the etched copper region comprises copper overburden.

15. The method of claim 6, wherein the copper is etched at a rate of at least about 1,000 Å/minute.
16. The method of claim 6, further comprising stopping the etching process by increasing the pH of the wet etching solution.
17. The method of claim 16, wherein increasing the pH of the wet etching solution comprises adding a basic pH-adjustor to the wet etching solution.
18. The method of claim 6, wherein the contacting comprises spraying the wet etching solution onto the rotating substrate.