An aqueous polishing composition for chemical mechanical polishing to remove copper from a buffer material, the composition comprising, an oxidizing agent, a complexing agent, an inhibitor, a dishing reducing agent, and abrasive particles comprising organic polymer particles for clearing relatively soft copper from the buffer material by chemical mechanical polishing while minimizing dishing and avoiding removal of the buffer material.
POLISHING COMPOSITION HAVING ORGANIC POLYMER PARTICLES

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation in part of application Ser. No. 09/826,525, filed Apr. 5, 2001.

FIELD OF THE INVENTION

[0002] The invention is directed to chemical mechanical polishing, CMP, of a semiconductor substrate having a copper metal circuit.

BACKGROUND OF THE INVENTION

[0003] A semiconductor substrate comprises, a semiconductor wafer and multiple layers of materials including, a layer of an insulating material, such as, silica, that is deposited and provided with troughs, and a metal conductor, such as, copper, that is deposited as a layer, and is in the troughs to form a copper circuit. The metal conductor is separated from the insulating material by a buffer material, such as, tantalum or tantalum nitride.

[0004] CMP is performed as a process for removing excess copper. According to a process of CMP, a polishing pad is pressed against the substrate and is moved across the surface of the substrate while an aqueous polishing composition is interposed between the polishing pad and the surface of the substrate being polished. Abrasive particles in the polishing composition apply abrasion to increase the rate of removal by polishing. Prior to the invention, inorganic abrasive particles included, alumina, silica, ceria, germania, diamond, silicon carbide, titania, zirconia, boron nitride, boron carbide and mixtures thereof.

[0005] The copper layer on the wafer is polished by performing CMP until the copper is cleared from the surface of the substrate. CMP desirably removes copper material from peaks or protrusions of the copper layer, which are those portions that are above the average surface height of the surface being polished. Copper material in valleys or recesses, including the copper circuit in the troughs, are below the average surface height. Removal of copper primarily from the peaks is desired, and is accomplished by removing the copper material from the peaks at a rate of removal that is faster than that of the copper material in valleys. However, the process of CMP has a tendency to remove copper in both the peaks and valleys. While polishing a copper circuit, i.e. copper in the troughs, more of the center is polished and removed, as compared to, or rather than, the edges. The result is a low center. This is an observed problem known as “dishing”. A need exists for an invention to significantly reduce, i.e., minimize, dishing.

SUMMARY OF THE INVENTION

[0006] According to the invention, a polishing composition has organic polymer particles as abrasive particles. The copper layer on the wafer is polished by CMP using the polishing composition, according to the invention, to remove peaks of the copper layer. Copper is cleared from the surface of the substrate or wafer, with minimized, i.e., substantial reduction in, dishing of the copper circuit. Planarization herein refers to clearing the copper layer from the semiconductor substrate with minimized dishing of the copper in the troughs. Planarized herein refers to a flat polished surface of the semiconductor substrate, and the copper in the troughs having minimized dishing, resulting from a process of CMP that has removed the copper layer.

[0007] Embodiments of the invention will now be described by way of example with reference to the following detailed description.

DETAILED DESCRIPTION

[0008] The organic polymer particles apply abrasion during CMP to remove “high spots” of the copper layer of semiconductor circuit and provide a planarized copper circuit. The polymer particles do not provide the same level of abrasion as inorganic particles but provide a substantially lower level of abrasion. Copper is a relatively soft metal and is easily eroded by polishing with the organic polymer particles. The organic polymer particles are selective in that only relatively soft copper is polished for clearing, i.e., removal and planarization, and not other layers of relatively hard material, such as, tantalum or tantalum nitride, of the buffer material.

[0009] An embodiment of the polishing composition does not have inorganic abrasive particles. Another embodiment does have 0.01% up to 3% by weight of inorganic abrasive particles, for example, alumina and silica or mixtures thereof, to adjust an increase in the removal rate of copper during CMP.

[0010] The polishing composition contains 0.1-5.0% by weight, based on the weight of the composition, of polymer particles having a number average molecular weight of at least 500,000 determined by GPC (gel permeation chromatography). One embodiment has a Tg (glass transition temperature) of at least 25°C. A further embodiment of the composition contains 0.25-1.0% by weight, based on the weight of the composition, of polymers having a number average molecular weight of 500,000 to 3,000,000 and a Tg of 25 to 130°C. An alternative of the further embodiment has a Tg of 25 to 90°C.

[0011] The Tg of the polymer is measured using differential scanning calorimeter (DSC) from Texas Instruments (model 2010), and performing a known procedure, wherein, polymer samples are heated in nitrogen starting at ambient temperature and heating at 20°C per minute through the glass transition temperature recording mid point values.

[0012] Embodiments of the polymer particles include those that have diameters in the range of 5 to 5,000, and those that have diameters in the range of 50 to 1,500 μm.

[0013] The polymer particles are formed by: a homogeneous polymer, a copolymer, a terpolymer, blends of two or more polymers, crosslinked homogeneous polymers, crosslinked blends of polymers, core-shell polymers in which the core is of a different composition from the shell or graft copolymers. These polymer particles can be solid particles or can be in the form of a hollow sphere.

[0014] The polymer particles include particles of polymers, including, but not limited to, styrene, copolymers and terpolymers of styrene, acrylonitrile, methyl methacrylate, copolymers and terpolymers of methyl methacrylate and an alkyl acrylate wherein the alkyl group has 1-18 carbon atoms or an alkyl methacrylate where the alkyl group has
2-18 carbon atoms and can contain small percentages of polymerized ethylenically unsaturated carboxylic acids, such as, methacrylic acid or acrylic acid or hydroxy alkyl acrylates or methacrylic esters or amino alkyl acrylates or methacrylates. The polymers can be crosslinked with monomers such as, divinyl benzene. One useful polymer is a polymer of styrene crosslinked with divinyl benzene, which can be in particle form of hollow spheres.

[0015] The polymer particles include, and are not limited to, a graft copolymer, for example, a graft copolymer having a backbone of relatively high Tg polymer, like polymethyl methacrylate and side chains of a comparatively low Tg polymer of an alkyl acrylate, like butyl acrylate. Further, for example, the graft copolymer can have a backbone of a low Tg polymer, such as, 2 ethylhexyl acrylate and side chains of macromonomers containing a major amount of polymethyl methacrylate. Polymer particles of a core shell polymer can be used in which the shell is of a high Tg polymer, such as, poly(methyl methacrylate) and the core is a lower Tg polymer, such as, ethyl acrylate.

[0016] Monomers that form the polymers of the particles are, for example, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, pentyl methacrylate, hexyl methacrylate, octyl methacrylate, lauryl methacrylate, stearyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, pentyl acrylate, hexyl acrylate, octyl acrylate, lauryl acrylate, stearyl acrylate, cyclohexyl acrylates and methacrylates, acrylonitrile, styrene, alpha methyl styrene, vinyl toluene, hydroxy alkyl acrylates and methacrylates such as hydroxy ethyl acrylate, hydroxy propyl acrylate, hydroxy butyl acrylate, hydroxy ethyl methacrylate, hydroxy propyl methacrylate, hydroxy butyl methacrylate, amino alkyl acrylates and methacrylates such as amino ethyl acrylate, amino propyl acrylate, amino butyl acrylate, amino ethyl methacrylate, amino propyl methacrylate, amino butyl methacrylate. Other suitable monomers that may be used include: acrylamide, methacrylamide, alkoxymethyl acrylamides and methacrylamides.

[0017] The polymers particles are formed by known techniques. An aqueous latex can be formed and added to form the polishing composition of this invention. Alternatively, solution polymerization techniques are used to form polymer particles, followed by having solvent removal. The polymer particles are dispersed in water and added directly to the polishing composition.

[0018] An embodiment of the polishing composition contains about 0.05-2.0% by weight, based on the weight of the composition, of carboxylic acid polymer particles comprising polymerized unsaturated carboxylic acid monomers and has a number average molecular weight of about 20,000 to 1,500,000. Blends of high and low number average molecular weight carboxylic acid polymers also can be used and are preferred for many polishing uses. These carboxylic acid polymers are in solution or are in the form of an aqueous dispersion. The number average molecular weight of the aforementioned polymers are determined by GPC (gel permeation chromatography). For some polishing compositions, high carboxylic acid containing copolymers and terpolymers can be used in which the carboxylic acid component comprises 5-75% by weight of the polymer. Typical of such polymer are polymers of (meth)acrylic acid and acrylamide or methacrylamide; polymers of (meth-}
Unsaturated carboxylic acid monomers include, and are not limited to, unsaturated monocarboxylic acids and unsaturated dicarboxylic acids. Typical unsaturated monocarboxylic acid monomers contain 3 to 6 carbon atoms and include acetic acid, oligomeric acetic acid, methacrylic acid, crotonic acid and vinyl acetic acid. Typical unsaturated dicarboxylic acids contain 4 to 8 carbon atoms and include the anhydrides thereof and are, for example, maleic acid, maleic anhydride, fumaric acid, glutaric acid, itaconic acid, itaconic anhydride, and cyclohexene dicarboxylic acid. Water soluble salts of the aforementioned acids also can be used.

An embodiment of the polishing composition is an aqueous composition that has a pH under 5.0. A further embodiment has a pH of 2.8 to 4.2. Yet a further embodiment has a pH of 2.8 to 3.8.

EP 0 913 442 A2 discloses a polishing composition having a dining reducing agent in the form of a polycrylic acid to adhere to copper and minimize dining during CMP.

The term “poly(meth)acrylic acid”, means polymers of acrylic acid or polymers of methacrylic acid. Particularly useful are poly(meth)acrylic acids having a number average molecular weight of about 20,000 to 150,000, preferably 25,000 to 75,000 and more preferably, 25,000 to 40,000. Blends of high and low number average molecular weight poly(meth)acrylic acids are particularly preferred. In such blends or mixtures of poly(meth)acrylic acids, a low number average molecular weight poly(meth)acrylic acid having a number average molecular weight of 20,000 to 100,000 and preferably, 20,000 to 40,000 is used in combination with a high number average poly(meth)acrylic acid having a number average molecular weight of 200,000 to 1,500,000, preferably 150,000 to 300,000. Typically, the weight ratio of the low number average molecular weight poly(meth)acrylic acid to the high number average molecular weight poly(meth)acrylic acid is 10:1 to 1:10, preferably 4:1 to 1:4, and more preferably 2:1 to 1:2. An embodiment comprises a polycrylic acid having a number average molecular weight of about 30,000 and a polycrylic acid having a number average molecular weight of about 250,000 in a 1:1 weight ratio. Embodiments of very low number average molecular weight poly(meth)acrylic acid polymers in the aforementioned blend include, for example, poly(meth)acrylic acid polymers having a number average molecular weight of 1,000 to 5,000.

The polishing composition may further contain pH buffers, such as, amines, and may contain surfactants, deflocculants, viscosity modifiers, wetting agents, cleaning agents and the like.

The following polishing pads can be used with the polishing composition to polish copper; a metal pad described in U.S. Pat. No. 6,022,268, a polishing pad containing particles for polishing described in U.S. Pat. No. 5,489,233, a polishing pad of polymer impregnated fiber matrices sold by Rodel Inc., Newark, Del., USA, under the trade name SUBA, a pad of a polymer sheet containing void spaces formed by in situ production or incorporation of hollow fill materials (sold by Rodel Inc. under the trade name P/LTEX and IC 1010), a pad of polymer sheets containing solid particles that are added as fillers that may optionally contain void spaces, effected either by in situ production or by incorporation of hollow filler materials (sold by Rodel Inc. under the trade name MH), and a composite pad of multiple layers of materials whose outer substrate that contacts the surface of the semiconductor being polished is one of the pads selected from the above.

The following examples further describe the invention. All parts and percentages are on a weight basis unless otherwise indicated and molecular weights are determined by gel permeation chromatography unless otherwise indicated.

Example 1

The following polishing compositions were prepared:

Control Polishing Composition

The polishing composition was prepared by blending the following constituents:

0.3 parts benzotriazole, 0.22 parts malic acid, 0.09 parts of polyacrylic acid having a number average molecular weight of 30,000, 0.9 parts of polyacrylic acid having a number average molecular weight of 250,000 and 9.0 parts hydrogen peroxide and sufficient deionized water to bring the total parts of polishing composition to 100.

Polishing Composition 1

(1% “Sunpheres)—identical to the above control composition except that 1% by weight of “Sunpheres” polymer particles was blended with the control composition. “Sunpheres” have a diameter of 350 nm, are manufactured by Rohm and Haas Company and are hollow spheres composed of polystyrene crosslinked with divinyl benzene and have a Tg of 81°C.

Polishing Composition 2

(1% “Rovace” 661)—identical to the above control composition except that 1.0% “Rovace” 661 was blended with the control composition. “Rovace” 661 have diameter of 300 nm, are manufactured by Rohm and Haas Company, and are polymer particles of polyvinyl acetate (PVA) having a number average molecular weight of approximately 1 million and have a Tg of 21°C.

Polishing Composition 3

(1% “Ropaque” HP-1055)—identical to the above control composition except that 1% “Ropaque HP-1055 was blended with the control composition. Ropaque HP-1055 are polymer particles having a diameter of 1000 nm, are manufactured by Rohm and Haas Company, are polymer particles of polystyrene that are crosslinked and have a Tg of 83°C.

Polishing Composition 4

(1% HG 74 P)—identical to the above control composition except that 1% HG 74 P was blended with the control composition. HG 74 P are polymer particles manufactured by Rohm and Haas Company, are polymer particles of polymethyl methacrylate having a number average molecular weight of approximately 1 million and have a Tg of 29°C.

Conventional Polishing Composition 5

(1% “Klebosol”—identical to the above control composition except that 1% “Klebosol was blended with the
control composition. “Klebosol” is colloidal silica having a particle diameter of 12 nm, has inorganic abrasive characteristics and is manufactured by Clariant Corporation.

[0043] Test for Dishing of Copper of a Copper Pattern Wafer

[0044] Wafer tested—electroplated 200 mm copper pattern wafer of silicon dioxide (100 um copper lines) and having Sematech 931 mask.

[0045] Test Pad—Metal 26 pad manufactured by Rodel Inc. Newark, Del. (described in U.S. Pat. No. 6,022,268).


[0047] The wafer was polished with the control polishing composition using the following polishing parameters until the end point was detected by the polishing machine.

[0048] Platen force-5 psi (351.5 g/cm²)

[0049] Platen Speed—93 rpm

[0050] Carrier Speed—87 rpm

[0051] Slurry Flow—250 ml/min

[0052] After the end point was detected, polishing was continued except the down force was reduced to 3 psi (210.9 g/cm²) until the endpoint trace on the polishing machine flattens (i.e., the slope of the curve is zero). At this point all removal of copper had stopped and no copper was present. The time was recorded for each of the above polishing steps.

[0053] The dishing of the copper pattern lines of the wafer was measured on a Tencor P1 profilometer. The 100 um lines in the center of the wafer were measured, the 100 um lines in the middle of the wafer were measured (i.e., half way between the center and edge of the wafer) and the 100 um lines near the edge of the wafer were measured (i.e., about 1 inch from the edge of the wafer). Separate wafers as described above were polished under the same conditions with each of the above prepared Polishing Compositions 1-5. The results are shown below in Table 1 for each of the polishing compositions.

<table>
<thead>
<tr>
<th>Polishing Composition</th>
<th>Dishing Center</th>
<th>Dishing Middle</th>
<th>Dishing Edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Composition</td>
<td>900 A</td>
<td>875 A</td>
<td>1500 A</td>
</tr>
<tr>
<td>0% Polymer Particles</td>
<td>700 A</td>
<td>900 A</td>
<td>750 A</td>
</tr>
<tr>
<td>Composition 1</td>
<td>700 A</td>
<td>900 A</td>
<td>750 A</td>
</tr>
<tr>
<td>1.0% Hollow cross-linked polystyrene particles</td>
<td>No removal</td>
<td>No removal</td>
<td>No removal</td>
</tr>
<tr>
<td>Composition 2</td>
<td>700 A</td>
<td>900 A</td>
<td>750 A</td>
</tr>
<tr>
<td>1.0% PVA particles</td>
<td>700 A</td>
<td>900 A</td>
<td>750 A</td>
</tr>
<tr>
<td>Composition 3</td>
<td>700 A</td>
<td>900 A</td>
<td>750 A</td>
</tr>
<tr>
<td>1.0% Polystyrene particles</td>
<td>—</td>
<td>1500 A</td>
<td>800 A</td>
</tr>
<tr>
<td>Composition 4</td>
<td>1500 A</td>
<td>2000 A</td>
<td>1800 A</td>
</tr>
<tr>
<td>1.0% PMMA particles</td>
<td>1500 A</td>
<td>2000 A</td>
<td>1800 A</td>
</tr>
<tr>
<td>Composition 5</td>
<td>1500 A</td>
<td>2000 A</td>
<td>1800 A</td>
</tr>
<tr>
<td>1.0% Colloidal silica particles</td>
<td>—</td>
<td>1500 A</td>
<td>800 A</td>
</tr>
</tbody>
</table>

A=Angstroms

[0054] The above results showed a decrease in dishing of copper lines on the addition of relatively hard polymer particles, such as, crosslinked polystyrene and PMMA, no polishing or dishing occurred with Composition 2 that contained relative soft polymer particles which is not acceptable for a polishing composition, and excessive dishing occurred with Composition 5 that contained a conventional abrasive of colloidal silica which also is not acceptable for a commercial polishing composition. The “step height” of Compositions 1, 3 and 4 that comprised relatively hard polymer particles was improved and dishing was reduced. “Step height” is a measure of the height difference between peaks and valleys on the surface of the wafer. Successful polishing of the surface by CMP reduces the step height to improve planarization and to minimize dishing upon clearing of a copper layer from the wafer by CMP.

What is claimed is:

1. An aqueous polishing composition for chemical mechanical polishing to remove copper from a buffer material, the composition comprising, an oxidizing agent, abrasive particles, a complexing agent, an inhibitor, and a dishing reducing agent, comprising:

- organic polymer particles of the abrasive particles for clearing relatively soft copper from the buffer material by chemical mechanical polishing while minimizing dishing of the copper in trenches and avoiding removal of the buffer material.

2. The aqueous polishing composition as recited in claim 1, further comprising:

- the organic polymer particles comprising, a water soluble carboxylic acid polymer of polymerized unsaturated carboxylic acid monomer having a number average molecular weight of about 20,000 to 1,500,000.

3. The aqueous polishing composition as recited in claim 1, further comprising:

- the organic polymer particles comprising 0.1 to 5.0% by weight in the aqueous polishing composition, and the organic polymer particles comprising a polymer having a number average molecular weight of at least 500,000 and a glass transition temperature of at least 250 C.

4. The aqueous polishing composition as recited in claim 1, further comprising:

- the organic polymer particles comprising polystyrene.

5. The aqueous polishing composition as recited in claim 1, further comprising:

- the organic polymer particles comprising hollow spheres of polystyrene crosslinked with divinyl benzene.

6. The aqueous polishing composition as recited in claim 1, further comprising:

- the organic particles comprising polymethyl methacrylate.

7. The aqueous polishing composition of claim 1, further comprising:

- the organic polymer particles have a diameter of 5 to 5,000 nm and a polymer of the organic polymer particles has a number average molecular weight of 500, 000 to 3,000,000 and a glass transition temperature of 25 to 130° C.

8. The aqueous polishing composition of claim 1, further comprising:

- the dishing reducing agent being a polyhydroxylic acid polymer comprising a blend of poly(meth)acrylic acid of a low number average molecular weight polymer
having a molecular weight of 20,000 to 100,000 and a high number average molecular weight polymer having a molecular weight of 200,000 to 1,500,000.

9. The aqueous polishing composition of claim 8 in which the polycarboxylic acid polymer consist essentially of a blend of polyacrylic acid having number average molecular weight of 30,000 and polyacrylic acid having a number average molecular weight of 250,000 in a 1:1 weight ratio.

10. A method of chemical mechanical polishing to remove relatively soft copper from a buffer material, comprising the steps of:

polishing the copper with a polishing pad and with a polishing composition having an oxidizing agent, a complexing agent, an inhibitor, a dishing reducing agent, and abrasive particles comprising organic polymer particles, and

removing the copper from the buffer material while minimizing dishing of the copper in troughs and avoiding removal of the buffer material.

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