A polishing liquid for components, preferably wafers, a process for producing a polishing liquid and a process for chemical mechanical polishing of components are provided. The polishing liquid has a polishing base liquid and an oxidizing agent. The aim is to provide an economical polishing agent which is also simple to produce, which can be used as an alkaline or acidic polishing agent and with which metallic layers in particular can be polished. Ozone, which is used as an oxidizing agent, is a strong oxidizing agent having a redox potential that is sufficient for oxidizing or polishing the metals in an acidic or alkaline environment.
POLISHING LIQUID FOR COMPONENTS, PREFERABLY WAFERS, PROCESS FOR PRODUCING POLISHING LIQUID AND PROCESS FOR CHEMICAL MECHANICAL POLISHING OF COMPONENTS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation of copending International Application No. PCT/DE99/02959, filed Sep. 16, 1999, which designated the United States.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The invention relates to a polishing liquid for polishing components, preferably wafers, in particular for chemical mechanical polishing of components of this type, having a base polishing liquid and an oxidizing agent. The invention also relates to a process for producing a polishing liquid of this type and to processes for using a polishing liquid of this type.

[0004] In the semiconductor industry, the ever decreasing size of structures leads to increasingly high demands being imposed on the planarity of the surfaces of components which are to be machined. One example of a conventional process for producing planar surfaces is chemical mechanical polishing (CMP). In this process, certain materials are abraded over previously patterned areas through the use of an abrasive-containing polishing liquid (also known as a slurry).

[0005] Particularly if metal layers are being polished, an oxidizing agent has to be added to the polishing liquids. As a result, the surface is chemically etched and the metal surface which has now been oxidized can be mechanically abraded or is dissolved. Oxidizing agents therefore allow controlled abrasion of metal at a sufficiently high rate.

[0006] Heretofore, either hydrogen peroxide (H₂O₂) or salts of elements of a high oxidation number (e.g. Fe(III), Ce(IV), S₅O₃²⁻) have been used as oxidizing agents. However, these substances have a number of drawbacks with a view to simple handling under production conditions.

[0007] Hydrogen peroxide is unstable, its decomposition being accelerated in the presence of extremely small metal impurities or by the action of light. This makes it more difficult, or under certain circumstances impossible, for the polishing apparatus to be continuously supplied with a polishing liquid of constant H₂O₂ concentration (in particular when a central chemical supply system is being used). Adding the polishing liquid in the immediate vicinity of the component which is to be polished (point of use), as is sensible in view of the instability of the peroxide, requires installations for mixing and storing liquid in the immediate vicinity of the production installations. However, this solution is not always desirable for various reasons.

[0008] The addition of solids, such as salts or the like, is often more complex than the addition of liquids, and the solubility of these solids is often pH-dependent. For example, in a neutral and alkaline medium, metals form hydroxides of low solubility which are deposited in the polishing apparatus and in feedlines, so that additional cleaning measures are required.

[0009] Therefore, for the above reasons the use of heavy metal salts (such as, for example, Fe(III) nitrate, ammonium cerium (IV) nitrate) is restricted to acidic polishing liquids. It is not possible to use alkaline polishing media, which may have better properties, for example with regard to stability, selectivity, mechanical abrasion or the like. Moreover, the metal-containing waste waters have to be disposed of.

SUMMARY OF THE INVENTION

[0010] It is accordingly an object of the invention to provide a polishing liquid for components, preferably wafers, a process for producing a polishing liquid and a process for chemical mechanical polishing of components, which overcome the heretofore-mentioned disadvantages of the heretofore-known products and processes of this general type and in which the liquid which can be produced in a simple, inexpensive manner and can be used as both an alkaline polishing liquid and an acidic polishing liquid.

[0011] With the foregoing and other objects in view there is provided, in accordance with the invention, an oxidizing polishing liquid for polishing components, comprising a base polishing liquid and ozone (O₃).

[0012] The result is a polishing liquid with oxidizing properties which can be used to polish components, such as wafers or the like, and in particular for the chemical mechanical polishing of components of this type. Ozone is a strong oxidizing agent, the redox potential of which is sufficient to polish the components in both an acidic environment and an alkaline environment. Particularly if metal layers are to be polished, ozone is especially suitable for oxidizing the metals employed.

[0013] The polishing liquid according to the invention makes it possible in principle to select any polishing liquid which may be suitable for the particular application as the base polishing liquid, to which ozone is then added. Since both the redox and the decomposition reactions of ozone take place without leaving any residues other than water and oxygen, special treatment of the waste water is not required.

[0014] Ozone is formed, for example in an ozone generator, from oxygen with energy input according to Equation 1 below and has a decomposition reaction according to Equation 2:

\[ 2O_2 \rightarrow 3O_3 \]  
\[ O_3 \rightarrow O_2 + O \]  
\[ \text{Equation 1} \]
\[ \text{Equation 2} \]

[0015] wherein O represents atomic oxygen.

[0016] The way in which an ozonized polishing liquid according to the invention acts for the polishing of metal layers can be represented in general terms by the following Equations 3 to 6. First of all, the ozone is reduced so as to form H₂O and O₂ in accordance with Equation 3:

\[ O_3 + 2H^+ + 2e^- \rightarrow H_2O + O_2 \]  
\[ \text{Equation 3} \]

[0017] Furthermore, the atomic oxygen which is formed as a decomposition product of ozone is reduced in accordance with Equation 4:

\[ O + 2H^+ + 2e^- \rightarrow H_2O \]  
\[ \text{Equation 4} \]
The oxidation of a metal $\text{Me}$ which is to be polished to form a metal ion $\text{Me}^{n+}$ takes place in accordance with Equation 5:

$$\text{Me}^{2-} + \text{Me}^{n+} + n \text{e}^- \rightarrow \text{Me}^{n+} \cdot$$  \hspace{1cm} (Equation 5)

Therefore, the above equations result in the following overall reaction for the action of the ozonized polishing liquid:

$$x/\text{O}_3 \cdot x/\text{H}_2\text{O} \cdot \text{Me}^{2-} \rightarrow x/\text{H}_2\text{O} \cdot x/\text{O}_3$$  \hspace{1cm} (Equation 6)

In preferred embodiments of the polishing liquid according to the invention, the base polishing liquid is a colloidal solution of small solid particles in an alkaline medium having a pH greater than 7 or an acidic medium having a pH less than 7. Particularly suitable colloidal solution polishing liquids include small solid particles of aluminum oxide, diamond, and/or silicon carbide. Colloidal solutions of suitable small solid particles are commercially available and can be selected according to requirements and the particular application.

The oxidizing agent is advantageously ozone dissolved in water.

The ozone solution according to the invention has a redox potential of at least 2.0V in the acidic range, and preferably has a redox potential of approximately +2.075V.

Furthermore, the ozone solution according to the invention has a redox potential of at least 1.2V in the alkaline range, and preferably has a redox potential of +1.246V.

The redox potential of ozone is therefore sufficiently great to be able to attack even metal layers which are difficult to oxidize, such as, for example, copper or the like, in both the acidic and the alkaline range. The redox potentials of customary oxidizing agents in aqueous solutions compared to ozone are given in Table 1 below.

<table>
<thead>
<tr>
<th>Redox system</th>
<th>Acidic solution</th>
<th>Alkaline solution</th>
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<tbody>
<tr>
<td>$\text{H}_2\text{O} / \text{O}_3$</td>
<td>$+2.075 \text{ V}$</td>
<td>$+1.246 \text{ V}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 / \text{O}_3$</td>
<td>$+2.422 \text{ V}$</td>
<td>$+1.504 \text{ V}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 / \text{H}_2\text{O}$</td>
<td>$+1.763 \text{ V}$</td>
<td>$+1.067 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Fe}^{3+} / \text{Fe}^{2+}$</td>
<td>$-0.771 \text{ V}$</td>
<td>$0.69 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Fe}^{2+} / \text{Fe}^{3+}$</td>
<td>$+1.72 \text{ V}$</td>
<td>$-0.7 \text{ V}$</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-} / \text{SO}_3^{2-}$</td>
<td>$+2.01 \text{ V}$</td>
<td>$+1.0 \text{ V}$</td>
</tr>
</tbody>
</table>

According to the invention, the quantity of ozone ranges from about 0.2 g to about 0.5 g.

This required quantity results from the fact that the solubility of ozone in water is at most 49% by volume, corresponding to approximately 1 g/l. It must be ensured that the dissolved quantity of ozone is sufficient to achieve the desired abrasion of metal. The maximum required quantities of various oxidizing agents for complete chemical conversion (i.e. oxidation) of 1 μm thick metal layers on 8 inch wafers are given in Table 2 below. For an average polishing liquid consumption of 500 ml per wafer to be polished, the maximum required quantity of ozone is as follows:

<table>
<thead>
<tr>
<th>Oxidizing agent</th>
<th>Aluminum</th>
<th>Metallic tungsten</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{3+}$</td>
<td>2.47</td>
<td>5.19</td>
<td>2.33</td>
</tr>
<tr>
<td>$\text{Ni}^{2+}$</td>
<td>6.56</td>
<td>11.78</td>
<td>5.28</td>
</tr>
<tr>
<td>$\text{Ni}^{2+}$</td>
<td>1.17</td>
<td>2.45</td>
<td>1.10</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>0.17</td>
<td>0.37</td>
<td>0.16</td>
</tr>
<tr>
<td>$\text{O}_3$</td>
<td>0.24</td>
<td>0.49</td>
<td>0.22</td>
</tr>
</tbody>
</table>

The polishing liquid according to the invention can be preferably used for polishing, in particular for chemical mechanical polishing of metal layers and/or contact layers and/or adhesion layers of components, in particular wafers.

Such layers can be formed, in particular, of a material which is selected from the group consisting of aluminum, tungsten, copper, titanium, titanium nitride, tantalum and tantalum nitride. Of course, other metals can also be polished using the polishing liquid according to the invention.

According to the invention, the polishing liquid can be used for the contact patterning and/or interconnect patterning of wafers.

With the above and other objects in view, there is also provided, according to a further aspect of the invention, a process for producing a polishing liquid for polishing components, preferably wafers, in particular a polishing liquid according to the invention as described above, comprising the following steps:

1. Providing a base polishing liquid comprising a colloidal solution of small solid particles;
2. Providing gaseous ozone as oxidizing agent; and
3. Introducing the gaseous ozone into the base polishing liquid.

Through the use of the process according to the invention, it is possible, in a simple and inexpensive manner, to produce a polishing liquid which can be used as both an alkaline and an acidic polishing liquid and which is particularly suitable for polishing metals. With regard to the advantages, actions, effects and functioning of the process according to the invention, reference is hereby made to the above statements relating to the polishing liquid and its use in their entirety.

The ozone which is used as the oxidizing agent can initially be produced as gaseous ozone in an ozone generator and can be added to the polishing liquid at a suitable point. Corresponding installations for mixing chemical solutions with ozone (also known as spiking) are commercially available and can be positioned in the immediate vicinity of the polishing apparatus. Special installations for mixing and storing liquid in the vicinity of the polishing apparatus, as are required, for example, in the prior art, can therefore be dispensed with. Existing central supply installations for polishing liquid can be retrofitted without any major structural outlay. In order to do this, it is merely necessary to install an ozone generator and corresponding safety devices and a metering unit. There is no need to repipe or add additional piping to the central supply network.
Through the use of the present invention, the use of ozone as oxidizing agent first of all leads to a particularly advantageous polishing liquid being formed. Furthermore, the ozone can be produced in situ and then added in the immediate vicinity of the polishing apparatus. Finally, it is possible to retrofit existing central supply networks without difficulty and without structural outlay.

Other features which are considered as characteristic for the invention are set forth in the appended claims.

Although the invention is illustrated and described herein as embodied in a polishing liquid for components, preferably wafers, a process for producing a polishing liquid and a process for chemical mechanical polishing of components, it is nevertheless not intended to be limited to the details shown, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

The construction and method of operation of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of specific embodiments when read in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A and 1B are diagrammatic, partly sectional views of a wafer which has been polished by using the polishing liquid according to the invention; and

FIGS. 2A and 2B are diagrammatic, partly sectional views of a further exemplary embodiment of a wafer which has been polished by using the polishing liquid according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the figures of the drawings in detail and particularly to FIG. 1A thereof, there is shown a wafer 10 which is to undergo chemical mechanical polishing by using an ozone-containing polishing liquid according to the invention as described above. The wafer 10 comprises a layer of silicon 11 as the base layer, in which there is a recessed metal layer 12. On the surface of the silicon layer 11 and in a recess therein there is a tungsten layer 14, which is joined to the silicon layer 11 and the metal layer 12 through a contact and adhesion layer 13.

In order to remove the excess tungsten, the wafer 10 is chemically mechanically polished using the ozone-containing polishing liquid. The resultant wafer configuration is illustrated in FIG. 1B. As can be seen from this figure, the residues of the tungsten layer 13 which remain in the recess in the silicon layer 11 after conclusion of the polishing process form a contact 15, through which it is possible to make contact with the metal layer 12 from outside the silicon layer 11.

FIGS. 2A and 2B show a further exemplary embodiment for the chemical mechanical polishing of a wafer 10. As can be seen in particular from FIG. 2A, the wafer 10 once again comprises a silicon layer 11 as the base layer in which there is a layer of metal 12. An aluminum layer 16 is disposed on the surface of the silicon layer 11 and in a recess in the silicon layer 11, through the use of a contact and adhesion layer 13. As an alternative to aluminum, it is also possible to use copper or the like, by way of example.

Through the use of the chemical mechanical polishing using the ozone-containing polishing liquid according to the invention, the aluminum layer 16 on the surface of the silicon layer 11 is abraded. Parts of the aluminum layer 16 remain, as can be seen from FIG. 2B, but only in the recess in the silicon layer 11. The remaining regions of the aluminum layer 16 form a contact/interconnect structure 17, through which the metal layer 12 can be brought into contact with other components inside and outside the wafer 10.

We claim:

1. An oxidizing polishing liquid for polishing components, comprising a base polishing liquid and ozone.

2. The polishing liquid according to claim 1, including a colloidal solution of small solid particles.

3. The polishing liquid according to claim 2, wherein said solution is alkaline.

4. The polishing liquid according to claim 2, wherein said solution is acidic.

5. The polishing liquid according to claim 1, wherein said ozone is dissolved in water.

6. The polishing liquid according to claim 4, including a redox potential of at least 2.0 V.

7. The polishing liquid according to claim 3, including a redox potential of at least 1.2 V.

8. The polishing liquid according to claim 1, wherein said ozone has a concentration range of from 0.2 g to 0.5 g per 500 ml of polishing liquid.

9. The polishing liquid according to claim 1, wherein the component is a wafer.

10. The polishing liquid according to claim 1, adapted for chemical mechanical polishing.

11. A process for producing an oxidizing polishing liquid, which comprises the following steps:

   a) providing a base polishing liquid having a colloidal solution of small solid particles;

   b) providing gaseous ozone as an oxidizing agent; and

   c) introducing the gaseous ozone into the base polishing liquid.

12. The process according to claim 11, wherein the base liquid is alkaline.

13. The process according to claim 11, wherein the base liquid is acidic.

14. The process according to claim 11, which further comprises producing the ozone with an ozone generator.

15. A process for polishing components with a polishing liquid, which comprises:

   providing a polishing liquid having a base polishing liquid and ozone; and

   chemical mechanical polishing of components with the polishing liquid.

16. The process according to claim 15, wherein the components are wafers.

17. The process according to claim 15, which further comprises polishing layers of a material selected from the group consisting of aluminum, tungsten, copper, titanium, titanium nitride, tantalum and tantalum nitride, with the polishing liquid.
18. The process according to claim 15, which further comprises contact patterning of wafers with the polishing liquid.

19. The process according to claim 15, which further comprises interconnect patterning of wafers with the polishing liquid.

20. The process according to claim 15, which further comprises chemical mechanical polishing of at least one of metal layers, contact layers and adhesion layers of components with the polishing liquid.

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