

## **A chemical mechanical polishing solution**

### **TECHNICAL FIELD**

The present invention relates to the field of chemical mechanical polishing, and to a chemical mechanical polishing fluid.

### **BACKGROUND**

Amorphous carbon film (Amorphous carbon), also known as diamond-like carbon film (Diamond-Like Carbon), has attracted much attention because of its high hardness, high strength, high thermal conductivity, high resistivity, high radiation resistance, high chemical stability, low friction coefficient, as well as good transmittance in infrared optics and other excellent properties. In high temperature, high frequency, high power and radiation-resistant high-density integrated electronic devices and other aspects have great potential for application.

As the semiconductor process becomes more advanced, the chip process needs to be more refined pattern improvement, photolithography laser wavelength is also gradually reduced with the process improvement. Generally by reducing the thickness of the photosensitive film to control the resolution of the pattern, however, too thin photosensitive film will lead to the photosensitive film before the lower material is etched away, resulting in pattern distortion, and thus the need to form a hard mask film in addition to the photosensitive film pattern on the lower material. In the past, silicon dioxide or silicon nitride was often chosen as the hard mask to ensure processing margins during the etching process to form the pattern. However, the hard mask along with the process improvement of the required thickness requirements are getting smaller and smaller, in order to obtain a higher resolution as well as to reduce the occurrence of material necking and foot shrinkage, usually more stable chemical properties and less diffuse reflection of the amorphous carbon film as a hard mask.

Amorphous carbon films can be formed by the well-known CVD (Chemical Vapor Deposition) and PVD (Physical Vapor Deposition) methods, and in the case of the PVD method represented by sputtering, the formation of amorphous carbon films is directional. Therefore, to form a uniform amorphous carbon film, it is necessary to take measures to rotate the substrate or place multiple targets in the device. The device for forming an amorphous carbon film is complex and expensive, and it is sometimes difficult to form an amorphous carbon film according to the shape of the substrate. The CVD method, in which an amorphous carbon film is formed by a reactive gas, has a simple and inexpensive device structure. Therefore, the prior art usually uses plasma CVD to form amorphous carbon films, i.e., hydrocarbons such as naphthalene, benzene, and toluene with

a benzene ring or multiple double bonds are usually used as reaction gases. However, in fine processes of 50 nm or less, there is a significant problem of residual vesicular carbon particles generated during the transfer of the amorphous carbon layer produced by the CVD process, as well as droplet carbon particles. By choosing the appropriate deposition technique and changing the deposition parameters, the C sp<sup>2</sup> and sp<sup>3</sup> hybridization ratio in the amorphous carbon film can be changed to further control the film properties.

Therefore, to improve the lithographic accuracy used in the manufacturing process of semiconductor devices, the interlayer flatness in each process is a very important factor. In patent CN109623581A, it is because the amorphous carbon material is usually very stable at room temperature, not easy to chemical reaction, and the more sp<sup>3</sup> hybridization content the greater the Mohs hardness, so there is a flattening processing difficulty, processing time-consuming and other difficulties and other issues, so the patent uses a combination of pre-rough casting and etching process to improve the removal rate of carbon material. In patent KR20200057566A, the use of cerium dioxide abrasive, by adding compounds such as subamino acids and formic acid can effectively remove the amorphous carbon film, but how to remove the cerium oxide and other residues generated during polishing is also a huge problem. In another patent CN102464944A, a large number of strong oxidizers are used, but the grinding rate of carbon materials is relatively low and cannot meet the semiconductor process requirements.

In order to make the amorphous carbon material film on the chip have a higher quality surface, there is a need for a grinding composition that meets the level of the grinding rate and can realize a good surface quality (e.g., a low number of scratches).

#### **DESCRIPTION**

The present invention provides a chemical-mechanical polishing solution capable of increasing the polishing rate of amorphous carbon. Specifically, the present invention provides a chemical-mechanical polishing solution for polishing an amorphous carbon material comprising abrasive particles, a compound containing a carboxyl group, and a compound containing two or more hydroxyl groups.

Preferably, the abrasive particles are silica, the abrasive particles having a particle size of 20-120 nm.

Preferably, the mass percentage content of the abrasive particles is 0.1-5%.

Preferably, the mass percentage content of the abrasive particles is 0.1-2%.

Preferably, the compound containing a carboxyl group is selected from one or more of a pyridine compound, a piperidine compound, a pyrrolidine compound and a pyrrole compound and derivatives thereof.

Preferably, the compound containing a carboxyl group is selected from one or more of 2-carboxypyridine, 3-carboxypyridine, 4-carboxypyridine, 2,4-dicarboxypyridine, 2-methyl-4-carboxypyridine, 2,6-dicarboxypyridine, 6-amino-2-dicarboxypyridine, 3,5-dicarboxypyridine, 2-carboxypiperidine, 3-carboxypiperidine, 4-carboxypiperidine, 2,3-dicarboxypiperidine, 2,4-dicarboxypiperidine, 2,6-dicarboxypiperidine, 3,5-dicarboxypiperidine, 1-methyl-piperidine-4-carboxylic acid, 2-carboxypyrrolidine, 3-carboxypyrrolidine, 2,4-dicarboxypyrrolidine, 2,5-dicarboxypyrrolidine, 2-carboxypyrrole, 3-carboxypyrrole, 2,5-dicarboxypyrrole, 3,4-dicarboxypyrrole.

Preferably, the mass percentage content of the compound containing a carboxyl group is 0.01-0.5%.

Preferably, the mass percentage content of the compound containing carboxyl groups is 0.01-0.2%.

Preferably, the compound containing two or more hydroxyl groups is selected from one or more of pentaerythritol, ethylene glycol, 1,2-propanediol, 2-methylpropanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol dimethylacetate, dipropylene glycol dimethyl acetate, trimethylolpropane and propylene trioxide, xylitol, dextrose, ascorbic acid, sorbitol, sucrose, methylcellulose, hydroxypropyl methylcellulose, hydroxyethylcellulose, carboxymethyl cellulose.

Preferably, the mass percentage content of the compound containing two or more hydroxyl groups is 0.05% to 3%.

Preferably, the compound containing two or more hydroxyl groups has a mass percentage content of 0.1-1%.

Preferably, the chemical-mechanical polishing solution has a pH of 2-6.

The chemical-mechanical polishing solution of the present invention may also contain additives commonly used in the field such as pH adjusters, fungicides and the like.

The chemical-mechanical polishing solution of the present invention can be prepared in concentrated form and can be diluted with deionized water to a concentration within the range of the present invention at the time of use.

Another aspect of the present invention provides a use of the chemical mechanical polishing solution described in any one of the above for polishing an amorphous carbon material.

The chemical mechanical polishing solution of the present invention has a high removal rate of amorphous carbon material and does not contain oxidizing agent, which can reduce the production cost, and the method of use is simple, without the need to carry out the rough polishing and etching treatment of the wafer in the preliminary stage, which has a good market prospect.

## **EMBODIMENTS**

The advantages of the present invention are further described below in connection with specific embodiments.

Table 1 gives the components and their contents (mass concentration) of the chemical-mechanical polishing solution of the present invention in embodiments 1 to 19. According to the formulations given in the table, dissolve and mix all the components, and replenish the mass percentage with water to 100%. The pH of the polishing solution is adjusted to the desired pH with a pH adjusting agent. pH adjusting agents are commonly used in the art.

Table 1 Components and their contents of the chemical mechanical polishing solution of Comparative embodiments 1-7 and embodiments 1-19

|                          | Abrasive particles |                    |            | First additive    |            | Second additive   |            | pH  | oxidizing agent   |            |
|--------------------------|--------------------|--------------------|------------|-------------------|------------|-------------------|------------|-----|-------------------|------------|
|                          | name               | particle size (nm) | Content, % | Specific compound | Content, % | Specific compound | Content, % |     | Specific compound | Content, % |
| Comparative embodiment 1 | SiO <sub>2</sub>   | 70                 | 0.2        |                   |            |                   |            | 7   | /                 | /          |
| Comparative embodiment 2 | SiO <sub>2</sub>   | 70                 | 0.2        |                   |            |                   |            | 1.5 | /                 | /          |
| Comparative embodiment 3 | SiO <sub>2</sub>   | 70                 | 0.2        |                   |            |                   |            | 4.0 | /                 | /          |

|                         |      |     |     |                             |      |                                         |     |     |                                   |     |
|-------------------------|------|-----|-----|-----------------------------|------|-----------------------------------------|-----|-----|-----------------------------------|-----|
| Comparative embodiment4 | SiO2 | 70  | 0.2 | 3-Carboxypyridine           | 0.02 |                                         |     | 4.0 | /                                 | /   |
| Comparative embodiment5 | SiO2 | 70  | 0.2 |                             |      | 1,4-Butanediol                          | 0.3 | 4.0 | /                                 | /   |
| Comparative embodiment6 | SiO2 | 70  | 0.2 |                             |      |                                         |     |     | hydrogen peroxide (H2O2) solution | 0.5 |
| Comparative embodiment7 | SiO2 | 70  | 0.2 |                             |      |                                         |     |     | potassium permanganate            | 0.1 |
| Comparative embodiment8 | SiO2 | 70  | 0.2 | 3-Carboxypyridine           | 0.02 | 1,4-Butanediol                          | 0.3 | 1.5 | /                                 |     |
| Comparative embodiment9 | SiO2 | 30  | 0.1 | 2-Carboxypyridine           | 0.02 | ethylene glycol                         | 0.3 | 7   | /                                 |     |
| Embodiment1             | SiO2 | 70  | 0.8 | 3-Carboxypyridine           | 0.03 | 1,4-Butanediol                          | 0.3 | 4.0 | /                                 | /   |
| Embodiment2             | SiO2 | 30  | 0.1 | 2-Carboxypyridine           | 0.05 | 1,4-Butanediol                          | 0.6 | 4.0 | /                                 | /   |
| Embodiment3             | SiO2 | 120 | 1   | 4-Carboxypyridine           | 0.02 | glucose C6H12O6                         | 0.3 | 4.0 | /                                 | /   |
| Embodiment4             | SiO2 | 60  | 5   | 2-Methyl-4-carboxypyridine  | 0.05 | ethylene glycol C2H4 (OH)2 (antifreeze) | 1.5 | 4.0 | /                                 | /   |
| Embodiment5             | SiO2 | 100 | 0.5 | 6-Amino-2-dicarboxypyridine | 0.15 | Dipropylene glycol monomer              | 1.5 | 4.0 | /                                 | /   |

|               |                    |     |     |                                      |      |                               |      |     |   |   |
|---------------|--------------------|-----|-----|--------------------------------------|------|-------------------------------|------|-----|---|---|
| Embodiment 6  | SiO <sub>2</sub>   | 50  | 2   | 3,5-Dicarboxypiperidine              | 0.04 | pentaerythritol               | 2    | 4.0 | / | / |
| Embodiment 7  | SiO <sub>2</sub>   | 60  | 0.8 | 2,3-Dicarboxypiperidine              | 0.2  | Methylcellulose               | 0.1  | 4.0 | / | / |
| Embodiment 8  | SiO <sub>2</sub>   | 40  | 1   | 2-Carboxypyrrolidine                 | 0.01 | hydroxyethylcellulose         | 2    | 2.5 | / | / |
| Embodiment 9  | SiO <sub>2</sub>   | 20  | 1.5 | 2-Carboxypiperidine                  | 0.08 | ethylene glycol               | 0.05 | 4.0 | / | / |
| Embodiment 10 | SiO <sub>2</sub>   | 80  | 0.4 | 3,4-Dicarboxypyrrole                 | 0.5  | fructose                      | 0.4  | 4.0 | / | / |
| Embodiment 11 | SiO <sub>2</sub>   | 90  | 2.5 | 2-Carboxypiperidine                  | 0.25 | 1,6-Hexanediol                | 0.3  | 2.0 | / | / |
| Embodiment 12 | SiO <sub>2</sub>   | 70  | 3   | 2,4-Dicarboxypiperidine              | 0.3  | Trimethylolpropane            | 0.8  | 3.0 | / | / |
| Embodiment 13 | SiO <sub>2</sub>   | 70  | 3.5 | 2-Carboxypyrrole                     | 0.35 | Dipropylene glycol monomer    | 0.5  | 3.5 | / | / |
| Embodiment 14 | SiO <sub>2</sub>   | 90  | 4.5 | 1-Methylpiperidine-4-carboxylic acid | 0.05 | xylitol                       | 1    | 5.0 | / | / |
| Embodiment 15 | SiO <sub>2</sub>   | 110 | 1.5 | 4-Carboxypyridine                    | 0.4  | neopentyl glycol              | 3    | 6.0 | / | / |
| Embodiment 16 | SiO <sub>2</sub>   | 40  | 1.5 | 4-Carboxypiperidine                  | 0.02 | glycerine                     | 0.5  | 4.0 | / | / |
| Embodiment 17 | SiO <sub>2</sub> A | 30  | 0.2 | 4-Carboxypiperidine                  | 0.03 | Hydroxypropyl methylcellulose | 0.2  | 4.5 | / | / |
|               | SiO <sub>2</sub> B | 50  | 0.1 | 3,5-Dicarboxypiperidine              | 0.01 |                               |      |     |   |   |
| Embodiment    | SiO <sub>2</sub> A | 50  | 1.5 | 3-Carboxypyridine                    | 0.05 | pentaerythritol               | 0.5  | 4.0 | / | / |

|              |        |     |     |                       |      |                  |     |     |   |   |
|--------------|--------|-----|-----|-----------------------|------|------------------|-----|-----|---|---|
| ent18        |        |     |     | dine                  |      | ol               |     |     |   |   |
|              | SiO2B  | 90  | 1   |                       |      | ethylene glycol  | 0.3 |     |   |   |
| Embodiment19 | SiO2A  | 60  | 0.5 | 2-Carboxypyridine     | 0.04 | neopentyl glycol | 0.5 | 3.5 | / | / |
|              | SiO2 B | 100 | 0.5 | 2,4-Dicarboxypyridine | 0.05 | glycerine        | 1   |     |   |   |

In order to illustrate the polishing performance of the above chemical-mechanical polishing solution, further polishing rate test. Specific polishing conditions: the polishing machine was Reflexion LK, polishing pad IC1010 polishing pad, 300 mm wafer, grinding pressure 1.0 psi, grinding disk speed 93 rpm, grinding head speed 87 rpm, polishing fluid flow rate 300 ml/min, and polishing time 1 min. The removal rate of each polishing fluid on carbon material was measured and recorded in Table 2.

Table 2 Polishing Rates of Amorphous Carbon Materials by Chemical-Mechanical Polishing Fluids of Comparative embodiments 1-9 and embodiments 1-19

| Chemical Mechanical Polishing Solution | Polishing rate (A/min) |
|----------------------------------------|------------------------|
| Comparative embodiment1                | 4                      |
| Comparative embodiment2                | 7                      |
| Comparative embodiment3                | 205                    |
| Comparative embodiment4                | 388                    |
| Comparative embodiment5                | 446                    |
| Comparative embodiment6                | 427                    |
| Comparative embodiment7                | 532                    |
| Comparative embodiment8                | 328                    |
| Comparative embodiment9                | 326                    |
| Embodiment1                            | 2741                   |

|              |      |
|--------------|------|
| Embodiment2  | 2448 |
| Embodiment3  | 2680 |
| Embodiment4  | 3512 |
| Embodiment5  | 2661 |
| Embodiment6  | 3268 |
| Embodiment7  | 2875 |
| Embodiment8  | 2231 |
| Embodiment9  | 2556 |
| Embodiment10 | 2312 |
| Embodiment11 | 2925 |
| Embodiment12 | 3101 |
| Embodiment13 | 3003 |
| Embodiment14 | 3179 |
| Embodiment15 | 3221 |
| Embodiment16 | 2651 |
| Embodiment17 | 2121 |
| Embodiment18 | 2812 |
| Embodiment19 | 2715 |

As can be seen from the test results in Table 2, polishing SiO<sub>2</sub> alone has essentially no rate of removal of amorphous carbon, as can be seen from Comparative embodiments 1-2. From Comparative embodiment 3 with Comparative embodiments 4,5 it can be seen that the addition of one or more carboxyl group compounds and two and more hydroxyl group containing alcohols alone, the rate of amorphous carbon is enhanced. From the results of the embodiments with Comparative embodiments 4 and 5, it can be seen that the addition of compounds with more than one carboxyl group and alcohols containing two and more hydroxyl groups simultaneously, there is a significant increase in the rate of removal of amorphous carbon. From the comparison of pairs of Comparative embodiments 6 and 7, and 8 and 9 with the embodiments, it appears that the pH environment of the present invention should be between 2 and 6. From the comparison of Comparative embodiments 6 and 7 with the embodiments, the present

invention without oxidizing agent has a higher removal rate for carbon materials than grinding particles with oxidizing agent alone.

In summary, the present invention significantly improves the removal rate of amorphous carbon materials by the addition of one or more carboxyl group compounds and polyols to the polishing solution.

Although the above specific embodiments of the present invention have been described in detail, they are only embodiments, and the present disclosure is limited to the embodiments described above. For those skilled in the art, any equivalent modification and substitution to the present invention is also covered in the present invention. Therefore, all these equivalent changes and modifications made without departing from the spirit and scope of the invention should be covered within the scope of the present invention.

## CLAIMS

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1. A chemical-mechanical polishing solution for polishing an amorphous carbon material, characterized in that the solution comprising abrasive particles, a compound containing a carboxyl group and a compound containing two or more hydroxyl groups.
2. The chemical-mechanical polishing solution as claimed in claim 1, characterized in that, the abrasive particles are silica, the abrasive particles having a particle size of 20-120 nm.
3. The chemical mechanical polishing solution as claimed in claim 1, wherein the mass percentage content of the abrasive particles is 0.1-5%.
4. The chemical mechanical polishing solution as claimed in claim 3, wherein the mass percentage content of the abrasive particles is 0.1-2%.
5. The chemical mechanical polishing solution as claimed in claim 1, characterized in that, the compound containing a carboxyl group is selected from one or more of a pyridine compound, a piperidine compound, a pyrrolidine compound and a pyrrole compound and derivatives thereof.
6. The chemical-mechanical polishing solution as claimed in claim 5, characterized in that, the compound containing a carboxyl group is selected from one or more of 2-carboxypyridine, 3-carboxypyridine, 4-carboxypyridine, 2,4-dicarboxypyridine, 2-methyl-4-carboxypyridine, 2,6-dicarboxypyridine, 6-amino-2-dicarboxypyridine, 3,5-dicarboxypyridine, 2-carboxypiperidine, 3-carboxypiperidine, 4-carboxypiperidine, 2,3-dicarboxypiperidine, 2,4-dicarboxypiperidine, 2,6-dicarboxypiperidine, 3,5-dicarboxypiperidine, 1-methyl-piperidine-4-carboxylic acid, 2-carboxypyrrolidine, 3-carboxypyrrolidine, 2,4-dicarboxythis pyrrolidine, 2,5-dicarboxythis pyrrolidine, 2-carboxypyrrole, 3-carboxypyrrole,, 2,5-dicarboxypyrrole, 3,4-dicarboxypyrrole.
7. The chemical-mechanical polishing solution as claimed in claim 1, wherein the mass percentage content of the compound containing a carboxyl group is 0.01-0.5%.
8. The chemical mechanical polishing solution as claimed in claim 7, wherein the mass percentage content of the compound containing carboxyl groups is 0.01-0.2%.
9. The chemical mechanical polishing solution as claimed in claim 1, characterized in that, the compound containing two or more hydroxyl groups is selected from one or more of pentaerythritol, ethylene glycol, 1,2-propanediol, 2-methylpropanediol, 1,4-butanediol, 1,6-hexanediol,

neopentyl glycol , diethylene glycol dimethylacetate, dipropylene glycol dimethyl acetate, trimethylolpropane and propylene trioxide, xylitol, dextrose, ascorbic acid, sorbitol, sucrose, methylcellulose, hydroxypropyl methylcellulose, hydroxyethylcellulose , carboxymethyl cellulose.

10. The chemical-mechanical polishing solution as claimed in claim 1, wherein the mass percentage content of the compound containing two or more hydroxyl groups is 0.05% to 3%.

11. The chemical mechanical polishing solution as claimed in claim 10, wherein the compound containing two or more hydroxyl groups has a mass percentage content of 0.1-1%.

12. The chemical mechanical polishing solution as claimed in any one of claims 1-11, wherein the chemical-mechanical polishing solution has a pH of 2-6.