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## DESCRIPTION



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### Etchant composition

#### 5    Technical Field

The present invention relates to an etchant composition for silver or a silver alloy.

#### Background Art

10            Members made of various conductive materials, for example, metals such as gold, silver, copper, aluminum or their alloys are arranged as electrodes or wiring members on a substrate made of ceramics or glass. In particular, silver and silver alloys have the characteristics such that their reflectance is high and their electrical  
15 resistance is small, and therefore they are commonly used as a reflecting material or wiring material. In the production of integrated circuit boards, flat panel displays, or the like, first a metal thin film of these materials is formed on a substrate, a resist having a predetermined pattern is formed on the thin film, and the metal thin  
20 film is etched, using the resist as a mask. For etching, an etchant suitable for the characteristics of the metal is used. For example, Japanese Laid-Open Patent Publications Nos. 10-130870 and 2000-100778 describe etchant compositions for aluminum and aluminum alloy thin films.

25            For etching of silver or silver alloys, an etchant containing phosphoric acid, nitric acid, acetic acid, and water is currently used. However, when a substrate on which a resist pattern having a plurality of identical resist pattern units has been formed is etched using this etchant, the sizes of the resultant pattern units of silver or  
30 silver alloys are not uniform between portions on the substrate, and a

difference of pattern width with etching and without etching is large. Furthermore, this etchant contains acetic acid in a high concentration, so that the etchant causes strong acetic acid odor, and thus, there are problems such as poor work environment.

5           Therefore, there is a demand for an etchant composition for silver or silver alloys that allows a pattern having pattern units of uniform size to be formed on a substrate surface, that causes a small difference of pattern width with etching and without etching, and that does not adversely affect work environment.

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#### Disclosure of Invention

The present invention is accomplished in order to solve the above problems.

15           An etchant composition for silver or a silver alloy of the present invention comprises a multi valence carboxylic acid, phosphoric acid, nitric acid and water.

20           In a preferred embodiment, the multi valence carboxylic acid is at least one selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, aconitic acid, ketoglutaric acid, maleic acid, citraconic acid, malic acid, tartaric acid and citric acid.

25           In a preferred embodiment, the multi valence carboxylic acid is contained in a ratio of 0.5 to 10% by weight, the phosphoric acid is contained in a ratio of 32 to 83% by weight, and the nitric acid is contained in a ratio of 0.4 to 19% by weight.

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#### Brief Description of Drawings

Figure 1 is a schematic view showing an area of a substrate on which a resist pattern is formed, wherein the substrate has a silver thin film on its surface.

30           Figure 2 is a partial enlarged view showing a striped resist

pattern on a substrate.

Figure 3 is a schematic view showing a cross-section taken along line X-X of Figure 2.

Figure 4 is a schematic cross-sectional view showing a silver striped pattern formed on a substrate by etching.

#### Best Mode for Carrying Out the Invention

An etchant composition for silver or silver alloys of the present invention (hereinafter, may be referred to as "the composition of the present invention) contains a multi valence carboxylic acid, phosphoric acid, nitric acid, and water.

There is no particular limitation regarding the multi valence carboxylic acid used in the present invention as long as it is a carboxylic acid having at least two valency carboxyl groups, and a multi valence carboxylic acid having a hydroxyl group is also preferably used.

Examples of preferable multi valence carboxylic acid include oxalic acid, malonic acid, succinic acid, glutaric acid, aconitic acid, ketoglutaric acid, maleic acid, citraconic acid, malic acid, tartaric acid, and citric acid. Examples of more preferable multi valence carboxylic acid include oxalic acid, succinic acid, glutaric acid, aconitic acid, ketoglutaric acid, maleic acid, citraconic acid, malic acid, and tartaric acid. Examples of even more preferable multi valence carboxylic acid include oxalic acid and maleic acid. These multi valence carboxylic acids can be used alone or in combination.

The multi valence carboxylic acid is preferably contained in the composition of the present invention in a ratio of 0.5 to 10% by weight. More preferably, the content is 1 to 7% by weight, and even more preferably, 2 to 4% by weight. When the concentration of the

multi valence carboxylic acid is excessively high, the multi valence carboxylic acid may be precipitated, so that precise caution is required.

Phosphoric acid is preferably contained in the composition of the present invention in a ratio of 32 to 83% by weight. More preferably, the content is 32 to 68% by weight, even more preferably, 39 to 61% by weight, and most preferably, 42 to 58% by weight.

Nitric acid is preferably contained in the composition of the present invention in a ratio of 0.4 to 19% by weight. More preferably, the content is 5 to 19% by weight, even more preferably, 7 to 17% by weight, and most preferably, 9 to 15% by weight.

Water is preferably contained in the composition of the present invention in a ratio of 6 to 59% by weight. More preferably, the content is 19 to 59% by weight, even more preferably, 29 to 49% by weight, and most preferably, 34 to 41% by weight. Water may be supplemented with an aqueous solution of multi valence carboxylic acid, phosphoric acid, or nitric acid.

The composition of the present invention may contain a surfactant, an antifoaming agent and the like that are commonly contained in an etchant composition.

An etchant can be obtained by mixing the multi valence carboxylic acid, phosphoric acid, nitric acid, water, and if necessary, a surfactant, an antifoaming agent, and the like that are the components of the above-described composition. Alternatively, aqueous solutions of each of the multi valence carboxylic acid, phosphoric acid and nitric acid may be separately prepared, and these solutions are mixed such that the concentrations of these substances in the resultant mixture are predetermined concentrations. There is no limitation to the order of mixing the solutions.

Using the thus obtained etchant, a silver or silver alloy film

formed on a substrate can be etched. For example, a predetermined pattern is formed on the surface of a silver film of a substrate by the use of a resist, and etching is performed with this resist as a mask. Then, the resist is removed with a photoresist stripper, so that a pattern of the silver film having the predetermined shape is formed. For the etching treatment of a silver or silver alloy film, the same conditions can be employed used as when a conventionally used etchant containing phosphoric acid, nitric acid, acetic acid, and water is used. The present etchant does not contain acetic acid, so that the work environment is not adversely affected. When a substrate on which a resist pattern having a plurality of identical pattern units has been formed is etched, the sizes of the pattern units are not different from portion to portion in the obtained pattern units of the silver or silver alloy film, and the units are uniform on the whole surface of the substrate, and the difference of pattern width with etching and without etching is small. Therefore, the etchant composition of the present invention can be used preferably for production of an integrated circuit board, a flat panel display or the like.

## 20 Examples

Hereinafter, the present invention will be described by way of examples, but the present invention is not limited thereto.

### (Example 1)

First, 64 parts by volume of a commercially available 85% (% by weight) phosphoric acid aqueous solution (specific gravity of 1.69) and 0.5 parts by volume of a commercially available 70% (% by weight) nitric acid aqueous solution (specific gravity of 1.42) were mixed, and then, 5 parts by volume of 35 wt% maleic acid aqueous solution (specific gravity of 1.12) was mixed with the resultant mixture, thereby

obtaining an etchant. Separately, a glass substrate having a silver film (made of 100% silver) with a thickness of 0.2  $\mu\text{m}$  on its surface was provided. This substrate was immersed in the etchant at 35°C for a period until the thin film dissolved. This period of time was measured,  
5 and the etching rate was calculated. Table 1 show the results.

(Examples 2 to 4)

The same procedure was repeated as in Example 1, except that the amount of the maleic acid aqueous solution was 10 parts by  
10 volume in Example 2, 15 parts by volume in Example 3, and 20 parts by volume in Example 4 and etching rates were calculated. Table 1 also shows the results.

Table 1

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| Example | 85% Phosphoric acid solution | 70% Nitric acid solution | 35% Maleic acid solution | Etching rate |
|---------|------------------------------|--------------------------|--------------------------|--------------|
|         | parts by volume              | parts by volume          | parts by volume          | Å/min.       |
| 1       | 64                           | 0.5                      | 5                        | 6154         |
| 2       | 64                           | 0.5                      | 10                       | 5879         |
| 3       | 64                           | 0.5                      | 15                       | 4627         |
| 4       | 64                           | 0.5                      | 20                       | 4202         |

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All the etchants of Examples 1 to 4 could etch silver. In the etchant containing a large amount of maleic acid of Example 4, the  
25 maleic acid was slightly precipitated, and the etching rate slightly lowered.

(Example 5)

An etchant containing 48.5 wt% of phosphoric acid, 11.5 wt%

of nitric acid, 1 wt% of oxalic acid, and 39 wt% of water was prepared. Separately, a glass substrate (10 cm  $\times$  10 cm) having a silver film with a thickness of 0.2  $\mu$ m on its surface was provided. A resist (novolak resin) film was formed on the silver film on the substrate, and a striped pattern was formed by exposure and development. This striped patterned resist was formed on the silver film 11 in a whole area of 9 cm  $\times$  9 cm in the central portion of the substrate as shown in Figure 1 (the area is shown by L in Figure 1). Each unit of this striped pattern was a rectangular pattern unit having a short side of 90  $\mu$ m and a long side of 300  $\mu$ m, and the pattern units were formed on the surface of the silver film with a distance of 7  $\mu$ m each in the vertical and horizontal directions as shown in Figure 2. Figure 3 is a schematic cross-sectional view taken along line X-X of Figure 2. The silver film 11 was formed on the substrate 1, and then the striped resist pattern 12 was formed on its surface. Then, the substrate on which the pattern was formed was immersed in the etchant at 40°C for 104 seconds for etching. This substrate was washed with water and dried, and then the resist was removed with acetone. Thus, as shown in Figure 4, a striped pattern 111 of the silver film was formed on the glass substrate 1. In the areas A, B, C, D and E on the substrate shown in Figure 1, a distance a ( $\mu$ m) between adjacent long sides of the silver film striped pattern units was measured. More specifically, in each area of A, B, C and D, the distance a ( $\mu$ m) between the long side of a striped pattern unit that is closest to a vertex of the square L shown in Figure 1 and the long side of its adjacent striped pattern unit was measured. In the area E, a distance a ( $\mu$ m) between the long sides of a striped pattern unit that is in the center of the square L shown in Figure 1 and its adjacent striped pattern unit was measured. The measured value a ( $\mu$ m) is the average of values obtained by three measurements in one

portion in each area. A value  $(a-7)/2$  obtained by dividing the difference between the distance  $a$  and the distance of 7  $\mu\text{m}$  (i.e., the distance between the original resist pattern units) by 2 was defined as a "one side loss of pattern width after etching". The one side loss of pattern width after etching was calculated in each of the areas A to E. Table 2 shows these amounts. The standard deviations of these amounts are calculated and shown in Table 2 as well.

(Example 6)

10           An etchant containing 83 wt% of phosphoric acid, 6.5 wt% of nitric acid, 3.4 wt% of citric acid, 1 wt% of malonic acid, and 6.1 wt% of water was prepared. Using this etchant, etching was performed with the same operations as in Example 5, and the one side loss of pattern width after etching and the standard deviation of these amounts were  
15           calculated. Table 2 also shows the results.

(Comparative Example 1)

20           An etchant containing 57.4 wt% of phosphoric acid, 0.74 wt% of nitric acid, 31.4 wt% of acetic acid, and 10.46 wt% of water was prepared. Using this etchant, etching was performed with the same operations as in Example 5, and the one side loss of pattern width after etching and the standard deviation of these amounts were calculated. Table 2 also shows the results.

Table 2

| Measurement area   | One side loss of pattern width after etching ( $\mu\text{m}$ ) |           |            |
|--------------------|----------------------------------------------------------------|-----------|------------|
|                    | Example 5                                                      | Example 6 | Com. Ex. 1 |
| A                  | 0.16                                                           | 1.7       | 3.8        |
| B                  | 1.10                                                           | 1.5       | 4.9        |
| C                  | 0.24                                                           | 2.1       | 1.6        |
| D                  | 0.85                                                           | 2.2       | 2.2        |
| E                  | 0.49                                                           | 0.6       | 0.8        |
| Standard deviation | 0.38                                                           | 0.64      | 1.7        |

From the results of Table 2, it can be seen that when the etchants of Examples 5 and 6 were used, a variation in the size of the silver pattern on the substrate is smaller than that when the etchant of Comparative Example 1 was used.

In the examples, acetic acid was not used, so that, needless to say, no acetic acid odor was produced, and thus, the work environment was significantly improved.

(Example 7)

First, 64 parts by volume of a commercially available 85% phosphoric acid aqueous solution (specific gravity of 1.69) and 10 parts by volume of 35 wt% maleic acid aqueous solution (specific gravity of 1.42) were mixed, and then 0.65 parts by volume of a commercially available 70% nitric acid aqueous solution (specific gravity of 1.12) was added to the mixture, thereby obtaining an etchant.. Separately, a glass substrate (10 cm  $\times$  10 cm) having a silver film with a thickness of 0.2  $\mu\text{m}$  on its surface was provided. Then, a striped resist pattern was formed on the silver film of the substrate in the same manner as in Example 5. This substrate on which a resist pattern has been formed

was subjected to a etching process by immersing the substrate in the etchant at a temperature of 35°C. The etching time was predetermined as a time to clear. Separately, the same procedure was repeated except that the immersing period was predetermined as twice  
5 as long as the time to clear or four times as long as the time to clear. The "time to clear" refers to a time during which a silver film having a thickness of 0.2  $\mu\text{m}$  formed on a glass substrate was dissolved when an etching process is conducted at 35°C using the above etchant. After etching, the substrate was washed with water, and dried, and then the  
10 resist was removed with acetone.

With respect to the obtained substrate, the distance  $a$  ( $\mu\text{m}$ ) between the long sides of the adjacent silver film striped pattern units was measured. The value  $a-7$ , which is the difference between the distance  $a$  and the distance of 7  $\mu\text{m}$  (i.e., the distance between the  
15 original resist pattern units) was calculated, and this value was defined as "difference of pattern width with etching and without etching". Table 3 show the results.

#### (Comparative Example 2)

20 First, 64 parts by volume of a commercially available 85% phosphoric acid aqueous solution and 48 parts by volume of glacial acetic acid were mixed, and 1.25 parts by volume of a commercially available 70% nitric acid aqueous solution was added to the mixture, thereby obtaining an etchant. Using this etchant, etching was  
25 performed with the same operations as in Example 7, and the difference of pattern width with etching and without etching was calculated. Table 3 also shows the results.

Table 3

| Etching time                 | Difference of pattern width with etching and without etching ( $\mu\text{m}$ ) |                |
|------------------------------|--------------------------------------------------------------------------------|----------------|
|                              | Example 7                                                                      | Com. Example 2 |
| Time of clear                | 1.7                                                                            | 5.0            |
| Twice the time to clear      | 3.4                                                                            | 10.0           |
| Four times the time to clear | 6.7                                                                            | 16.0           |

The results of Table 3 indicate that the difference of pattern width with etching and without etching is small when the etchant of the present invention is used.

#### Industrial Applicability

According to the present invention, as described above, an etchant composition containing a multi valence carboxylic acid, phosphoric acid, nitric acid and water is provided. When this etchant composition is used, patterns of a metal thin film, in particular, a silver or silver alloy film can be formed uniformly on the surface of a substrate. In more detail, when a substrate on which a resist pattern having a plurality of identical resist pattern units has been formed is etched, the obtained pattern units of the metal thin film on the surface of the substrate are uniform without having a different size from portion to portion on the substrate, and the difference of pattern width with etching and without etching thereof is small. Furthermore, since the etchant does not contain a compound that emits a pungent odor such as acetic acid, the work environment is not adversely affected. Therefore, the etchant composition for silver or an silver alloy of the present invention is useful in a wide range of fields such as production of integrated circuit boards, production of flat panel displays or the like.

## CLAIMS

1. An etchant composition for silver or a silver alloy, which comprises a multi valence carboxylic acid, phosphoric acid, nitric acid, and water.

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2. The etchant composition for silver or a silver alloy of claim 1, wherein the multi valence carboxylic acid is at least one selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, aconitic acid, ketoglutaric acid, maleic acid, citraconic acid, malic acid, tartaric acid, and citric acid.

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3. The etchant composition for silver or a silver alloy of claim 1, wherein the multi valence carboxylic acid is contained in a ratio of 0.5 to 10% by weight, the phosphoric acid is contained in a ratio of 32 to 83% by weight, and the nitric acid is contained in a ratio of 0.4 to 19% by weight.

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