

METHOD FOR REMOVING HYDROGEN PEROXIDE AND PROCESSING AGENT FOR REMOVING HYDROGEN PEROXIDE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application is based on, and claims priority from, Taiwan Patent Application No. 103104478, filed February 11, 2014, the disclosure of which is hereby incorporated by reference herein in its entirety.

TECHNICAL FIELD

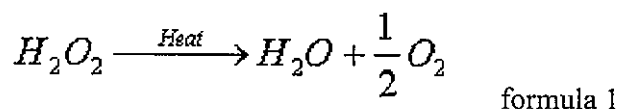
[0002] The present invention generally relates to a method for removing hydrogen peroxide and a processing agent for the method, and more specifically to a method for removing hydrogen peroxide from a sulfuric acid- hydrogen peroxide solution and a processing agent for the method.

BACKGROUND

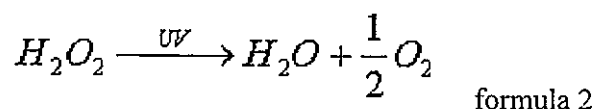
[0003] In the general semiconductor process, hydrogen peroxide (H_2O_2) as an oxidizer is often used together with sulfuric acid (H_2SO_4) to serve as a removing agent or an etching agent for a photo resist agent. Thus, more than 30% to 40% of waste liquid generated in the semiconductor process is sulfuric acid waste liquid, which is mostly the sulfuric acid- hydrogen peroxide solution.

[0004] Since the sulfuric acid- hydrogen peroxide solution exhibits strong oxidizing property, for the sake of safe storage and recycle/re-use, it is needed to remove hydrogen peroxide to reduce the overall oxidizing property. Some commonly used treatments are described as below.

[0005] The first is thermal decomposition as specified by formula 1. Heating up to more than 140°C may cause hydrogen peroxide to strongly decompose and generate oxygen gas. This method has one drawback that the reaction at high temperature is substantially dangerous because the reaction heat of formula 1 is up to -98 KJ/mol.



[0006] The second method is implemented by ultra-violet decomposition as specified by formula 2. It is well known that hydrogen peroxide may decompose by absorption of ultra-violet with wavelength in a range of 3200Å to 3800Å. The shortcoming of this method is that other components in the solution to be treated may absorb ultra-violet such that the absorption efficient of ultra-violet for hydrogen peroxide is greatly reduced. It is commonly needed to increase the intensity of ultra-violet. In addition, some photo-chemistry side products are adversely generated.



[0007] The third one uses catalyst material to react with hydrogen peroxide. Specifically, some ions of metal elements like manganese (Mn), nickel (Ni), copper (Cu) and iron (Fe) are helpful to cause hydrogen peroxide to decompose. However, too many metal ions are needed and a pollution risk is potentially resulted in. It is adverse to latter treatment or recycle/re-use.

[0008] The forth method is to add other organic or inorganic compound as reactant to react with hydrogen peroxide. The reaction should be controlled at a specific temperature for safety and efficiency, and the side products generated may

cause difficulties in the latter treatment for waste liquid. Therefore, this method is still not suitable.

[0009] If the above problems in the prior arts are overcome, the etching waste liquid generated by the semiconductor process can be effectively recycled and re-used. The environmental impact is thus greatly reduced, and industrial competitiveness is improved.

SUMMARY OF THE INVENTION

[0010] The primary object of the present invention is to provide a method for removing hydrogen peroxide from a sulfuric acid-hydrogen peroxide solution. The method of the present invention comprises adding nitric acid with a weight percent concentration of 0.05%-5.09%(w/w) into the solution containing sulfuric acid and hydrogen peroxide so as to obtain a product solution. The solution has an initial reaction temperature between 45°C and 60 °C while being added by nitric acid. When a weight percent concentration of sulfuric acid contained in the solution is less than 55%(w/w), it is needed to add additional sulfuric acid to the solution such that the weight percent concentration of sulfuric acid contained in the solution attains to 55%(w/w).

[0011] Another object of the present invention is to provide a method for removing hydrogen peroxide from a sulfuric acid-hydrogen peroxide solution. The method comprises adding a processing agent into the solution containing sulfuric acid and hydrogen peroxide so as to obtain a product solution. The solution has an initial reaction temperature between 45°C and 60 °C. The processing agent comprises nitric acid with a weight percent concentration of 0.05%-5.09%(w/w) and sulfuric acid with a weight percent concentration of 91.0%-97.9%(w/w), and a volume ratio of the solution to the processing agent is 20:1 to 5:1.

[0012] In one embodiment of the present invention, the weight percent concentration of hydrogen peroxide contained in the solution to be treated is between 0.5% and 10% (w/w), and the weight percent concentration of sulfuric acid contained in the solution is 45% (w/w).

[0013] In another embodiment of the present invention, the sulfuric acid-hydrogen peroxide solution is waste liquid from semiconductor processes or common factories.

[0014] In a yet embodiment of the present invention, the product solution contains hydrogen peroxide has a concentration less than 90 ppm.

[0015] Thus, the method of the present invention previously check the concentration of sulfuric acid in the sulfuric acid-hydrogen peroxide solution to be treated, then increase the temperature of the solution up to 45°C and 60 °C, and selectively directly add nitric acid or the processing agent previously prepared into the solution in accordance with a predetermined setting, thereby implementing the effect of removing hydrogen peroxide from the solution.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The present invention will be apparent to those skilled in the art by reading the following detailed description of a preferred embodiment thereof, with reference to the attached drawings, in which:

[0017] FIG. 1 is a view showing the test using the flask for the method for removing hydrogen peroxide according to one embodiment of the present invention;

[0018] FIG. 2 is a test result showing an effect of adding different amount of 70% nitric acid at different reaction temperature on the reaction rate according to the embodiment of the present invention;

[0019] FIG. 3 is a test result showing an effect of adding different amount of 70% nitric acid and concentrated sulfuric acid on the reaction rate according to the embodiment of the present invention; and

[0020] FIG. 4 is a test result showing an effect on the reaction rate by adding different amount of sulfuric acid according to the embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

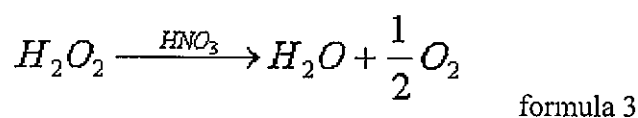
[0021] The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

[0022] In generally, the present invention can be implemented by two different methods. First, one of the two methods is described in detail. Nitric acid with a weight percent concentration of 0.05%-5.09%(w/w) is added into the solution containing sulfuric acid and hydrogen peroxide so as to obtain a product solution. Specifically, the solution has an initial reaction temperature between 45°C and 60 °C while being added by nitric acid. When a weight percent concentration of sulfuric acid contained in the solution is less than 55%(w/w), it is needed to add additional sulfuric acid to the solution such that the weight percent concentration of sulfuric acid contained in the solution attains to 55%(w/w).

[0023] Furthermore, the other method of the present invention comprises adding a processing agent into the solution containing sulfuric acid and hydrogen peroxide so as to obtain a product solution. The solution has an initial reaction temperature between 45°C and 60 °C. The processing agent comprises nitric acid with a weight

percent concentration of 0.05%-5.09%(w/w) and sulfuric acid with a weight percent concentration of 91.0%-97.9%(w/w), and a volume ratio of the solution to the processing agent is 20:1 to 5:1.

[0024] In an actual operation, a given amount of volume of the solution to be treated is taken and placed into a reactor before the reaction. The concentration of sulfuric acid in the sulfuric acid-hydrogen peroxide solution is checked, and then the temperature of the solution is increased up to 45°C and 60 °C. When the weight percent concentration of sulfuric acid contained in the solution is more than 55%(w/w), nitric acid is directly added. When the weight percent concentration of sulfuric acid is not more than 55%(w/w), appropriate amount of sulfuric acid is additionally added to attain the preset concentration of sulfuric acid in the solution. Alternatively, according to the check result, appropriate amount of the processing agent is added. During the reaction, hydrogen peroxide in the solution decomposes to generate products like water (H₂O) and oxygen gas (O₂), which is specified by formula 3. As a result, hydrogen peroxide H₂O₂ starts to decompose under the presence of nitric acid,, and it is believed that nitric acid is a catalyst in this decomposing reaction.



[0025] Then, hydrogen peroxide generates oxygen gas due to nitric acid. The generation rate of oxygen gas is thus used to measure and compare the decomposing reaction rate of hydrogen peroxide. When no more oxygen gas generated, the decomposing reaction of hydrogen peroxide finishes. Some related experiments are described as below.

Experiment 1: the test of removing hydrogen peroxide by adding different amounts of nitric acid at different temperature

[0026] As shown in FIG. 1, a given volume 50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 60% sulfuric acid and 6% hydrogen peroxide is placed in the flask 2, and then 1ml, 2.5ml or 5ml of 70% nitric acid solution is added to the flask 2. The flask 2 is placed in a thermal bath 3 kept at 35°C or 45 °C for horizontal vibration so as to cause sulfuric acid and hydrogen peroxide to react. The thermometer 4 is used to measure the reaction temperature, and the gas generated is collected by a volumetric gas flow rate meter 6 through an outlet 5. The accumulated volume of oxygen gas generated is recorded at a predetermined period.

[0027] The effect of adding different amount of 70% nitric acid at different reaction temperature on the reaction rate is shown in FIGs. 2A to 2F. Specifically, FIG. 2A indicates 1ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 60% sulfuric acid and 6% hydrogen peroxide at 35°C, FIG. 2B indicates 2.5ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 at 35°C, FIG. 2C indicates 5ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 at 35°C, FIG. 2D indicates 1ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 at 45°C, FIG. 2E indicates 2.5ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 at 45°C, and FIG. 2F indicates 5ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 at 45°C.

[0028] The analysis result of the above experiment show: (1) As increasing the volume of nitric acid added to the solution 1, the reaction rate of removing hydrogen

peroxide increases, like FIG. 2F illustrating that the reaction is completed in 5 to 6 minutes in case of 5ml of nitric acid added at the initial temperature 45°C; and (2) The initial temperature also directly affects the reaction rate. By comparing FIG2. 2C and 2F, it is clear that it takes 20 minutes at the initial temperature 35°C and the reaction rate of hydrogen peroxide decomposition speeds up to finish in 5 to 6 minutes if more nitric acid added. A great deal of heat in such an exothermic reaction results in a temperature increase of about 90°C to 100°C. Thus, the present invention presets the initial temperature starting at 45°C.

Experiment 2: the test of removing hydrogen peroxide by adding different amounts of nitric acid to the sulfuric acid-hydrogen peroxide solution containing different concentrations of sulfuric acid

[0029] To test the effect of different concentrations of sulfuric acid on the decomposition reaction of hydrogen peroxide, this experiment uses two concentrations of sulfuric acid such as 60% and 70%. A given volume 50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 60% sulfuric acid and 6% hydrogen peroxide or 70% sulfuric acid and 6% hydrogen peroxide is placed in two flasks 2. Next, 1ml, 2.5ml or 5ml of 70% nitric acid solution is added. The flask 2 is placed in a thermal bath 3 kept at 35°C for horizontal vibration so as to cause sulfuric acid and hydrogen peroxide to react. The gas generated is collected by a volumetric gas flow meter 6 through an outlet 5. The accumulated volume of oxygen gas generated is recorded at a predetermined period.

[0030] The effect of adding different amounts of 70% nitric acid to different concentrations of sulfuric acid on the reaction rate of the solution 1 is shown in FIGs. 3A to 3F. Specifically, FIG. 3A indicates 1ml of 70% nitric acid solution is added to

50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 60% sulfuric acid and 6% hydrogen peroxide at 35°C, FIG. 3B indicates 2.5ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 60% sulfuric acid and 6% hydrogen peroxide at 35°C, FIG. 3C indicates 5ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 60% sulfuric acid and 6% hydrogen peroxide at 35°C, FIG. 3D indicates 1ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 70% sulfuric acid and 6% hydrogen peroxide at 35°C, FIG. 3E indicates 2.5ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 70% sulfuric acid and 6% hydrogen peroxide at 35°C, and FIG. 3F indicates 5ml of 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 70% sulfuric acid and 6% hydrogen peroxide at 35°C.

[0031] The above result shows that the decomposition reaction of hydrogen peroxide greatly speeds up by increasing the concentration of sulfuric acid. As shown in FIGs. 3D, 3E and 3F, when 70% nitric acid solution is added to 50ml of the sulfuric acid-hydrogen peroxide solution 1 containing 70% sulfuric acid and 6% hydrogen peroxide, the decomposition reaction of hydrogen peroxide is completed in one minute. In other words, if the concentration of sulfuric acid in the solution 1 is too low, the present invention may selectively add additional 98% sulfuric acid so as to accelerate the decomposition reaction.

Experiment3: the test of removing hydrogen peroxide by increasing the amount of sulfuric acid in the processing agent and the reaction temperature

[0032] Since nitric acid can cause hydrogen peroxide to decompose, when the temperature at the final stage of the reaction exceeds 70°C due to the exothermic effect, concentrated nitric acid may generate a great deal of yellow gas, nitrogen dioxide(NO₂). Therefore, the concentration of nitric added should be controlled as low as possible, or it is needed to try reducing the amount of nitric acid and increasing the temperature so as to maintain the decomposition rate of hydrogen peroxide.

[0033] The present experiment actually measures the sulfuric acid-hydrogen peroxide solution generated by common semiconductor factories. Before the experiment, the concentration of sulfuric acid in the solution is measured as 56.9%, and the concentration of hydrogen peroxide is 5.1% by titration of potassium permanganate (KMnO₄). The initial reaction temperature is preset to 55 °C. The processing agent is added to 50ml of the solution containing 56.9% sulfuric acid and 5.1% hydrogen peroxide, wherein the processing agent is formed by mixing 15, 10 or 5ml of 98% sulfuric acid and 0.2ml of 70% nitric acid, as shown in FIGs. 4A to 4C. Additionally, FIG. 4D illustrates 0ml of 98% sulfuric acid and 0.2ml of 70% nitric acid used.

[0034] Specifically, FIG. 4A indicates that 50ml of the solution containing 56.9% sulfuric acid and 5.1% hydrogen peroxide is added by the processing agent containing 15ml of 98% sulfuric acid and 0.2ml of 70% nitric acid, FIG. 4B indicates that 50ml of the solution containing 56.9% sulfuric acid and 5.1% hydrogen peroxide is added by the processing agent containing 10ml of 98% sulfuric acid and 0.2ml of 70% nitric acid, FIG. 4C indicates that 50ml of the solution containing 56.9% sulfuric acid and 5.1% hydrogen peroxide is added by the processing agent containing 5ml of 98% sulfuric acid and 0.2ml of 70% nitric acid, and FIG. 4D indicates that 50ml of the

solution containing 56.9% sulfuric acid and 5.1% hydrogen peroxide is added by the processing agent containing only 0.2ml of 70% nitric acid.

[0035] The above experiment shows that more concentrated sulfuric acid added, faster the increase rate of the reaction temperature. At the final stage of the decomposition reaction of hydrogen peroxide, the temperature is highest, and after the final stage of the reaction, hydrogen peroxide is completely decomposed. As shown in FIG. 4A, the processing agent the processing agent containing 15ml of 98% sulfuric acid and 0.2ml of 70% nitric acid is added, and the decomposition reaction of hydrogen peroxide finishes in about 3.5 minutes. It is proved that increasing the concentration of sulfuric acid speeds up the decomposition reaction of hydrogen peroxide. In addition, the processing agent the processing agent containing 5ml of 98% sulfuric acid and 0.2ml of 70% nitric acid is added as shown in FIG. 4C, and the decomposition reaction of hydrogen peroxide finishes in about 5 to 7 minutes. At the same time, since the exothermic effect of the decomposition of hydrogen peroxide causes the solution temperature to increase up to 91°C from 55°C, the concentration of hydrogen peroxide after the test is measured as 86ppm by KMnO_4 standard titration. That is, the concentration of hydrogen peroxide in the product solution after the treatment is reduced to less than 90ppm. However, it takes 20 minutes to complete the decomposition of hydrogen peroxide without adding sulfuric acid solution, as shown in FIG. 4D.

[0036] For the method of the present invention, if the primary components of the processing agent comprise electronic degree sulfuric acid and nitric acid, in which the pollutants of metal ions can be controlled within 1 to 10ppb, the product solution after treatment is still the sulfuric acid product with sub-electronic degree for recycle and re-use. Apparently, the present invention does not increase metal pollution.

[0037] If the sulfuric acid-hydrogen peroxide solution to be treated by the method of the present invention contains sulfuric acid lower than 55% (w/w), the reaction with nitric acid becomes slow. It is thus helpful to directly add sulfuric acid to increase the concentration of sulfuric acid up to 55% so as to accelerate the decomposition reaction of hydrogen peroxide.

[0038] The processing agent of the present invention primarily comprises 91.0%-97.9% (w/w) sulfuric acid and 0.05%-5.09% (w/w) nitric acid. The concentration of nitric acid is specified because too concentrated nitric acid will generate a great deal of yellow gas NO_2 , which adversely affects the working environment and limits recycle of subsequent products.

[0039] It is preferred that the volume ratio of the sulfuric acid-hydrogen peroxide solution to the processing agent is 20:1 to 5:1. The mixing ratio of sulfuric acid and nitric acid depends on the concentration of sulfuric acid in the solution to be treated. The concentration of sulfuric acid is currently increased up to 55% by adding 98% sulfuric acid, and more sulfuric acid added can accelerate the decomposition rate of hydrogen peroxide in the solution at the same initial reaction temperature. Accordingly, more concentrated nitric acid may accelerate the decomposition reaction of hydrogen peroxide.

[0040] If 100ml of the sulfuric acid-hydrogen peroxide solution containing 50% sulfuric acid and 5% hydrogen peroxide is taken as a baseline, more than 5ml of the processing agent containing 98% sulfuric acid and 70% nitric acid is added (the resultant weight percent concentration of sulfuric acid is 53.2%), and it is preferred that 10ml of the processing agent is added for better reaction rate (the resultant weight percent concentration of sulfuric acid is 55.8%). More amount of the processing agent is added, more concentrated nitric acid exists. As a result, the decomposition rate of

hydrogen peroxide is increased. Since the decomposition of hydrogen peroxide is exothermic, the temperature fast increases as the decomposition speeds up.

[0041] From the above mention, one primary feature of the present invention is that the decomposition of hydrogen peroxide is triggered by adding sulfuric acid and nitric acid. When the concentration of sulfuric acid in the solution to be treated is more than 55%, it is proved that nitric acid can cause hydrogen peroxide to decompose without adding sulfuric acid. However, since more nitric acid may generate a great deal of yellow gas NO_2 , it is preferred to limit the amount of nitric acid such that the sulfuric acid-hydrogen peroxide solution after treatment is available for recycle and re-use or other applications, thereby effectively improving utilization of valuable resources and reducing the cost.

[0042] Although the present invention has been described with reference to the preferred embodiments thereof, it is apparent to those skilled in the art that a variety of modifications and changes may be made without departing from the scope of the present invention which is intended to be defined by the appended claims.

WHAT IS CLAIMED IS:

1. A method for removing hydrogen peroxide from a sulfuric acid-hydrogen peroxide solution, comprising:

adding nitric acid with a weight percent concentration of 0.05%-5.09%(w/w) into the solution containing sulfuric acid and hydrogen peroxide so as to obtain a product solution, the solution having an initial reaction temperature between 45°C and 60 °C while being added by nitric acid,

wherein additional sulfuric acid is added to the solution when a weight percent concentration of sulfuric acid contained in the solution is less than 55%(w/w) such that the weight percent concentration of sulfuric acid contained in the solution attains to 55%(w/w).
2. A method for removing hydrogen peroxide from a sulfuric acid-hydrogen peroxide solution, comprising:

adding a processing agent into the solution containing sulfuric acid and hydrogen peroxide so as to obtain a product solution, the solution having an initial reaction temperature between 45°C and 60 °C,

wherein the processing agent comprises nitric acid with a weight percent concentration of 0.05%-5.09%(w/w) and sulfuric acid with a weight percent concentration of 91.0%-97.9%(w/w), and a volume ratio of the solution to the processing agent is 20:1 to 5:1.
3. The method as claimed in claim 1 or 2, wherein the weight percent concentration of hydrogen peroxide contained in the solution is between 0.5% and 10% (w/w), and the weight percent concentration of sulfuric acid contained in the solution is 45% (w/w).
4. The method as claimed in claim 1 or 2, wherein the product solution contains hydrogen peroxide having a concentration less than 90 ppm.

5. A processing agent for removing hydrogen peroxide from a sulfuric acid-hydrogen peroxide solution, comprising nitric acid with a weight percent concentration of 0.05%-5.09%(w/w) and sulfuric acid with a weight percent concentration of 91.0%-97.9%(w/w).
6. The processing agent as claimed in claim 5, wherein the weight percent concentration of hydrogen peroxide contained in the solution is between 0.5% and 10% (w/w), and the weight percent concentration of sulfuric acid contained in the solution is 45% (w/w).