

Dissolution Characteristics of Copper Oxide in Gas-liquid Hybrid Atmospheric Pressure Plasma Reactor Using Organic Acid Solution

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Abstract

In this study, a gas-liquid hybrid atmospheric pressure plasma reactor of the dielectric barrier discharge method was fabricated and characterized. The solubility of copper oxide in the organic acid solution was increased when argon having a larger atomic weight than helium was used during plasma discharge. There was no significant effect of mixing organic acid solutions under plasma discharge treatment on the variation of copper oxide's solubility. As the applied voltage for plasma discharge and the concentration of the organic acid solution increased, the dissolution and removal power of the copper oxide layer increased. Solubility of copper oxide was more affected by the concentration in organic acid solution rather than the variation of plasma applied voltage. The usefulness of hybrid plasma reactor for the surface cleaning process was confirmed.

Keywords: Gas-liquid hybrid, Plasma reactor, Cleaning process, Copper oxide, Organic acid solution, Solubility

1. Introduction

As the degree of integration of semiconductor devices increases, the adoption of a multilevel metal interconnection process employing low-resistance copper (Cu) and low-k materials has become indispensable. However, since copper generates metal halides with a very low vapor pressure in plasma etching to form a wiring structure, it is difficult to apply a direct etching process, so the damascene method is applied as an alternative copper interconnection process[1]. During the etching process of the insulating film for the damascene process, various post etch residues (PER) composed of polymeric organic materials, inorganic materials such as copper oxide or copper fluoride, and Si containing materials on the sidewalls of via and trench are formed[2,3]. The removal of etch residues proceeds as the next step in the etch process, and a cleaning process that forms a surface free of residues is very important. It is necessary to develop a cleaning solution and a cleaning method that can suppress copper corrosion and deterioration of low-k materials (etch damage and increase dielectric constant, etc.), and effectively remove etch residues[4-6]. In the evaluation of cleaning effect, the compatibility of cleaning solution with various types of low-k materials and compatibility with copper interconnection processes should be considered. Since dry cleaning using plasma is difficult to remove metal contaminants such as copper, the use of wet cleaning is more practical[7]. If possible, combining plasma dry cleaning and wet cleaning may be a novel and innovative cleaning method, which

would encompass the advantages of each.

In the low-pressure plasma process in a condition containing a liquid phase, continuous plasma discharge is difficult due to a change in process conditions because the liquid phase is easily vaporized at low pressure. Therefore, it is possible to estimate that cleaning components in the liquid phase can improve the reactivity of the cleaning solution through gas-liquid contact with various active species generated in plasma discharge through atmospheric pressure plasma[8,9]. It is valuable to analyze whether the cleaning properties are improved through the generation of cleaning active species in the cleaning solution by combining with atmospheric pressure plasma discharge.

In this study, a gas-liquid hybrid atmospheric pressure plasma reactor was firstly fabricated, and the effect on the solubility change of copper oxide, which is applicable to the cleaning process for copper interconnection, was analyzed. This study would define that the usefulness of the wet-dry combined cleaning method can be applied to semiconductor device manufacturing and ultra-precision surface cleaning process.

2. Experimental

Figure 1 shows the schematic diagram of the gas-liquid hybrid atmospheric pressure plasma reactor fabricated. Atmospheric pressure plasma of a dielectric barrier discharge method was used. The reactor has an inner diameter of 22 mm. A 250 mm-long quartz tube was used, and a 250 mm-long stainless steel was used for the inner electrode, and an outer electrode was made by wrapping it around using a copper plate. To protect the inner electrode from corrosive solution, a 150 mm long quartz tube was applied to enclose the electrode. A Teflon material with high chemical resistance and insulation was used

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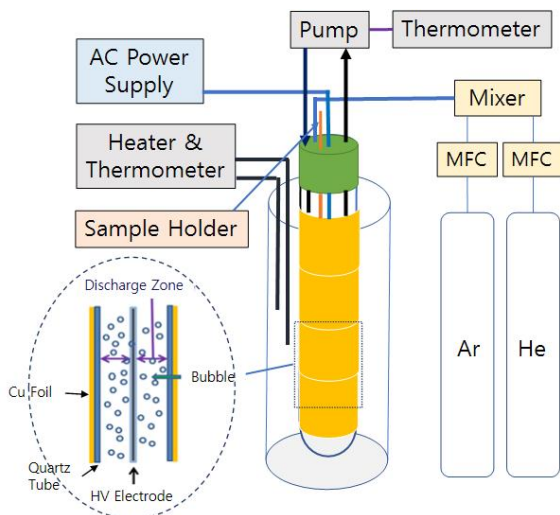


Figure 1. Schematic of gas-liquid hybrid atmospheric pressure plasma reactor. Including the cross section of plasma discharge zone and the reactor cap design.

as the reactor cover. Five passage holes were made for solution input and output, gas input, power grounding, and sample holder (gas output), and quartz tubes with an outer diameter of 4 mm and lengths of 120 and 190 mm, respectively, were installed to circulate the solution in the reactor. Mixing of the upper layer solution and the lower layer solution was facilitated. For the gas input, a quartz tube having an outer diameter of 4 mm and a length of 190 mm was placed in the solution to form bubbles in the solution. A liquid pump was installed to control the temperature of the solution through internal circulation. A thermostat was installed to control the reactor temperature, and a reflux condenser was installed to prevent evaporation of the solution due to plasma discharge and heat generation. The solution temperature was measured by inserting an electronic thermometer (pH 610, Thermo) into the reactor. It was injected into the reactor by controlling the gas flow rate with a mass flow controller (MFC). AC power supply (HVP, AP Plasma Power Supply) reveals its performance such as a maximum frequency of 30 kHz, a maximum voltage of 15 kV, and a maximum power of 2000 W.

For the preparation of copper oxide sheet, first, the copper thin film (0.5 T, 99.999%, Sigma-Aldrich) cut appropriately after washing with acetone to remove organic contaminants on the surface was added to glacial acetic acid (99.7%, Daejung) heated to 35 °C. After removing all the oxide film by putting it in for a minute, it is prepared at room temperature without treatment with deionized water[10] The copper thin film treated in this way is immediately put into a furnace and then heated at 400 °C in an air ambient for 12 hours to form a copper oxide film on the surface. A copper sheet covered with copper oxide was prepared. The organic acids used in the experiment were aspartic acid [(99.5%, Wako), citric acid (99.5%, Daejung), succinic acid (99.5%, Wako), oxalic acid (98%, Junsei), lactic acid (99.5%, Daejung)], and ultrapure water (DIW, Deionized Water) was used as a solvent. The effects of solution temperature, plasma discharge condition, gas activation, and mixing of organic acid solution on the solubility of copper

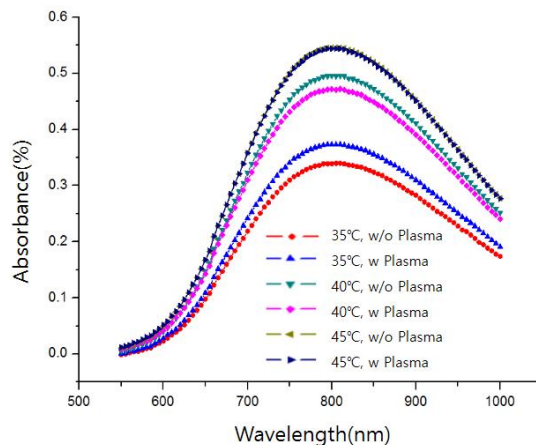


Figure 2. Effects of the variation of absorption peak intensity of copper(II) oxide at 800 nm according to the on/off of plasma and the temperature of 1 M lactic acid solution.

oxide were analyzed.

Inductively Coupled Plasma Spectrometer (ICP, OPTIMA 7300 DV, Perkin-Elmer) analysis was performed in Radial Mode. For analysis, 1 ml of a sample is taken and completely dissolved in 9 ml of 1 M H₂SO₄ for one day, and then analyzed. For UV-Vis Spectrophotometer (OPTIZEN α , MECASYS, Korea) analysis, 200 μ L of sample was taken and placed in a micro quartz cell, and the analysis range was 300-900 nm with an interval of 10 nm and a measurement rate of 100 nm/min. Solubility can be compared relative to the size of the absorption peak at 800 nm, which indicates the dissolution characteristics of copper oxide[11].

3. Results and Discussion

Figure 2 shows the UV/Vis results of measuring and comparing the effects of plasma discharge and solution temperature on the solubility of copper oxide. It was shown that the solubility of copper oxide increased as the solution temperature increased to 35 °C, 40 °C, and 45 °C regardless of plasma discharge. Here, in the comparison of solubility according to the presence or absence of plasma discharge treatment, the case of 45 °C showed almost the same solubility characteristics regardless of discharge. At a temperature lower than this, the difference in solubility increased further. These results indicate that the generation of hydrogen peroxide in solution during plasma discharge and the activation of reactive species due to the plasma discharge affected the copper oxide dissolution characteristics. However, at a high solution temperature, the plasma discharge effect becomes relatively small, so it is thought that the effect on the solubility of copper oxide is reduced.

It was reported that hydrogen peroxide is generated in the solution by the contact between 1 M lactic acid solution and plasma discharge, and the generated hydrogen peroxide affects copper oxide dissolution [12]. Plasma process conditions were set to 5 kV, 30 kHz, Ar gas 200 sccm, and a circulation flow rate of 200 ml/min of the solution, and the reaction was maintained for 20 minutes. The degree of decom-

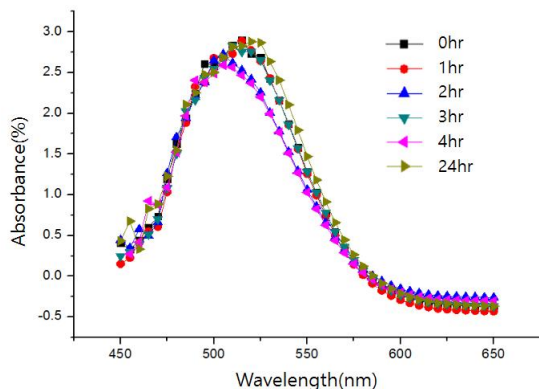


Figure 3. Variation of hydrogen peroxide concentration according to the idle time, which generated in lactic acid solution by plasma treating for 20 min.

position of hydrogen peroxide generated in 1M lactic acid solution treated with plasma discharge was observed over time. The 2,9-dimethyl-1,10-phenanthroline (DMP) solution was mixed with the solutions collected at intervals of 1, 2, 3, 4, and 24 hours and analyzed with a UV/Vis spectrophotometer [13]. As shown in Figure 3, there was no significant difference and no regular tendency in the relative comparison of the absorbance, resulting that the hydrogen peroxide generated in the solution after plasma treatment maintains the concentration until 24 hours. In order to exclude the dissolution effect by hydrogen peroxide and analyze only the plasma effect, first, 1M lactic acid solution and copper oxide were added at the same time, the solution temperature was maintained at 40 °C, and plasma discharge was performed, and then the solubility of copper oxide was measured. Next, the organic acid solution was subjected to plasma discharge treatment, and copper oxide was added while the solution temperature was maintained at 40 °C to measure the solubility. Here, it was assumed that the total amount of hydrogen peroxide produced in the solution was the same. The solubility of copper oxide through the two methods was measured by UV/Vis absorbance and the relative values are shown in Figure 4. The solubility was higher when copper oxide was included in the lactic acid solution during plasma discharge. Although the difference is not large, the difference in solubility is expected to be larger when plasma discharge treatment is applied, considering the process time of about 5 minutes to reach the maximum temperature of the solution during plasma processing.

Table 1 lists the results of copper concentrations and pH values according to the various solution conditions. In comparison of temperature factor and plasma discharge effect, plasma discharge was effective in increasing the solubility of copper oxide in an organic acid solution, and the solubility of copper oxide increased effectively when Ar was used as a plasma discharge gas than when He was used. It is considered to further increase the solubility of the solute by accelerating the generation of hydrogen peroxide or reactive molecular active species in the solution by transferring the reaction energy to the molecules in the solution more effectively than He because the molecular weight of Ar gas is higher than He gas. The lower the pH is, the higher the

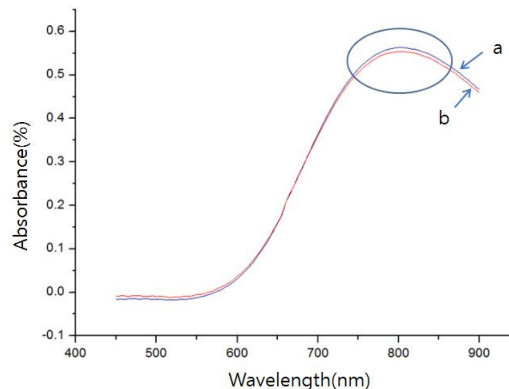


Figure 4. Comparison of copper(II) oxide's solubility in 1 M lactic acid solution. "a" indicates the solubility under the plasma treatment, "b" indicates the solubility without the direct plasma treatment.

Table 1. Copper Concentration and pH Values According to the Organic acid Species and Kinds of Plasma Treatment. Copper(II) Oxide 0.1 g was Inserted to the Organic Acid Solution 55 ml.

Solution and Plasma Treatment	Cu Concentration [mg/L]	pH
1M Citric acid solution	10.482	1.86
1M Citric acid solution + Ar Plasma 20min	21.239	1.84
1M Citric acid solution + He Plasma 20min	13.013	1.92
1M Oxalic acid solution	17.919	1.19
1M Oxalic acid solution + Ar Plasma 20min	102.98	1.22
1M Oxalic acid solution + He Plasma 20min	39.438	1.20
1M Succinic acid solution	4.0552	2.74
1M Succinic acid solution + Ar Plasma 20min	29.699	2.74
1M Succinic acid solution + He Plasma 20min	9.411	2.85

Table 2. Experimental Parameters for Copper(II) Oxide Dissolution in Organic Acid Solution. Copper(II) Oxide 0.1 g was Inserted to the Organic Acid Solution 55 ml.

Parameters	
E1	1M Lactic acid solution (55ml) + Ar Plasma Treatment for 20min
E2	1M Lactic acid solution (55ml) + Aspartic acid 0.05g + Ar Plasma Treatment for 20min
E3	1M Lactic acid solution (55ml)
E4	1M Lactic acid solution (55ml) + Aspartic acid 0.05g

solubility of copper oxide in organic acid solutions is yielded [12,14,15]. When looking at the pH change, pH change in the organic acid solution after plasma discharge treatment is slightly different, but the solubility value is significantly different. This shows that the solubility difference due to the plasma discharge effect is dominant rather than the effect of pH in the process of dissolving copper oxide.

The effect of organic acid mixed solution on copper oxide solubility under plasma discharge conditions was analyzed. Table 2 shows the experimental parameters of the mixed organic acid solution used. As

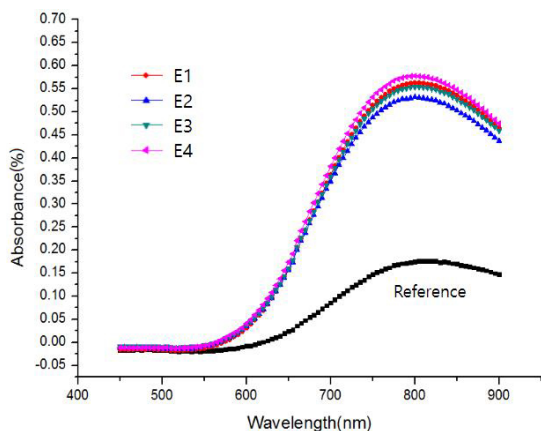


Figure 5. Effects of copper(II) oxide's solubility in 1 M lactic acid solution under the conditions showed in Table 2.

shown in Figure 5, the solubility of copper oxide was found to be high in the order of E4, E1, E3, and E2 conditions, but there was no significant difference in the comparison of absorbance at 800 nm, which indicates solubility. These results can be compared with the absorbance of a standard solution containing 1000 ppm copper oxide. In a solution of 55 ml of 1 M lactic acid and 0.05 g of aspartic acid, it had the highest solubility of copper oxide in the absence of plasma discharge. However, when the mixed solution is subjected to plasma discharge treatment, the solubility of copper oxide is decreased.

The dissolution shape of the copper oxide film surface following plasma discharge treatment in citric acid solutions was observed. As plasma discharge conditions, the applied voltage was set to 3, 4, and 5 kV, respectively, and 30 kHz, the circulating flow rate of the solution 200 ml/min, Ar 200 sccm, and the reaction treatment time were fixed at 15 min. For the experiment, 0.1 M, 0.01 M and 0.001 M citric acid solutions were prepared, respectively. Figure 6 shows the surface shape of the copper oxide thin film according to the applied voltage and the concentration of citric acid solution. It was shown that the degree of removal of the copper oxide layer clearly increased as the applied voltage and the concentration of citric acid solution increased. It can be seen from this result that the removal effect of copper oxide according to the concentration change of citric acid can act more than the effect on the plasma applied voltage. Therefore, in the process of removing copper oxide from the surface, it is preferable to apply the plasma discharge voltage and the concentration of the organic acid used as high as possible within the allowable range.

4. Conclusions

A gas-liquid hybrid atmospheric pressure plasma reactor of the dielectric barrier discharge method was fabricated, and the dissolution characteristics of copper oxide were analyzed using an organic acid solution. The solubility of copper oxide in the organic acid solution was increased when Ar having a larger atomic weight than He was used during plasma discharge. Mixing of organic acid solutions did not yield an effect on the variation of copper oxide solubility regardless

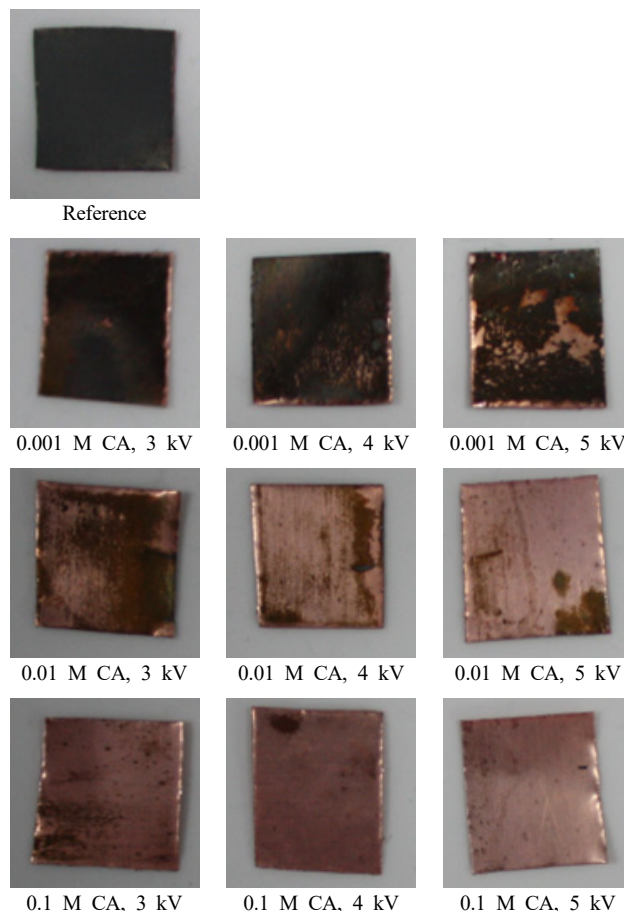


Figure 6. Effects of copper(II) oxide's solubility in 1 M lactic acid solution under the conditions showed in Table 2.

of plasma discharge treatments. As the applied voltage for plasma discharge and the concentration of the organic acid solution increase, the dissolution of the copper oxide layer increases. Here, the copper oxide removal effect according to the concentration change of the organic acid was greater than the effect on the plasma applied voltage. Based on the results of this study, the usefulness of the hybrid plasma reactor for the surface cleaning process could be confirmed.

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