The Method of Vacuum Plasma Reduction without Gas

S. Ueno, M. Yamahara, K. Noborio and K. Taguchi

Sakigake Semiconductor Co., Ltd., Kyoto, Japan

Abstract: Copper and silver are essential materials for electronic components, however natural oxidation has often caused problems. As a solution, chemical treatment using reducing agents and plasma reduction treatment using hydrogen gas have been used, but the peripheral equipment and other costs have been high. On the other hand, we have proposed a gas-free film forming technique in the past. In this study, we propose a new gas-free reduction method based on this technology.

Keywords: Reduction, Gas Free, Vacuum Plasma,

1. Back Ground

Metals are used in a variety of fields, from industry and medical equipment to daily necessities and accessories, so much so that not a day goes by that we do not see them in our daily lives. In electronic devices in particular, aluminum and other metals are pretty common in containers and lead frames, while gold and copper are used for circuits and terminals. Precious metals such as gold, silver, and copper are known for their high electrical conductivity and are essential materials in the modern electronics industry due to their low electrical conductivity loss. However, it is also well known that silver and copper oxidize naturally in the atmosphere. As is the case with other metals, when copper and silver oxidize, their conductive performance deteriorates, which often causes problems such as defects and reduced yields.

Wet treatments such as chemical treatment using glycol or glycerol as a reducing agent [1, 2] have been used to remove such metal oxide films. However, there were problems with the process, such as high temperatures and high environmental impact. As a dry process, reduction using hydrogen gas has also been used [3], but hydrogen gas is difficult to handle, and its introduction has often been hesitated. 4% or less diluted gas is easier to handle, but it greatly reduces the reaction rate and increases costs.

On the other hand, we have previously proposed DH-CVD (Direct Humidity-Chemical Vapor Deposition) [4], a gas-free film deposition method. This technique is an innovative film deposition method in which the film-forming material is placed in a liquid state in a vacuum vessel. In this study, we propose a gas-free plasma reduction method by introducing a reducing agent into the vacuum chamber instead of the film forming material. Although there have been previous processes using a reducing agent [1, 2], they were wet processes and required cleaning as a post-process. In contrast, the proposed method is a dry plasma process and does not require any post-processing. In addition, the proposed method is very compact and does not require complicated operations because it does not use an external feeder such as a bubbler as a means of introducing raw materials. In other words, the cost of the reduction process can be significantly reduced while at the same time reducing the environmental impact.

2. Experiment Methods

We prepared ten-yen coin and copper foil (C1020P 0.03, The Nilaco Corporation) for treatment. We used glycerol (CAS RN®: 56-81-5, Fujifilm Wako Pure Chemicals Co.) as the reducing agent. The glycerol exists as a liquid in the pressure range (5-20 Pa) and temperature range (293K-333K) in this experiment.

We treated the samples using a CCP (Capacitively Coupled Plasma) vacuum plasma equipment (CPE-200AHM, Sakigake Semiconductor). We placed the reducing agent in a container and positioned off the electrodes, as shown in Fig. 1.

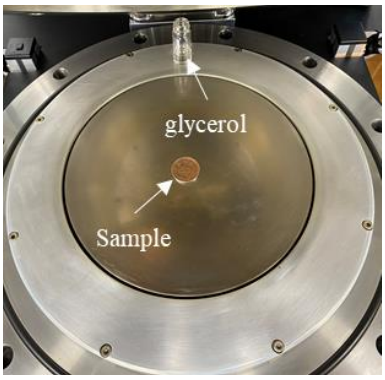

Fig. 1. Layout of sample in vacuum chamber.

We used the following three methods to evaluate this experiment.

(A). Visual evaluation of 10-yen coin and copper foil

We visually evaluated the color changes before and after treatment.

(B). Surface analysis of copper foil using XPS (X-ray photoelectron spectroscopy) (PHI5000 VersaProbe II, ULVAC-PHI, inc.).

We performed each surface analysis on the copper foil before and after treatment. As a comparative evaluation, we also performed Ar etching on the untreated copper foil to remove the natural oxide film while performing the measurements.

(C). Elemental evaluation using Q-mass (quadrupole mass spectrometer) (Qulee BGM-102, ULVAC inc.) in exhaust.

We measured elements in the exhaust before and after the plasma discharge in three conditions: I. empty chamber, II. glycerol only, and III. glycerol and copper foil.

3. Experiment Results

(A). Visual evaluation

As shown in Fig. 2(a), clear discoloration was observed on the surface of the 10-yen coin. Also, in Fig. 2(b), the color of the copper foil changed before and after the treatment.

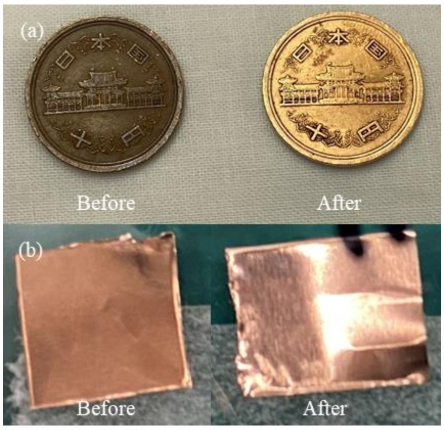

Fig. 2. Visual evaluation results before and after treatment. (left: before treatment, right: after treatment)
(a) Evaluation for 10-yen coin,
(b) Evaluation for Copper Foil

(B). Surface analysis by XPS

As shown in Fig. 3(a), the peaks indicating oxygen decreased after treatment. Also, etching decreased oxygen as in this method. On the other hand, as shown in Fig. 3(b), peaks indicating copper increased after treatment. For copper, the peaks indicating copper also increased after etching.

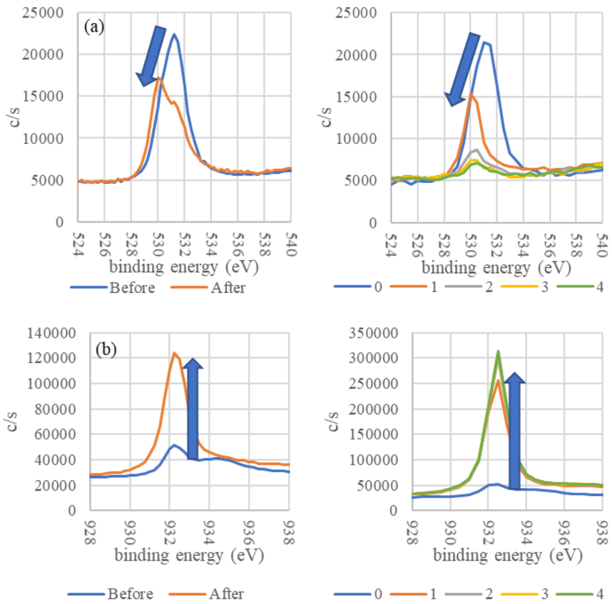

Fig. 3. Evaluation results using XPS. (left: comparison before and after processing, right: comparison against the number of etchings)
(a) Oxygen (O1s) spectrum (b) Copper (Cu2p3) spectrum

(C) Elemental evaluation using Q-mass

We did not obtain direct results indicating reduction.in each of the conditions. However, as shown in Fig. 4, we observed many active species contributing to the reduction reaction, such as CO and CH_2.

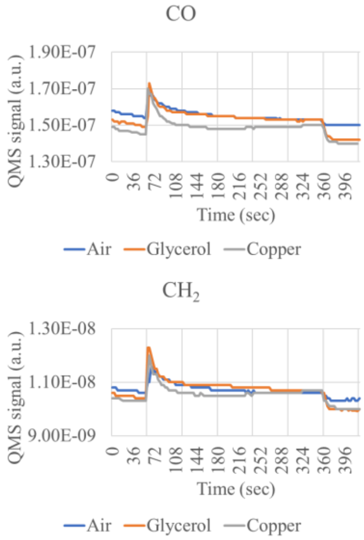

Fig. 4. Some of the evaluation results using Q-mass. In both cases, we started the discharge at 60 seconds and stopped it at 360 seconds.
(Air: empty chamber, Glycerol: glycerol only, Copper: glycerol and copper foil.)

4. Discussion

The colour change in Fig. 2 are also considered to be caused by reduction.

In Fig. 3, the spectra are similar to etched ones by using this method. Although the copper has not yet reached pure copper, it is considered to be in the process of reduction. Extending the processing time may bring it closer to pure copper.

Fig. 4 suggests that the active species contributing to the reduction were obtained when glycerol entered the plasma state.

5. Conclusion

In this study, we have successfully reduced copper without using gas by placing the reductant in a chamber. We hope that this research will contribute to cost reduction in the electronics industry.

6. References

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