# **Controlling Cu Corrosion in Single Wafer Cleaning Process**

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# 1. Introduction

In the damascene method, which has been widely used for fabricating Cu interconnects, organic byproducts formed after etching and ashing are removed by wet chemical cleaning. However, this wet cleaning often causes low-k film damage and Cu corrosion, so it is necessary to carefully select the wet chemicals and optimize the cleaning method as the device scale decreases. TEM images of Cu corrosion at the via bottom, which happened after post-etching wet cleaning, are shown in Fig. 1. This type of corrosion is often observed in an isolated via [1] and causes via contact failure or degrades reliability.

This via corrosion is thought to be related to the single wafer cleaning process, especially to the rinse step after the chemical cleaning step, because it mainly occurs at the wafer edge even though cleaning chemicals are not used. Thus, we investigated the mechanism of Cu corrosion by focusing on dissolved oxygen (DO) [2] and the oxidation-reduction potential (ORP) [3] of deionized water (DIW) in the rinse step.

#### 2. Experimental

Two types of 300-mm single wafer cleaning equipment were used in this work (Fig. 2). One is a simple system developed for cleaning experiments, and the other is a cleaning system for mass production use.

The dissolved oxygen in the DIW was measured in the cleaning test equipment (Fig. 2(a)). First, air was sucked from the DIW and then  $N_2$  gas was dissolved. DIW flows on the plastic board of the equipment from the center to the edge at 1 L/min, which reproduces the actual rinse water flow on a wafer. Four small holes were made in the plastic board at distances of 0, 38, 75, and 140 mm from the nozzle point to sample the DIW through tubes and measure the dissolved oxygen. The process chamber was closed to control oxygen concentration in the atmosphere, and  $N_2$  atmosphere was also available.

A schematic of our cleaning system, in which a rotating shield plate is brought close to a wafer in parallel at distances between 2 and 180 mm during the rinsing and drying steps, is shown in Fig. 2(b). A low oxygen (< 2%) atmosphere was obtained by introducing  $N_2$  gas onto the wafer center through the shield plate.

A Kelvin via ( $\phi$  120 nm) with a two-level damascene structure was observed by TEM after the ashing step to determine Cu corrosion in a patterned wafer. The Cu etched amount within a non-patterned wafer was measured using a 50-nm-thick blanket Cu film by sheet resistance change. To quantify the amount of Cu corrosion, we accelerated the rinse step for 10-30 times longer than the normal rinse time.

#### 3. Results and Discussion

3-1. Cu corrosion by dissolved oxygen in DIW rinse

A TEM image of Cu corrosion of a wafer after a 10-min DIW

rinse but no chemical cleaning is shown in Fig. 3. Compared with the wafer in Fig. 1(b), which was cleaned with chemicals followed by a 1-min DIW rinse, corrosion was also observed at the via bottom of the wafer edge. Thus, we examined the effect of dissolved oxygen in DIW on corrosion. The results showed that the Cu etching rate increased as the dissolved oxygen increased (Fig. 4).

Next, we investigated the effect of oxygen in the air on the dissolved oxygen in the rinse DIW by using the equipment shown in Fig. 2(a). The dissolved oxygen in the DIW increased to more than 0.6 ppm as the flow distance from the nozzle point increased (Fig. 5). However, it decreased to less than 0.1 ppm when the air atmosphere was replaced with N<sub>2</sub> atmosphere. Therefore, oxygen from the air is thought to dissolve into the DIW for a short moment after the DIW starts to flow on the wafer surface.

3-2. Corrosion suppression by oxygen shield plate

We applied a corrosion suppression technique to our cleaning system for mass production use. By decreasing the distance between the wafer and shield plate to less than 20 mm and increasing the N<sub>2</sub> flow rate to more than 60 L/min, we were able to suppress the oxygen concentration in the atmosphere above the wafer to less than 2% (Fig. 6). The Cu etched amount within a non-patterned wafer was evaluated after a 30-min DIW rinse with this condition (Fig. 7). In air, the etched amount increased at the wafer edge, but this was suppressed when the air atmosphere was replaced with N<sub>2</sub> atmosphere. Cu corrosion at the via bottom was also suppressed (Fig. 8).

We also studied the dependence of Cu etching on wafer rotational speed in the air and  $N_2$  atmosphere during rinsing (Fig. 9). The results showed that the etched amount at a wafer edge increased as the rotation speed increased. This is assuming that more oxygen was involved due to the ruffled flow of DIW at the wafer edge caused by high speed wafer rotation [2]. Therefore, we must reduce the dissolved oxygen to prevent Cu corrosion and obtain a good rinse effect at higher wafer rotation speeds.

Besides dissolved oxygen, we examined  $H_2$  water with a low ORP [3]. As shown in the Pourbaix diagram (Fig. 10(b)), Cu corrosion at the via bottom was suppressed by wafer with the lowest ORP, -550 mV. Furthermore, when  $N_2$  atmosphere was used during  $H_2$  water rinsing, via-bottom corrosion was minimized. Therefore, not only cleaning chemical damage on low-k film, but also quality control of rinse DIW will become more essential when device patterns are shrunk.

### 4. Conclusion

To suppress Cu corrosion at the via bottom of the wafer edge, control of the dissolved oxygen and ORP in rinse DIW by decreasing oxygen concentration in the atmosphere and using  $H_2$ water is necessary. This will become indispensable in the cleaning process of next generation Cu interconnects.

## References

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Fig. 1 Cu corrosion in isolated via after wet chemical cleaning to remove polymers.



Fig. 3 Cu corrosion after accelerated DIW rinse test.



Fig. 6 Oxygen concentration dependency on  $N_2$  flow rate and distance from wafer to shield plate.



Fig. 9 Cu etched amount dependency on wafer rotational speed and  $air/N_2$  atmosphere.



Fig. 4 Cu etch rate dependency on dissolved oxygen in rinse DIW.



Fig. 7 Cu etched amount within wafer in air and in  $N_2$  atmosphere.

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Fig. 2 Schematics of (a) cleaning equipment for measuring dissolved oxygen and (b) cleaning system with shield plate.



Fig. 5 Dissolved oxygen in rinse DIW dependency on  $air/N_2$  atmosphere and distance from DIW nozzle.



Fig. 8 Cu corrosion at via bottom (a) after cleaning in air and (b) that in  $N_2$  atmosphere.



Fig. 10(a) Cu corrosion at via bottom dependency on ORP of rinse DIW and  $air/N_2$  atmosphere and (b) Pourbaix diagram of Cu.