

# The Mechanism of Cu Seed Residue Formation

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## Abstract

**This paper presents Cu seed residue defects commonly encountered in wafer-level Cu Bump fabrication process. Through analysis of the defects, we proposed a hypothesis for the formation of the defects. The hypothesis was tested with controlled experiments, and mechanism for the formation of Cu seed residue defects during bump plating and post plating was revealed.**

## INTRODUCTION

Cu Bump or Cu Pillar bumping technology has been integrated into semiconductor device wafer level fabrication in recent years because of its reduced cost compared to wire bonding process, and more importantly it enables fine pitch flip-chip process for integration of high density electronic components.

A basic Cu Bump fabrication process includes the flowing process blocks:

- 1) Deposit a blanket Cu seed metal (with an adhesion layer) on wafer using a PVD process;
- 2) Define where Bumps are to be formed using photolithography;
- 3) Plate Cu pillar followed by Sn solder plating on top;
- 4) Strip patterning photoresist;
- 5) Etch off Cu seed metal using wet chemistry

One of the common process upsets in Cu bump fabrication is formation of “white-ring” defects in the vicinity of plated Cu bumps on the Cu seed as shown in Figure 1, as has been reported in [1][2][3]. The defects would lead to incomplete Cu seed etch removal during Cu seed wet etch, and there is no effective rework procedure for this type of defects.

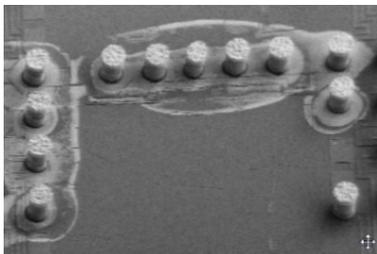


Fig. 1. Examples of Cu seed residue.

A number of factors that could contribute to the formation of the defects were investigated, including photo process, oxygen plasma clean before plating, plating chemistry, post plating DI water rinses, plating resist strip chemistry and process, as well as seed metal etch process. However, there is a lack of understanding of the mechanism for the defects formation.

## DEFECT ANALYSIS

Auger Electron Spectroscopic (AES) analysis over the Cu seed residue, and SEM-EDS analysis of the plated bump in the affected area were performed to reveal the nature of the defects. Based on AES analysis, at the surface of Cu seed residue, there was presence of Sn, carbon, and oxygen. Source of Sn is definitely originated from Sn solder plating chemistry. To estimate the thickness of the Sn layer, Ar sputter etch was performed during Auger analysis, and Sn was detected 50 Å to 500Å beneath the defect surface. Figure 2 shows Auger spectra of Cu seed residue at different depth levels.

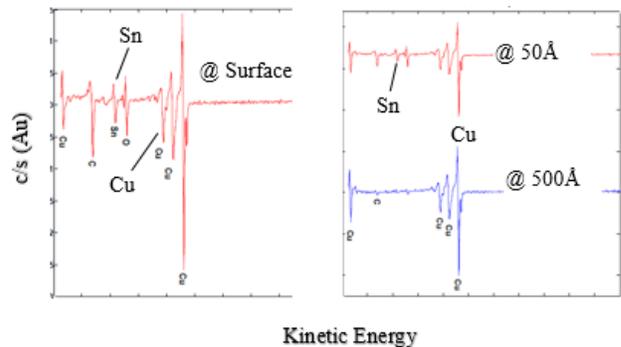


Fig. 2. Auger spectra over Cu seed residue.

For Cu bumps in the affected area, FIB cross-section and SEM inspection of the entire Cu pillar and solder cap were performed, and a grainy and porous layer of material over the bulk electroplated metal was observed as shown in Figure 3.

Energy Dispersive X-Ray Spectroscopy (EDX) analysis was performed along with SEM inspection at locations 1 through 5, with location 1 at solder cap region, location 2 at

Cu and solder boundary, and location 3 to 5 in plated Cu pillar region in Figure 3. Both Cu and Sn were detected at all 5 locations. Figure 4 shows normalized EDX counts at 5 EDX locations, with solid grey bar for Sn signal, and shaded bar for Cu signal.

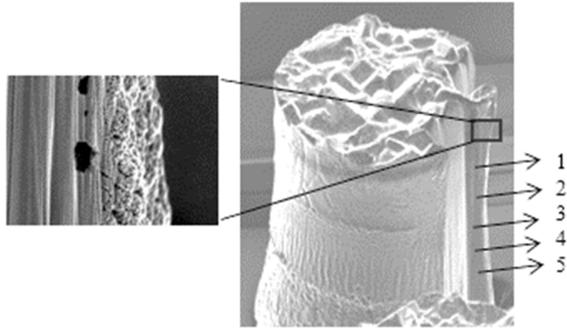


Fig. 3. Sn “Curtain” over plated Cu pillar.

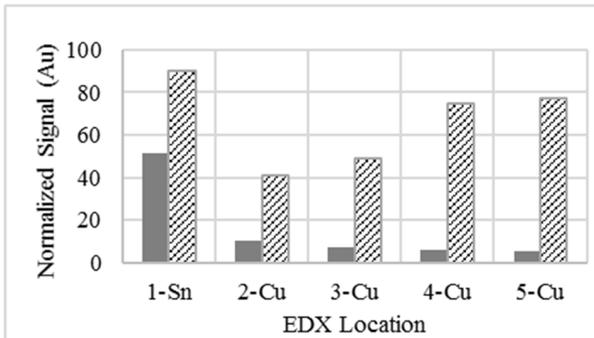


Fig. 4. Sn and Cu signal at 5 EDX locations.

At location 1, there was a coat of Cu over the plated Sn, along with oxygen and carbon signals, see Figure 5.

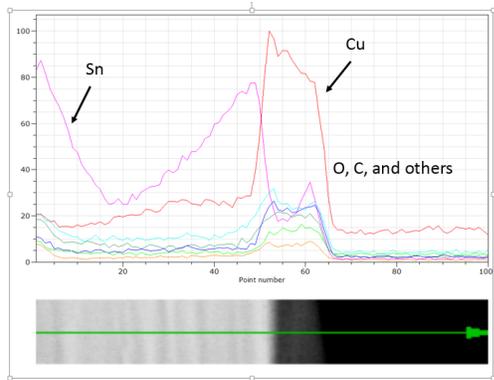


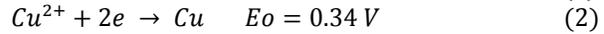
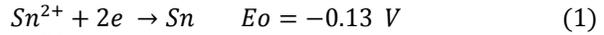
Fig. 5. A thin layer of Cu detected over plated Sn surface.

#### INITIAL HYPOTHESIS FOR THE DEFECT FORMATION

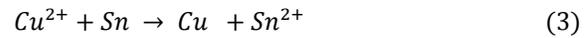
Based on defect analysis, we propose a hypothesis to explain three phenomena associated with the defect formation.

**Phenomenon 1:** Cu detected at Sn skin: This Cu over Sn skin could be formed from two paths;

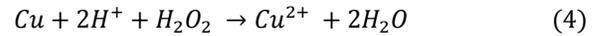
**Path 1.** Entrapment or absorptions of Cu plating chemicals in photoresist, and then  $\text{Cu}^{2+}$  was released during solder plating, and co-plated on Sn solder. Half-cell reaction for electrochemical deposition (ECD) of Sn and Cu can be written as:



**Path 2:** Entrapment of  $\text{Cu}^{2+}$  ions in photoresist was reduced by elemental Sn through replacement chemical reaction, and deposited on Sn solder surface. The replacement chemical reactions can be expressed as:



**Path 3:** There is a third path which can take place during Cu seed metal etch, where elemental Cu (Cu seed and plated Cu pillar) was oxidized by  $\text{H}_2\text{O}_2$  in acid environment, and dissolved into  $\text{Cu}^{2+}$  ions, chemical equation can be written as:

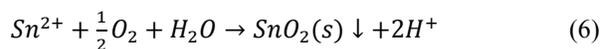
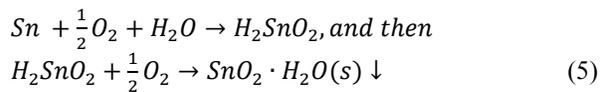


and then  $\text{Cu}^{2+}$  ions were subsequently reduced by elemental Sn through replacement chemical reaction, see Equation 3. This third path is not in our scope of interest, because white-ring defects can be observed before Cu seed etch.

Cu and Sn formed through ECD are expected to be dense and showing crystalline structure, while SEM inspection observation showed porous and grainy appearance, ECD hypothesis could not be substantiated, and  $\text{Cu}^{2+}$  ion reduction through replacement chemical reaction hypothesis fits well for this phenomenon (Path 2).

**Phenomenon 2:** Sn detected over Cu pillar surface. Since Sn is more active than Cu in metal activity series, the reduction of  $\text{Sn}^{2+}$  by Cu through replacement chemical reaction can be ruled out. One possible route is  $\text{Sn}^{2+}$  is reduced to Sn during solder plating as stated in Equation (1) because of Sn plating chemicals wicking down Cu pillar along photoresist sidewall.

Another route is Sn or  $\text{Sn}^{2+}$  oxidation through dissolved oxygen forming  $\text{SnO}_2$  deposits, as explained in Equation (5) and (6).



**Phenomena 3:** “white ring” defects over Cu seed metal could be explained using the same mechanism as described in phenomena 2, the necessary condition is delamination of photoresist on Cu seed metal, allowing access of Sn plating solution for ECD of Sn, or formation of insoluble SnO<sub>2</sub> from dissolved oxygen chemical reactions

#### DEFECTS REGENERATION

To validate the initial hypothesis, we conducted two groups of experiments to reproduce the defects in a controlled manner. To our surprise, the results from our experiments could not substantiate initial hypothesis for explaining phenomenon 2 (Sn “curtain” over Cu pillar) or 3 (white-ring defects). The experiment splits and results were summarized in Table 1 and Table 2.

Prior to splits, all experimental legs were processed according to standard procedures through photoresist patterning, pre-plate dry/wet cleaning, and then were processed with different experimental conditions following the left-to-right sequence as shown in Table 1 or Table 2. The plating steps in the splits were also carried out following standard procedures.

For the first group of experiments in Table 1, after completed splits in plating steps, wafers were dipped into a still Sn plating solution, and soaked for 2 hours without stripping photoresist. Sn plating solution was kept at ambient conditions during the experiments.

For the second group of experiments in Table 2, Cu pillar plating step was skipped, and other experimental conditions were kept the same as in first group.

TABLE 1.  
SOAK SPLITS WITH PHOTORESIST NOT STRIPPED.

Splits	Cu Plating	Sn Plating	Soak in Sn Solution	White-ring Defects
1	Yes	Yes	No	No
2	Yes	Yes	Yes	Yes
3	No	No	Yes	No
4	Yes	No	Yes	No
5	No	Yes	Yes	Yes
6	No	Yes	No	No

TABLE 2.  
SOAK SPLITS WITHOUT CU PILLAR PLATING.

Splits	Sn Plating	Soak in Sn Solution	White-ring Defects
1	Yes	No	No
2	Yes	Yes	Yes
3	No	Yes	No
4	No	Yes	No

After completed soak experiments, wafers were then sent for photoresist strip with standard procedures, and then wafers were inspected using automated optical inspection equipment (AOI). Figure 6 shows an example of AOI map with “white-ring” defects. The line drawn in the figure indicates Sn plating solution level in soak experiment.

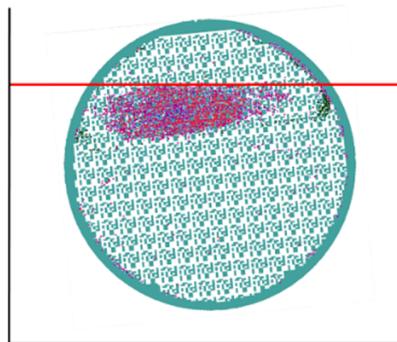


Fig. 6. Schematic of wafer soaked in Sn plating tank.

The experimental results can be summarized as following:

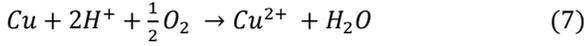
- (1) Elemental Sn from EDC or plating was essential for the formation for white-ring defects. Without Sn plating, even wafers were soaked in Sn plating solution, there would be no white-ring defects to form.
- (2) Cu plating was not a necessary condition for the formation of defects. This could be easily understood because with or without Cu plating, wafers had elemental Cu from PVD Cu seed metal process.
- (3) Post Sn plating, soaking wafer in Sn solution was necessary for the formation of defects, without soak in Sn plating solutions, no white-ring defects were observed.
- (4) Defects if formed were near the Sn solution surface, indicating the formation of defects is related to exposure of atmosphere.

The experimental results puzzled us in two aspects, first it demonstrated that after Sn solder plating, with soak in Sn solution only (no external power supply was required), white-ring defects were formed; and secondly, it nullified the hypothesis that defects were formed from oxidation of Sn or Sn<sup>2+</sup> forming SnO<sub>2</sub> deposits. There must be a new mechanism responsible for the formation of white-ring defects without external power supply.

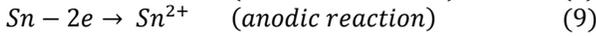
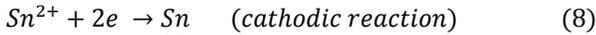
#### MECHANISM DEDUCTION

We started with a new hypothesis: Elemental Cu was first oxidized into Cu<sup>2+</sup> in Sn plating solution through dissolved oxygen, and formed an internal battery cell, and the battery cell provides close-loop circuit for Sn<sup>2+</sup> reduction on Cu surface. The full reactions mechanism can be simplified as:

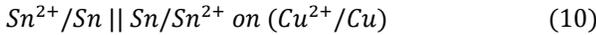
First, Cu oxidation into  $\text{Cu}^{2+}$  through dissolved oxygen



Then  $\text{Cu}^{2+}$  ions generated from Equation 7 formed a  $\text{Cu}^{2+}/\text{Cu}$  half-cell on the Cu seed metal, where cathodic reduction of  $\text{Sn}^{2+}$  into elemental Sn (see Equation 8) takes place; and on elemental Sn in plated solder together with  $\text{Sn}^{2+}$  ions in plating solution formed anodic half-cell, where elemental Sn is oxidized into  $\text{Sn}^{2+}$  (see Equation 9). Two half-cells formed a close-loop galvanic cell (Equation 10).

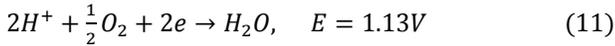


Overall galvanic reaction can be expressed as:



For this mechanism to function, two necessary conditions need to be met: first, Equation 7 dissolved oxygen needs to provide greater than 0.34V oxidation potential to drive Cu seed oxidation; and second,  $\text{Cu}^{2+}$  concentration from dissolved oxygen oxidation reaction needs to be above certain level so that  $\text{Cu}^{2+}/\text{Cu}$  half-cell potential is greater than 0.13V, large enough to drive oxidation reaction of Sn into  $\text{Sn}^{2+}$  on Cu surface.

Let's examine the dissolved oxygen reduction potential first. The cell reaction can be expressed as:



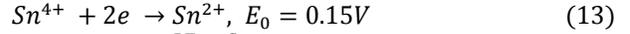
Applying Nernst-Equation for Equation (11), where  $E_0=1.23\text{V}$  ( $E_0$ : standard half-cell oxygen reduction potential),  $R=8.314 \text{ J}/(\text{mol}\cdot\text{K})$  ( $R$ : universal gas constant),  $T=298\text{K}$  at  $25^\circ\text{C}$  for temperature,  $z=2$  for mole of charges transferred for 1 mole of oxygen-atom reduction,  $F=96485 \text{ C}/\text{mol}$  ( $F$ : Faraday constant), the activity of  $\text{H}^+$  is estimated to be 1M (calculated based on Debye-Hückel mean ionic activity theory), and  $\text{O}_2$  concentration= $2.5 \times 10^{-7}\text{M}$  using 8mg/L saturated dissolved oxygen concentration at  $25^\circ\text{C}$ , then dissolved oxygen reduction potential in acid environment is calculated to be 1.13V, greater than 0.34V required for driving Cu oxidation.

Next let's check the minimum  $\text{Cu}^{2+}$  concentration required for  $\text{Cu}^{2+}/\text{Cu}$  half-cell to provide greater than 0.13V potential to drive  $\text{Sn}^{2+}$  reduction on Cu seed. Applying Nernst-equation for Equation 12, with  $E_0=0.34\text{V}$  and  $E=0.13\text{V}$  for  $\text{Cu}^{2+}/\text{Cu}$  cell,  $T=298\text{K}$ ,  $z=2$ ,  $F=96485 \text{ C}/\text{mol}$ , and  $R=8.314 \text{ J}/(\text{mol}\cdot\text{K})$ ,  $\text{Cu}^{2+}$  ion concentration is calculated to be  $7.8 \times 10^{-8}\text{M}$ , which is close to 30% of dissolved oxygen concentration.

$$E = E_0 + \frac{RT}{zF} \ln \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}}}, \quad a_{\text{Cu}^{2+}} = 7.8 \times 10^{-8}\text{M} \quad (12)$$

Both conditions for Equation (7) through (10) used for explaining the formation mechanism of white-ring defects are examined and validated based on Equation (11) and (12).

Lastly,  $\text{Sn}^{2+}$  oxidation to  $\text{Sn}^{4+}$  on Cu seed metal is not favored compared to Cu oxidation to  $\text{Cu}^{2+}$  to serve as cathode in galvanic cell. because  $\text{Sn}^{4+}/\text{Sn}^{2+}$  cell potential with assumption of full conversion of dissolved oxygen is approximately -0.068V, less than 0.13V required to drive  $\text{Sn}^{2+}$  reduction to Sn.



$$\text{And } E = E_0 + \frac{RT}{2F} \ln \frac{a_{\text{Sn}^{4+}}}{a_{\text{Sn}^{2+}}} = -0.068\text{V} < 0.13\text{V} \quad (14)$$

## CONCLUSIONS

In Summary, Cu seed etch residue could be formed via two mechanisms: (1) if defects were formed during the plating process, then photoresist delamination and Sn deposition through ECD with external power accounted for the defects formation; (2) and if defects were formed post Sn plating, then dissolved oxygen oxidation of Cu forming galvanic cell that drives deposition of Sn was the dominant force. Cu coat over Sn solder was formed mainly via replacement chemical reaction. With the understanding of the defect formation mechanisms, final root cause of the problem was found

## ACKNOWLEDGEMENT

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## ACRONYMS

FIB: Focused Ion Beam  
 ECD: Electrochemical Deposition  
 EDS: Energy Dispersive X-Ray Spectroscopy  
 SEM: Scanning Electron Microscope