Low Thermal Expansion Coefficient Electrodeposited Copper and its Contraction Phenomena with Annealing

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1. Introduction

Electrodeposited copper has been widely used both in three dimensional packaging and printed circuit boards (PCB). This is because copper has lowest resistivity, next to silver. However, the disadvantage of using electrodeposited copper is its large thermal expansion coefficient (TEC). The TEC of copper $1.7 \times 10^{-5}/\text{K}$ is nine times larger than TEC of silicon $2 \times 10^{-6}/\text{K}$. This TEC mismatch causes several failures such as extrusion of copper and cracking or stress in surrounding silicon.

Through-silicon via (TSV) filling by copper electrodeposition is the key technology used in three dimensional packaging. Copper TSV is exposed to a high temperature between 400 $\degree$C and 600 $\degree$C in SiO$_2$ formation process. The high exposure temperature induces the extrusion of copper out of silicon surface (or called “pumping”). This copper pumping destroys wiring above TSV.

There are several studies on pumping. F. X. Che$^{11}$ and N. Nabio$^{12}$ used finite element analysis for simulation of the pumping in TSV. I. De Wolf reported that multiple chemical mechanical polishing (CMP) and annealing can effectively reduce the TSV pumping$^{5}$. J. De Messemaker used optical profilometry for the copper pumping measurement. The copper pumping values were lognormal distributed with an intrinsically large spread. With multiple CMP, low pumping was found with annealing at the higher temperature and with a longer time$^{16}$. However, the CMP is a very expensive process. Hence, less CMP reduces the total TSV cost.

Another solution to overcome TEC problems is using low TEC metals and/or alloys to replace copper$^{17-20}$. However, the resistivity of these metals and alloys is higher than that of copper, and furthermore, etching is impossible. For example, Y.-T. Lin have applied a Ni-W plating formula for filling TSVs. The Ni-W alloy showed a smaller TEC$_{\text{Cu,Ni,W}}$ value (approximately $1.4 \times 10^{-5}/\text{K}$) as compared with the TEC of copper$^{21}$. M.-H. Roh tried to suppress the extrusion of copper in TSV by using Cu-W alloys. The results showed that the TEC of Cu-7.6$\%$wt W was only $10.8 \times 10^{-6} /\text{K}$. And the extrusion height decreased from 1.369 $\mu$m for Cu to 0.465 $\mu$m for Cu-7.6$\%$wt W$^{22}$.

In this study, we have found that our new copper electrodeposited contracts with annealing. Phenomena of the contraction with annealing is reported. No one to date has done any study to reduce copper TEC, thus this study is very original.

2. Experimental

The base electrolytes for copper electrodeposition were CuSO$_4$, H$_2$O and H$_2$SO$_4$. The additives used in this study consisted of Leveler, Accelerator, Inhibitor, C$_1$, and low TEC additive.

Copper pipes were made for measuring TEC of electrodeposits by the thermal expansion meter (TD5020SA, NETZSCH). The copper pipe was heated in an argon atmosphere with a quartz as the reference. The copper pipe expansion lengths were measured.

Copper electrodeposited microstructure was observed on in-situ SEM annealing stage (HSEA-500, TSL solutions). The sample was annealed with a ceramic heater in scanning electron microscopy (SEM) chamber. X-ray diffraction (XRD) profiles were measured by a Ringaku SmartLab X-Ray Diffractometer using Cu K$_\alpha$ radiation ($\lambda = 1.5406 \text{Å}$) operated at 45 kV and 200 mA in a scanning speed of 5$\degree$/min.

3. Results and Discussion

Figure 1 shows the thermal expansions of electrodeposited copper with and without low TEC additive. The x-axis is the copper expansion length and the y-axis is the temperature. Without additive A, the sample is conventional electrodeposited copper and the expansion length increases linearly with temperature (red line). The thermal expansion coefficient, slope, is constant with temperature. With low TEC additive, the electrodeposited copper starts to contract at $120 \degree$C (blue curve). The discrepancy between red line and blue curve gets larger in the range temperature from $203 \degree$C to $310 \degree$C. The discrepancy becomes much larger, about $47 \mu$m at

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400 °C.

Figure 2 shows the in-situ SEM microstructure of electrodeposited copper at different annealing temperatures. Microstructure a is 203 °C, b is 310 °C, c is 350 °C and d is 450 °C. In Fig. 2 a, about 1 μm electrodeposited copper grains are observed. While no dark spot is observed at 203 °C, several 100 nm dark spots start emerging at 310 °C (Fig. 2 b). These dark spots form at triple grain points. The number of dark spots increases with the increase of temperature as shown in Fig. 2 c at 350 °C and Fig. 2 d at 450 °C. From the FE-AES analysis, these 100 nm dark spots are carbon precipitates.

Figure 3 shows the X-ray diffraction results of electrodeposited copper with and without annealing. Cu(400), Kα1, Kα2, Cu(400) are selected at high 2θ in order to indicate significant differences in the 2θ. The position of Cu(400) peak shifts to a higher 2θ value from 116.950 for as-deposited copper to 117.180 after annealing at 420 °C in 1 hour. This 2θ shift corresponds to a change in lattice constants from d = 3.6147 Å for as-deposited copper to d = 3.6104 Å after annealing. The decrease from 47 to 04 in third and fourth decimal places indicates that the copper lattice contracts after annealing at 420 °C for 1 hour.

Furthermore, the TEC measurement and X-ray diffraction are consistent. The ratio of expansion length between room temperature and after annealing at 400 °C and the copper pipe original length is 47/15000, since the copper pipe original length is 15000 μm. The ratio of lattice constant difference at room temperature and after annealing at 420 °C and as-deposit lattice constant is 0.0043/3.6147. The order of magnitude of these two ratios are in good agreement.

4. Conclusion

1. Electrodeposited copper with low TEC additive starts to contract at 120 °C. This discrepancy between conventional copper and electrodeposited copper with low TEC additive becomes larger with annealing.

2. The dark spots exist in SEM image at 310 °C and their number increases with increasing annealing temperature.

3. From the X-ray diffraction, lattice constant contracts with annealing at 420 °C, 1 hour.

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References


7) K. Kondo ; PCT/JP2016/084499.


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Fig. 2 SEM micrographs of the electrodeposited copper after annealing. a) 203 °C, b) 310 °C, c) 350 °C and d) 450 °C.

Fig. 3 X-ray diffractions of electrodeposited copper with and without annealing.