Microvia Filling with Nickel-Tungsten Alloy to Decrease the Coefficient of Thermal Expansion of Electronic Circuit Interconnections

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A nickel-tungsten alloy plating formula was developed to electrochemically fill the microvias of printed circuit boards and the through-silicon vias (TSVs) of wafers. The plating solution was composed of Ni(SO3NH2)2, citric acid, sodium citrate, Na2WO4, chloride ions, and 2-mercapto-5-benzimidazolesulfonic acid. Avoid-free Ni-W superfilling of a microvia and a TSV were achieved. The tungsten content in the filled alloy varied from 1.5 atom% to 5.5 atom%, depending on the plating temperature. The coefficient of thermal expansion of the filled Ni-W was theoretically calculated according to the tungsten content, which was lower than that of copper.

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Microvia filling by copper electroplating has been widely employed to fabricate state-of-the-art printed circuit boards (PCBs) for interconnection, especially for integrated circuit (IC) packaging substrates.1–5 Recently, through-silicon vias (TSVs) have also been metallized by copper electroplating for the interconnection of three-dimensional (3D) IC chip stacking packaging.6–13 Copper is a good conductor but its coefficient of thermal expansion (CTE) is high. Therefore, issues related to CTE mismatch between the conducting materials and the dielectric materials arise in PCB and 3D packaging with high-density interconnections.

Numerous authors have reported that the high CTE of the copper filled in the TSVs results in stress impacts on silicon substrates.14–17 Copper atoms diffuse from the TSV due to thermal cycling, leading to void formation in the TSV.18,19 The copper protrusion on the TSV caused respectively by thermal expansion and diffusion of copper lattices and atoms may destroy stacked IC chips.20–22 Copper must be replaced by tungsten23 or nickel24,25 to overcome the issue of CTE mismatch.

Although the CTE of tungsten is very low,14,15 it cannot be electrochemically plated in an aqueous electrolyte. Fortunately, tungsten can be induced to co-deposit with nickel.27–32 In this work, a Ni-W alloy plating formula that can achieve Ni-W bottom-up filling of microvias was developed. This plating formula can fill the microvias of PCBs and can also fill TSVs. The Ni-W filled TSVs exhibit good thermal stability after being annealed at 500 C for 4 h.

Experimental

The dimensions of the PCB fragments cut for the Ni-W filling plating were 4.2 × 6.0 cm2. The microvias were formed by CO2 laser ablation. The diameter and depth of the microvias were 80 μm and 40 μm, respectively. The sidewalls of the microvias were metallized by electroless copper plating in advance to deposit a 2–3 μm thick layer of copper before the filling plating.

TSVs were formed by a deep reactive ion etching (DRIE) process (i.e., the Bosch process). The thickness of the isolation layer (i.e., SiO2) in the TSVs formed by thermal oxidation was approximately 1–3 × 103 Å. The barrier layer was a TiN film with a thickness of 500 Å, which was conformably deposited by atomic layer deposition (ALD) for 600 cycles. The seed layer was deposited by sputtering to form a copper film with a thickness of 1.2 × 103 Å.

For the Ni-W filling plating, the copper seed was unnecessary. After these pretreatment processes, the TSV diameters were 20, 30, 40, and 50 μm, and their depth was 70 μm.

The base electrolyte for Ni-W plating consisted of 1.0 M Ni(SO3NH2)2, 0.05 M citric acid, 0.12 M sodium citrate, and 0.06 M Na2WO4. The additives used in this work were 60 ppm Cl−, 30 ppm 2-mercapto-5-benzimidazolesulfonic acid (MBIS), and 220 mL·L−1 commercial wetting agent that mainly contained sodium 2-ethylhexyl sulfate. The plating time was 1 h for PCB at a current density of 1.08 A·dm−2 (ASD) and 4 h for TSV at a current density of 0.27 ASD. The flow rate of air-bubble agitation during the filling plating was 2.0 L·min−1 for PCB and 1.5 L·min−1 for TSV. An uniform bubble distribution were controlled by a small tube with many small holes to be embedded at the bottom of the plating bath.33 A commercialized copper plating formula was used to fill TSVs for comparison of thermal reliability.

The cross-sections of PCB and TSV were observed using optical microscopy (OM, Olympus BX51). Three-dimensional imaging of the Ni-W pillars after silicon removal by immersion in a concentrated NaOH solution at 80 C were taken by scanning electron microscopy (SEM, Zeiss UltraPlus). The tungsten content in the Ni-W alloy was measured by energy-dispersive X-ray spectroscopy (EDS) (JEOL JSM-6010LA).

Results and Discussion

Figure 1a1, 1a2 and 1b1, 1b2 show that the Ni-W plating solution can achieve bottom-up filling of microvias at 25 C and 40 C. When the plating temperature was elevated to 55 C, the filling performance significantly decreased (see Fig. 1c1, 1c2) and even conformal deposition occurred at 60 C, as shown in Fig. 1d1, 1d2. The conformal content incorporated into the Ni-W deposit increased with increasing plating temperature, as confirmed by curves (a) and (b) in Fig. 1c1. In fact, temperature rather than the WO4−2 concentration was the critical factor for increasing the tungsten content in the plated Ni-W alloy.34–35 The tungsten content was not uniformly distributed inside the microvias. The tungsten content deposited at the via bottom was greater than that at the via top, as demonstrated by the curves (a) and (b) in Fig. 1e. The gradient of the tungsten content may be caused by the consumption of WO4−2 during the filling plating. The adhesion of the Ni-W film onto the copper substrate improved with increasing the plating temperature.

To evaluate the CTE issue of the filled materials in the microvias, TSVs were filled by copper electroplating and were subjected to a thermal annealing test. Figure 2 shows that the filled copper was not

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The plating formula was composed of $1.0 \text{ M Ni(SO}_3\text{NH}_2)_2$, $0.05 \text{ M citric acid}$, $0.12 \text{ M sodium citrate}$, $0.06 \text{ M Na}_2\text{WO}_4$, $60 \text{ ppm Cl}^-$, $30 \text{ ppm MBIS}$, and $220 \text{ mL}\text{L}^{-1}$ wetting agent. The current density was $1.08 \text{ ASD}$. The plating time was $60 \text{ min}$. The flow rate of air-bubble agitation during plating was $1.5 \text{ L}\text{min}^{-1}$. The plating temperature was $(a1, a2) 25^\circ \text{C}$, $(b1, b2) 40^\circ \text{C}$, $(c1, c2) 55^\circ \text{C}$, and $(d1, d2) 60^\circ \text{C}$. The depth and diameter of the microvias were $40 \mu\text{m}$ and $80 \mu\text{m}$, respectively. $(a2-d2)$ were shown to confirm the reproducibility of $(a1-d1)$.

The same thermal test was conducted again with the TSVs filled with Ni-W alloy, as shown in Fig. 3. Figure 3a1–1d1 shows that the Ni-W plating solution also can achieve void-free superfilling of TSVs, similar to the copper plating solution (see Fig. 2). The filled Ni-W alloy exhibits excellent thermal stability because the incorporated tungsten decreases the average CTE of the filled Ni-W alloy. Therefore, metallic cracks, voids and protrusions were not observed after the thermal annealing test at $500^\circ \text{C}$ for $4 \text{ h}$, as confirmed by the OM images shown in Fig. 3a2–3d2 and the SEM images shown in Fig. 3e, 3f. No Cu$_3$Si compound was observed in Fig. 2e because the barrier layer (i.e., TiN) was tightly and densely deposited on the sidewall of the TSVs.

To verify the Ni-W alloy pillars, a silicon wafer was removed by chemical dissolution in a concentrated NaOH solution at $80^\circ \text{C}$. Figure 4a–4d shows that these Ni-W alloy pillars with different aspect ratios are perfect, without voids. The tungsten content incorporated into the Ni-W alloy pillars was measured by EDS; the results are shown in Fig. 4e. Similarly, the higher plating temperature resulted in greater tungsten content. The tungsten content deposited at the via bottom was always higher than that at the via top. In addition, when we compare the cure (a) shown in Fig. 1e with the curve (a) shown in Fig. 4e, it shows that a high aspect ratio of the via feature results in a high tungsten content at the via bottom due to different deposition rate and the corresponding WO$_4^{2-}$ consumption rate during the plating.

Regarding the average CTE of Ni-W alloy, Dosovitskiy et al. derived a simple empirical equation to calculate the average CTE (from $20^\circ \text{C}$ to $800^\circ \text{C}$) value for Ni-W alloys as follows

\[
\text{CE}_{\text{average}} = \left[15.63 - 0.416[W]\right] \times 10^{-6} \cdot \text{K}^{-1} \times 10^6 \cdot \text{C}^{-1}
\]
The diameters of the TSVs were (a, b) 30 μm, (c) 40 μm, and (d) 50 μm. The depth of the TSVs was 70 μm.

where [W] is the tungsten content in atom%. According to equation 1, the CTE_{average} of the filled Ni-W was decreased theoretically from $15.63 \times 10^{-6}$ C$^{-1}$ of a pure nickel to approximately $14.2 \times 10^{-6}$ C$^{-1}$ of the filled Ni-W alloy at 55°C, as shown by curve (c) in Fig. 1e for the PCB. For TSV, the CTE_{average} of the filled Ni-W was decreased theoretically from $15.63 \times 10^{-6}$ C$^{-1}$ of a pure nickel to approximately $14 \times 10^{-6}$ C$^{-1}$ of the filled Ni-W alloy at 55°C, as shown by curve (c) in Fig. 4e. These average CTE values are very close to the theoretical and calculating results, and is lower than the CTE of $17 \times 10^{-6}$ C$^{-1}$ of a pure copper at 25°C. Hence, after the thermal test, the filled Ni-W alloy was still stable.

Conclusions

Microvias of a PCB and TSVs of a wafer were superfilled with Ni-W alloy using an electroplating process. The Ni-W plating formula composed of citric acid, sodium citrate, MBIS, and a wetting agent achieved void-free Ni-W superfilling of microvias and TSVs. The theoretically calculated CTE_{average} of the filled Ni-W alloy can be reduced from $15.63 \times 10^{-6}$ C$^{-1}$ of a pure nickel to approximately $14 \times 10^{-6}$ C$^{-1}$ at the plating temperature of 55°C, resulting in an average tungsten content of 4 atom%, which is in agreement with the previous works. The filled Ni-W alloy has a low CTE_{average} and exhibits excellent thermal stability compared with the copper process.

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Figure 4. SEM images of the Ni-W pillars, the tungsten content incorporated into the Ni-W pillars, and their corresponding average CTE obtained from Equation 1. The Ni-W pillars were obtained after TSVs were fully filled with Ni-W deposit and the silicon wafer was removed by chemical dissolution in a concentrated NaOH solution. The plating formula conditions were the same as those in Fig. 3. The diameters of the TSVs were (a, b) 30 μm, (c) 40 μm, and (d) 50 μm. The depth of the TSVs was 70 μm.