Five-Minute TSV Copper Electrodeposition

Kazuo Kondo,a,* Chikara Funahashi,a Yuko Miyake,b Yasuhiro Takeno,a Taro Hayashi,a,** Masayuki Yokoi,a,* Naoki Okamoto,a,* and Takeyasu Saitoa***

aDepartment of Chemical Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan
bTosetzu Inc., Itakano-shi, Saitama 358-0054, Japan

TSV (Through Silicon Via) is a promising interconnection for the next generation smartphone, driving assistance and medical care system because of its high speed image processing and low energy consumption. Conventional TSV electrodeposition requires 15 minutes to 1.5 hour due to the application of a low current of less than 10 mA/cm². Two shapes of vias have been used, columnar and conical shapes. Columnar shape via has acute edges at via mouth and the current lines concentrates at these edges, hence introducing void. In conical shape via, the acute angle at via bottom concentrates the current lines, hence improving bottom up filling. Using conical vias, we are able to electrodeposit a 6 μm diameter and 25 μm deep TSV via within 5 minutes. A very high on-current of 90 mA/cm² is available without any void formation.

© The Author(s) 2014. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0751414jes] All rights reserved.

Manuscript submitted June 24, 2014; revised manuscript received September 5, 2014. Published October 17, 2014. This was Paper 1679 presented at the Cancun, Mexico, Meeting of the Society, October 5–9, 2014.

TSV is a promising interconnection for the next generation smartphone, driving assistance and medical care system because of its high speed image processing and low energy consumption. Columnar shape via has acute edges at via mouth and the current lines concentrates at these edges, hence introducing void. Conventional TSV electrodeposition requires several 15 minutes to 1.5 hours due to the application of a low current of less than 10 mA/cm². This long time electrodeposition prevents TSV realization.

K.Kondo have electrodeposited a 10 μm diameter and 70 μm deep via within 35 minutes. O.L. Oulou, A.RAdicic and P.M. Verecken have used a partially covered Ta cap layer and 15 minutes was required to electrodeposited the via. By using the same commercial additives, a 5 μm diameter and 40 μm deep via has electrodeposited in 1.5 hours. H.Kadota have used a pulse current with a long off-time of 1.0 sec at a current density of 10 mA/cm². It takes 90 minutes to electrodeposited the 10 μm diameter and 70 μm deep via. T.P.Moffat has electrodeposited donut shaped via using Cl and poloxamine additives at a potential of −0.650 V SSE with 17 minutes. Hence a further time reduction to several minutes is demanded.

Another issue to preventing TSV realization is that TSV consumes part of the device area. With RIE (Reactive Ion Etching), our conical-shaped via forming from the back side of a device, the device consumption can be avoided. This is because the smaller conical shape bottom areas are facing device side.

Experimental

Two via shapes have used, i.e., columnar and conical shapes. A 0.1 μm tantalum and 3 μm copper layers have sputtered. The times required to perfectly electrodeposited these vias have determined by evaluating the maximum current without voids. Figure 1 shows a cross section of a 30 μm diameter and 50 μm deep conical via (a) and of a 6 μm diameter and 25 μm deep conical via (b). For the Fig. 1a via, the electrodeposition time has compared to the columnar via of 30 μm diameter and 50 μm depth. For the (b) via, the electrodeposition time has compared to the columnar via of 5 μm diameter and 30 μm depth. By gradually increasing the current density and observing the void in the cross section, the maximum current density without voids gives the minimum electrodeposition time. We further have compared the minimum electrodeposition times to the electrodeposited columnar and conical vias. For the 6 μm diameter and 30 μm deep conical via (b), the columnar via of 5 μm × 30 μm has compared. This columnar via is already known to electrodeposited within 25 minutes.

The basic bath consists of 200 g/L CuSO₄ · 5H₂O, and 25 g/L H₂SO₄, HCl, SPS ((bis (3-sulfopropyl) disulfide, PEG) polyethylene glycol) and a leveler. A rotating disk electrode has used for the electrodeposition. The current source is an HA-151 potentiostat/galvanostat (Hokuto Dneko). The TSV via silicon substrates have attached to the cathode of the rotating disk electrode. The speed of the rotating disk electrode is 1000 r.p.m. Phosphorous copper is used as the anode. The current wave has controlled by an HB-21 pulse.

Figure 1. Cross sections of conical vias of 30 and 6 μm diameters. (a) 30 μm diameter (b) 6 μm diameter.

Figure 2. Periodic reverse current waveform.
generator (Hokuto Denko). The periodic reverse current waveform (PR current) has used for the electrodeposition. The PR current consists of three periods of $T_{on}$ (On-time), $T_{rev}$ (Reverse time) and $T_{off}$ (Off-time) (Fig. 2). The on-time is 200 ms, the reverse time is 10 ms and the off-time is 100 ms. The ratio of $i_{rev}/i_{on}$ is set equal to two. All the TSV samples have electrodeposited at room temperature. Prior to the electrodeposition, oxygen gas have bubbled through the solution for 30 minutes.

The via cross sections have prepared by polishing. The via silicon substrate has initially molded using a photo solidification resin and polished with emery papers and 0.3 μm Al2O3 colloidal silica. The silicon via cross sections have been observed by FESEM (Hitachi-4300). We have examined the void in the cross sections by gradually increasing the on-time current, $i_{on}$. The maximum $i_{on}$ without a void gives the minimum electrodeposition time.

**Results**

**Electrodeposition of columnar via of 30 μm diameter and 50 μm depth.**— Figure 3 shows the cross sections of the columnar via electrodeposited at $i_{on} = -5$ mA/cm$^2$, $-10$ mA/cm$^2$, $-15$ mA/cm$^2$. The bright dark portion in the SEM micrograph center is the electrodeposited via and dark portions on both sides of the via is the silicon. At $-5$ mA/cm$^2$, a 120 minute electrodeposition time has required. For $-10$ mA/cm$^2$, 60 minute and for $-15$ mA/cm$^2$, 40 minute times have required. For both $-5$ mA/cm$^2$ and $-10$ mA/cm$^2$, no voids are present. On the contrary, at $-15$ mA/cm$^2$, voids form at the via bottom (indicated by the arrow). Sixty minutes at $-10$ mA/cm$^2$ is the minimum electrodeposition time.

**Electrodeposition of conical via of 30 μm diameter and 50 μm depth.**— Figure 4 shows the cross sections of the conical via electrodeposited at $i_{on} = -5$ mA/cm$^2$, $-10$ mA/cm$^2$, $-15$ mA/cm$^2$. At $-5$ mA/cm$^2$, a 100 minute electrodeposition time is required. For $-10$ mA/cm$^2$, 50 minute and for $-15$ mA/cm$^2$, 35 minute times are required. For $-5$ mA/cm$^2$, $-10$ mA/cm$^2$ and $-15$ mA/cm$^2$, no voids are present. Additional high currents should be applied for this conical via.

Figure 5 shows the cross sections of the conical via electrodeposited at $i_{on} = -26$ mA/cm$^2$, $-28$ mA/cm$^2$, $-30$ mA/cm$^2$. At $-26$ mA/cm$^2$, a 20 minute electrodeposition time is required. At $-28$ mA/cm$^2$, 20 minute and for $-30$ mA/cm$^2$, 18 minute times are required. For both $-26$ mA/cm$^2$ and $-28$ mA/cm$^2$, no voids are present. On the contrary, $-30$ mA/cm$^2$ forms voids at the via bottom (indicated by the arrow). Twenty minutes at $-28$ mA/cm$^2$ is the minimum electrodeposition time. A reduction in the electrodeposition time of 67% is obtained by changing from a columnar to conical via with the same 30 μm diameter.

**Electrodeposition of columnar via of 5 μm diameter and 30 μm depth.**— Figure 6 shows the cross section of a columnar via of 5 μm diameter and 30 μm depth. This columnar via is already known to be electrodeposited within 25 minutes at $i_{on} = -5.5$ mA/cm$^2$ and $i_{rev}/i_{on} = 6.9$.

**Electrodeposition of conical via of 6 μm diameter and 30 μm depth.**— Figure 7 shows the cross sections of conical via electrodeposited at $i_{on} = -80$ mA/cm$^2$, $-90$ mA/cm$^2$ and $-100$ mA/cm$^2$. At $-80$ mA/cm$^2$, a 10 minute electrodeposition time is required. For $-90$ mA/cm$^2$, 5 minutes and for $-100$ mA/cm$^2$, 4 minutes. At $-100$ mA/cm$^2$ a void forms at the via bottom (indicated by the arrow). Five
minutes at $-90 \text{ mA/cm}^2$ is the minimum electrodeposition time. A reduction in the electrodeposition time of 75% is obtained by changing from a columnar to conical via with a 6 $\mu$m diameter.

There are two reasons which make possible to apply the high $i_{on}$ of $-90 \text{ mA/cm}^2$ for the conical via of 6 $\mu$m diameter. One is due to the concentration of current lines at the conical via bottom and may improve bottom up filling. The other is the formation of a recirculating vortex of Cu(I)thiolate, the accelerator, at the conical via bottom due to the electrolyte flow.8–14

**Figure 7.** Cross sections of conical via of 6 $\mu$m diameter. (a) $-80 \text{ mA/cm}^2$ 10 min (b) $-90 \text{ mA/cm}^2$ 6 min (c) $-100 \text{ mA/cm}^2$ 4 min.

**Conclusions**

TSV (Through Silicon Via) is a promising interconnection for the next generation smartphone, driving assistance and medical care system because of its high speed image processing and low energy consumption. Two shapes of via have been used, columnar and conical shapes.

1. To electrodeposit a columnar via of 30 $\mu$m diameter and 50 $\mu$m depth, 60 minutes is required at $-10 \text{ mA/cm}^2$. For the conical via of 30 $\mu$m diameter and 50 $\mu$m depth, a shorter time of 20 minutes is required at $-28 \text{ mA/cm}^2$.
2. To electrodeposit a columnar via of 5 $\mu$m diameter and 30 $\mu$m depth, 25 minutes is required at $-5.5 \text{ mA/cm}^2$. For the conical via of 6 $\mu$m diameter and 30 $\mu$m depth, an extremely shorter time of 5 minutes is required. A very high on-current of 90 mA/cm$^2$ is able to be used without void formation.

**References**

1. K. Kondo, *J. Electrochem. Soc.*, 156(12), D548 (2009).
2. K. Kondo, *J. Electrochem. Soc.*, 152(11), H173 (2005).
3. O. Luhn and A. Radisic, *Electrochem. & S-S Lett.*, 12(5), D39 (2009).
4. O. Luhn and C. Van Hoof, *Electrochimica Acta*, 54, 2504 (2009).
5. A. Radisic and O. Luhn, *Microelectronic Eng.*, 88, 701 (2011).
6. H. Kadota, *IEEE*, 13(3), 213 (2010).
7. T. P. Moffat and D. Josell, *J. Electrochem. Soc.*, 159(4), D208 (2012).
8. K. Kondo and T. Yonezawa, *J. Electrochem. Soc.*, 152(11), H173 (2005).
9. K. Kondo, *J. Electrochem Soc.*, 143(6), 1880 (1996).
10. K. Kondo, *J. Electrochem Soc.*, 144(2), 466 (1997).
11. K. Kondo, *J. Electrochem Soc.*, 145(3), 840 (1998).
12. K. Kondo, *J. Electrochem Soc.*, 145(9), 3007 (1998).
13. K. Kondo, *J. Electrochem Soc.*, 156(12), D548 (2009).
14. T. Hayashi and K. Kondo, *J. Electrochem Soc.*, 160, D1 (2013).