Communication—Conical TSV Filling within 30 Seconds

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Copper electrodeposition is a reliable technology to make through silicon via (TSV). However, the TSV processing cost is still high. 1, 2 The shortening of electrodeposition time directly lowers the electrodeposition cost by using less expensive equipment and clean-room area while the production capacity remains.

New additive finding and the optimization of electrodeposition conditions have reduced electrodeposition time and improved the reliability of TSVs. 3–5 Besides, applying an optimized PPR current in TSV electrodeposition significantly reduces the formation of void inside TSVs and increases current density. 6–13 Hong, S. C. et al. applied TSV electrodeposition significantly reduces the formation of void in columnar TSVs which have the same volume. The filling time of 30 μm columnar TSVs in 80 min and eliminated all defects. 7 Kondo et al. archived 60 min of filling for 10 × 70 μm columnar TSVs using the PPR current. 13 TSV electrodeposition time has dramatically reduced by using conical TSV shape, and new levelers. 8, 9, 10 Kondo et al. have successfully applied a higher current density to conical TSVs in comparison with columnar TSVs which have the same volume. The filling time of the 30 × 50 μm columnar TSVs was 60 minutes at −10 mA/cm2 while that of the conical TSVs was 20 min at −28 mA/cm2. 11 Hoang and Kondo filled 3 × 27 μm conical TSVs in 3 minutes with a electrolyte containing 10 mg/L of sulfonated diallyl dimethyl ammonium chloride copolymer (SDDACC). 10

In this research, a new leveler was characterized. The leveler contributed to the strong inhibition on TSV walls, therefore, a two-steps electrodeposition process including PPR current and DC were capable of being a higher current density, and reduced the filling time of 2 × 16 μm conical TSVs.

Table I. Electrodeposition conditions.

| Parameters                  | Conditions |
|-----------------------------|------------|
| Leveler                     | SDDACC     |
| TSV (μm)                    | 20 × 50    |
| Pulse (ms)                  | 100/200:10 |
| iion (mA/cm²)               | −30        |
| t (s)                       | 1200       |
|                            | 10 × 25    |
|                            | 100/200:10 |
|                            | −5/−30 DC  |
|                            | 20/10 DC   |

| Leveler         | NM         |
|-----------------|------------|
| TSV (μm)        | 20 × 50    |
| Pulse (ms)      | 100/200:10 |
| iion (mA/cm²)   | −30        |
| t (s)           | 1200       |
|                  | 10 × 25    |
|                  | 100/200:10 |
|                  | −5/−30 DC  |
|                  | 20/10 DC   |

The TSV silicon substrate chips were placed on a rotating disk (RD) and then deposited at 25°C and 1000 rpm. The PPR consists of three periods: 100 ms off time, 200 s on time, and 20 ms reverse time. An ion beam of JEOL IB90910CP polisher was applied for the cross-sectional sample preparation of 2 × 16 μm TSVs and the cross sections were observed by FE-SEM (Hitachi-4300).

The characteristic of electrolytes was monitored by the Cyclic Voltammetric Stripping (CVS) method at 1000 rpm and 10 rpm. The basic electrolytes contained 200 g/L CuSO4, 1H2O, 25 g/L H2SO4, the concentration of additional additives were 70 mg/L Cl−, 2 mg/L SPS, 25 mg/L polyethylene glycol 10000 (PEG). The concentrations of SDDACC and NM levelers are in Table I. The rotating disk electrode (RDE) is platinum with an area of 0.196 cm2. The voltage scan range was −0.5 V to 0.8 V vs. saturated calomel electrode (SCE) at 10 mV/s rate.

Electrolyte velocity flows over the TSVs was calculated from “Boundary Layer Theory” of H. Schlichting, 1979. 15 The flow pattern inside 2 × 16 μm TSV was simulated by COMSOL Multiphysics1 Modeling Software ver. 5.1. Table II show simulation parameters with open walls were slip walls, and TSV surfaces were non-slip walls.

Results and Discussion

The CVS of electrolytes containing different additives is shown in Fig. 1. The solid lines and the dash lines are the CVS of electrolytes measuring at 1000 rpm, and 10 rpm, respectively. In Figure 1a, the electrolytes contain 2 mg/L SPS and 70 mg/L Cl−. The cathodic area of CVS at 10 rpm shows a smaller electrodeposition rate, and less sensitive to potential than that at 1000 rpm. The forward cathodic current at 10 rpm reaches minimum at about −0.4 V vs SCE then

Table II. Electrolyte characteristics and parameters using in simulation.

| Para. | Value | Description       |
|-------|-------|-------------------|
| ρ     | 1140[kg.m⁻³] | Electricity density |
| cint | 1[ mole.L⁻¹ ] | Initial conc. |
| μ    | 1.9E-3[Pa.s] | Dynamic viscosity |
| Eeq  | 0[V] | Relat. equi. potent. |
| D1   | 5.7E-10[m².s⁻¹] | Diffusivity Cu²⁺ |
| D2   | 1.38E-9[m²/s] | Diffusivity Cu⁺ |
| R    | 9685.3365[cm.mol⁻¹] | Faraday cons. |
| T    | 8.3144621[J.mol⁻¹.K⁻¹] | Gas Cons. |
| η    | 298[K] | Over potential |
| n    | 1 | Exchange elec., 1 step |
Figure 1. Characteristic of leveler NM: CVS at 10 rpm and 1000 rpm of 2 mg/L SPS, 70 mg/L Cl\(^{-}\) electrolyte (a); 2 mg/L SPS, 70 mg/L Cl\(^{-}\), 25 mg/L PEG (b); 2 mg/L SPS, 70 mg/L Cl\(^{-}\), 25 mg/L PEG, 16 mg/L NM (c); 2 mg/L SPS, 70 mg/L Cl\(^{-}\), 25 mg/L PEG, 16, 64 and 128 mg/L NM (d).

Figure 2. Flow pattern of electrolyte inside 2 × 16 μm conical TSV.

slightly goes up at −0.5 V. That indicates the mass transfer of Cu\(^{2+}\) to the electrode surface reaches limit at 10 rpm and −0.4 V. This mass transfer limit causes the anodic area at 10 rpm is smaller than that at 1000 rpm.

The addition of PEG to the electrolyte makes a clear reduction of cathodic current at both 10 rpm, and 1000 rpm (Fig. 1b). The cathodic currents measuring at 1000 rpm, −0.5 V (vs SCE) and 10 rpm, −0.5 V (vs SCE) are −21.5 mA, and −19 mA, respectively. However, the anodic area at 1000 rpm is much smaller than that at 10 rpm. It is explained by more PEG accumulates on the RDE surface at 1000 rpm.\(^{10}\) The charge for stripping copper is less than the requirement, because, instead of becoming the cupric ions, a part of copper atoms becomes cuprous ions then disperses to the electrolyte especially at a higher rotating rate.\(^{10,16–18}\) Then, they are oxidized to cupric by dissolving oxygen in bulk.

In the presence of 16 mg/L NM, the positive polarization part of CVS at 1000 rpm shows a redirection point at 0.46 V vs SCE (Fig. 1c). That means there were two layers of copper, which are different in resistivity, covered on the RDE surface. The inside layer requires a higher overpotential to prevent the reduction of dissolution rate at redirection point, this account for the formation of an inhibition layer by NM at the high rotating rate. The present of this leveler with repeating ammonium groups also causes the resistance of copper electrodeposition until −0.2 V vs SCE.

Fig. 1b and Fig. 1c, the dash lines have a similar shape and area, hence, the effect of 16 mg/L NM on CVS at 10 rpm is not clear. However, the effect of NM on CVS at 10 rpm increases with the higher concentrations (Fig. 1d). The anodic area reduces clearly, especially at 128 mg/L.

The flow pattern of liquid in the 2 × 16 μm depth TSV is shown in Fig. 2, vortexes reach to the two-thirds of the TSV. When a PPR current is applied, the reverse period generates massive cuprous ions in the form of Cu(I) thiolate trapping inside vortexes, accumulating at the via bottom and preferring accelerates via bottom.

Normally, the copper electrodeposition fills TSVs by forming and building up a conical surface.\(^{5,9,13}\) The Fig. 3a, conical surfaces resulted from the columnar TSVs filling which used the PPR current, and the standard four-additive electrolyte including Cl\(^{-}\), SPS, PEG, and SDDACC. The conical surfaces form because of the electrodeposition rate gradually increases from the top to the bottom of TSVs by the contribution of additives and the acceleration of Cu(I)thiolate at the TSV bottom. However, the novel NM leveler shows a different behavior, the electrodeposition rate on TSV wall is small, and the bottom raises up (Fig. 3b). This only appears at a certain condition with a high concentration of leveler NM. That means the leveler NM contributes to the formation of a strong inhibition layer on the TSV
current is applied as a first step before applying a DC to get the fast bottom-up filling. An extreme fast filling was obtained in 30 s by two steps electrodeposition: 20 s using the PPR, and 10 s using the DC. The first step in 20 s prevents the TSV mouths close and forms the inhibition layer on the TSV walls and the acceleration area at the bottom of TSVs. The second step in 10 s applied a very high current density to fill full TSVs (Table I).

Conclusions

Leveler keeps an important role in TSV filling, being a polymer containing ammonium groups it acts as an inhibitor on the TSV outside and wall. Electrolyte bath containing 16 mg/L NM reduced significantly the anodic area at 1000 rpm and showed a strong TSV wall inhibition. Copper electrodeposition on the walls of 20 μm diameter and 50 μm depth TSVs was small, therefore, the TSV bottom raises up.

The conical TSV was successful filling in a very short time by applying the two-step electrodeposition; the second step was applied the high DC density. The result obtained thanks to the advantage of the conical shape and the new leveler.

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