Cu superconformal filling of through glass vias (TGV) of aspect ratios (AR) 6:1 and 10:1 for glass interposer applications is achieved by DC electroplating in the presence of the additives tetraniobutiric acid Cl\(^{-}\) (TNBT) and nitroblue tetrazolium Cl\(^{-}\) (NTBC) in acidic CuSO\(_4\)/H\(_2\)SO\(_4\)\(\cdot\)H\(_2\)O formulations. Filling takes place by the so-called ‘butterfly’ mechanism that nucleates hemispherical or X-shaped Cu plugs in the centers of TGV’s while keeping the thickness on external surfaces low. Holes of AR 6:1 are filled in 3 h at 2.5 mA cm\(^{-2}\), using a bath composed of 40 ppm TNBT, 80 ppm Cl\(^{-}\), 0.88 M CuSO\(_4\), and 0.5 M CH\(_3\)COOH under stagnant conditions. Increasing [TNBT] to 80 ppm and [Cl\(^{-}\)] to 120 ppm in the presence of 0.3 M CH\(_3\)COOH allows filling of 10:1 AR holes in 12.5 h at 1.0 mA cm\(^{-2}\) while maintaining thin surface plating. In the case of NTBC, 6:1 holes are filled in 4–5 h at 2.5–4.0 mA cm\(^{-2}\), and 10:1 holes are filled in 12–13 h at 1.0 to 1.5 mA cm\(^{-2}\) in a slowly stirred bath containing 0.88 M CuSO\(_4\), 80 ppm Cl\(^{-}\), 0.6 M H\(_2\)SO\(_4\), and 45–50 ppm NTBC. Optimization of bath composition is necessary to avoid void-formation in the holes. Effects of composition on overvoltage and Cu surface topography are discussed.

The drive toward higher circuit density and higher operating frequencies in electronic packaging has led to the employment of interposers between the Si chip and the underlying package. Si was the initial material used for interposers because of its coefficient of thermal expansion (CTE) match to the Si chip and the familiarity of wafer fabrication facilities in Si processing. Recently, glass has gained attention as a candidate interposer material. The CTE of borosilicate glass, 3.2, is reasonably close to that of Si, 2.9, and a wide range of CTE’s is available by changing the glass composition. Methods have been developed for producing and handling glass in thin, flexible roll formats offering the prospect of low cost, and a wider range of size options than Si. Along with that, glass manufacturers have developed high speed methods for producing through-holes in glass with thicknesses between 100 and 500 \(\mu\)m. The high dielectric constant of glass and the minimal diffusion of Cu into glass simplify processing by eliminating the barrier layers (e.g., TiN, TaN) needed with Si, and allows higher operating frequencies.

Through glass vias (TGV) are needed to make electrical connections between the top and bottom surfaces of interposers. This can be done with conformal Cu plating, but especially in the case of glass it is also desirable to completely fill the TGVs with Cu to compensate for the poorer thermal conductivity of glass compared to Si and improve the overall thermal conductivity of the interposer. Filling also enables formation of a flat surface for buildup of subsequent layers or for component attachment. Superconformal filling techniques have already been developed starting in the 1990’s for filling ‘blind’ features such as trenches and vias by Cu electroplating using combinations of suppressors, accelerators and leveling agents. Models have been developed to explain the preferential filling at the bottoms of ‘blind’ features through the interplay of “accelerators” such as SPS and suppressors such as PEG. In the case of Si, through vias (TSV) have been generated by first filling vias as blind vias, then thinning the back side of the wafer by CMP until the bottoms of the filled vias are interdigitated, thereby producing filled TSVs or by first sealing one end of the TSVs then filling them as blind vias. In the case of glass, where through-holes may be formed directly into the glass without the need for mechanical thinning, it is our intent to develop Cu plating processes to fill these holes as TGVs (open on both ends) instead of as blind vias. The aforementioned plating methods for filling of blind vias do not work well when directly applied to filling of TGVs, and a different approach is needed.

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be reducible to highly colored species,\textsuperscript{29,30} and loss (consumption) of these additives is proposed to occur through their reduction during Cu plating. Simulations and plating results for through-hole Cu filling in a proprietary 3 additive (suppressor, accelerator, leveler) Cu / methane sulfonic acid system have recently been presented by Shi et al.\textsuperscript{31} Previous work by our group applied TNBT to the filling of higher aspect ratio TGVs, AR = 6 (diameter = 50 μm, thickness = 300 μm) in glass samples. This was accomplished in 3 hours at a current density of 2.5 mA cm\textsuperscript{-2} under stagnant conditions in both “acid-free” and 0.1 M CH\textsubscript{3}COOH-containing Cu sulfate solutions.\textsuperscript{18} Stirring was found to lead to voids in the TGVs.\textsuperscript{18} In the present work we extend the use of TNBT in 0.3 M CH\textsubscript{3}COOH under stagnant conditions to the filling of 10:1 AR holes by optimization of current density, and report on the use of the related additive NTBC for filling of both 6:1 and 10:1 AR holes. An optimum level of solution agitation was found to be necessary to ensure continuous, void-free filling in the case of NTBC.\textsuperscript{15} Voltages during constant current plating and the effects of added acids on voltage are compared for TNBT and NTBC. The observed voltages are compared to literature values for the reduction potentials of TNBT and NTBC and call into question the degree of reduction taking place under our operating conditions. Cu surface topographies are examined by SEM and compared for various plating formulations. Cross sections of plated TGV’s are examined by optical microscopy.

**Experimental**

**Reagents.**— The following chemicals were used in this work as received from the suppliers: CuSO\textsubscript{4}·5H\textsubscript{2}O (Sigma-Aldrich), H\textsubscript{2}SO\textsubscript{4} (doubly distilled, GFS), HCl (doubly distilled, Sigma Aldrich), HNO\textsubscript{3} (JT Baker 69%), TNBT (Sigma Aldrich), NTBC (Sigma Aldrich), NaCl (JT Baker), CH\textsubscript{3}COOH (GFS Double distilled), HCOOH (JT Baker 69%), TNBT (Sigma Aldrich), NTBC (Sigma Aldrich), NaOH 99%-100% JT Baker, amino propyl triethoxy silane (Sigma-Aldrich), PdCl\textsubscript{2} (GFS Chemicals, 99.999%), dodecyl sulfate sodium salt (JT Baker 88%), ethanol (Pharmco-AAPER, 200 proof ACS/USP grade), NaClO (JT Baker 98%), NaCl (JT Baker 99%), potassium citrate (98% Alfa Aesar), PdCl\textsubscript{2} (GFS Chemicals, 99.999%), dodecyl sulfate sodium salt (Sigma-Aldrich ≥ 99%), Polyvinyl pyrrolidone (MW 29,000, Sigma-Aldrich), Cu wire (99.99% Sure Chemetals), 0.04–0.06% P, phosphorized Cu anode (Kocour). All solutions were prepared with Barnstead Nanopure water with resistivity above 18.2 MΩ cm.

**Cu metallization.**— All plating experiments were done on Corning Eagle XG borosilicate glass substrates supplied by Corning Inc that were 300 μm or 500 μm thick containing 50 μm (nominal) diameter holes drilled with a proprietary process on 100 or 200 μm centers. Test samples of 1.75 cm × 1.75 cm were cut from 7 cm × 7 cm glass panels with 20 × 20 arrays of TGVs in the center of the sample. They were subjected to the hybrid approach for metallization of glass interposers as shown in Figure 2.\textsuperscript{7} The Cu coated glass samples were then transferred to the superfilling bath. Different bath compositions and plating conditions were used to achieve superfilling and different qualities of plated Cu. Electrochemical processes were done in a three-electrode configuration using a Princeton Applied Research Model 173 Potentiostat/Galvanostat with a model 276 Interface and model 270/250 Research Electrochemistry Software 4.00, or a Princeton Applied Research Model Versastat 3 Potentiostat/Galvanostat and Versa-studio v 2.2 software. Phosphorized Cu was used as counter electrode, and Cu wire or a saturated mercury sulfate electrode (MSE) were used as reference electrodes. pH measurements were made at room temperature with an Oakton model pH Testr 30. A Fisher Isotherm Digital Stirring hotplate (11-300-49SHP) was used to provide a controlled and reproducible stirring rate. Plating was done in a 150 mL beaker. A 2.5 cm stir bar was used when stirring was required. Two anodes with a combined area of about 9 cm\textsuperscript{2}, three times the sample area, were placed opposite each other in the beaker. Samples were placed in the center of the beaker above the stir bar with their holes parallel to the line between the two parallel anodes which are separated by a distance of about 5 cm in a 150 mL beaker.

**Cross sections.**— Samples were cut with a diamond scribe and mounted in epoxy resin which had air bubbles removed by vacuum before curing at room temperature for 8–12 hours. Care was taken to prevent damaging the TGV’s. Mounted samples were ground on a rotating disc using a series of Si carbide papers (iC grades No. 240, 400, 600, 800 and 1200) followed by an ultrasonic water rinse after each grade. Polishing was done on polishing discs covered with soft cloth impregnated with alumina slurry with particles from 5 μm to 1 μm diameter. Final imaging was done with a Carl Zeiss Axiosc mager 2 at 200× magnification using AxioVision software. Scanning electron microscopy (SEM) performed for morphological characterization (top view) was carried out using a high resolution FEG-SEM Zeiss Supra 55 VP (variable pressure) coupled with a through-the-lens detector at an accelerating voltage of 8–10 kV for imaging at magnification as high as 20,000 times.

**Results**

**Superfilling of AR 6 and AR 10 holes using TNBT.**— Earlier work by our group\textsuperscript{18} demonstrated the nucleation and further development of

\[\text{Nitrotetrazolium blue Cl- monohydrate (NTBC)}\]

\[\text{Tetranitroblue tetrazolium Cl- (TNBT)}\]

![Figure 1. Molecular structures of NTBC and TNBT.](image)

![Figure 2. Process flow for Cu metallization of TGVs.](image)
of the superfilling process of 6:1 AR, 50 micron diameter holes in glass in 3 h at 2.5 mA cm$^{-2}$ in stagnant, TNBT-containing 0.88 M CuSO$_4$ baths with no added acid (Fig. 2 in Ref. 18). It was also observed that the addition of 0.1 M HCOOH or 0.1 M CH$_3$COOH and 0.5 M Na$_2$SO$_4$ eliminated the brownish color that developed on the Cu surface in the “acid-free” TNBT bath, possibly due to decreasing the level of additive incorporation. Increasing the Cl$^-$ concentration from 20 ppm to 80 ppm reduced the thickness of Cu plated on the surface (Fig. 3 in Ref. 18). Finally it was shown that increasing current density to 4 or 5 mA cm$^{-2}$ in the acid-free bath leads to formation of voids in the holes (Fig. 1 in Ref. 18). In the present work we illustrate in Figure 3 the progression of the superfilling process in Cl$^-$ and TNBT-containing Cu plating bath with the addition of 0.3 M CH$_3$COOH. The shape of Cu deposits in the presence of acid, Figures 3A and 3B, shows a more pronounced X-shape nucleated preferentially at the center of the hole after 0.5 hour of plating, unlike the hemispherical shape in the absence of acid (Fig. 2A and 2B in Ref. 18). The X-character remains more or less preserved not only for 2 hours when a plug first forms in the middle of the hole and then keeps growing toward the TGV openings (Figures 3B and 3C, respectively), but remnants of it (two “V”s) can be seen until the very end of the filling process (as already shown in Fig. 3E in Ref. 18). These observations suggest that the presence of CH$_3$COOH in the plating solution results in linearization of the gradient in the amount of adsorbed TNBT from the TGV opening to the middle of the hole thus leading to a clear X-shaped Cu nucleation and growth during the deposition process. Overall, the superfilling results obtained in the absence and presence of CH$_3$COOH demonstrate a behavior quite similar to the “butterfly” plating described earlier by Dow et al. 17 Generally, the addition of CH$_3$COOH to the plating solution was done to lower the pH thus reducing the risk of incorporation of organics when plating in ‘acid-free’ bath. 8, 20 Our experience in using higher concentrations than 0.1 M CH$_3$COOH suggests that up to 0.3 M (in this study) added to the standard Cu plating bath along with 0.5 M Na$_2$SO$_4$ improves the quality of hole filling after 3 h plating as shown in Figure 4A (TGVs filled completely with little deposit on the flat surface). However, when 0.5 M H$_2$SO$_4$ was added for this purpose, filling was not achieved, and instead excess plating at the entrances eventually resulted in complete blockage and led to formation of large voids in the middles of the holes as shown in Figure 4B. Dow et al. observed a similar effect for H$_2$SO$_4$ addition except when used at a low and very narrow concentration range, 3.06 × 10$^{-2}$ to 1.98 × 10$^{-2}$ M. 20 Overall, TNBT itself appears to be stable when sulfuric acid is added to the plating bath, but once plating potential is applied a light yellow precipitate forms and becomes suspended in solution before settling out. A precipitate also forms in solutions containing 0.3 M CH$_3$COOH, but at a much lower rate, requiring over 15 h to become significant. Plating voltages over time for acid-free TNBT Cu plating baths at current densities from 1 to 5 mA cm$^{-2}$ are shown in Figure 5A. Addition of 0.3 M CH$_3$COOH to the TNBT bath, Figure 5B, has the effect of increasing the overpotential (potential shifts from −0.503 V to −0.575 V vs MSE while the current density in both cases is 2.5 mA cm$^{-2}$). If CH$_3$COOH were acting simply as an electrolyte it would be expected to slightly decrease the overpotential by increasing the solution conductivity (though the contribution to solution conductivity would be small since CH$_3$COOH with a pK$_a$ of 4.76 is mostly un-dissociated at the pH of about 3.1 typical of a CuSO$_4$ solution). The change in the opposite direction could be due to adsorption of CH$_3$COO$^-$ ion or CH$_3$COOH causing an increase in the charge transfer resistance.

Attempts to superfill TGVs of 10:1 AR using a current density of 2.5 mA cm$^{-2}$, effective for 6:1 TGVs, led to the formation of two plugs, one below each entrance, leaving large voids at the centers of the holes, as shown in Figures 6A, and 7A. This problem was solved by reducing the current density. Comparisons of Figures 6A and 6B, and 7A and 7B show that the sizes of the voids at the centers of the holes are reduced by lowering the current density to 1.5 mA cm$^{-2}$. Further reduction of current density to 1.0 mA cm$^{-2}$ leads to formation of a single plug after about 4.5 h as shown in Figure 6C, and nearly complete filling of the holes in 12.5 h without formation of voids in the middles, as shown in Figure 7C. The observation of double plugging of 10:1 AR holes at higher current densities (2.5 and 1.5 mA cm$^{-2}$) may be explained by the hypothesis that the slow rate of diffusion of TNBT to the middle is not able to “keep up with” the rate of Cu deposition, and is thus not able to provide the level of inhibition needed to suppress plating near the entrances. Another important observation is that the combination of high [Cl$^-$], 120 ppm, and the addition of 0.3 M CH$_3$COOH leads to a very low surface Cu thickness even after 12.5 hours of plating as shown in Figure 7C. This is a highly desirable result in cases where surface planarization is to be employed.

Superfilling of 6:1 and 10:1 aspect ratio holes using NTBC.— The structure of NTBC is the same as that of TNBT except for the absence of two NO$_2$ groups, as shown in Figure 1. While addition of H$_2$SO$_4$ to plating solutions containing TNBT appears to eliminate the
Figure 5. Potential transients for Cu plating for different bath compositions and current densities. (A) standard bath containing 0.88 M CuSO₄, 40 ppm TNBT, 40 ppm Cl⁻ at current density as labeled; (B) standard bath composition as for A + 0.3 M CH₃COOH at current density of 2.5 mA cm⁻²; (C) plating bath containing 0.88 M CuSO₄, 45 ppm NTBC, 40 ppm Cl⁻ + 0.6 M H₂SO₄ in the current density range of 1.0–4.0 mA cm⁻².

desired concentration gradient between surface and holes producing a more conformal deposit, addition of a relatively high concentration of H₂SO₄, 0.5 M to 0.6 M, to a bath employing NTBC leads to good superfilling following a ‘butterfly’ growth progression. Prolonged plating (e.g. 12 h) leads to pale yellow precipitate formation. Figures 8A and 8B show an “X” shaped plug in cross sections of 6:1 and 10:1 AR holes after plating for 3 h at 2.5 mA cm⁻², or 7.5 h at 1.5 mA cm⁻², respectively, in this solution. AR 6 holes are filled in 4 h at the relatively high current density of 4 mA cm⁻² or in 5 h at lower current density of 2.5 mA cm⁻² using slow stirring (50 rpm) in both cases, as shown in Figures 9A and 9B. A current density between 2.5 and 4 mA cm⁻² was found to work best for 6:1 AR holes. Holes of AR 10 are filled in 12 h at 1.5 mA cm⁻² and in 13 h at 1 mA cm⁻² as shown in Figure 10. The time required for filling is longer than for TNBT baths, but plating under the acidic conditions used with NTBC is expected to reduce incorporation of organics and result in a higher quality Cu deposit.

Plating with NTBC/H₂SO₄ in a stagnant environment even at the relatively low current density of 2.5 mA cm⁻² leads to serious voiding as seen in Figure 9C. Voiding is also a problem at higher stirring rates as shown in Figure 9D where stirring was done at 500 rpm presumably causing loss of the needed concentration gradient between surface and holes. Thus, some intermediate level of stirring is needed.

As shown in Figure 5C and Table I, the voltages measured while plating in NTBC baths containing 0.6 M H₂SO₄ are more negative than those for plating in an ‘acid-free’ TNBT bath at identical current densities. The addition of H₂SO₄ would be expected to lower the solution resistance and reduce the necessary applied voltage. The shift in the opposite direction suggests that a more effective inhibiting layer is formed on the Cu surface by NTBC/H₂SO₄. As mentioned above, the addition of 0.3 M CH₃COOH to the TNBT bath, which causes a decrease in pH from 3.1 to 2.4, also shifts the voltage while plating at 2.5 mA cm⁻² down to −0.58 V vs MSE, closer to that for the NTBC/H₂SO₄ bath at its even lower pH near 0.6. In that case, the adsorption of CH₃COOH/CH₃COO⁻ is suspected to be one of the contributors to this shift.

SEM images of the various surface topographies of Cu deposited from three TNBT containing solutions and one NTBC containing solution are compared in Figure 11. The CuSO₄ and Cl⁻ concentrations are the same in all cases, and the additives are present at 40 ppm. The acid-free TNBT bath and TNBT/H₂SO₄ bath represent two
extremes. The former is known to produce deposits with high levels of incorporated organic material\(^1\) (Figure 11A) while the latter (Figure 11B) does not involve the same extent of incorporation,\(^1\) but also does not provide effective hole filling. The surface topographies from these two baths are quite different, and both differ from the topographies produced by the CH\(_3\)COOH/TNBT bath (Figure 11C) or the NTBC/H\(_2\)SO\(_4\) bath (Figure 11D). Topographies 11C and 11D look quite similar despite the use of different additives and different acids as supporting electrolytes.

**Discussion**

Inhibiting effect of the additives.— Clearly, both of the tetrazolium salts used in this work are capable of inhibiting plating on the surface and near TGV entrances while allowing faster plating in the middles of the holes, thereby leading to filling. Dow et al. have discussed many factors potentially contributing to the establishment of the gradient in plating rate needed to achieve filling.\(^{20}\) Specific adsorption of Cl\(^-\) and SO\(_4^{2-}\) ions onto the Cu is expected to increase the adsorption of the positively charged tetrazolium ions through electrostatic interactions.\(^{20}\) Adsorption of the large, flat tetrazolium ions is expected to increase the charge transfer resistance by simple physical blocking, reducing the available Cu surface area.\(^{20}\) According to Dow’s view the inhibiting effect of TNBT as well as its rapid adsorption onto a Cu surface, are reflected by the large and rapid cathodic shift in voltage that accompanies the addition of TNBT to a CuSO\(_4\) solution during constant current plating.\(^{17}\) Also, the plating voltage is driven more negative as the stirring rpm is increased showing that greater inhibition is achieved by increasing the flux of the tetrazolium ion to the surface at the low concentrations typically used, e.g. 4.6 × 10\(^{-5}\) M (40 ppm).\(^{17}\) This simple adsorption blocking effect can be exploited to create a gradient in the degree of ‘inhibition’ by selectively increasing the flow of solution over the surface while leaving the solution inside the holes relatively stagnant. Less inhibition inside the holes allows a higher plating rate there, while plating on the surface is suppressed. Even under stagnant conditions the flux to the interior of a hole will be less than that to the exposed surfaces.
Effect of the solution pH.— Solution pH is an important parameter when plating in the presence of TNBT. Dow et al. showed that addition of 0.08 M H$_2$SO$_4$ while plating at a constant current density of 1.62 mA cm$^{-2}$ in a CuSO$_4$ bath containing 43 ppm TNBT caused a rapid shift in voltage from −0.43 V to −0.56 V (vs MSE reference electrode), indicating an increase in the interfacial resistance$^{20}$ (opposite the direction expected for an increase in solution conductivity). The contribution of the added sulfate ion to this change in potential is expected to be small since that bath already contained 0.88 M CuSO$_4$, and most of the effect can be associated with the increase in [H$^+$]. Further additions of sulfuric acid had little effect on the voltage indicating that a threshold had been crossed after which the surface was no longer sensitive to the acid. Weak organic acids were capable of the same rapid shift in voltage to more negative values if they were added no longer sensitive to the acid. Weak organic acids were capable of the same rapid shift in voltage to more negative values if they were added.

Table I. Steady state potentials developed during Cu electrodeposition at various current densities. The most negative values observed over approximately 2 h are shown in the table.

| Solution composition | Average current density (mA cm$^{-2}$) | Observed steady state potential vs MSE (from Fig. 4) | Potentials vs NHE |
|---------------------|--------------------------------------|---------------------------------------------------|------------------|
| TNBT (40 ppm), Cl$^-$ (40 ppm) | 1.0 | −0.436 | 0.218 |
| TNBT (40 ppm), Cl$^-$ (40 ppm) | 2.5 | −0.503 | 0.151 |
| TNBT (40 ppm), Cl$^-$ (40 ppm) | 4.0 | −0.565 | 0.089 |
| TNBT (40 ppm), Cl$^-$ (40 ppm) | 5.0 | −0.615 | 0.04 |
| TNBT (40 ppm), Cl$^-$ (40 ppm) | 2.5 | −0.575 | 0.079 |
| + 0.3 M CH$_3$COOH | 1.0 | −0.585 | 0.069 |
| NTBC (45 ppm), Cl$^-$ (40 ppm), H$_2$SO$_4$ (0.6 M) | 2.5 | −0.585 | 0.069 |
| NTBC (45 ppm), Cl$^-$ (40 ppm), H$_2$SO$_4$ (0.6 M) | 4.0 | −0.620 | 0.034 |

Figure 10. OM images of cross-sections of 10:1 AR TGVs plated with NTBC. Bath composition: 0.88 M CuSO$_4$, 45 ppm NTBC, 80 ppm Cl$^-$, and 0.6 M H$_2$SO$_4$. (A) 1.0 mA cm$^{-2}$, 13 h, (B) 1.5 mA cm$^{-2}$, 12 h.

Possible additive reduction.— Umemoto et al. have reported that the reduction of the tetrazolium ring of NTBC$^{2+}$ occurs at about −0.28 V vs SCE (−0.04 V vs NHE) in DMSO, and proceeds via a complicated 4 electron process including a parallel disproportionation of the monoformazan into the diformazan and NTBC$.^{32}$ They showed that constant potential electrolysis at −0.4 V vs SCE first yielded the radical NTBC$^{-}$ followed by the monoformazan of NTBC with the addition of a second electron. The formation of the final, 4-electron reduction product, the insoluble diformazan of NTBC, requires the addition of two protons and thus makes the process sensitive to pH. Independent work gives the potentiographic $E_{1/2}$ of NTBC in a 0.1 M phosphate buffer at pH 7.2 as −0.05 V vs NHE,$^{37}$ close to Umemoto’s value in DMSO.$^{35}$ Reference 37 also mentions that the $E_{1/2}$ for TNBT under the same conditions is “above” that of NTBC without giving further details, though a shift to less negative values would be expected from the two additional “electron withdrawing” nitro groups in TNBT.

Of greater relevance to the plating conditions used in our work, Dow et al. did LSV measurements on TNBT in Cu-free solutions in 0.48 M H$_2$SO$_4$ and attributed reduction peaks at −0.68 V and −0.8V (vs MSE, or −0.03 and −0.15 vs NHE) to the first and second reductions of TNBT.$^{20}$ Interestingly, the authors did not see these there may be an effect associated with adsorption of the acids or their anions on Cu.

There are other important consequences of the operating pH. In early work of Dow et al. with TNBT where plating was done without the addition of any acid, good filling of holes was achieved, but cross sections revealed a layered or ‘chap-like’ structure in the deposit, and EDX analysis showed high levels of incorporation of C, N, and O.$^{37,20}$ Addition of 0.5 M H$_2$SO$_4$ eliminated the ‘chap-like’ features, but led to poor filling of the holes. When weak organic acids were added to the plating solutions in place of H$_2$SO$_4$ Dow et al. observed that peeling occurred between the plated Cu and the foil Cu on the surface of his PCB samples when the solution pH was above 2.75. This suggests that at higher pHs some kind of ‘weak boundary layer’ was left on the Cu surface after plating.$^{5,15,17,19,20,27,28}$ Parts plated in solutions below pH 2.75 did not exhibit this peeling. Interestingly the pH of the above ‘acid-free’ plating solution is expected to be approximately 3.1 due to hydrolysis of Cu(H$_2$O)$_6$.$^{2+}$, i.e. above the limit at which residual organic material on the surface is suspected.$^{20}$ The question then becomes, what is happening on the surface to cause the increase in ‘inhibition’ evidenced by the rapid shift in potential to more negative values when acid is added? A possible answer comes from the fact that tetrazolium salts may be reduced at relatively modest potentials.

This, and the fact that the reduction products tend to be intensely colored has led to their use in bioanalytical studies at physiological pHs$^{32}$ for detecting reducing agents such as superoxide ion (aqueous formal potential −0.31 vs Ag/AgCl),$^{29}$ NADH (−0.32 V vs NHE, pH 7),$^{32}$ etc.
the diformazan by Cu(II) could conceivably shift the reduction potential of TNBT into our operating range, provided that this irreversible process could get to the point of some level of diformazan production. However, we have observed that the diformazan of TNBT exhibits practically no solubility even in a concentrated CuSO₄ solution, suggesting that we should observe this intensely colored species on the cathode surface if it were forming, but we have not. Further questions could be raised about the possible interaction of Cu(I) produced during Cu(II) reduction¹¹ and the diformazan, noting that Cu(I) halide complexes of related ligands such as 1,10-phenanthroline or 2,2′-bipyridyl have been reported.²⁰ At the even lower current density of 1 mA cm⁻² where the best filling of 10:1 AR holes was achieved, the potential is +0.22 V, and the case for TNBT reduction is even weaker. We do see the formation of a precipitate after plating in TNBT, but the color is the pale yellow of the original TNBT-Cl₂ rather than the intense dark red of the diformazan of TNBT.

In the case of plating with NTBC at 2.5 mA cm⁻² in a much more acidic electrolyte of 0.54 M H₂SO₄ and CuSO₄, we observe a voltage of −0.585 V vs MSE, or +0.07 vs NHE. This too is above the value of −0.05 V vs NHE reported in DMSO. So again, the plating voltage is not low enough to clearly support the idea that reduction is occurring. In addition, we have no visual evidence of formation of a colored product in the case of NTBC (though a colored product could be masked by the blue color of the Cu²⁺ hydrated ion) or an intensely colored precipitate as would be expected for diformazan formation. No unusual color is seen on the Cu plated surface either, as might be expected if an insoluble product were being formed by reduction.

So, under the plating conditions that we have used to produce effective hole filling in this work, we do not see strong evidence for reduction of either NTBC or TNBT, though their reduction potentials are close enough to our operating potentials that we cannot rule out some slow rate of reduction. According to the models for leveler mediated filling in ‘blind’ features, this increases the possibility that the consumption mechanism for these additives is that of incorporation into the Cu deposit. However, it should be noted that in the early stages of TGV filling, the surface area of the initially formed ring of plating at the middle of the hole is greater than that of the flat cylindrical surface near it. Furthermore, until the plug is formed the surface area of this ring is increasing. It is conceivable that the increasing surface area coupled with slow diffusion of the additive may be enough to serve as the ‘loss mechanism’ without requiring loss via incorporation or reduction. The geometry of the early stages of ring formation in the middle of the hole resembles the ‘convex’ surface in the CEAC model of Moffat et al.²¹

Conclusions

Superconformal filling of TGVs of both aspect ratios 6:1 and 10:1 is successfully performed using DC plating in CuSO₄ solutions consisting of TNBT and CH₃COOH. The TNBT facilitates the nucleation of hemispherical Cu clusters at the TGV’s center, whereas addition of 0.3 M CH₃COOH leads to a X-shaped deposit. The NTBC + H₂SO₄ bath also supports good filling in TGVs of AR 6:1 and 10:1. Addition of 0.5 M H₂SO₄ to the TNBT bath leads to poor hole filling. A current density of 2.5 mA cm⁻² is the optimum for the superfilling TGV’s of AR 6:1 for both TNBT and NTBC baths. A current density of 1.0 mA cm⁻² is the optimum for superfilling of TGVs of AR 10:1. The time required to fill TGV’s of AR 6:1 using the TNBT + CH₃COOH bath at 2.5 mA cm⁻² is 3 h while 5 h is needed for the NTBC bath. The surface topographies of Cu deposited from the TNBT + CH₃COOH bath and the NTBC + H₂SO₄ bath are very similar. Plating voltages measured in this work were not negative enough to convincingly support the idea that reduction of the tetrazolium inhibitors is occurring nor did we see visual evidence suggesting the formation of the insoluble diformazan end products of tetrazolium ion reduction. Yet, given the complex nature of the reduction of tetrazolium ions including possible interactions with Cu(II) ions, we cannot reject the possibility that some degree of reduction is occurring. Further work is...
underway to better understand the behavior of tetravalent ions during low current density Cu deposition.

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