Nitro blue tetrazolium chloride (NTBC) and thiazolyl blue tetrazolium bromide (MTT) are the organic additives applied successfully in Cu superconformal filling of through glass vias (TGVs) with aspect ratios 6:1 and 10:1. However, traces of purple inclusion were observed through the cross-sectioning of electroplated samples indicating that a reduction could likely be occurring during the plating process. In this work, the reduction propensity of NTBC and MTT in the course of Cu superconformal plating was assessed in the absence of Cu(II) ions by cyclic voltammetry, controlled-potential electrolysis (CPE), and UV-Vis spectroscopy. A CPE potential of ~0.25 V vs Ag/AgCl reference electrode was selected aiming at studying the reduction process as close as possible to the actual potential range of Cu deposition. The CPE and UV-Vis results suggest that both additives reduce steadily with time generating different (by)products. Also, it is shown that the MTT reduces itself at a rate that is substantial at lower pH, producing both surface precipitates and soluble reduction products. Unlike that, the NTBC reduction exhibits weaker pH dependence and generates lower quantity of surface precipitates only. Thus, the reduction of MTT is expected to impact considerably stronger than NTBC the Cu superconformal plating process in TGVs.

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There has been a rapid development of electronic devices in the recent decades. The extrinsic features and particularly the size of the devices have become smaller thus promoting their portability. The multi-functionality associated with these devices is rather complex, so the demand for increasing the circuit density to provide higher bandwidth, I/O ratio, and faster speed led to the introduction of interposers as indispensable element of the 2.5D and 3D electronic packaging.1–3 The interposer features a pattern developed on insulating separator slides, made out of silicon or glass and used for signal distribution between vertically stacked chips and BGAs. The processing strategy of silicon is mature and also its coefficient of thermal expansion (CTE) matches the chip’s one,a rendering silicon one of best candidates for practical use. Glass, on the other hand, has advantages over silicon especially regarding signal degradation when superconformally plat- ing Cu in TGVs4–8 as Cu tends to diffuse into silicon in the absence of a barrier layer, but glass is not impacted by this issue. In addition, the CTE of glass could be tuned to match the chip’s onea thus making glass interposers a cost-effective alternative to silicon.

In the previous work of our group, promising results on supercon- formal filling of TGVs with aspect ratio (AR) 6:1 and 10:1 have been obtained.9,10 Organic additives were introduced in the plating solutions to help suppressing most of the Cu electroplating on the flat surface of the glass sample, while allowing for substantially faster rate of depo- sition in the center of the TGVs. This was realized by maintaining a gradient of the additive concentration that decreases from the TGV’s entrance to its center thus insuring that Cu nucleation takes place at the very center of the TGV.11,12 The center-targeted nucleation serves to minimize the risk of void formation during the Cu plating throughout the TGV.10,12 While at least three different additives have been successfully used in the superconformal TGV-filling process, reports have been made in the literature about simultaneous additive reduc- tion along with the Cu plating. Such reduction results in generation of potentially inactive by-products and in effectively lower additive concentration that in turn could potentially cause plating-performance degrada- tion.13 The odds of additive reduction in the course of Cu superconformal plating mediated by TNBT were assessed in a recent work of W.P. Dow’s,13 whereby the authors present both, a proposed chemical mechanism and experimental observations. The TNBT ad- ditive has a tetrazolium ring that can be protonated and reduced to form a radical. In addition, this radical can also accommodate a proton and an electron that in turn leads to opening of the tetrazolium ring thus forming a formazan.13–17 Because the studied additives for Cu superconformal plating feature two tetrazolium rings, this formazan can further accommodate another proton and accept one more electron to eventually open the second tetrazolium ring. The resulting compound featuring purple or blueish color constitutes the ultimate reduction product. Owing to its limited solubility in water this reduc- tion product can easily precipitate in water-based electrolytes.a In earlier work of our group, the formation of purple color was detected occasionally from the cross-section of the electroplated samples,10 thereby implying potential additive reduction. Normally, during Cu superconformal plating, the applied current density is relatively low (of order of a mA/cm2). However, due to substantial passivation of the flat-surface that could potentially halt the deposition, one could estimate the actual current density in the holes to be much higher than the experimentally applied one to carry out the overall plating process. Should such non-uniform current density power up the plating process, the higher current in the holes could serve as promoting factor for incorporation in the Cu deposit of additive molecules and/or its reduction (by)products. Such incorporation, already reported for the use of TNBT as additive,13 could substantially compromise the quality of Cu fills and lead eventually to higher resistance and poor solderability.24,25 Of accordingly deposited Cu. Also, it has been shown in the literature that coupled electron transfer/proton transfer reactions associated with electroactive suppressor additives used for Cu superconformal plating are pH dependent.24–26 The uncertainty associated with the actual current density and the varying plating solution pH along with the reduction propensity of additives used in our TGV superconformal filling, like TNBT, NTBC, and MTT serve as strong motivation for a detailed phenomenological additive-reduction study. The specific goals of that study are (i) to assess the odds of reduction to take place and (ii) to study the reduction impact on the quality and reliability of Cu deposits in the superconformal filling process. Herein, we report on a study of the reduction behavior of two additives, NTBC and MTT (Figure 1) that have both been successfully used in the glass interposer fabrication process.9,10 Our study provides the insight on durability of the plating bath and furthering the understanding of the additives’ behavior. In its immediate context, the study assesses two
aspects of the potential reduction process, (i) its pH-dependence and (ii) time-dependence within realistic time limits of the Cu deposition process lasting up to either 4 h (at AR 6:1) or 12 h (at AR 10:1). The stability of NTBC and MTT in the entire range of plating potentials is first assessed by cyclic voltammetry (CV), then the reduction is studied by a chrono-amperometry while running constant potential electrolysis (CPE), and the reduction product accumulation is characterized by UV-Vis. Finally, the results are critically compared with related ones on obtained earlier in TNBT reduction.13

**Experimental**

**Reagents.**—The following chemicals were used in this work: MTT (Biosynth International, CAS-No. 298-93-1), NTBC (99%, Alfa Aesar), NaCl (JT Baker, reagent), H$_2$SO$_4$ (doubly distilled, GFS), CH$_3$COOH (GFS, double distilled), MSA (99%, Acros), NaOH (JT Baker, reagent), methanol (99.9%, Pharmco-Aaper), pH 7.00 buffer (Fisher, certified pH 6.99 - 7.01 @ 25 °C), pH 4.00 buffer (Fisher, certified pH 3.99 - 4.01 @ 25 °C), pH 1.68 buffer (Oaklon), DMSO (Acros, c grade, 99.9%).

**Test samples, solutions, and setups.**—All CV and CPE experiments were performed on Cu disks, with diameter of 0.6 cm. A Au disk was also used to compare the results with those generated using Cu disks. All samples were immersed in the electrolyte in hanging meniscus configuration.24,25 the potential was applied right after the sample was brought in contact with the solution. Different solution compositions, current ranges and applied potentials were used. All electrochemical experiments were done using BASI-Epsilon potentiostat in a three-electrode configuration whereby along with the Cu and Au working electrodes (WE), a Pt wire was used as the counter electrode (CE), Ag/AgCl in 3 M KCl (SHE) served as the reference electrode (RE). All potentials in this work are also reported versus the Ag/AgCl (3 M KCl) reference electrode.

**Sample preparation.**—All samples were polished manually using 5.0 μm alumina powder (Buehler), proceeding to 1.0 μm micropolish II alumina powder (Buehler), and finishing up with 0.05 μm micropolish II powder (Buehler) to diminish the interference of oxidation products on the surface in further electrochemical work. An electropolishing step was exploited as well because of its simplicity and ability to render the surface clean and smooth.

**Working solutions.**—All solutions were made with Barnsted Nanopure water (>18MΩ cm). The NTBC solution formulation used in this work was NTBC (0.05 mM or 40 ppm), Cl$^-$ (added as NaCl, 0.67 mM or 40 ppm), H$_2$SO$_4$ (0.6 M) or CH$_3$COOH (0.5 M), operating pH values between 2.00 and 6.00, adjusted by addition of acid or NaOH palettes/solutions. The MTT working bath was consisted of MTT (0.30 mM or 126 ppm), Cl$^-$ (0.61 mM or 36 ppm), methane-sulfonic acid (MSA, 1.0 M), and the pH was adjusted in the range of 2.00 to 6.00 by addition of acid or NaOH palettes/solutions.

**Electrochemical experiments.**—Before conducting any experiment in the three-electrode cell, all samples were mechanically polished following steps described earlier in the Sample Preparation section to make sure the surface was bright and smooth. This was followed by rinsing with Barnsted Nanopure water and drying in ultrapure N$_2$ atmosphere.24 During the CV experiments, the entire potential range was set according to the compositions of solutions, since the behavior of different additives and acids varied. Attempts were made with random ranges to determine the practical interval needed for CV work. Our results show the optimum potential interval for MTT solution is 0.00 to −1.00 V and for NTBC solution is 0.00 to −0.58 V. Once these regions were established, different sweep rates in the range of 0.02 to 0.150 V/s were applied for the solutions. Furthermore, CPE was performed to run long-term MTT reduction and potentially generate reduction product precipitating on the electrode surface or dissolving in the electrolyte. After the CPE, UV-Vis spectra were registered to study trends in peak position and absorption of both additives and reduction products at different conditions. A potential of −0.25 V was chosen for the CPE based on the CV curves analysis. The electrolyte composition was chosen in accordance with that used for Cu superconformal plating and included 0.05 mM NTBC, 0.67 mM Cl$^-$ ions and 0.6 M H$_2$SO$_4$ or 0.30 M MTT, 0.61 mM Cl$^-$ ions and 1 M MSA dissolved in Barnstead Nanopure water. No CuSO$_4$ was used to avoid interference of the overwhelming Cu reduction current with that resulting from the MTT reduction process. In addition, short-term chrono-amperometry experiments were performed at the CPE potential to assess the reduction current in both open and N$_2$ purged solutions. In the latter case, N$_2$ purged the solution for at least 25 min before starting electrolysis. The latter experiments are aimed at assessing the contribution of oxygen reduction to the overall reduction current.

**Initial solution for UV-Vis.**—Ultraviolet-visible spectroscopy (UV-Vis) performed for analyzing accumulation of reduction product was carried out using a HP 8452A Diode Array Spectrophotometer. This technique was used for quantitatively analyzing the analytes such as additive-formazan or additive-diformazan. The volume for all tested solutions was 1 mL. The solvents to dissolve reduction products of NTBC and MTT are methanol and DMSO, respectively. An initial solution, which was used as the baseline, was prepared with dissolving the pure organic additive in corresponding organic solvent. The concentration of this solution was 100 μM by dissolving either 2.4 mg NTBC in 2 mL methanol or 2.4 mg MTT in 2 mL DMSO. Because the final volume was 1 mL, the initial solution of NTBC consisted of 66.7 μL NTBC and 933.3 μL methanol, and that of MTT had 34.5 μL MTT and 965.5 μL DMSO. These solutions only contained the original additives, i.e. they were pre-electrolysis solutions used to compare with post-electrolysis solution.
Results and Discussion

The strong inhibiting effect of several additives in Cu superconformal TGV filling was confirmed in earlier work of our group,\textsuperscript{9,10,16} whereas the reduction propensity of these additives still remains unclear. A close look at W.P. Dow’s study on reduction behavior of TNBT\textsuperscript{13} suggests that there is a likelihood that NTBC and MTT exhibit similar reduction propensity because of the common structural features that these additives have with TNBT.\textsuperscript{9,10,13,14} This work focuses on the addressing of two key questions: (i) does any reduction take place at all in the course of Cu plating and (ii) if it does, what are the similarities and differences of the NTBC and MTT behavior in comparison with the TNBT reduction studied earlier by W.P. Dow.\textsuperscript{911} As stated above, the substantially higher current in the holes than that on the surface is a result of a different extent of passivation realized by the establishment of additive-adsorption gradient from the hole-center to the entrances of the holes. The dynamics of that gradient formation warrants application of different growth regimes in the stage of Cu nucleation, Cu plug formation, and completion of the hole filling process as detailed in our previous work.\textsuperscript{10} Therefore, it is necessary to conduct a CV experiment that is the most comprehensive approach to assess the redox activity corresponding different potentials applied to power up the deposition in the above mentioned growth regimes associated with the real-life TGV-filling process.

Reduction of NTBC.—The formation of reduction product is analyzed in electrolytes with different composition. The electrochemical reduction of organic additives depends directly on the pH (acidity) of the solution, not on the concentration of the acid itself, as weak and strong acids release different amount of dissociated hydrogen ions (protons, H\textsuperscript{+}).\textsuperscript{13} The proton released from the strong acid, such as H\textsubscript{2}SO\textsubscript{4}, leads to a higher chemical activity that facilitates an attack of the additives’ amine group. Such attack makes more likely potential structural changes of the additive thus promoting the reduction propensity.\textsuperscript{13} CV experiments have been done in this work with a strong acid, H\textsubscript{2}SO\textsubscript{4}, and a weak one, CH\textsubscript{3}COOH, to compare the potential regions where a reduction process is likely to occur and the magnitude of the corresponding reduction current.

CV results.—In Figure 2A, the peak current density of the curve at pH 0.76 is much higher in comparison with all other pH values. This could be due to the higher concentration of H\textsuperscript{+} ions in the solution that makes more of these ions available for immediate reduction and as a result of that, the evolution of H\textsubscript{2} has a higher possibility to occur. Consequently, the H\textsubscript{2} evolution would gain more strength in the competition with the NTBC reduction. To minimize this side-process impact one needs to generally decrease the H\textsuperscript{+} ion concentration. Following these thoughts, the extent of NTBC reduction during CPE was expected to increase gradually with increase of the solution pH. Considering the structural similarity between TNBT and NTBC, it is likely the NTBC reduction to follow the reaction pathway, presented in Figure 3, similarly to the TNBT reduction mechanism proposed earlier by W.-P. Dow.\textsuperscript{13} Thus, the NTBC alike with TNBT emphasizes two-peak cathodic polarization curve (Fig. 1). In this curve, the more positive peak occurring around −0.1 V is assigned to the first ring opening of NTBC (the 3\textsuperscript{rd} step in Fig. 3), and the one with a more negative potential is associated with the second ring opening of NTBC (the 5\textsuperscript{th} step in Fig. 3) combined with SO\textsubscript{4}\textsuperscript{2−} desorption that also contributes to the large second peak area. The distinct reduction steps that could take place simultaneously or sequentially are preceded by a conversion of tetrazolium ring to a radical resulting in a formation of a resonance structure right after the additive adsorption on the Cu surface. The resonance structure then undergoes all reduction transitions as presented in Figure 3.\textsuperscript{13} According to Dow’s view the reduction propensity increases in the presence of more electrons and protons. Meanwhile, the higher concentration of protons provides a better environment for H\textsubscript{2} evolution. Therefore, when the solution pH is low, there is abundance of protons to boost the reduction thus generating the higher current seen in Figure 2A. Considering the actual Cu plating conditions\textsuperscript{9} whereby the cell is open to the ambient, the contribution of O\textsubscript{2} to the overall reduction activity should be taken into consideration as well. In Figure 2B, experiments are performed to check the impact of O\textsubscript{2} on the system in both open to the ambient and N\textsubscript{2} purged cells. In the open cell, the reduction current is higher (in magnitude) and at the dominant peak potentials are more negative. On the other hand, N\textsubscript{2} purging eliminates the oxygen reduction reaction (ORR) contribution which leads to slightly lower peak currents and positive potential shift.

Except providing information on the reduction current, the CV curves in Figure 2 also show the suitable range to choose a potential for performing a CPE experiment at. Therefore, the constant potential was chosen taking into account the actual (practically relevant) plating potential range as well as the range whereby additive reduction is most likely to occur. There are two peaks shown in Fig. 2, with the one between 0.0 and −0.2 V being closer to that observed from the Cu deposition work.\textsuperscript{9} Therefore, eventually a potential of −0.25 V was chosen for the CPE study. The CPE process was performed in two different ways. Firstly, the experimental time was fixed and chrono-amperograms were registered in solutions with various

![Figure 2](image-url)
Figure 3. Electrochemical reduction reactions of NTBC to change gradually from a radical, resonance structure to a complete formazan.

Figure 4. (A) CPE in NTBC containing solution at different pH in open cell and N₂ purging. The solution composition is 0.05 mM NTBC, 0.67 mM Cl⁻ ions, 0.6 M H₂SO₄ and pH ranging from 2 to 6, adjusted with adding NaOH. Plot (B) presents a magnified current density range of the steady-state behavior of the de-oxygenated cell experiment.
pH values, as shown in Figure 4. Secondly, same type of experiments was carried out for different times of up to 24 hours, as presented later in this work. The second approach was performed to study if the accumulation of reduction product on the electrode surface was time-dependent process as this dependence directly correlates with the additive stability.

**Choice of solvent for UV-Vis characterization.**—Unlike the results of W.P. Dow on the reduction of TNBT suggesting a distinct color change in the solution,13 the CPE experiments presented in this work did not result in any apparent change of the solution color. Presumably, the accordingly realized rate of product accumulation in this work was substantially lower in comparison with the experiments reported in the TNBT reduction work of W.P. Dow et al. We believe that the difference in the rates of product accumulation can be associated with the substantially lower pH levels in Dow’s work. In extra support to this hypothesis, all TNBT reduction experiments carried out at comparable or higher than our pH values yielded no detectable product accumulation either.13 Therefore, to address the absence of color changes, we decided to monitor the reduction product accumulation employing an approach used by Marques et al.14 This approach takes into account only the reduction product formed on the electrode surface. The associated experimental procedure involves a quantitative dissolution of the reduction product from the electrode in appropriate solvent followed by a UV-Vis spectrometry analysis. In our work, alike with the original work of Marques methanol was used for dissolving the NTBC reduction product14 whereas for obtaining best results in the MTT reduction study a decision was made to employ DMSO as solvent.28 The choice was based both on the DMSO’s higher dielectric constant and on a parallel testing of both organic solvents’ ability to dissolve specifically the MTT reduction product.28

**Electrolysis and UV-Vis analysis.**—The CPE experiments were aimed at studying the relationship between the NTBC reduction product accumulation on one hand and the solution pH and/or time on the other. In addition, tests of the impact of the environment on the chrono-amperometry results including open and N2-purged (deoxygenated) cells were performed to assess the effect of dissolved O2 on the overall reduction current. The comparison of both experimental environments suggested that the steady-state currents in an open cell are higher than these measured in N2-purged electrolyte at identical pH values (Figure 4). Apparently, when the cell is open to the ambient, the concentration of O2 is higher, thus increasing the impact of the O2 reduction. The chrono-amperograms in open cell suggest higher rate of the overall reduction activity at low pH and very close to virtually identical reduction rates at higher pH, in the range 2.8 to 5.9. This result is generally consistent with a NTBC reduction mechanism involving participation of H+ ions.13 The lack of distinct trend seen at higher pH values could be explained by a masking contribution of the local alkalization resulting from the concomitantly occurring ORR.

Afterwards, the effort was focused on investigation of whether the NTBC reduction is pH-and time-dependent. In both cases, a surface accumulation of reduction product can be easily seen through a comparison with a reference freshly polished Cu sample, as shown in Figure 5B. Also, before the CPE, when reduction process has not started, the UV-Vis spectra in Figs. 5A and 5B, feature only one peak at 266 nm reflecting the absorption of the original NTBC additive. After 4 h, 8 h and 24 h of electrolysis, the intensity of this peak increases with time. Also, the curve between 290 nm and 390 nm features, unlike the baseline, two consecutive peaks that both become more evident with time. Furthermore, another distinct broad peak appears between 500 nm and 600 nm. Judging by the shape of the peaks and their increasing magnitude (absorption), one would expect the reduction not only to occur, but also to emphasize all respective structural changes as discussed earlier in relevance with the detailed steps of the process laid out sequentially in Figure 3.

According to Beer-Lambert Law, the concentration is directly proportional to absorption.29 Therefore, one can conclude that the reduction product concentration increases with pH as clearly evidenced by the UV-Vis spectra presented in Fig. 5A. Also, as seen in the inserted pictures of Fig. 5B, the reduction product accumulation is time-dependent as the color becomes more intensive when the CPE is carried out for a longer time. The latter agrees with the results on TNBT reduction.13 Overall, no saturation of the reduction product accumulation was observed for a period of 24 h as the intensity of all peaks in Fig. 5B keeps increasing. This implies that in an actual Cu deposition process, the amount of reduction product might be higher in longer-plated samples, i.e. in Cu superconformal plating of TGVs with higher AR.

In Figure 5A, the UV-Vis spectra obtained in solutions with different pH suggest accumulation of more reduction product with the pH increase. More specifically, after 4 h of electrolysis, besides the original peak at 266 nm, an appearance of peaks with increasing intensity as the solution pH becomes higher is observed at 322 nm, 392 nm and 610 nm. This trend seemingly opposes the results in

![Figure 5](image-url)
Figure 6. UV-Vis spectra recorded before and after 24 h of CPE at different pH aimed at assessing the presence/absence of reduction product(s) in the electrolyte.

Figure 4A where current transients in open cell show highest reduction rate at lowest pH. However, the latter result could be better understood taking into consideration the current-time curves after thorough solution de-oxygenation (Fig. 4B) where one can see a generally weak pH dependence of the reduction rate with yet the highest reduction rate being measured at the highest pH. Given the limitation of Marques’ approach that measures only surface deposits and has no hold of reduction product dispersed elsewhere, a long term experiment was carried out to assess additional quantities of reduction product potentially dissolved/crystallized in the solution. The results of that experiment are presented in Figure 6 where by the UV-Vis spectra of the initial working solution and filtrate of working solution after 24 h of CPE dissolved in methanol are compared. Apparently, no features could be found outside of 200–300 nm range where the original NTBC peaks are normally located. This indicates no quantities of reduction product to that documented in Figure 5A could be reported. Overall, the weak pH dependence and the generally low reduction currents seen in Figures 4A and 4B and the limited amounts of reduction product resulting from as long as 24 h of CPE presented in Figures 5 and 6 hint at anticipation of relatively minor impact of the NTBC reduction process on the Cu superconformal plating in the process of glass-interposer fabrication described in detail in Ref. 9.

Reduction of MTT.— In a recent development on the Cu superconformal filling of TGVs resulting in remarkable high-quality filled TGVs with AR 6:1 and 10:1 our group used successfully a cost-effective solution provided by the use of the organic additive MTT. Yet, during the Cu plating work a trace of purple product was observed along with the electrodeposited Cu when some of the sample cross-sections were examined. Even though the phenomenon was occasionally seen in a large number of accordingly plated samples, it is still essential to assess quantitatively the odds of MTT reduction to occur in the actual Cu plating conditions. To perform this study in the presence of MTT, CV and CPE experiments were performed, generally following the approach used and described in detail for the NTBC reduction study.

CV result analysis.— In electrodeposition with MTT, Cu methane sulfonate (CuMSA) was introduced due to its ability to produce a higher concentration of Cu ions and thus to overall accelerate the Cu deposition process. Coordinating with the new plating solution, a methane sulfonic acid (MSA) was used in the reported herein MTT reduction study. The solution consisted of 126 ppm MTT, 40 ppm Cl and 1 M MSA. As previously stated, different pH values and sweep rates were monitored by CV experiments. Afterwards, in the CPE chrono-amperometry work, various pH values and operational times were applied to generate surface deposits of MTT reduction product. Alike with the NTBC case, the experiments were aimed at assessing both the potential pH dependence the MTT reduction and the proportionality of MTT degradation to the polarization time. The UV-Vis spectra were analyzed based on studying samples obtained by the Marques’ approach. The analysis of CV curves suggests appearance of a peak around −0.2 V that could be associated with initialization of the MTT reduction process (see Figure 7). The peak potentials falls in a region identified also as ‘reduction range’ in Marques’ work. A further result interpretation in said work associates the formation of two peaks in the CV curves with a two-electron process generally following the reduction pathway presented earlier in Figure 3 and thus yielding a MTT-diformazan compound. The potential of the first peak is close to the range where the Cu deposition takes place in a real plating process. When pH is above 5, the first peak potential shifts negatively in conjunction with a general decrease of the current density to about 0.1 mA/cm². As mentioned in the previous section, the decrease of H⁺ ion concentration could cause both, reduction-
The reduction process outcome comprised two separate assays accounting for reduction product formed on the electrode and in the solution and following routines described earlier in this work regarding results in Figures 5 and 6, respectively. The only difference in this case is the use of DMSO instead of methanol to dissolve the filtered floccules after 24 h of CPE. The results of this characterization experiment are presented in Figures 10A and 10B.

**MTT reduction products.**—In Figure 10 one could see a clear difference between the rates of MTT reduction product accumulation at pH 2.82 on one hand and that at higher pH (3.84 and 5.30) on another. The latter observation is in perfect agreement the observed trend in the CPE current density with pH. Even more convincingly, this agreement applies identically for each of both independent assays ruling out major impact of secondary factors like pH dependence of reduction products’ solubility and/or effects of local pH elevation near the Cu electrode as a result of the reduction process. The only noticeable distinction of the UV-Vis results in Figures 10A and 10B is the difference of the dominant reduction product’s adsorption band registered after CPE at pH 2.82, 650 nm vs 510 nm, respectively. It is also noteworthy that complementary minor contributions of reduction products with counterpart’s adsorption band are present as peak/shoulder in both plots. Finally, Figure 10A shows presence of the same reduction product (adsorption band at 650 nm) at higher pH, albeit accumulated at substantially lower rate. The latter result suggests that the accumulation of reduction product on the Cu surface is governed by a common mechanism in the pH range of interest. Overall, combining the contributions from the flaky precipitate and surface deposited reduction product at pH 2.82 (Figs. 10A and 10B) leads to a conclusion that there is a significant rate of MTT reduction in the potential range of Cu superconformal deposition. This, in turn, makes likely to expect more substantial impact of the MTT reduction activity on the quality of accordingly deposited Cu as compared to the case where NTBC is used for the same purpose. Further insight on the impact of reduction products generated by MTT and NTBC in the Cu superconformal plating process could be obtained directly by a high sensitivity elemental analysis performed by secondary ion mass spectroscopy (SIMS),19,20 Also, indirect information of impurity incorporation could be obtained by a study of the voiding propensity.
at the interface of Pb-free solder and accordingly electrodeposited Cu.\textsuperscript{31,32} Such informative characterization studies are yet to be made.

Conclusions

In this work, the reduction behavior of organic additives used in Cu superconformal filling of TGVs at different pH and solution operational times is studied in a typical plating baths but in the absence of Cu\textsuperscript{2+}. The reduction is believed to be a two-electron process that forms formazan (for MTT) and diformazan (for NTBC). Cyclic voltammetry preceding the CPE, chrono-amperometry in the course of CPE, and UV-Vis spectroscopy methods used post-factum are all employed to assess the reduction behavior. The CV curves feature two peaks appearing at $-0.2$ V and $-0.6$ V where steps of the reduction process likely occur. A potential of $-0.25$ V was chosen to perform CPE because of its being close to the potential range where actual Cu plating takes place. A key observation from CPE in the presence of each of studied additives is the formation of a purple deposit on the cathode surface, and also in the MTT-containing electrolyte, the formation of a purple flocculate precipitate after at least 16 h of reduction. The assessment done by UV-Vis spectroscopy clearly suggests a trend of reduction product increase with time in both additive reduction cases. Also the chrono-amperometry and UV-Vis results suggest directly and indirectly, respectively, highest reduction rate for NTBC at highest pH and absence of reduction products in the working solution after CPE. Unlike that, the same characterization routines provide direct evidence for highest reduction rate at lowest pH and product accumulation both on the cathode and in the working electrolyte after CPE. Overall, from the standpoint of product accumulation at relatively low operational pH, these observations hint at lower odds of NTBC reduction impact on the superconformal Cu plating in comparison with case when MTT is used as additive. Information on the immediate propensity of incorporation of accordingly generated reduction product in both additive cases will be obtained in a future study.

Acknowledgments

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