

## Effects of organic acids on through-hole filling by copper electroplating



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### ABSTRACT

Through-hole (TH) filling of a printed circuit board (PCB) by copper electroplating was performed using formic acid, acetic acid and propionic acid instead of  $H_2SO_4$ . Tetranitroblue tetrazolium chloride (TNBT) was used as an inhibitor to perform a fast copper protruding deposition at the hole center during plating. The use of an organic acid instead of  $H_2SO_4$  overcomes two issues caused by  $H_2SO_4$ : poor copper filling performance at high  $H_2SO_4$  concentrations and a chap-like copper structure in the filled TH at low  $H_2SO_4$  concentrations. The filling performance using an organic acid was evaluated through the experimental examination of cross-sections of THs. The inhibition mechanism of TNBT on copper deposition was characterized by galvanostatic measurements with real-time injection of various acids, cyclic voltammetry (CV), linear sweep voltammetry (LSV) and UV–vis spectrophotometry. The results show that TNBT is electrochemically reducible only in the presence of protons. Its inhibiting strength and mechanism depend on the pH value, the chloride ion concentration and the cathodic potential. An electrochemical reaction mechanism was proposed herein to explain the filling plating behaviors and results.

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### 1. Introduction

Recently, copper filling in micron-sized through holes (THs) by electroplating has become an important topic in the field of fabrication of advanced printed circuit boards (PCBs) with high-density interconnections (HDIs) [1–5]. The copper plating formulas that have been devised for TH filling differ from those formulated for microvia filling because of the different geometric shapes [6–18]. The plating solution can flow through THs but cannot flow through microvias [19–23]. Therefore, the copper plating formulas that work for microvia filling cannot be applied to TH filling. In addition, the plating solutions used for TH filling usually do not contain accelerators, which are commonly present in the plating solutions for microvia filling because THs have no “bottom.” The bottom-up filling behavior of the plating solution for microvia filling relies on the effect of an accelerator that cannot be used in TH filling. Instead, the TH is filled in a filling mode such that copper is preferentially deposited at the hole center to form a butterfly-shaped copper cross-section in the filled TH [13–15,18,24,25].

The butterfly technology (BFT) for TH filling by copper electroplating has numerous advantages: (1) the fastest copper deposition rate occurs at the hole center rather than at the hole mouth, thereby

ensuring a void-free copper filling [13–15,24,25]; (2) copper can be directly filled in the TH without the use of a conductive template followed by a photoresist process [26–32], thereby reducing the number of processing steps and the complexity; (3) BFT can be performed using direct-current (DC) plating, thereby avoiding the use of a complicated period pulse reverse (PPR) plating; and (4) BFT can be applied not only to PCB fabrication but also to the metallization process of wafer and chip packaging, thereby providing comprehensive applicability. However, BFT also possesses disadvantages, including a long plating time and a chap-like (i.e., crack-like) copper structure caused by additive incorporation when  $H_2SO_4$  is absent in the copper plating solution [13,14,25]. These disadvantages can be overcome through adjustments to the forced convection using cathodic rotating motion equipment and through the replacement of  $H_2SO_4$  with  $K_2SO_4$  or  $Na_2SO_4$  [15,25].

For a high copper throwing power in plated through hole (PTH), an organic additive, namely a leveler, is significantly effective. Those levelers which are able to enhance the copper throwing power of a PTH have a specific functional group, namely quaternary ammonium cation [33]. Usually, one leveler molecule bears one quaternary ammonium cation. Since the leveler is an organic cation, it prefers to adsorb onto the cathode during plating, especially at the area of high current density. They either physically inhibit copper deposition at a peak position or electrochemically share the charge for copper deposition at the peak position. Both amine and quaternary ammonium cation are electrochemically reducible. Therefore, when the leveler preferentially adsorbs at the peak position, the

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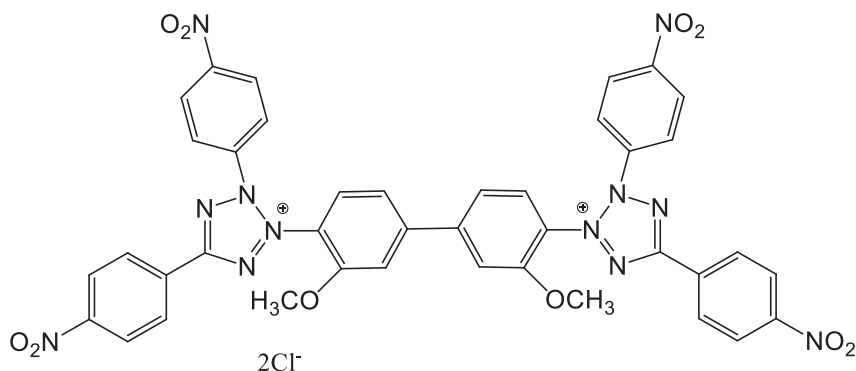


Fig. 1. Molecular structure of tetranitroblue tetrazolium chloride (TNBT).

local charges at the peak position will be donated to the leveler rather than copper ions [34]. Hence, copper ions will be forced to deposit elsewhere, leading to a leveling effect.

The reducibility of these levelers means that they are consumed during plating. Therefore, a concentration gradient of a leveler will be established from the hole mouth to the hole center. This is the root cause of enhancement in copper throwing power as the leveler is added in the plating solution. TNBT has two quaternary ammonium cations and four nitro groups, as illustrated in Fig. 1. These specific function groups enable TNBT to be potential-dependent adsorption on a cathode and easily electrochemically reducible at a cathodic surface because quaternary ammonium cations prefer to adsorb on a cathode and nitro groups are strong electron-withdrawing groups, leading to an easy ring-opening of TNBT (i.e., electrochemical consumption) [13,14,25,34]. Therefore, TNBT can strongly dominate the secondary current density distribution of copper plating inside the TH, which leads to the fastest copper deposition occurring at the center position of the TH and results in a butterfly-shaped deposition profile of the filled TH cross-section at the early plating stage.

Electrochemical analysis and experimental filling results from previous works [14,15,25] have indicated that the adsorption and inhibition properties of the organic additives that can produce the butterfly-shaped copper filling of a TH, such as nitrotetrazolium blue chloride monohydrate (NTBC) and tetranitroblue tetrazolium chloride (TNBT), are related to the  $H_2SO_4$  concentration. A high  $H_2SO_4$  concentration leads to a solid copper deposit in the filled TH, with poor filling performance. In contrast, a low  $H_2SO_4$  concentration, even the absence of  $H_2SO_4$ , results in excellent filling performance; however, a chap-like copper deposit in the TH is also obtained.

Based on the previous work, both the acid concentration and the acidity (i.e., the pH value) can be reasonably inferred to affect the chemical adsorption of NTBC and TNBT on the copper surface and to influence the inhibiting strength of NTBC and TNBT on the copper electrodeposition. Therefore, three weak acids (organic acids), instead of a strong acid (i.e.,  $H_2SO_4$ ), were employed in this work to explore the effects of acid concentration and strength on the adsorptive and inhibiting capabilities of TNBT in copper electrodeposition for TH filling.

## 2. Experimental

### 2.1. Filling plating of THs

PCB fragments with THs formed by mechanical drilling were used as plating samples. The dimensions of the PCB fragments were  $6\text{ cm} \times 4.4\text{ cm}$ . Before undergoing metallization, the THs underwent a desmearing process to remove the smear that was formed by mechanical drilling and coated on the hole wall. After the

desmearing process, copper electroless plating was used to metallize the sidewalls of the THs. The PCB was passed through a commercial copper electroless deposition process, including cleaner/conditioner, microetching, activation in Sn/Pd colloid, Sn removal, and then copper electroless deposition. The thickness of the electroless copper layer coated on the sidewall was around  $2\text{--}3\text{ }\mu\text{m}$ . Thereafter, we used copper electroplating to thicken the electroless copper layer to prevent the oxidation of the electroless deposited copper. The PCB fragment was plated by direct current with a current density of  $1.5\text{ A ft}^{-2}$  (ASF). Two phosphorus-containing copper plates were used as anodes and were placed directly in the plating bath with a working volume of 700 mL. The plating bath is detailed elsewhere [35].

The plating formula that was used to directly fill the THs was composed of 0.88 M  $CuSO_4$ , 43 ppm tetranitroblue tetrazolium chloride (TNBT, Fluka), 20 ppm  $Cl^-$  and various acid concentrations. The molecular structure of TNBT is shown in Fig. 1. The plating solution was maintained at  $28^\circ\text{C}$ . Polarization curves associated with the filling plating were recorded using a saturated mercury-mercurous sulfate electrode (SMSE) as a reference electrode. The filling performance was assessed according to cross sections of the filled THs, which were examined using an optical microscope (OM, Olympus BX51). The microstructures of the filled copper deposits were also examined using the OM. Before OM examination, copper deposits were polished and etched to allow clear characterization of their microstructures. The detailed sample pre-treatment is described elsewhere [25].

### 2.2. Electrochemical analyses

The electrochemical effects of additives on copper electrodeposition were characterized by galvanostatic measurement, cyclic voltammetry (CV) and linear sweep voltammetry (LSV) using a PGSTAT30 (Auto-Lab) potentiostat with a three-electrode cell. Galvanostatic measurements with various acid injections were performed in 50 mL of an electrolyte that was composed of 0.88 M  $CuSO_4$ , 20 ppm  $Cl^-$  and 43 ppm TNBT. The current density was fixed at  $1.5\text{ A ft}^{-2}$  (ASF). The spin rate of the copper-coated rotating disk electrode (Cu-RDE, working electrode) was fixed at 900 rpm. The counter electrode was Pt foil placed in a glass tube that contained 0.88 M  $CuSO_4$ , which was isolated by a porous plug. A saturated mercury sulfate electrode (SMSE) was employed as the reference electrode (RE). Various acids were injected into the base electrolyte at 500 s, 1000 s, 1500 s, 2000 s and 2500 s. Each injection of the various acids resulted in a concentration increase of 0.08 M and the final acid concentration was 0.4 M. The temperature of the electrolyte was maintained at  $28^\circ\text{C}$ .

CV was performed in 50 mL of an electrolyte that was composed of 0.88 M  $CuSO_4$ , 20 ppm  $Cl^-$  and 43 ppm TNBT. The scan rate was  $50\text{ mV s}^{-1}$ , and the potential range was  $-0.4\text{ V}$  to  $-0.7\text{ V}$

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