Available online at www.sciencedirect.com

ScienceDirect

Electrochimica Acta 53 (2008) 3610–3619

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Enhancement of filling performance of a copper plating formula at low chloride concentration

Wei-Ping Dow [a,*], Ming-Yao Yen [a], Cheng-Wei Liu [b], Chen-Chia Huang [b]

[a] *Department of Chemical Engineering, National Chung Hsing University, Taichung 40227, Taiwan*
[b] *Department of Chemical and Materials Engineering, National Yunlin University of Science & Technology, Yunlin 64002, Taiwan*

Received 14 August 2007; received in revised form 1 December 2007; accepted 12 December 2007
Available online 24 December 2007

Abstract

In this work, microvia filling was performed by copper electroplating using two plating formulas with and without a leveler at a low concentration of chloride. The base plating solution contained $CuSO_4$, H_2SO_4, polyethylene glycol (PEG), bis (3-sulfopropyl) disulfide (SPS) and Cl^-. When the Cl^- concentration was lower than 30 ppm, the plating formula without a leveler became dead for bottom-up filling, resulting in conformal deposition. The addition of 1 ppm Alcian Blue, used as a leveler, could effectively recover the filling performance of the plating formula with low chloride concentration. Electrochemical analyses revealed possible mechanisms. The results demonstrate that the usage of Alcian Blue can widen the operation window of chloride concentration, since it can assist PEG in competing with SPS in adsorption at low chloride concentration.

Keywords: Copper electroplating; Leveler; Microvia; Filling; Chloride concentration

1. Introduction

Consumer electronic products are becoming smarter, lighter, smaller, thinner, shorter, and faster. Therefore, the inner conducting lines of integrated circuits (ICs) and printed circuit boards (PCBs) must be made by copper metallization process which is based on electroplating [1–5]. Most advanced IC chips must be assembled on packaging substrates. A connection between an IC chip substrate and the corresponding PCB is achieved using a solder ball array. Stacked microvia in IC substrates, to connect the contact points of IC chips, have been used in mass-production, to increase the pattern density of the packaging substrate. Specifically, these microvias have to be fully filled by copper electroplating without void [6–9].

Based on the consideration of process integration of PCB, a dimple formation is not acceptable on the top of a filled microvia after copper electroplating. Otherwise, the next microvia is not easily stacked well on the filled microvia [9]. An issue of planarization between two dielectric layers of an IC substrate will arise if the microvia is not completely filled with the plated copper. However, a copper bump (i.e., overplating) may form on the top of a filled microvia because of a plating accelerator [8,10], also raising the issue of planarization. Therefore, a leveler must be added to the plating solution in order to level off the copper surface of the filled microvia.

Numerous papers [4,9–14] have demonstrated that Janus Green B (JGB) is an effective leveler for copper filling. It not only enhances the filling performance of a plating solution but also levels off any copper bump on the filled microvia [9,10]. Moreover, JGB can interact with the suppressor, polyethylene glycol (PEG), to form a composite suppressor, whose suppressing effect on copper electrodeposition is superior to that of PEG [9]. A detailed electrochemical behavior of JGB was explored by Bozzini et al. using surface enhanced Raman spectroelectrochemistry (SERS) [15]. More recently, a number of new levelers have been found, such as branched polyethyleneimine (PEI) [16], dodecyltrimethylammonium chloride (DTAC) [17], polyvinylpyrrolidone (PVP) [18] and benzyl-phenyl modified polyethyleneimine (BPPEI) [19]. Another leveler, Alcian Blue (a pyridine variant) (ABPV), has been reported to be effective for microvia filling [10,20]. However, its electrochemical properties have not been comprehensively elucidated yet.

According to previous works, Cl^- is a key additive in a copper plating solution that is used for microvia filling. It

---

[*] Corresponding author. Tel.: +886 4 22859152; fax: +886 4 2284734.
E-mail address: dowwp@dragon.nchu.edu.tw (W.-P. Dow).

0013-4686/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2007.12.048

interacts with PEG as a suppressor [21–25], with 3-mercapto-1-propanesulfonate (MPS) or bis (3-sulfopropyl) disulfide (SPS) as an accelerator [26,27], and with PEG-JGB as a composite suppressor [9,12]. These organic additives competitively adsorb on the copper surface, on which the final predominance of these additives is determined crucially by the concentration range of Cl^- and the impact of forced convection [9,10]. In other words, both the suppressor and the accelerator rely on Cl^- to exert their functions on the copper electrodeposition. However, the operating window of Cl^- concentration that can be used in the copper plating bath is narrow. Normally, it ranges from 50 to 70 ppm for the microvia filling. When the Cl^- concentration falls outside the operating window, the filling performance of the copper plating solution declines. This work demonstrated that the addition of ABPV can recover the filling performance of a copper plating solution at a very low Cl^- concentration. In other words, the addition of ABPV can widen the operation window of Cl^- concentration for microvia filling. Corresponding electrochemical analyses were also carried out to explain these results.

2. Experimental

PCB fragments with many microvias formed by CO_2 laser ablation were used as plating samples. The dimensions of the PCB fragment were 4.5 cm × 6 cm. The microvias had two diameters. One was around 110 μm; the other was around 130 μm. The depth of all microvias was around 85 μm regardless of diameter. Before metallization, the microvias were conducted through a so-called desmear process in order to remove the smear that was formed by laser ablation at the microvia bottom. The desmear process could thoroughly clean the via bottom to make sure of its conductivity. Following the treatment of desmear process, electroless copper plating was used for sidewall metallization of the microvia. Following that, an electroplated copper layer with a thickness of 2–3 μm was deposited on the sidewall in order to increase the thickness of electroless copper layer for prevention of electroless copper oxidation.

The PCB fragment was plated at a current density of 18 $A\,ft^{-2}$ (ASF) for 70 min. Two phosphorus-containing copper plates were used as anodes and placed directly in the plating bath with a working volume of 700 mL. The plating solution was constantly agitated by continuously flowing air bubbles at a flow rate of 2.5 $L\,h^{-1}$ during the electroplating to ensure good convection. The plating bath was detailed elsewhere [28].

The composition of the base electrolyte used in all plating tests was 0.88 M $CuSO_4{\cdot}5H_2O$ (Riedel-de Haën, ACS), 0.54 M H_2SO_4 (Merck, 96%, Ultrapure) and 200 ppm PEG with a molecular weight of 8000 (Fluka). The other additives, such as SPS (Raschig GmbH, Germany), Cl^- (NaCl, Fisher, Certified ACS) and ABPV (Aldrich), were individually added to the plating bath through dilution from stock solutions of these additives at appropriate concentrations. The temperature of the plating solution was maintained at 28 °C. The filling performance was assessed according to the cross-sections of microvias, which were examined using an optical microscope (OM) (Olympus BX51).

The electrochemical behavior of these additives was characterized by potential steps and galvanostatic measurements at different rotation speeds of a working electrode (WE). All of the electrochemical measurements were performed in a glass vessel containing 100 mL of electrolyte solution and using a potentiostat (PGSTAT30, Auto-Lab) with a three-electrode cell. A platinum rotating disk electrode (Pt-RDE) with a diameter of 3 mm was employed as a base of WE. Before each electrochemical analysis, a thin copper layer with a thickness of 500 nm was predeposited onto the Pt-RDE in a predeposition bath, which only contained 0.88 M $CuSO_4{\cdot}5H_2O$ and 0.54 M H_2SO_4, to prepare a Cu-RDE. The counter electrode (CE) was a small copper bar, which was placed in a small glass tube that contained an electrolyte (i.e., 0.88 M $CuSO_4{\cdot}5H_2O$ + 0.54 M H_2SO_4). The end-side of the small glass tube was sealed by a porous polymer material to prevent the additives from direct contact with the CE during analysis, yielding unfavorable byproducts. A saturated mercury-mercurous sulfate electrode (SMSE) served as a reference electrode (RE). The temperature of the electrolyte was maintained at 28 °C during the electrochemical analysis. Millipore Direct-Q DI water (18.2 MΩ cm) was used to make all solutions those were used in the electrochemical analysis.

Potential step measurements were carried out by setting a step of 0.02 V. The cathodic potential ranged between −0.58 V and −0.64 V *versus* SMSE, which corresponded with the practical plating condition. Galvanostatic measurements of additive injection were carried out using the Cu-RDE at a current density of 18 ASF in the same cell as mentioned above. At the beginning of the galvanostatic measurement, the glass vessel contained only the base electrolyte and 10 ppm Cl^-. After the galvanostatic measurement had been performed for ca. 500 s, the second additive was injected into the glass cell. Subsequently, the third additive was injected into the glass cell at 1×10^3 s. The last additive was injected into the glass cell at 2×10^3 s. Each plating formula was galvanostatically measured twice; once at 100 rpm, the other at 1000 rpm. In addition, two plating formulas with and without ABPV were also characterized by galvanostatic measurement for the same time used in practical plating.

Normally, the rate of copper electrodeposition on a cathode is directly proportional to the strength of forced convection of a plating solution, since forced convection leads to a thinner diffusion boundary layer of Cu^{2+}. However, not only Cu^{2+} but also many additives are present in the plating solution, hence the mass-transfer of the copper plating solution onto a cathode becomes complex. Recent papers [10,29] demonstrated that the rate of copper electrodeposition is inversely proportional to the strength of forced convection, if the copper plating formula is effective for microvia filling. The key point was attributed to the mass-transfer and potential-dependent adsorption of chloride ion, because chloride ion bears negative charge. Moreover, both the suppression of PEG and the acceleration of SPS need the participation of chloride ion and they compete with each other to interact with the adsorbed chloride [29]. Considering the mass-transfer equation in electrochemistry, only convection term is beneficial for the transport of chloride ion onto a cathode. Therefore, convection-dependent adsorption (CDA) was named according to the convection effect on chloride transport and the