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### Void-free and high-speed filling of through ceramic holes by copper electroplating

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#### ABSTRACT

In order to achieve void-free and high-speed filling for through ceramic holes (TCHs) to prepare direct plated copper (DPC) ceramic substrates, copper electroplating technology combined with nano-carbon coating process was used in this work. The nano-carbon coating process was adopted to form a nano-carbon film as a conductive layer on the hole wall. For the TCH electroplating, an ameliorative plating additive mixture was proposed, which consists of accelerator thiazolyl dithio-propane sodium sulfonate (SH110), leveler nitrotetrazolium blue chloride (NTBC) and inhibitor polyethylene glycol (PEG, MW = 8000). Experimental results indicate that the optimized formula of the additives is 6 ppm SH110, 5 ppm NTBC, and 200 ppm PEG. By this optimized formula, the filling speed was further improved by duly increasing current densities. Consequently, TCHs with high aspect ratios (ARs) of 6.25 (500 µm depth and 80 µm diameter) were completely and void-free filled at the high current density of 1.5 ASD for 2 h, which promotes the development of vertical interconnection for DPC ceramic substrates and enhances their reliability for high power packages.

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#### 1. Introduction

Due to its high mechanical strength, high thermal conductivity, excellent corrosion resistance, and low coefficient of thermal expansion, ceramic has been widely applied as a heat spreader or submount for power electronic packaging, such as light-emitting diodes (LEDs), laser devices (LDs), and power controllers [1–3]. In recent years, direct plated copper (DPC) ceramic substrate has been developed to satisfy high power device packaging, which can realize precise and controllable metal layer for heat conduction and electrical interconnection [4–6]. Moreover, in order to improve the integration level and miniaturization, laser drilling and filling of through ceramic holes (TCHs) are adopted as a feasible and effective method for the preparation of DPC ceramic substrates. But it still has some technical challenges to realize the void-free and high-speed filling of TCHs in the DPC process.

Copper electroplating is the main filling technology for throughholes (THs), especially in the field of printed circuit boards (PCBs), through glass vias (TGVs) and through silicon vias (TSVs) [7–9]. Currently, two electroplating approaches, bottom-up electroplating and double-sided electroplating, have been proposed for the TH filling [10, 11]. Although bottom-up electroplating can achieve compact TH filling, it is not suitable for the TCH filling during DPC process because the TCH with large diameter is difficultly sealed to prepare blind hole by

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http://dx.doi.org/10.1016/j.microrel.2017.06.074 0026-2714/© 2016 Elsevier Ltd. All rights reserved. electroplating [12,13]. On the contrary, double-sided electroplating can effectively fill the TH with large diameters, but voids always occur in the filled TH, leading to the low packaging reliability of DPC substrates. Notably, the filling quality and efficiency are greatly affected by power supply, plating additives, current densities, and hole wall metallization. Thus, a compact fill and high efficiency can be obtained by optimizing these factors.

For the TH filling of PCB and glass interposer by electroplating, single plating additive, such as nitrotetrazolium blue chloride (NTBC), thiazolyl blue tetrazolium bromide (MTT), and sodium thiazolinyldithiopropane sulfonate (SH110), has been developed [14–16]. By using these single additives, a void-free filling is achieved for THs with different aspect ratios (ARs) and diameters [13,16]. But this void-free filling process is only conducted at a low current density and results in a low filling efficiency, since the voids resulted from irregular copper depositing always appear in Cu fills at a high current density under the small concentration gradient of inhibitor in THs [8,15]. W. P. Dow et al. and N. Dimitrov et al. addressed the matter by pre-adsorbing an inhibitor-free or weak accelerator-containing electrolyte before plating the THs in the bath composed by DI water, acid, sodium salt, chlorine ion and inhibitor. The method can quickly form plugs in the center of high AR TGVs with small diameters and complete void-free filling at a higher speed [17,18]. However, this process also requires long time for the void-free filling of the TH with large diameter, especially for TCHs with diameters of 80-150 µm, because it is difficult to prepare copper plug in this TH center [18]. Alternatively, periodic-pulse-reverse (PPR) plating is developed to solve this problem [19]. In this PPR method, a

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pause time allows copper ions to diffuse to the center in THs. And the reverse current can increase the copper ions concentration in THs, also it can preferentially strip the copper deposited at the entrance, which can prevent THs blocking and defects forming [20,21]. Nevertheless, the PPR method requires expensive power supply and special plating additives, which is much more complex than the DC plating method [12]. For these reasons, multiple plating additives, including accelerator, inhibitor, and leveler, have been researched for the TH filling by DC plating. These plating additives can increase the copper deposition speed at the center and reduce the speed at the mouth of a TH during the electroplating process and then form butterfly profile, which is benefit to achieve void-free filling with high filling efficiency and low cost [17]. However, these plating additives have not been systematically investigated in the TCH filling with high ARs. In addition, electroless plating is usually used to deposit metal seed layer on the sidewall for THs electroplating, but it is harmful to humans and the environment [22,23]. Therefore, in order to realize void-free and high-speed TCH filling for the preparation of vertical interconnecting DPC ceramic substrates, it is necessary to systematically study the TCH electroplating process, including plating additives, current density, and hole wall metallization.

In this work, void-free and high-speed TCH filling for DPC substrate was achieved by nano-carbon coating process and direct current copper electroplating. The nano-carbon coating process with non-pollution was firstly employed to form a conductive layer on the hole wall of TCHs, followed by DC copper electroplating for TCHs filling. A plating additive mixture including accelerator SH110, inhibitor polyethylene glycol (PEG, MW = 8000), and leveler NTBC, was proposed and optimized. Furthermore, the highest filling efficiency for TCHs was investigated by duly improving current densities with the optimized formula of the additives. The TCH electroplating experiments were carried out and the main performances of fully filled TCHs were examined.

#### 2. Experiments

Fig. 1 shows the schematic diagram of TCH filling process. Firstly, Alumina ceramic substrates (Al<sub>2</sub>O<sub>3</sub>) with TCH arrays were prepared by laser drilling. The dimension of ceramic substrate is about 6.2 imes6.4 cm<sup>2</sup>. In order to achieve various ARs, the depth of TCHs is designed as 380 µm and 500 µm, and the diameter of TCHs is designed as 80 µm, 100 µm and 120 µm, respectively. Some smear left in TCHs by laser ablation was cleaned by acetone, ethanol, and deionized (DI) water in an ultrasonic bath for 10 min in turn, and then dried with nitrogen (N<sub>2</sub>) gas. After that, a seed layer with Ti (200 nm) and Cu (300 nm) was deposited on the surface of ceramic substrate, and 5-6 µm Cu layer was electroplated on this seed layer. Then, the nano-carbon coating process was adopted herein to deposit a conductive layer in the TCH, and a continuous nano-carbon film was fixed on the hole wall for following electroplating. Next, the photolithography and developing process were finished to prepare the pattern. At last, the ceramic substrate was put into the electroplating bath and placed between two anodes to complete the TCH filling. The bath was equipped with the air agitation and cathode (ceramic substrate) swing, which were used to reduce the concentration gradient of plating electrolyte. And vertical spraying was designed on both sides of cathode for super filling, which can establish the convection difference of plating electrolyte along TCHs and provide ample Cu<sup>2+</sup> at the center of TCHs. A DC power (HY3003F-3, Hangzhou huayi electronics industrial co., LTD, China) was used to supply various current densities for the TCH electroplating.

In this work, nano-carbon coating process was applied to replace the harmful electroless plating, in which a conductive nano-carbon film was formed for TCHs electroplating [24]. The nano-carbon coating process was described in detail, as illustrated in Fig. 2. Firstly, the ceramic substrates were dipped into a conditioner at 55 °C following by ultrasonic cleaning. And the hole walls were cleaned and fixed with positive



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 Charge
 Adsorption of
 Carbon film
 Copper

 conditioning
 nano-carbon colloid
 fixation by Drying
 microetching

Fig. 2. Nano-carbon coating process for carbon film formation and fixation.

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