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Ultra-Uniform Copper Deposition in High Aspect Ratio Plated through Holes via Pulse-Reverse Plating

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Abstract: The uniformity and microstructure of the copper deposition in the high aspect ratio plated through holes (penetrating holes) are crucial for the performance of printed circuit board. We systematically investigated the effects of reverse pulse parameters in the period pulse reverse (PPR) plating on the uniformity and microstructure of the copper deposition, including reverse pulse frequency, reverse pulse duty cycle and reverse pulse current density. The Cu deposition behavior (throwing power) and its crystallographic characteristics, including grain size, crystallographic orientation, and grain boundary, were characterized by means of field-emission scanning electron microscopy (FE-SEM), X-ray diffractometer (XRD), and electron backscatter diffraction (EBSD). Our results clarify that the reverse pulse current density and duty ratio should be low to achieve the full filling and high uniformity of the through holes. The reverse pulse frequency of 1500 Hz would prevent the through holes to be fully filled. The copper electrodeposition in PTH prepared by double pulse electrodeposition has the good (111) surface texture and grain boundary distribution. This work demonstrated that the period pulse reverse (PPR) plating provides unique advantages in achieving the ultra-uniform copper deposition in the high aspect ratio plated through holes.

Keywords: pulse-reverse plating; ultra-uniform copper; plated through holes; high aspect ratio; reverse pulse frequency

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1. Introduction

With the miniaturization of modern electronics, the multi-layer, thin, and high-density wiring printed circuit boards (PCBs) are the research and development direction [1]. The high-density interconnected printed circuit boards (HDI-PCBs) offer significant advantage in improving the device performance and reliability [2]. Hole metallization is the core technology in HDI-PCBs to achieve the high quality interlayer connections [3]. Copper is the most widely used metal in the hole metallization due to the superior comprehensive properties of high ductility, low cost, high electrical, and thermal conductivity [4]. Among various copper deposition methods, such as PVD (Physical Vapor Deposition), CVD (Chemical Vapor Deposition) [5], and sputtering, the electrochemical methods have proven to be costless, highly productive, readily adoptable, and the most general route employed to obtain metallic films of adequate thickness, porosity-free structure, and good adhesion. In the development of HDI-PCBs integration, the aspect ratio of through holes increases significantly, where the aspect ratio (ε) is defined as the depth (D) of the hole divided by its width (W). In high aspect ratio plated through holes, the diffusion of the reactants would be constricted by the very narrow and deep holes, leading to the concentration polarizations of copper ions, which would impede the copper deposition process [6–8]. Although many strategies have been developed to address the above mentioned limitations [9–12], it is still challenging to realize uniform copper superfilling of the plating through a hole with high aspect ratio.

The period pulse reverse (PPR) plating [13,14], in which cathodic pulses are followed by anodic pulses, is a promising technology to achieve uniform copper deposition in high aspect ratio holes [15–18]. The periodically reverse current could dissolve the over-deposited copper in the current crowding position (PTH entry or exit). Meanwhile, the metal ions consumed in the cathode area can be replenished, thus effectively slowing down the concentration polarization [19,20]. Moreover, the PPR reduced the consumption of copper ions and organic additives in a via structure [21,22]. The peak current density in the PPR electrodeposition method increases the over potential of the cathode and benefits the nucleation and grain refinement [23].

Much research on period pulse reverse plating in plating through hole has been done to partially reveal the effects of processing parameters on plating performance, such as comparison of period pulse reverse plating and direct current plating for the uniformity of copper deposition plated through holes [24–26], microstructure of copper deposition with various pulse reverse frequency [27]. However, there is still a lack of comprehensive study on the effects of a battery of pulse reverse parameters [28] and underlying mechanism on copper deposition in high aspect ratio PCB plating through a hole. In this paper, a comprehensive study has been performed to investigate the effect of pulse reverse parameters, including pulse reverse frequency, duty cycle and current on lattice strut size, morphology, surface structure, and internal porosity. On this basis, the mechanism of the reverse pulse in the electrodeposition behavior was discussed. The presented results can enhance the understanding and enable the subsequent adjustable craft of period pulse reverse plating for the ultra-uniform copper deposition in high aspect ratio PCB plating through hole.

2. Experimental

2.1. Plating through Hole (PTH)

The PCBs were composed of FR-4 epoxy resin and copper. The microvia fabricated by mechanical drilling had an aspect ratio of 1.5 mm/0.3 mm (depth/diameter). Electroplated copper was used to characterize the cross sections. Before metallization, a desmearing process was done to remove the smear formed by the mechanical drilling on the hole wall of the THs. A thin Cu film was predeposited on the hole wall by electroless (ELS) copper deposition. The electroless copper acts as the catalytic seed layer of copper plating. The electroless copper was also an important step of the current PCB through-hole metallization process, which affects the final uniformity of the through-hole plating and the device performance. The phosphor copper plate is used as the anode and the PCB is used as the cathode. In our procedure, four anode plates were adopted and the PCB board was located in the middle of the rectangle enclosed by the anode plates. The overall size of the electroplating tank is 9 cm × 9 cm × 8 cm. We placed four identical anode plates inside the plating tank, and the thickness of the anode plate is 0.2 cm. When the cathode and anode are facing each other, the distance is approximately 4.3 cm. The cathode was rotated, and the speed was 100 revolutions/min. The electroplating bath temperature was 40 °C, and the SMD-30 was used as the period pulse reverse power supply. The four-anode system is adopted, and the rotation of the cathode was adopted to improve the uniformity of PTH. The experimental device was illustrated in Figure 1.

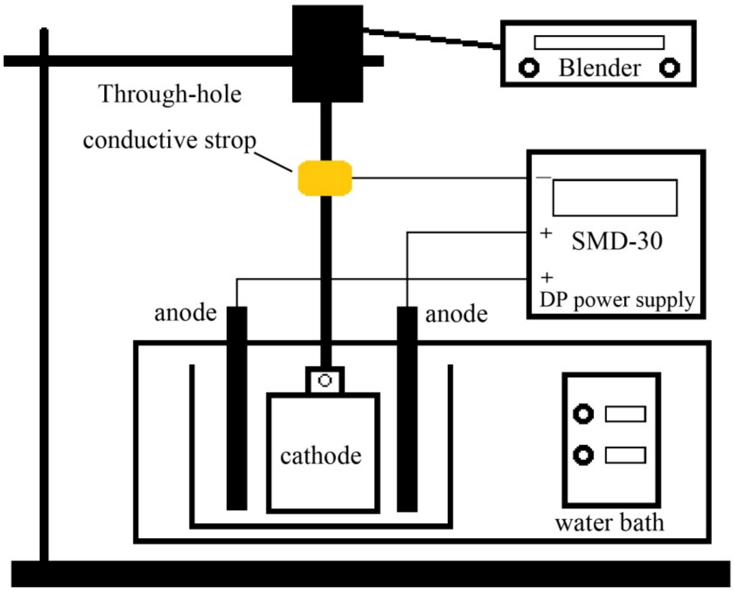

Figure 1. Schematic diagram of the experimental device.

The copper electroplating bath solution was composed of 70 g/L $CuSO_4{\cdot}5H_2O$, 200 g/L sulfuric acid, 200 ppm polyethylene glycol (PEG, MW10000), 60 ppm Cl^- and 10 mg/L thiazolinyl dithio propane sulfonate (SH110). The current density of the copper plating was controlled at 2 A/dm^2 (ASD) and the electroplating time was 2 h. Imposed pulse current included forward pulse current and reverse pulse current (Figure 2). The forward duty ratio is 0.4, the pulse frequency is 100 Hz, the forward working time is 100 ms, and the reverse working time is 20 ms. The reverse pulse current density, reverse pulse duty cycle, and frequency are summarized in the Table 1.

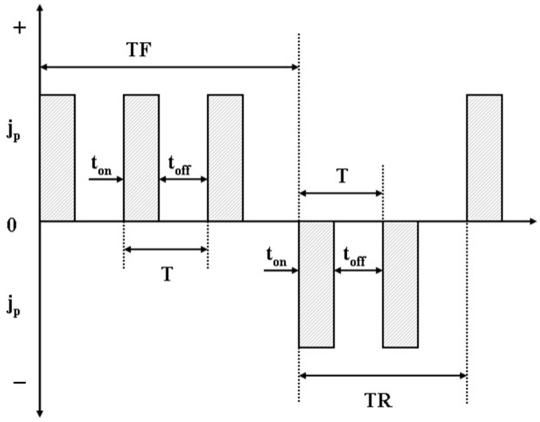

Figure 2. The schematic diagram of forward- and reverse-pulse currents to prepare copper, $+j_p$ is the forward pulse current density, $-j_p$ is the reverse pulse current density, t_{on} is the pulse current on-time, t_{off} is the pulse current off-time, T is a pulse power-on and power-off cycle, $T = t_{on} + t_{off}$, TF is the working time of a set of forward pulses, and TR is the working time of a set of reverse pulses.

Table 1. Experimental parameter design.

Conditions	a1	a2	a3	a4	b1	b2	b3	b4	c1	c2	c3	c4
reverse pulse frequency (HZ)	100	500	1000	1500	100	100	100	100	100	100	100	100
reverse pulse duty cycle	0.4	0.4	0.4	0.4	0.2	0.4	0.6	0.8	0.4	0.4	0.4	0.4
reverse pulse current density (A/dm^2)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.4	1

2.2. Characterization Methods

The throwing power (TP) is the parameter which is defined as the ability of an electroplating solution/method to uniformly deposit metal on the cathode and can be calculated via the following equation:

$$\text{Throwing Power} = \frac{(Y1+Y2+Y3+Y4+Y5+Y6)/6}{(X1+X2+X3+X4)/4} \times 100\% \quad (1)$$

where X1–X4 and Y1–Y6 are δ surf and δ TH at different regions, as illustrated in Figure 3.

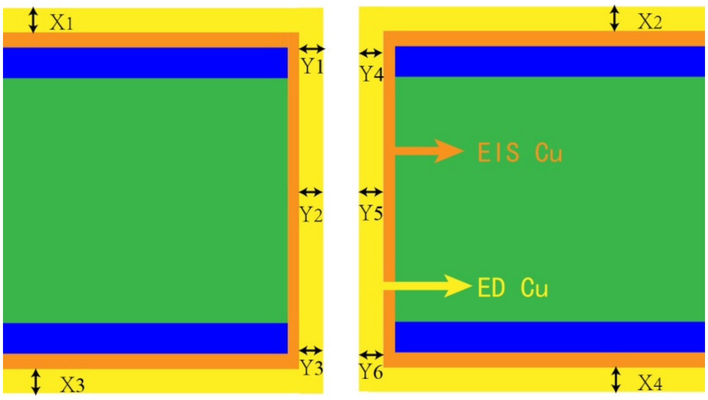

Figure 3. Definition of the throwing power (TP) in a plating through hole (PTH) structure.

After being precisely polished, the filled microvia cross-section's morphology of were observed under field emission scanning electron microscopy (FE-SEM, ThermoFisher Scientific Aperos S, Waltham, MA, USA) to calculate the TP.

All electrochemical measurements were performed in a three-electrode system using a Gamry electrochemical workstation (Gamry, Philadelphia, PA, USA) at 24 ± 1 °C. In the test, different rotation speeds of the rotating disk electrode (RDE) are used to simulate different convection strengths of the solution on the cathode surface. In this paper, the rotation speed of 100 rpm (space, the same below) and 1000 rpm were used to simulate the center of the hole during the electroplating process and the convection strength of the bath at the orifice. The working electrode, reference electrode, and counter electrode are Cu-RDE, mercurous sulfate electrode, and platinum electrode, respectively. The electrochemical test method was galvanostatic chronopotentiometry curve test. The current density used in the E~t curve test is 2 A/dm^2.

The XRD pattern was recorded through a X-ray diffractometer (X'Pert PRO, Dy2198, PANalytical B.V., Almelo, The Netherlands) with Cu Kα radiation. Preferred orientation was also studied by using the relative texture coefficient (RTC, $TC_{(hkl)}$), which is given by the following expression.

$$TC_{(hkl)} = \frac{I_{(hkl)}/I^0_{(hkl)}}{\sum I_{(hkl)}/I^0_{(hkl)}} \quad (2)$$

where $I_{(hkl)}$ and $I^0_{(hkl)}$ are the diffraction intensities of each (hkl) line in the XRD patterns of the deposits and randomly oriented copper powder sample (JCPDS No. 02-1225), respectively. When the texture coefficient of each diffracting plane is the same, the crystal plane orientation is random; if the TC value of a certain (hkl) plane is higher than the average value, the crystal plane has a preferred orientation. The TC value is positively correlated with the preferred orientation degree.

The microstructures of the Cu electro deposition in the PTHs were examined using the electron back-scatter diffraction (EBSD, Oxford Instrument, Oxford, UK) analysis system and AztecCrystal, software (version 7.0 published by EDAX, Inc., Philadelphia, PA, USA).

3. Results and Discussion

3.1. Bath Solution Design

In general, the composition of the plating solution in through-hole plating compared required careful tailoring from the blind-hole plating solution in HDI-printed boards. The through-hole plating solution required the higher concentration of acid and the relatively lower concentration of copper ions than those in blind-hole plating solution. Previous studies on through-hole plating suggest that the optimal composition consists of copper ions concentration ranges from 70 to 100 g/L and the sulfuric acid concentration ranges from 180 to 220 g/L [29]. In this experiment, the plating bath was composed of 70 g/L $CuSO_4{\cdot}5H_2O$, 200 g/L sulfuric acid, 60 mg/L Cl^-.

The addition of additives into the base bath is necessary to achieve the uniform copper deposition in the hole. The additives can be classified as inhibitors, brighteners, and levelers by their roles in the copper deposition process. Polyethylene glycol was a common inhibitor, the molecular weight and concentration of which would affect the filling effect. According to previous reports [6,7,21], 200 mg/L polyethylene glycol (PEG10000) was used at plating. The role of the accelerator includes the acceleration of the copper deposition rate, promoting the formation of copper crystal nucleus, thus improving the uniformity of the copper layer. At present, SPS, MPS, SH110, etc., were widely used as the accelerator in plating [30]. Wang et.al. [31] showed that SH110 was an excellent additive exhibiting bi-role as the accelerator and the inhibitor, and exhibits superior performance than the conventional additive, SPS. Meanwhile, SH110 exhibited higher bottom-up filling ability than SPS over a wider potential range.

Figure 4 shows the results of galvanostatic measurements of PEG10000 and SH110 injection during copper electroplating. When 200 mg/L PEG was injected to the base plating solution, the cathode potential shifted to negative rapidly, indicating that PEG was adsorbed on the cathode surface as an inhibitor, increasing the cathode polarization. So, the growth rate of copper crystals decreased accompanied by the increase of nucleation rate, and there was a certain grain refinement. After 1 mg/L SH110 was injected, it acted as an accelerator and exhibited a competitive adsorption with the inhibitor PEG adsorbed on the cathode surface, and the absorptive strength was higher than PEG. So, the addition of SH110 enables depolarization of copper deposition. With a SH110 concentration increase, the concentration of inhibitor fragments decomposed by SH110 gradually increased, and the cathodic polarization increased [30,31]. Different potential changes were gradually displayed under strong and weak convection. When 10 mg/L SH110 was injected, the polarization of cathode surface decreases from 1000 to 100 rpm. So, the electrodeposition rate under strong convection at the orifice was lower than that in the weak convection inside the hole, thus leading to high TP. When 20 mg/L SH110 was injected, the concentration of the decomposed inhibitor fragments further increased. Under the strong convection at 1000 rpm, the higher polarization of the cathode leads to a negative shift of the cathodic potential. The cathode potential at 100 rpm had smaller negative shift than at 1000 rpm. Therefore, SH110 exhibits both acceleration and inhibition effect, and the concentration should be moderate, and 10 mg/L was found to be the optimized value in this system.

3.2. Effect of Reverse Pulse Parameters on Uniformity of Cu Electrodeposition

In this experiment, the forward current density was 2 A/dm^2, the duty cycle was 40%, the forward frequency was 100 Hz. The forward working time and reverse working time was 100 and 20 ms, respectively. The key parameters of reverse pulse were reverse pulse frequency, reverse pulse duty cycle, and reverse current density. The experiments with different reverse pulse parameters are shown in Table 1. The uniformity of Cu electrodeposition in PTH of the experiments is shown in Figure 5.

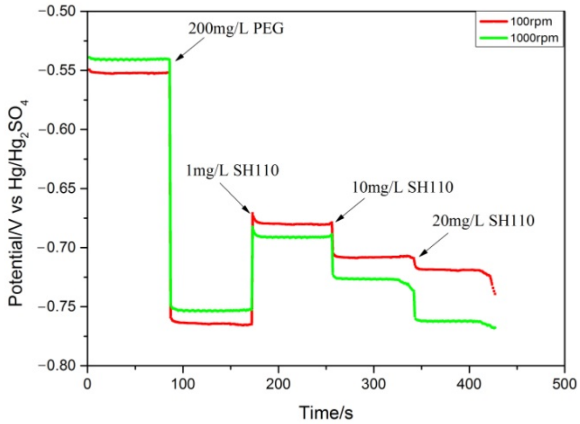

Figure 4. Galvanostatic measurements with 200 mg/L PEG10000 and 1~20 mg/L SH110, and the rotating speed 1000 rpm or 100 rpm. The plating solution was composed of 70 g/L $CuSO_4{\cdot}5H_2O$, 200 g/L sulfuric acid, 60 mg/L Cl^-.

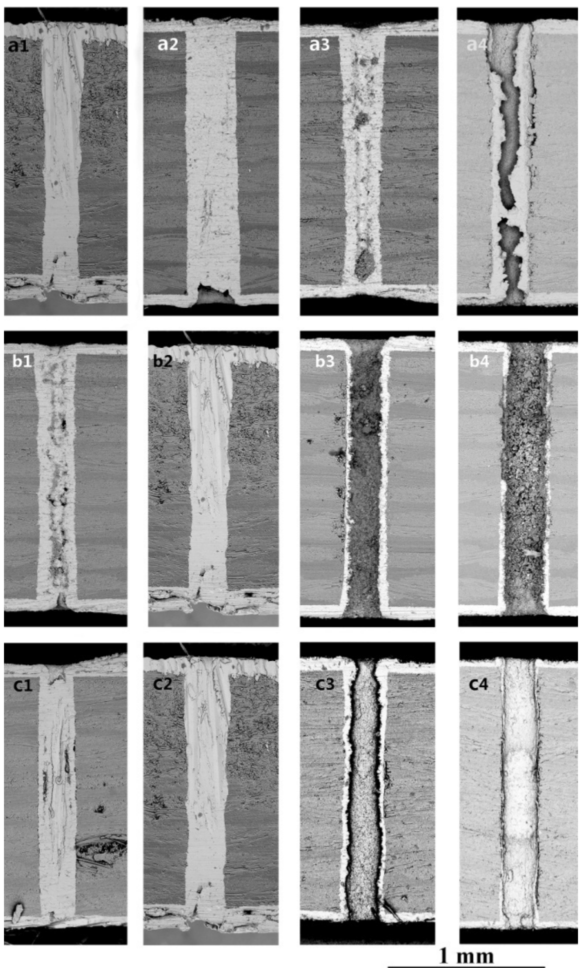

Figure 5. Cross-sectional observations of the filled PTH by PPR plating. (**a1**–**a4**) is reverse pulse frequency (HZ). (**b1**–**b4**) is reverse pulse duty cycle. (**c1**–**c4**) is reverse pulse current density (A/dm^2).

The void-free filling of copper was achieved with the reverse frequency of 100, 500 Hz. The uniformity of copper in PTH deteriorated and the voids appeared when the reverse frequency increases to 1000 or 1500 Hz. These voids lead to poor thermal reliability and conductivity of copper in PTH.

When the pulse reverse duty cycle was 20% or 40%, full filling of the copper in PTH was achieved, and shows superior uniformity than the samples prepared under the pulse reverse duty cycle of 60% or 80%. When the on-time of the pulse reverse increases, the dissolution effect was enhanced, resulting in an inferior filling effect of the copper in PTH. When the pulse reverse duty cycle was 20%, voids appeared in the coating, the peak current density was higher than others of duty cycle parameters with the same average current density. The significant oxidation of the cathode would cause the uneven dissolution of the copper, resulting in large voids in the coating. Meanwhile, the increase of the reverse pulse peak current may have a deactivation effect on the additive, resulting in an inferior filling effect.

When the reverse current density was low, such as 0.1 or 0.2 A/dm^2, the high uniformity and the void-free filling of copper in PTH were achieved. The current efficiency decreases when the reverse current density increases to 0.4 or 1 A/dm^2. The reason is that the large reverse current density leads to the large amount of anodic dissolution on the surface of the copper coating during the reverse pulse. Therefore, the current efficiency and the coating thickness would decrease, resulting in an inferior filling effect.

The TP values of PTHs obtained from electroplating with different experimental parameters of Table 1 are shown in Table 2. The TP value higher than 100% means a thick copper layer depositing at the center of PTHs, and a relatively thin layer at the mouths, then indicating PTH filling without any defects. The TP values of different reverse pulse frequency were higher than 100%. That means it could deposit the copper in PTH filling without any defects. The average current density and duty cycle of the reverse pulse should not be too high such as the experiments of b3, b4, and c4, which will lead to a decrease in TP value. In addition, the uniformity of copper in PTH was inferior in the experiments of b3, b4, and c4.

Table 2. The thickness of copper and the TP value.

Experiment	a1	a2	a3	a4	b1	b2	b3	b4	c1	c2	c3	c4
Copper inside the hole/μm	136.39	142.71	126.26	82.22	114.69	136.39	36.46	33.26	135.38	136.39	42.18	24.71
Copper of surface/μm	77.14	60.21	73.31	64.31	88.39	77.14	54.58	52.42	88.30	77.14	40.06	43.07
TP/100%	176.80	237.03	172.23	127.84	129.75	176.80	66.80	63.45	153.31	176.80	105.28	57.37

Compared with the reverse pulse frequency, reverse pulse duty cycle and current density have a higher impact on the coating filling and uniformity. When the reverse frequency ranges from 100 to 1000 Hz, the uniformity of copper in PTH improves to achieve the full filling of the through hole. The reverse pulse current density should not be too high, preferably 10% of the forward current density, and the optimal reverse duty cycle should preferably be 20%~40%. Therefore, considering the TP value and uniformity of the coating, the optimal reverse pulse parameters were 100 Hz, -0.2 A/dm^2, and 40%.

During the period pulse reverse plating, the peak current density increases the cathode over potential and the nucleation process was accelerated, which caused the grain refinement of the copper. The reverse pulse also affects the growth and nucleation process of the copper coating. The reverse pulse has influence on the overpotential of the cathode surface. During forward electrodeposition, additives were adsorbed on the cathode surface to tailor the nucleation and crystal growth process. During reverse dissolution, the additives would be desorbed on the surface. When it was transformed into forward electrodeposition again, the additive is resorbed on the surface of the cathode. Duplex or three-fold diffusion layer on the cathode surface was reconstructed, thus affecting the overpotential and deposition process. This leads to a change in TP value and thickness of the copper in PTH. The existence of the reverse pulse also affected the crystal growth process of copper plating. The reverse pulse had a leveling effect on the coating, and had an advantage in promoting the uniform copper growth of the copper. In the process of direct current electrodeposition, it tends to grow priorly in the orifice part, in which the ion concentration was high and the concentration polarization was low. The concentration polarization becomes significant in the hole with the high thickness-to-diameter ratio, which limits the copper growth of the coating. Therefore, overgrowth copper would be dissolved by the reverse pulse, leading to higher uniformity of the copper. Meanwhile, the oxidation occurs in the reverse pulse process to dissolve the copper layer, so that the cathode could replenish copper ions and suppress the concentration polarization. Therefore, the period pulse reverse plating benefits the ultra-uniform thickness growth of copper plating with high aspect ratio.

3.3. Copper Texture

The texture of copper is critical to the performance of the HDI-PCB interconnect coating. Copper with strong (111) crystallographic orientation is preferable as it can improve thermal stability in high temperature manufacturing process, and have higher resistance to electromigration and mechanical properties. The copper with strong (111) crystallographic orientation is related to its crystal growth mode. Studies have shown that copper with strong (111) crystallographic orientation can be obtained by adjusting the period pulse reverse plating parameters. Zhan et.al. [32] reported that the pulse frequency and pulse off time contribute to the growth of twin crystals. The spiral feature of the hexagonal pyramid on top of the nt-Cu indicated that the formation of periodic twin structures is owing to the screw dislocation-induced growth.

Figure 6 and Table 3 show the XRD data and the texture coefficients of different crystal planes of copper prepared by different experimental parameters as shown in Table 1. It can be seen from Figure 6 that copper prepared with different reverse pulse parameters all have copper standard XRD diffraction peaks, and the (111) plane is the preferred orientation, which benefits the interconnection performance of copper. When the reverse duty cycle was 0.4, the TC value of (111) plane reaches maximum as 68.21%, and the TC value of (111) plane decreased with the increase of reverse duty cycle. The copper prepared with different reverse pulse frequency were all with high portion (111) textured copper. The reverse pulse frequency has little effect on the TC value of (111) plane, the same trend was observed in the copper uniformity. The TC value of (111) plane decreased when reverse pulse frequency was 1500 Hz. When the reverse pulse frequency was 100 Hz, the TC value of (111) plane reaches its peak. According to the texture coefficients data, TC value of (111) plane decreased when reverse current density is either too high or too low. When the reverse current density was 0.2 A/dm^2, the TC value of (111) plane was the highest. The result indicates that the reverse pulse affects both the growth of copper (111) plane and its texture coefficient. For DC plating, the current does not change, and the crystal plane orientation is determined by the orientation of the substrate, the current density of the components and the plating solution. For pulse-reverse plating, there are forward growth and reverse dissolution processes; T_{on} and T_{off} also affect the crystal growth. The difference in grain orientation of the copper coating has a close relationship with the formation of twins during the growth process. Twin formation is one mechanism by which new crystal directions appear on the oriented substrates. The period pulse reverse deposit a barrier layer at points of high current density. This inhibits Cu deposition at these points and reduces, compared to DC plating, the required amount of organic additives. Furthermore, the PPR plating favors grain nucleation thus increases the number of grains per unit area. The reverse pulse can dissolve the cathode surface, which leads to possible changes in the orientation of the crystal planes of the substrate and ultimately affects the texture coefficient of the crystal planes. Therefore, different reverse pulse parameters will affect the texture coefficient of the crystal planes. With different reverse pulse parameters, all prepared samples possess high-portion (111) textural copper, which is beneficial to the stability of copper and the interconnect performance of plating. Based on the TC values, the optimal reverse pulse parameters are 100 Hz, -0.2 A/dm^2, and 40%, which also have higher TP value and copper uniformity.

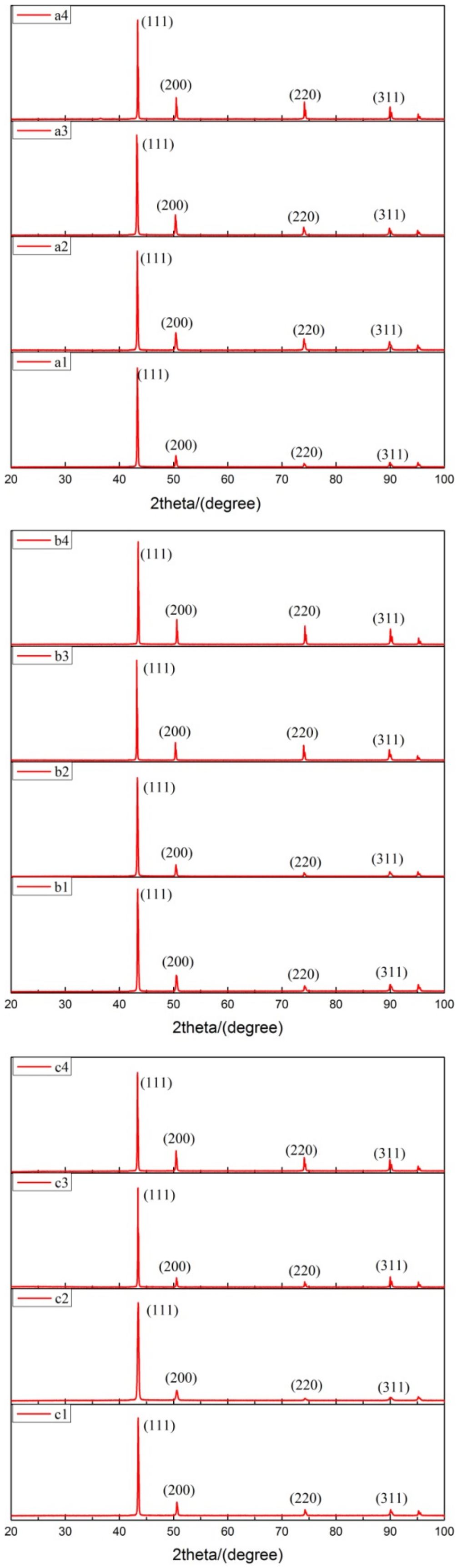

Figure 6. XRD of Cu electrodeposition in PTH. (**a1**–**a4**) is reverse pulse frequency (HZ). (**b1**–**b4**) is reverse pulse duty cycle. (**c1**–**c4**) is reverse pulse current density (A/dm^2).

Table 3. The TC value of copper.

TC/100%	(111)	(200)	(220)	(311)
a1	68.21	13.34	6.93	11.52
a2	59.23	16.10	12.03	12.64
a3	64.92	16.08	8.80	10.20
a4	51.23	17.09	15.6	16.08
b1	66.66	15.42	6.72	11.20
b2	68.21	13.34	6.93	11.52
b3	56.20	15.47	14.13	14.20
b4	54.01	18.00	13.69	14.30
c1	59.90	16.25	9.92	13.93
c2	68.21	13.34	6.93	11.52
c3	66.66	10.28	7.26	15.80
c4	51.91	17.92	14.06	16.11

The crystallographic characteristics of the PR plated copper, including grain sizes, crystallographic orientations, and grain boundaries were characterized using EBSD. Figure 7 shows the EBSD result of the cooper prepared with the reverse pulse frequency at 100 Hz, reverse pulse duty cycle of 40%, the reverse current density of 0.2 A/dm^2. The scanning step sizes utilized in the EBSD analysis was 0.20 μm. Each color corresponds to an individual crystallographic orientation, as represented in the stereographic triangle.

The Figure 7 showed that the blue crystal grains representing the (111) orientation account for the majority, indicating that the copper surface is dominated by the (111) plane orientation. There was a preferred orientation of the (111) plane of copper crystal grains in the copper of electrodeposition in PTH, which was proved in the orientation map and IPF map, and it was consistent with the XRD data analysis. Meantime, the pole figure showed the strong (111) surface texture. The grain boundary was considered to be the area between two adjacent pixels in the orientation map with a disorientation angle (θ) above a specified value. The white line represents grain boundaries with θ of 2°–15° (i.e., low angle grain boundaries, LAGBs), the black line represents high angle grain boundaries (HAGBs) with θ > 15°, which demonstrated a similar GB distribution (HAGBs: 0.863; LAGBs: 0.137). Copper had many TBs. A high density of HAGBs in Cu could effectively block the slip deformation and stimulate secondary slip systems. TBs (Σ3) are a special type of coherent boundary that are capable of blocking dislocation motions, thereby strengthening metals. In contrary, LAGBs provide poor resistance for the glide of mobile dislocations, decreases the micro-structural integrity and stability. The mobility of TBs was relatively low, and the structure stability was high. Moreover, the resistance of TBs was significantly lower than those of non-coherent large-angle grain boundaries.

In the fabrication process of high (111) texture nano-copper with PPR plating, the mechanism of action has been investigated previously. Delilah A. Brown et al. [33] investigated the growth law of copper thin films under different electroplating conditions, including no additives and in the presence of various additives under DC electroplating, pulse electroplating. This study showed that the growth structure of copper crystals has a great relationship with the substrate. The ultimate crystal planes were determined by the different growth trends. For example, Zhan et al. [32] prepare high portion (111) textured nano-twinned copper in additive-free electrolytes via the PPR plating technology. The pulse frequency is medium-frequency (10~100 Hz). By changing the pulse frequency, highly (111) specific copper close-packed coherent nano twins were prepared, and the theoretical growth model of screw dislocation growth was explained at the same time. The prepared copper coating has good thermal stability and mechanical properties, which broadens the application of pulse electrodeposition technology in this field. From the EBSD results and XRD texture analysis, it confirms that the copper prepared by the PR plated have good stability and a nti-migration ability. The copper with better through-hole filling uniformity also has better texture coefficient.

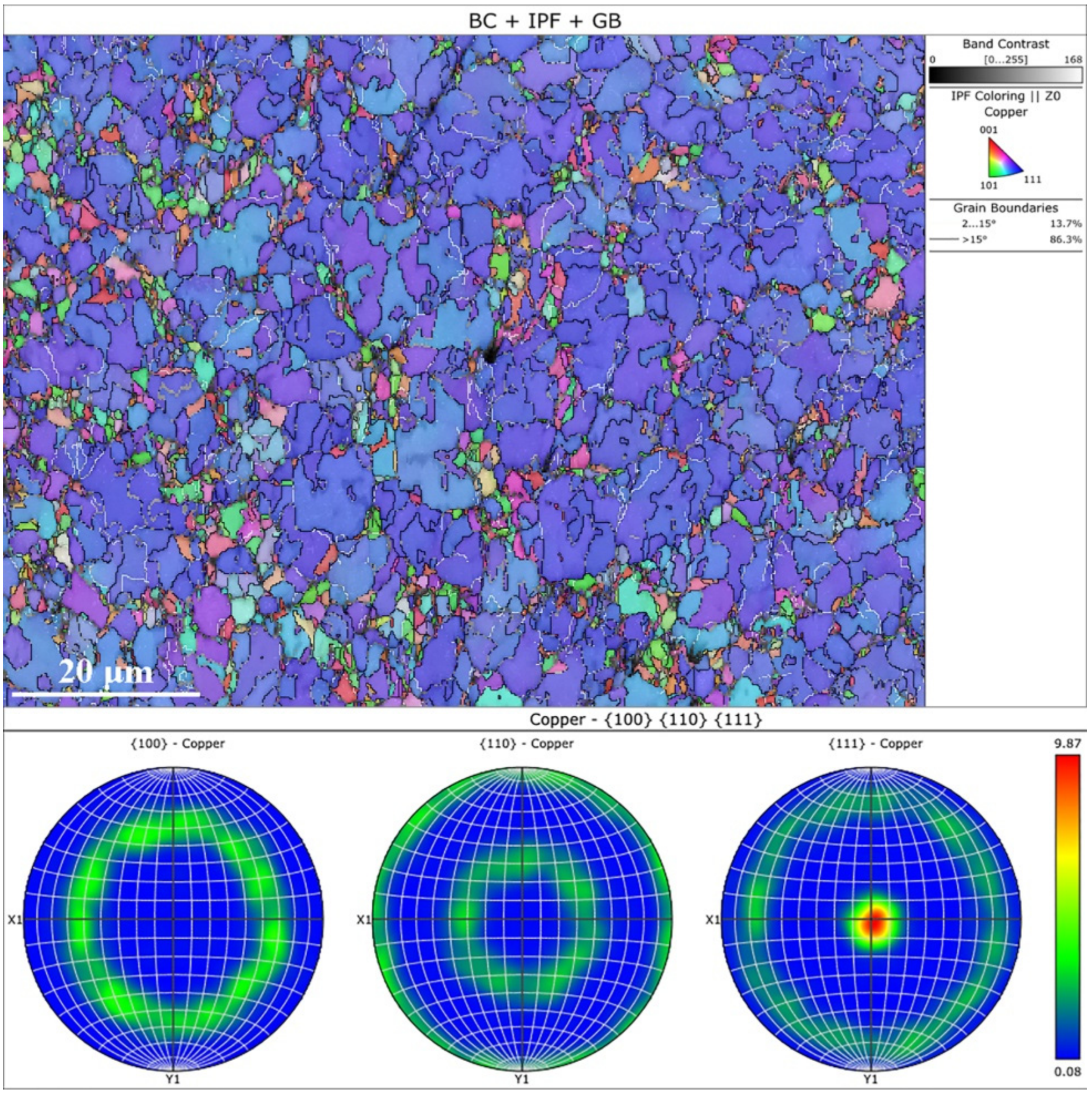

Figure 7. EBSD orientation maps (TD), grain boundary and the pole figure of Cu electrodeposition in PTH.

3.4. Copper Surface Morphologies of PTH

Figures 8–10 show the SEM images of copper surface prepared by different experimental groups as shown in Table 1. When the reverse pulse frequency was 100 Hz, the reverse duty cycle was 20% or 40%, and the reverse current density was 0.1 A/dm^2 or 0.2 A/dm^2; the flat and dense surface is obtained. This result was consistent with the previous uniformity of copper, TP value and XRD texture analysis. The dense copper surface is closely arranged of uniform and small spherical particles clustering. In high magnification SEM, planar morphology was a hexagonal pyramid with a clear step-and-terrace structure. The hexagonal pyramid structure at the surface of (111) copper is owing to screw dislocation growth [32]. When the reverse pulses increase to 1000 and 1500 Hz, the planar morphology of the copper is the accumulation of copper crystals with a longer hexagonal pyramid structure, with larger particles. Some pores were observed as the copper was not tightly arranged. The spherical hexagonal pyramid structure of the copper transformed into a long needle-like hexagonal pyramid structure. That morphology would deteriorate the stability of copper and the interconnect performance of copper. A similar situation occurs when the reverse duty cycle was 60% or 80%, with the current density of 0.4 A/dm^2. In addition, when the reverse pulse current density increases to 1 A/dm^2, the copper surface structure was mostly a large block crystal, and large gaps appear. The PPR plating has both the deposition process and the dissolution process, which influence the surface morphologies. The cathode peak current density of plating, while increasing the deposition rate creates more densely packed nano-twins. The reverse pulse results in the copper dissolution process. The reverse pulse would make the surface of the cathode supplemented by copper ions, which will affect the copper deposition process and final surface morphology. In addition, the reverse pulse can directly act on the surface of the copper crystal to tailor the surface morphology. Different reverse pulse parameters will affect the dissolution process of copper, such as dissolution rate and area. Therefore, different reverse pulse parameters have an effect on the surface state of copper, which in turn affects its interconnect performance.

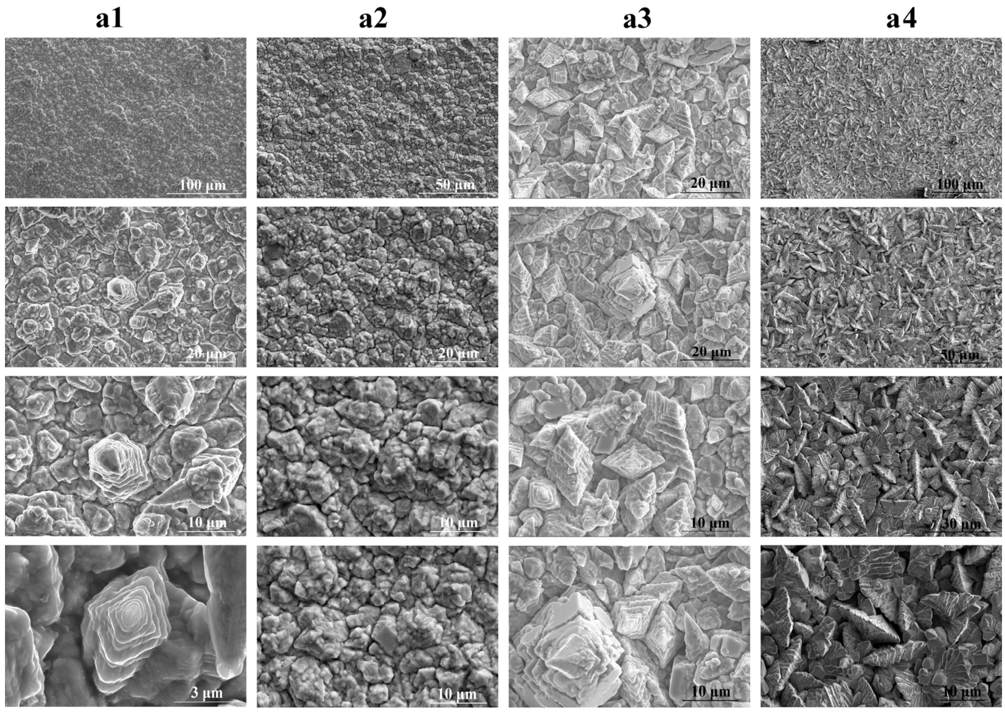

Figure 8. SEM images of copper surface under different reverse pulse frequency. (**a1**) is 100HZ; (**a2**) is 500HZ; (**a3**) is 1000HZ; (**a4**) is 1500HZ.

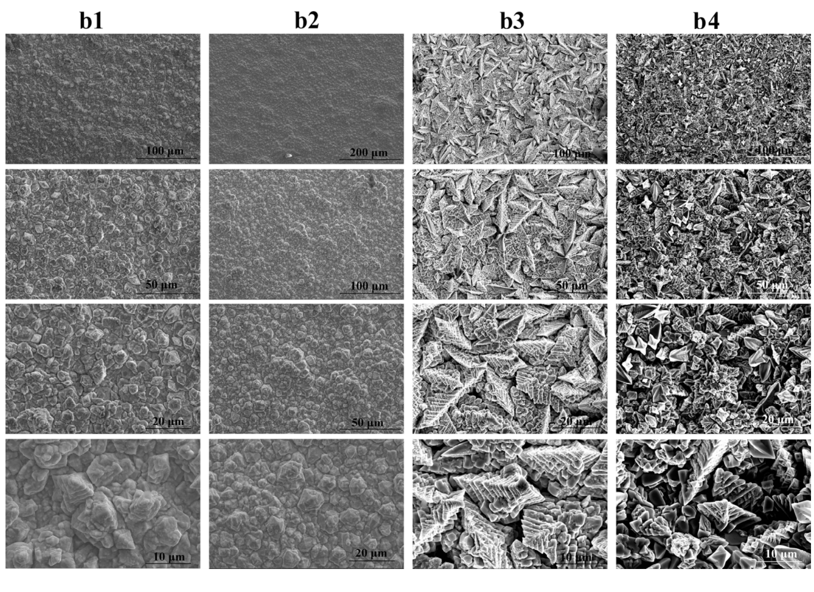

Figure 9. SEM images of copper surface under different reverse pulse duty cycle. (**b1**) is 20%;(**b2**) is 40%;(**b3**) is 60%;(**b4**) is 80%.

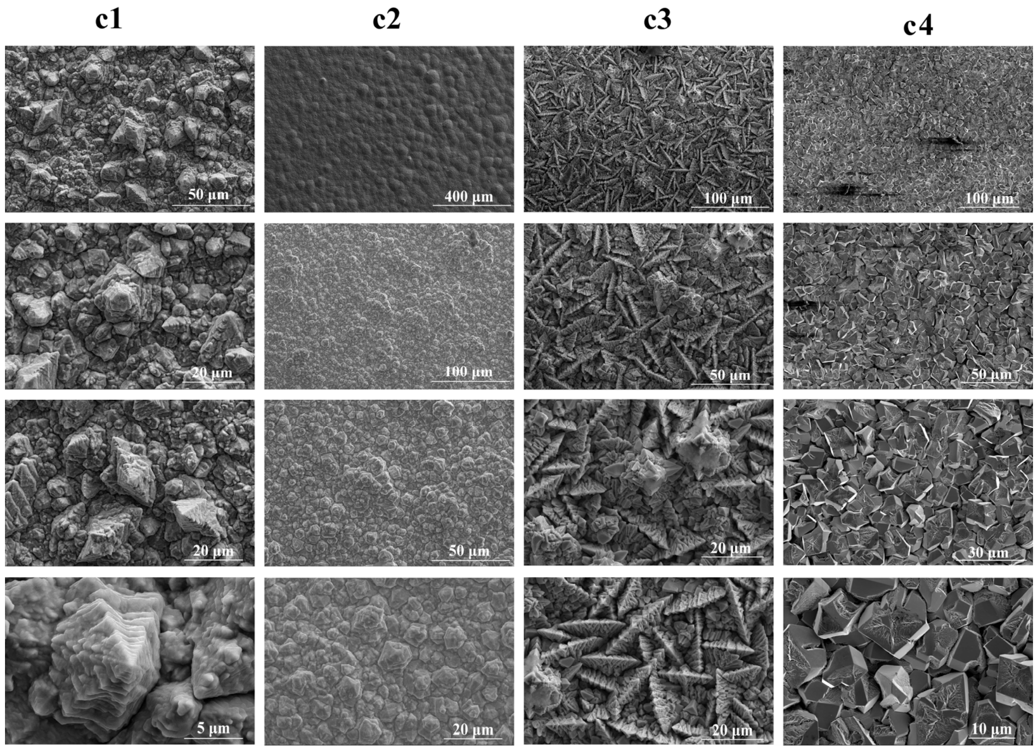

Figure 10. SEM images of copper surface under different reverse pulse current density. (**c1**) is 0.1A/dm^2; (**c2**) is 0.2A/dm^2; (**c3**) is -0.4A/dm^2; (**c4**) is 1A/dm^2.

From the surface morphology of copper crystal arrangement, the optimal reverse pulse parameters are 100 Hz, -0.2 A/dm^2 and 40%, which are consistent with the TP value and copper uniformity results. Therefore, we can conclude that the surface state of the copper is consistent with the uniformity of the copper. The copper with good surface state also has good uniformity by the same reverse pulse parameter.

4. Conclusions

This work systematically investigated the effect of reverse pulses parameters in reverse pulses plating route on copper uniformity in high aspect ratio through holes. The uniformity, copper texture, and surface morphologies of the copper plating were characterized via SEM, XRD, and EBSD. The reverse pulse frequency can be tailored in a wide range of 100~1000 Hz. The reverse current density and the reverse duty cycle are more sensitive parameters. To achieve the high uniformity of the through-hole plating, the reverse current density was preferably 10% of the forward current density, and the reverse duty cycle should be 20%–40%. Distinct reverse pulse parameters have an effect on the surface state of copper, which in turn affects its interconnect performance. The surface roughness of the copper is consistent with the uniformity of the copper. The copper with low surface roughness also has good uniformity by the same reverse pulse parameter. The optimal reverse pulse parameters are 100 Hz, -0.2 A/dm^2, and 40%, and copper with ultra-uniformity and strong (111) crystallographic orientation were successfully prepared. The refined crystal grains and the large-angle grain boundaries enables good stability of filling copper. This study has presented the unique advantage of reverse pulses plating for the development of high-density wiring printed circuit boards.

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