

2022-06-28

Application of Numerical Simulation Method in Periodic Pulse Reverse Electroplating Through Hole

Yuan-Hang Zhang

Mao-Zhong An

MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, Heilongjiang, China;
mzan@hit.edu.cn

Pei-Xia Yang

Jin-Qiu Zhang

Recommended Citation

Yuan-Hang Zhang, Mao-Zhong An, Pei-Xia Yang, Jin-Qiu Zhang. Application of Numerical Simulation Method in Periodic Pulse Reverse Electroplating Through Hole[J]. *Journal of Electrochemistry*, 2022 , 28(6): 2104511.

DOI: 10.13208/j.electrochem.210451

Available at: <https://jelectrochem.xmu.edu.cn/journal/vol28/iss6/4>

This Article is brought to you for free and open access by Journal of Electrochemistry. It has been accepted for inclusion in Journal of Electrochemistry by an authorized editor of Journal of Electrochemistry.

数值模拟方法在周期换向脉冲电镀通孔中的应用

张远航, 安茂忠*, 杨培霞, 张锦秋

(哈尔滨工业大学化工与化学学院, 新能源转换与储存关键材料技术工业和信息化部重点实验室,
黑龙江 哈尔滨 150001)

摘要: 5G 通信技术的升级使得通信背板层数增加, 板上通孔的厚径比也相应增加, 使用传统直流电沉积进行互连难度提高。而周期换向脉冲电镀方法对高厚径比通孔均匀电镀有明显的改善。通过使用数值模拟方法对周期换向脉冲在通孔电镀中的参数进行了研究, 并使用正交实验方法对周期换向脉冲电镀的各参数对通孔均镀能力的影响主次顺序和影响规律进行了分析。筛选出了优水平组合为: 正向峰值电流密度 $1 \text{ A} \cdot \text{dm}^{-2}$, 正反向峰值电流密度比 1:4, 反向峰宽 1 ms, 正反向峰宽比 30:1, 正向占空比 1, 反向占空比 1, 正向峰个数 2, 反向峰个数 3。研究表明, 与直流电镀相比, 数值模拟方法优化后的周期换向脉冲电镀参数能够有效提高通孔的均镀能力, 并且能够应用于实际电沉积通孔中。该实验结果可为数值模拟方法对周期换向脉冲电镀的优化提供理论支持和新思路。

关键词: 数值模拟; 通孔电镀; 周期换向脉冲电镀; 均镀能力; 正交实验

1 引 言

在电子产品中, 印制电路板起到了承载电路的作用。随着 5G 时代的到来, 人类对智能、轻便的电子产品提出了更高的要求, 使得电路板的发展逐渐向高密度化、高集成性发展^[1]。为了满足需求, 电路板的层数增加, 层与层之间的电路导通孔的尺寸逐渐变小, 这使得导通孔的金属化过程变得更加困难。

周期换向脉冲电镀是一种能够有效提高通孔电镀质量的方法。与直流电沉积相比, 周期换向脉冲电沉积能够在阳极脉冲过程对沉积金属离子产生反方向的电迁移, 从而提高阴极表面金属离子浓度, 降低浓差极化导致的不同对流区域的镀速差异。另外, 在阳极脉冲过程能够对阴极进行一个“反镀”过程使得通孔表面和孔口附近的金属溶解, 从而有效抑制了表面沉积过厚和孔口附近提前封孔的现象的产生。同时, 周期换向脉冲电镀含有多个可以调控的参数, 如电流密度、脉冲峰宽、

占空比、峰个数等^[2-3]。这些参数对正向过程和反向过程均可调节, 而直流电源仅有电流大小和沉积时间两个参数可以控制。但参数过多对于工艺的优化过于繁琐, 逐个实验费时费力, 采用数值模拟方法优化周期换向脉冲电镀参数就具有一定的优越性。

数值模拟是一种新兴的研究方法, 对不规则镀件在电镀过程中的物理场的变化分析有直观的展示^[4-5]。在通孔电镀过程中, 包含电荷迁移、物质传递、流场、电化学动力学场和温度场等多个物理过程, 这些过程可以用带有边界条件的偏微分方程进行描述求解^[6]。COMSOL Multiphysics 能基于有限元算法分析求解偏微分方程并且耦合多物理场实现对物理现象的仿真, 从而对研究给予一定的理论指导作用^[7]。通过对通孔电镀过程仿真的结果进行分析, 缩小实验范围, 减少实验数量从而提高实验效率。本文通过使用数值模拟方法对通孔周期换向脉冲电镀过程进行了模拟,

Cite as: Zhang Y H, An M Z, Yang P X, Zhang J Q. Application of numerical simulation method in periodic pulse reverse electroplating through hole. *J. Electrochem.*, 2022, 28(6): 2104511.

收稿日期: 2022-02-28, 修订日期: 2021-04-10. * 通讯作者, Tel: (86-451)86413721, E-mail: mzan@hit.edu.cn

国家自然科学基金项目 (No. 21972037) 和城市水资源和环境重点实验室 (哈尔滨工业大学) 项目 (No. 2021TS07) 资助

并通过正交实验的方法对周期换向脉冲参数进行了优化,并将优化的结果应用于实际的通孔电镀中,为周期换向脉冲电镀通孔提供了指导方向。

2 实验

2.1 通孔电镀模型的建立

基于通孔的实际尺寸,建立通孔镀铜过程的简化二维仿真模型,如图 1 所示。数值模拟通孔周期换向脉冲电沉积铜的参数与实际电沉积铜的参数保持一致,数值模拟模型主要包括上下对称的两个阳极和作为阴极的通孔内外壁两个部分,模拟过程的相关参数如表 1 所示。

2.2 模型控制方程及边界条件

在通孔电镀过程中,孔内外存在电势差和浓度差异,符合三次电流分布。通过使用 COMSOL Multiphysics 中的“包含三次电流分布的 Nernst-Planck 电化学分布接口”模块,能够对物质扩散、电迁移等进行计算^[6]。电解质中的离子传质守恒符合 Nernst-Planck 方程:

$$\frac{dc_i}{dt} = -\nabla \cdot N_i$$

$$= -\nabla \cdot \left(-D_i \nabla c_i - z_i c_i D_i \frac{F}{RT} \nabla \phi_i + c_i \mathbf{u} \right) \quad (1)$$

其中, N_i 为离子通量, c_i 为离子的浓度, D_i 为离子扩散速率, z_i 为离子所带电荷数, F 为法拉第常数, R 为玻尔兹曼常数, T 为开尔文温度, ϕ_i 为溶液电势, \mathbf{u} 为溶液速度流场。

电解质中离子电荷守恒表示为:

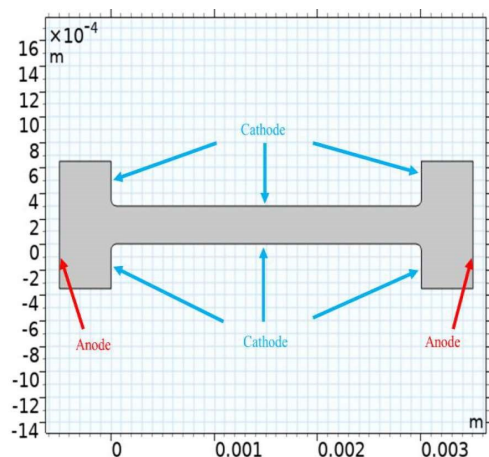


图 1 数值模拟模型。(网络版彩图)

Figure 1 Model of numerical simulation. (color on line)

表 1 通孔电沉积模拟参数

Table 1 Parameters of through hole electrodeposition simulation

Parameter	Value	Units
Concentration of Cu^{2+}	300	$\text{mol} \cdot \text{m}^{-3}$
Diffusion coefficient of Cu^{2+}	5.5×10^{-10}	$\text{m}^2 \cdot \text{s}^{-1}$
Temperature	298	K
Reaction charge	2	-
Transfer coefficient	0.5	-
Exchange current density	0.106	$\text{A} \cdot \text{dm}^{-2}$
Density of Cu	8960	$\text{kg} \cdot \text{m}^{-3}$
Atomic mass of Cu	63.55	$\text{g} \cdot \text{cm}^{-3}$

$$\sum_i z_i c_i = 0 \quad (2)$$

电解质中的电流密度可以用所有物质通量的总和来描述:

$$i_l = F \sum_i z_i \left(-D_i \nabla c_i - z_i c_i D_i \frac{F}{RT} \nabla \phi_i \right) \quad (3)$$

由于电镀液中存在大量的 H_2SO_4 作为支撑电解质,忽略其对溶液中产生的电势差,溶液中的电势符合 Laplace 方程:

$$\nabla^2 \phi = 0 \quad (4)$$

电解质的电导率为^[8]:

$$\kappa \equiv F^2 \sum_i \frac{D_i}{RT} z_i^2 c_i \quad (5)$$

在无添加剂作用时,阴极表面电流密度依据 Butler-Volmer 方程表示为:

$$i_c = -i_0 \frac{c_{\text{Cu}^{2+}}^s}{c_{\text{Cu}^{2+}}^\infty} \left[\exp \left(-\frac{\alpha_c F \eta}{RT} \right) \right] \quad (6)$$

其中, i_c 为阴极电流密度, i_0 为交换电流密度, $c_{\text{Cu}^{2+}}^s$ 和 $c_{\text{Cu}^{2+}}^\infty$ 分别为阴极表面和溶液中 Cu^{2+} 浓度, α_c 为阴极传递系数, η 为过电势。

2.3 正交实验设计

式(1)-(6)对通孔电镀过程提供了理论支持。通过在数值模拟过程中加入周期换向脉冲边界条件,改变脉冲电流波形,分析正反向峰值电流密度($i_{t,p}$ 、 $i_{r,p}$)、正反向脉冲时间(t_f 、 t_r)、正反向占空比(d_f 、 d_r)、正反向峰个数(n_f 、 n_r)对通孔电镀的影响。采用正交实验的方法进行了研究,分别选

表 2 正交实验因素水平表

Table 2 Factors and levels of orthogonal test

Factor	i_{ip} (A·dm ²)	i_{rp}/i_{ip}	t_r (ms)	t_f/t_r	d_f	d_r	n_f	n_r
1	1	1:3	1	10:1	1	1	1	1
Level 2	2	1:4	10	20:1	0.8	0.8	2	2
3	3	1:5	100	30:1	0.6	0.6	3	3

表 3 正交实验设计表

Table 3 Orthogonal experimental design

Test number	i_{ip} (A·dm ²)	i_{rp}/i_{ip}	t_r (ms)	t_f/t_r	d_f	d_r	n_f	n_r
1	1	3	1	10	1	1	1	1
2	1	3	1	20	0.8	0.8	3	3
3	1	3	1	30	0.6	0.6	2	2
4	1	4	100	10	0.8	0.6	1	2
5	1	4	100	20	0.6	1	3	1
6	1	4	100	30	1	0.8	2	3
7	1	5	10	10	0.6	0.8	1	3
8	1	5	10	20	1	0.6	3	2
9	1	5	10	30	0.8	1	2	1
10	2	3	100	10	0.6	0.8	3	2
11	2	3	100	20	1	0.6	2	1
12	2	3	100	30	0.8	1	1	3
13	2	4	10	10	1	1	3	3
14	2	4	10	20	0.8	0.8	2	2
15	2	4	10	30	0.6	0.6	1	1
16	2	5	1	10	0.8	0.6	3	1
17	2	5	1	20	0.6	1	2	3
18	2	5	1	30	1	0.8	1	2
19	3	3	10	10	0.8	0.6	2	3
20	3	3	10	20	0.6	1	1	2
21	3	3	10	30	1	0.8	3	1
22	3	4	1	10	0.6	0.8	2	1
23	3	4	1	20	1	0.6	1	3
24	3	4	1	30	0.8	1	3	2
25	3	5	100	10	1	1	2	2
26	3	5	100	20	0.8	0.8	1	1
27	3	5	100	30	0.6	0.6	3	3

择设计正交实验水平表和正交实验表 2 如表 3 和表所示。测量模拟结束后通孔孔内和表面的镀层厚度,计算均镀能力作为正交实验指标^[9]。

2.4 通孔电沉积

通孔电沉积实验在哈林槽中完成,镀液组成为: CuSO₄·5H₂O 75 g·L⁻¹, H₂SO₄ 240 g·L⁻¹, Cl⁻ 0.06 g·L⁻¹。

为了避免添加剂由于阳极脉冲的作用使其吸附行为发生变化, 仅研究周期换向脉冲参数对工艺的影响, 故在电镀液中不加入添加剂^[10]。阳极采用磷铜板, 并采用空气搅拌以提高传质速率。阴极为含有一些通孔的双面覆铜板碎片, 通孔直径为 300 μm, 板厚为 3 mm。将阴极经过酸洗、除油、预浸后电沉积铜 2 h、电镀完成后将碎片切割并用环氧树脂制备金相样品, 对金相样品进行磨抛后采用光学显微镜(Olympus DSX510)测试镀层厚度, 通孔截面示意图如图 2 所示, 并用式(7)对通孔电沉积均匀性进行评价。

$$TP = \frac{2 \times (d_3 + d_4)}{d_1 + d_2 + d_5 + d_6} \quad (7)$$

式中, d_1 、 d_2 、 d_5 、 d_6 为通孔表面的镀层厚度, d_3 、 d_4 为通孔中心的镀层厚度。

3 结果与讨论

3.1 正交实验结果和极差分析

对模拟结束后通孔内镀层厚度和表面厚度测量, 并计算对应的均镀能力如表 4 所示。

各因素对均镀能力的影响结果如表 5 和图 3 所示。均值 K 为某一因素在同一水平下的不同实验指标的均值, 极差 R 为该因素不同水平实验指标均值的最大值和最小值之差^[11]。比较极差大小可

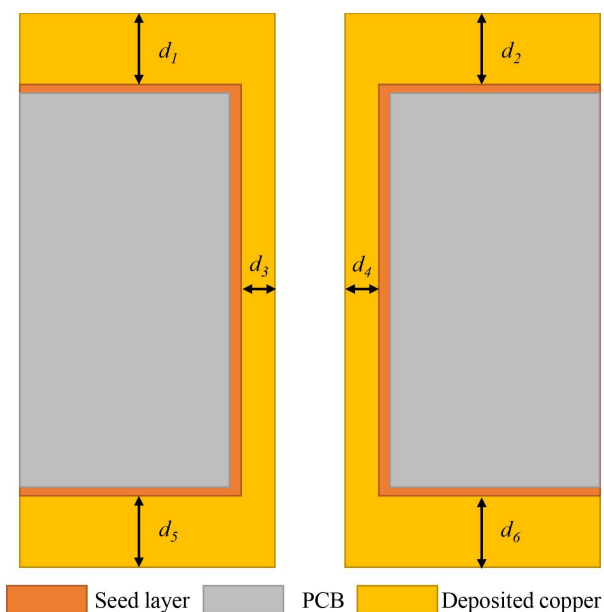


图 2 通孔截面示意图。(网络版彩图)

Figure 2 Schematic diagram of through hole section. (color on line)

表 4 正交实验结果

Table 4 Orthogonal experimental results

	Hole center thickness (μm)	Surface thickness (μm)	Throwing power
1	13.458	14.621	0.920
2	12.964	16.529	0.784
3	10.365	13.512	0.767
4	10.541	12.554	0.840
5	14.354	22.524	0.637
6	6.395	6.466	0.989
7	28.884	104.780	0.276
8	8.922	12.545	0.711
9	12.392	20.927	0.592
10	22.172	55.561	0.399
11	24.694	59.051	0.418
12	13.577	14.629	0.928
13	23.982	37.897	0.633
14	21.272	34.430	0.618
15	19.960	30.476	0.655
16	14.171	17.066	0.830
17	9.766	8.026	1.217
18	33.026	42.216	0.782
19	42.547	85.170	0.500
20	28.063	37.459	0.749
21	39.192	52.623	0.745
22	27.512	36.676	0.750
23	44.879	71.538	0.627
24	37.210	51.107	0.728
25	21.566	48.325	0.446
26	28.638	72.153	0.397
27	30.844	56.101	0.550

以得到因素主次序为 $t_r > d_r > t_f/t_r > i_{tp} > i_{tp}/i_{rp} > n_r > n_f > d_f$, 其中 t_r 的影响较大, d_r 、 t_f/t_r 和 i_{tp} 的影响次之, i_f 和 d_f 极差曲线呈下降趋势, 说明降低 i_f 和 d_f 可以提高均镀能力。

3.2 优水平模拟实验结果

对表 5 中得到的优水平组合进行模拟实验, 所得到的实验结果和直流电沉积实验结果如图 4 所示。使用优水平工艺得到的通孔内厚度为

表 5 均镀能力极差分析表
Table 5 Range analysis of average throwing power

	i_{tp} ($A \cdot dm^{-2}$)	i_{tp}/i_{rp}	t_r (ms)	t_f/t_r	d_f	d_r	n_f	n_r
K1	6.517	6.211	7.407	5.148	6.272	6.851	6.175	5.945
K2	6.480	6.477	5.478	5.762	6.217	5.740	6.297	6.041
K3	5.492	5.802	5.604	6.186	6.000	5.898	6.018	6.503
K1/9	0.724	0.690	0.823	0.572	0.697	0.761	0.686	0.661
K2/9	0.720	0.720	0.609	0.640	0.691	0.638	0.700	0.671
K3/9	0.610	0.645	0.623	0.687	0.667	0.655	0.669	0.723
R	0.114	0.075	0.214	0.115	0.030	0.123	0.031	0.062
Priorities	$t_r > d_r > t_f/t_r > i_{tp} > i_{tp}/i_{rp} > n_r > n_f > d_f$							
Optimal horizontal	$i_{tp,1}$	$d_{f,2}$	$t_{r,1}$	$t_f/t_{r,3}$	$d_{f,1}$	$d_{r,1}$	$n_{f,2}$	$n_{r,3}$
Optimal combination	$i_{tp,1} d_{f,2} t_{r,1} t_f/t_{r,3} d_{f,1} d_{r,1} n_{f,2} n_{r,3}$							

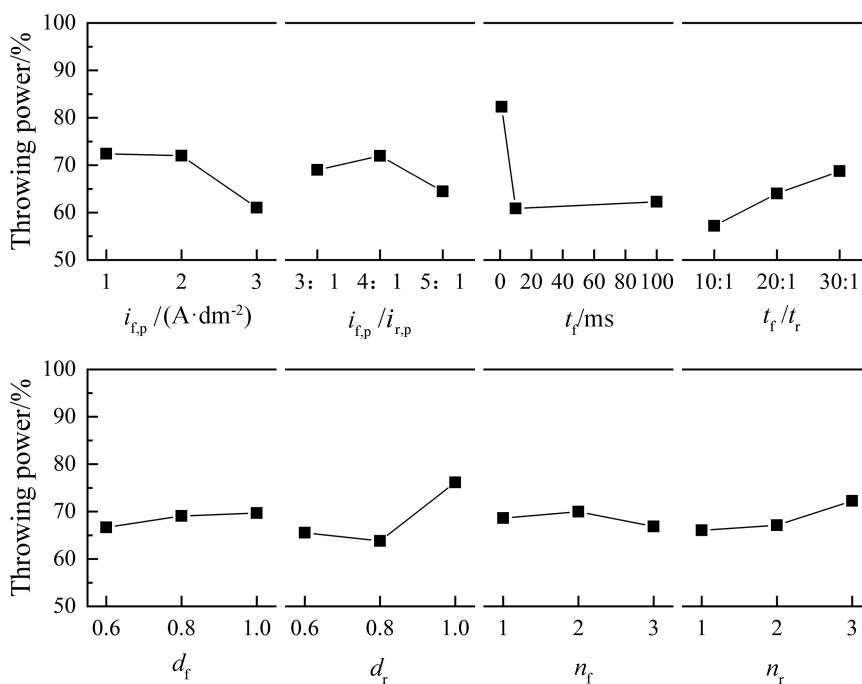


图 3 正交实验中各因素对均镀能力的影响

Figure 3 Influences of various factors on throwing power in the orthogonal experiment

30.593 μm , 表面厚度为 11.940 μm , TP 为 256.2%, 而直流电沉积通孔内厚度为 16.342 μm , 表面厚度为 42.174 μm , TP 为 38.7%。可见使用数值模拟对脉冲工艺参数的优化有一定的优越性。

3.3 电沉积实验结果

将模拟后的参数应用于电沉积实验, 并与相

同电流密度的直流电沉积和文献^[12]中使用的工艺参数 ($i_{tp} = 1 A \cdot dm^{-2}$, $i_{tp}/i_{rp} = 1/3$, $t_r = 1 ms$, $t_f/t_r = 20/1$)进行比较, 如图 5 所示。三种电沉积条件得到的通孔的 TP 分别为 71.9%、82.2%和 90.2%。使用数值模拟优化后的工艺参数使通孔的 TP 得到提升, 对周期换向脉冲电沉积实验的优化有一定的

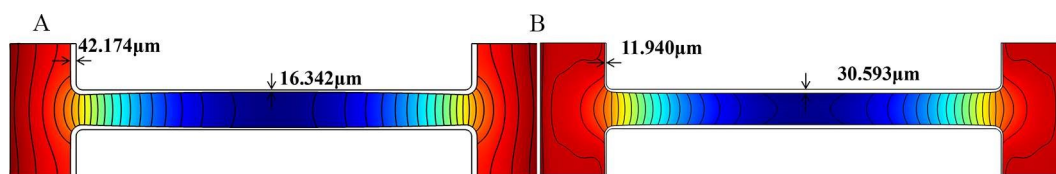


图 4 模拟结果比较:(A)直流;(B)周期换向脉冲最优水平组合。(网络版彩图)

Figure 4 Comparison of simulation results. (A) direct current; (B) Periodic pulse reverse optimal combination. (color on line)

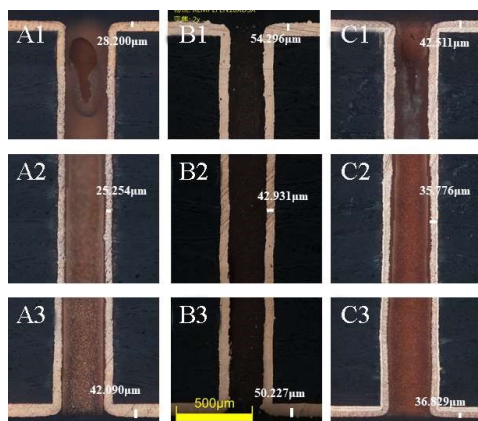


图 5 通孔电沉积实验结果:(A)直流电沉积;(B)文献^[12]工艺参数;(C)数值模拟优组合工艺参数。(网络版彩图)

Figure 5 Experimental results of through hole electrodeposition. (A) direct current; (B) process parameters in reference^[12]; (C) Numerical simulation of optimal combined process parameters. (color on line)

理论指导意义。

4 结论

通过数值模拟方法对通孔电沉积过程进行了正交实验研究,分析了周期换向脉冲电镀中正反向峰值电流密度、正反向脉冲宽度,正反向占空比以及正反向峰个数对通孔电沉积均镀能力的影响情况。结果表明,周期换向脉冲参数最佳水平组合为 $i_{fp} = 1 \text{ A} \cdot \text{dm}^{-2}$, $i_{fp}/i_{rp} = 1/4$, $t_r = 1 \text{ ms}$, $t_f/t_r = 30/1$, $d_f = 0.1$, $d_r = 1$, $n_f = 2$, $n_r = 3$ 。将其应用于实际电沉积,与直流电沉积相比,通孔的均镀能力从 71.9% 提升到 90.2%,有效减轻了通孔内外沉积厚度不均的现象。数值模拟研究能够有效优化周期换向脉冲电沉积参数,为进一步实验研究提供了依据。

参考文献(References):

[1] Abbaspour R, Brown D K, Bakir M S. Fabrication and electrical characterization of sub-micron diameter through-

silicon via for heterogeneous three-dimensional integrated circuits[J]. J. Micromech. Microeng., 2017, 27(2): 025011.

[2] Wang Q(王卿), Zhang Y B(张勇斌), Chen J M(陈金明), Wang F(王峰). Effects of current modes on gold electroplating in a citrate system[J]. China Surf. Eng.(中国表面工程), 2019, 32(3): 88-98.

[3] Chang L M(常立民), Chen D(陈丹), Shi S Y(石淑云). Electrochemical study of corrosion resistance of electroplated Zn-Ni alloy coatings[J]. Mater. Protec.(材料保护), 2008, (10): 17-9+3.

[4] Su S D(苏世栋), Ji L X(冀林仙). Copper filling of microvia in printed circuit based on multiphysics coupling[J]. Electr. Comp. Mater.(电子元件与材料), 2018, 37(7): 22-28.

[5] Fei X Y(费翔昱), Gong B K(宫本奎), Dong Z C(董志超), Feng R(冯锐), Sun Y M(孙玉梅), Nie J W(聂继伟). Numerical simulation and experimental study on electrodeposition of copper foil with through holes[J]. Electroplat. Finsh.(电镀与涂饰), 2021, 40(5): 343-351.

[6] Ji L X(冀林仙). Investigation of copper electrodeposition for printed-circuit interconnection based on multiphysics coupling method[D]. Chengdu: University of Electronic Science and Technology of China, 2016.

[7] Fu D G(付定国), Luo H J(罗华江). The simulation of connector parts gold-plated by comsol multiphysics[J]. Guangdong Chem. Ind.(广东化工), 2019, 46(11): 104-106.

[8] Ji L X, Wang S X, Wang C, Chen G Q, Chen Y M, He W, Tan Z. Improved uniformity of conformal through-hole copper electrodeposition by revision of plating cell configuration[J]. J. Electrochem. Soc., 2015, 162(12): D575-D583.

[9] Chen X L(陈雪丽), Wang C(王翀), He W(何为), Zhang W H(张伟华), Chen Y M(陈苑明), Tao Y G(陶应国). Application of periodic pulse reverse plating for through hole interconnection of communication backplane board[J]. Printed Circuit Infor. (印制电路资讯), 2021, 29(5): 7-11.

[10] Zhu Q S, Zhang X, Liu C Z, Liu H Y. Effect of reverse pulse on additives adsorption and copper filling for through silicon via[J]. J. Electrochem. Soc., 2018, 166(1): D3006-D3012.

- [11] Xu J M(徐建民), Yan Y F(严艺飞), Yan X S(严新松). Research on electrochemical descaling characteristics based on orthogonal experiment[J]. *Mod. Chem. Ind.*(现代化工), 2021, 41(10): 172-176.
- [12] Huang B C, Yang C H, Lee C Y, Hu Y L, Hsu C C, Ho C E. Effect of pulse-reverse plating on copper: Thermal mechanical properties and microstructure relationship[J]. *Microelectron Reliab.*, 2019, 96: 71-77.

Application of Numerical Simulation Method in Periodic Pulse Reverse Electroplating Through Hole

Yuan-Hang Zhang, Mao-Zhong An*, Pei-Xia Yang, Jin-Qiu Zhang

(*MIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, Heilongjiang, China.*)

Abstract: The upgrade of the fifth generation (5G) communication technology increases the number of communication backplane layers and the aspect ratio of through holes on the board, making it more difficult to use traditional direct current deposition for interconnection. Direct current electrodeposition is more prone to uneven coating in the hole, resulting in poor contact between the coating and components, and open circuit. This has a serious impact on the stability of printed circuit board. The periodic pulse reverse plating method can significantly improve the uniformity of high aspect ratio through-hole plating and improve the production quality of through-hole plating through the dissolution and electromigration of the coating in the reverse pulse process. Compared with direct current method, periodic reverse pulse has multiple controllable parameters. Changing these parameters will have different effects on the quality of through-hole electroplating. However, to study all parameters one by one, the number of experiments is huge and time-consuming. Numerical simulation is a newly developing research method, which intuitively studies the influence of a variety of physical fields. And it can be completed only by calculation, which avoids the loss of a large number of experiments. In this work, the influences of periodic pulse reverse parameters in through hole electroplating were studied by numerical simulation. Based on the orthogonal experiments, the influence order and rule of the periodic pulse reverse parameters on throwing power (*TP*) of through hole were analyzed. Among them, the reverse pulse duty ratio has a great influence on the *TP* of through-hole. The optimal combination is screened as: Forward peak current density $1 \text{ A} \cdot \text{dm}^{-2}$, ratio of positive and reverse peak current density 1:4, reverse peak width 1ms, ratio of positive and reverse peak width 30:1, forward duty cycle 1, reverse duty cycle 1, number of forward peak 2, number of reverse peak 3. Using the optimized parameter combination in the simulation results, *TP* is greatly improved as compared with direct current electrodeposition. The parameters of periodic pulse reverse electroplating optimized by numerical simulation method can effectively improve the uniform plating capacity of through holes, and can be applied to actual electrodeposition of through holes. Using the optimized parameters, the *TP* of through hole with the aspect ratio of 1:10 is improved efficiently. The experimental results provide theoretical support and new ideas for the optimization of periodic pulse reverse electroplating by numerical simulation method.

Key words: numerical simulation; through hole electroplating; periodic pulse reverse electroplating; throwing power; orthogonal test