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Optimization of Pulse Plating Additives and Plating Parameters for High Aspect Ratio Through Holes

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高深径比通孔脉冲电镀添加剂及电镀参数的优化

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摘要: 本文采用毒性小,价格低廉的 2, 2′-二硫代二吡啶(2, 2′-Dithiodipyridine, DTDP)作为通孔电镀铜添加剂,对添加剂体系的浓度及脉冲电镀参数进行了优化。首先,对 DTDP 能否在高深径比通孔脉冲电镀过程中起到整平作用进行探究,并对包含其在内的四种添加剂的浓度进行正交优化,得到了当电镀效果较好时的最优添加剂浓度,但是该条件电镀后的通孔呈“狗骨状”。其次再利用正交优化后的电镀液,采用单因素分析法对脉冲电镀参数进行优化,得出此时较优的脉冲电镀参数,并消除上述通孔“狗骨”现象。在电镀试验后,通过采用扫描电子显微镜(SEM)和浸锡热应力实验对电镀后的实验板进行性能测试。

关键词: 电镀添加剂; 脉冲电镀; 高深径比通孔; 正交设计试验; 深镀能力

1 引 言

在现今第五代通信技术(5G)迅速发展的时代中,电子产品发展速度迅猛,而电子产品的发展离不开印制电路板(printed circuit board, PCB)的支持[1-4]。随着电子产品“薄、轻、小”的要求越来越高,PCB 也在向着高密度高要求发展[5-7],这就使得通孔电镀成为行业的一大研究热点,尤其是通过对高深径比的通孔孔金属化从而提高层与层之间的连通,实现 PCB 上各种电子元件的电气连接[8, 9]。此外,为了 PCB 上更易布线,通孔的直径要求越来越小,深度要求越来越高[10],从而导致在电镀过程中存在孔内外的对流和电位差,使得孔内较难镀上铜,即使镀液的分散能力变差。

为了提高镀液的分散能力,要在电镀液中加入添加剂。添加剂种类可分为加速剂、抑制剂和整平剂,这些添加剂在镀液中通过协同或竞争作用[11],从而改善阴极的极化作用,进而改善镀液的深镀能力(*TP*)。整平剂常用健那绿 B(Janus green B, JGB)[12, 13]和一些季胺类化合物,这些化合物通常分子量较大,毒性也较大,而 DTDP 价格低廉,毒性小,故被王旭[14, 15]等人作为电镀添加剂的一种,研究了其在高深径比通孔直流电镀中的应用,结果得出当通孔的深径比为 10:1 时,镀液 *TP* 值在 112%左右,表面铜的厚度在 18 μm 左右。

但在通孔电镀过程中,使用传统直流电镀,会出现孔口处的电流密度大于孔中的电流密度,从而造成狗骨现象,严重甚至会出现孔封口现象[16]。由于脉冲电镀具有正向和反向电流,并且具有周期性,可以提高电镀液在通孔中的交换能力,从而达到改善镀液的 *TP* 值和提高表面平整的效果,故脉冲电镀在高深径比通孔电镀研究中越来越被重视[17-19]。陈雪丽[20]等人使用罗门哈斯 PPR-II 系列添加剂,在通孔深径比为 18:1 的情况下,通过优化脉冲电镀参数,最终得到当正反向脉冲电流幅值比为 1:3、正反向脉冲时间比为 20:1、正向电流密度为 1.5 A·dm^{-2} 时,该参数组合下镀液 *TP* 值可达 78%,但是表面铜的厚度较厚,不利于线路板后续工序加工。

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本文将 DTDP 作为整平剂应用到深径比为 14.5:1 的通孔脉冲电镀中，通过正交实验优化添加剂浓度，验证了其在脉冲电镀中也可起到整平效果，最后镀层符合行业要求；后又对脉冲电镀参数进行单因素分析，研究了正/反向时间比、正向电流密度和正/反向电流比对脉冲电镀的影响，得到在此电镀液的情况下的较优参数，并对其镀层进行测试，结果符合行业要求，且可减小表面铜的厚度；并对单段脉冲电镀和分段脉冲电镀进行了对比和分析，为后续高深径比通孔脉冲电镀的研究提供了一定思路和研究方向。

2 实 验

2.1 试剂与仪器

试剂：浓硫酸（H_2SO_4, 98%）、硫酸铜（$CuSO_4\cdot 5H_2O$, 99%）、盐酸(HCl, 98%)购自天津市化学试剂三厂；聚二硫二丙烷磺酸钠(sodium 3, 3'-dithiodipropane sulfonate, SPS, > 97%)购自江苏梦得电镀化学品有限公司；聚乙二醇 8000（Polyethylene glycol 8000, PEG-8000）、2, 2'-二硫代二吡啶(DTDP)购自上海泰坦科技股份有限公司；除油液(120±20 $mL\cdot L^{-1}$)、微蚀液（20±10 $ml\cdot L^{-1}$ H_2SO_4, 80±10 $g\cdot L^{-1}$ 过硫酸钠)、酸浸液(40±10 $mL\cdot L^{-1}$ H_2SO_4)购自杰希优贸易有限公司)；无水乙醇(C_2H_5OH, 99.9%)购自广东光华科技有限公司。所涉及溶液均由去离子水配制。

仪器：超景深显微镜(VHX-950F, 基恩士有限公司)；正负脉冲电源(Max pulse 整流器，广州精原科技有限公司)；扫描电子显微镜(TM4000P, 日本高新(深圳)科技公司)。

2.2 电镀实验

2.2.1 电镀液的配制

本实验采用的电镀液体系为"高酸低铜"体系[21]，基础镀液为 2.04 $mol\cdot L^{-1}$ 的 H_2SO_4 和 0.45 $mol\cdot L^{-1}$ 的 $CuSO_4\cdot 5H_2O$，添加剂为 Cl^-、SPS、EG-8000、DTDP。

添加剂的配制：分别称取 8 g PEG-8000 和 0.25 g SPS 置于烧杯中，加少量水搅拌使其溶解，之后分别转移至 250 mL 容量瓶中定容。量取 1 mL 浓 HCl 于烧杯中，加少量水搅拌稀释，之后转移至 1 L 容量瓶中定容。由于本实验采用的整平剂为 DTDP，其不溶于水，故每次配制电镀液时，直接称取所需用量放入 H_2SO_4 中使其溶解。

电镀液的配制：每次称取 144 g $CuSO_4\cdot 5H_2O$ 与烧杯中，加少量水使其溶解，再量取 217.3 mL 浓 H_2SO_4，称取一定量的整平剂 DTDP，使其溶于 H_2SO_4 中，之后缓慢倒入 $CuSO_4\cdot 5H_2O$ 溶液中，不断搅拌，再依次加入一定体积的加速剂、抑制剂，最后转移至 2 L 容量瓶中定容。

2.2.2 实验用板的制作

实验板材制作时是将生益科技的型号为 S1000H(1.3 mm, 铜厚 1/1 oz)的基材经过开料(一块平均分成四块)、压合、锣边、机械钻孔、沉铜、闪镀、电铣和真空包装等工序制成尺寸为 6 × 13 cm，厚度为 2.9 mm 的实验用板，其上通孔孔径为

表 1 $L_9(3^4)$ 因素-水平表

Table 1 $L_9(3^4)$ orthogonal factor level design

Factors Level	DTDP ($mg\cdot L^{-1}$)	SPS ($mg\cdot L^{-1}$)	PEG-8000 ($mg\cdot L^{-1}$)	Cl^- ($mg\cdot L^{-1}$)
1	1	4	300	90
2	2	5	400	100
3	3	6	500	110

表 2 脉冲电镀参数单因素设计表

Table 2 The single factor design of pulse electroplating parameters

Pulse electroplating parameter	1	2	3
Forward and reverse time ratio/ms	40	50	60
Forward current/ASD	1	2	3
Forward and reverse current ratio	1:1.5	1:2	1:2.5

0.2 mm。

2.2.3 电镀实验设计

先对电镀液的添加剂配方进行正交优化，正交设计表如表 1，得出各添加剂较优浓度，采用的电镀参数为正向电流密度为 2.15 ASD、正/反向电流比为 1:2.5 + 1:1.5、电镀时间为（80 + 40）min、正/反向时间比为(50:1) ms；其次再对脉冲电镀参数进行单因素分析，设计表如表 2，得出各参数较优结果，拟采用的脉冲电镀参数单因素为：正/反向时间比：40:1、正向电流密度：2 ASD、正/反电流比：1:2.5、电镀时间为 2 h。

2.3 性能检测方式

2.3.1 深镀能力测试

在评价通孔的电镀效果，通常用填孔率、*TP* 或者均匀性来作为评价指标。图 1 为通孔电镀示意图，*TP* 计算公式如下：

$$TP=\frac{(e+f+g+h+m+n)/6}{(a+b+c+d)/4}$$

其中，a、b、c、d 为电镀后孔口表面铜厚度；e、f、g、h、m、n 为电镀后孔内铜厚度。

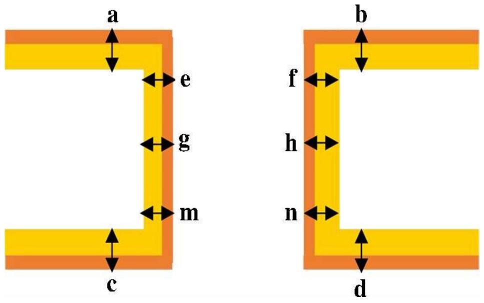

图 1 通孔电镀能力表征示意图。(网络版彩图)

Figure 1 Schematic diagram of through-hole plating capability. (color on line)

2.3.2 镀层性能测试

(1) 浸锡热应力测试：测试前将切片置于 150 ℃ 烘箱中干燥 4 h，冷却至室温。测试时将切片先放置松香中浸泡，然后将切片浸入 288 ℃ 的无铅锡炉中，静置 10 s，取出后放于松香中冷却，重复该操作 5 次，测试完成。一般要求测试后的实验板无

表 3 正交实验结果

Table 3 The results of orthogonal experiments

	A	B	C	D	Throwing power /%
	DTDP (mg·L^{-1})	SPS (mg·L^{-1})	PEG-8000 (mg·L^{-1})	Cl$^-$ (mg·L^{-1})	
1	1	4	300	90	72.1
2	1	5	400	100	82.8
3	1	6	500	110	81.8
4	2	4	400	110	80.4
5	2	5	500	90	79.2
6	2	6	300	100	73.5
7	3	4	500	100	73.6
8	3	5	300	110	67.6
9	3	6	400	90	61.9
K1	236.7	226.1	213.2	213.2	-
K2	233.1	229.6	225.1	229.9	-
K3	203.1	217.2	234.6	229.8	-
k1	78.9	75.4	71.1	71.1	-
k2	77.7	76.5	75.1	76.7	-
k3	67.7	72.4	78.2	76.6	-
R	11.2	4.1	7.1	5.6	-

爆板、孔裂现象。

(2) 扫描电子显微镜检测：采用 SEM 对电镀后实验板镀层表面形貌进行观察，要求电镀后的镀层表面颗粒均匀细小且无明显铜瘤，具有一定平整性。

3 结果与讨论

3.1 正交优化添加剂配方

根据正交结果，在选定的添加剂浓度范围内，四种添加剂对电镀液的 *TP* 值均有一定影响。表 3 中极差结果表明，四种添加剂对 *TP* 值的影响次序为 DTDP > PEG-8000 > Cl^- > SPS，并得到添加剂最优组合为 A1B2C3D2，即 DTDP 为 1 $mg\cdot L^{-1}$，PEG-8000 为 500 $mg\cdot L^{-1}$，Cl^- 100 $mg\cdot L^{-1}$，SPS 浓度为 5 $mg\cdot L^{-1}$。选用最优添加剂组合进行电镀实验，结果如图 2 所示，得到最终 *TP* 值为 86.2%，表面铜的平均厚度为 37.985 μm，并对切片进行 SEM 测试和浸锡热应力测试。从图 3 可以看出采用正交优化后的镀液电镀后的通孔孔口处铜厚较厚，整个通孔呈“狗骨”状，若电镀时间再加长，通孔极易形成封口现象，原因可能是因为在电镀过程中，由于“尖端效应”，使得孔口处的电流密度要比其他区域的电流密度大，从而使带正电荷的 DTDP 优先在孔口处吸附，但 DTDP 和 SPS 不仅有对抗作用，还存在协同作用，即当 DTDP 吸附在孔口起整平作用时，SPS 的加速作用仍然存在，并且 DTDP 会吸引更多 SPS 在此吸附起加速作用，从而造成导致铜沉积的速度较快，形成“狗骨现象”。

为了方便看出正交实验最后结果，将基础电镀液、正交优化后的镀液(不含 DTDP)和正交优化后的镀液(含 DTDP)采用同样的电镀参数进行电镀实验，并进行 SEM 测试，结果见图 4。从图 4(A)中可以看出当电镀液不加任何添加剂时，镀层表面凹凸不平，且晶体结构不规则，导致镀层平整性较差，表明添加剂对镀层结晶至关重要。图 4(B)是在电镀液中加入 SPS、Cl^-、PEG-8000，不加 DTDP 时的镀层表面形貌图，可以看出此时，镀层大颗粒减少，很多区域结晶较细，但仍有大块结晶存在，表面不平整。当向电镀液中加入这三种电镀添加剂时，对 Cu^{2+} 的析出和沉积都有一定的抑制作用，所以晶核成型较慢，故会有大颗粒生成[22]。当向加有 SPS、Cl^-、PEG-8000 的电镀液中加入整平剂 DTDP 时，可以从图 4(C)看出镀层表面颗粒变得细致均匀，且无大颗粒生产，表面较为平整，表明 DTDP 可以在表面高电流区吸附，从而抑制该处 Cu^{2+} 的沉积，达到整平效果。综合所有结果表

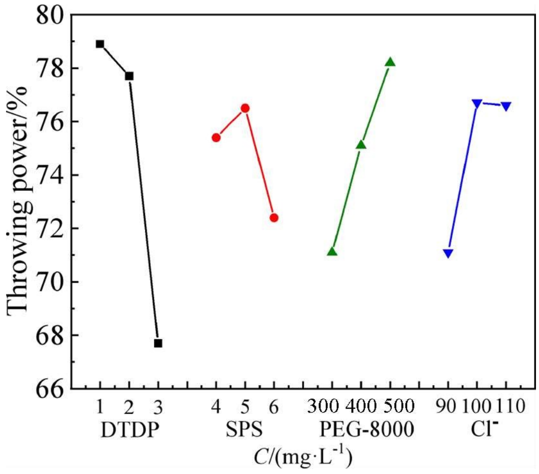

图 2 深镀能力指标因素图。(网络版彩图)

Figure 2 The index factor diagram of throwing power. (color on line)

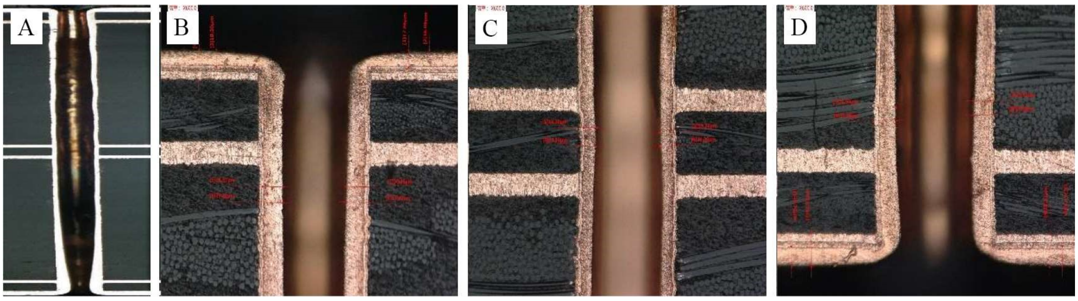

图 3 采用正交最优镀液电镀后的通孔横截面图：A. 全貌；B. 上段；C. 中段；D. 下段。(网络版彩图)

Figure 3 Cross-sectional views of through holes plated with orthogonal optimal results. A. Overall view; B. Upper section; C. Middle section; D. Lower section. (color on line)

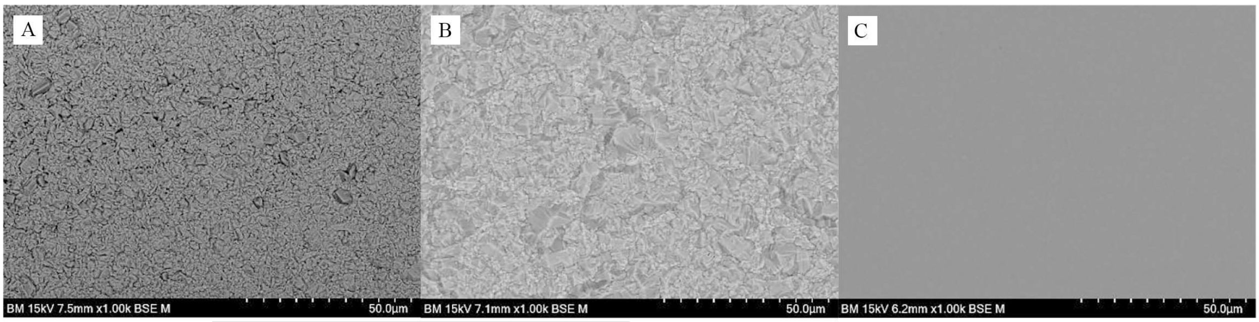

图 4 不同镀液电镀后镀层表面形貌:(A) 基础镀液;(B) 正交优化后的镀液(不含 DTDP);(C) 正交优化后的镀液(含 DTDP)

Figure 4 Surface morphologies of coatings after electroplating with different plating solutions. (A) Base bath, (B) orthogonal optimized bath (without DTDP) and (C) orthogonal optimized bath (with DTDP).

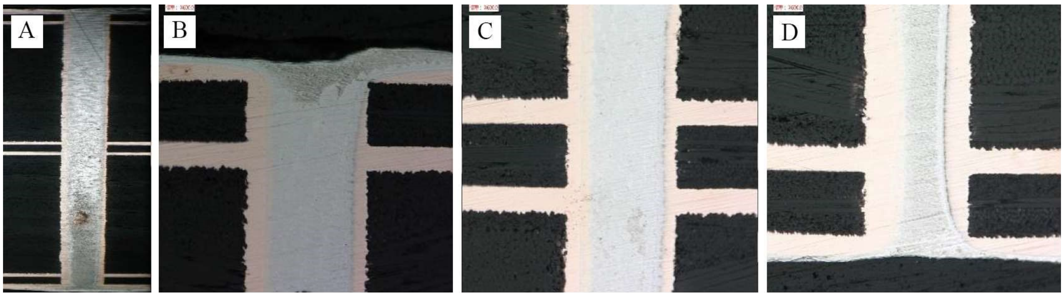

图 5 电镀后通孔浸锡热应力测试截面图:A. 全貌; B. 上段; C. 中段;D. 下段。(网络版彩图)

Figure 5 Cross-sectional views of planted THs after the immersion tin thermal stress test. A. Overall view; B. Upper section; C. Middle section; D. Lower section. (color on line)

明,在电镀液中加入 DTDP 后,经过和其他添加剂相互作用后, 可以使镀层表面更加平整光滑,即 DTDP 可以作为整平剂应用于高深径比脉冲通孔电镀。图 5 为正交结果切片的热应力测试,未发现实验板有爆板,孔裂现象。此结果也证明 DTDP 可在高深径比通孔脉冲电镀中可以起到整平的效果,使镀层表面更加细致、平整。

3.2 脉冲电镀参数单因素分析

通过图 2 可知正交结果中电镀液 *TP* 值在 86%左右,表面铜的平均厚度在 38 μm 左右,不利于线路板后续工序, 故对脉冲电镀参数进行单因素分析, 结果见表 4、表 5、表 6。结果可以看出, 当正/反向时间比为 50:1、正向电流密度为 1 ASD、正反向电流比为 1:2 时电镀液 *TP* 值较大。表 7 为最优脉冲电镀参数实验结果。通孔横截面图如图 6 所示, 此时电镀液 *TP* 值在 74.5%左右, 表面铜的平均厚度在 27.6 μm 左右,电镀液 *TP* 值较使用分段脉冲电镀时低, 可能原因为通孔的深径比较高, 单段脉冲电镀实验时, 镀液进入通孔阻力较大从而导致孔内镀层较薄,镀液分散能力降低。表面铜

表 4 正反向时间比的影响

Table 4 Influences of forward and reverse time ratios

Forward and reverse time ratio/ms	40:1	50:1	60:1
Forward current/ASD	2	2	2
Forward and reverse current ratio	1:2.5	1:2.5	1:2.5
Throwing power/%	70.6	77.3	73.8
Average copper thickness/μm	43.06	40.44	40.27

表 5 正向电流的影响

Table 5 Influence of forward current

Forward and reverse time ratio/ms	40:1	40:1	40:1
Forward current/ASD	1	2	3
Forward and reverse current ratio	1:2.5	1:2.5	1:2.5
Throwing power/%	86.9	53.1	58
Average copper thickness/μm	24.16	41.05	56.72

表 6 正反向电流比的影响

Table 6 Influences of forward and reverse current ratios

Forward and reverse time ratio/ms	40:1	40:1	40:1
Forward current/ASD	2	2	2
Forward and reverse current ratio	1:1.5	1:2	1:2.5
Throwing power/%	69.6	74.6	67.1
Average copper thickness/μm	41.76	41.31	42.1

表 7 最优电镀参数实验结果

Table 7 Experimental results of optimal electroplating parameters

Forward and reverse time ratio/ms	40:1
Forward current/ASD	1
Forward and reverse current ratio	1:2
Throwing power/%	74.5
Average copper thickness/μm	27.6

的厚度有所减小，可能原因为经优化后的脉冲电镀参数中正向电流密度为 1 ASD，正/反向电流比为 1:2，相对于上节采用的脉冲电镀参数来讲,正/反向电流密度均较小,电镀时间均为 2 h,故而电镀后表面镀铜层厚度较小。通过图 6 和图 2 的对比可以看出，尽管采用优化后的电镀参数后镀液的分散能力有所下降,但是解决了通孔的“狗骨”现象,可能原因为在此时的脉冲电镀条件下,溶液处于搅动状态,当向阴极通反向脉冲电流时,会对阴极 Cu^{2+} 的沉积有一定的抑制效果，并去除孔口处的加速剂的吸附，从而使高电流密度区的铜生长缓慢,当向阴极通反向电流时,会使孔口处的铜部分溶解,故而“狗骨”状的通孔会消失,从而使电镀效果较为完美。

图 7 和图 8 为切片的 SEM 和浸锡热应力测试结果。通过切片的 SEM 图，可以看出镀层表面颗粒较为细致、均匀、平整,说明在此时的电镀参数条件下，可以使晶核成型速度大于晶核生长速度，故而可实现镀层表面颗粒细致且均匀，并在添加剂的协同作用下使镀层平整。经过 5 次浸锡热应力测试,实验板无孔裂和爆板现象，符合行业要求。

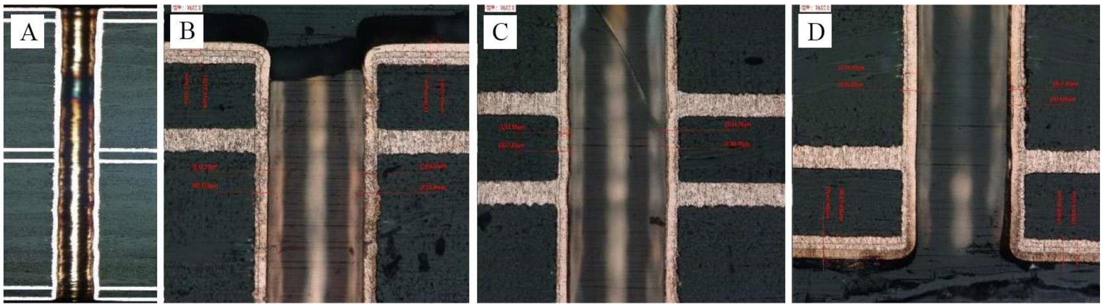

图 6 采用最优脉冲电镀参数电镀的通孔横截面图：A. 全貌；B. 上段；C. 中段；D. 下段。(网络版彩图)

Figure 6 Cross-sectional views of a through hole plated with the optimal pulse plating parameters. A. Overall view; B. Upper section; C. Middle section; D. Lower section. (color on line)

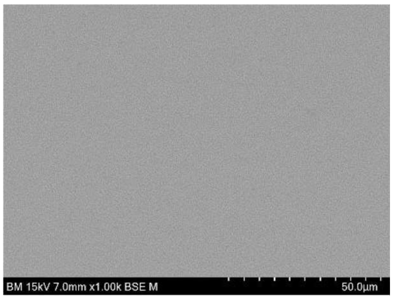

图 7 最优脉冲电镀参数电镀后镀层形貌

Figure 7 The morphology of the coating after the electroplating using the optimal pulse electroplating parameters

4 结 论

本文采用 DTDP 作为电镀添加剂，并采用正交实验对电镀液添加剂配方进行优化，最终得出最优添加剂配比为 Cl^- 100 $mg \cdot L^{-1}$，PEG-8000 为 500 $mg \cdot L^{-1}$，SPS 5 $mg \cdot L^{-1}$，DTDP 浓度为 1 $mg \cdot L^{-1}$。此时镀液 *TP* 值在 86%左右,表面铜的平均厚度在 38 μm 左右，且表面平整度要比无 DTDP 镀液的

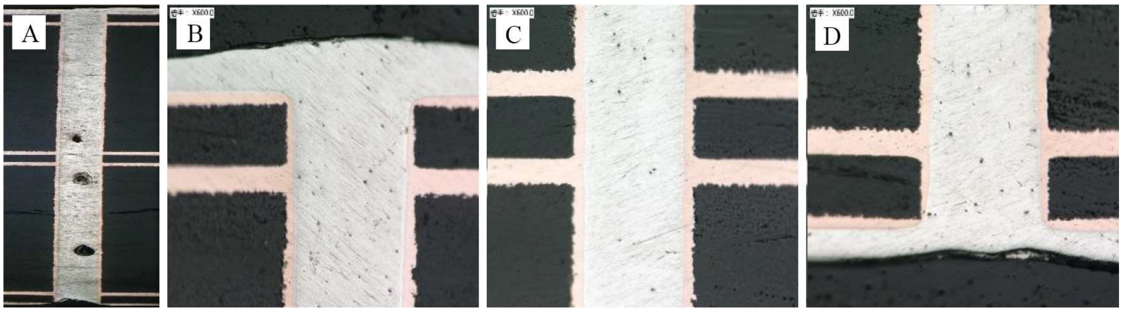

图 8 最优参数电镀后通孔浸锡热应力测试截面图：A. 全貌；B. 上段；C. 中段；D. 下段。(网络版彩图)

Figure 8 Cross-sectional views of the planted THs with the optimal pulse electroplating parameters. A. Overall view; B. Upper section; C. Middle section; D. Lower section. (color on line)

平整度要好。说明其有望应用于高深径比通孔脉冲电镀。

对脉冲电镀参数进行单因素分析，结果显示当正/反向时间比为 40:1 ms、正向电流密度为 1 ASD、正/反向电流比为 1:2 时，镀液 *TP* 值在 74.5%左右，表面铜的平均厚度在 28 μm 左右，相对于分段脉冲电镀，表面铜的厚度有所减小，且电镀后通孔“狗骨”现象消失。

本文中对添加剂配方进行优化时，采取的是分段脉冲电镀，虽然可使镀液 *TP* 值提高，但是通孔呈“狗骨”状，且表面铜的厚度偏大，不利于后续工序操作；脉冲电镀参数单因素分析时考虑了单段脉冲电镀，使得“狗骨”现象消失，表面铜的厚度降低，使其便于线路板后序加工，但同时也使镀液 *TP* 值有所降低。故后续需要进一步实验，使镀液 *TP* 值保持较高的同时降低表面铜的厚度。

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Optimization of Pulse Plating Additives and Plating Parameters for High Aspect Ratio Through Holes

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Abstract: As an important component in electronic products, printed circuit board (PCB) plays a supporting and interconnecting role for the electronic components in it. With the development of communication technology, electronic products are developing in the direction of "thin, light and small", and high density interconnection (HDI) comes into being. Due to the high-density interconnection characteristics of HDI boards, the thickness of the board is increasing. At the same time, in order to reserve space for the laying of fine lines on the subsequent board surface, the diameter of the through holes on the board is also decreasing, so the depth-diameter ratio of the through holes is increasing. In order to ensure the electrical interconnection between the middle layers of the HDI board, the through-hole plating technology has become the key. In the process of through-hole electroplating, due to the relatively small diameter of the through-hole, the current density distribution inside and outside the hole is uneven, and the dispersion ability of the plating solution is poor, resulting in uneven copper plating layer and thick surface copper layer, which is not conducive to subsequent fine circuits laying. An effective way to overcome this drawback is to add electroplating additives to the bath, and to use bidirectional pulse electroplating technology. Therefore, 2, 2'-dithiodipyridine (DTDP) with low toxicity and low cost was used as an additive in the plating solution, and its application in pulse plating of high aspect ratio through holes was studied. The additive concentration and pulse plating parameters were optimized. It was concluded that DTDP could be applied to pulse plating of high aspect ratio through holes. And through orthogonal optimization experiments, the optimal concentration of additives suitable for the high aspect ratio (14.5:1) through-hole electroplating was obtained. Finally, the throwing power of the plating solution was measured at about 86%, and the average thickness of surface copper was about 38 μm. It is not conducive to the operation of the subsequent process, and the through hole is in the shape of a "dog bone"; then the single factor analysis of the pulse parameters was carried out, and finally, the optimal single-stage pulse plating parameters were obtained. At this time, the throwing power of the plating solution was about 75%, and the average thickness of the surface copper was about 27.6 μm, which is convenient for the subsequent processing and solves the above-mentioned "dog bone" phenomenon. SEM test and tin immersion thermal stress test were performed on the experimental boards of the two experiments separately. The SEM images found that the coating particles of the two experimental boards were fine and uniform, and relatively flat; the tin immersion thermal stress test results did not find any cracks. These phenomena are all in line with industry requirements, so it provides a certain basis for the research of high aspect ratio through-hole pulse electroplating. Further experiments are needed in the follow-up to make the plating solution higher in throwing power and at the same time reduce the surface copper thickness.

Key words: plating additive; pulse electroplating; high aspect ratio through hole; orthogonal design tests; throwing power