

Use of Modulated Current Technology for High Performance Pulse Reverse Plating

Myung C. Chu, and Chan Won Seo
CSS Technologies Company Limited
Seoul, Korea

Abstract

Among the many advantages of Periodical Pulse Reverse (PPR) technology, improvement in throwing power and plating thickness uniformity are the most obvious. Traditionally, the biggest drawback of the technology is that it plates well in one size hole but poorly in others, when there are several sizes of holes within a board or different current density areas. Modulated Current Technology Controller (McTc) is a new technology in PPR, which generates modulated complex waves to overcome such drawbacks of the current technologies. High aspect ratio holes of various sizes on a board and irregularly distributed circuitry in pattern plating boards may all achieve more uniform plated thickness and throwing power using this technology

Introduction

The IT industry is growing every day and the boards have become very complicated and, in most cases, include various sizes of holes. The line spacing and the conductor width are getting narrower every year

Conventional DC plating with the help of organic leveling agents has come to a threshold and is not capable of adequately meeting today's processing requirements. Pulse Reverse plating technologies became high-lighted from mid 1990's. Since then, many related technologies have been introduced to the printed circuit board and precious metals industries. However, specifically in the PCB industry, none of them can fabricate all types of boards; *i.e.* boards carrying various sizes of holes, especially when combined with isolated very narrow line and space circuitries.

T. Yamamoto¹ et al. made microscopic measurements to identify the relationship between the vertical and horizontal etched distances, and derived a mathematical model of etching progression. The model estimates that a line/space pattern of 75/75 μm through panel plating requires a 12 μm thick copper foil clad laminate with 15 μm thick copper plated on it. 50/50 μm line/space requires 5 μm clad copper and 15 μm deposited copper. The model predicts that a circuit pattern of L/S of 30/30 μm cannot be formed with panel plating. In addition, circuitry produced through subtraction has an intrinsic problem of shape factor. The conductor cross section is significantly different from place to place. Therefore, many a prototype PCB must be produced before an electronic good is brought to market. Therefore, the need for pattern plating technology is growing. However, conventional pattern plating technologies produce defects such as deposit over hang, severe conductor thickness variation, seepage under photo resist, etc. If these conventional faults in pattern plating can be

solved, producing relatively uniform copper deposition at high productivity, it would have the following advantages:

- High yield
- Extreme fidelity of pattern transfer and shape replication
- Easier fabrication of high aspect ratio structures
- Rapid and low cost processing

Another difficulty is that a mixture of hole sizes as well as a variety of other structures is often found in conjunction with high aspect ratio holes and blind vias within a board. In such cases, throwing power required to uniformly plate the various structures varies significantly. Simple pulse reverse systems cannot handle the variety in the plating environment. This paper tries to explore the possibility of obtaining uniform throwing power over various aspect ratio structures. The theoretical derivation of a pulse reverse system is briefly reviewed to demonstrate that a simple pulse reverse cannot yield sufficiently high throwing powers over various sizes of holes.

McTc technology is introduced as one of the possible solutions for the high yield pattern plating and aspect ratio structures of various sizes within a board

Pulse Plating

As the circuitry becomes finer and denser, many more kinds of vias and/or conductors are required to be fabricated, and the importance of mass transfer to the cathode area becomes more and more significant. Pulsed current electrolysis reduces irreversibility from mass transfer limitations, which results in an increase in the concentration of the reacting species in the diffusion layer and thereby reduction in the concentration over potential. Consequently high values of instantaneous currents have often been applied in practice. A. A. Bedrssiyan and H. Y. Cheh² derived a theoretical equation for the concentration overpotential in a pulse system. The ratio of concentration overpotential to DC

concentration overpotential, denoted as h_c hereafter, is plotted as a function of $(a\tau)$ at $a\theta = 0.5$ and duty cycle $= 0.4$, where $a = \pi^2 D / \delta^2$, θ is one cycle time and τ is the time at a specific cycle of concern. The η_c increases as $(a\tau)$ increases during on time cycle, and decreases during off time cycle, due to the fact that the reacting metal ion is depleted during on time cycle and replenished during off time cycle. At very low currents, the application of pulsed current has little effect on the mass transfer of the system. On the other hand, the η_c decreases as the pulse current density increases, due to the fact that the ratio of η_c in pulsed current to that in DC decreases as the DC limiting current density is approached. In the presence of an excess supporting electrolyte, the η_c is calculated from the total overpotential subtracted by activation overpotential.²

However, Pesco and H. Y. Cheh¹⁰ reported that pulsed current yields worse distribution than DC. Pulsed current certainly has an effect to reduce η_c . However, the diffusion boundary layer has been increased by the increased average current density and the detrimental increase is more severe than the relaxation that occurs during the off time cycle. If the off time cycle is further increased to improve the reacting metal ion diffusion, productivity is sacrificed. Otherwise deposit uniformity will get worse due to the increased average current density. The reversed current in pulse reverse system helps the relaxation without losing the productivity. and, in fact, results obtained with pulsed plating were improved over DC plating.

The activation overpotential contributes a significant portion of the total over potential. In the presence of an excess supporting electrolyte, η_c is calculated from the total overpotential subtracted by activation overpotential in the presence of excess supporting electrolyte.

Pulse Reverse

As it was shown in the previous section, pulsed current exhibits some effect on concentration relaxation in the diffusion layer. However, due to the fact that it has to increase the average current density, instantaneous current density must be increased in order to maintain productivity, and the resultant deposit uniformity decreases. Therefore pulse alone cannot meet the requirements of the modern electronic industry.

Pulse reverse system plays a very important role in fabricating modern electronic circuits, which have high aspect ratio holes of various sizes within a board. Pattern plating seems the only economical solution for the ever decreasing dimensions of conductor lines and spaces. However, the

theoretical level of understanding of a pulse reverse system and all interactions in a specific plating application is not yet sufficiently well developed to completely design the pulse reverse cycles to meet all the requirements without at least some optimization testing. The complete interaction between complex pulse reverse waves, the geometry of the plating cell, and the features to be plated can only be understood qualitatively. In fact, based on the level of understanding of the simple pulse system and the mass and diffusion transfer related electrochemistry, an iterative type approach is generally made to find an optimal plating program. The shortcoming of the simple pulse reverse system is that, while it may generate effective control on a specific cathode surface, it cannot be as effective in other cathode areas of different geometry. Figure 1 shows a schematic concentration overpotential of two different cathode environments within a board. As the resultant η_c is different, a simple pulse reverse cannot fabricate boards that have a wide range of aspect ratio structures. The ideal pulse reverse cycle is the one which can yield uniform η_c regardless of the different level of patterns and vias of blind and common through holes.

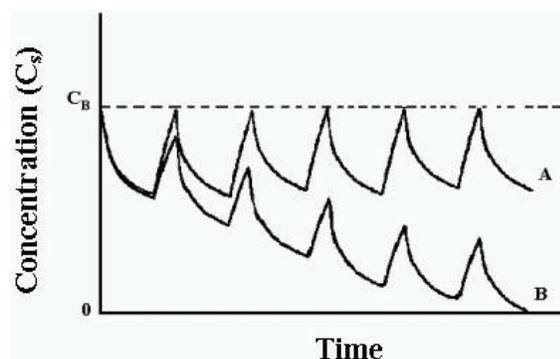


Figure 1 - Schematic Concentration Profile in the Diffusion Layer During Pulse Reverse Plating (A: In Case Electrolyte is Sufficient in the Cathode Area; B: In case Electrolyte is Insufficient in the Cathode Area)

Theory

The diffusion model for pulse reverse plating is completely analogous to that of pulsed plating. The only difference is in the boundary condition involving the form of the applied current density at the electrode surface. During reversed current, the replenishment of reacting metal ion increases rapidly influencing the diffusion boundary layer, and the concentration over potential is reduced. A schematic concentration profile in the diffusion boundary layer is as shown in Figure 1. The only difference is the faster relaxation during reverse current cycle.

For a simple pulse reverse current, H. Y. Cheh⁴ outlined a theoretical method for the calculation of limiting current density. η_c increases during the forward cycle and decreases during the reverse cycle. The average value of the η_c under pulsed conditions as a function of applied pulsed current density and duty cycle is reported. Utilizing the fact that the limiting current plateau at its maximum in deposition rate, the limiting current density was found to be dependent on the rotation speed of the rotating electrode. At over 1600 rpm, both DC and pulsed system produced 100% throwing power on a triangle shape groove of which depth is 35.8 μ m and the opening is 78.2 μ m. The beneficial results of the pulse reverse system were, firstly, as high as 70 % of the DC limiting current density could be applied, and secondly, it produced high throwing power. In their experiment, they obtained some additional important results not discussed at all in the original paper. At 27.4 mA/cm², the throwing power showed a strong dependence on both the pulse and the relaxation times.⁵ At very low pulse time of 0.0067 second and 0.027 seconds of about four times longer relaxation time, the throwing power was only 40%, while it is 110% at (0.013/0.020). At (0.013/0.020) and (0.010/0.040), the throwing powers were both 110%. Their experimental result stresses the importance of the ratio of the pulse and the relaxation times on throwing power.

During deposition, the applied potential between the through hole and the nonpolarized counterelectrodes, V, consists of ohmic losses in the electrolyte phase, ϕ_o , surface overpotential due to the charge transfer reaction, η_s , and η_c .

$$V(t) = \phi_o(x,t) + \eta_s(x,t) + \eta_c(x,t) + E_r \quad (1)$$

E_r is the equilibrium potential at bulk concentration conditions. The η_c depends on axial position and time, and is expressed by,

$$\eta_c(x) = \frac{RT}{nF} \ln \left[\frac{C_s(x,t)}{C_B} \right] \quad (2)$$

$C_s(x,t)$ is the metal ion concentration, which is greatly affected by both the cathode geometry and the solution transportation to the cathode surface. The potential distribution in the electrolyte phase corresponds to the solution of the Laplace equation. Applying the cylindrical coordinates,

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial f}{\partial r} \right) + \frac{\partial^2 f}{\partial x^2} = 0 \quad (3)$$

Assuming that mass transfer occurs within a thin diffusion layer, transient mass transfer is described

by the following equation.

$$\frac{\partial C_s}{\partial t} + \frac{2V_{\max}}{R} y \frac{\partial C_s}{\partial y} = D \frac{\partial^2 C_s}{\partial y^2} \quad (4)$$

M. Pesco and H. Y. Cheh¹⁰ introduced Equations (1) and (2) to the Butler-Volmer equation, and solved with equations (3) and (4) numerically with proper boundary conditions. The numerical solutions prove the strong dependence of throwing power in a hole on the reacting metal ion and its diffusion to the reacting site. As the aspect ratio increases at a set value of average current density and pulse reverse frequency, the time averaged current density becomes less uniform in the interior regions of the holes. Also at a set value of average current density, the time averaged current density varies as the pulse reverse frequency changes. In other words, the current density distribution in the hole varies with the aspect ratios, average current densities at a set pulse reverse frequency and other processing parameters such as mass transfer and diffusion coefficient.

As may be seen from the Figure 1, the reacting metal ion concentration is not zero in hole A while it is zero in hole B. The metal ion transport is also directly related to the geometry of the holes to be plated, or to cathode environment of circuitry patterns in case of pattern plating. The transition time may be shorter in high aspect ratio holes or around highly populated circuit areas than in cathode electrode areas with excess supporting electrolyte. Therefore, it can be concluded that simple pulse reverse system can improve the deposit thickness uniformity to some extent. And if the pulse and reverse cycle is well selected, it can plate even high aspect ratio holes with good uniformity. But, as the electrolyte transport to various level of structures are not equal, the thickness uniformity can not be the same from one structure to another.

Results of work plated with simple pulse reverse current on a board of mixed holes of various size are shown in table 1. Leveling agent developed for pulse reverse system was used with cathode and solution agitation. In order to improve the mass transfer, many different levels of solution and cathode agitation were tried and the result are shown for the best one among the runs. The forward and reverse times, and the frequency used were kindly provided from a shop, which adopted an early form of the technology more than three years ago.

Table 1 – Hoes of Various Sizes

Board thickness, mils	126				
Plating	55 min / 28 ASF				
Hole f, in mils	31	20	14	10	8
T.P, in %	156	132	100	88	52

H. Y. Cheh⁴ reported numerical results of the ratio of the instantaneous cathode limiting current density for pulse reverse plating to that of DC plating for various ratios of the periods of forward current to reverse current with a ratio of reverse current to forward current of -0.2 . With the increase in the forward cycle, the limiting current density at the pulse reverse decreased indicating that the diffusion layer thickness increases as the proportion of forward cycle increases. This calculation proves that reverse cycle retards the growth of diffusion layer thickness. Andricasos and Cheh⁵ used rotating disk electrode system and obtained experimental data of limiting current density at various rotation speed. As the disk electrode rotates faster, the limiting current density of pulse reverse current increased. However, there was no clear evidence that it improves throwing power. They tried to vary pulse and relaxation times to find a relation of the throwing power to the relaxation time as it certainly affects the boundary layer thickness, but they were only able to conclude that at 1600 rpm, the throwing powers were about 100% regardless of the pulse time varying from 0.0016 to 0.17 seconds and relaxation time from 0.0064 to 0.68 seconds. It can be explained that although solution transfer is sufficient, the reacting metal ion depletion rate and the retardation speed must be well matched. Other wise, diffusion layer thickness will increase and result in poor current density distribution.

Effect of Leveling Agent

Tuner and et. al.⁶ proposed that sulfur groups are cathodically reduced and the precipitate interferes with crystals growth by inhibiting the surface diffusion of copper atoms to growth sites. It could even completely block a growth site from deposition and thereby force renucleation. This mechanism was proposed based on the kinetic measurement that indicated that leveling agents reduced the cathodic charge transfer coefficient and changed the value of the exchange current density. Other agents such as gelatin appeared to affect the crystal growth of copper deposition by adsorption at the growth site. The function of leveling agents comes from its adsorption capability. In the Kardos' proposed⁷ diffusion controlled inhibition mechanism, two criteria were necessary for leveling to occur: (1) increased polarization caused by the leveling agents and (2) the dimension of surface imperfections

to be smaller than the thickness of the mass transfer boundary layer. J. E. Chern and Huk Y. Cheh⁹ mathematically derived the effect of the leveling agent from adsorption kinetics and mass transfer for convective diffusion. The results showed strong dependence of the leveling desorption rate constant, k_2 , of the agent. At higher k_2 and $(K \cdot C_{A,B})$, the deposit uniformity was better. K is the adsorption and desorption equilibrium constant and the $C_{A,B}$ is the concentration of the leveling agent in the bulk solution. It can be understood that the higher concentration of the leveling agent in the solution, the higher possibility of the agent to be delivered to the cathodic area of low current density.

With respect to pulse reverse system, the leveling agent can improve the deposit uniformity. However, the leveling agent's effectiveness is limited by the mass transfer and performs limited improvement in mixed holes or pattern plating.

Modulated Current Technology Controller

With a fixed pulse reverse frequency and its characteristic forward to reverse ratio, various hole sizes and geometries within a board can not be plated uniformly. Similarly, conductor lines of different geometries, or different locations on the panel can not be plated to have uniform distribution. Previous studies^{9,10} have shown that the conductors and holes of different geometry can not be plated uniformly at a fixed simple forward and reverse current cycle unless mass transport of the reacting ion to diffusion layer of all the conductors and holes of different geometries is sufficient such that the concentration gradient of the reacting metal ion near the cathode is negligible. This may happen at very low current density. However, this approach is not practical due to the loss in productivity. McTc, Modulated Current Technology Controller, generates multiple trains of pulse reverse of various frequencies, which are the programmed specifically to the plating conditions.

The basic advantage of the technology lies in the flexibility of programming the cycle times and the relaxation times. A schematic drawing of the pulse reverse system is shown in Figure 2.

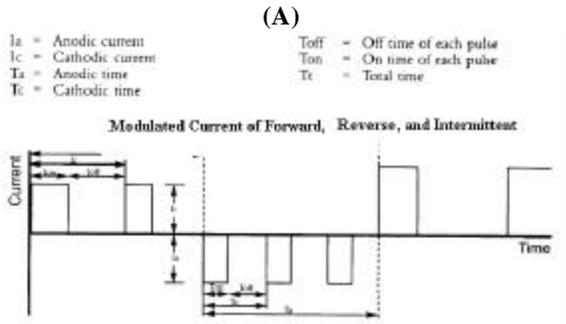
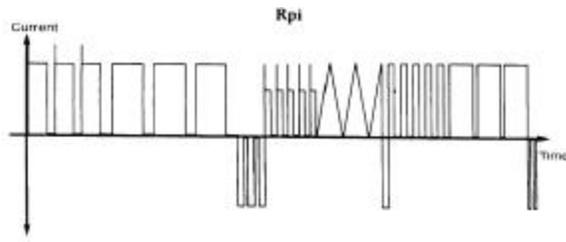


Figure 2 - A Schematic Drawing of McTc Pulse Reverse System

It has multiple trains of forward and reverse waves, and each of them can be programmed as needed. As reviewed in the earlier sections, each wave has its own characteristic influences on each of the cathodic structures and the metallurgy plated there from. It is to be concluded that each set of waves consisting of on time and off time has a certain weight factor to each of the cathodic areas. The resulting deposit thickness can be expressed as follows.

$$\zeta_i \propto \sum_{k=1}^{k=N} w_k \theta_k \quad (5)$$

ζ_i is the deposit thickness of i -th cathodic surface and w_k and θ_k are the weighting factor and the set of on time and off time of k th train of wave. The effectiveness of the particular series (“trains”) of waves is known to depend on the leveling agent chosen. Each of the trains are still manually combined to produce an optimized program. The capability of plating holes of different size within a hole is shown in Table 2.

Table 2 - Capability of Plating Holes of Different Size Within a Hole

Board, in mil	126				
Plating	55 min / 28 ASF				
Hole ϕ , in mils	.031	.020	.014	.010	.008
T.P, in %	91	94	95	92	88

Figures 3 through 6 are the results obtained from the McTc technology. All of them show its capability of plating different level of geometries with uniformity.

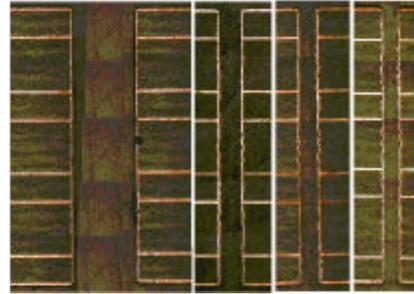
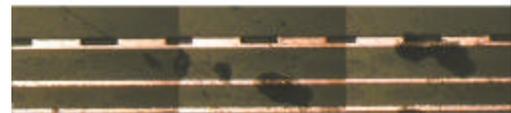
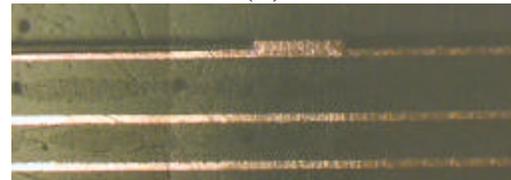


Figure 3 - Holes of Different Size within a Board Plating Condition: 55minutes, 28 ASF – Board thickness: 150 mils. Hole Diameters: 40, 16, 14, and 12 mils from the left - The Throwing Powers: 103, 95, 92, and 90 % Respectively



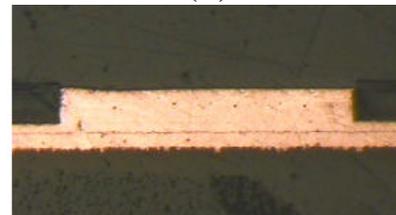
(A)



(B)



(C)



(D)

Figure 4: Some Examples of Pattern Plating. Plated at 27 ASF for 69 Minutes - Thickness Uniformity: less than 15% Across the Board

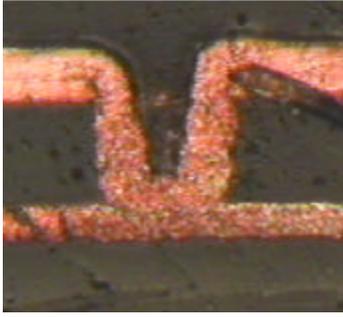


Figure 5 - Blind via Hole (85mm Wide, 65mm Deep) - Plated for 85 Minutes at 20 ASF - Throwing Power at the Bottom: 100%, Side: 110%



Figure 6 - High Aspect Ratio Hole in Pattern Plating - Board Thickness: 252 mils, HAR: 11.6:1, Throwing Power: 80%, Plating Condition: 110 minutes at 24 ASF

Conclusion

The theories on the pulse reverse current plating have been reviewed mostly from the mass transfer and diffusion convective perspectives. It was concluded that simple waves of pulse reverse current cannot meet the today's complicated cathodic surface geometries. McTc technology, which incorporates many trains of different waveforms is proposed as a solution.

Acknowledgement

The authors would like to acknowledge to many dedicated colleagues at A.S.E.T, Florida and RBP Chemicals, Milwaukee. In particular, Moti Holtzmann gave us invaluable advice and Marc Carter and Dr. Mohs shared their experimental results with ours without any reservation. And finally we would like to express our sincere appreciation to Mr. One Kyu Son who has continuously supported and encouraged us for the tedious experimental works.

References

1. Yamamoto, T. Kataoka, and J. Andresakis, S07-3, IPC Proceedings, April, (2000).
2. Bedrossian and H. Y. Cheh, J. Electrochem. Soc., v128, 2536 (1981).
3. J. Newman, "Electrochemical Systems", Prentice Hall, Englewood Cliff, NJ (1973)
4. H. Y. Cheh, J. Electrochem. Soc., **118**, p551 (1971)
5. P. C. Andricacos, H. Y. Cheh and H. B. Linford, Plating and Surface Finishing, Sept., p44 (1977).
6. Bedrossian and H. Y. Cheh, J. Electrochem. Soc., v128, p2536 (1981).
7. D. R. Tuner and G. R. Johnson, J. Electrochem., v109, p918 (1962).
8. O. Kardos, Plating, v61, p129 (1974)
9. Ja-Wern E. Chern and Huk Y. Cheh, J. Electrochem. Soc., v143, p3144 (1996).
10. Anthony M. Pesco and H. Y. Cheh, J. Electrochem. Soc., v131, p2259 (1984).
11. J. R. White and R. T. Galasco, Plating and Surface Finishing, May, p122 (1988).