Selective Pulse Plating From an Acid Copper Sulfate Bath

By N.R.K. Vilambi and D-T. Chin

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Pulsed current was used to selectively deposit copper from an acid sulfate bath on a localized area of an unmasked cathode. The deposits produced by pulse plating were brighter and contained larger crystallite than those applied using direct current.

elective plating (also called spot plating) has received increasing attention in the metal finishing industry because of the high cost of noble metals and the need to localize deposits in selected areas. The use of pulsed current (Pc) to selectively apply metals on a localized area of an unmasked cathode is the subject of this report.

The problem of current and metal distribution in pulse plating is not well understood. There are contradictory reports in the literature. Sheshadri¹ concluded that PC reduced the grain size of copper deposits and resulted in greater leveling. Enchev² used pc in the electrowinning of non-ferrous alloys and obtained higher-quality deposits and higher" current efficiency. Teschke and Soares³ obtained smoother, denser, more coherent deposits when nickel was electrodeposited at high current densities with periodic-reverse rectangular pulsed current.

The effect of pc on the initial stages of gold deposition was studied by Lin et al.,⁴ who said that high pulse frequencies and large duty cycles improved coating coverage. Chin and Zhang⁵ reported that pulse plating of chromium from the standard aqueous chromic acid baths containing sulfate catalyst reduced the coulombic efficiency of the deposition reaction and produced deposits with a needle-like structure compared with a hemispherical nodular growth in direct current (de) plating.

Chin et al.⁶⁷ found that pc enhanced the nucleation rate and produced more uniform zinc deposits in acid zinc chloride and alkaline zincate solutions. With a pasted zinc battery electrode in a nickel-zinc cell, the superimposition of a rectangular pulsed current on dc during the charging period caused deeper penetration of current into the porous electrode matrix and more zinc deposits were obtained at the silver current collector grid on the back side of the zinc electrode.⁶

Pulsed current has also been used in color anodizing aluminum.^{9/10} The color of the anodic coating appeared to be brighter with PC because of deeper penetration of metallic dye ions into the micropores of the oxide film on the aluminum surface.

Some of these effects can be attributed to the capability of PC to enhance the mass-transport process, rate of nucleation, and kinetics of electrodeposition. Pulsed current produces a pulsating diffusion layer wherein the

JANUARY 1988

concentrations of the ionic species fluctuate periodically with time near the electrode surface.^{11,12} The resulting concentration and surface overpotentials depend not only on the magnitude of the pulse current density but on the frequency of the pulse.

Chin" presented a theory on mass transfer and the current-potential relationship in pulse electrolysis with rectangular PC, periodic-reverse current, and double rectangular pc with relaxations; He showed that very high instantaneous mass-transfer rates corresponding to 100-1000 times the dc limiting current density can be obtained with short current pulses at high frequencies. He also showed that current pulses can profoundly change the current-potential relationships and thus the current distribution on the electrode surface.

Ibl¹⁴ discussed the problem of current distribution. Because the instantaneous current density during pulsing is usually higher than that in dc plating, he believed the primary current distribution would prevail in pulse deposition and the current distribution would be less uniform than when using dc. This would suggest that selective plating of metal on localized areas can be achieved using small electrode gaps and high current pulses.

The objective was to study the effect of rectangular pulsed current on the selective plating of copper from an acid sulfate bath. The copper deposition is localized by directing a small insoluble anode toward a large, unmasked cathode and by applying a high Pc. The effects of pulsed current, duty cycle, and anode-cathode gap on the metal distribution and morphology of the copper deposits are described here. The Wagner number evaluated from the slopes of the polarization curves with pulsed current is used to discuss the current distribution in pulse plating.



Fig. I—Experimental cell for plating experiments (B, constant-temparatura bath H, heater; M, magnetic stirrer; P, pump R, solution reservoir Ref, reference electrode; S, stirrer, S, and S₂, micrometer heads; T, thermometer TC, temperature controlled and V, vent).

Experimental Procedure

Figure 1 shows the experimental setup, including the rectangular Plexiglas cell. A yellow brass plate (5x5x0.038 cm) was used as the cathode. Suitable grooves were cut on the cell walls to support the cathode vertically and facilitate easy insertion and removal. The insoluble anode was a lead dioxide circular disc, 0.4cm in diameter, flush-mounted on a Teflon sleeve. It was secured at one end of the cell with its exposed plane parallel to that of the cathode. A saturated calomel electrode located in a Luggin capillary was used as the reference electrode. A thermometer inserted through the cell cover was used to measure electrolyte temperature.

The bath consisted of 0.75M copper sulfate and 0.75M sulfuric acid. No chlorides or other additives were used. The electrolyte was stored in a solution reservoir housed inside a constant-temperature water bath. A plastic pump was used to transfer the electrolyte from the solution reservoir to the experimental cell. Purified nitrogen gas was bubbled through the solution before and during the experiment to remove dissolved oxygen and prevent corrosion of the brass cathode, which was previously polished with 0.3 μ m alumina compound and cleaned with water and methanol. The cathode was dried and weighed to an accuracy of ±0.1 mg. It was then catholically treated in dilute sulfuric acid before transfer to the test cell.

A constant rectangular pc of known pulse period (ontime plus off-time) and duty cycle (percent on-time in one period) was then applied. The pc control circuit included a dc function generator^a connected to a mini-pulsir^b across a variable resistor (R) to generate a rectangular pulsating voltage signal of desired magnitude, duty cycle, and frequency, The signal was fed to a high-power potentiostat^c and converted to pulsating current by operating the potentiostat at the galvanostatic mode. A digital dataacquisition system using a microcomputer^d and accessories was used to monitor the average plating current, average potential drop between the cathode and reference electrode, average anode-cathode cell voltage, and root mean square of the periodic potential components, The waveforms of applied PC and the resulting cathode potential were examined on an oscilloscope."

A digital coulometer was used to record the number of dc coulombs (based on the average current) passed during the experiment. After a desired number of coulombs was passed, the cathode was removed from the cell, washed, dried, and weighed to determine the weight of copper deposited. The deposition area was also noted. All experiments were performed at a constant temperature of $25 \pm 1^{\circ}$ C.

Model 3311A, Hewlett Packard, Palo Alto, CA.
'LWD Scientific, San Francisco, CA.
'Model Wenking HP-72, Brinkmann Instruments Inc., Westbury, NY.
'Commodore PET 4032, Commodore Business Machines. Westchester, PA.
'Model 214, Tektronix, Beaverton, OR.



3-Effect of anode-cathode gap on copper thickness distribution with current density of 0.1 A/cm². Dimensionless anode-cathode gap varied from 1 to 8.



2-Copper thickness distribution obtained with dc current densities of 0.05 to 0.5 A/cm². Dimensionless anode-cathode gap was 1.



Fig. 4-Copper deposits obtained at average current density of 0.3 A/cm² and dimensionless anode-cathode gap of 1 using (a) dc and (b) pc with 5 percent duly cycle and 10-msec pulse period.

PLATING AND SURFACE FINISHING

After the plating experiment, photomicrographs of the cathode surface were taken with a scanning electron microscope to study the morphology of the copper deposits. The local coating thickness was measured using a coulometric thickness gage⁹. A 1-mm circular mask was used for the measurements, and the thickness values represented the average over a circular area 1 mm in diameter.

The active cathode area where copper was deposited varied with the experimental conditions. Unless otherwise noted, the current density values reported here are based on a constant anode area. Plating experiments were conducted at pulsed currents of 0.05 to 10 A/cm², duty cycles of 1 to 100 percent and pulse periods of 1 to 100 msec. The average current density varied from 0.05 to 0.5 A/cm². Two anode-cathode gaps were examined: $H^* = 1$ and 2, where H^* was a dimensionless anode-cathode gap defined as the ratio of anode-cathode distance to the anode radius. The plating was terminated for each experimental run after 30 coulombs was passed through the cell.

Metal Distribution

Figure 2 shows the results of metal distribution for dc plating from 0.05 to 0.5 A/cm' at a dimensionless anodecathode gap of $H^* = 1$. The local thickness of electrodeposited copper is plotted as a function of the dimensionless radial position, X*, defined as the distance from the center of the deposit divided by the anode radius. The copper deposit was thickest at the center and became thinner with increasing radial position. With increasing dc current densities, the thickness at the center increased and the coverage^b of the copper deposit decreased.

Figure 3 shows the thickness distribution with H* varying from 1 to 8 at a dc current density of 0.1 A/cm². The coverage of copper deposits, as determined by the radius of the copper deposition area, increased as the gaps became wider. The thickness of the electrodeposits at the center



Fig. 5—Copper thickness distribution obtained with pulse plating at dimensionless anode-cathode gap of 1. Average current density was 0.1 A/cm² end pulse period was 10 msec.

increased as the anode-cathode gap decreased. For example, with $H^*=1$, the thickness of the copper deposit at the center was almost 10 times greater than that at $H^*=8$. The results of dc plating experiments indicate that more localized copper deposits can be obtained by increasing the dc current density and decreasing the anode-cathode gap.

Figure 4a shows a copper deposit obtained with dc at 0.3 A/cm². Figure 4b shows the deposit produced with Pc at an average current density of 0.3 A/cm², a pulse period of 10 msec, and a 5 percent duty cycle. The black dot in each photograph represents the anode size. The copper deposition area was reduced by pc. The deposit obtained by Pc also had a better-defined edge.

Experiments were conducted to investigate the effect of pulse current density, duty cycle, pulse period, and anodecathode gap on metal distribution. Figure 5 shows the results obtained with a dimensionless anode-cathode gap of $H^* = 1$. In these runs, the average current density was 0.1

*Coverage is defined as the cathode area covered by a layer of visible copper.







Fig. 7-Effect of average current density on copper thickness distribution. Duty cycle wee 5 percent, pulse period was 10 meet, pulse current density varied from 1 to 6 A/cm², and dimensionless anode-cathode gap was 1.

JANUARY 1988

¹Model 640, The Electrosynthesis Co., Inc., Amherst, NY.

Model CM-100, Veeco-UPA Technology, Syosset, NY.

A/cm', the pulse period was 10 msec, and the duty cycle varied from 1 to 100 percent. Because the magnitude of pulse current density was equal to the average current density divided by the duty cycle, the results covered a pc range of 0.1 to 10 A/cm². A 100 percent duty cycle corresponded to dc plating.

The center thickness of pulse-plated deposits was greater than that of de-plated coatings and increased with decreasing duty cycles. Also, the coverage of copper deposits declined with decreasing duty cycles.¹⁵ For example, with a 1 percent duty cycle, the center thickness of copper deposits was almost five times that obtained with dc.

Figure 6 shows the results obtained at the larger anodecathode gap of $H^* = 2$. The average current density was again kept at 0.1 A/cm², the pulse period was 10 msec, and the duty cycle varied from 1 to 100 percent. The results were similar to those obtained at $H^* = 1$. Thus, PC improved the selectivity (or localization) of copper deposition by decreasing the total coverage of the deposit but increasing the thickness in the central area facing the anode. The selectivity improved with. decreasing duty cycles. A decrease in the anode-cathode gap also significantly increased the thickness of copper deposits in the central region.

The effect of pc current density on the metal distribution of copper is shown in Fig. 7. These experiments were conducted at 1 to 6 A/cm², a pulse period of 10 msec, and a duty cycle of 5 percent. The dimensionless anode-cathode gap was 1. The thickness of copper deposits at the center increased with increasing pc current densities the effect was similar to that of increasing the current density in dc plating. Plating experiments were also performed for pulse periods ranging from 1 to 100 msec with a duty cycle of 5 percent. The pulse period did not affect the metal distribution and coverage of copper deposits.

Morphology of Deposits

The effect of pulsed current on the morphology of copper electrodeposits was examined with a scanning electron microscope (SEM). The results of PC current density, duty cycle, and radial position (X^*) were compared to those obtained by dc plating.

Figure 8 shows the effect of current density on the morphology of copper after dc plating. The photomicrographs were taken at the center of the deposits. With a current density of 0.1 A/cm², compact crystalline deposits (crystallite) of 1 to 2 μ m were obtained. Increasing the current density to 0.5 A/cm² resulted in an increase in the crystallite size to 8 to 10 μ m.

Figures 9a-c are photomicrographs of the centers of copper deposits obtained with Pc at 100, 10, and 1 percent duty cycles, respectively. The average current density was 0.1 A/cm² and the dimensionless anode-cathode gap was 1. "he sample with a 100 percent duty cycle corresponded to



IFig. 8-Copper deposits obtained by dc plating at (a) 0.1 A/cm² and (b) 0.5 A/cm². Photos were taken at center of deposits. Dimensionless anodecathode gap was 1.



Fig. 9.-Copper deposits obtained with (a) dc, (b) pc with a 10 percent duty cycle and 10-msec pulse period, and (c) pc with 1 percent duty cycle and 10-msec pulse period. Averge current density was 0.1 A/cm² and dimension-fess anode-cathode gap was 1. Photos were taken at center of deposits.

dc plating. Pulsed current significantly modified the morphology of the electrodeposits. With pc, the deposits were brighter and the individual crystals more perfect and larger than with dc. These effects increased with decreasing duty cycle and increasing PC current density. For example, with a 1 percent duty cycle, the individual crystals were 20 to 30 times larger than those obtained with dc plating (Figs. 9a and c).

Figures 10a-c show the centers of copper deposits obtained at pc current densities of 2, 6, and 10 A/cm². The duty cycle was 5 percent, the pulse period 10 msec, and the dimensionless anode-cathode gap, 1. At pc current densities greater than 2 to 4 A/cm², a secondary nucleation was observed and the deposits changed from a crystalline to a nodular-type growth. Figure 10a shows the deposit obtained with a PC current density of 2 A/cm². Figures 10b and c show burnt deposits at 6 and 10 A/cm², respectively. The copper grains at 6 A/cm² were hemispherical and nodular and very different from the large crystallite obtained at 2 A/cm². Increasing the PC current density to 10 A/cm² resulted in spherical, nodular deposits with fine secondary growths (Fig. 10c). Thus, the deposits were transformed from crystalline structures at low pc current densities to nodular structures with secondary growths at high pc current densities.



Fig. 10-Copper deposits obtained by pulse plating with 5 percent duty cycle and pulse period of 10 msec. Pulse current densities were (a) 2 A/cm^2 (b) 6 A/cm^2 , and (c) 10 A/cm^2 . Photos were taken at center of deposit Dimensionless anode-cathode gap during plating was 1.

JANUARY 1988

The nature of the copper electrodeposits was also examined as a function of the radial position from the center of the deposit. Figure 11 shows three SEM photomicrographs of various areas on a deposit obtained by PC. Near the edge, the single-layer-thick deposit was composed of well-defined crystallite with an average size of 1 to 2 µm. A magnified view (5X) of the crystallite is shown on the right side of the photograph. Closer to the center, the deposits became denser and more compact. The crystallites grew in size and gradually became transformed from well-defined polygons to elongated structures midway between the center and the edge (Fig. 11 b). At the center, significant growth was observed in the size of the crystallites. Figure 1 la shows that the copper crystallite at the center were almost 20 to 30 times larger than those near the edge of the deposit.

Thus, pc strongly affected the morphology of copper electrodeposits. The coatings deposited with Pc were brighter and the crystallite larger than those plated with dc. The crystallite size increased with decreasing duty cycle (or increasing pc current density) and with decreasing distances from the center of the deposit.

Polarization and Current Distribution

The current efficiency of copper deposition was 100 percent for dc and pulse plating. Thus, the characteristics of metal distribution can be described by the current distribution at the cathode. In the potential theory, an important quantity that characterizes the uniformity of current distribution is the value of a dimensionless group called the Wagner number:

$$Wa = \frac{k\left(\frac{d\eta_{dc}}{di_{dc}}\right)}{L}$$
(1)

where k is the conductivity of the electrolyte, $(d\eta_{dc}/di_{dc})$ is the slope of the dc polarization curve (average potential vs. average current density) of the cathodic deposition reaction, and L is the characteristic length of the plating system. For the present geometric configuration, the diameter of the anode may be chosen as the characteristic length. The Wagner number represents the ratio of the activation or charge-transfer resistance to the ohmic resistance of the electrolyte. The current distribution is generally more uniform at large Wagner numbers. In other words, the deposit at the cathode is more localized when the Wagner number is small.

To interpret the present results using the potential theory, experiments were conducted to determine the polarization behavior of copper deposition in the standard acid sulfate bath under pc conditions. A copper rotating disk electrode with a surface area of 0.071 cm² was used to experimentally determine the relationship between average electrode potential and average cathode current. A constant pc of known pulse period and duty cycle was applied to the electrode, and the instrumentation was constructed to measure the average electrode potential with respect to a reference electrode as a function of the average current density of the pulsed current. The experimental technique is discussed in References 5 and 16.

Figure 12 shows data for average potential vs. average current density obtained with the rotating disk electrode at 2500 rpm for a pulse period of 10 msec. The polarization curves are given for five duty cycles ranging from 1 to 100 percent. An anodic dc polarization curve is also shown in the figure as a reference. The results agreed qualitatively with a theoretical calculation made earlier¹¹ for the acid copper sulfate bath. Pulsed current behaved as a depolarizer and reduced the average overpotential required for the plating process. The extent of the overpotential reduction increased with a decreasing pc duty cycle. In other words, Pc reduced the slope of the polarization curves and shifted them to a more horizontal position (Fig. 12). Thus, for a given average current density, the Wagner number is smaller with pulsed than with direct current:

$$(Wa)_{pc} < (Wa)_{dc} \tag{2}$$

This implies that the current distribution is less uniform with pc than with dc plating and that more localized deposits can be obtained with pc. This notion agrees qualitatively with the results presented in Figs. 4-6. However, any quantitative comparison between the theory and the experiments would require a simultaneous solution of the potential and electrokinetic equations (the subject of another paper). The type of polarization curves shown in Fig. 12 appears to be useful in estimating the secondary current distribution in pulse plating.



Fig. 11-Copper deposit obtained at pc current density of 2 A/cm², pulse period of 10 msec, and duty cycle of 5 percent. Photos were taken (a) at center of deposit ($X^* = 0.0$), (b) midway between edge end center ($X^* = 1.3$ and (c) at edge ($X^* = 2.3$). Dimensionless anode-cathode gap was 1.

Conclusions

In a study carried out by directing a small insoluble anode toward a large unmasked cathode, a pulse current density of 0.05 to 10 A/cm² greatly improved the selectivity (or localization) of copper deposition. Pulsed current produced thicker deposits and smaller deposition areas than dc. The extent of the improvement increased with decreasing duty cycles (or increasing peak Pc density) and with decreasing anode-cathode gaps. Pulsed current also produced much larger crystallite than dc.

The polarization characteristics of the plating bath examined with a copper rotating disk electrode demonstrated that PC served as a depolarizer and reduced the average overpotential of the process. The Wagner number generated from the slope of the polarization curves was used to discuss the current distribution in pulse plating.

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Fig. 12—Effect of pc with 10-msec pulse period on polarisation curves of copper deposition in standard acid sulfate bath at 25° C. Copper rotatingdisk electrode was used.

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Chin

Vilambi

About the Authors

Dr. Der-Tau Chin is a professor in the Dept. of Chemical Engineering, Clarkson University, Potsdam, NY 13676. He has more than 20 years of research experience in electrodeposition, corrosion, electrochemical energy conversion, and electrolytic processes. Prior to joining Clarkson in 1975, he was a senior research engineer at General Motors Research Laboratories. Dr. Chin received his PhD degree from the University of Pennsylvania in 1969.

N.R.K. Vilambi is a principal scientist at Physical Sciences Inc., Andover, MA. He recently completed the requirements for a PhD degree in chemical engineering from Clarkson University and was a research assistant for AESF Research Project 68. Dr. Vilambi also holds an MS from Clarkson and a BS from Regional Engineering College, Tiruchi, India.