

Influence of Pulse Plating on Surface Distribution And Metallurgy of Copper Deposits

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Coupons with variably spaced, 50- μ m-wide lines were plated with different pulse parameters in a copper sulfate/sulfuric acid electrolyte with and without additives. In general, the thickness distribution of pulse-plated coatings was less uniform than that of deposits obtained using constant average current density. Additive-free baths employing reverse pulsed current yielded surface distributions and deposit properties typical for dc plating in additive-containing solutions.

One of the problems encountered in electrolytic pattern plating of printed circuit boards is the non-uniform distribution of plated line heights. Isolated lines, in contrast to densely packed ones, tend to plate higher. In the absence of mass-transfer effects, the non-uniform distribution can be described in terms of the dimensionless parameter known as the Wagner number (W_a), which is the ratio of the kinetic (activation) and ohmic resistances (R_p/R_o) and which can be related to the characteristic width of the circuit line (L), the solution conductivity (k), and the slope of the polarization curve (dE/di), according to the following equation¹³:

$$W_a = R_p/R_o = k/L (dE/di) \quad (1)$$

where it is assumed that $L < d$, the anode-to-cathode distance. For $W_a < 1$, the plating is under resistive control. The distribution approaches the primary one and is non-uniform. Conversely, for $W_a > 1$, the plating is under kinetic control and the distribution is more uniform. In the Tafel region, W_a can be expressed as:

$$W_a = k \cdot b/L \cdot i \quad (2)$$

where b is the Tafel slope and i the current density.

This study was designed to examine the effects of pulse plating (PP) and reverse pulse plating (RPP) on the surface thickness distribution of line heights obtained during copper pattern plating. The distribution obtained with direct current was examined for comparison. The impact of PP and RPP on the properties of copper plated from baths

with and without organic additives was also elucidated. The objective was to define a set of pulse parameters and bath composition that would optimize copper properties and surface-distribution uniformity.

Pulse plating of copper has been studied by a number of investigators and a literature review is available.⁴ Compared with dc plating, PP provides an increase in plating rate,⁵ finer grain structure,⁷ and improved mechanical properties.¹⁰ There is also evidence that throwing power can be enhanced with PP.¹¹

Experimental Procedure

Coupons of approximately 5 x 12 cm cut from electrolytic copper foil and having the lined pattern shown in Fig. 1 were prepared using standard photoresist and imaging techniques. They were plated using the bath compositions shown in Table 1. Solution 1 contained a multicomponent additive⁷ to improve the metallurgical properties of the deposit. Solution 2 was identical to the first except that the additive was eliminated. The solutions were prepared with distilled water and reagent-grade chemicals. The coupons were mechanically agitated with reciprocating movement and air was bubbled through the solutions during plating to ensure appropriate mass transfer. The resultant copper deposits did not show the burned or powdery appearance typical of mass-transfer effects.

The coupons were plated with either a reverse-pulse or dc supply. The deposit was plated to a height of 35.6 μ m and line heights were measured with a profilometer. Plating was performed under constant-current conditions. The counterelectrodes were commercially available, phosphorized copper anodes of approximately the same dimensions as the coupons, from which they were positioned about 12 cm. The average current density was kept constant for all experiments; the plating time was 1 hr. The percent elongation was determined with a bulge tester for 50- μ m-thick foils 7.6 x 7.6 cm.¹²

*GS 818, Schering/Chemcut, Berlin, W. Germany.

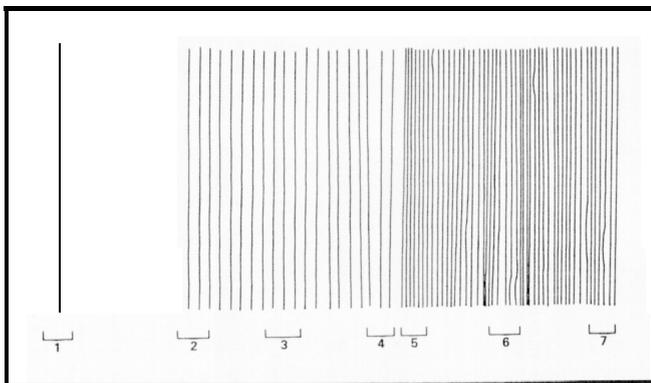


Fig. 1—Schematic line pattern for all experiments. All lines were 50 μ m wide. They were spaced 0.1, 1, and 10 mm apart for Groups 5-7, Groups 2-4, and Group 1, respectively.

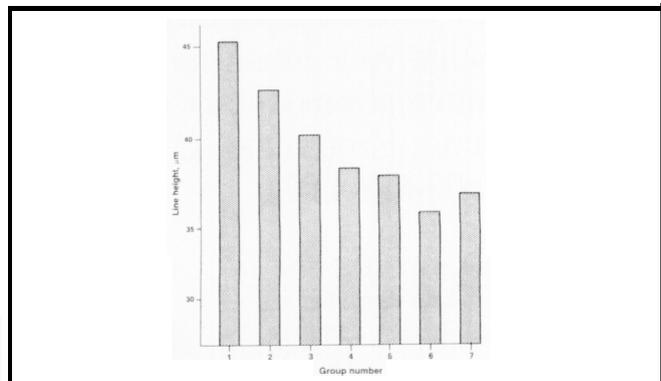


Fig. 2—Average deposit height as a function of group number for representative plated coupon. Locations of group numbers are shown in Fig. 1. For Group 1, only one line was used; for Groups 2-4, three line heights were averaged; for Groups 5-7, five lines.

Surface Distribution

Typical results for a coupon plated with dc at 25 mA/cm² are shown in Fig. 2. The isolated line (Group 1) plated the highest, and line heights decreased monotonically to the central region of the densely packed lines (Group 6). The height increased for Group 7 because this region is close to the edge of the coupon where higher current densities are generally encountered. The basic pattern was observed in all experiments with the only difference being changes in relative line heights.

To compare the distributions obtained under various conditions, an arithmetic mean of line heights for the seven groups was obtained. This is not a weighted average and therefore has no physical significance. The difference from the mean for each average group height was obtained and plotted vs. the group number. Figure 3 is a representative plot and shows the effect of current density on surface distribution for dc plating. Of the samples discussed here, this was the only one in which overall plating rate and time were not held constant. The replicate data for the lower current density shows the magnitude of error observed for most experiments. The error was greater for the isolated and central lines because there were fewer to average. Lower current densities were observed to yield more uniform distributions consistent with Eq. 1 and previously reported results.

For PP and RPP, the average plating current density, i_{av} , is defined by Eq. 3, where i_c and t_c are the peak cathodic current density and duration, and i_a and t_a are the peak anodic current density and duration, respectively

$$i_{av} = (i_c \cdot t_c - i_a \cdot t_a) / (t_c + t_a) \quad (3)$$

To maintain a constant value of i_{av} , for symmetric pulsing ($t_a = t_c$), the value of i_c will be greater than the cathodic current density for dc conditions. For pulse plating ($i_a = 0$), W_s under Tafel kinetics (Eq. 2) predicts that the distribution would be less uniform than that of the comparable dc plating distribution. This prediction is supported by the data shown in Fig. 4. No significant frequency dependence was observed. Thus, in terms of the macroscopic distribution, there appears to be no benefit derived from high-frequency pulsing.

Asymmetric PP where $t_a > t_c$ further degrades the distribution compared with dc or symmetric PP (Fig. 5)

because values of i_c must be higher. For example, the value of i_c must be 275 mA/cm² (11 times the dc value) to maintain i_{av} constant for $t_a = 10 t_c$. Again, the height distribution appears to depend primarily on the magnitude of i_c and, for constant i_{av} , cannot be improved when compared with dc plating. As before, there appears to be no frequency dependence. This case is of practical interest because there has been some evidence that long off-times favor more frequent nucleation, and finer-grained deposits may be obtained.⁸

Asymmetric pulse plating where $t_c > t_a$ is not considered here. As $t_c/t_a \rightarrow 0$, the distribution approaches that obtained for dc plating. Furthermore, there is no benefit derived, in terms of metallurgical properties, from plating with these parameters.

The discussion until now has focused only on PP; there has been no anodic component. Some improvement in distribution can be obtained for an appropriate set of RPP parameters. As the deposits are stripped during the anodic cycle, the lines plated with copper to a greater thickness during the cathodic pulse would also be etched to a greater extent because they are regions of high current density for both the anodic and cathodic pulses. The net result would be a more uniform deposit. For copper, the relative magnitude of this effect can be enhanced if the slopes of the polarization curves for deposition and dissolution are taken into account (Eq. 1). The Tafel slopes for deposition and dissolution of copper have been reported at 118 and 40 mV/decade, respectively.¹³ Assuming $i_a = i_c$, the lower Tafel slope implies that copper dissolution during the anodic cycle will be less uniform than deposition during the cathodic cycle (i.e., W_s is smaller for the anodic cycle). Therefore, under the appropriate conditions, RPP should improve the height distribution compared with dc plating.

Two general experimental cases were examined to test the aforementioned hypothesis. The first is shown in Fig. 6. The value of i_c was as low as possible in order to maintain a constant i_{av} and was applied for a relatively long time (i.e., $t_c > t_a$). The anodic current took the form of a sharp spike; relatively high current was applied for a short duration. The results show that the distribution again was worse than that obtained with dc. This was surprising because the parameters were expected to be those most favorable for obtaining uniform deposits.

Large values of i_a should exaggerate the asymmetry of distribution during the anodic pulse, while low values of i_c

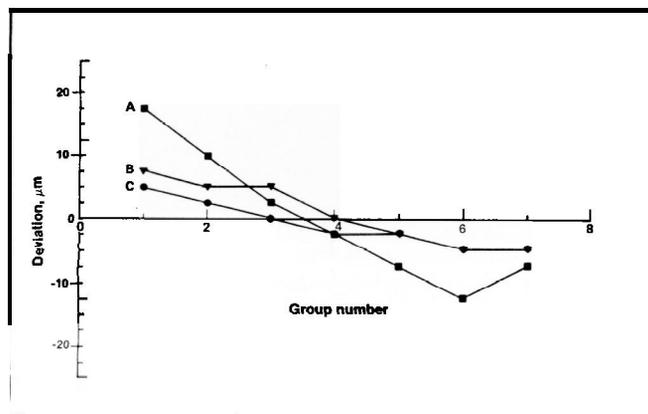


Fig. 3—Variation in deposit height as a function of group number for dc densities of 50 mA/cm² (Curve A) and 25 mA/cm² (Curves B and C). Coupons were plated from Bath 1.

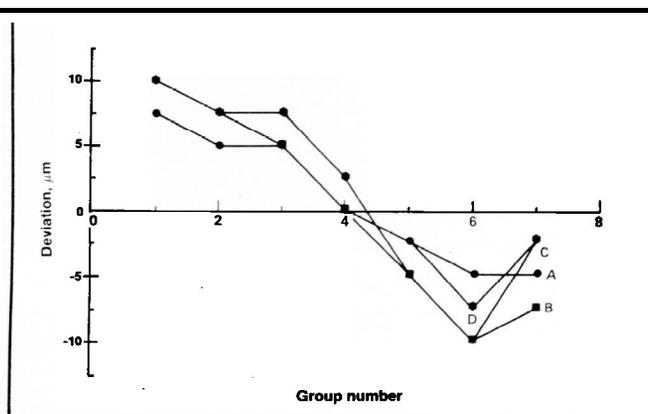


Fig. 4—Variation in deposit height as a function of group number for coupons plated from Bath 1 using dc at 25 mA/cm² (Curve A) and pulsed current at $t_c = t_a = 10$ msec (Curve B), $t_c = t_a = 1$ msec (Curve C), and $t_c = t_a = 0.1$ msec (Curve D). For pulse-plated samples, $i_c = 50$ mA/cm² and $L = 0$.

favor a more uniform distribution during the cathodic pulse. In practice, however, during dissolution at high current densities, copper passivates either by oxide formation or precipitation of CuSO_4 at the interface. Visual inspection of the coupon showed blackening of the deposit,

signifying oxide formation. Furthermore, because the deposit on the isolated line is etched faster at a higher current density compared with the more densely packed lines, it has a tendency to passivate preferential y. Clearly, i_a must be adjusted so it is large enough to affect the distribution but not so large that the surface is passivated.

The set of RPP parameters shown in Fig. 7 met these criteria and resulted in improved distribution compared with that obtained by dc. In this case, i_a was large enough (5 mA/cm^2) to improve distribution without causing deleterious oxide formation or passivation.

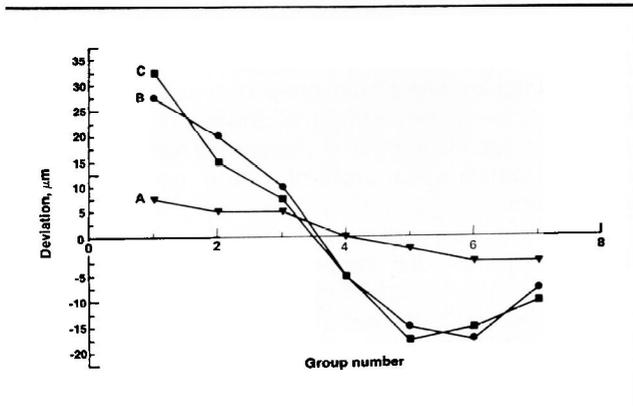


Fig. 5—Variation in deposit height as a function of group number for coupons plated with dc at 25 mA/cm^2 (Curve A); pulsed current at $t_c = 10 \text{ msec}$ and $t_r = 100 \text{ msec}$ (Curve B); and pulsed current at $t_c = 1 \text{ msec}$ and $t_r = 10 \text{ msec}$ (Curve C). For Curves B and C, $i_c = 275 \text{ mA/cm}^2$ and $i_r = 0$. All coupons plated from Bath 1.

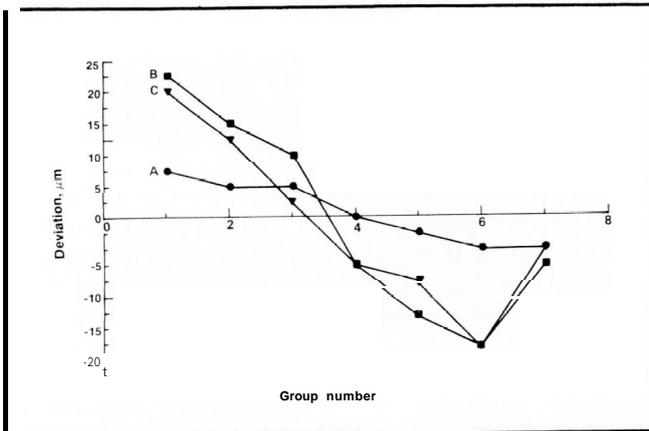


Fig. 6—Variation in deposit height as a function of group number for coupons plated with dc at 25 mA/cm^2 (Curve A) and reverse pulsed current at $t_c = 10 \text{ msec}$, $t_r = 50 \text{ msec}$, $i_c = 100 \text{ mA/cm}^2$, and $i_r = 50 \text{ mA/cm}^2$ (Curves B and C). Bath 1 was used for Curves A and B Bath 2 for Curve C.

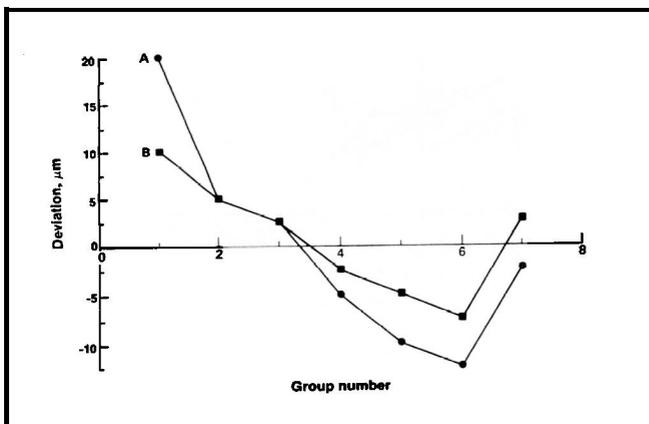


Fig. 7—Variation in deposit height as a function of group number for coupons plated with dc at 25 mA/cm^2 (Curve A), and reverse pulsed current at $t_c = t_r = 10 \text{ msec}$, $i_c = 55 \text{ mA/cm}^2$, and $i_r = 5 \text{ mA/cm}^2$ (Curve B). All coupons plated from Bath 1.

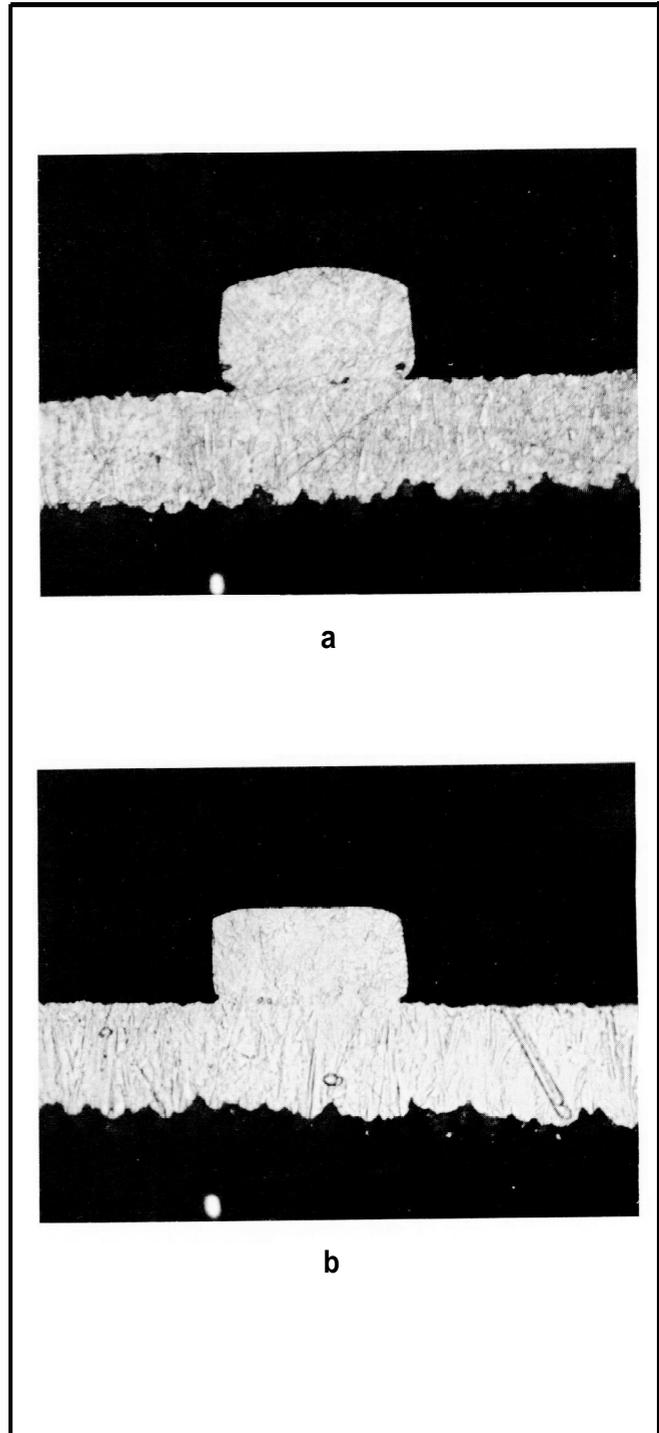
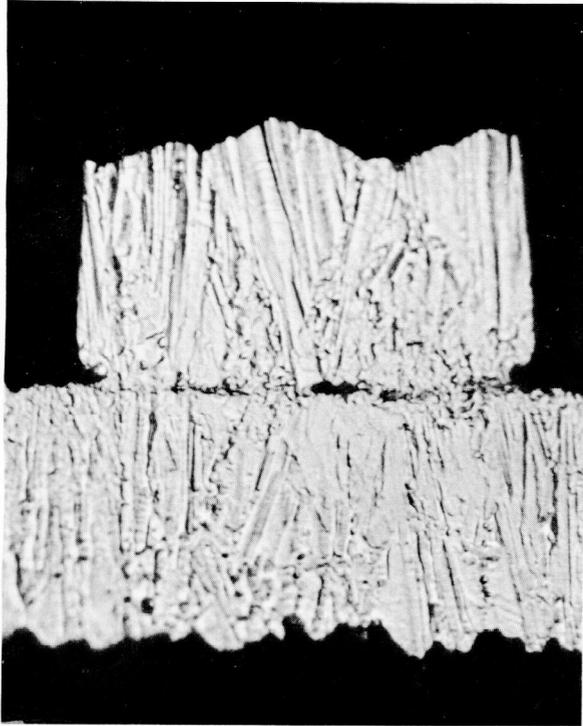


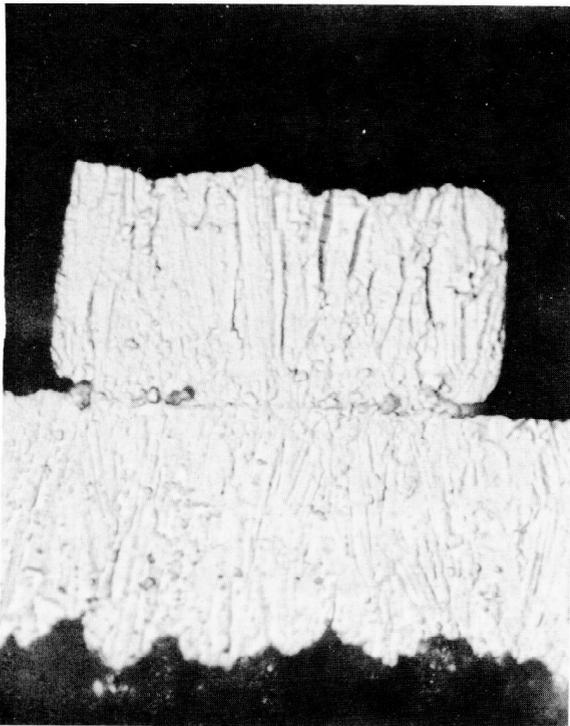
Fig. 8—Cross-sectional micrographs (640X) of coupons plated with (a) dc at 25 mA/cm^2 and (b) pulsed current at $t_c = t_r = 10 \text{ msec}$, $i_c = 50.5 \text{ mA/cm}^2$, and $i_r = 0.5 \text{ mA/cm}^2$. samples a and b were from Group 6. All coupons plated from Bath 1.

Table 1
Copper Plating Solutions

Constituent	Bath 1	Bath 2
CuSO ₄ ·5H ₂ O, g/L	78.6	78.7
H ₂ SO ₄ , g/L	200	200
Cl, mg/L	50	50
Additive, %	1	None



a



b

Fig. 9—Cross-sectional micrographs (1200X) of coupons plated with (a) dc at 25 mA/cm² and (b) pulsed current at $t_r = t_c = 10$ msec, $i_c = 50.5$ mA/cm², and $i_a = 0.5$ mA/cm². All coupons plated from Bath 2.

Metallurgy

Figure 8 shows cross-sectional micrographs of coupons plated from additive-containing copper baths (Table 1) using direct and pulsed current. The deposits showed fine, equiaxed grains. However, the ductility of deposits obtained by PP and RPP decreased to some extent compared with dc coatings (Table 2). This indicates an inconsistency between the electrochemical parameters and the effect of the additives. Pulsing seems to have some effect on the capability of the additives to promote the desired ductility. Investigations will continue on the microscopic nature of these deposits to elucidate the causes of ductility decreases when using pulse plating.

There was no effect on the microleveling capabilities of the additives; all deposits were bright, probably due to the similar grain structures observed in each. Interestingly, the lines obtained with dc had a domed appearance, which can be attributed to mass-transfer limitations near the edge of the resist. The copper deposits were 35 μ m thick and the resist was 55.9 μ m thick. The domed configuration was prominent for 50.8- μ m-wide lines but was not observed for wider line channels. Pulsing the current appears to reduce this effect, yielding a flatter profile—an effect that is also under further investigation.

Deposits from baths containing no additives and employing dc (Fig. 9a) had a pronounced columnar grain structure with an associated decrease in ductility (Table 2) and were quite rough (i.e., exhibited poor microleveling). In baths without additives, RPP (Fig. 9) disrupted the columnar structure to some extent, resulted in an increase in ductility compared with the dc case (Table 2), and somewhat improved microleveling. The set of electrochemical RPP parameters that enhanced ductility also provided the most uniform deposits.

Conclusion

The surface height uniformity on circuit lines generally degrades as plating current densities are increased. With PP, parameters previously shown to enhance metallurgical properties also tended to degrade height distribution. However, RPP improved height distribution although the magnitude of the anodic current pulse had to be limited to avoid passivation of the surface.

Additives formulated for dc plating of ductile copper may not function properly under pulsed conditions. With no additives in the bath, RPP—given the appropriate parameters—yields copper deposits having structures, ductility values, and surface height distributions comparable to those obtained by dc plating with additives. Thus, the additives and the process control difficulties they impose can be eliminated.

Table 2
Elongation Data

Type of current ^a	Bath no.	Elongation, %
Direct	1	7
Pulsed ^b	1	3
Reverse pulsed ^c	1	4
Direct	2	3
Pulsed ^b	2	3
Reverse pulsed ^c	2	5

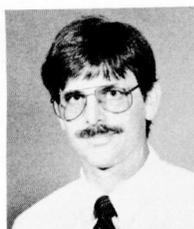
^aAll samples plated with $50 \pm 2.5 \mu\text{m}$ copper.

^bPulse plated at $t_a = t_c = 10$ msec.

^cReverse pulse plated from Bath 1 at $t_a = t_c = 10$ msec, $i_c = 55 \text{ mA/cm}^2$, and $i_a = 5 \text{ mA/cm}^2$.

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