Pulsed Electrodeposition of Copper

By G. Devaraj and S.K. Seshadri

Pulsed electrolysis of copper has been systematically investigated by electrodepositing copper from a copper sulfate bath. Pulse duty cycles of 5 to 80 percent, at frequencies from 10 to 100 Hz with current densities ranging from 2.5 to 7.5 A/dm^2 were employed. The appearance of Hull Cell panels with both direct current and pulsed current was recorded. The influence of pulsed current on current efficiency, cathode potential, and properties of the deposit, such as hardness and porosity, were studied and compared with the same characteristics obtained with conventional d-c plating.

Table 1
Pretreatment for Copper Cathodes

1. Mechanically polishing and buffing to a mirror finish.
2. Decreasing with trichloroethylene or acetone.
3. Anodic and cathodic cleaning in a bath of 35 g/L NaOH and 25 g/L Na_2CO_3 at 15 A/dm^2 for 3 to 5 min.
4. Rinse.
5. Neutralization in 10% H_2S0_4.
6. Rinse.

Electrodeposition by pulsed current has received much attention in recent years for improvement of the mechanical and chemical properties of a de-posit.[1] The advantages of pulsed plating are numerous, such as reduction of porosity,[2] lower gas content,[3] high purity, fine-grained deposits, and deposits having low electrical resistance.[4-6] Pulsed plating of alloys has proved beneficial as well.[7,8] It is also possible to produce harder, pore-free deposits by pulsed plating.[9,10]

A review of pulsed plating has already been presented by the authors." Various reports review the application of pulse techniques for copper deposition.[12] Surface roughness of copper deposits is reduced with pulsed current at higher frequencies. [13] Leveling of copper was found to be good with pulsed current but the macrothrowing power was poor.[14] Reduced level of stress and increased plating rate were reported for copper deposition.[15]

There are three parameters which can be varied independently in pulsed plating—pulse current, pulse on time and pulse off time, which determine the physical characteristics of the deposits obtained from the given electrolyte.[4]

In the present study, a systematic investigation of copper deposition from an acid copper sulfate bath has been undertaken with the application of square wave pulse current. The influence of pulse conditions on current efficiency, cathode potential and physical properties, such as hardness and porosity have been studied in detail and compared with those for conventional direct-current copper deposits.

Experimental Procedure

An electrolyte, consisting of 210 g/L $CuS0_4 \bullet 5H_20$ and 52.5 g/L of 1.84 sp. grav. H_2S0_4 was prepared (pH less than 0.1) and purified by charcoal treatment and dummying at 0.5 A/dm^2. Deposition of copper was on copper cathodes (20 cm^2 **area).** The procedure used for pretreatment of the cathode is given In Table 1. The plating solution was stirred magnetically during deposition.

Hull Cell experiments were performed in a 267-mL standard cell, The average current densities used for pulse plating were selected based on Hull Cell experiments. Pulse plating was done at 35 “C, using one liter of the electrolyte and employing rolled electrolytic copper anodes. Pulse frequencies ranging from 10 to 100 Hz and duty cycles ranging from 5 to 80 percent were used. Table 2 shows the various pulse parameters used.

Hardness of the copper deposits (50 µm) was measured at a load of 50 g. Porosity of copper deposits of 5 µm thickness was determined electrographically, using a nickel

Table 2
Details of Pulse Conditions

Duty cycles, %.	Pulse frequency, Hz: 10	25	50	100	Current density, A/dm^2: Peak	Average
	Pulse times (on-off) msec					
5	5-95	2-38	1-19	0.5-9.5	50, 100, 150	2.5, 5.0, 7.5
10	10-90	4-36	2-18	1-9	25, 50, 75	2.5, 5.0, 7.5
20	20-80	8-32	4-16	2-8	12.5, 25, 3.75	2.5, 5.0, 7.5
40	40-60	16-24	8-12	4-6’	6.25, 12.5, 18.25	2.5, 5.0, 7.5
80	80-20	32-8	16-4	8-2	3.12, 6.25, 9.38	2.5, 5.0, 7.5

$$\% \text{ Duty cycle} = \frac{\text{On time}}{\text{On time} + \text{Off time}} \times 100 \qquad \text{Average current} = \frac{\text{On time}}{\text{Total time}} \times \text{Peak pulse current} \qquad \text{Peak current} = \frac{\text{Average current}}{\text{Duty cycle}}$$

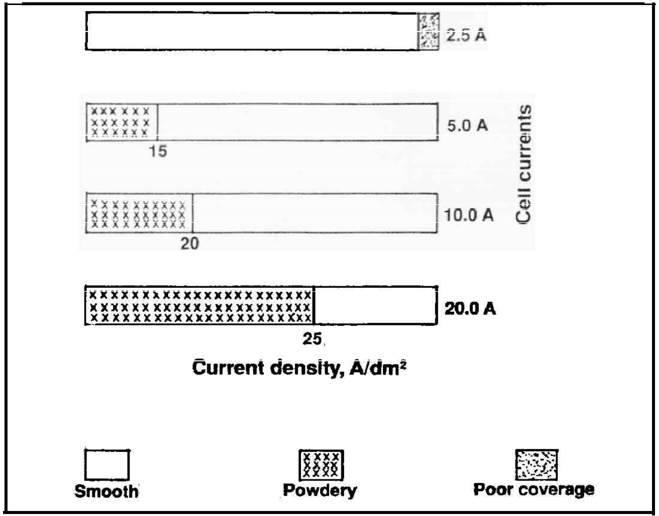

Fig. 1—Hull Cell panels plated with copper at different cell currents (DC).

undercoat per ASTM B583-83. The porosity was measured as number of pores over 10 cm^2 of copper deposit. D.C. experiments were also carried out, for the purpose of comparison, at a current density equal to the average pulse current density and the various properties measured.

Results and Discussion

Hull Cell Studies

The appearance of copper deposits obtained at different cell currents (D. C.) is shown in Fig. 1. At a lower current of 2.5 A, throwing of copper was poor at the extreme low-current-density (LCD) end of the panel. At higher currents, from 5 to 20 A, the throwing was good, but powdery deposits appeared at the high-current-density (HCD) range of the panel. This study shows that from the given electrolyte, copper may deposit smoothly up to 25 A/din'.

The Hull Cell patterns produced under different pulse conditions are shown in Fig. 2. It is observed that, in general, the throwing of copper was poor at lower pulse duty cycles (five percent). With increase in cell current, deposition is seen to be improved. Throwing power appears to get poorer with increase in pulse frequency. Another distinct feature observed was the absence of powdery deposits at the HCD end of the panels at 50 and 100 Hz pulsed current.

Although peak pulse currents at low duty cycles are higher, good throw was not obtained under these conditions. This may be because the peak current was on only for shorter periods of time, followed by longer off times. When the current is on, higher peak current favors deposition at the HCD end of the panel, resulting in poor coverage at the LCD end. A similar finding, showing poor macrothrowing power with pulsed currents has been reported.[14] Deposition improved, however with increasing duty cycle because the peak current is lower for the same average current.

Macrothrowing of copper from a still copper sulfate bath is better, compared to an agitated bath, as reported by Graham.[16] This is because, with agitation, mass transport of the cations is favored at the high-current-density end of the Hull Cell panel, leading to poor coverage at the LCD end. A similar observation was made in the case of pulsed plating; with increasing frequency of pulses, there **was** absence of powdery deposits at high current density because of negligible polarization and poor throwing at the LCD end of the Hull Cell panel.

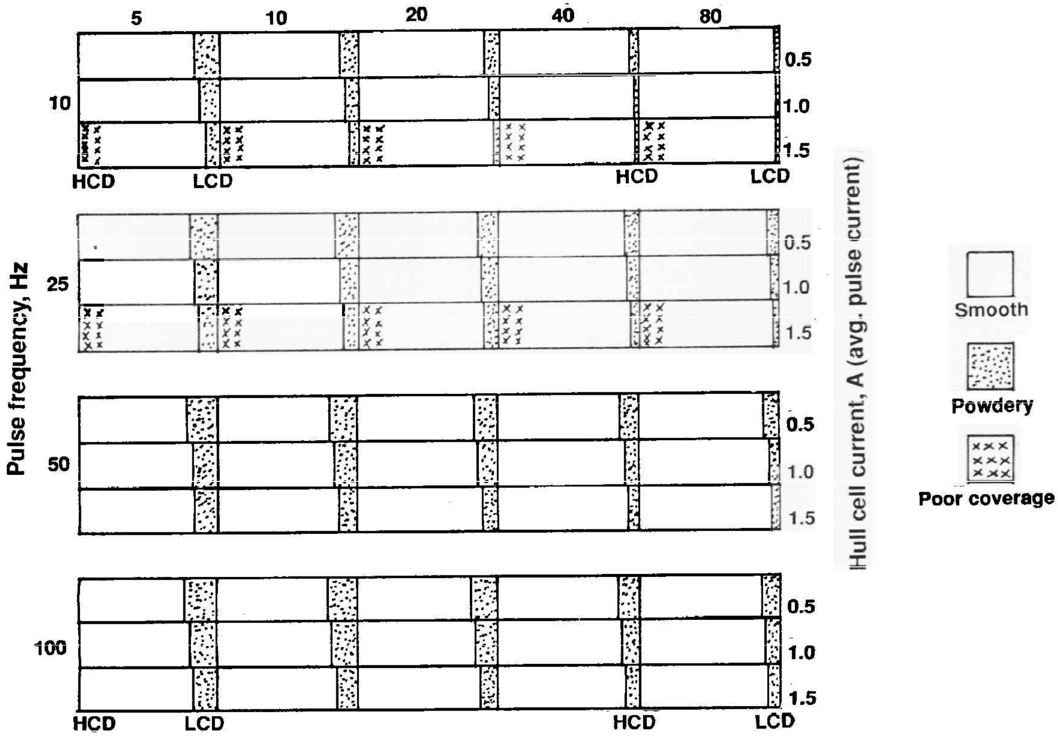

Fig. 2—Hull Cell panels plated under different pulse conditions.

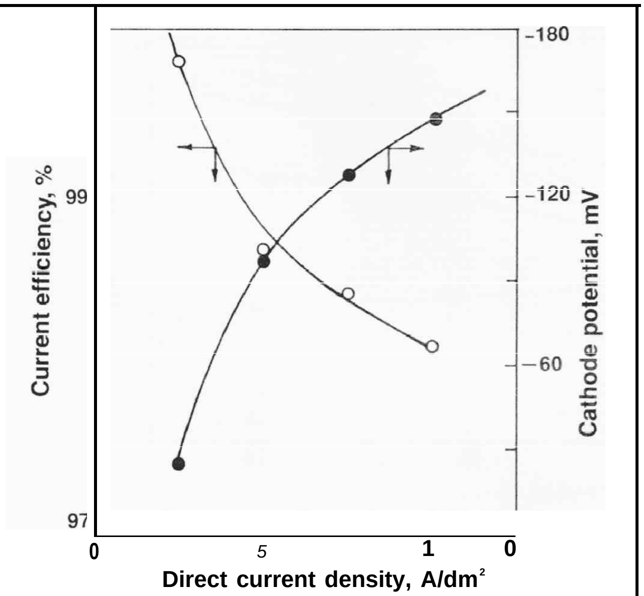

Fig. 3—Effect of current density on current efficiency and cathode potential *copper deposition (DC).*

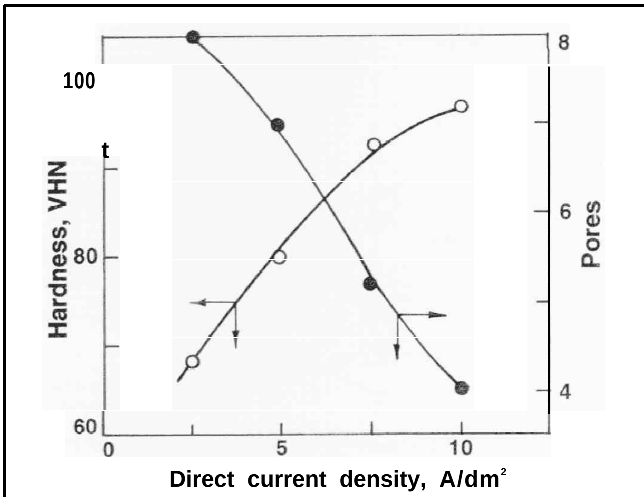

Fig. 4—Effecf of direct current density on hardness and porosity of copper *deposits.*

Based on the above observations, the average current densities for pulsed deposition were chosen as *2.5,5* and 7.5 A/dm^2, which fall in the smoother, good deposition range in all the pulse conditions studied.

Effects of Current Density

Figure *3* shows the effect of **current density on current** efficiency and cathode potentials for electrodeposition of copper. Current efficiency decreased with increasing current density, a normal observation for acid baths. More negative cathode potentials were recorded as current density increased, showing increased cathodic polarization with current. Hardness of the deposit increased with current density, as shown in Fig. 4. In general, copper deposited from copper sulfate baths shows hardness ranging from 45 to 180 VHN.[17-19]

Deposition occurring at more negative potentials and exhibiting hardness may be a result of formation of finer grains at higher current densities. Porosity of the copper deposit was also observed to decrease with increasing current density. This would lead to formation of dense deposits having greater hardness.

Effects of Pulse Duty Cycle

At 2.5 A/dm^2 average pulse-current density

Higher current efficiency (98.3 to 99.4 percent) was recorded for deposition of copper at 80-percent pulse duty cycle, while at a low duty cycle of five percent, the cathode current efficiency (CCE) was lower (97.6 to 98.2 percent) as shown in Fig. 5. The CCE also increased with pulse frequency, but the general observation is that there is a reduction in CCE for deposition of copper with pulsed current, compared to d-c deposition. Wan et al. reported reduced current efficiency with pulsed plating because of formation of cuprous ions in the bath.[12] The cathodic reactions were described as

$$Cu^{++} + e^- \rightarrow Cu^+ \quad (1)$$

$$Cu^+ + e^- \rightarrow Cu^o \quad (2)$$

During the first interval of pulsing, reaction (1) is found to be greater than reaction (2), resulting in the accumulation of cuprous ions in the bath.

The cathode potentials of pulsed copper deposition were found to be more negative compared to d-c deposition, as can be seen from Fig. 5. This was true for both duty cycle and

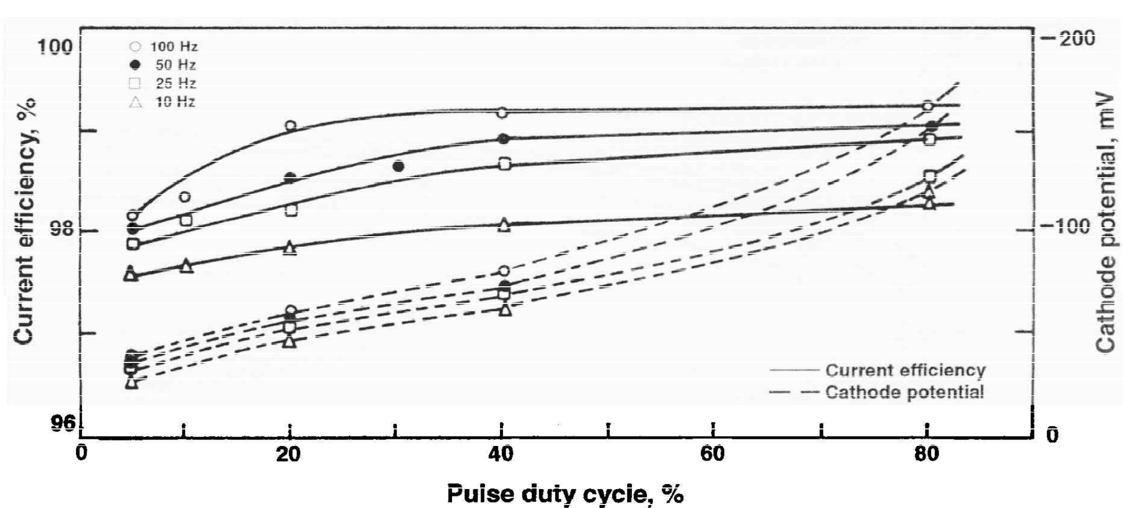

Fig. 5-Effect of pulse duty cycle on cathode current efficiency and cathode potentials of copper deposition at 2.5 A/dm^2 average current density.

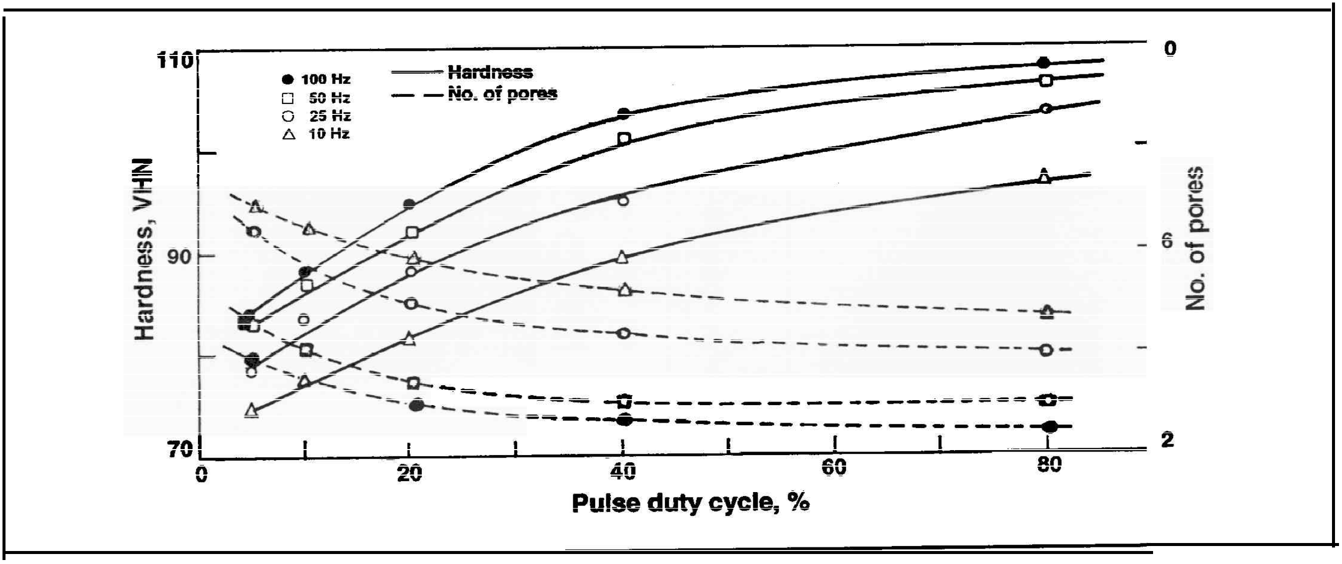

Fig. 6—Effect of pulse duty cycle on hardness and porosity of copper deposits at 2.5 A/dm² average current density.

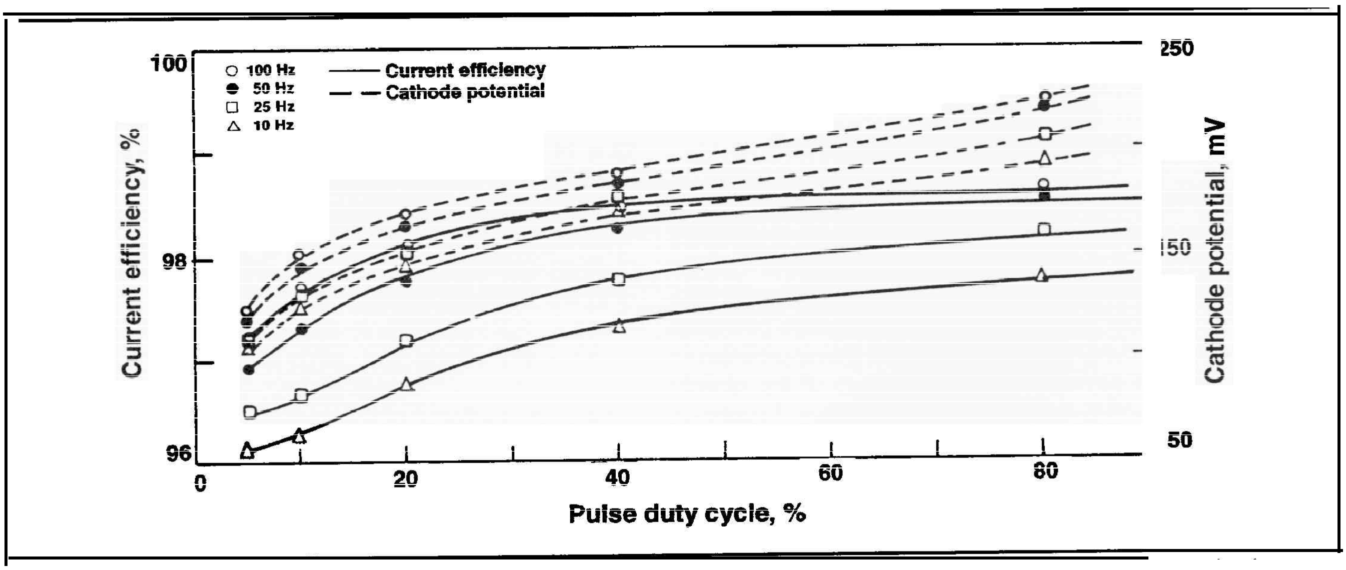

Fig. 7—Effect of pulse duty cycle **on** *cathode current efficiency and cathode potentials of copper deposition at 5 A/dm² average current density.*

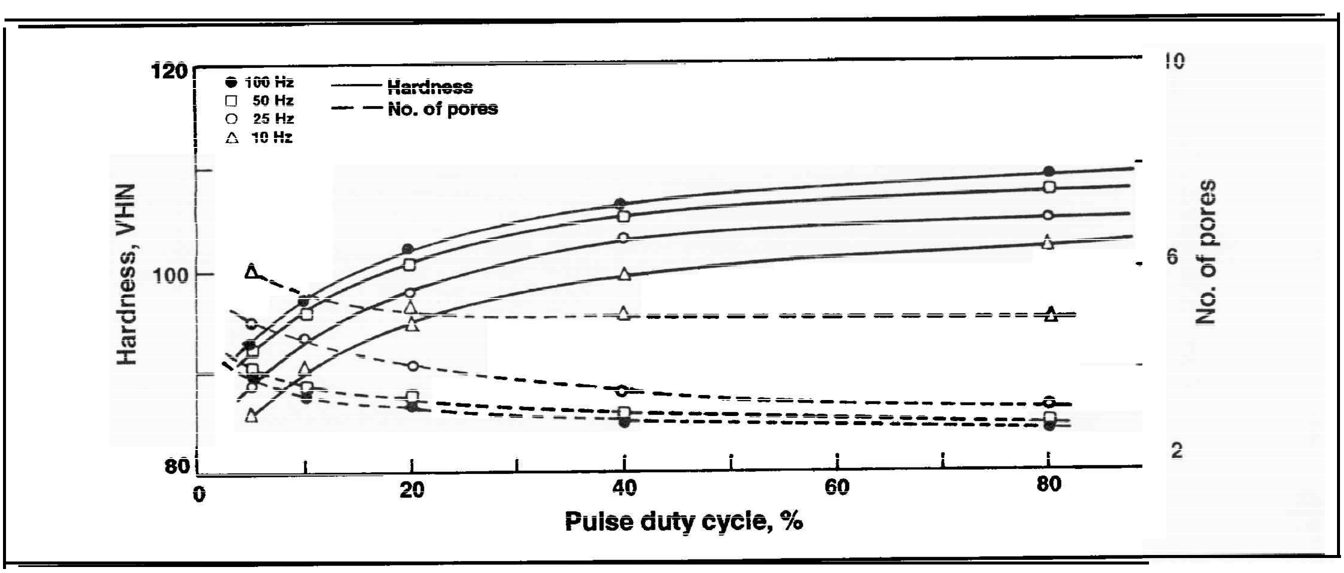

Fig. 8—Effect of pulse duty cycles on hardness and porosity of copper deposits at 5 A/dm² average current density.

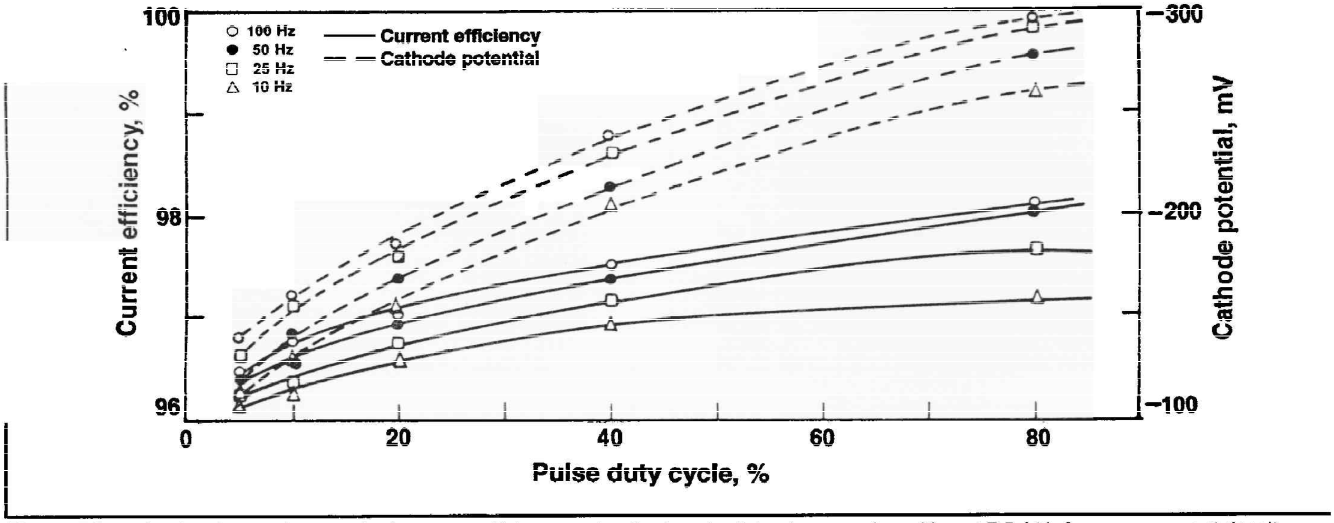

Fig. 9—Effect of pulse duty cycle on cathode current efficiency and cathode potentials of copper deposition at 7.5 A/dm² average current density.

frequency variations. Such large polarization favoring fine-grained deposits maybe responsible for increasing the hardness of copper deposits, as indicated in Fig. 6, when compared to deposits obtained by d-c plating at the same average current density. Higher pulse frequency and longer duty cycles produced greater hardness of copper deposits. It was also observed that there was **a** reduction in porosity of the copper deposits obtained with pulsed current. With d-c plating, for the same current density, the number of pores recorded was eight, but this number decreased in the case of pulsed plating.

At 5.0 A/dm² average pulse current density

Current efficiency increased with pulse duty cycle and frequency, as shown in Fig. 7. The trend is similar to that obtained with 2.5 A/dm² average current density, but the values were lower because of the higher current density. The cathode potentials were still more negative **than those obtained with 2.5** A/dm² and with pulsed operation. The more negative cathode potentials were responsible for greater hardness of copper deposits, with varying pulse duty cycles and frequency (Fig. 8). Reduction in porosity noticed in this **case is** consistent with the greater hardness obtained with increased pulse duty cycles and frequency. The change in hardness and porosity was observed to occur over a narrow range at 50 and 100 Hz pulse frequency.

At 7.5 A/dm² average pulse current density

The results obtained with pulsed plating at 7.5 A/dm² are shown in Figs. 9 and 10. The CCE was low at five-percent duty cycle and higher at 80 percent. Because the **average current density was higher,** the CCE was larger than that obtained with 2.5 and 5.0 A/dm². The cathode potentials were again more negative compared to DC and lower average pulse current densities. Similarly, the copper deposits showed greater hardness, which increased with pulse duty cycles as before. The number of pores detected were reduced considerably for deposits obtained with pulse frequencies of 50 and 100 Hz.

These results show that the introduction of pulsed current improves the hardness of copper deposits and reduces their porosity. In pulsed plating, when the current is turned *on,* metallic ions adjacent to the cathode are depleted and the cathode film is enriched with nonmetallic ions present in the bath. When the current is off, the gas bubbles and impurities that have been adsorbed on the cathode are desorbed into the solution. The

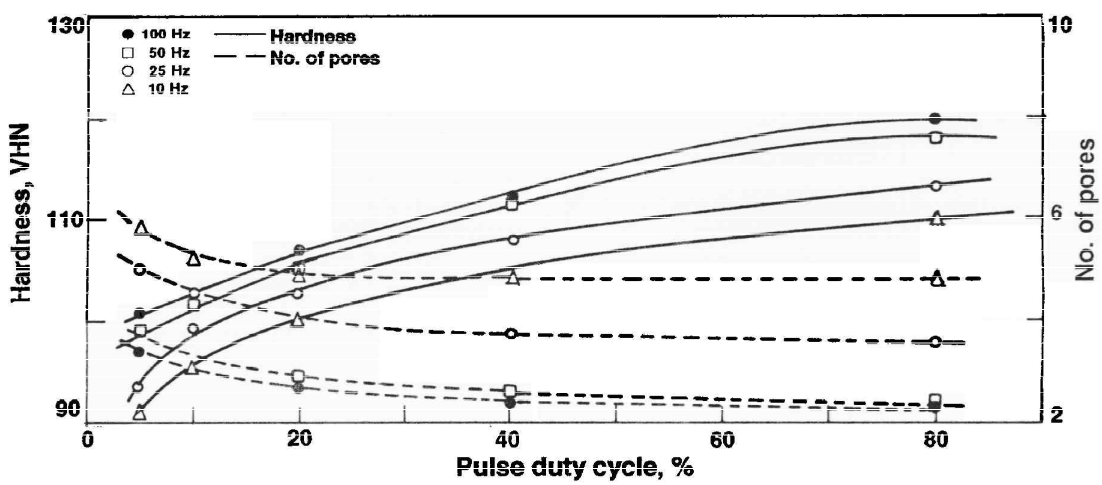

Fig. 10-Effect of pulse duty cycle on hardness and porosity of copper electrodeposited at 7.5 A/dm² average current density.

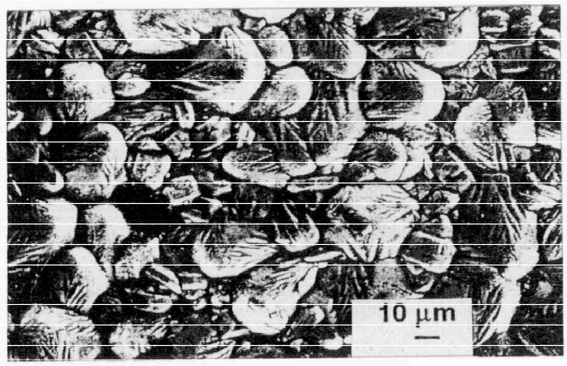

Fig. 11—SEM photograph of copper deposited at five-percent duty cycle and 25 Hz frequency, showing coarser structure.

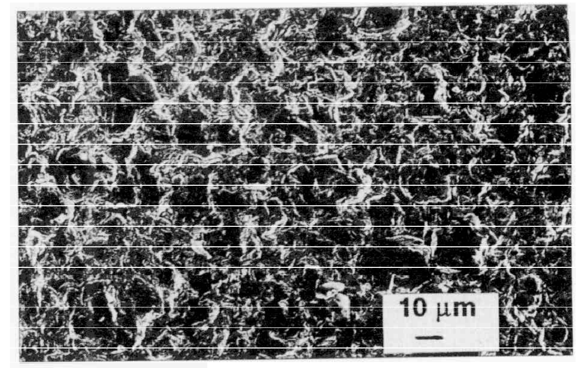

Fig. 12—SEM photograph of copper deposited at 80-percent duty cycle and 25 Hz frequency, showing finer structure.

increase in hardness and decrease in porosity in pulsed plating is accounted for by this resorption phenomenon .[5,9,10]

The hardness of the deposit when plating at 80-percent duty cycle was always greater than that obtained at five-percent duty cycle. With a low duty cycle, the hardness was lower, even though the peak current density was much higher. This could be because a much larger number of nuclei would have formed and, with the longer off period, there is more time available for grain growth as a result of recrystallization. Conversely, with an 80-percent duty cycle, the off time is very much shorter; the grains remained stable and did not have adequate time for grain growth. A reasonable conclusion is that the possibility of grain growth because of longer off times is a factor in lower hardness values of these deposits. SEM photographs (Figs. 11 and 12) show larger and finer grains of copper deposits at five- and 80-percent duty cycles, respectively.

With longer off times, large grains of copper deposits resulting from recrystallization were also observed by Puippe et al.[20] It is also reported that for deposition of gold from an acid bath, an increase in grain size was accompanied by an overlong off time in the absence of any strong adsorption of ionic species.[21]

Conclusions

Compared to direct current deposition, pulsed plating, using various duty cycles, improved the hardness of copper deposited from a copper sulfate bath without addition agents. The cathode current efficiency was lower with pulsed current, but appreciable reduction in the porosity level of the copper deposit was observed with increasing average pulse current densities. Improvement in hardness and reduction in porosity of copper deposit were achieved at 80-percent pulse duty cycles and at 50 to 100 Hz pulse frequencies.

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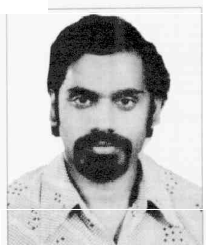

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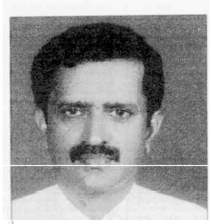

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