Throwing Power & Cathode Efficiencies of Gold Electroplating Solutions Under Pulse Regimes

By D.L. Rehrig & N.V. Mandich

Throwing power, the property that expresses the capability to produce uniform thickness on non-planar substrates is measured for pulse-plated gold deposits using the Haring Cell. Throwing power was found to vary in parallel with cathode efficiency except in the eight- and nine-msec *on* times range, where throwing power increased while cathode efficiency decreased. Cathode efficiency decreased with increased *on* time. With long *on* times (8-9 msec), the metal ions adjacent to the cathode were depleted and hydrogen evolution occurred.

Wave Forms

Brugnatelli[1] was the first to report electrodeposition of gold by direct current, in 1805. Since that time, advances in gold electrodeposition have primarily resulted from improvements in bath chemistry. Observations on the use of non-direct current in electrochemical systems dates from nearly the beginning of gold electroplating. During the 19th century, it was found that in non-stationary regimes [*e.g.*, when alternating current (AC) and AC superimposed on DC are used, there is a frequency-dependent effect on the corrosion rate of metals in electrolytic systems].[2] Decreased polarization and dependence of anodic dissolution (corrosion) on a-c frequency were well characterized by 1909, when Wohlwill[3] reported the first commercial application of superimposed AC on DC. The Wohlwill method was used to control anodic corrosion in gold refining. A variation of a-c waveforms was the bipolar DC or periodic reverse current (PRC) method first described by Rosing[4] in 1896. Patents were filed during the first half of the twentieth century on various electroplating methods with periodic reverse currents.[5-9]

The first reference on practical pulse electroplating appeared in 1934 when Winkler[10] was issued a patent for changing the alloy composition by varying the voltage, which is in essence pulse electroplating. In addition, unipolar or pulsed current (PC) could deposit certain Ni-Au alloy compositions that could not be plated by other methods. This phenomenon has since been verified with a number of other alloys, such as Fe-Ni,[10] Ag-Sn,[11] Au-Cd-Cu,[12-15] Cr-Mo,[16] Pd-Ni,[17] Cu-Zn-Sn,[18] and Ni-P.[19] In 1953, Bertolere[20] used direct current with superimposed alternating current for gold electroplating. In 1955, Rockafellow[21] obtained a patent describing copper and cadmium electroplating. This method was later recognized as a form of pulse plating.

When using non-stationary currents in the form of PC or PRC for electroplating, it was observed, some years before, that either a deposit of much finer grain size could be obtained from cyanide[22] or acid copper solutions.[23,24] Other research workers have confirmed this for nearly all deposited metals. Gardman and Tisdwell[25] further discussed gold electroplating in 1954, covering also electrodeposition of gold and alloys by a new method. Because of lack of commercial power supplied at that time, applied research and industrial application did not develop as would be expected. Recently it was found that with certain pulse frequencies, better leveling can be obtained for bright nickel, bright gold and bright acid copper solutions with much smaller quantities of organic brightening agents needed.[26]

It was known that the morphology of gold and gold alloys would be influenced by PRC or PC, but great interest developed when it was realized that pulse-plated gold deposits

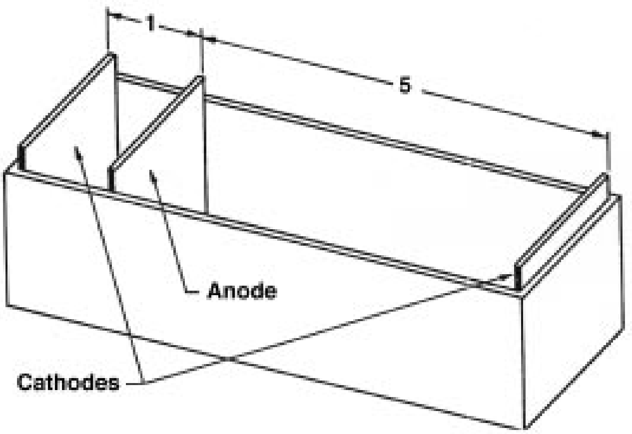

Fig. 1—Haring Cell.

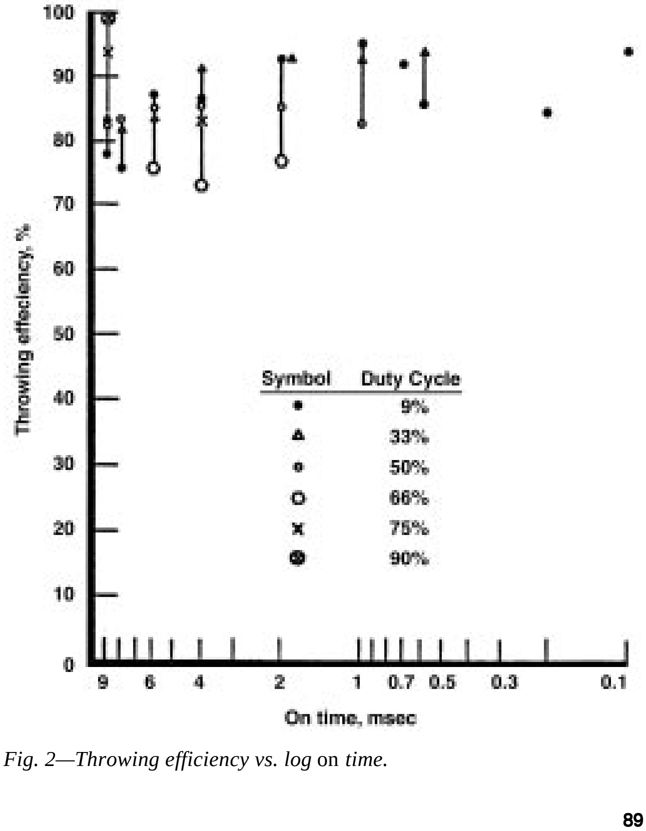

Fig. 2—Throwing efficiency vs. log on *time.*

proved superior to DC-plated deposits for certain electronic applications. The age of electronics and material shortages gave new importance to gold as a commodity and a boom in gold prices led to a demand for ways of reducing gold consumption. Pulsing proved to be an answer, and this justified the expensive pulse rectifiers required. After that, theoretical contributions were made.

A comprehensive literature search reveals that the majority of the previous theoretical work was done outside the United States. Practical applications were first implemented here, however.

It is known that the application of periodically changing (pulsed) current or potential leads to improvement in the quality of electrodeposits.[27,28] By using periodically changing rates, compared with the deposits obtained by DC, smoother deposits of gold can be obtained from cyanide solutions,[11,12,21] with the average current densities and electroplating times being kept equal. In addition, equal or better quality deposits of gold are obtained at higher current density under PC than under DC conditions.[30,31] A decrease of grain size of the pulse-plated deposits is generally found[29,31] to lead to increased coverage of the substrate with the same quantity as well as quality of the deposited metal, decreased porosity, surface resistance and increased density of the metals. It can be expected that an increase in compactness is associated with a decrease in internal stresses, and increased ductility and hardness of metal deposits. While the effect of nonstationary currents (PC and PRC) on morphology is well documented, current density distribution of the macroprofiles in pulsed regimes has been treated in relatively few papers.[30,32] It seems that this distribution improves deposition if done by PRC. In situations where hydrogen is codeposited (current efficiency less than 100%), the current density distribution can be better in nonstationary regimes as compared with direct current.

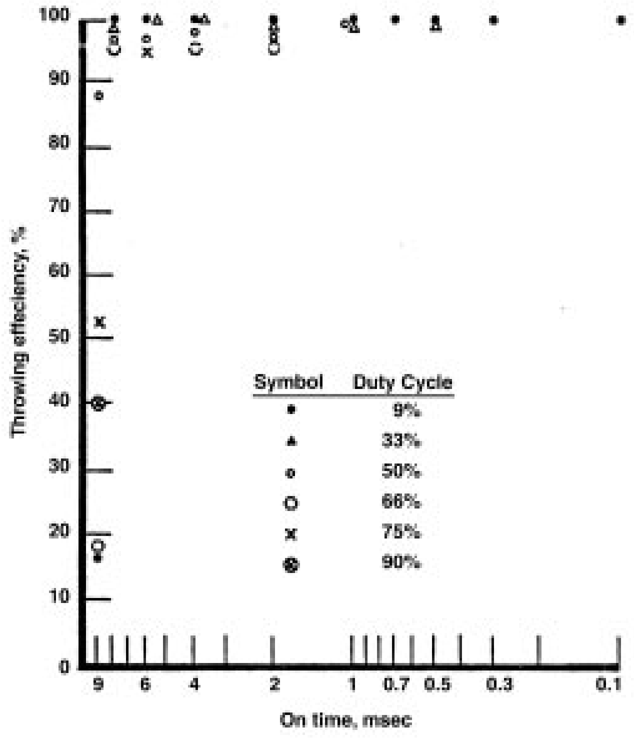

Fig. 3—Cathode efficiency vs. log on *time.*

Throwing Ability & Cathode Current Efficiencies

Thickness distribution for deposits that are not planar, but are irregular, can be quantitatively measured in terms of throwing efficiency. Throwing Power (TP) is a term also used, qualitatively, plus somewhat different equations.

The throwing power was obtained for each of the pulse waveforms, using the method developed by Haring and Blum.[33] The object was to determine what effect the nature of the pulse waveform would have on the metal distribution when deposition occurs on irregular substrates.

Cathode efficiency is a measure of the current actually utilized in deposition compared to the theoretical maximum current available for deposition. The difference is indicative of the amount of current involved with side reactions. The objective in determining cathode efficiency is to determine the effect pulse waveform variations produced on the cathodic deposition reaction.

The actual current contributing to the deposition reaction is measured by the weight gain of the sample. The theoretical weight deposited is calculated according to Faraday’s laws. For the gold system being considered, the equivalent weight is 122.7 mg/amp-min.

Haring-Blum Cell

A typical Haring-Blum cell is a rectangular electroplating tank containing positions for an anode and two cathodes (Fig. 1). Simple, though versatile, it can be used to measure solution conductivity, polarization and throwing power. The sample substrates, in our case, were brass Hull Cell panels arranged in parallel. This arrangement places a uniform electric field on the cathodic substrates when they are electrically connected. The perforated anode is positioned so that the distance from one sample is L times greater than the distance from the other. This gives a primary (or linear) current density ratio, L, between the two equipotentially placed plane cathodes at different distances from the anodes, typically 5 to 1. The weight of each sample cathode is recorded before and after deposition. The ratio of the weight

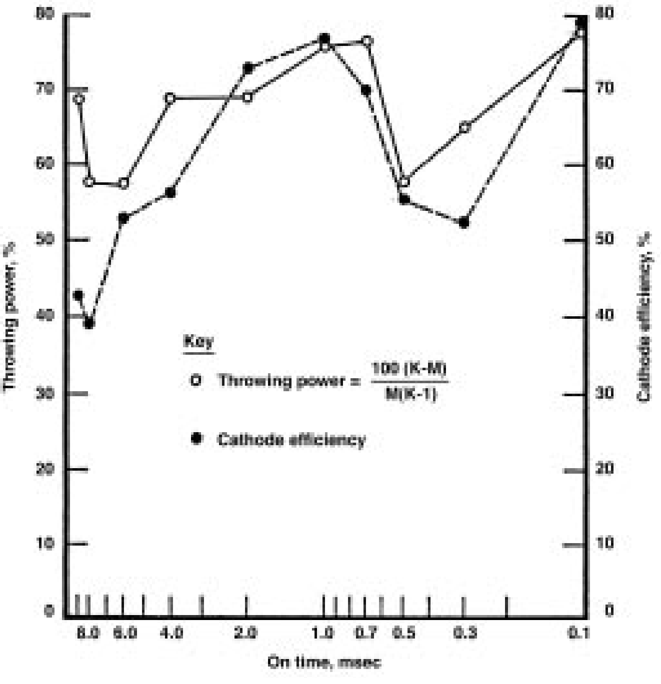

Fig. 4—Throwing power vs. log on *time and cathode efficiency vs. log* on *time for 9% duty cycle.*

gains gives the metal distribution ratio, M. If, in an experiment in a cell with L = 5, the weight of the deposit on the near cathode is, for example, four times that on the far cathode, M = 4. From the Haring-Blum expression for throwing power:

$$[TP]_{HB} = \frac{100(L-M)}{L} \qquad (1)$$

or, in this case, (5-4)/5 x 100 = 20%. For "perfect" throwing power, that is, M = 1 (equal weights of deposit on both far and near cathodes), this formula yields a throwing power of 80 percent. Intuitively, one would prefer "perfect" TP to be called 100 percent. Further, for no deposit on the far cathode, TP comes out to minus infinity; again, one intuitively dislikes a plating variable to be expressed as infinity. Also, the result depends on the value chosen for P (usually, as stated, either 2 or 5).

According to the suggestions of Pan[34] and Heatley[35], the Throwing Efficiency, the term used by them for TP, was calculated from the modified Haring-Blum relationship:

$$[TP]_{P} = \frac{100(L-M)}{L-1} \qquad (2)$$

This expression, similar to Eq. (1), produces values for TP of +100 to -∞. Both expressions are difficult and confusing to interpret. A formula for TP that avoids those objections is that of Fields:[36]

$$[TP]_{F} = \frac{100(L-M)}{L+M+2} \qquad (3)$$

In this expression, when M = 1 (perfect TP), $[T]_F$ = 100% regardless of the value of L. When L = M, $[TP]_F$ = 0; and when M = ∞ (no deposit on far cathode), $[TP]_F$ = -100% instead of -∞.

One other method for calculating throwing ability will be used—the expression for throwing power by Subramanian:[37]

$$[TP]_{S} = \frac{100(L-M)}{M(L-1)} \qquad (4)$$

Equation (4) was used for the most of the calculations because it provides a wider spread in numerical values (100% to 25%) that can be plotted clearly on the same coordinates as cathode efficiency. Objections to use of Eq. (1)-(4) have been raised by Jelinek and David[38] because use of different equations will result in different numerical values for a given plating bath and TPs calculated will vary with different linear ratios. They offered a graphical method for analyzing the TP measurements directly in terms of a Linear Throwing Index. By plotting the M vs. L values, the reciprocal of the slope indicates the TP. D-T. Chin further developed the throwing index concept by using log-log coordinates for M and L.[39] This Logarithmic Throwing Index gives the best fit for experimental data and still retains a single-valued parameter for measurements of TP: $M = L^{1/A}$ where A is constant for a given plating bath at given operating conditions.

Experimental Procedure

Cleaning

1. Removal of protective plastic coating from brass Hull Cell panels.
2. Acetone rinse - 5 min.
3. Methanol rinse - 5 min.
4. Water rinse - 5 min.
5. 15% HCl dip - 2 min.
6. Water Rinse - 5 min.
7. Second water rinse - 5 min.
8. Final cleaning - following deposition all samples were cleaned with cascade water rinse, followed by two distilled water dip rinses, then dried.

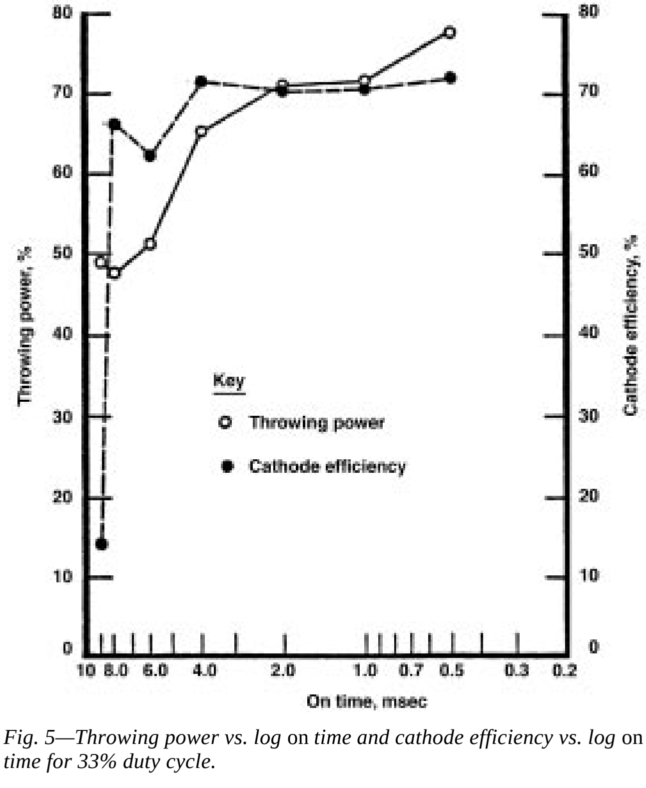

Fig. 5—Throwing power vs. log on *time and cathode efficiency vs. log* on *time for 33% duty cycle.*

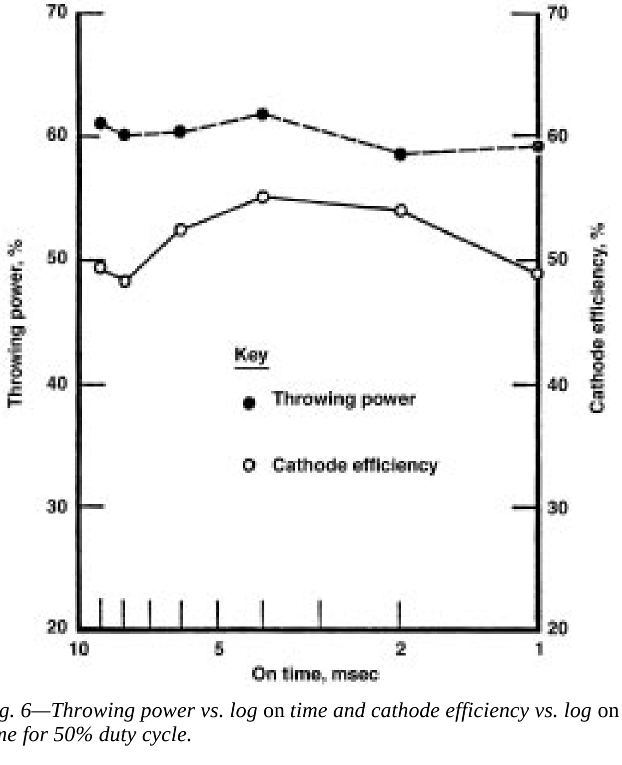

Fig. 6—Throwing power vs. log on *time and cathode efficiency vs. log* on *time for 50% duty cycle.*

Bath Chemistry

Deposition was carried out in an Engelhard-type bath having the following chemical composition: 75 g/L dibasic ammonium citrate, 75 g/L ammonium sulfate and 20 g/L potassium gold cyanide.

Bath Parameters

The pH was maintained at a constant 5.0 - 5.5 with additions of citric acid or potassium hydroxide as needed. Agitation was vigorous and constant, using an external pump and a magnetic stirrer. The temperature was maintained at 60 °C, with current density of 0.5 A/dm^2.

Power Supply

The power supply[a] leads to the plating electrodes were twisted and kept short as feasible to minimize RC effects. An oscilloscope was coupled to the electrodes to monitor the shape of the voltage waveform continuously.

[a] Model 2010, Pulsco.

Experimental Results

The cathode efficiencies were calculated for samples deposited at each of the waveform conditions as plotted in the figures. One sample set had constant agitation; another was deposited without agitation. This second set was deposited in the Haring Cell for measuring macrothrowing power in the form of TP. The calculated values of TP are plotted against log *on* time in Fig. 2.

At duty cycles less than 50 percent, a similar pattern in TP duty cycles exists. With the exception of the outlying point at 0.1 msec *on* for 9%, there is an upward trend in efficiency with *on* time reaching a maximum at 1 msec. For *on* times greater than one msec, TP tends to decrease.

Haring Cell Results

No.	Duty Cycle, %	On-Off time	Cathode Effic., %	Throwing Effic., %*	Throwing Power, %**	Throwing Power, %***
1	9	0.1-1	78.2	94.8	75.9	78.6
2	9	0.3-3	64.8	84.8	67.9	52.8
3	9	0.5-5	57.3	86.0	68.8	55.1
4	9	0.7-7	76.3	92.1	73.7	70.0
5	9	1.0-10	76.2	94.5	75.6	77.5
6	9	2.0-20	69.2	93.1	74.5	72.9
7	9	4.0-40	68.3	86.6	69.3	56.5
8	9	6.0-60	57.4	86.7	68.0	53.0
9	9	8.0-80	58.0	76.3	61.0	39.2
10	9	9.0-90	71.9	78.3	62.7	42.0
11	33	0.5-1	72.2	94.0	75.2	77.8
12	33	1.0-2	70.8	92.6	74.1	71.4
13	33	2.0-4	70.0	92.4	73.9	70.8
14	33	4.0-8	71.4	90.3	72.3	65.1
15	33	6.0-12	61.5	83.7	66.9	50.6
16	33	8.0-16	66.3	81.7	65.4	47.3
17	33	9.0-18	14.3	83.0	66.4	49.4
18	50	1.0-1	59.3	82.5	66.0	48.4
19	50	2.0-2	59.0	85.3	68.2	53.7
20	50	4.0-4	61.8	85.8	68.6	54.8
21	50	6.0-6	60.5	84.6	67.6	52.2
22	50	8.0-8	60.9	82.3	65.8	48.2
23	50	9.0-9	61.2	82.8	66.3	49.1
24	66	2.0-1	57.3	76.6	61.3	39.6
25	66	4.0-2	51.9	73.3	58.6	35.4
26	66	8.0-4	54.9	75.8	60.6	38.5
27	75	6.0-2	48.5	82.9	66.3	49.2
28	75	9.0-3	29.5	93.7	74.9	74.8
29	90	9.0-1	38.5	99.0	79.2	95.3
30	2.5	1.0-3	56.9	84.6	67.2	52.4
31	D.C.		63.6	90.9	72.7	66.6

*After Pan $\frac{100(K-M)}{K-1}$ **After Fields $\frac{100(K-M)}{K}$ ***After Subramanian $\frac{100(K-M)}{M(K-1)}$

Exceptions to this trend were samples deposited at long *on* times and high duty cycles. Duty cycles of 75 and 90 percent, with 9 msec *on*, had high TP of 94 and 99 percent, respectively. Direct current deposition had an efficiency of 91 percent. The same increase in macrothrowing power has been found for long cycles with periodic reverse current in copper deposition.[40]

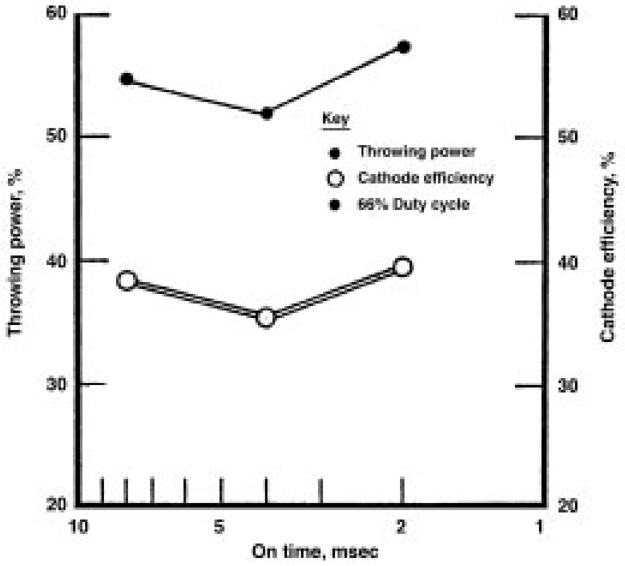

Fig. 7—Throwing power vs. log on *time and cathode efficiency vs. log* on *time for 66 duty cycles.*

The cathode efficiency results are plotted in Fig. 3 as Cathode Efficiency vs. log *on* time for the set of samples with high agitation. There is a decrease in efficiency with increased *on* time. The most drastic reduction in efficiency occurs with 9 msec *on*. This is attributable to the local depletion of metal ion species available for deposition at the cathode during peak current flow for long *on* times. The result is hydrogen evolution from water electrolysis and drastic reduction in cathode efficiency.

The cathode efficiencies (CE) of the samples deposited in the Haring Cell without agitation are plotted in Figs. 4-7. As in the case of the samples deposited with agitation, the cathode efficiency decreases with increasing *on* time. The lack of agitation increased side reactions at shorter *on* times as well. The efficiencies for the samples were 20 to 40 percent lower than for the same deposition conditions with agitation. The deposits formed by direct current at low agitation had a CE of 63 percent and a throwing power of 72 percent.

Plots of TP vs. log *on* time were made along with plots of CE vs. log *on* time on the same sets of coordinates. A plot at the 9% duty cycle is shown in Fig. 4, 33% duty cycle in Fig. 5, 50% duty cycle in Fig. 6 and 66 duty cycle in Fig. 7. The plots illustrate that the TP closely follows cathode efficiency.

The exception is the 9 msec *on* time with 75 and 90 percent duty cycles as shown in the Table, Nos. 28 & 29. In these two cases, TP increases notably while CE drops and hydrogen evolution occurs.

The overpotential for hydrogen evolution is reached at long *on* times. The concentration of depositing species, a gold complex, at the cathode interface is only a fraction of the species concentration in the bulk solution. As these species are depleted by deposition, the resistance at the cathode increases. In other words, the limiting rate of mass transfer of the deposition species governs charge transfer. Greater voltage is required to maintain constant current flow and the potential for hydrogen evolution is reached as the depositing ions are depleted at long *on* times. The increase in throwing power suggests the overpotential for H_2 evolution being reached preferentially in the specimen areas that experience higher deposition rates at lower duty cycles not accompanied by H_2. There is an improvement in the distribution for deposition accompanying the hydrogen liberation. The improvement in throwing power is not of practical value, however, because the deposit obtained is spongy and brown as a result of the H_2 evolution, making it unsuitable in most applications of gold deposits.

Findings

The throwing power of pulse electroplating was found greater than DC with a certain pulse waveform, less with other waveforms. The throwing power was also linked to cathode efficiency; the two characteristics were found to parallel each other. For long *on* times (*i.e*., 8 and 9 msec *on*), exceptions existed. In these cases, CE dropped, hydrogen evolution occurred, and a brown deposit formed; TP, however, increased. Best TP, coupled with high CE and bright gold deposits were found with short duty cycles (*i.e*., 9 and 33%).

Gold deposits formed by pulsed current have specific characteristics not common to other deposition methods. Pulses can be produced with a multitude of frequencies, durations, and magnitudes. From the observations made by exploring 30 pulse waveform conditions, TP and CE are clearly affected the pulse waveform. The apparent advantage of pulse deposition is its capability to alter those two deposit properties by simple electronic manipulation of the pulse waveform, rather than by involved chemical variations, the more traditional approach to tuning electrodeposition.

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About the Authors

David L. Rehrig is a member of the technical staff at Lucent Technologies where he is responsible for the metrology and characteristics of silicon crystals used in development and global manufacture of microelectronic devices. He holds a BS in chemistry from Lafayette College and a Master's Certificate in Global Business Management from George Washington University. He is a past president of the AESF Lehigh Valley Branch and a recipient of the AESF Silver Medal for his papers and publications.

Dr. Ned V. Mandich, CEF, FIMF, is president of HBM Electrochemical & Engineering Co., 2800 Bernice Rd., Lansing, IL 60438. He holds the Dipl. Ing. degree in chemical engineering from the University of Belgrade, Yugoslavia, an MS in theoretical chemistry from Roosevelt University, Chicago, and a PhD in electrochemical engineering from Aston University, Birmingham, UK. He has published more than 50 papers and holds 12 patents. He is a former chairman of the AESF Hard Chromium Plating Committee and is a Fellow of the IMF. He received AESF Board Recognition Awards in 1991 and 1995.*

** To whom correspondence should be addressed.*