The Effects of Duty Cycle and Frequency On the Crystal Size of Pulse-Plated Gold

By Yao Qi-Xia

Pulsed current can be used effectively to plate fine-grained gold in an ammonium sulfite bath without additives. With a fixed average current density, grain size decreased when the duty cycle was lowered from 15 or 20 to 5 or 10 percent and the pulse frequency raised from 0.5 to 1.0 kHz.

Interest and progress in pulse plating to control the properties of electrodeposits has been increasing in recent years.[1-3] However, there is need for a better understanding of the process and how deposition parameters should be chosen.

In gold plating, pulsed current can give smooth and bright deposits with excellent physical properties. As grain size is refined, hardness is increased and porosity and contact resistance can be reduced. Wear resistance may improve. This report focuses on the crystal size of gold electroplated in a cyanide-free, ammonium sulfite bath.

Theoretical Aspects

There are many types of waveforms available for pulse plating, including modified sine-wave and unipolar varieties. The square wave is the most popular because it offers the widest latitude of plating parameters. One of the most important expressions is the duty cycle, defined as the ratio of on-time (T) to the sum of on-time plus off-time (T'):

$$\text{Duty cycle, } \% = 100\ (T/T+T') \qquad (1)$$

A duty cycle of 100 percent corresponds to conventional direct current because there is no off-time. Depending on the desired properties and deposit characteristics, duty cycles vary, for example, from 5 to 40 percent. However, other chemical and electrochemical parameters must be established, often by trial and error, for a pulsed-current process to succeed.

The sum of T and T' constitutes one pulse. During the on-time, the concentration of metal ions is reduced near the cathode surface. After a finite time, pulsed-current plating produces a pulsating diffusion layer at the cathode surface and an essentially stationary layer adjacent to it. The stationary layer exists because the pulsating layer does not penetrate into the region where there is mass transport by convection.

The pulsating diffusion layer pulsates at the same frequency as the applied pulsating current. Its thickness is related to the peak current density. Although the concentration of metal ions at the cathode surface fluctuates periodically, the thickness of the pulsating diffusion layer reaches a limited value governed primarily by the diffusion coefficient of the metal ions.

The activation overpotential becomes larger with an increasing pulsed-current density and more free energy is available for increasing the rate of nucleation. According to the theory of Damjanovic and Bockris,[4] the nucleation rate (R) can be expressed by:

$$R = 2\pi r_c n^2 (KT/2\pi m)^{1/2} \times \exp[-(\Delta F_c + E)/KT] \qquad (2)$$

where r_c is the critical radius of the host crystal, n is the number of absorptive adions per cm^2, ΔF_c is the variable free energy of nucleation, $\bar{E}$ is the activation energy of surface diffusion, K is the Boltzmann constant and T is the temperature of crystallization.

The definition of m is complicated: $m = (p/D)^{1/2}$, where D is the diffusion coefficient; and $p = (i_o/ZFC_o) \bullet \exp[(1-\beta)ZF\eta/RT]$, where Z, F, β, R, and T have their usual meaning, η is the constant overpotential, C_o is the equilibrium adion concentration, and i_o is the equilibrium current density of charge transfer.

With a short on-time, the peak pulsed-current density must be increased to retain the same deposition rate and ΔF_c and E are increased. As $\exp[-(\Delta F_c + E)/KT]$ is increased, more nuclei are generated. Thus, fine-grained deposits can be obtained by pulsing the current.

During off-time periods, there is an opportunity for the replenishment of the pulsating diffusion layer by diffusion and convection. The activation overpotential produces a high instantaneous mass transfer of metal ions into the depleted region adjacent to the cathode surface through the essentially stationary layer. This process is enhanced by hydrodynamic effects; thus pulsing the current enhances the nucleation rate, the kinetics of electrodeposition and the mass-transfer process to provide fine-grained deposits.

The peak current density (i,) is equivalent to the average current density (i_a) divided by the duty cycle:

$$i_p = i_a/100\ T/(T+T') \qquad (3)$$

The peak current density becomes larger with a decreasing duty cycle when the average current density is constant and can be expressed as follows:

$$i_p = Z \times F \times N_p \qquad (4)$$

where Z is the charge equivalent number, F is the Faraday constant and N_p is the flux density of the metal ions in the pulsating diffusion layer during a pulse and is calculated from:

$$N_p = D\ (C_s - C_p)/\delta_p \qquad (5)$$

where D is the diffusion coefficient of the metal ions, C, is the concentration of metal ions in the stationary diffusion layer, C_p is the concentration in the pulsating diffusion layer, and δ_p is the thickness of the pulsating diffusion layer at the end of the pulse cycle.

Substituting equation (5) for N_p in equation (4):

$$i_p = ZFD(C_s - C_p)/\delta_p \qquad (6)$$

During a study of the influence of duty cycle when i_a is kept constant, i_p is increased when the duty cycle is decreased. The diffusion gradient in the pulsating diffusion layer is proportional to the peak current density. Extremely thin pulsating diffusion layers can be obtained by using small duty cycles that are sufficient to allow restoration of the bulk concentration of metal ions near the cathode surface. More nuclei are then formed, due to the enhancement of nucleation by the resulting free energy.

Whereas the concentration gradient in the essentially stationary layer is proportional to the average current density, a high peak current density in combination with turbulent cathode surface flow should enhance the relaxation of the essentially stationary layer.

As the duty cycle is decreased and the peak current density increased, the kinetics of electrodeposition will be further enhanced. In this case, the off-time is longer than necessary to activate growth centers or recrystallize the adion species. The larger grains are more stable. Thus for gold deposition, an increase in grain size will accompany an overlong off-time.

On the other hand, gold deposition will occur when anions near the cathode surface are strongly absorbed during an overlong off-time, which will block the growth centers at the cathode and force the creation of new nuclei at each new pulse. The equilibrium potential of gold in an acid sulfite solution is more positive than the zero charge potential. Thus the ionic species can break away from a strong absorption by acquiring sufficient free energy.

Table 1
Gold Plating Bath Composition

Constituent	Concentration, g/L
Gold	10-20
Ammonium sulfite	150-250
Potassium citrate	80-120
pH	8.5-9.5
Temperature, °C	60-70
Anodes	Platinum
Agitation	Mechanical stirring

Table 2
Effect of Duty Cycle on Crystal Size*

Duty cycle, %	On-time, μsec	Peak current density, A/dm^2	Crystal size, μm
5	50	6.4	0.28
10	100	3.2	0.20
15	150	2.1	0.74
20	200	1.6	0.98

“The average current density was 0.32 A/din’ and the pulse frequency was 1.0 kHz.

Table 3
Effect of Pulse Frequency on Crystal Size*

Pulse frequency, kHz	On-time, μsec	Crystal size,μm
1.0	100	0.20
0.5	200	0.35

‘The duty cycle was fixed at 10 percent. Average and peak current densities were 0.32 and 3.2 A/dm^2, respectively.

The concentration of metal ions in the pulsating diffusion layer and the surface overpotentials depend not only on the value of the pulse current density but also on the frequency of the pulse. An increase in the fluctuating periodicity of the pulsating diffusion layer accompanies an increase in pulse frequency. Thus, fine-grained deposits can be obtained with an increase of pulse frequency that favors an increase in the rate of nucleation.

Experimental Conditions and Results

With the plating bath given in Table 1, gold was deposited with square-wave current pulses at a fixed average current density of 0.32 A/dm^2, while the duty cycle was varied from 5 to 20 percent and the peak current density from 1.6 to 6.4 A/din’. The cathodes were sections of copper-coated, printed-circuit boards. Crystal size was determined by electron microscopy.

The results obtained with a fixed pulse frequency of 1.0 kHz are shown in Table 2. Crystal size was greatly increased when the duty cycle was increased from 5 or 10 percent to 15 or 20 percent. This increase agrees with the prediction of theoretical considerations.

Table 3 shows the results of changing the pulse frequency while the average current density was fixed at 0.32 A/dm^2. The higher pulse frequency produced the finer grains.

Discussion

The results show that a low duty cycle of 10 percent and a pulse frequency of 1.0 kHz effectively decreased the crystal size of gold deposited in an ammonium sulfite bath while using pulsed-current. Although pulse plating favors the rate of grain nucleation and produces finer-grained deposits with improved characteristics and properties, pulse plating is not a panacea and is still an evolving technology. There is a continuing need for identifying plating solutions that are capable of producing deposits with improved properties and characteristics. New plating solutions combined with appropriate pulsing conditions can be expected to provide effective processes in the future.

References

1. *N.* Ibl, *.Surface Technology,* 10, 81 (1980).
2. M.F. El Shazly, J.L. White and E.W. Brooman, *Plat. and Surf. Finish., 74, 136,* (May 1987).
3. J. Cl. Puippe and N. Ibl, ibid., 67,68 (Jun. 1980).
4. H. Damjanovic and J. O’M. Bockris, J. *Electrochem.* Soc., 110, 1035 (1963).

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