Combination of Pulse- & Constant-current Plating for the Creation of Desirable Surface Microgeometry

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Effects of low- and medium-frequency pulsing on the microgeometry of nickel deposits have been studied under galvano- and potentiostatic conditions. When low-frequency pulsing is used, the ratio of electric charge passed in the alternating high- and low-amplitude pulses plays a major role in controlling the formation of surface morphology. For medium-frequency pulsing, only galvanostatic pulses of a single amplitude were used. Charging and discharging of the electric double-layer played the role of low-amplitude pulses in this case. Additional steady-state electrodeposition after pulse plating, which is always accompanied by geometric leveling, may be used to mechanically strengthen the deposits.

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Introduction

Role of Mass Transport in Microdistribution

The microgeometry of a surface obtained in the course of electrochemical deposition of a metal depends on three major factors:

- (1) microgeometry of the original surface;
- (2) microdistribution of the rate of electrodeposition;
- (3) average thickness of the deposited layer.

To a lesser extent, the structure of the depositing metal can also play a role in this process. In the absence of brightnening or leveling additives, the electro-crystallization process continuously creates submicro-irregularities which can gradually grow in size to the point that they alter the light relfection properties of the surface. Geometric leveling acts in the opposite manner and smoothens the cathode surface.

During the electrodeposition process, the depth of the micro-recesses and the height of the micro-protrusions on the original surface can either be made to increase or decrease. Under conditions of true leveling, surface irregularities are gradually smoothened and eventually disappear. Alternatively, negative leveling or anti-leveling conditions result in self-accelerated growth of surface irregularities. Dendritic growth and the formation of spongy deposits represent an extreme case of anti-leveling which occurs when transport of metal ions to the cathode surface becomes the rate determining step. Thus, metal deposits ranging from mirror-bright to spongy are obtainable on any type of substrate through the proper choice of bath composition, plating conditions and average thickness of the deposited layer.

Mass transport phenomena in the cathode diffusion layer is the sole factor which controls local metal deposition rates under conditions of nonuniform microdistribution. In situations of true leveling, additives (leveling agents), acting as inhibitor species, diffuse to the tips of microprotrusions faster than they diffuse into recessed areas. Analogously, under anti-leveling conditions, metal ions diffuse more rapidly to protrusions on the cathode surface. For surface leveling to occur, the current density must be kept far below the limiting value for discharge of the metal ions, and it is usually held constant; using higher currents could result in uncontrolled deposit morphology due to the existence of both leveling and anti-leveling conditions during electroplating. On the other hand, if the creation of surface roughness is desired then leveling additives should be omitted from the solution, and the cathode current density should be close to, or above, the limiting current.

Earlier^{1,2} it was demonstrated for cathodic copper and nickel deposition that periodic changes in current density (or cathode potential) can be used to meet two seemingly contradictive requirements: to produce a deposit that is mechanically strong and that has a large true surface area, i.e. that avoids formation of weak, spongy deposits which are typically obtained at high current densities. The major objective of our investigation was to follow, by means of electron microscopy, the evolution of the surface morphology of nickel deposits as a function of periodic changes in cathode potential or current.

Experimental

Electrodeposition experiments were carried out with one type of nickel bath (Table 1) using either potentiostatic or galvanostatic equipment.

Component	Concentration (mole/l)
Nickel Sulfate	0.09
Ammonium Sulfate	0.11
Sodium Sulfate	0.17
Sodium Chloride	0.17
Boric Acid	0.20
pH	2.5 - 3.0
Temperature, C	20 - 25

Table I: Plating Bath Composition

Electrolytic copper foil (both matte and shiny sides) and rolled copper foil were used as cathode materials (Figs. 1 to 3). Scanning electron micrographs were taken at a 45 degree angle with respect to the sample plane. All plating experiments were conducted at room temperature without agitation. Nickel foil was used as the anode. A saturated calomel electrode



Figure 1. Matte side of electrolytic copper foil.



Figure 2. Shiny side of electrolytic copper foil.



Figure 3. Surface of rolled copper foil.

served as a reference and was placed about 1 mm away from the cathode surface. Cathodic current efficiency was not determined, so the exact values of the average deposit thickness are unknown. It should be noted that at high values of cathode polarization the current efficiency was considerably lower than 90 to 95 percent as is typically obtained for normal nickel plating conditions at these pH values. Copper foil samples in Figs. 12 to 15 were pre-plated with nickel at 2.5 mA/cm² immediately preceding the experiment (Q = 0.5 coul/cm²).

Results and Discussion

Deposition under Steady Potentiostatic Conditions

An initial series of plating experiments was carried out under potentiostatic conditions (Figs. 4 to 6) in order to determine the character of the microdistribution of nickel at different cathode potentials. These conditions corresponded to current density regimes that were (1) much less than, (2) comparable to and (3) much greater than the limiting current. It should be remembered that the third condition results in much lower plating efficiency,



Figure 4. Nickel deposited onto the matte side of electrolytic copper foil at constant potential -1.0V (vs. sat. cal. El.); current density was gradually decreasing from 5 to 3 mA/cm². Overall charge passed, Q = 6 coul/cm².

and thus the amount of electric charge passed during electrolysis does not accurately reflect the plated quantity of nickel. Nevertheless, dramatic changes in the surface morphology are observed in this particular sample (Fig. 6). It is covered by a very fine bushy deposit. This contrasts with low polarization conditions (Fig. 4) where the original microgeometry underwent only minor changes consistent with geometric leveling, i.e. the filling of narrow recesses along with uniform nickel deposition on flat surfaces. The intermediate situation (Fig. 5) represents strong anti-leveling conditions where there is a transition from dense to spongy deposits. Branched dendrites have grown on the tops of the original copper peaks (where the diffusion flow of nickel ions is most favorable) while the very little nickel appears to coat the base of the peaks—a major portion of the cathode surface.

Using these results as a guideline, we carried out a subsequent series of plating experiments using potentiostatic pulses that alternated between the extremes of -0.95V and -1.4V.



Figure 5. Nickel deposited onto the matte side of electrolytic copper foil at constant potential -1.3V; current density was gradually decreasing from 21 to 9 mA/cm². Overall charge passed, $Q = 6 \text{ coul/cm}^2$.



Figure 6. Nickel deposited onto the matte side of electrolytic copper foil at appr. -1.8V; current density was gradually increasing from 90 to 102 mA/cm². Q = 3 coul/cm². Strong evolution of H₂ occurred during the electrolysis.

Deposition Using Potentiostatically Controlled Alternating High- and Low-Polarization Pulses (<0.1 Hz)

A series of plating experiments was performed using rectangular unipolar current pulses at frequencies ranging from 0.040 - 0.025 Hz (see Figs. 7 to 9). Low polarization pulses of long duration were used to ensure sufficient time for the concentration of nickel ions near the cathode surface (both peaks and valleys) to be restored to bulk values. As a consequence, the subsequent high-polarization pulses resulted in the formation of three-dimensional nuclei over much of the cathode surface. The principal difference between Fig. 7 and 9 is the ratio of nickel deposited under conditions of high antileveling to that deposited with uniform microdistribution. When this ratio is small (Fig. 7), uniform microdistribution dominates the formation of the deposit morphology. It should be noted that even at the highest ratio (Fig. 9), relatively few individual tree-like deposits have grown on the tops of the copper peaks. This differs from the results obtained in the previous potentiostatic experiment (Fig. 5) even though it was conducted at a slightly lower polarization (-1.3V vs. -1.4V).



Figure 7. Nickel deposited onto the matte side of ED Cu foil by alternating potentiostatic pulses: -1.4V (5sec.) and -0.95V (20 sec.); Q = 6 coul/cm².



Figure 8. Nickel deposited onto the matte side of ED Cu foil by alternating potentiostatic pulses: -1.4V (10sec.) and -0.95V (20 sec.); Q = 6 coul/cm².



Figure 9. Nickel deposited onto the matte side of ED Cu foil by alternating potentiostatic pulses: -1.4V (20sec.) and -0.95V (20 sec.); Q = 6 coul/cm².

The surface morphology obtained by the pulse plating process can easily be altered by the addition of a subsequent direct current-plating step. Figs. 10 and 11 illustrate this point. Initially, nickel was pulse plated under conditions which favored strong dendritic growth, i.e. using a high ratio of $t_{\rm H}/t_{\rm L} = 20 {\rm sec}/10 {\rm sec}$ (Fig 10). In a second step, additional metal was plated from the same solution at a constant low-polarization potential (Fig. 11). The amount of nickel deposited under this condition of uniform microdistribution corresponded to an average thickness of about 1 μ m.



Figure 10. Nickel deposited onto the matte side of ED Cu foil by alternating potentiostatic pulses: -1.4V (20sec.) and -0.95V (10 sec.); Q = 6 coul/cm².



Figure 11. Same as Fig. 10 with additional postplated layer at -0.95V; additional Q = 3 coul/cm².

Medium Frequency Galvanostatic Pulsed Plating (10 – 100 Hz)

Electrode potentials do not decay instantaneously during the off-time of a pulsed plating cycle³. Some charge remains stored in the double layer capacitor at the cathode/solution interface. This capacitor discharges by reducing metal ions at the interface. As a result, metal

deposition takes place as the cathode potential gradually decreases below the limiting value. At higher frequencies, metal deposition under these circumstances becomes more important because a significant fraction of the deposit is plated during the "off" period. In our experiments, the decay portion of the pulse cycle was used as a substitute for the low-polarization pulse used in the preceding potentiostatic experiments. By varying pulse currents and the ratio of t_{n}/t_{off} , it is possible to adjust the average current density according to equation (1).

$$i_{AV} = i_{pulse} \quad x \quad [t_{on}/(t_{on} + t_{off})] \qquad (1)$$

Likewise, both the average concentration gradient in the diffusion layer and the total amount of metal deposited under non-diffusion-controlled conditions are influenced by the ratio i_{AV}/i_{lim} . Therefore, if the objective is to produce rough deposits evenly over a non-flat surface (like matte Cu foil) then major efforts should be directed towards the proper choice of plating parameters which ensure maintainence of the inequality shown in equation (2).

$$i_{AV} \le 20-33\%$$
 of i_{lim} . (2)

Our initial unipolar pulse plating experiments using a 33% duty cycle (Figs. 12 and 13) produced nodular and dendritic deposits that were similar in size and shape to those obtained in the corresponding D.C. experiment (Fig. 14). The main difference was that the pulsed samples contained less nickel deposit—a result of lower current efficiency under these conditions. However, when i_{AV} was decreased by a factor of three (to 11% duty cycle), a spectacular change in deposit morphology took place: the substrate was populated only with nodules; not a single dendrite had formed on the tops of the copper peaks (Fig. 15).



Figure 12. Nickel deposited onto the matte side of ED Cu foil by galvanostatic pulses: 10 Hz; 0.25 A/cm²; 33% duty ($t_{orr}/t_{off} = 1:2$); t = 34 secs. (Q = 2.8 coul/cm²).



Figure 14. Nickel deposited onto the matte side of ED Cu foil by DC at 0.25 A/cm²; t = 11 secs. (Q = 2.8 coul/cm^2).



Figure 13. Nickel deposited onto the matte side of ED Cu foil by galvanostatic pulses: 83 Hz; 0.25 A/cm^2 ; 33% duty ($t_{on}/t_{off} = 1:2$); t = 34 secs. (Q = 2.8 coul/cm²).



Figure 15. Nickel deposited onto the matte side of ED Cu foil by galvanostatic pulses: 100 Hz; 0.25 A/cm²; 11% duty ($t_{on}/t_{off} = 1:9$); t = 100 secs. (Q = 2.8 coul/cm²).

It should be noted that controlling dendritic growth on the matte side of electrolytic copper foil is much more difficult than is the case for smooth substrates, such as rolled foil or the shiny side of electrolytic foil. Figs. 16 and 17 illustrate this point for copper foil. The smooth surfaces of these samples lack any asperities which act as initiators for preferential and auto-accelerating growth of tall, branched dendrites.



Figure 16. Nickel deposited onto the shiny side of ED Cu foil by galvanostatic pulses: 83 Hz; 0.25 A/cm²; 33% duty ($t_{on}/t_{off} = 1:2$); t = 34 secs. (Q = 2.8 coul/cm²).



Figure 17. Nickel deposited onto rolled Cu foil by galvanostatic pulses: 83 Hz; 0.25 A/cm²; 33% duty $(t_{on}/t_{off} = 1:2)$; t = 34 secs. (Q = 2.8 coul/cm²).

Conclusions

(1) We have observed that different types of galvano- and potentiostatic current pulses can be used to vary the microdistribution of electrodeposition rates ranging from uniform to strongly anti-leveling.

(2) Discharge of metal ions can be directed to occur at specific sites on the cathode surface by using pulsed currents and proper bath fomulations (e.g., by introducing leveling additives).

(3) Medium-frequency pulses can be used to reduce the amplitude of rough electrodeposits by keeping the average deposition current below the limiting value.

References

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