The Hydrodynamic Electroplating Test Cell

By Shi-Chern Yen and I-Min Lu

A new electroplating test cell has been proposed to analyze the performance of plating solutions in electroplating processes. The hydrodynamic electroplating test cell is composed of a rotating cylinder, an electrolytic cell, and two electrode plates. Because in this study the cathode and anode plates are placed in the radial direction, which results in a distance variation between the two electrodes, a variation of current density or deposit thickness on the cathode panel may occur. To enhance the mass transfer near the cathode plate, as in high-speed electroplating, the plating solution can be stirred strongly by use of a rotating cylinder. As employed in this study, a rotating cylinder can provide stable and well-controlled hydrodynamic conditions, and enhance plating stability and performance. Also, this test cell can be operated with high currents for high-speed electroplating tests.

he Hull cell,¹⁻⁴ developed by R.O. Hull in 1939, is a quite versatile tool for electroplaters to analyze the performance of plating solutions. The geometry of a 267-mL Hull cell is sketched in Fig. 1. It is trapezoidal, with the two parallel sides insulated. The slant side supports the cathode and the normally inclined side supports the anode. Because the cathode is placed at an inclined angle to the anode, the Hull cell offers variable solution resistance between the electrodes. Therefore, metals can be deposited over a wide range of current densities across the cathodic panel at given currents. On the other hand, the Hull cell also provides the deposit properties at various current densities on a single test panel, making it a useful tool for quality control in electroplating.

Although a Hull cell can yield deposit properties with a wide range of current densities across a single cathodic panel, it does not possess reproducible and well-defined hydrodynamic conditions. In high-speed electroplating processes, it is often necessary to stir the electrolyte vigorously to improve mass transfer at the electrodes. Usually, a magnetic stirrer or air agitation near the cathode is employed in a traditional Hull cell, but neither provides reproducible mass transfer. Numerous studies have been made to improve mass transfer in the Hull cell or other types of test cells⁵⁻⁸. In those studies, a rotating electrode, in the form of a cone or cylinder, was employed to provide well-defined hydrodynamics and increase the magnitude of operating cathodic current densities. In this investigation, a novel hydrodynamic electroplating test cell (HETC), consisting of a rotating cylinder, an annular electrolytic cell, and two electrode plates, has been developed to provide well-defined hydrodynamic conditions. The cathode and anode plates are placed in the radial position, so that a variation of current density across the cathode plate is produced. The rotating cylinder provides a stable hydrodynamic flow and enhances the plating current.

Hydrodynamic Electroplating Test Cell (HETC)

It is well known that mass transfer conditions have a strong influence on the properties of deposits. If metals are deposited at limiting currents, the deposit tends to be powdery, with poor adhesion to electrode surface. Nevertheless, if a deposit is formed at a lower current density, the structure of the deposit will exhibit dendrites, bunched layers, spiral or other forms. Accordingly, it is important to provide reproducible mass transfer, which can result from a well-defined hydrodynamic flow, for assessing the performance of an electrolyte.

The proposed hydrodynamic electroplating test cell is sketched as shown in Fig. 2. The surface of the rotating cylinder is insulated. The two electrode plates can be set at any angle—90° in this case. The region enclosed by the two electrodes and the rotating cylindrical surface is a sector called the reaction zone. The radius of the rotating cylinder is 2.5 cm, and the width and height of the electrodes are 10 and 6.5 cm, respectively. The geometry of the HETC provides continuous variation in solution resistance between electrodes in the outward direction from the surface of the rotating cylinder. During electroplating, metal deposition is possibly limited by mass transfer, which may dominate the structure of the deposit, at the region of high current density. Therefore, this HETC was developed to enhance the mass transfer of metal ions and retain the feature of current density variation of the traditional Hull cell. The dimensionless current distribu-



Fig. 1—The traditional Hull cell.

Fig. 2—The hydrodynamic electroplating test cell.



Fig. 3—The thickness and current distributions for the Hull cell and the hydrodynamic electroplating test cell (HETC) without agitation.

tion (i/i_m) along the cathodic surface can be derived analytically, and is expressed (\mathbf{R}_{S-R})

$$\frac{1}{i_m} = \frac{(R_2 - R_1)}{\ln(R_2/R_1)} \frac{1}{R_1 + x}$$
(1)

where R_1 is the radius of rotating cylinder, R_2 is the radius of the outer cylindrical surface in the plating zone, and x is the position on the cathodic plane away from the inner cylindrical surface that is at the high-current-density end. The quantity i_m is the average current density across the test panel. In this study, R_1 and R_2 are 2.5 and 12.5 cm, respectively. A rotating cone or cylindrical electrode, as proposed in the literature, ^{5,7,8} is not convenient for electroplaters to analyze the thickness or structure of deposits.

The HETC employs two planar electrodes that serve as cathode and anode. The longer the cathode, the wider the range of current densities provided by the HETC. The HETC

Fig. 4—Cathode placement for the hydrodynamic electroplating test cell: (a) rotating impingement type; (b) rotating drag type.

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Fig. 5—Polarization curves for the hydrodynamic electroplating test cell (HETC).

employs the same size of cathode and anode to avoid excessive anodic polarization, which can be produced if an anode of insufficient size is used. The volume of a traditional Hull cell is 267 mL. A 2-gram addition of additive to 267 mL is



equivalent to 1 oz per U.S. gallon. An error of 10 mL in electrolyte volume, however, would invalidate the precise current density relationship, because of the small volume of the traditional Hull cell. A volume of 1068 mL was selected for this new cell, and the depth of solution is about 4 cm, the same as that of the traditional Hull cell. If 8 g of additive are added to 1068 mL, the additive concentration will be 1 oz per U.S. gallon. The volume of electrolyte included within the reaction zone is about 470 mL.

Experimental Procedure

The dimensions of the electrode plates used in the HETC are 6.5 x 10 cm, the same as the cathode used in the 267-mL Hull cell. The ratio of the maximum and minimum current densities for the HETC has been calculated as 5.0, from the primary current distribution ($R_1 = 2.5$ cm and $R_2 = 12.5$ cm). The anode was a plate of pure copper, and a plate of 316 stainless steel instead of brass was chosen as the cathode. The rotation rate was monitored by a tachometer. The plating solution contained copper sulfate and sulfuric acid. A copper wire was placed near the cathode as a reference electrode when the polarization curves were measured. Electrodeposition was performed potentiostatically or galvanostatically, and the charge passed through the cell was measured by a coulometer. The electrodes were pretreated by electrochemical cleaning, and the backs of the electrodes were insulated with epoxy. After electroplating, the cathode plate was removed, washed with double-distilled water, and dried. The copper thickness distribution along the cathode plate was measured by X-ray fluorescence.

Results and Discussion

A comparison of thickness distribution between the 267-mL Hull cell and the HETC, with electrolytes not agitated, is shown in Fig. 3. The charge passed through the electrolytic cells was 2000 Coulombs, and the total current applied to the cells was 0.5 A. For the HETC, the angle between cathode and insulating planes at the region of high and low current densities was 90°, which leads to a finite current density at the edge of the cathode for primary current distribution.

As shown in Fig. 3, the deposit obtained from the Hull cell



Fig. 8—Thickness distribution for the HETC with rotation rate of 1400 rpm.

at the region of high current density is thicker than that obtained from the HETC. In the low-current-density region, however, the deposit obtained from the Hull cell is thinner than that obtained from the HETC. Because the Hull cell has the acute and obtuse angles at both ends of the cathode, the range of current density distribution provided is wider than that of the HETC, but the HETC covers almost the same useful range of the electroplating test panel (10 to 90 percent) as the Hull cell.

To assess the stability of agitation provided by the HETC, the mass transfer performance was analyzed. The two positions of the cathode in the HETC, with the cylinder rotating counterclockwise, are shown graphically in Figs. 4a and 4b. In Fig. 4a, the rotating flow impinges on the cathode plate near the rotating cylinder, and in Fig. 4b, the rotating cylinder drags the flow from the cathode. The results are that if the cathode is plated as in Condition 1 for Fig. 4a, the high-current-density region will be located on the upstream fluid flow, where the diffusion layer is thin. In the contrary situation, plated as in Condition 2, the high-current-density region will be located on the downstream fluid flow, where the diffusion layer gets thicker. Therefore, the current obtained from Condition 1 is larger than that from Condition 2 at the same rotation rate, if the operating condition is in the region of mass transfer control. Figure 5 shows the polarization curves of various rotation rates (0 to 2000 rpm) for 0.02 M CuSO, revealing that the HETC offers higher limiting current plateaus as the rotation speed increases. The overall mass transfer coefficient, k_{m} (cm/sec), can be correlated as a function of rotation rate for each condition, as shown in Figs. 4a and 4b. For rotating impingement, Condition 1, the mass tranfer correlation is

$$k_m = 0.98 \times 10^{-4} \ \omega^{0.6} \tag{2}$$

where ω is the rotation rate with unit rpm. For rotating drag, Condition 2, the mass transfer correlation is

$$k_m = 1.36 \times 10^{-4} \ \omega^{0.45} \tag{3}$$

As shown in Fig. 5, Condition 1 provides higher limiting current than Condition 2. The deposit thickness distributions obtained from Conditions 1 and 2 were measured at the region of mass transfer control and are shown in Fig. 6. Because of the direction of fluid flow, the thickness distribution obtained from Condition 2 is not as sensitive as that from Condition 1. The thickness distribution from Condition 1 in Fig. 6 shows that the hydrodynamic flow provides higher mass transfer as it approaches the high-current-density end. Consequently, the rotating impingement flow of Fig. 4a, for the HETC, is better employed for investigation of plating performance. If the plating is performed at currents well below the limiting current, however, the deposit thickness distribution obtained from Condition 1 would be almost the same as that obtained in Condition 2.

Additional comparisons of the cathode current distribution at various applied voltages between the Hull cell and the HETC have been made at the region of mass transfer control. In Fig. 7, the deposit thickness distribution at 0.8 V is uniform because of the limited mass transfer of natural convection. At higher applied voltages (1.2 and 1.6 V), there is more gas evolution at the cathode and mass transfer is enhanced, resulting in greater current density at the region near the inner cylinder. With the same operating conditions, Fig. 8 shows





thickness distribution of the copper deposit for the HETC at 1400 rpm. The applied voltages of 0.8, 1.2 and 1.6 V were in the range of limited mass transfer for copper deposition, but higher voltages produced more gas evolution, inducing more mass transfer for cupric ions. As expected, there was greater current density near the inner cylinder. By adjusting the rotation rate, thickness distribution along the cathode plate can be made smoother and deposit thickness can be wellcontrolled. As can be seen in Figs. 7 and 8, the HETC provides more mass transfer at the cathode than the Hull cell. Consequently, higher limiting currents for metal ions can be obtained.

Figure 9 shows the comparison between experimental data and the theoretical results. The curve is very smooth and reproducible. Numerous experiments have been performed to verify the reproducibility of the HETC. LaPlace's equation was employed to derive the primary current distribution for the HETC with the assumptions of uniform concentration through the cell and negligible surface overpotentials at the anode and cathode. As shown in Fig. 9, the experimental data agree very well with the theoretical values of the primary current distribution if the plating parameters are restricted to those assumptions of the primary current distribution. The ratio of maximum to minimum current density is about 5.0, calculated according to Eq. (1). The ratio for a good Hull cell, however, is about 10. The variation of current density of the HETC can be enhanced by increasing the ratio of the radii of the outer and inner cylinders, or by placing an insulated flat plate between the two low-current-density ends of the electrodes.

Findings

The hydrodynamic electroplating test cell (HETC) was proposed for analyzing plating performance, especially highspeed electroplating. The HETC can provide reproducible mass transfer and achieve high limiting currents with high rotation rates. The experimental results agree very well with the theoretical values for primary current distribution. For this test cell, rotating impingement is better than that of rotating drag.

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