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An experimental study of mass transfer in pulse reversal plating

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An experimental study has been made of the limiting pulse current density for a periodic pulse reversal plating of copper on a rotating disc electrode from an acidic copper sulfate bath containing 0.05 M $CuSO_4$ and 0.5 M H_2SO_4. The measurements were made over a range of the electrode rotational speeds of 400–2500 r.p.m., pulse periods of 1–100 ms, cathodic duty cycles of 0.25–0.9, and dimensionless anodic pulse reversal current densities of 0 to 50. The experimental limiting pulse current data were compared to the theoretical prediction of Chin's mass transfer model. A satisfactory agreement was obtained over the range of a dimensionless pulse period of $DT/\delta^2 = 0.001 - 1$; the root mean square deviation between the theory and 128 experimental data points was ±8.5%.

Notation

C_b	bulk concentration of the diffusing ion ($\mathrm{mol\,cm^{-3}}$)
C_s	surface concentration of the diffusing ion ($\mathrm{mol\,cm^{-3}}$)
D	diffusivity of the diffusing ion ($\mathrm{cm^2\,s^{-1}}$)
F	Faraday's constant ($96\,500\,\mathrm{C\,equiv^{-1}}$)
i	current density ($\mathrm{A\,cm^{-2}}$)
i_1	cathodic pulse current density ($\mathrm{A\,cm^{-2}}$)
i_3	anodic pulse reversal current density ($\mathrm{A\,cm^{-2}}$)
i_3^*	dimensionless anodic pulse reversal density defined as $i_3/\lvert i_{\mathrm{lim}}\rvert$
i_{lim}	cathodic d.c. limiting current density ($\mathrm{A\,cm^{-2}}$)
$i_{\mathrm{lim,a}}$	anodic d.c. limiting current density ($\mathrm{A\,cm^{-2}}$)
i_{PL}	cathodic limiting pulse current density ($\mathrm{A\,cm^{-2}}$)
i_{PL}^*	dimensionless limiting pulse current density defined as $i_{\mathrm{PL}}/i_{\mathrm{lim}}$
m	dummy index in Equation 1
n	number of electrons transferred in the electrode reaction (equiv/mol)
t	time (s)
t_1	cathodic pulse time (s)
t_3	anodic pulse reversal time (s)
T	pulse period equal to $t_1 + t_3$ (s)
T^*	pulse period defined as DT/δ^2 (dimensionless)

Greek letters

δ	thickness of the steady-state Nernst diffusion layer (cm)
η	electrode potential (V)
η_{dc}	time-averaged electrode potential (V)
λ_m	eigenvalues given by Equation 2 (dimensionless)
θ_1	cathodic duty cycle (dimensionless)
θ_3	anodic duty cycle in pulse reversal plating (dimensionless)
ν	kinematic viscosity ($\mathrm{cm^2\,s^{-1}}$)
ω	electrode rotational speed ($\mathrm{rad\,s^{-1}}$)

1. Introduction

The mass transfer process with pulsating currents has been studied by many investigators. Cheh *et al.* [1–3] made an analysis of mass transfer to a rotating disc electrode; they obtained an infinite series solution for the regular pulse plating and an implicit expression for the limiting current density in a periodic pulse reversal plating. Ibl *et al.* [4, 5] introduced the concept of a pulsating diffusion layer and proposed a simple duplex diffusion layer model. Datta and Landolt [6, 7] modified Ibl's model and presented a semi-empirical equation for the calculation of the limiting pulse current density on a rotating hemisphere electrode. Chin [8] developed a generalized mass transfer theory for a periodic double rectangular pulse current wave; the model could be simplified to the special cases of regular pulse current and pulse reversal current waves. He presented numerical results for the concentration fluctuations, current–potential responses and limiting pulse current densities under various pulsed current conditions.

The experimental mass transfer measurements for pulse plating using a regular cathodic pulsating current wave have been made by Datta and Landolt [6] and Chin *et al.* [9]. Their limiting pulse current measurements agreed with the predictions of Chin's mass transfer model [8] and Ibl's duplex diffusion layer model [4, 5]. For the pulse plating using a periodic anodic pulse reversal current, few exper-

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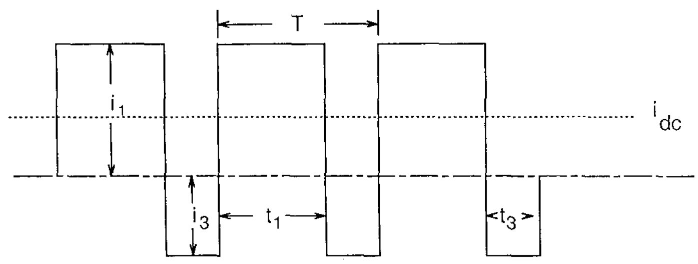
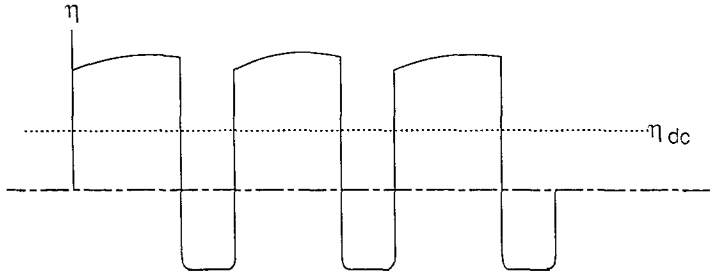
(a) Current wave



(b) Overpotential



(c) Overpotential

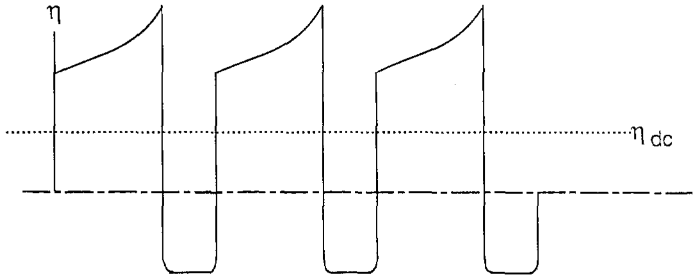


Fig. 1. Schematic representation of current and potential waves in pulse reversal plating: (a) applied current wave showing a cathodic current density of i_1 during a cathodic pulse time of t_1, and an anodic pulse reversal current density of i_3 during the anodic pulse time of t_3; (b) overpotential response wave when i_1 is small; and (c) overpotential response wave when i_1 become equal or greater than the limiting pulse current density of i_{PL}.

imental works were reported in the open literature. In the present work, the limiting pulse current densities for the periodic pulse reversal plating of copper have been measured with a rotating disc electrode under various convective conditions. The experimental data are compared to the theoretical predictions of Chin's generalized mass transfer model [8].

2. Theoretical background

Pulse reversal plating refers to a plating process where the current at the cathode reverses its polarity to the anodic direction at a periodic time interval. A pulse reversal current wave is schematically shown in Fig. 1a, where the peak current density during the cathodic time period, t_1, is i_1; and the peak current density during the anodic time period, t_3, is i_3. The sum of the cathodic and anodic time periods, $T = t_1 + t_3$, is called one pulse period of the applied current wave. The fraction of the cathodic time in one period, $\theta_1 = t_1/T$, is called the cathodic duty cycle; likewise, the fraction of the anodic time in one period, $\theta_3 = t_3/T$, is called the anodic duty cycle. For the pulse reversal current wave shown in Fig. 1a, the sum of the θ_1 and θ_3 is equal to one. The limiting pulse current density is defined as a peak cathodic current density, at which the surface concentration of the depositing metal ion drops to zero at the end of the cathodic period. This quantity can be experimentally determined by observing the potential response of the electrode during the plating process. For a given pulse reversal current, i_3, the potential response would exhibit a near rectangular wave as shown in Fig. 1b when the applied cathodic pulse current density, i_1, is small. As the cathodic pulse current density, i_1, increases, the metal ion concentration at the electrode surface would decrease with the time, and reach to a minimum value at the end of the cathodic period, t_1. This causes the potential response wave to be distorted from the rectangular form. When the applied cathodic current density, i_1, reaches the limiting pulse current density of i_{PL}, the surface concentration of the metal ion becomes zero at the end of the cathodic period, and the corresponding potential value would increase sharply to a high value as shown in Fig. 1c. It has been found that for a given anodic pulse reversal current of i_3, if one plots the time-averaged value of the potential

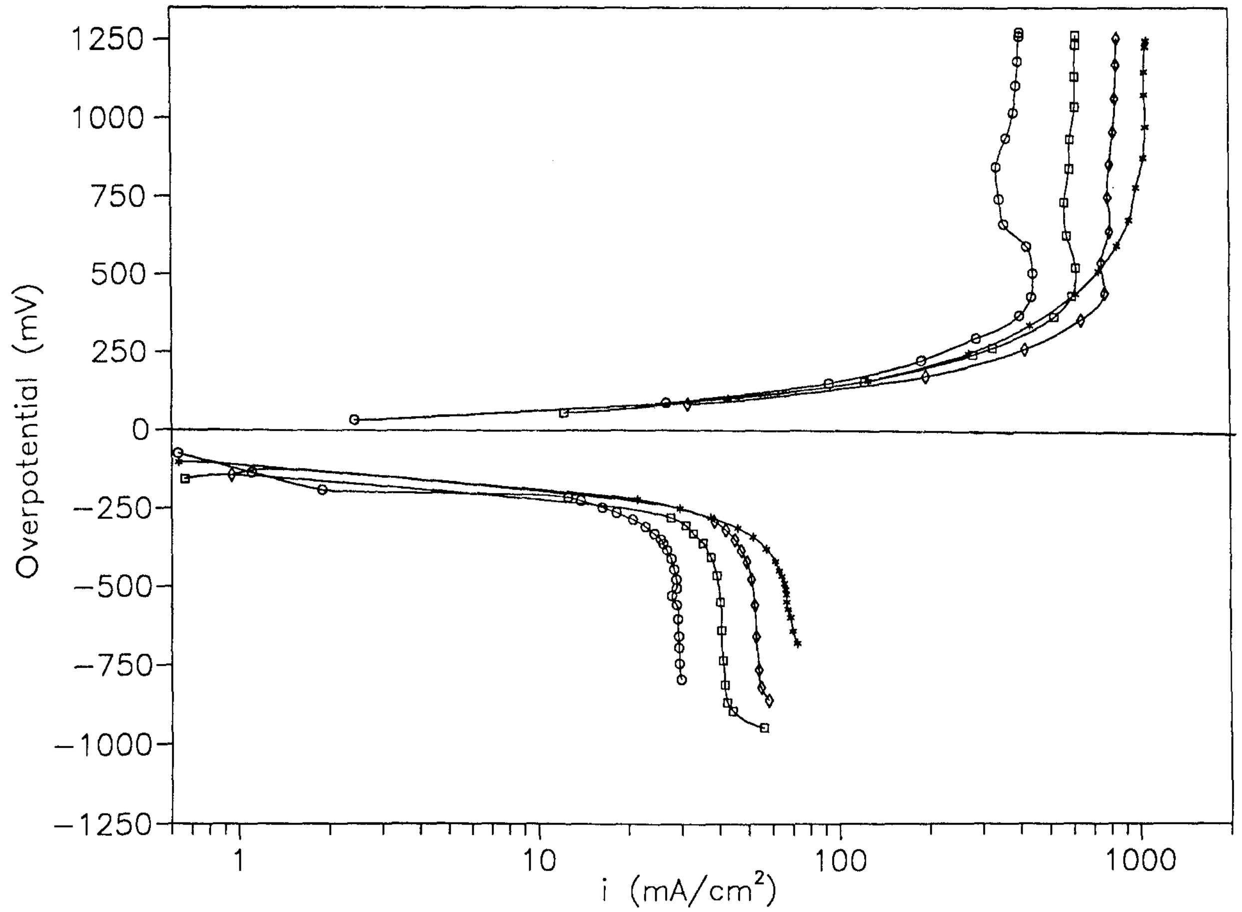


Fig. 2. Anodic and cathodic d.c. polarization curves for a rotating Cu disc electrode in an acid copper sulfate bath containing 0.05 M $CuSO_4$ and 0.5 M H_2SO_4. ω/r.p.m.: (○) 400, (□) 900, (◇) 1600 and (∗) 2500.

response wave, η_{dc}, against the applied peak cathodic current density, i_1, on a linear plot, a sharp transition occurs near the value of i_{PL}. Two linear lines are obtained on the plot: one is through the data points below i_{PL}; and the other is through the data points above i_{PL}. The point of intersection of the two linear lines would give the value of the pulse limiting current density, i_{PL}. The accuracy of this method was checked by measuring the limiting pulse current density of regular cathodic pulse plating of copper on a rotating disc electrode from an acid copper sulfate bath, and the results agreed with those of [8, 9] to within ± 5.9%. A similar method has also been used successfully in the determination of the limiting current in a.c. electrolysis [10, 11].

A theoretical analysis of mass transfer to a rotating disc electrode in pulse reversal plating has been made by Chin [8]. His analytical solution of the limiting pulse current density for a periodic pulse reversal wave of an anodic current density of i_3, a pulse period of T, and a cathodic duty cycle of θ_1, may be expressed by the following equations:*

$$i_{PL}^* = i_{PL}/i_{lim}$$

$$= \left\{1 + 2i_3^*T^* \sum_{m=1}^{\infty} \frac{\exp(-\lambda_m\theta_1) - \exp(-\lambda_m)}{\lambda_m[1 - \exp(-\lambda_m)]}\right\} \Bigg/$$

$$\left\{2T^* \sum_{m=1}^{\infty} \frac{1 - \exp(-\lambda_m\theta_1)}{\lambda_m[1 - \exp(-\lambda_m)]}\right\} \qquad (1)$$

$$\lambda_m = \pi^2 T^*(m - \tfrac{1}{2})^2 \qquad (2)$$

$$T^* = DT/\delta^2 \qquad (3)$$

$$i_3^* = i_3/|i_{lim}| \qquad (4)$$

where i_{PL}^* is the dimensionless limiting pulse current density defined as the ratio of the limiting pulse density, i_{PL}, to the cathodic d.c. limiting current density, i_{lim}; i_3^* is the dimensionless anodic pulse reversal current density defined as $i_3/|i_{lim}|$; D is the diffusivity of the diffusing ion; δ is the thickness of the steady-state Nernst diffusion layer in d.c. plating; T^* is the dimensionless pulse period defined as DT/δ^2; m is a dummy index in the infinite series; and λ_m is an eigenvalue of the infinite series. The sign convention used in the above equations is that the current density in the anodic direction has a positive value, and the current density in the cathodic direction has a negative value (i.e. i_3 is positive, and i_1, i_{PL} and i_{lim} are negative). On a rotating disc electrode, the cathodic d.c. limiting current density, i_{lim}, and the thickness of the steady-state Nernst diffusion layer, δ, are related to the bulk concentration of the diffusing ion, C_b, the diffusivity, D, the kinematic viscosity of the electrolyte, ν, and the electrode rotational speed, ω (in rad s^{-1}), by the following expressions [12]:

$$i_{lim} = -0.62nFC_bD^{2/3}\nu^{-1/6}\omega^{1/2} \qquad (5)$$

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* Correcting the misprint in [8], the form of f_3 (as $p \to \infty$) for the derivation of Equation 1 should be: $f_3 = 2T^* \Sigma_{m=1}^{\infty} \{\exp(-\lambda_m\theta_1) - \exp[-\lambda_m(\theta_1 + \theta_3)]\}/\{\lambda_m[1 - \exp(-\lambda_m)]\}$.

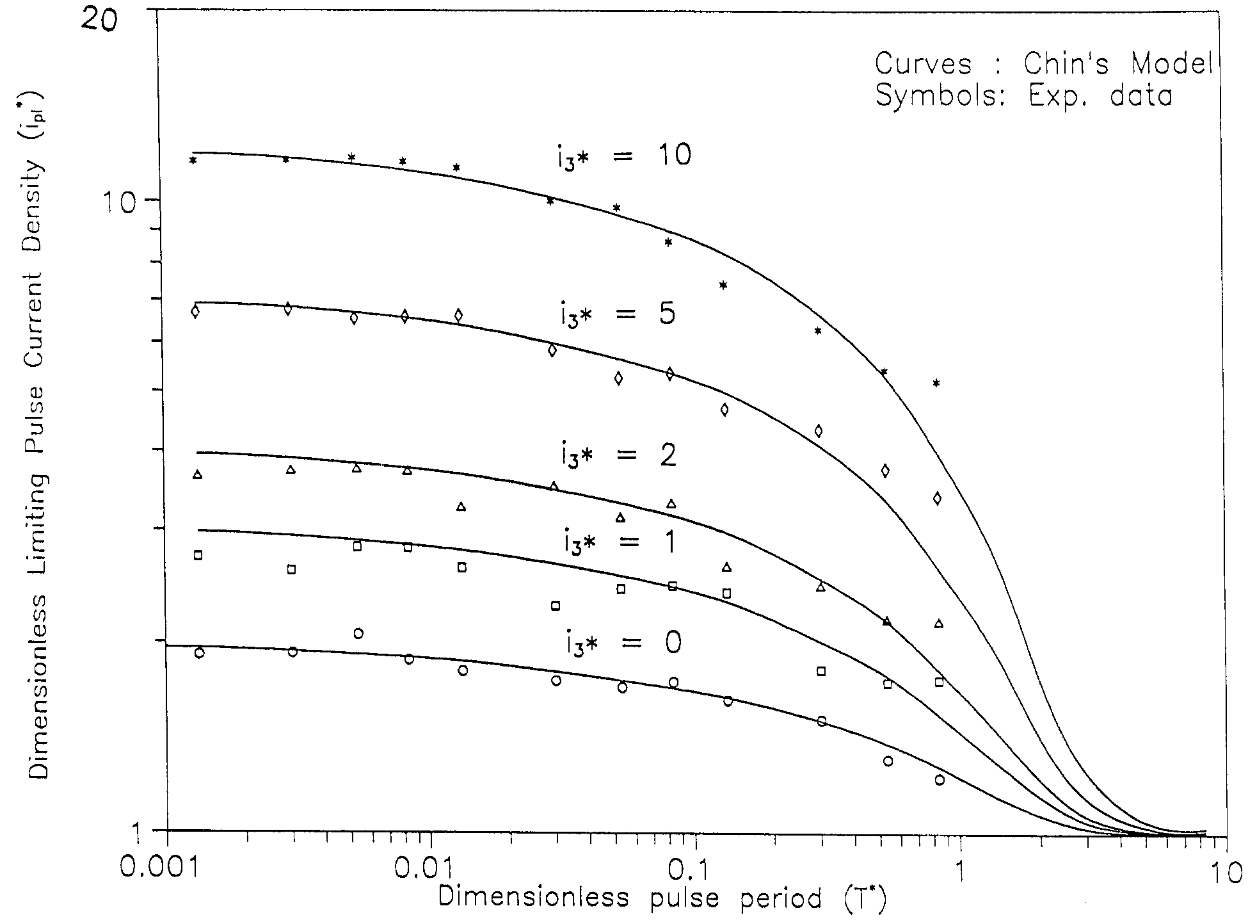

Fig. 3. Dimensionless limiting pulse current density against the dimensionless pulse period for a pulse reversal plating at a cathodic duty cycle of $\theta_1 = 0.5$, and the dimensionless anodic pulse reversal current densities of $i_3^* = 0, 1, 2, 5$, and 10.

$$\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \qquad (6)$$

Equations 1–4 indicate that the dimensionless limiting pulse current density, i_{PL}^*, is a function of the dimensionless pulse period, T^*, the cathodic duty cycle, θ_1, and the dimensionless anodic pulse reversal current density, i_3^*.

3. Experimental details

The electrodeposition of copper on a rotating copper disc electrode from an acid copper sulfate bath at 21 ± 1°C was used for the mass transfer measurements. The bath concentration was 0.05 M $CuSO_4$ and 0.5 M H_2SO_4; it was prepared by dissolving ACS certified reagent grade chemicals into the distilled water. The physical properties of the electrolyte at 21°C were: density, 1.038 $\mathrm{g\,cm^{-3}}$; viscosity, 0.0108 poise; and diffusivity of Cu^{2+} ion, $5.93 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$.

A copper rotating disc electrode having an exposed area of 0.317 $\mathrm{cm^2}$ was used as the working electrode. A copper wire located in a Luggin capillary tube served as the reference electrode. A copper plate of 4.5 cm × 4.5 cm in size was used as the counter-electrode. For each experiment, the working electrode was polished to a 1 μm smoothness with alumina powder. It was cleaned with detergent, degreased with methanol, and rinsed with distilled water. The working electrode was further electrolytically cleaned in a 5% H_2SO_4 solution at a cathodic current density of 1.0 $\mathrm{A\,cm^{-2}}$ for 1 min. The cleaned electrode was dipped in a solution containing 0.05 M $CuSO_4$ and 0.5 M H_2SO_4, and was quickly transferred into the plating bath. A high speed rotator (Pine Instrument ASR2) was used to rotate the working electrode at a desired speed during the experiment.

The limiting pulse current density was measured with a galvanostatically controlled circuit described in the previous studies [13, 14]. A MiniPulsir (LWD Scientific) connected to a d.c. source (Hewlett Packard 3311A) was used to generate a rectangular cathodic pulse voltage signal of a desired magnitude, duty cycle, and pulse period. The signal was fed to a potentiostat (Wenking HP72), and was converted to a controlled pulse current by operating the potentiostat on a galvanostatic mode. The magnitude of the anodic pulse reversal current, i_3, was set by an internal control of the potentiostat. The resulting pulse reversal current was applied to the cell, and its waveform was observed on an oscilloscope (Tetronix 214). A digital multimeter (Keithley 178) was used to measure the time-averaged value of the potential response of the rotating disc electrode with respect to the reference electrode. The limiting pulse current density was determined by gradually increasing the cathodic pulse current density, i_1, and by plotting the time-averaged potential, η_{dc}, against i_1 as described in Section 2. Approximately 2 min of experimental time was needed

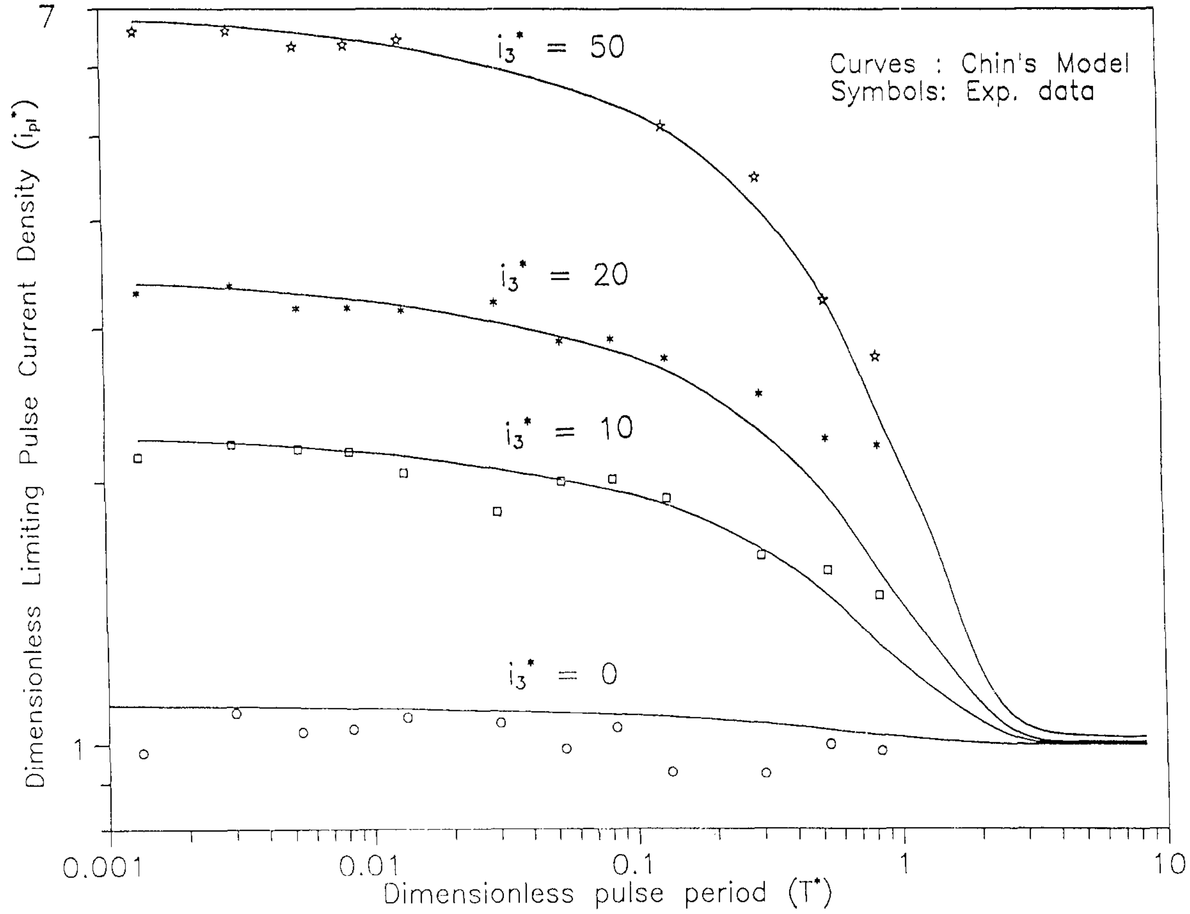

Fig. 4. Dimensionless limiting pulse current density against the dimensionless pulse period for a pulse reversal plating at a cathodic duty cycle of $\theta_1 = 0.9$, and the dimensionless anodic pulse reversal current densities of $i_3^* = 0$, 10, 20, and 50.

to complete each limiting pulse current measurement. During this time period, the amount of electric charge passing through the cell was generally less than 4 C, which corresponded to a maximum copper deposit of 5 μm in thickness on the rotating disc electrode. This thickness did not cause an appreciable change in the surface roughness of the rotating disc electrode to affect the accuracy of the limiting pulse current measurement.

4. Results and discussion

To determine if the acid copper sulfate bath might be complicated by the passivity or oxygen evolution reaction during the periodic anodic pulse reversal plating, a particular set of runs were made to examine the cathodic and anodic polarization behaviour of the copper rotating disc electrode under the d.c. plating condition. Figure 2 shows the d.c. polarization curves at the rotational speeds of 400, 900, 1600 and 2500 r.p.m. For a given rotational speed, a limiting current was observed at both the cathodic and anodic directions. The cathodic polarization curves represented the electrodeposition reaction of Cu^{2+} ion to Cu on the rotating disc electrode. A plot of the cathodic limiting current density against the square root of the rotational speed was linear; the diffusivity of Cu^{2+} ion as calculated from the slope of the linear line using Equation 5, was 5.93×10^{-6} cm^2 s^{-1}. The anodic polarization curves represented the anodic dissolution reaction of Cu rotating disc electrode to Cu^{2+} ion in the electrolyte. No passivity was observed within the overpotential range investigated. The anodic limiting current arose from the saturation of $CuSO_4$ at the surface of the rotating disc electrode when Cu dissolved into the electrolyte at sufficiently high anodic overpotentials. For a given rotational speed, the magnitude of the anodic limiting current was more than 20 times greater than that of the cathodic limiting current. A plot of the anodic limiting current density against the square root of the rotational speed was again a linear line passing through the point of origin. This suggested that the anodic limiting current density on the present rotating disc electrode system followed the modified form of Levich's equation:

$$i_{\mathrm{lim,a}} = 0.62nFD^{2/3}\nu^{-1/6}(C_s - C_b)\omega^{1/2} \qquad (7)$$

The surface concentration, C_s, of Cu^{2+} ion as calculated from the slope of the linear line using a diffusivity value of 5.93×10^{-6} cm^2 s^{-1} was 0.84 M. This value agreed with an experimental concentration of 0.841 M for a saturated $CuSO_4$ solution in 0.5 M H_2SO_4 at 21° C.

In the present study, the limiting pulse current density on the rotating disc electrode was measured for the dimensionless anodic pulse reversal current densities of $i_3^* = 0$, 1, 2, 5, 10 at a cathodic duty

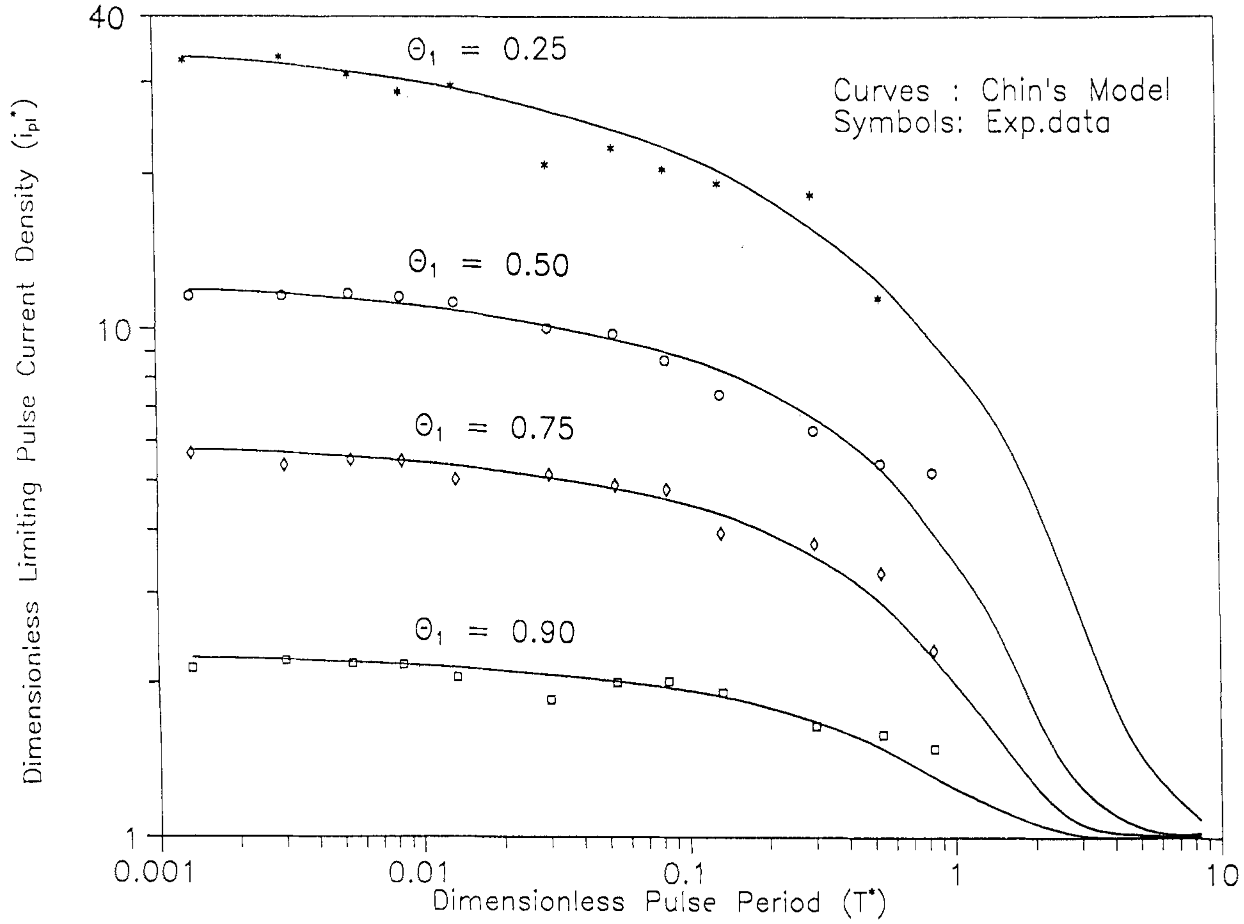

Fig. 5. Dimensionless limiting pulse current density against the dimensionless pulse period for a dimensionless anodic pulse reversal current density of $i_3^* = 10$ at the cathodic duty cycles of $\theta_1 = 0.25$, 0.5, 0.75, and 0.9.

cycle of $\theta_1 = 0.5$, and for $i_3^* = 0$, 10, 20, 50 at a cathodic duty cycle of $\theta_1 = 0.9$. The measurements were made over a range of pulse periods of 1–100 ms, and the electrode rotational speeds of 400–2500 r.p.m. To compare with the mass transfer theory of Equations 1–4, the measured limiting pulse current density was converted into a dimensionless quantity, i_{PL}^*, by normalizing it with the d.c. cathodic limiting current density obtained at the same rotational speed. Figures 3 and 4 are a plot of i_{PL}^* against the dimensionless pulse period of $T^* = DT/\delta^2$ for the cathodic duty cycles of $\theta_1 = 0.5$ and 0.9, respectively. The experimental data covered a range of T^* from 0.001 to 1 by varying both the pulse period and electrode rotational speed. The measured dimensionless limiting pulse current densities are given in the figures as the data points; the solid lines are the predictions from Chin's mass transfer model of Equations 1–4. The results indicate that for a given dimensionless pulse period of T^*, the value of i_{PL}^* increased with increasing magnitude of i_3^*. This is because during the anodic pulse reversal period, the surface concentration of Cu^{2+} ion increased due to the dissolution of Cu to Cu^{2+} ion. The higher the magnitude of applied i_3^*, the higher is the surface concentration of Cu^{2+} ion at the beginning of the cathodic pulse period, and the higher will be the limiting cathodic pulse current density to reduce the surface concentration of Cu^{2+} ion to zero at the end of the cathodic pulse period. The results also indicate that there is a satisfactory agreement between the experimental data and the theoretical predictions over the range of the dimensionless periods of $T^* = 0.001 - 1.0$. The deviation between the theory and the experimental data became larger near $T^* = 1.0$. This was primarily caused by the experimental limitation to accurately measure the pulse current and potential response by the digital multimeter (Keithley 178) at a pulse period larger than 100 ms (or a frequency below 10 Hz). The root mean square deviation between the data and the theory was: ±8.2% for Fig. 3 and ±8.9% for Fig. 4.

The effect of cathodic duty cycle on the dimensionless limiting pulse current density was also examined by keeping i_3^* at a constant value and by changing the cathodic duty cycle from 0.25 to 0.9. The experiments were carried out over the range of pulse periods of 1–100 ms and the electrode rotational speeds of 400–2500 r.p.m. Figure 5 shows a plot of i_{PL}^* against T^* for the cathodic duty cycles of $\theta_1 = 0.25, 0.5, 0.75$, and 0.9 at $i_3^* = 10$. The experimental data are represented by the symbols, and the theoretical predictions are represented by the solid lines. The results indicate that the dimensionless limiting pulse current density increased with decreasing cathodic duty cycles. For a $T^* = 0.0013$, the value of i_{PL}^* increased from 2.2 to 28.9 when θ_1 decreased from 0.9 to 0.25. A good agreement was also obtained between the experimental

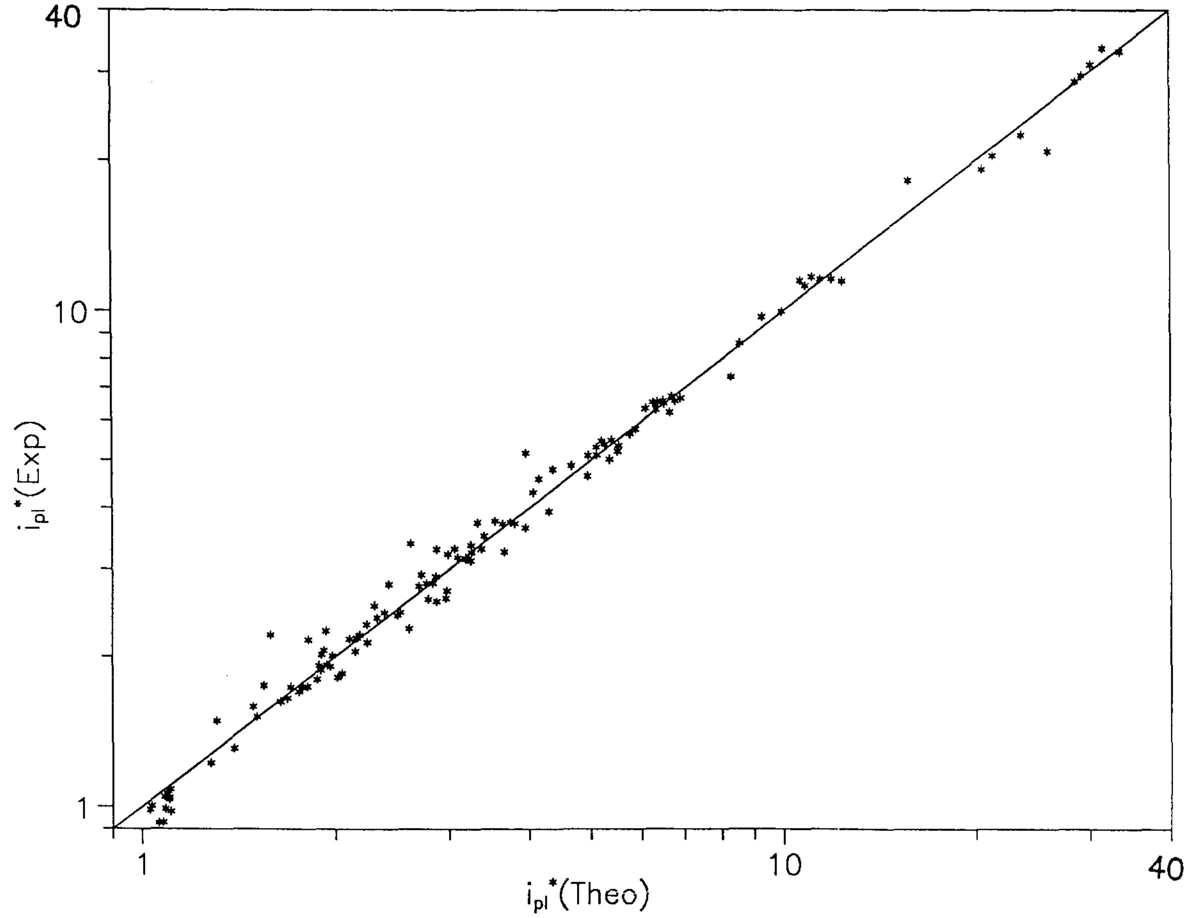

Fig. 6. Comparison between the experimental and theoretical dimensionless limiting pulse current densities.

data and theoretical predictions. Figure 6 shows an overall comparison between the experimental and theoretical limiting pulse current densities for the range of $T^* = 0.001$ to 1.0, $\theta_1 = 0.25$ to 0.9, and $i_3^* = 0$ to 50. The root mean square deviation between the theory and 128 experimental data points was ±8.5%.

5. Conclusion

An experimental study has been made of the limiting pulse current density for the pulse reversal plating of copper on a rotating disc electrode from an acidic copper sulfate bath containing 0.5 M $CuSO_4$ and 0.5 M H_2SO_4. The measurements were made over a range of the electrode rotational speeds of 400–2500 r.p.m., pulse periods of 1–100 ms, cathodic duty cycles of 0.25–0.9, and dimensionless anodic pulse reversal current densities of 0 to 50. When the measured limiting pulse current density was normalized by the d.c. limiting current density at the same rotational speed, the resulting dimensionless limiting pulse current density, $i_{PL}^* = i_{PL}/i_{lim}$, depended only on the cathodic duty cycle, θ_1, the dimensionless pulse period, $T^* = DT/\delta^2$, and the dimensionless anodic pulse reversal current density defined as $i_3^* = i_3/|i_{lim}|$. The value of i_{PL}^* increased with increasing magnitudes of i_3^*, and with decreasing values of T^* and θ_1. The experimental data were compared to the theoretical prediction of Chin's mass transfer model of Equations 1–4. A satisfactory agreement was obtained over the range of $T^* = 0.001 - 1$; the root mean square deviation between the theory and 128 experimental data points was ±8.5%.

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