**Electrode Response During Low and High Frequency Pulse Plating of Copper at a Rotating Disc Electrode**

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Electrodeposition by pulse plating has been shown to have advantages over DC plating by producing finer grain-sized, more compact and lower porosity deposits [1,2]. In addition, it provides more parameters to enable better control of the deposition process [3]. However, it is normally limited to a range of low pulse frequencies (<200Hz) in order to avoid the electrical double layer effect. The conventional view has been that the electrode response at high frequency will approach that of a DC signal so that the advantages of pulse plating are nullified and deposit properties similar to those obtained by DC plating are expected. Thus, electrodeposition carried out by pulse plating at high frequency and the electrical double layer effect occurring during electrodeposition have not received much attention from researchers. Recently, work in our laboratory has shown, however, that the application of frequencies as high as 200 kHz can lead to an improvement in deposit properties [4].

This research focuses on an experimental and modelling study of the use of both low and high frequency galvanostatic pulse plating of copper from $CuSO_4$-$H_2SO_4$ solutions at a rotating disc electrode. SEM images and measurements of microhardness, roughness and specular reflectivity are being used to characterize the deposits obtained by DC, pulsed current and pulse reverse modes of plating. In addition, the electrode potential and current are monitored during electrodeposition via a digital oscilloscope. A mathematical model incorporating diffusive, convective and migrational transport, electrode kinetics, homogeneous reaction and the electrical double layer has been developed to thoroughly describe the electrode response.

In most previous pulse plating models, either the effect of the double layer has been excluded or the value of the double layer capacitance has been assumed to be constant. This has been justified on the basis of these models being mostly applied to low frequency pulse plating. To more closely account for the effect of the double layer, we have allowed the capacitance $C_{DL}$ to be dependent on the electrode potential and electrolyte concentration at the electrode surface according to Gouy-Chapman theory and to have an inverse square root dependence on pulse frequency [5]. Thus, the boundary condition at the electrode surface relating the faradaic current density $i_{f,j}$ for each electrode reaction to the total applied current density $i_{total}$ becomes

$$i_{total} = \sum_j i_{f_j} + C_{DL}\frac{dE}{dt} \qquad (1)$$

where

$$C_{DL} = \frac{\varepsilon}{\lambda(2\pi f)^{0.5}}\cosh\frac{zFE}{2RT} \qquad (2)$$

In these expressions, $E$ represents the potential drop at the electrode surface, $\varepsilon$ is the permittivity of the solution, $\lambda$ is the Debye length based on surface concentrations and $f$ is the pulse frequency.

The measured electrode potentials during pulsed current plating of copper from a 0.1 M $CuSO_4$-1.0 M $H_2SO_4$ solution at an average current density of 4 A $dm^{-2}$, 50% duty cycle, 50 Hz frequency and 500 rpm rotational speed is given in Fig. 1. Superimposed on the plot are computed responses for 3 cases: $C_{DL}$ = 0.5 F $m^{-2}$, $C_{DL}$ varies according to Eq.(2) and $C_{DL}$ = 0 (no double layer effect). The experimental data reveal that a noticeable capacitative effect is observed, particularly during the off-times, even at this low frequency where such effects have usually been ignored. Comparison with the computed results shows that $C_{DL}$ is variable during pulse plating and that the use of Eq.(2) gives excellent agreement with the measured response. These results are very promising in view of the fact that the theoretical response has been obtained without the need for any adjustable parameters to fit the experimental data.

Fig. 2 shows a similar comparison for pulse plating at 50 kHz frequency. The experimental data show that the electrode response does not approach that of a rippled DC signal, as is conventionally viewed. This conventional view is based on the assumption that $C_{DL}$ is constant, as the results in Fig. 2 for $C_{DL}$ = 0.5 F $m^{-2}$ indicate. However, once again if $C_{DL}$ is allowed to vary according to Eq.(2), excellent agreement between measured and computed electrode potentials is obtained.

**References**

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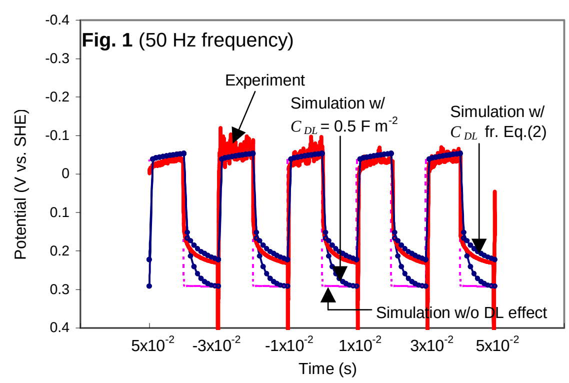


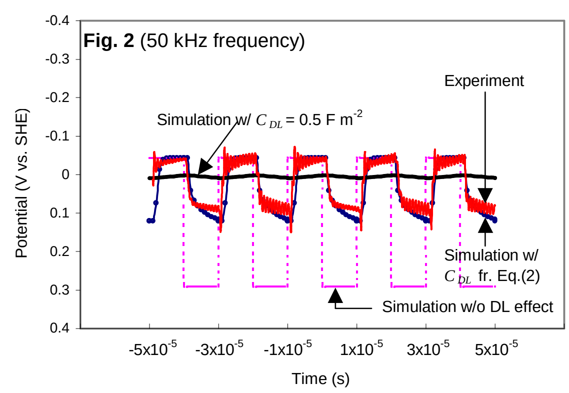


***Fig. 1 and 2*** *The simulated and experimental electrode potentials during 50 Hz (Fig. 1) and 50 kHz (Fig. 2) pulse plating at the average current density of 4 A* $dm^{-2}$ *with 50% duty cycle.*