Ionic Mass Transfer Rate Accompanying Pulsed Current Electrodeposition of Silver

S. Kawai, Y. Fukunaka* and S. Kida
Department of Mechanical Engineering and Science, Kyoto University, Yoshida-Honnachi, Sakyo-ku, Kyoto 606-8501, Japan.
* Nano Technology Research Center, Waseda University, 513 Tsurumaki-cho, Shinjyuku-ku, Tokyo 162-0041, Japan.
e-mail: fukunaka@energy.kyoto-u.ac.jp

Transient mass transfer rate of Ag⁺ ion associated with natural convective electrolyte flow developing along the vertical plane electrodes immersed in a stagnant AgNO₃ aqueous electrolyte solution is numerically analyzed under both direct and pulsed current conditions. The cathodic concentration profile of Ag⁺ ion caused by silver electrodeposition was measured by the holographic interferometer. Calculated results are compared with the measured values. Under direct current condition, it is found that quantitative agreement between calculated and measured results is obtained at the lower current density, while an obvious deviation is noticed at the higher one due to the laser beam deflection effect as well as the concentration dependence of transport properties. Additionally, it may be related to the fact that the effective cathode surface area apparently increases due to the roughening of the cathode surface by silver electrodeposition. Under pulsed current condition, reasonable agreement is obtained even at the higher pulse current density. It may be ascribed to the fact that pulse electrolysis reduces the nodular growth, edge build up, and surface roughness development.

Key words: Natural convection, Silver electrodeposition, Numerical simulation, Holographic interferometry

1. INTRODUCTION

With the great progress in the fields of electrometallurgy, electrocatalysis, and microelectronics, the production of smooth, compact, and coherent deposited thin film is of greatest importance. The additive technique has been widely adopted in not only the large scale industrial electrolytic process but also the microelectronic fabrication field in order to prevent the dendritic growth or to modify certain physical and mechanical properties [1-9]. Although the control of shape evolution and surface microstructure can be realized by this technique, it is not always acceptable due to the inclusion of impurities. It is thus desired to develop the additive-free electrochemical processing.

The application of pulse electrolysis technique is another way to improve the quality of the electrodeposits and to reduce nodular growth, edge build up, and surface roughness development. As compared to the deposits obtained from direct current (DC) electrolysis, those obtained by pulse electrolysis with pulsed current (PC) and periodic reverse (PR) current have a variety of surface microstructures and mechanical properties depending on several pulse parameters such as the pulse current density \( j_p \), pulse cycle time \( T_p \), and duty cycle \( \theta \). These pulse parameters can be varied independently over a very broad range. It is thus expected to control the surface microstructure of electrodeposited thin film or to produce materials with tailored structure under the optimal pulse parameters. Many papers have been so far published on the relationship between the pulse scheduling and the electrodeposited film morphology [10-12], while very few studies have focused on the mass transfer rate of the electrodepositing metallic ions [13, 14]. The discussion about the effect of unsteady pulse electrolysis on the ionic mass transfer rate is indispensable to design the optimal electrolytic operation with high current density.

The understanding of physicochemical hydrodynamic phenomena in electrochemical system has been expanded with the developments of both theoretical and optical studies on the ionic mass transfer. Since Wagner has introduced the boundary layer theory to the electrochemical system [15] and Ibl has examined the ionic mass transfer rate by the interferometry technique [16], numerous studies have been carried out on the ionic mass transfer rate along the vertical electrode [17-21]. However, most studies have been carried out in copper electrolysis system, because its reaction mechanism has been investigated extensively for a long time and the macroscopic flatness of the cathode surface is generally maintained as far as the electrodeposited copper film is not too thick. Very few studies have been so far carried out in silver electrolysis system [14, 22].

The present study applies the previously developed mathematical model [23-26] to silver electrodeposition from a 0.5 M AgNO₃ aqueous electrolyte solution under both DC and PC conditions. The cathodic concentration profile of Ag⁺ ion developing along the vertical plane electrode was measured by the holographic interferometer. Calculated results are compared with the measurements.

2. EXPERIMENTAL SETUP

The experimental apparatus, setup and measurement procedure have been reported in detail previously [14, 22]. Two different electrolytic cells are employed; one is employed for DC experiments and the other for PC experiments. Figure 1(a) shows the schematic diagram of the electrolytic cell.
Ionic Mass Transfer Rate Accompanying Pulsed Current Electrodeposition of Silver

The heights of both effective electrode and insulated wall are also listed in Figure 1. A 10 mm thick electrolyte layer was sandwiched between two vertical plane electrodes.

The optical measurements were carried out before the cathode surface roughness accelerated. The interference fringe shift was taken several seconds after the cathode surface roughness accelerated. The measurement position of the refractive index was located at the middle of the profile was located 15 mm from the bottom in DC electroplating experiments, while it was located in the middle of the effective electrode height in PC experiments. The effective electrode condition and pulse schedule are listed in Table I.

![Fig. 1: Schematic diagram and computational grid of electrolytic cell.](image)

The heights of both effective electrode and insulated wall are also listed in Figure 1. A 10 mm thick electrolyte layer was sandwiched between two vertical plane electrodes.

The optical measurements were carried out before the cathode surface roughness accelerated. The interference fringe shift was taken several seconds after the cathode surface roughness accelerated. The measurement position of the refractive index was located at the middle of the profile was located 15 mm from the bottom in DC electroplating experiments, while it was located in the middle of the effective electrode height in PC experiments. The effective electrode condition and pulse schedule are listed in Table I.

Table I: Electrolytic conditions.

<table>
<thead>
<tr>
<th>Electrolysis Type</th>
<th>Average Current Density $i_{ave}$ [mA/cm$^2$]</th>
<th>$i$ [mA/cm$^2$]</th>
<th>$T_1$ [s], $\theta$ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC Electrolysis</td>
<td>10, 20, 30, 60, 100, 120, 180</td>
<td>60</td>
<td>2, 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>2, 0.5</td>
</tr>
<tr>
<td>PC Electrolysis</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. NUMERICAL ANALYSIS

The present study applies the previously developed mathematical model [23-26]. It is based on several assumptions such as the principle of electroneutrality, Boussinesq approximation, and constant physical properties. The governing equations include the unsteady advection-diffusion equation for the concentration of AgNO$_3$, the Poisson equation for the electric potential, and the continuity and Navier-Stokes equations for the incompressible viscous electrolyte motion due to buoyancy.

$$\nabla \mathbf{u} = \mathbf{0} \quad (3)$$

$$\partial \mathbf{u} / \partial t + (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \mathbf{D} + \mathbf{F} \quad (4)$$

Here, $m$ and $D$ express the concentration and diffusion coefficient of AgNO$_3$, $\phi$ the electric potential, $\mathbf{u}$ the fluid velocity, $g$ the gravitational acceleration, $\nu$ the kinematic viscosity, $\rho_0$ the fluid density of bulk electrolyte solution, $P$ the pressure, $m_0$ the initial bulk electrolyte concentration of AgNO$_3$, $\alpha$ the densification coefficient of AgNO$_3$, and $t$ is the time. $C_1$ and $C_2$ are the concentrations of Ag$^+$ and NO$_3^-$ ions, respectively.

The present study assumes that only the electrochemical deposition and dissolution of silver take place on the electrode/electrolyte interface and no other electrochemical reaction such as the gas evolution is considered. The boundary conditions for the concentration of AgNO$_3$ and the electric potential on the effective electrode surface can be expressed as follows, based on the principle of electroneutrality

$$\partial m / \partial n = -(1/\nu) i_{ave} F D \quad (6)$$

$$\partial \phi / \partial n = -RT(1/\nu) i_{ave} z_1^2 F P \quad (7)$$

Here, $z_1$ and $i_{ave}$ express the valency and transference number of Ag$^+$ ion, $i$ the applied current density, $F$ the Faraday constant, $R$ the universal gas constant, $T$ the electrolyte temperature, and $n$ the normal direction to the boundary. Both anodic and cathodic current density distributions are calculated along the vertical direction. The electric potential gradient toward the effective electrode surface can be corrected from the constraint that the integration of local current density over the whole effective electrode surface area must be equal to the applied constant electrolytic current $I$ [25]

$$i_{ave} = \frac{\sum i(z) \cdot (z_1^2 F^2 D / (1/\nu) RT) m_0(z) \partial \phi (z) / \partial n}{\sum \partial \phi (z) / \partial n} \quad (8)$$

Here, $A$ denotes the whole effective electrode surface area, and $i_{ave}$ the applied average current density. The subscripts $A$ and $C$ express the anode and cathode surfaces, respectively. The boundary conditions on both insulating wall and electrolyte free surfaces can be expressed as follows, because no electrochemical reaction takes place on these interfaces

$$\partial m / \partial n = \partial \phi / \partial n = 0 \quad (11)$$

The boundary condition modeling for fluid velocity and pressure fields is the same as in previous studies [23-26]. No-slip boundary condition is imposed on both the effective electrode and insulated wall surfaces, and both shear stress and vertical component of the fluid velocity are assumed to be zero along an electrolyte free surface. As the initial condition, the aqueous electrolyte solution is assumed to have an homogeneous bulk electrolyte concentration and to be at rest before the electrolysis

$$m = m_0 = 0.5, \mathbf{u} = (u_v, v) = (0.0) \quad (for \ t = 0) \quad (12)$$

The two-dimensional mathematical model is
numerically analyzed using the finite difference method and deterministic relaxation techniques. The calculation procedure is based on the MAC (marker-and-cell) method. The computational mesh of 120×42 cells is employed in the DC experiments as shown in Figure 1(b), while that of 120×36 cells is employed in the PC experiments as shown in Figure 1(c). The physical properties used in the present numerical calculations are listed in Table II. The effect of the electric double layer on both concentration and potential responses is assumed to be negligible.

Table II: Physical properties used in calculation.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$ [m²/s]</td>
<td>$0.965 \times 10^9$</td>
</tr>
<tr>
<td>$D$ [m²/s]</td>
<td>$1.4 \times 10^9$</td>
</tr>
<tr>
<td>$\alpha$ [m²/mol]</td>
<td>$1.305 \times 10^4$</td>
</tr>
<tr>
<td>$\rho_i$ [-]</td>
<td>0.482</td>
</tr>
<tr>
<td>$\rho_e$ [kg/m³]</td>
<td>$1.067 \times 10^3$</td>
</tr>
</tbody>
</table>

4. RESULTS AND DISCUSSION

Figure 2 shows the time evolutions of the cathode surface concentration at the middle of the effective electrode height. The solid lines correspond to the calculated results, while the dashed lines to the analytical solutions for unsteady one-dimensional diffusion equation in semi-infinite media which can be expressed as follows

$$C_{10}(t) = C_{10} + \left[2(1-t_0)/t_{1/2}(t'/\pi D)^{1/2}\right]$$

In PC electrolysis, the average value between the cathode surface Ag⁺ ion concentrations at the pulse on and off periods is plotted at 5 pulse cycle times interval. In the case of DC electrolysis, calculated results are plotted at 6 seconds interval.

As the time progresses, the calculated cathode surface concentration converges to a substantially steady state value due to the development of natural convection. It is seen that the slopes estimated from calculated results quantitatively agree with the analytical ones within 1 % of error. The overshoot followed by oscillation behavior may be related to the interaction between cathodic upward and anodic downward natural convections, as previously reported [23]. It is clearly seen that the buoyancy convection plays an important role in the transient ionic mass transfer rate even under PC condition.

4.1 Morphological variations of silver electrodeposits

Figure 3 shows the morphological variations of silver electrodeposits obtained in a 0.5 M AgNO₃ aqueous electrolyte during DC electrolysis at various current densities.

It was seen that the grain size became smaller when increasing the applied current density, and morphology transited from block or pyramid type one to three-dimensional nucleation and lateral growth. Above $i_{j}=60$ mA/cm², the preferential dendritic growth appeared around the edge of the effective cathode. Furthermore, above $i_{j}=180$ mA/cm², such a dendritic silver growth was observed even at the center part of the effective cathode.

Figure 4 compares the morphology of silver electrodeposits in DC electrolysis at $i_{j}=30$ mA/cm² with that in PC electrolysis at $i_{j}=60$ mA/cm² with $T_p=2$ seconds and $\theta=0.5$.

It was clearly seen that pulse electrolysis reduced the grain size and enhanced the nucleus number density, which resulted in the smooth surface with finer grain size.

4.2 Comparisons between numerical calculations and optical measurements

Figure 5(a) compares the calculated concentration profiles of Ag⁺ ion with the optical measurements 600
seconds after starting DC electrolysis. It is seen that better agreement is obtained at the lower current density less than \(i_p=30 \text{ mA/cm}^2\), while an obvious deviation is noted at \(i_p=120 \text{ and } 180 \text{ mA/cm}^2\). It is due to the apparent increase of the effective cathode surface area due to the roughening of the cathode surface by silver electrodeposition [22]. Because the present calculation is based on a geometrically flat electrode surface, the enhancement of the surface roughness is thus a crucial problem.

![Image](Fig. 5: Cathodic concentration profile of Ag\(^+\) ion.)

Figure 5(b) shows the calculated concentration profiles of Ag\(^+\) ion 600 seconds after starting PC electrolysis. The solid lines correspond to the calculated results at the end of the pulse on period, while the dashed lines to those at the end of the pulse off period. Both the pulsating and stationary concentration boundary layers can be clearly described. Thus, the calculated results qualitatively agree with the optical measurements by the holographic interferometry.

5. CONCLUSION

Transient mass transfer rate of Ag\(^+\) ion associated with natural convection induced by silver electrodeposition from AgNO\(_3\) aqueous electrolyte solution is numerically calculated under both DC and PC electrolytic conditions. Calculated results are compared with the optical measurements by the holographic interferometry.

It is found that better agreement is obtained at the lower current density, while an obvious deviation is noted at the higher current density under DC condition. It is related to the fact that electrodeposited silver from a nitrate electrolyte solution without supporting electrolyte and additives readily grows in dendritic manner, and the effective cathode surface area apparently increases due to the surface roughness development. In PC silver electrodeposition, the present calculation reasonably predicts the duplex boundary layer structure. The measured concentration of Ag\(^+\) ion on the cathode surface agrees well with calculated result. The better agreement under PC condition is partially due to the fact that pulse electrolysis reduces the nodular growth, edge build up, and surface roughness development. The numerical simulation based on the present methodology must be further discussed to understand the coupling phenomena with micro-structural texture evolution rate. Such a study may be reasonably combined with the optimal design of pulse plating scheduling.

References


(Received April 17, 2009; Accepted November 13, 2009)