The Analysis of the Cu Surface Morphology Evolution During Electropolishing

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Abstract

The work examining the evolution of the rough Cu surface morphology during the electropolishing process is presented. The surface width, \( w \), is measured for different length scale, \( l \), and time of the electropolishing experiments, \( t \), and the data are analyzed within the scope of the scaling concept and predictions of electropolishing theory. The experimental data indicates that surface width as a function of the length scale maintains two scaling regimes (\( l \leq l_C; w \sim l_C^\alpha \), and, \( l \geq l_C; w \approx \text{const} \)). The roughness exponents (\( \alpha \)), extracted from the data obtained for different polishing times show the time dependence described by linear regression. The decrease of surface width with polishing time is well described by exponential decay predicted by the mathematical model of an ideal electropolishing process. The semi-empirical function is proposed to describe the surface width decrease during the electropolishing and the example of its practical application is discussed.

Introduction

The electropolishing has been used for various purposes in research and industry for many years (1). The appropriate formulation of the electropolishing solutions, electropolishing conditions and the process application itself were and are still the subject of numerous trade secrets and patents(2,3,4). Although the fundamental concept and mathematical description of an ideal electropolishing process have been known for some time (5), the kinetic surface smoothening during electropolishing is still not well understood. Because the electropolishing is gaining more and more applications in different areas of microelectronics and nanofabrication (6,7), the correlation between parameters of electropolishing process and the resulting surface smoothening needs to be established.

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The scaling analysis as a concept has been already established in the literature (8) to describe the kinetic roughening of the surface during the non-equilibrium deposition or erosion processes. In this approach, the surface is treated as self-affined fractal geometry where the surface width \( w \), describing the average surface corrugation in statistical sense (eq. 1), is observed over the different length scale \( l \) and time \( t \) as two independent variables. The surface width is defined as the root-mean–square of the average fluctuations of the surface height \( h(r,t) \) with respect to some referent plane over the system of size \( l \) measured over the \( N \) different points, (eq.1) (8);

\[
w(l,t) = \left( \left( h(r,t) - \bar{h}(r,t) \right)^2 \right)^{0.5}.
\]  

In the most studies of surface morphology evolution using scaling analysis, the observed systems where found to obey normal (9) (eq. 2), and anomalous (10) (eq. 3) scaling laws. The common formulations of these scaling laws are presented below, (9,10)

\[
w(l,t) \sim l^{\alpha} f(t/l^{\alpha/\beta}) , \tag{2}
\]

\[
w(l,t) \sim l^{\alpha} f_l(t/l^{\alpha/\beta}) . \tag{3}
\]

Here the scaling function \( f \) is such that \( w(l,t) \sim l^{\alpha} \) for \( (t/l^{\alpha/\beta}) > 1 \) and \( w(l,t) \sim t^\beta \) for \( (t/l^{\alpha/\beta}) < 1 \) (normal scaling). The length scale at which two scaling regimes cross is called critical length scale and it is commonly noted as \( l_c \). The \( \alpha, \beta \) in the above expressions are the roughness and growth exponents. In the case of anomalous scaling, the additional exponent, the so-called local growth exponent, \( \beta_{loc} \), is necessary to describe the surface morphology evolution for the length scale \( l \leq l_c \), (eq. 3).

The suitable studies of the surface morphology evolution during an erosion process that could be applied to electropolishing phenomenon have been carried out through the simulations using algorithms for Diffusion Limited Annihilation model (DLA) (11). In simulations as well as in the analytical model (5) and in mechanistic studies of electropolishing,(12) the random walk or diffusive type of the transport in the phase carrying out the chemically active component to the interface is assumed to be the dominant phenomenon governing the evolution of the surface morphology. Both, the theory and simulations, predict that the corrugations of the surface would diminish exponentially as a function of time, independent on the length scale of observation. (5,11,12)

The focus of this paper is to investigate the evolution of the surface morphology during the electropolishing process of rough Cu surfaces. The surface width measurements of the samples polished for different times are performed on different length scale using Atomic Force Microscope (AFM). The data are analyzed within the scope of both, scaling analysis (8) and predictions of the electropolishing theory (5) and a
semi-empirical function is proposed to describe the surface width evolution during electropolishing process.

**Experimental**

The rough Cu surfaces were produced by electrodeposition from 0.1 M Cu SO$_4$ + 0.1 M H$_2$SO$_4$ solution using -50mAcm$^{-2}$ current density for 2 hours at $\omega$=1000 rpm. The electropolishing was carried out in H$_2$O + PEG (MW=400) + H$_3$PO$_4$ solution (1) using constant current of 50 mA·cm$^{-2}$. The representative galvanostatic scan is shown in Figure 1, where the three different current density regions are indicated as function of the Cu surface they produced during electropolishing. In region one, $(0 < j < 40$ mA·cm$^{-2}$) the Cu surface is rough and this part represents just the electrochemical etching. The Cu surface does not show any signs of smoothing. The subsequent increase of current density beyond 40 mA·cm$^{-2}$ (region two) leads to the passivity of the Cu, and it is characterized by large increase in voltage for almost no change in current density. In this region, besides the Cu surface oxidation, a salt film is forming, yielding the necessary conditions for good electropolishing (1). Right after the passivity region is passed, for the current densities of $\approx 50 \pm 3$ mA·cm$^{-2}$, the smoothes Cu surface was observed (dotted region). This current density has been determined to be the optimum one for our solution. Further increase in current density beyond 50 mA·cm$^{-2}$, does not result in good polishing. The obtained Cu surface looked bright and smooth on macro scale, however, the AFM Cu surface analysis revealed a large number of pits, and additional roughening as compared to the ones obtained in dotted region (Figure 1). Further increase of current density above the 100 mA·cm$^{-2}$ leads to significant gas evolution (O$_2$) which produces even rougher Cu surfaces.

![Figure 1](image-url)

**Figure 1.** Galvanostatic scan for Cu surface in the polishing solution. Reference electrode is Cu$^{2+}$/Cu, and current density scan rate is 1 mA·s$^{-1}$. See text for more details.
Immediately after the polishing, the samples were rinsed by DI water and ethanol to prevent any additional corrosion induced surface morphology changes. The AFM measurements were performed using an E-AFM scanner and Nanoscope IIIa ADC5 controller from Digital Instruments-Veeco Instruments Company. The AFM images were analyzed using Matlab-based custom image processing software. This software has enabled the maximum possible number of measurements of the surface width for desired size of observation window (length scale) over the 15 x15 μm AFM images. The fitting of the data was performed using the least square method, and the standard deviations of the fits are presented as the intervals for error bars of the fits unless it is stated differently in the text.

Results and Discussion

Starting Rough Cu Surfaces. The representative AFM image of the starting Cu surface used in electropolishing studies is presented in Figure 2A. The initial Cu surface produced by electrodeposition shows two scaling regimes dependent on the length scale of observation (Figure 3, data for \( t = 0 \) sec.). The critical length \( l_C \) at which two scaling regimes are crossing, \( l_C \), is determined to be between 7.5 μm and 8 μm \( (l_C \approx 7.85 \, \text{μm}, \) Figure 3). For \( l \leq l_C \), the surface width evolution follows the power law, \( w \sim l^{\alpha} \), having the roughness exponent \( \alpha = 0.56 \pm 0.039 \). This value of \( \alpha \) is expected for electrodeposits exhibiting 3D columnar type of surface morphology \((13,14,15,16)\). For \( l \geq l_C \) the surface width is \( \text{const} \), having its saturation value of \( w_{\text{sat}} \approx 340 \pm 7 \, \text{nm} \) (Figure 3). The value of \( l_C \) observed for our starting Cu surface could be correlated to the average lateral size of the 3D columnar grains \((14,17)\) indicated in Figure 2A. For the length scale of the observation being within the average dimension of these grains \( (l \leq l_C) \), the scaling behavior is defined by the surface morphology confined in the perturbing columns or recessed regions \((13)\). However, if the length scale of observation is larger than the lateral size of the columnar grains \( (l \geq l_C) \), the surface width is then predominantly defined by an average normal distance of these grains from a common arbitrary plane (Figure 2A).

![Figure 2. The representative AFM images of (A) starting Cu surface, (B) Cu surface after 80 sec. and (C) 135 sec. of electropolishing. The approximate lateral sizes of the Cu grains of the initial and electropolished surfaces are indicated for illustration purpose \((l_C \approx 7 – 8 \, \text{μm})\).](image-url)
**Surface Width Evolution during Electropolishing.** The results from *ex-situ* measurements for the surface width evolution during the Cu electropolishing are presented as a function of the length scale for different polishing time intervals, Figure 3. The same data are re-plotted in Figure 4A and B emphasizing the time dependence of the surface width for the fixed length scale. The data in Figure 3 show the existence of two scaling regimes and critical length $l_C$. It is important to notice that the values of $l_C$ for polished surfaces do not express any changing trend but rather differ insignificantly from the value measured for initial, rough Cu surface. Knowing that an error bar is involved in determination of $l_C$ (18,19), we can state that initial value of $l_C$ stays relatively constant during the time frame of our polishing experiments ($7 \mu m < l_C < 8 \mu m$, for $t \geq 0$).

![Figure 3](image-url)

**Figure 3.** The log-log plot showing the Cu surface width data measured for different length scale and time of electropolishing. The dashed lines are shown for illustration purpose representing the best power law fits for $t = 0$ sec and $t = 375$ sec data and indicating crossover of two scaling regimes (dashed and full line) from which the approximate value of $l_C$ is determined.

Our analysis of the experimental data shows that decrease of surface width as a function of time is not described by the power which excludes the normal or anomalous scaling formalism to evaluate the growth exponents (20) However, this functionality is well described by the exponential decay predicted theoretically (5) and in simulations involving DLA algorithms. (11) In order to develop the formalism to analyze our data we consider, for the moment, the main results of the electropolishing theory. (5)
If the surface corrugations are presented with the periodic sine wave function of an amplitude \( b \), and wavelength \( \lambda \), then, the average displacement of the surface, \( u \), during the electropolishing process is described by:

\[
u = \frac{\lambda \cdot \left[ \ln \left( \frac{b_0}{b} \right) \right]}{2\pi}.
\]

Here, \( b_0 \) and \( b \) are the initial amplitude of the surface corrugations at \( t_0 = 0 \) and after the certain time interval \( \Delta t \) where \( t = t_0 + \Delta t \). Assuming the anodic current efficiency of an electropolishing process to be 100\%, and taking the electropolishing of copper to be the case where Cu\(^{2+}\) is the only form of dissolved Cu (21), the average displacement of the surface due to the advancement of the dissolution front during the electropolishing can be described as:

\[
u = \frac{j \cdot M_{Cu} \cdot t}{2F \cdot \rho_{Cu}}.
\]

The terms \( j, M_{Cu}, F \) and \( \rho_{Cu} \) in above expression represent the polishing current density \([\text{mA-cm}^{-2}]\), molar mass of copper \([\text{g-mol}^{-1}]\), Faraday’s constant \([\text{C-mol}^{-1}]\) and the density of Cu \([\text{g-cm}^{-3}]\). The substitution of eq.(2) in to eq.(1) and after the rearrangement yields the exponential decay for the sinusoidal corrugations of the Cu surface during the electropolishing process as:

\[
b(t) = b_0 \cdot \exp \left( -\frac{\pi \cdot j \cdot M_{Cu} \cdot t}{2F \cdot \rho_{Cu}} \cdot \frac{1}{\lambda} \right).
\]

In order to make the direct use of the polishing theory and the surface width (roughness) measurements, we make an attempt to interpret the surface morphology quantified by the surface width with an analogy to the corresponding sine wave profile. For this purpose, the real, rough surface is represented by a sine wave with an amplitude \( w \cdot \sqrt{2} \) where \( w \) is the value of the surface width measured experimentally. The term \( \lambda \) is assumed to be the characteristic wavelength of the real surface with roughness \( w \). Now, the eq.(6) can be rewritten in a such way where the amplitude of the sine wave \( b_0 \) and \( b(t) \) are replaced by the value of the experimentally measured initial surface width \( w_0 \cdot \sqrt{2} \) and \( w(t) \cdot \sqrt{2} \). The resulting expression reads as:

\[
w(t) = w_0 \cdot \exp \left( -0.115 \left[ \text{um/s}^{-1} \right] \cdot \frac{t}{\lambda} \right).
\]

In this expression the factor has the value of 0.115 \( \text{um/s}^{-1} \) estimated for the case of our electropolishing conditions (22). The eq.(7) is used to fit the data in Figure 4A and Figure 4B having \( w_0 \) and \( \lambda \) as the only fitting parameters. The fitting procedure could have been
performed using $\lambda$ as the only fitting parameter while the $w_0$ term is taken from the data for $t = 0$ sec. In both cases, very similar values of $\lambda$ are obtained. The representative fits are shown as dashed lines in Figure 4.

For the case $l \geq l_C$, Figure 4A, the values of $\lambda$ extracted from the fits are very close, all being between 15.33 $\mu$m and 15.74 $\mu$m. This difference is smaller than the error bar of the fitting ($\pm 0.6$ $\mu$m) and it can be concluded that the characteristic wavelength of the surface does not show appreciable dependence on $l$, i.e. $\lambda(l \geq l_C) \approx \text{const}$. This is not surprising since we observe that for different polishing times the $w(l \geq l_C) = w_{\text{sat}} \approx \text{const}$ and the result $\lambda(l \geq l_C) \approx \text{const}$ is just mathematical reconfirmation of this observation. The important result of this analysis is the fact that the extracted value of $\lambda$ for $l \geq l_C$, is approximately equal to $2l_C$ measured for the initial Cu surface ($t = 0$ sec, $l_C \approx 7.85$ $\mu$m, Figure 3). In another words, the characteristic wavelength of the polished surfaces shows a direct correlation with the critical length of the initial Cu surface for which the surface width saturates. To some extent, this result is expected since we do not see the change in the scaling behavior of polished surfaces (maintained two scaling regimes) or change in $l_C$ values but rather a significant reduction $w$ and $w_{\text{sat}}$ with an increasing time of polishing (Figure 2, and Figure 3). The origin of $l_C$, as we mentioned before, can be related to the lateral size of the columnar grains (Figure 1A), and these grains, although being significantly reduced in their height ($w_{\text{sat}}$), continue to maintain their lateral dimensions during the polishing process which yields relatively constant values of $l_C$ (see, the images in Figure 2B and Figure 2C). The surface profile of these grains can be mathematically approximated by a half of the sine wave with amplitude $w_{\text{sat}}\sqrt{2}$ and, it that sense, the relation $\lambda(l \geq l_C) \approx 2l_C$ obtained from the fits has the physical meaning and it is in agreement with the mathematical model of the electropolishing process. (5)

![Figure 5](image-url)

Figure 5. The semi-log plot of the Cu surface width data measured for different polishing times and length scale: (A) $l \geq l_C$ and (B) $l \leq l_C$. In (B), the data for $l = 4, 6, \text{and } 7$ $\mu$m are omitted for clarity. The short dashed lines in (A) and (B) are shown for illustration purpose indicating the best fits of eq.(7) to experimental data.
w vs. t dependence for \( l \leq l_C \). The fit of \( w \) vs. \( t \) experimental data (Figure 4B) by eq. (7) yields increasing values of \( \lambda \) for decreasing length scale, i.e. \( \lambda \uparrow \) for \( l \downarrow \). These data are shown in Figure 5. Figure 6 shows the values of roughness exponents \( \alpha \) obtained from the power law fits to the experimental results for different polishing times. The extracted roughness exponents show a decreasing trend as the polishing time extends from 0 sec. to 375 sec. This observation goes along with what one would expect by looking at a simplistic picture of an ideal electropolishing process. The successful electropolishing leads to gradual reduction of surface width with time and after very long time, \( t_{++} \), the surface would reach the minimum surface width, \( w_{\text{min}} \), being constant for any length scale (\( w = w_{\text{min}} \approx \text{const} \) for \( l \leq l_C \) and \( l \geq l_C \)). This means that the roughness exponent would gradually decrease to zero for \( t = t_{++} \). The same conclusion follows if we analyze the necessary condition for existence of both, the self-affinity of Cu surface during electropolishing, and the exponential decrease of the surface width for increasing polishing time which are both observed in our experiments. Using mathematical framework, this condition could be defined starting from scaling relation for \( w_{\text{sat}}(l_C,0) \) and \( w(l,0) \), (eq.(2)),(8,9,23) expressed as:

\[
 w_{\text{sat}}(l_C,0) = w(l,0) \cdot \left( \frac{l_C}{l} \right)^{\alpha_0} \quad (8)
\]

The same is true for the Cu surface morphology obtained after some polishing time \( t \),

\[
 w_{\text{sat}}(l_C,t) = w(l,t) \cdot \left( \frac{l_C}{l} \right)^{\alpha(t)} \quad (9)
\]

Dividing eq.(9) by eq.(8) and substituting eq.(7) instead of \( w_{\text{sat}}(l_C,t)/w_{\text{sat}}(l_C,0) \) and \( w(l,t)/w(l,0) \), after rearrangement yields:

\[
 \exp\left(-0.115[\mu\text{m/s}^{-1}] \cdot \frac{t}{\lambda_C} \right) = \exp\left(-0.115[\mu\text{m/s}^{-1}] \cdot \frac{t}{\lambda} \right) \cdot \left( \frac{l_C}{l} \right)^{\alpha(t) - \alpha_0}. \quad (10)
\]

Performing the logarithm of the left and right side, the eq.(10) is presented in a form which is more convenient for discussion;

\[
 \frac{\alpha(t) - \alpha_0}{t} = \frac{0.115[\mu\text{m/s}^{-1}] \cdot \left( \frac{1}{\lambda} - \frac{1}{\lambda_C} \right) \ln \left( \frac{l_C}{l} \right)}{\ln \left( \frac{l_C}{l} \right)} = \text{const} \quad (11)
\]

The right side of the above expression represents the fraction between the experimentally measured parameters which are only dependent on the conditions of polishing process and material (0.115 \( \mu \text{m/s}^{-1} \)), morphology of the starting Cu surface \( (l_C, \lambda_C) \) and the length
scale of the observation \((l, \lambda)\). This means that the right hand side of eq.(11) yields a constant value, independent of \(t\) and the same statement has to be valid for the left side as well. Mathematically, this is possible only if \(\alpha(t)\) is linear decreasing function of time having the form:

\[
\alpha(t) = \alpha_0 - B \cdot t , \tag{12}
\]

where, \(B\) is the positive constant and \(\alpha_0\) is the roughness exponent measured for initial Cu surface \((t = 0)\).

**Figure 5.** The values of \(\lambda\) obtained from the fit of eq.(7) to the data in Figure 4B. The full line in this figure represents the fit of eq.(13) to the \(\lambda\) vs. \(l\) values with coefficient \(B\) as the only fitting parameter \((l_C = 7.85 \, \mu m)\). The obtained value of \(B\) is \(0.00072 \pm 0.00003\) s\(^{-1}\).

**Figure 6.** The values of roughness exponent \(\alpha\) obtained from the power law fits of the data in Figure 3, \(l \leq l_C\) for different electropolishing times. The full line represents the best fit of \(\alpha\) vs. \(t\) dependence with linear regression (eq.(12)). The \(\alpha_0 = 0.56\) is determined from the experimental data for \(t = 0\) sec. and the coefficient \(B\) is the only fitting parameter \((B = 0.00058 \pm 0.00008)\).

Considering the experimentally observed decreasing trend for \(\alpha(t)\) shown in Figure 6, we can state that in order to have consistency between the selfaffinity of the Cu surface during electropolishing expressed by two scaling regimes, and the exponential decay of surface width predicted by electropolishing theory, it is necessary that roughness exponent \(\alpha\) has the time dependence described by linear regression defined by eq.(12). Substituting eq.(12) into eq.(11) and having \(\lambda_C \approx 2l_C\), after rearrangement, the characteristic surface wavelength \(\lambda\) as a function of \(l\), for \(l \leq l_C\), is then defined in terms of constants \(B [s^{-1}], l_C [\mu m]\) as:

\[
\lambda \approx \frac{1}{2l_C} \cdot \frac{1}{\frac{B}{0.115 [\mu m/s^{-1}]} \cdot \ln \left(\frac{l_C}{l} \right)} , \tag{13}
\]
The fit of the eq.(13) to the data in Figure 5 with coefficient $B$ as the only fitting parameter is shown as solid line. The extracted value of $B$ from this fit is $= 0.00072 \pm 0.00003 \text{ s}^{-1}$. This is slightly higher than what is obtained in the case of the liner fit of the data in Figure 6. However, considering the experimental error bars (Figure 3), and error bars of the fits, we can say that these results are in agreement and they support our analysis.

It is important to emphasize that the value of $B$ can be calculated from eq.(13) using the assumption for an ideal electropolishing process. The $\lambda$ vs. $l$ dependence for $l \leq l_C$ described by equation (13) shows that as the $l$ is decreasing the value of the surface characteristic length $\lambda$ is increasing as it is observed experimentally. In the case of an ideal electropolishing we can expect that $\lambda \rightarrow \infty$ for $l = a$, where $a$ is the minimum length at which the surface can still be considered as continuum. Mathematically this means that the expression in the denominator of the right side of eq.(13), has to be equal zero for $l = a$. We can take $a$ to be the length of the Cu lattice unit cell as the first approximation, $a = 0.361 \text{ nm}$ (24), and having $l_C = 7.85 \mu\text{m}$, from eq.(13), the estimated value of $B$ is $0.00073 \text{ s}^{-1}$. As one can see, this is very close to the $B$ value obtained by fitting eq.(13) to the data in Figure 5, and this result additionally supports the physical meaning of our analysis. The extrapolation of eq.(13) at $l \rightarrow a$ limit could also be found very useful in predicting the surface width evolution as a function of time for $l \leq l_C$, without having experimentally determined $D$ vs. $t$ dependence. The details of this procedure will be discussed it in the next paragraph.

Conclusion

The morphology evolution of rough Cu surface during the electropolishing process has been described using a combined approach of scaling analysis and predictions of the electropolishing theory. During electropolishing, the surface morphology maintained the existence of two scaling regimes although the roughness exponent $\alpha$ has shown a time dependence characterized by linear regression. The surface width data measured for the constant length scale but different polishing times indicate strong time dependence as well. This dependence was fitted using an exponential decay suggested by electropolishing theory and interpreted in our case where the surface is described in statistical sense. The surface wavelength used in theoretical description of the polishing phenomenon in this analysis has adopted a new meaning of the characteristic surface wavelength. For the $l \geq l_C$ case, the characteristic surface wavelength was found constant and being in direct correlation with an average width of the columnar grains originating from the starting rough Cu surface. However, for $l \leq l_C$ case, the characteristic wavelength of the surface was found dependent on the length scale of observation and this dependence is described by eq.(13). Based on these results and analysis, the general function is proposed that can be used to describe the surface width evolution during electropolishing of rough Cu surfaces having two different formulations depending on the length scale:
and,

\[ w(l \leq l_C, t) = w(l \leq l_C, 0) \cdot \exp \left(-\psi \cdot \frac{t}{\lambda C}\right), \]  

where \( \lambda \) is defined by eq.(13). In the case where the coefficient \( B \) is not determined from fitting eq.(12) to experimentally obtained \( \alpha \) vs. \( t \) dependence or eq(13) to \( \lambda \) vs. \( l \) dependence, the good approximation of \( B \) could be obtained from the extrapolation of eq(13) at \( l \to a \) limit \((0.5 l_C = B/0.115[\mu m s^{-1}] \ln(l_C/a))\).

In conclusion, the proposed functionality for \( l \geq l_C \), eq.(14), was used to predict the polishing time required to reduce the \( w_{sat} \) of the rough Cu studs (Figure 7) fabricated using electrodeposition through-mask process (\( w_{sat} = 1200 \pm 115 \text{ nm}, l_C \approx 9 \mu \text{m} \)). The obtained results were found in a good agreement with predictions of the developed function (\( w_{sat-measured} = 20 \pm 6 \text{ nm} \) vs. \( w_{sat-predicted} = 26 \text{ nm} \) for \( t = 600 \text{ sec} \)) demonstrating the usefulness of our results for applications in different areas of microelectronics and MEMS fabrication.

**Figure 7.** The representative SEM images of (A) rough Cu stud produced by electrodeposition through photoresist mask and (B) electropolished Cu stud which has initial roughness as the one in (A). The photoresist is removed after the electropolishing process.

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References

2. J. D. Reid, *US Patent* # 6,653,226, November (2003),
20. The term ‘growth’ exponent in this case can be considered only conditionally since the electropolishing phenomenon involves smoothing of the surface rather than roughening.
21. The dissolution reaction of the Cu in this case is assumed to be completely confined in the form of $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$
22. $\frac{\pi \cdot j \cdot M_{\text{Cu}}}{F \cdot \rho_{\text{Cu}}} = 0.115 \mu \text{m}^{-1}$ is calculated using the values $j = 50 \text{ mA cm}^{-2}, M_{\text{Cu}} = 63.5 \text{ g mol}^{-1}, F = 96500 \text{ C mol}^{-1}$ and $\rho_{\text{Cu}} = 8.96 \text{ g cm}^{-3}$.
23. The eq.(8) is derived using scaling formalism, $y \sim x^\alpha, Y \sim X^\alpha$, which implicates $Y/y = (X/x)^\alpha$ or $Y = y \cdot (X/x)^\alpha$.