



Cu Surface Morphology Evolution during Electropolishing

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The work examining the evolution of the rough Cu surface morphology during the electropolishing process is presented. The initial Cu surface was produced by electrodeposition under kinetic control. 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 results indicate that surface width as a function of the length scale for different times of polishing maintains two scaling regimes ($l \leq l_C$; $w \sim l^\alpha$ and $l \geq l_C$; $w \approx \text{const}$). The roughness exponents (α) extracted from the same data show the time dependence described by linear regression. Our analysis of the experimental data demonstrates that decrease of surface width with polishing time is well described by exponential decay predicted by the mathematical model of an ideal electropolishing process. A semiempirical function is proposed to describe the surface width decrease during the electropolishing, and an example of its practical application is discussed.

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Manuscript submitted June 13, 2007; revised manuscript received October 5, 2007. Available electronically November 7, 2007.

Electropolishing has been used for various purposes in research and industry for many years.¹ Traditionally regarded as an art more than a science, the appropriate formulation of the electropolishing solutions, electropolishing conditions, and the process application itself are the subject of numerous trade secrets and patents.²⁻⁴ Although the fundamental concept and mathematical description of an ideal electropolishing process have been known for some time,⁵ the kinetic surface smoothing during electropolishing is still not well understood. Because electropolishing is gaining more and more applications in different areas of microelectronics and nanofabrication,^{6,7} the correlation between the underlying science of electropolishing and the resulting surface smoothing needs to be established.

In the literature, there is already a well-established concept of scaling analysis⁸ to describe the kinetic roughening of the surface during the nonequilibrium deposition or erosion processes. The surface is treated as self-affine 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

$$w(l,t) = \langle (h(r,t) - \bar{h}(r,t))^2 \rangle^{0.5} \quad [1]$$

Although the kinetic roughening during surface growth or erosion is a complex phenomenon involving many different processes, most systems where the surface can be represented as a self-affine fractal geometry are well described by a normal⁹ (Eq. 2), and for some systems, by anomalous¹⁰ (Eq. 3) scaling laws. The common formulations of the scaling laws are presented as follows^{9,10}

$$w(l,t) \sim l^\alpha f\left(\frac{t}{l^{\alpha/\beta}}\right) \quad [2]$$

$$w(l,t) \sim l^\alpha t^{\beta_{\text{loc}}} f\left(\frac{t}{l^{\alpha/\beta}}\right) \quad [3]$$

Here the scaling function f is such that $w(l,t) \sim l^\alpha$ for $(t/l^{\alpha/\beta}) \gg 1$ and $w(l,t) \sim t^\beta$ for $(t/l^{\alpha/\beta}) \ll 1$ (normal scaling). The length scale at which two scaling regimes cross is called the critical length scale, commonly noted as l_C . The α , β in Eq. 2 and 3 are the roughness and growth exponents. In the case of anomalous scaling, the additional exponent, the so-called local growth exponent β_{loc} is

necessary to describe the surface morphology evolution for the length scale $l \leq l_C$ (Eq. 3).

Because the electropolishing is the process opposed to electrodeposition, one might expect to see similar scaling behavior. However, the major difference is that, during electropolishing, the most exposed leading parts of the surface are removed first, while in the case of electrodeposition, these would be the ones to receive the largest flux of the material. 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 the diffusion limited annihilation (DLA) model.¹¹ In simulations¹¹ as well as in the analytical model⁵ and in mechanistic studies of electropolishing,¹² the random walk or diffusive type of 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 of the length scale of observation.^{5,11,12}

The focus of this paper is to investigate the evolution of 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 an atomic force microscope (AFM). The data are analyzed within the scope of both scaling analysis⁸ and predictions of the electropolishing theory,⁵ and a semiempirical function is proposed to describe surface width evolution during the electropolishing process.

Experimental

The rough Cu surfaces were produced by electrodeposition from 0.1 M CuSO₄ + 0.1 M H₂SO₄ solution using -50 mA cm^{-2} current density for 2 h at $\omega = 1000 \text{ rpm}$. The electropolishing was carried out in H₂O + PEG (Mw = 400) + H₃PO₄ solution¹ using constant current density of 50 mA cm^{-2} . Immediately after polishing, the samples were rinsed by deionized (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 enabled the maximum possible number of measurements of the surface width for desired size of observation window (length scale) over the $15 \times 15 \text{ } \mu\text{m}$ AFM images. The fitting of the data was performed using the least-squares method, and the standard deviations of the fits are presented as the intervals for error bars of the fits, unless stated differently.

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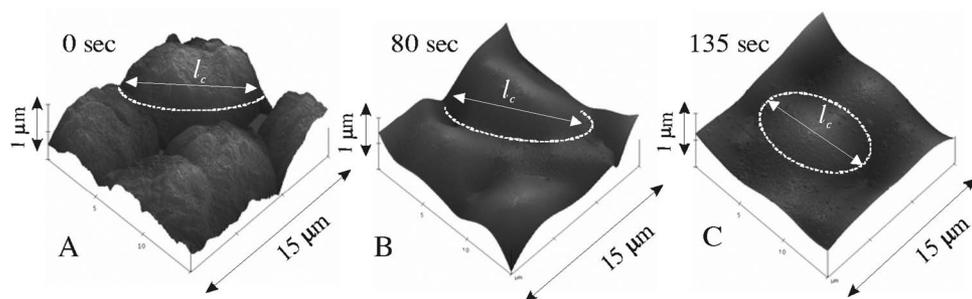


Figure 1. The representative AFM images of (A) starting Cu surface, (B) Cu surface after 80 s, and (C) 135 s of electropolishing. The approximate lateral sizes of the Cu grains of the initial and electropolished surfaces are indicated for illustration purpose ($l_c \approx 7\text{--}8 \mu\text{m}$).

Results and Discussion

Starting rough Cu surfaces.— The representative AFM image of the starting Cu surface used in electropolishing studies is presented in Fig. 1A. The initial Cu surface produced by electrodeposition shows the self-affine fractal geometry characterized by two scaling regimes dependent on the length scale of observation (Fig. 2, data for $t = 0$ s). The critical length at which two scaling regimes are crossing l_c is determined to be between 7.5 and 8 μm ($l_c \approx 7.85 \mu\text{m}$, Fig. 2). 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 α is predicted for electrodeposits exhibiting a three-dimensional (3D) columnar type of surface morphology,¹³ which is commonly seen in electrodeposition experiments producing polycrystalline deposits.^{14–16} For $l \geq l_c$, the surface width is constant, having its saturation value of $w_{\text{sat}} \approx 340 \pm 7 \text{ nm}$ (Fig. 2). 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 Fig. 1A. 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 (Fig. 1A).

Surface width evolution during electropolishing.— The results from ex situ measurements for the surface width evolution during Cu electropolishing are presented as a function of the length scale

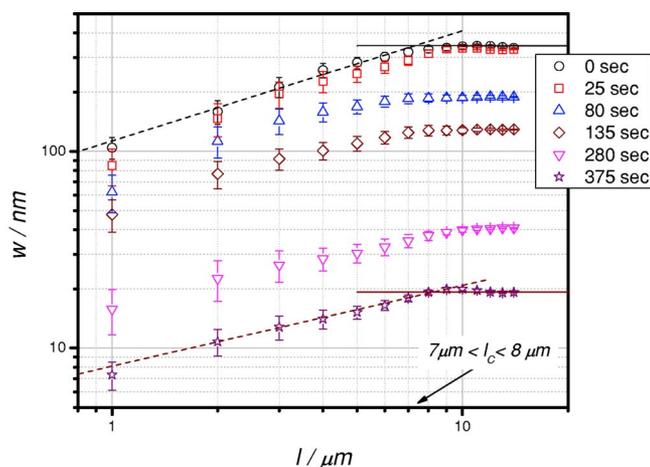
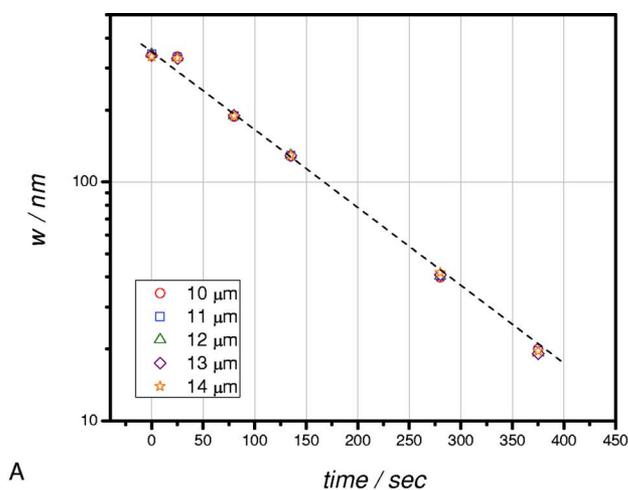
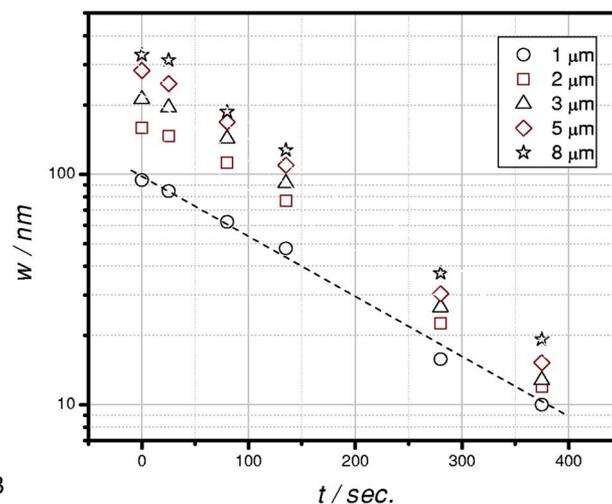


Figure 2. (Color online) The log-log plot showing the Cu surface width data measured for different length scale and time of electropolishing. The dashed lines are shown for illustration purposes, representing the best power law fits for $t = 0$ s and $t = 375$ s data and indicating crossover of two scaling regimes (dashed and solid lines) from which the approximate value of l_c is determined.

for different polishing time intervals (Fig. 2). The same data are replotted in Fig. 3A and B, emphasizing the time dependence of the surface width for the fixed length scale. The data in Fig. 2 show the existence of two scaling regimes and l_c . This is an indication that the Cu surface maintains the self-affine fractal geometry throughout the polishing experiment. It is important to note that the values of l_c for polished surfaces do not express any changing trend but rather differ insignificantly from the value measured for the initial, rough Cu surface. Knowing that, in general, an error bar is involved in the



A



B

Figure 3. (Color online) The semilog 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 $l = 4, 6, \text{ and } 7 \mu\text{m}$ are omitted for clarity. The short dashed lines in (A) and (B) are shown for illustration purposes, indicating the best fits of Eq. 7 to experimental data.

determination of l_C ,^{18,19} we can state that the initial value of l_C stays relatively constant during the time frame of our polishing experiments ($7 \mu\text{m} < l_C < 8 \mu\text{m}$, for $t \geq 0$).

w vs t dependence for $l \geq l_C$ case.—The use of the normal or anomalous scaling formalism in order to evaluate the growth exponents^a in our case is precluded because the experimentally observed decrease of surface width as a function of time is not described by the power law. In fact, this functionality is well described by the exponential decay predicted theoretically⁵ and in simulations involving DLA algorithms.¹¹ For the purpose of a better formulation of this exponential functionality, we will 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 λ , then the average displacement of the surface u during the electropolishing process is described by⁵

$$u = \frac{\lambda[\ln(b_0/b)]}{2\pi} \quad [4]$$

Here, b_0 and b are the initial amplitude of the surface corrugations at $t_0 = 0$ and after the certain time interval Δt 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,^b the average displacement of the surface due to the advancement of the dissolution front during the electropolishing can be described as

$$u = \frac{jM_{\text{Cu}}}{2F\rho_{\text{Cu}}}t \quad [5]$$

The terms j , M_{Cu} , F , and ρ_{Cu} in Eq. 5 represent the polishing current density (mA cm^{-2}), molar mass of copper (g mol^{-1}), Faraday's constant (C mol^{-1}) and the density of Cu (g cm^{-3}). The substitution of Eq. 2 into Eq. 1 and after the rearrangement yields the exponential decay for the sinusoidal corrugations of the Cu surface during the electropolishing process as

$$b(t) = b_0 \exp\left(-\frac{\pi j M_{\text{Cu}} t}{F \rho_{\text{Cu}} \lambda}\right) \quad [6]$$

However, the real rough surfaces are not just simple sine wave corrugations. In fact, their mathematical description involving a continuum model is still a challenging task. The surface width is a statistical interpretation of the surface corrugations or roughness (Eq. 1) that can be easily deduced from the experimental data. In general, the real surface could be represented as an infinite series of sin and/or cos functions with different wavelengths using the Fourier series.²⁰ In this sense, the dominant terms in Fourier series with appropriate wavelengths and frequencies and with dominant contribution to the value of the surface width would be the one to consider as representative. In order to make 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 $w\sqrt{2}$, where w is the value of the surface width measured experimentally. The term λ is assumed to be the characteristic wavelength of the real surface with roughness w . Now, 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 $w_0\sqrt{2}$ and $w(t)\sqrt{2}$. The resulting expression reads as

$$w(t) = w_0 \exp\left(-\Psi \frac{t}{\lambda}\right) \quad [7]$$

In this expression, the factor $\Psi = \pi j M_{\text{Cu}} / F \rho_{\text{Cu}}$ is a constant having the value of $0.115 \mu\text{m s}^{-1}$ estimated for our electropolishing conditions.^c Equation 7 is used to fit the data in Fig. 3A and B, having w_0 and λ as the only fitting parameters. The fitting procedure could have been performed using λ as the only fitting parameter while the w_0 term is taken from the data for $t = 0$ s. In both cases, very similar values of λ are obtained. The representative fits are shown as dashed lines in Fig. 3. For the case $l \geq l_C$ (Fig. 3A), the values of λ extracted from the fits are very close, all being between 15.33 and $15.74 \mu\text{m}$. Knowing that this difference is smaller than the error bar of the fitting ($\pm 0.6 \mu\text{m}$), we conclude 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 because 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 that the extracted value of λ for $l \geq l_C$ is approximately equal to $2l_C$ measured for the initial Cu surface [$t = 0$ s, $l_C \approx 7.85 \mu\text{m}$ (Fig. 2)]. Thus, 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 because 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 of w and w_{sat} with an increasing time of polishing (Fig. 1 and 2). The origin of l_C , as previously mentioned, can be related to the lateral size of the columnar grains (Fig. 1A), and these grains, although being significantly reduced in their height (w_{sat}), continue to maintain their lateral dimensions during the polishing process, which yields relatively constant values of l_C (see Fig. 1B and C). The surface profile of these grains can be mathematically approximated by half of the sine wave with amplitude $w_{\text{sat}}\sqrt{2}$, and, in that sense, the relation $\lambda(l \geq l_C) \approx 2l_C$ obtained from the fits has physical meaning, which is in agreement with the mathematical model of the electropolishing process.⁵

w vs t dependence for $l \leq l_C$.—The fit of w vs t experimental data (Fig. 3B) by Eq. 7 yields increasing values of λ for decreasing length scale, i.e., $\lambda \uparrow$ for $l \downarrow$. These data are shown in Fig. 4. The results, at first look, might be counterintuitive. However, more physical sense of the λ vs l results is transparent if one looks at the overall data shown in Fig. 2 and extracted corresponding values of α . Figure 5 shows the values of roughness exponents α obtained from the power law fits of the experimental results for different polishing times. The extracted roughness exponents show a decreasing trend as the polishing time extends from 0 to 375 s. This observation goes along with what one would expect by looking at a simplistic picture of an ideal electropolishing process. Successful electropolishing leads to gradual reduction of surface width with time, and after a very long time t_{++} the surface would reach the minimum surface width w_{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 the 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 the scaling relation for $w_{\text{sat}}(l_C, 0)$ and $w(l, 0)$ (Eq. 2),^{8,9,d} expressed as

^a The term *growth* exponent in this case can be considered only conditionally because the electropolishing phenomenon involves smoothing of the surface rather than roughening.

^b The dissolution reaction of the Cu in this case is assumed to be completely confined in the form of $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$.

^c $\pi j M_{\text{Cu}} / F \rho_{\text{Cu}} = 0.115 \mu\text{m s}^{-1}$ is calculated using the values $j = 50 \text{ mA cm}^{-2}$, $M_{\text{Cu}} = 63.5 \text{ g mol}^{-1}$, $F = 96,500 \text{ C mol}^{-1}$, and $\rho_{\text{Cu}} = 8.96 \text{ g cm}^{-3}$.

^d The Eq. 8 is derived using scaling formalism, $y \sim x^\alpha$, $Y \sim X^\alpha$, which implicates $Y/Y = (X/x)^\alpha$ or $Y = y(X/x)^\alpha$.

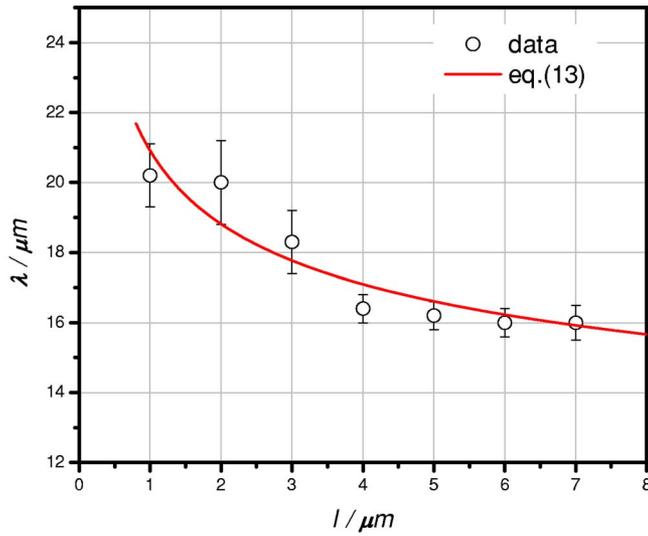


Figure 4. (Color online) The values of λ obtained from the fit of Eq. 7 to the data in Fig. 3B. The solid line represents the fit of Eq. 13 to the λ vs l values with coefficient B as the only fitting parameter ($l_C = 7.85 \mu\text{m}$, $\Psi = 0.115 \mu\text{m s}^{-1}$).

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

The same is true for the Cu surface morphology obtained after some polishing time t

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

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

$$\exp\left(-\Psi \frac{t}{\lambda_C}\right) = \exp\left(-\Psi \frac{t}{\lambda}\right) \left(\frac{l_C}{l} \right)^{\alpha(t) - \alpha_0} \quad [10]$$

Performing the logarithm of the left and right side, Eq. 10 is presented in a form that is more convenient for discussion

$$\frac{\{\alpha(t) - \alpha_0\}}{t} = \frac{\Psi[(1/\lambda) - (1/\lambda_C)]}{\ln(l_C/l)} = \text{const} \quad [11]$$

The right side of Eq. 11 represents the fraction between the experimentally measured parameters, which are only dependent on the conditions of polishing process and material (Ψ), morphology of the starting Cu surface (l_C, λ_C), and the length scale of the observation (l, λ). This means that the right 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 a linear decreasing function of time having the form

$$\alpha(t) = \alpha_0 - Bt \quad [12]$$

where B is the positive constant and α_0 is the roughness exponent measured for initial Cu surface ($t = 0$). Considering the experimentally observed decreasing trend for $\alpha(t)$, shown in Fig. 5, we can state that in order to have consistency between the self-affinity 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 α 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 λ as a function of l , for $l \leq l_C$, is then defined in terms of constants B

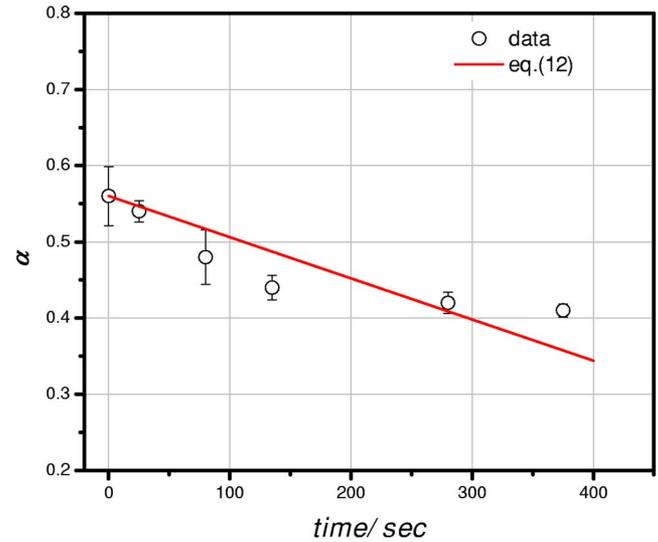


Figure 5. (Color online) The values of roughness exponent α obtained from the power law fits of the data in Fig. 2, $l \leq l_C$ for different electropolishing times. The solid line represents the best fit of α vs t dependence with linear regression (Eq. 12). The $\alpha_0 = 0.56$ is determined from the experimental data for $t = 0$ s and the coefficient B is the only fitting parameter ($B = 0.00058 \pm 0.00008$).

(in seconds to the -1), l_C (in micrometers), and Ψ (in micrometers per second) as

$$\lambda \approx \frac{1}{\frac{1}{2l_C} - \frac{B}{\Psi} \ln(l_C/l)} \quad [13]$$

The fit of the Eq. 13 to the data in Fig. 4 with coefficient B as the only fitting parameter is shown as a 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 linear fit of the data in Fig. 5. However, considering the experimental error bars (Fig. 2) and error bars of the fits, we can say that these results are in agreement and they support our analysis.

Conclusion

The morphology evolution of a 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 α 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 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, a 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

$$w(l \geq l_C, t) \approx w(l \geq l_C, 0) \exp\left(-\psi \frac{t}{2l_C}\right) \quad [14]$$

and

$$w(l \leq l_C, t) \approx w(l \leq l_C, 0) \exp\left(-\psi \frac{t}{\lambda}\right) \quad [15]$$

where λ is defined by Eq. 13.

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 fabricated using an electrodeposition through-mask process ($w_{\text{sat}} = 300 \pm 15$ nm, $l_C \pm 5$ μm). The obtained results were found in a good agreement with predictions of the developed function ($w_{\text{sat-measured}} = 91 \pm 6$ nm vs $w_{\text{sat-predicted}} = 95$ nm for $t = 100$ s), demonstrating the usefulness of our results for applications in different areas of microelectronics and MEMS fabrication.

Acknowledgments

This work is supported by NSF, Division of Industrial Innovation and Partnership (contract no. IIP 0638195) and the 2006 GEAR program at University of Houston.

University of Houston assisted in meeting the publication costs of this article.

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