

Scaling of Roughness in Silver Electrodeposition

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The electrodeposition of silver from thiosulfate solutions and its surface roughness are studied using scaling methods. Although silver electrodeposition from photographic fixing baths containing thiosulfate has been done successfully for many years, the vast majority of information about this process remains empirical. A comparison is made between plating silver from ammonium- and sodium-thiosulfate-containing solutions. Atomic force microscopy is used to study surface roughness, which is then analyzed by scaling methods. Silver electrodeposition from sodium-thiosulfate-containing solutions. The obtained scaling exponents, found after correction for local effects, depend strongly on the nature of the electrolyte; the growth exponents β are 0.13 and 0.71 for sodium and ammonium thiosulfate solutions, respectively. Local effects are observed only for the sodium but not for the ammonium thiosulfate solution. (© 2003 The Electrochemical Society. [DOI: 10.1149/1.1567267] All rights reserved.

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The goal of this work is to further the electrochemical and morphological understanding of silver electrodeposition from thiosulfate solutions. The recovery of silver from photographic fixing solutions is a well-established practice in the photographic industry. A comprehensive description of the mechanism of electrodeposition is complicated by the large number of variables that affect the process, including surface and local morphology, solution-surface interactions, solution chemistry, and transport mechanisms. In recent years, ammonium thiosulfate has been considered to replace sodium thiosulfate for environmental reasons.

This work represents the first attempt to obtain quantitative insight into silver electrodeposition that can be directly compared with other electrodeposited surfaces using scaling analysis. Scaling analysis of silver electrodeposited onto vapor-deposited silver substrates was done to gain a better understanding of the differences in plating from sodium and ammonium thiosulfate, in the presence of strong silver ion complexing agents. Empirical observations of silver plated from sodium and ammonium thiosulfate solutions indicate that the electrodeposits obtained from sodium thiosulfate solution are macroscopically smoother than those obtained from the ammonium-thiosulfate-containing solution. Atomic force microscopy (AFM) images of the surface topography were analyzed using scaling methods to gain insight into the differences in morphology and surface roughening.

Theory

Scaling methods have been used to identify the dominant growth processes during deposition and etching of vapor-deposited surfaces.¹ These methods have been used to study copper electrodeposition on gold in the presence of thiurea and benzotriazole,² copper deposition,³ dissolution,⁴ copper deposition with additives,⁵ and local effects in copper deposition.⁶ Silver electrodeposition has been extensively studied,⁷ as well as underpotential silver deposition,^{8,9} and roughness of silver electrodeposition from silver nitrate in water dioxane solutions.¹⁰ It has been shown that the nature of the electrolyte affects the structure of underdeposited silver. As yet, scaling analysis has not been applied to silver.⁹

The quantitative measure of surface roughness is obtained from the standard deviation of the perpendicular surface variation, σ , also known as the root mean square (rms) height of the surface

$$\sigma = \sqrt{\langle [H(x,y) - [\langle H(x,y) \rangle]]^2 \rangle}$$
[1]

where H(x,y) represents the height of the surface relative to the arbitrary plane, generally taken as the average value at the ordinates

x, *y*. The value of σ depends on the extent of the surface examined. For example, if the length scale used for the calculation of the rms height is chosen small enough to fall on top of an individual nucleus of growth, the value of σ will be much smaller than a value calculated for a larger surface region that includes a number of nuclei. If the length scale is small enough, placing it in two different areas of the surface, vastly different σ values can be observed. Measuring on the top of an individual nucleus, or on the side of a sharp peak gives very different results. Inherent in this analysis is the fact that as the length scale used to calculate σ increases, the value of σ also increases up to a certain magnitude and then levels off, unchanging as the analysis region is taken larger and larger. This saturation of σ is a characteristic of the system being studied. This scaling behavior provides considerable insight into the operative microscopic mechanism of electrodeposit growth.

The scaling behavior of σ is considered below. If the growing surface is such that H(r) is indistinguishable from $\kappa' H(\kappa r)$ for $\kappa' \neq \kappa$, then the surface is said to be self-affine. Self-affine objects change morphology when a scale change is made in all directions. If a scale change is made that is different for each direction, then self-affine surfaces do not change morphology. For self-affine surfaces, additional information can be extracted for the way in which σ scales with length. The rms of self-affine surfaces scales as¹¹

$$\sigma(L,t) = L^{\alpha} f(t/L^{\alpha/\beta})$$
[2]

where α and β are defined as the static and dynamic scaling exponents, respectively. The exponents α and β are also known as the roughness and growth exponents, respectively. The growth exponent characterizes the time-dependent dynamics of the roughness of the saturated interface.¹¹ The function $f(t/L^{\alpha/\beta})$ is defined so that $\sigma \propto L^{\alpha}$ for $t/L^{\alpha/\beta} \ge 1$, and $\sigma \propto t^{\beta}$ for $t/L^{\alpha/\beta} \le 1$. Self-affine surfaces are also characterized by a limiting value, denoted as ξ_L , which is the limiting value of σ for large analysis regions. The characteristic length, above which the rms height of the surface does not change, is known as the critical scaling length, L_c . For a self-affine surface, a plot of σ vs. L on a log-log scale yields a straight line with slope $0 < \alpha < 1$ for $L \leq L_c$. The roughness exponent, α , will be equal to 1 for a self-similar surface.

Huo and Schwartzacher⁶ have recently shown that for copper electrodeposition, an extra scaling exponent is required to characterize the time evolution of the local roughness

$$\sigma(L,t) = L^{\alpha} t^{\beta_{\text{loc}}} f(t/L^{\alpha/\beta})$$
[3]

The influence of local effects on the growth exponent β is applied here by calculating β_{loc} at a length scale well below the correlation length. This is done by selecting a length scale (*e.g.*, L=1,000 nm)

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Table I. Comparison of scaling parameters for silver electrodeposition from ammonium and sodium thiosulfate solutions to theoretical models.

Solution	Growth exponent β	Roughness exponent α	Growth exponent β corrected for local effects
Experimental results			
Ammonium thiosulfate	0.71 ± 0.05	0.62 ± 0.05	0.71 ± 0.1
Sodium thiosulfate	0.88 ± 0.05	0.36 ± 0.03	$0.13~\pm~0.08$
Continuum models			
Surface diffusion ¹¹	0.25	1.0	
Surface diffusion and step growth ¹¹	0.20	0.67	
KPZ equation ^{11,19,20}	0.25	0.39	
Ballistic ^{11,21,22}	0.23	0.3	

and log-plotting the roughness rms vs. time. The obtained β_{loc} is then subtracted from the experimental β to obtain the universal β .

Various models have been used to describe surface growth. Scaling parameters calculated from experimental data are commonly compared to results of continuum growth models to gain insight on surface growth. This is done even though the strict theoretical limitations required by continuum growth models are seldom entirely satisfied by actual experimental results. One commonly used model to describe surface growth is the Kardar, Parisis, and Zhang (KPZ) equation.^{11,17} The KPZ equation is given by

$$\frac{\partial h(\mathbf{r},t)}{\partial t} = v \nabla^2 h + \frac{\lambda}{2} (\nabla h)^2 + \eta(\mathbf{r},t)$$
 [4]

where *v* is the surface tension and $\nabla^2 h$ describes the relaxation of the interface caused by surface tension. The $(\nabla h)^2$ term reflects the presence of lateral growth and $\eta(\mathbf{r},t)$ is a noise term. The basic nature of the equation is that the growth rate at any point depends on the local surface geometry and stochastic noise.¹² The KPZ equation has been found to predict parameters that are close to experimentally observed results.¹³ The precise physical interpretation of the KPZ equation is still a topic of discussion, but is generally accepted to apply to cases where the dominant surface relaxation mechanism is not surface diffusion, as the equation does not conserve particle numbers.¹⁴ The equation does take into account smoothing processes on surfaces as the result of the filling in of recesses and the erosion of asperities.¹¹

A comparison between theoretical and experimentally obtained exponents provides a valuable perspective on surface growth. Table I gives the accepted roughness and growth exponents for the KPZ model, surface diffusion, and surface diffusion with step growth models. Huo and Schwarzacher⁶ attempted to explain anomalous scaling of the surface width during copper electrodeposition by introducing a local growth exponent β_{loc} , which was found to become significant when the rate approached the diffusion-limiting current in the electrolyte. The current data was obtained at a current density (0.8 mA/cm²) well below the diffusion-limiting current.

Experimental

The silver plating solutions were prepared by dissolving silver bromide into solutions containing sulfite and thiosulfate, because silver bromide is not soluble in water and must be complexed with thiosulfate. The ammonium thiosulfate plating solution contained 0.10 M of silver bromide, 0.20 M ammonium sulfite, and 0.25 M ammonium thiosulfate. The natural pH of this solution is between 6.8 and 7.2 and was not changed. The sodium thiosulfate plating solution contained 0.10 M of silver bromide, 0.20 M sodium sulfite, and 0.25 M sodium thiosulfate. In both solutions this represents a ratio of 2.5 moles of thiosulfate for every 1 mole of silver. A preplating solution containing 0.5 M of ammonium or sodium sulfate was used so that the thiosulfate solutions would not dissolve the silver off the vapor-deposited silver substrate at open circuit at the start of the experiment. All chemicals and silver wire were obtained from Aldrich in the highest purity available and were used without further purification. Millipore-Q water was used as the solvent in all experiments.

An AFM flow cell (Digital Instruments) was used as the reaction vessel for all experiments. A silver wire reference electrode was placed in the inlet port, the counter electrode was a silver wire placed in the outlet port, and a vapor-deposited silver substrate served as the working electrode. A silver wire was connected to the 0.30 cm² working electrode with silver epoxy (Chomerics, Woburn, MA). The anode, cathode, and reference electrodes were connected to an EG&G PAR model 273A potentiostat controlled by an IBM 386 computer using EG&G model 270/259 software. The cell was cleaned prior to each experiment by soaking in concentrated sulfuric acid and rinsing in Millipore-Q water.

Deposition times were used so as to pass 0.20, 0.25, 0.30, 0.35, 0.40, and 0.45 coulomb (C) of charge per cm^2 . The corresponding low thickness of the deposits was such that crystallization was minimized. A constant current density of 0.8 mA/cm² was used to ensure that the current distribution was fairly uniform, as confirmed by the uniform deposit thickness at various locations along the electrode. This low current density was chosen so as to prevent depletion of silver ions at the interface during electrodeposition. Flow analysis in the AFM cell has indicated that the flow at the center of the substrate was uniform.¹⁵ Consequently imaging of substrates for this work was done in the center between the inlet and outlet ports. The volume of the AFM flow cell is very small, below 0.5 mL. To maintain silver concentration in the bulk solution of the cell, the plating solution was delivered to the cell at a very low flow rate, on the order of 1 mL/min. This flow rate was enough to prevent depletion of silver ions, as monitored by the cathode potential, which remained constant throughout the experiments.

Vapor-deposited silver substrates were prepared at room temperature at a pressure of 1.5×10^{-5} Torr and an evaporation rate of 15.0 Å/s on 0.15 cm thick quartz. The resulting silver surface had a thickness of 2.0 μ m. Each substrate was 1×1 cm and all the substrates used in the experiments were made at the same time to insure uniformity from experiment to experiment.

Prior work by Schmidt et al.² with copper electrodeposition from copper sulfate was done in situ where copper was plated on gold substrates, imaged with the AFM, and then continued to be plated and imaged. Due to the slow capturing speed of the AFM scanning mechanism, this method does not allow for real time data acquisition. Unfortunately, thiosulfate is such a good silver solvent that the plating solution used here could dissolve the substrate, making the use of in situ methods impossible. As a result, the experiments were carried out such that each experiment used a total of six substrates, one for each level of silver plate. After electrodeposition, the surfaces were carefully and thoroughly washed and dried and were individually imaged using the AFM. It was expected that the oxidation of the surface due to exposure to air did not alter the surface morphology and roughness. Imaging with the AFM was done in contact mode, using gold-coated Si₃N₄ cantilevers from Digital Instruments.

Results and Discussion

Silver electrodeposition on evaporated silver surfaces from ammonium and sodium thiosulfate solutions was studied by galvanostatically depositing various amounts of silver and then imaging these surfaces using AFM. It was essential that the original substrate be as flat as possible so that this initial surface will have as little influence as possible on the electrodeposited surface characteristics. The rms of the original substrates was on the order of a few nanometers. Silver electrodeposition from ammonium thiosulfate solution.—Figure 1 contains $15 \times 15 \mu$ m AFM images of silver electrodeposited from ammonium thiosulfate solution. During the initial stages of electrodeposition, small nuclei are formed on the surface. These nuclei continue to grow by incorporation of adatoms diffusing toward them. Substantially fewer growth sites are observed, suggesting that smaller sites have combined to form larger growths. The number of growth sites significantly decreases when going from 0.20 to 0.45 C/cm² of charge passed, and these growth sites are seen to be taller and more lateral growth appears on the surface. As the amount of silver plating increases, the surface roughness increases and the sites become larger, probably due to the mechanism of Schwoebel barriers.

Analysis of the images for roughness was done using the AFM software.¹⁶ Each image was analyzed at different length scales, the largest being 15 \times 15 μ m, from which the rms height of the surface was found as a function of length scale. Especially for small length scales, up to 40 sites were measured and averaged. It was observed that increasing the number of sites beyond 40 did not affect the rms height results. Plots of the rms height *vs.* the length scale are included in Fig. 2. Each data point in the figure represents a different roughness measurement. For each surface the rms height increases with length and then levels off, so that the rms height does not change as the length scale is further increased. Each level of charge used is represented in the figure with a different symbol.

The saturation rms height was determined by averaging the last few data points in the saturation region. Figure 3 presents a logarithmic plot of the saturation rms height *vs*. the deposition time for the ammonium, as well as for the sodium thiosulfate systems. The slope of the resultant straight line is β , the growth exponent, which gives the time dependence of the total interface width. A linear regression analysis of the data was done to determine the slope, β =0.71. These results, as well as the results with the sodium system, are included in Table I. This β is significantly higher than the β associated with any of the continuum model values included in Table I, and probably associated with the large and rapid surface growth of a few selected points. The local growth exponent $\beta_{loc}=0$ was calculated according to Eq. 3 and hence the universal growth exponent remains $\beta = 0.71$.

The static scaling or roughness exponent, α , is determined by linear regression analysis of the slope of the log-log plot of rms height *vs.* length scale, in the region below the rms height saturation. An average was calculated for each of the six levels of charge passed $\alpha = 0.62 \pm 0.05$. This α corresponds best to that of surface diffusion and step growth ($\alpha = 0.67$) in Table I, indicating that silver electrodeposition from ammonium thiosulfate solution is a self-affine surface dominated by surface growth mechanism. Kahanda *et al.*¹² observed similar behavior for copper electrodeposition, where the value of α agreed well with a continuum model, but the value of β was significantly higher than predicted by any of the continuum models.

Silver electrodeposition from sodium thiosulfate solution.—Figure 4 contains $15 \times 15 \mu m$ AFM images of silver electrodeposited from sodium thiosulfate solution after the passage of 0.20, 0.25, 0.30, 0.35, 0.40, and 0.45 C/cm² of charge. Progressing from 0.20 to 0.45 C/cm², the number of nucleation sites decreases with increasing charge passed, and there are fewer, wider, and higher peaks present on the surface.

Plots of the rms height variation with length scale are included in Fig. 5. Each data point represents an individual roughness measurement. As was found with the ammonium thiosulfate system, the rms height increases with increasing measurement length scale for each of the surfaces and then levels off to the saturation rms height. The saturation rms height for each level of charge passed are plotted *vs.* deposition time in Fig. 3 for the sodium thiosulfate system. A linear regression of the data was done to determine the slope for this system, $\beta = 0.88$. This value is included in Table I along with results



Figure 1. Silver electrodeposits from ammonium thiosulfate solution at (a, top left) 0.20, (b, bottom left) 0.30, (c, top right) 0.45 Vertical scale: 1, μ m/div; horizontal scale: 5 μ m/div.

from the ammonium thiosulfate system. The value for β is relatively large, larger than any of the continuum models, and represents surface growth of a few selected points that rapidly increase the roughness of the surface. The local growth exponent $\beta_{loc} = 0.75$ was



Figure 2. Roughness rms vs. length scale for silver electrodeposition from ammonium thiosulfate solution with coverage of 0.20 to 0.45C.

calculated according to Eq. 3 and hence the universal growth exponent becomes $\beta=0.88-0.75=0.13.$

The static scaling or roughness exponent, α , is determined by linear regression analysis of the slope of the log-log plot of rms height *vs.* length scale, below saturation. The average calculated $\alpha = 0.36 \pm 0.03$. This level of α corresponds best to the KPZ model.^{17,18} This agreement suggests that for the sodium thiosulfate



Figure 3. Saturation roughness rms vs. deposition time for silver electrodeposition form ammonium and sodium thiosulfate solutions.



Figure 4. Silver electrodeposits from sodium thiosulfate solution at (a) 0.20, (b) 0.35, (c) 0.45 C. Vertical scale: 1 μ m/div; horizontal scale: 5 μ m/div.

system, the smoothing of self-affine surface is not dominated by surface-diffusion processes, but rather by the erosion of asperities and filling in of surface recesses.¹¹

Comparison of results from ammonium and sodium systems.—A



Figure 5. Roughness rms vs. length scale for silver electrodeposition from sodium thiosulfate solution.

comparison of the AFM images for silver electrodeposition from ammonium and sodium thiosulfate solution indicates some significant differences. At each level of charge passed, the surfaces plated from the ammonium thiosulfate solutions are rougher than those plated from sodium thiosulfate solutions. There are more nucleation sites on the initial surface plated from sodium thiosulfate than from ammonium thiosulfate solution. The surface plated from sodium thiosulfate has more nucleation sites, and they are noticeably smaller in magnitude. This trend is maintained throughout the series of images.

Figure 3 is a plot of saturated rms height for both the ammonium and sodium thiosulfate systems. The rms height is greater in magnitude for the ammonium thiosulfate system at all deposition times. The slope of the line through these points gives the growth exponent, which is larger for the sodium thiosulfate system than for the ammonium thiosulfate system. This suggests that the timedependent dynamics of the roughening process is greater for the sodium than for the ammonium thiosulfate system, which indicates that the surfaces plated from sodium thiosulfate are increasing in roughness with time faster than those plated from ammonium thiosulfate. This does not mean to suggest that silver plated from the sodium thiosulfate system is rougher, but rather that the increase with time is faster in the sodium system. The growth exponents, after being corrected for local effects, support this trend; the corrected β for the ammonium thiosulfate ($\beta = 0.71$) is significantly larger than that for the sodium thiosulfate-supported electrolyte $(\beta = 0.13)$. The incorporation of the rms height at a common deposition time helps to clarify that plating from the ammonium system is significantly rougher. The larger β for the sodium thiosulfatesupported electrolyte appears to be due to local effects (diffusionlimited current) as evident by the large $\beta_{loc} = 0.75$. Ammonium ion is known to complex silver ion, although the complexation is weaker than that of the anionic thiosulfate.

The value of the roughness exponent, α , is larger for the ammonium thiosulfate system. This suggests that the growth process for silver electrodeposition from the ammonium thiosulfate system is more dominated by surface diffusion and step growth than plating from the sodium thiosulfate system. The value of α for the sodium thiosulfate system corresponds closely with what would be predicted by the KPZ equation.

Exchange current density results²³ indicate that sodium ions slow down the kinetics as indicated by the lower value of the exchange current density for the sodium thiosulfate system. This lower value of i_0 would result in a larger surface overpotential, which contributes to a smoother deposit from the sodium thiosulfate system.

Incorporating the rms height at a particular point of deposition, *e.g.*, the saturation rms height of the system after the passage of 0.35 C of charge, shows that the level of roughness in the ammonium system was 44% greater in magnitude than in the sodium system. This parameter can be used to make further comparisons of surfaces, especially when the differences are less obvious.

Different β_{loc} are obtained for the sodium and ammonium thiosulfate systems, 0.75 and 0, respectively. The universal β , corrected for local effect, are therefore 0.13 and 0.71, respectively. It is not clear why the local effect, which depends on the proximity to the diffusion-limiting current, is significant in the sodium thiosulfate system and is insignificant in the ammonium thiosulfate system. Ammonium ion is known to be a complexing agent for the silver ion, however its complexing strength is weaker than that of the thiosulfate ion. This might explain the difference in roughness and roughness exponents, especially since the thiosulfate-complexed silver ion is negatively charged, while the ammonium-complexed silver is positively charged. Chen *et al.*⁹ also observed that, during underpotential deposition of silver on gold, the structure of the Ag monolayer depends on the nature of the electrolyte.

Discussion

The growth of silver surfaces by electrodeposition from the two thiosulfate solutions cannot be explained in terms of the simplistic models like equivalent weight, KPZ, or the molecular beam epitaxy models of surface diffusion. Indeed, in none of the systems we looked at, did both scaling exponents α and β simultaneously fit the values of any of these models. Moreover, the widely different exponents found for deposition from ammonium and sodium thiosulfate solutions and from no thiosulfate at all, imply that the notion of universality fails in these systems. The scaling exponents change from system to system and thus do not fall into a few universal classes. The reasons for that are not well understood but could originate from the following phenomena:

I. Nonlocal growth.—All the above theoretical models assume that the growth rate at a point depends only on few lower derivatives of the surface height at that point. However, the interaction between the ion and the surface boundary extends to a finite range given by the screening length. Thus, depending on the extent of the screening length, the assumption of locality might not apply. If the length is large, local tips will grow even faster, resulting in rougher surfaces (in the extreme case of large screening length, this effect gives rise to diffusion-limited aggregation clusters which are full fractal and not just self-affine).

2. *Crystallization.*—If the deposited metal crystallizes, then the size of the microcrystals is another important length scale of the system. In the present work, we extracted the exponents in the regime in which the correlation length is larger than the microcrystalite size. In this regime, the paradigm of an amorphous self-affine surface may still apply, but with a local correction (due to the crystal formation) just as we find for the sodium system.

3. Convection.—The motion of the ions toward the surface is accompanied by a convective motion of the electrolyte. Near the surface these convection flows have a component parallel to the surface as well. The effect of the convective flow on the surface morphology has not been elucidated yet, although we observed that the flow affects the scaling exponents.²³

Other phenomena may also contribute to the failing of universality in our systems. The surface diffusion of silver adatoms was measured by Porter and Robinson²⁵ at the Ag(111)/water interface and

was found to be similar to that obtained in ultrahigh vacuum, indicating little effect of the liquid water. The surface-diffusion length was estimated at $>40 \ \mu m$. The observed exchange current at atomic steps was found to be ten orders of magnitude higher than at the planar surface,²⁵ which might contribute to the disagreement among scaling exponents and the lack of universality in the present work.

It is important to make it clear that the KPZ model and the Schwoebel effect have no relation to each other. Indeed, the Schwoebel effect is present only in crystalline growth. Its origin is in the energy barrier for an adatom from one terrace to fall down the stair to a lower terrace. Since no such barrier exists for an adatom of the lower terrace to diffuse and stick to the step (and effectively extending the upper terrace) the Schwoebel effect is responsible for a bias in the diffusion from the lower terrace to the higher one. On a coarse-grained scale this gives rise to an effective flux of adatoms in the direction of elevating height.

The KPZ model describes a surface which grows locally in the normal direction to itself. On a coarse-grained scale it gives rise to a term proportional to the square of the local gradient, resulting in a higher growth velocity for the surface segments with higher slopes. Crystalline surfaces do not grow in the normal direction and thus are not described by the KPZ model (note that in crystalline models used in simulations, like the ballistic deposition and the Kim-Kosterlitz models,²⁶ the effect of lateral growth is achieved through nonrealistic growth rules).

In the early stage of electrodeposition, competition between nucleation and growth determines the granularity and roughness of the surface.²⁴ The forms of the growing crystals determine the structure and appearance of the deposit. The subsequent growth of crystalline faces depends on the orientation of the seed crystal. The growing front in the case of silver can be one of the close-packed faces of the single-crystal: octahedral (111), cubic (100), or rhombododecahedral (110). The emergence points of the screw dislocations emerge as growth pyramids. Quadrangular pyramids are obtained from Ag(100), whereas triangular pyramids are obtained from Ag(111). The slope of the growing pyramids depends on the current density employed.²⁴ Indeed, upon prolonged silver electrodeposition, especially subjected to periodic partial dissolution, crystalline pyramids were observed.

Conclusions

Comparison of silver electrodeposition from sodium and ammonium thiosulfate solutions after the passage of 0.20 to 0.45 C/cm² of charge shows that silver electrodeposition from ammonium thiosulfate solutions produced noticeably rougher surfaces than those plated from sodium thiosulfate solutions when comparing surfaces after the passage of the same charge.

Comparison of the roughness exponent, α , for these two systems suggests that the difference in roughness is due to the fact that the ammonium system is surface-diffusion-limited while the sodium thiosulfate system is dominated by the erosion of asperities and filling in of surface recesses. This difference is determined by the agreement of α for the two systems with accepted continuum models. The values for β obtained for silver electrodeposition in these two systems do not correspond well to any of the continuum models. This suggests that there are important factors involved in the electrodeposition process that are not being taken into account in the continuum models. The lower exchange current density, found for plating from sodium thiosulfate, might contribute to this difference.

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