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The Effect of Rate of Surface Growth on Roughness Scaling

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The effect of rate of deposition on the scaling properties of roughness during surface growth is studied by silver electrodeposition in a flow cell and atomic force microscopy measurements. The rate of growth is controlled by the applied current density. The Ag-electrodeposited surface becomes rougher as the current density increases, approaching the diffusion limiting current. Furthermore, as the current density increases, the number of growth sites decreases and the lateral surface features become wider. Scaling analysis of the self-affine surface indicates that the saturated root-mean-square height increases with increasing current density, over a range of 2 decades; however, below saturation, the dependence is more complicated: Initially, there is no local effect; however, as the rate increases, negative local effect is observed, indicating that the local roughness grows more slowly at higher rates, as the current approaches the diffusion limiting current in the electrolyte. The discrepancy between the obtained average roughness exponent $\alpha = 0.52$ and the growth rate exponent $\beta_r = 0.3$, similar to experiments under low deposition rate and for various deposition times ($\alpha = 0.62$, $\beta_t = 0.71$), indicates that the rate plays a decisive role in the selection of the growth kinetics by affecting the initial number of nucleation sites and their subsequent merge. Only at low rates, the rate and the time of growth behave interchangeably, and therefore the roughness scales with the average height, the product of the rate, and the time of growth.
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Kinetic roughening of self-affine surfaces has been the subject of intense investigation during the last decade. Surface growth represents an example of scaling of nonequilibrium systems, where the main issue is the establishment of scale invariance and universality, as has been observed in equilibrium critical phenomena and nonlinear dynamics. Surface roughness has been studied primarily from the point of view of scaling behavior,[1-5] surface width,[6] height velocity,[4] maximal height,[7] and cyclical surface growth,[8-10] among others. The effect of growth rate has been recently addressed[11] for the case of kinetic roughening in polymer film growth by vapor deposition. The growth rate was controlled by the pressure of the deposition chamber. It was found that the scaling behavior did not change for growth rate spanning almost 1 order of magnitude,[11] despite the fact that the rate at which material arrives at the surface is expected to affect the kinetic roughening. The effect of the growth rate of the surface on its scaling properties has not been extensively studied, mainly because it is usually difficult to control the rate of growth. Electrodeposition offers a convenient way to investigate this effect because the rate of growth can be easily controlled and manipulated by the applied current. The rate of growth is directly proportional to the current density through Faraday's law. Thus, the scaling exponents obtained from experiments conducted under various current densities (under constant deposition time) can be compared with scaling exponents obtained from experiments conducted under various growth times (under constant current density). Agreement or disagreement between the obtained scaling exponents could reveal the unique role of the rate in determining the growth mechanism. The effect of the current density on roughening scaling was attributed to local growth exponent,[12] which becomes significant as the surface growth rate approaches the diffusion-limiting current from the bulk.

Self-affine growing surfaces can be described by scaling analysis of the surface roughness. The width of the surface $W(L,t)$, where L is the spatial size and t is the time, is defined by

$$W(L,t) = \langle [h(r,t) - \langle h(r,t)\rangle]^2\rangle^{1/2} \qquad [1]$$

and it scales as

$$W(L,t) \sim L^{\alpha} f(L/t^{1/z}) \qquad [2]$$

where f is the scaling function. For large time $t \gg L^z$

$$W \sim L^{\alpha} \qquad [3]$$

while for $t \ll L^z$

$$W \sim t^{\beta} \qquad [4]$$

where $\beta = \alpha/z$ is the growth exponent. It is expected that all processes with the same universality class share the same critical exponent.

In the present paper, we focus on the effect of growth rate on the scaling exponents of electrochemically deposited growing surfaces. The growth rate can be easily maintained and manipulated by the applied current density. For electrodeposition, it is proposed here that the roughness scales as before with the length and with the average thickness of the deposited layer, rather than simply with the time

$$W(L,h) = L^{\alpha} f[L/(h)^{1/z}] \qquad [5]$$

The average thickness under constant growth rate (or constant current density) is given by

$$h \propto it \qquad [6]$$

where i is the current density (rate of growth) and t is the electrodeposition time. Then, the width scales with the lateral length and current density according to

$$W(L,it) = L^{\alpha} f[L/(it)^{1/z}] \qquad [7]$$

If the time of electrodeposition is maintained constant, then

$$W(L,i) = L^{\alpha} f[L/i^{1/z}] \qquad [8]$$

Thus, for current density $i \gg L^z$

$$W \sim L^{\alpha} \qquad [9]$$

while for $i \ll L^z$

$$W \sim i^{\beta} \qquad [10]$$

where $\beta = \alpha/z$ is the growth exponent. This is expected under constant time, and as long as the current is significantly lower than the diffusion limiting current (no diffusion effect).

Thus, by logarithmically plotting the root-mean-square (rms) of the height as a function of the length, one can obtain the roughness exponent α (Eq. 9), and by logarithmically plotting the saturated rms height as a function of the current density, under constant deposition time, one can obtain the growth exponent β_r (Eq. 10). These exponents then can be compared with the time exponent β_t obtained under constant current density and for various deposition times (Eq. 4). An agreement between the growth exponents will indicate that

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the surface roughness scales with the current density, the growth rate of the surface, and the roughness scales with the average height, Eq. 5. A disagreement will indicate that the roughness scales with the rate in a more complicated way, as the rate determines the various growth kinetics regimes.

Silver electrodeposition from its thiosulfate solution was selected to test the effect of growth rate on roughness scaling because silver reduction is a relatively simple one-electron reaction and well-studied system. The subject of silver electrodeposition has been previously reviewed.[13]

Experimental

Experiments of surface growth were conducted in a flow channel by silver electrodeposition from silver thiosulfate solution

$$[\mathrm{Ag}(\mathrm{S_2O_3})_2]^{3-} + \mathrm{e} = \mathrm{Ag}^0 + 2\mathrm{S_2O_3^{2-}}$$

The plating solution was prepared by dissolving 0.1 M AgBr in solution containing 0.20 M ammonium sulfite and 0.25 M ammonium thiosulfate or sodium thiosulfate in Millipore-Q water. The ratio of 2.5 mol of thiosulfate to every mole of silver was chosen to ensure that all the silver ions were complexed by the excess thiosulfate ions. The natural pH of this solution is around 7, and was not adjusted. The electrodeposition was performed in a glass flow cell to ensure adequate supply of silver ions and to minimize any diffusion limitations. The current efficiency for silver deposition was close to 100%, eliminating the possibility of any side reaction. Silver substrates served as the cathodes for the electrodeposition experiments. The 1 × 1 cm substrates, prepared from pure silver (99.999% Alfa Aesar, Inc.), were polished down to 50 nm with alumina, rinsed in an ultrasound water bath, and fitted into the bottom of the flow cell. Platinum foil served as the anode facing the silver cathode.

The AFM flow cell (Digital Instruments), 10 cm long, 0.5 cm wide, and 0.25 cm high and horizontally placed, served as the electrodeposition cell. The electrodeposition occurred at the cathode facing up. The counter anode was made of silver sheet. Constant currents of 0.2-8 mA/cm^2 for a period of 1250 s were applied by a PAR 273A potentiostat using EG&G 270/259 software. Experiments were also conducted under constant current density of 0.8 mA/cm^2 for various deposition times of 800-2000 s (which correspond to charge passed of 0.2-0.45 C/cm^2.) Before use, the glass flow cell was rinsed with 97% sulfuric acid and Millipore-Q filtered water. The plating solution was continuously fed into the flow cell by gravity from an elevated reservoir, and the flow rate was maintained at 65 cm^3/min, which corresponds to a linear velocity of 11 cm/s, parallel to the surface. The corresponding Reynolds number was 300, clearly within the fully developed laminar flow regime. All experiments were conducted under constant flow velocity, and the current density varied between 1 and 10 mA/cm^2. The electrodeposition time was held constant at 1250 s, which corresponds to average deposit thickness of 1.3-13 μm, while for the constant current experiments (0.8 mA/cm^2), the electrodeposition time varied from 800 to 1200 s.

The roughness of the electrodeposited silver surface was measured after each experiment by imaging the surface on a Digital Nanoscope III atomic force microscope (AFM), operated in a contact mode. Gold-coated pyramidal NanoProbe Si_3N_4 tips mounted on a gold-coated v-shaped cantilever were used to image the surface. The correction for the tilt distortion was applied and the image files were exported as text files to a spreadsheet program for numerical calculations of surface roughness at each pixel.[14]

Results and Discussion

The purpose of this work was to determine the effect, if any, of rate of growth on the roughness of electrodeposited surface, and to compare the obtained scaling exponents with those obtained under constant growth rate. The maximum rate of deposition can be found by measuring the limiting current density, which is the rate controlled by diffusion in the electrolyte. Figure 1 shows the limiting current density for the cell under a flow velocity of 11 cm/s, which corresponds to a Reynolds number of 300. The limiting current is measured at 19 mA/cm^2; thus, all experiments were conducted substantially below the limiting current density and consequently diffusion in the fluid plays little effect.

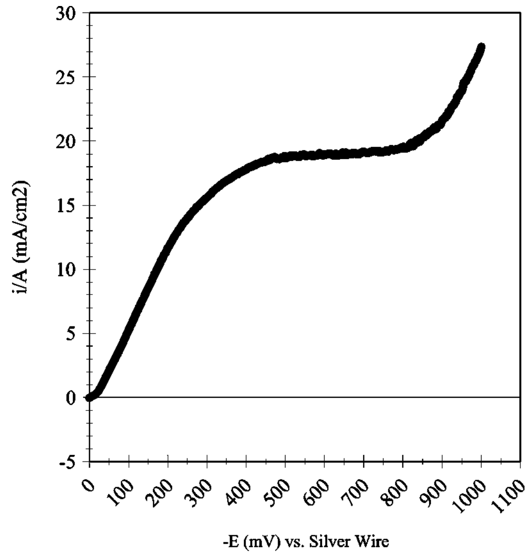

Figure 1. Limiting current density for silver electrodeposition under flow rate of 1.08 cm^3/s (Reynolds number is 300).

Figure 2 shows the AFM images of four surfaces under the various current densities. As the current density increases, the number of deposition sites decreases and the surface becomes rougher, as indicated by the higher measured rms of the surface roughness. The decrease in the number of bumps can be accounted for by the merging of roughness features, because in high current experiments the amount of deposited silver was the highest.

Figure 3 shows the logarithmic plots of the rms roughness versus length scale for silver electrodeposition under various current densities. The initial slopes are quite similar, resulting in an average roughness exponent of $\alpha = 0.52 \pm 0.11$, although the slope at the highest current density of 8 mA/cm^2 is significantly steeper, probably because the amount deposited was higher and merging of features occurred. It is not clear why at small correlation lengths the roughness for 8 mA/cm^2 is lower than that for 4 mA/cm^2, although the corresponding saturation roughness increases monotonically with current density, as expected,[11,12] indicating that the surface becomes rougher at higher growth rates. It is quite possible that because the magnitude of the roughness measured here is relatively high (>100 nm), hence the aspect ratios at small correlation lengths is relatively high. This might prevent the AFM tip from accurately measuring the roughness at very small correlation lengths.

Figure 4 shows a plot of the saturated roughness as a function of the current density. The increase in saturated roughness with rate is monotonic, as expected.[11,12] The slope, according to Eq. 10, gives a growth exponent $\beta_r = 0.30$.

For comparison, Fig. 5 and 6 show similar plots for silver electrodeposition at constant current density of 0.8 mA/cm^2 and under various deposition times: 800-2000 s.[10,13] Again, monotonic increase of roughness with time is observed only for the saturation region. The roughness exponent for these experiments was obtained as $\alpha = 0.62 \pm 0.05$ and the average growth exponent was found to be $\beta_t = 0.71 \pm 0.10$.[10,13] The slightly different slopes in Fig. 6 are probably due to the complexing ability of ammonium ion in comparison to the sodium ion. It appears that the growth exponent depends on the rate in a complicated way. Huo and Schwarzacher[12] 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 ap-

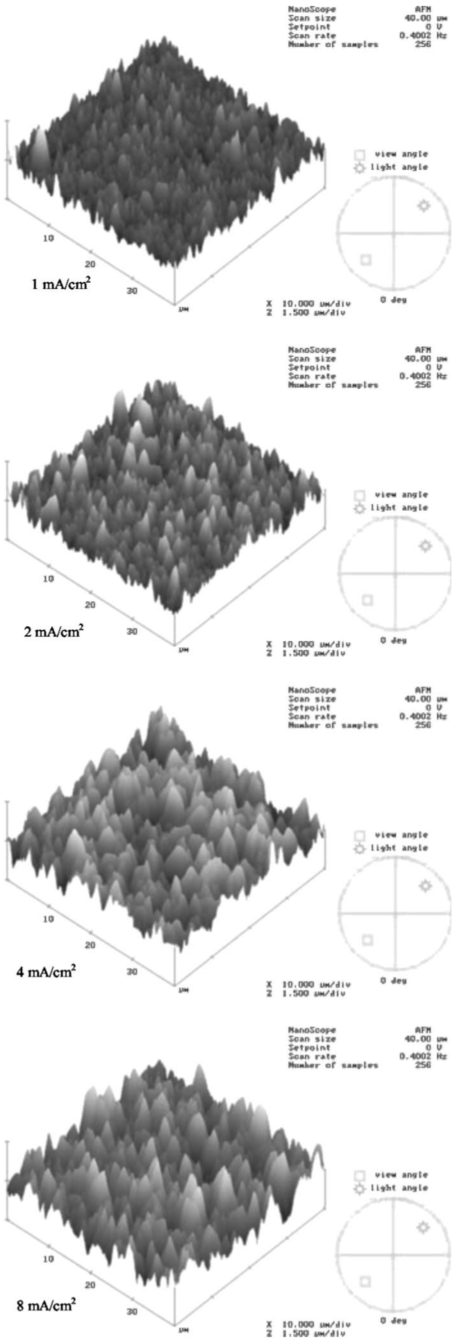

Figure 2. AFM images of silver electrodeposition under various current densities: 1, 2, 4, 8 mA/cm^2.

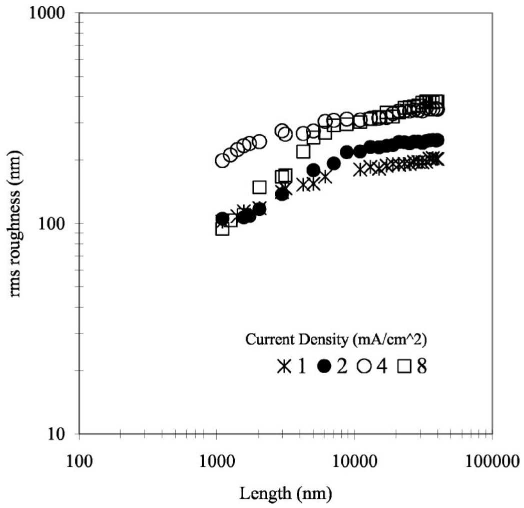

Figure 3. Logarithmic plot of surface roughness *vs.* current densities: 1, 2, 4, 8 mA/cm^2.

proached the diffusion-limiting current in the electrolyte. Similar analysis of the current data resulted in $\beta_{\text{loc}} = 0$ at low rates ($i < 2$ mA/cm^2), because in this range, the employed current densities were well below the diffusion limiting current of 19 mA/cm^2, as shown in Fig. 1. For higher rates ($i = 4$-8 mA/cm^2), a negative local growth exponent is observed, $\beta_{\text{loc}} = -0.61$, indicating that the local roughness grows more slowly as the rate of deposition starts to approach the diffusion-limiting current. The growth exponent for the higher current regime is calculated as the difference between the experimental and the local growth exponent: $\beta = 0.30 - (-0.61) = 0.91$. Both experiments, at constant time and at constant rate, establish the lack of local growth effect at low rates of growth, in agreement with Huo and Schwarzacher,[12] who related the local effect to the effect of diffusion in the electrolyte, which is expressed by the fraction of the limiting current. The disagreement between the present rate growth exponent $\beta_r = 0.3$ and the time growth exponent $\beta_t = 0.71$ indicates that the roughness scales with the growth rate and with the growth time in a dissimilar way. Zhao *et al.*[11] concluded that the scaling behaviors of the growth front, in the case of polymer deposition, do not change for growth rate spanning almost 1 order of magnitude. This apparent discrepancy can be resolved if one looks into the rates involved. The polymer growth rates from the vapor phase in Ref. 11 ranged from 5.5 to 13.9 nm/min, while the present current densities for silver deposition correspond to much higher rates of 100-1000 nm/min. In addition, silver deposition from a liquid phase is expected to be more diffusion limited than in the case of vapor deposition; thus, the local effect is expected to be more pronounced.[12] Using SEM cross-sectional studies of copper electrodeposition, Kang and Gewirth[15] showed that identical scaling parameters do not necessarily ensure identical growth mechanism. This might be true in the present case, especially at the highest current density of 8 mA/cm^2, where the slope below saturation is

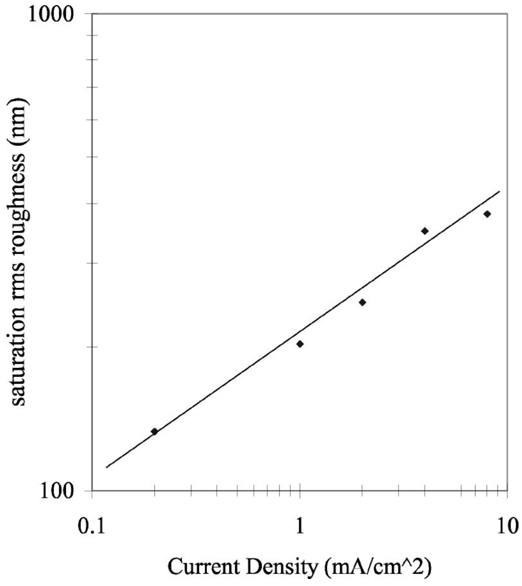

Figure 4. Logarithmic plot of saturation rms roughness *vs.* various current densities: 1, 2, 4, 8 mA/cm^2.

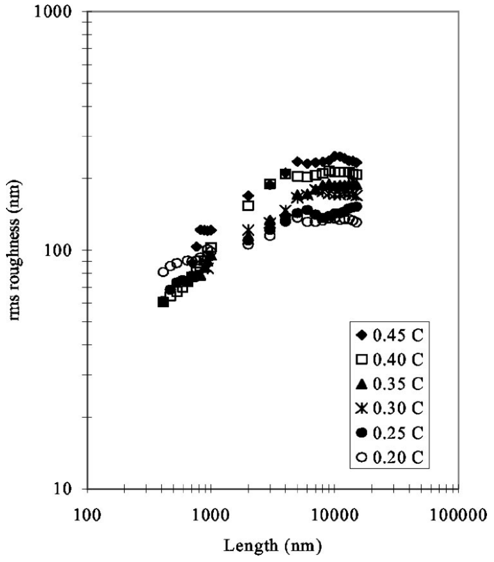

Figure 5. rms roughness *vs.* length scale for various deposition times (800-2000 s) under constant current density 0.8 mA/cm^2.

significantly steeper (see Fig. 3), resulting in a higher α value at higher rate and indicating different mechanism of merging of roughness features, as has been observed in copper electrodeposition.[14] The scaling of the saturation roughness with the average height (i times t), observed for silver electrodeposition in the presence of either sodium or ammonium thiosulfate, resulted in a growth exponent based on the average height, of $\beta_h = 0.36$. The growth exponent predicted from the ballistic and the KPZ models is 0.23 and 0.25, respectively.[2]

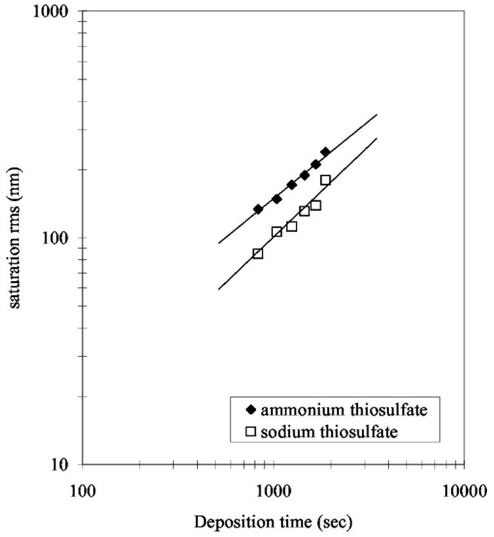

Figure 6. Logarithmic plot of saturation rms roughness *vs.* deposition time under constant current density of 0.8 mA/cm^2.

The effect of the growth rate might have been more highlighted by comparing the time growth exponents under various growth rates, rather than by the present approach of comparing the time and the rate growth exponents; however, this comparison requires a large number of experiments which the present approach is attempting to avoid. It should be pointed out that the range of average height in the constant time experiments (1.25-10 C/cm^2) is higher than the range in the constant current experiments (0.64-1.6 C/cm^2); however, this difference has little effect on the calculated exponents because the saturation roughness was achieved much earlier.

Conclusions

The effect of growth rate on the roughness scaling was studied using silver electrodeposition and AFM roughness measurements. As the growth rate is increased, the surface becomes rougher with larger lateral feature size. The obtained roughness exponent $\alpha = 0.52$ is in good agreement with a value of 0.62, obtained from silver electrodeposition under constant current.[10] It slightly increases with increasing the current density. The rate growth exponent $\beta_r = 0.3$, obtained over 2 decades from the dependence of the roughness on the current density, is in disagreement with $\beta_t = 0.71$, obtained under constant rate and various times, indicating that the rate of growth affects the kinetics of roughness growth. Even after correction for local effects, it is found that the rate determines the scaling exponents by affecting the initial number of nucleation sites and their subsequent merge. The scaling analysis of the self-affine surface indicates that the roughness scales with the average height of the growing surface, in accordance with Eq. 10 and the growth exponent is $\beta = 0.36$.

Acknowledgments

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