Columnar Growth and Kinetic Roughening in Electrochemical Deposition

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We performed electrochemical deposition of copper at very slow rates so that local growth effects such as surface relaxation and stochastic noise can compete with the nonlocal Laplacian effects. We observed that the initial growth pattern is consistent with the conventional Mullins-Sekerka instability. This is followed by coarsening and roughening of the surface that leads to a columnar structure with deep crevices. The surface roughness for length scales below the typical column width shows a power-law behavior with an exponent $\alpha=0.55\pm0.06$, consistent with the prediction of Kardar, Parisi, and Zhang (KPZ). However, the time dependence of the total interface width is not the $t^{1/3}$ power law predicted by KPZ.

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The growth of rough and fractal surfaces is a subject of much practical importance and fundamental interest [1]. Theoretical studies fall into two classes [2]. The first one treats mainly *nonlocal* effects such as those occurring in all the Laplacian growth phenomena: diffusion limited aggregation (DLA) and directional solidification, etc. They emphasize how the growth at any point on the surface can affect the growth everywhere else through a Laplacian field in the bulk. The other class of theories treats mainly local effects such as those occurring in reaction-limited aggregation (RLA), the Eden model, and kinetic percolation. Transport current in the bulk is assumed to be irrelevant and the growth rate at any point is assumed to be controlled by local mechanisms such as reaction rates, surface relaxation rates, and stochastic noise. A common approach is to write down Langevin equations to describe the continuous space-time evolution of the interface. One of the best known examples is the Kardar, Parisi, and Zhang (KPZ) equation [3] in which a single-valued function $h(\mathbf{x},t)$ describes the height profile above a basal plane with coordinates $\mathbf{x}$ and its time evolution obeys the equation

$$\frac{\partial h}{\partial t}=\gamma\nabla^2 h+\frac{\lambda}{2}|\nabla h|^2+\eta(\mathbf{x},t)\,. \qquad (1)$$

Here, the γ term represents surface tension, the λ term represents lateral coarsening, and $\eta(\mathbf{x},t)$ is a white noise. Depending on what other physical mechanisms one might want to consider, other derivatives of h and different noise functions may be included. The essence is that the growth rate $\partial h/\partial t$ at any point depends only on the local surface geometry and a stochastic noise. Clearly, these two classes of theories represent idealized limits and surface growth in physical systems is likely to have both local and nonlocal effects.

Electrochemical deposition is an ideal system for studying the competition between local and nonlocal growth effects. The reason is that, at low current densities, the deposition rate is limited by the activation of cations in the double layer over a potential barrier caused by the intervening water molecules. As such, the addition of atoms to the surface is similar to the RLA or Eden models to which the KPZ equation was intended to apply. At high current densities, the cations in the double layer are depleted and the growth is controlled by mass transfer in the electrolyte by migration and diffusion currents. Growth patterns in this regime have been extensively studied by both electrochemists [4] and physicists [5-11] and they are among the best known examples of Laplacian growth phenomena. Earlier experiments on the deposition of zinc and copper have found a variety of dendritic and fractal patterns and there is a characteristic noise spectrum associated with each [9]. The cause of the different behavior is still not fully understood. The resistance of the deposits [7] and electrolyte convection [11] are believed to be important factors. Even excluding such complications, Suter and Wong [9] have noted that the variation of growth velocity (v) results in a competition between the migration and diffusion currents, and that could lead to different growth patterns. To gain more insight into this problem, we have chosen to study the growth phenomena in the low velocity limit to see how the local effects might compete with the nonlocal effects. Compared to previous experiments that covered a range of v above 1 mm/h, we worked with velocities in the range $0.2>v>0.01$ mm/h ($54>v>2.7$ nm/sec).

Slow deposition experiments had previously been attempted by Kahanda and Tomkiewicz (KT) using zinc and $ZnSO_4$ solutions [10]. Unfortunately, because the potential for zinc deposition is very close to that for hydrogen evolution, the growth was always interrupted by the appearance of hydrogen bubbles at the cathode. For this reason, we have chosen to deposit copper from $CuSO_4$ solutions. Since our goal is to observe the roughening of a surface due to local growth effects, we use a linear working electrode (WE) in a quasi-2D rectangular cell similar to the one used by KT. The WE (cathode) is a 25-μm-thick copper foil sandwiched between two horizontal acrylic plates of dimensions 13 mm×25 mm. The straight edge of the foil is exposed along one of the short sides as the initial surface for growth. The counter electrode (CE, anode) is a copper rod placed in a fluid well connected to the opposite side of the cell. It has a large contact area with the electrolyte so that the surface current density is low enough to avoid any anomalous effect. A micro standard calomel electrode (SCE) is placed 5 mm in front of the WE off to one side. It acts as a reference electrode (RE) to control the interfacial bias voltage on the WE. $2M$ $CuSO_4$ solution fills the thin gap of the cell and the well that holds the CE. This near-saturation concentration minimizes the resistive voltage drop between the working and reference electrodes so that the WE-RE voltage is as close to the true interfacial voltage as possible. The deposition was controlled by a Solartron 1286 electrochemical interface operated in the three-terminal potentiostatic mode such that the cell voltage (WE-CE) is adjusted by a feedback circuit to keep the interfacial voltage (V_i) between the WE and RE constant. The rest potential (V_0) of Cu is +0.099 V relative to SCE. We applied small overpotentials η (defined as $\eta \equiv V_i - V_0$) between -0.1 and -0.5 V such that the deposition currents were in the range of 0.1-0.5 mA.

The evolution of the interface profile is recorded by a video microscopy imaging system. The image is captured by a charge-coupled-device camera with 610×490 (H $\times$V) pixel resolution. The camera output can be either recorded by a SVHS video recorder or sent to an image digitization board in a microcomputer for direct frame-by-frame time-lapse digital recording. The digitized image has 640×480 square pixels. The highest resolution of the system is 1 μm/pixel. In most cases, we used a resolution of 4.9 μm/pixel so that the optical illumination would not heat up the cell. This gives a field width of 2.35 mm for 480 pixels. To record the interface geometry over the entire 13 mm length of the WE, we mounted the microscope on a horizontal linear positioning track to capture the entire interface in six separate video fields. The two outer fields were discarded because of edge effects of the cell. The four inner fields cover a total width of 8.8 mm and they can be printed on a 300 dpi laser printer.

Figure 1 shows the time series of the interface profiles for four different values of η. Figure 1(a) corresponds to $\eta = -0.5$ V. Successive profiles are separated by 15-min intervals. They show the developments of usual DLA-like branching structure except that, given the rather slow growth rate, the widths of the branches are comparable to the spacing between them. The deposit and the empty space appear to have a reversal symmetry and the pattern is *critical* in the sense that a slight decrease in η would destroy the DLA-like pattern. Figure 1(b) shows that the pattern at $\eta = -0.35$ V exhibits a columnar morphology. This is due to the fact that the coarsening of the initial tips causes them to merge with neighboring ones leaving some holes behind. Such columns can never grow tall enough above the neighboring ones to develop side branches. In the context of the KPZ equation, we can say that the lateral growth mechanism modeled by the λ term in Eq. (1) is of dominant importance. Qualitatively the same behavior is seen in Figs. 1(c) and 1(d) for which $\eta = -0.25$ and -0.15 V, respectively. They all show columns of comparable width with noise-induced surface roughness. These columns are separated by narrow crevices that can be closed off as the neighboring columns merge. Additional experiments were performed at $\eta = -0.1$, -0.2, -0.3, and -0.4 V and similar behavior was observed.

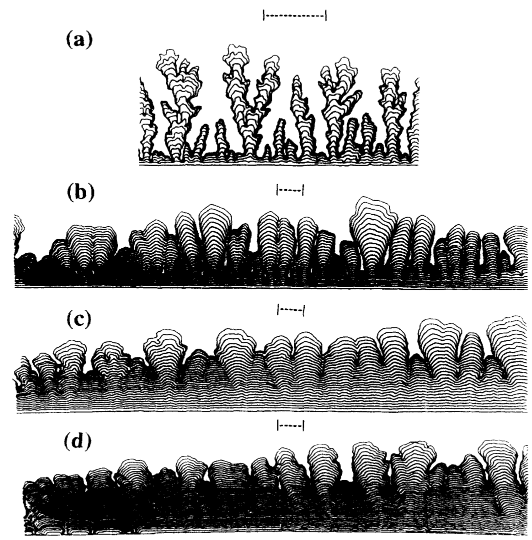

FIG. 1. Time-lapse interface profiles for different overpotentials. (a) $\eta = -0.5$ V, 15-min intervals, 5 h total; (b) $\eta = -0.35$ V, 1-h intervals, 25 h total; (c) $\eta = -0.25$ V, 2-h intervals, 50 h total; (d) $\eta = -0.15$ V, 2-h intervals, 76 h total. Scale bar is 0.5 mm.

In order to quantify the pattern to compare with the predictions of KPZ [3] and the linear stability theory of Laplacian growth [2,12], we construct a single-valued height profile $h(x)$ by taking the highest point for each horizontal position x and calculate its power spectrum $S(k) \equiv \langle |F(k)|^2 \rangle$, where $F(k)$ is the Fourier transform of $h(x)$. Figure 2 shows the log-log plot of $S(k)$ vs k for the $\eta = -0.25$ V interfaces in Fig. 1(c) at different times. It is striking to observe that $S(k)$ approaches a power law at late times which implies that the interface has a self-affine roughness, i.e., it has a root-mean-square width w_L that increases with the linear size L according to a power law $w_L \propto L^\alpha$ with $\alpha < 1$ and $S(k) \propto 1/k^{1+2\alpha}$ [1]. Since the cell thickness (δ) is about 25 μm, and the column width (W_c) is about 500 μm, we performed least-squares fits to determine the exponent α over the range $0.01 < k < 0.25$, which corresponds to wavelengths λ in the range of $\delta \lesssim \lambda \lesssim W_c$. The six fitted lines in Fig. 2 give α values between 0.52 and 0.58, each with a statistical error about ± 0.03. Thus we estimate that $\alpha = 0.55 \pm 0.06$. Similar fits for interface profiles obtained for other values of η all resulted in α's between 0.5 and 0.6. This variation is partly statistical because it is impractical to perform a large number of runs for these very slow experiments. There is little doubt that the underlying columnar structure over long length scales also introduced some systematic errors that could not be easily estimated. Nevertheless, it is noteworthy that KPZ predict $\alpha = 0.5$ in 2D, which is within our estimated error limits.

KPZ also predict that the total interface width W

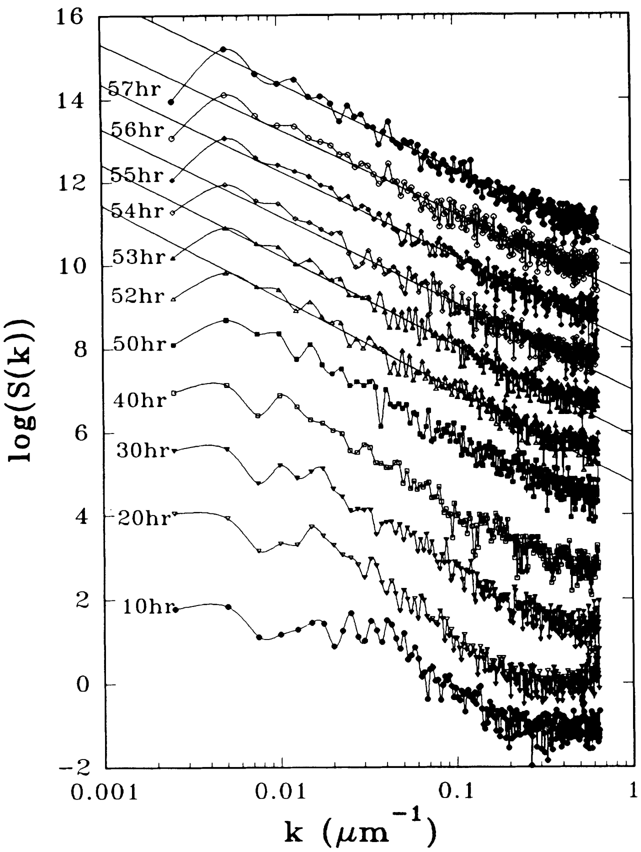

FIG. 2. Log-log plots of the roughness power spectrum $S(k)$ vs k at different times for $\eta = -0.25$ V. Least-squares fits over the range $0.01 < k < 0.25$ give slopes in the range -2.04 and -2.17 with errors of ± 0.06. They correspond to $\alpha = 0.55 \pm 0.06$.

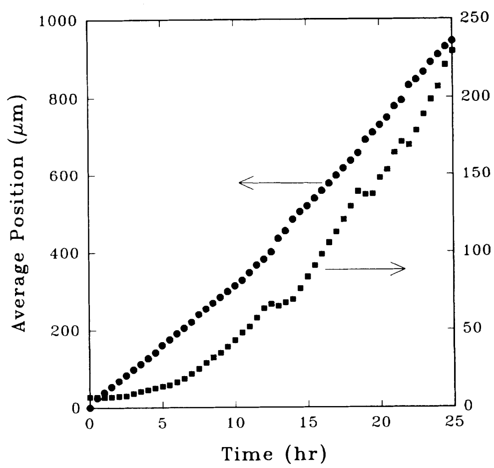

FIG. 3. Average interface position and total interface width for the $\eta = -0.35$ V profiles shown in Fig. 1(b). The discontinuities are due to the merging of neighboring columns (see text).

grows with time as t^{β} with $\beta = \frac{1}{3}$ in 2D. However, since the large amplitude surface features are columns of similar width and not the self-affine roughness assumed by KPZ, we should not expect this prediction to apply. Figure 3 shows the time dependence of the total interface width W for a single video field ($L = 2.35$ mm) and its average position $\langle x \rangle$ for $\eta = -0.35$ V. The large glitches in the data are due to the merging of neighboring columns that leaves behind a hole. Our calculations of all the interface properties exclude such holes since they are not part of the moving interface. The curvature of the W vs t plot implies that any power-law fit to the data would result in $\beta > 1$, in disagreement with the KPZ prediction. A more intuitive explanation of the columnar structure is that they originate from the usual Mullins-Sekerka (MS) instability of Laplacian growth [12]. To test this, we take the mode amplitude $F(k)$ for each k and check if it obeys the MS prediction of $F(k) \propto e^{\omega(k)t}$ with

$$\omega(k) = v_0 k (1 - d_0 l_D k^2) , \tag{2}$$

where v_0 is the average velocity of the interface and d_0 is the capillary length related to the intrinsic surface tension. Figure 4(a) shows three examples of semilogarithmic plots of $F(k)$ vs t for the early time profiles in Fig. 1(b) ($\eta = -0.35$ V). The k values (0.01, 0.02, and 0.025 μm^{-1}) correspond to wavelengths $\lambda \approx W_c$. The different slopes show that the growth rate ω varies with k. We analyzed all the profiles in Figs. 1(b)-1(d) this way and summarize the corresponding $\omega(k)$ dependence in Fig. 4(b) for $k < 0.031$. Fitting the data by Eq. (2) gave $v_0 = 3.17$ and 5.15 nm/sec for $\eta = -0.25$ and -0.35 V, respectively. The $\langle x \rangle$ vs t data in Fig. 3 gave measured velocities $v_m = 6$ and 8.6 nm/sec for these two cases. The agreement is remarkable since the MS prediction applies to the infinitesimal amplitude ($t = 0$) limit while we have to use data at late enough times with measurable amplitudes when local effects have already taken place. In other words, $v_0 < v_m$ is to be expected. In addition, we note the peak positions of the parabolas ($k \approx 0.023$ μm^{-1}) are given by $3 d_0 l_D k^2 = 1$. Following Ref. [9], we used the cell length (25 mm) for l_D and found $d_0 \approx 20$ nm which is a reasonable value for the capillary length. Thus the MS theory appears to provide a semiquantitative explanation of the long-wavelength behavior. On the other hand, we note that for $\eta = -0.15$ V, we find $v_0 = 0.84$ nm/sec and $v_m = 4.1$ nm/sec, and the parabolic fit in Fig. 4(b) is poor. These suggest that local effects are so dominant at this voltage that Eq. (2) is inapplicable.

In summary, the columnar structure at low deposition rates can be explained as a crossover between the MS instability which controls the column width and the local kinetic effects which lead to lateral growth and surface roughness. The measured exponent $\alpha = 0.55 \pm 0.06$ is consistent with the KPZ prediction but that alone is not a proof that the KPZ equation is completely applicable. For example, the simpler Edwards-Wilkinson model [i.e., Eq. (1) without the λ term] also predicts $\alpha = \frac{1}{2}$ [13]. On

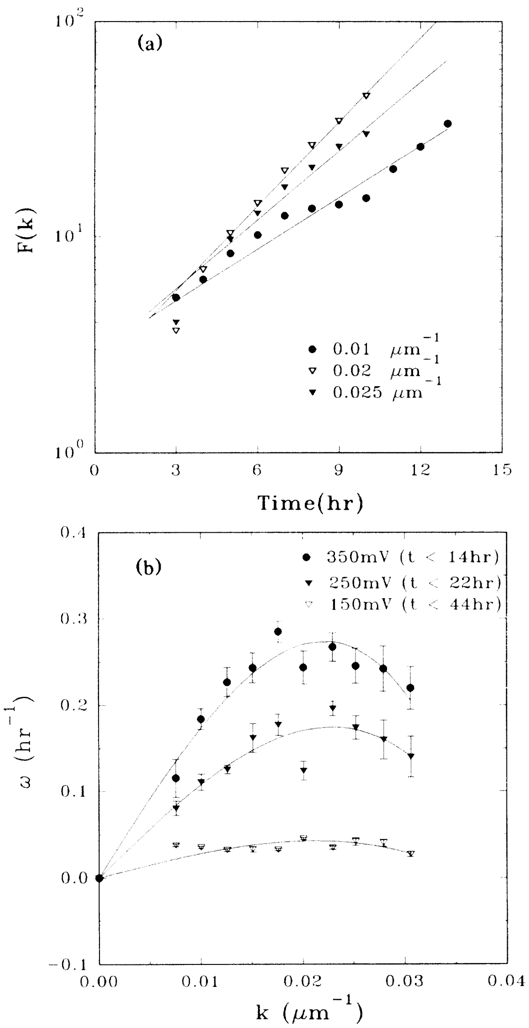

FIG. 4. (a) The Fourier amplitudes $F(k)$ for $\eta = -0.35$ V show that they have an approximately exponential growth in time. (b) The growth rate ω vs k is fitted well by Eq. (2) for the higher overpotential cases but not for the lowest overpotential case ($\eta = -0.15$ V).

the other hand, the visually apparent lateral growth in Fig. 1 provides strong evidence for the λ term, so the KPZ equation is at least a useful starting point. The issue is whether additional terms are necessary. For example, Bales, Redfield, and Zangwill [14] suggested that a linear h term could be included in Eq. (1) to mimic the MS instability, and others [15] have suggested that a $(\nabla^2)^2 h$ term can be added to model surface diffusion effects. The latter could destabilize the self-affine surface into a self-similar surface and this may explain the creation of holes in the pattern. Last, we should mention that the crossover from DLA to Eden growth has often been discussed in the context of computer simulation studies that vary the *sticking probability* [16]. The connection between such a microscopic approach and the KPZ-type continuum approach is an interesting issue that needs to be clarified.

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