Anomalous Scaling of the Surface Width during Cu Electrodeposition

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Kinetic roughening during thin film growth is a widely studied phenomenon, with many systems found to follow simple scaling laws. We show that for Cu electrodeposition from additive-free acid sulphate electrolyte, an extra scaling exponent is required to characterize the time evolution of the local roughness. The surface width $w(l,t)$ scales as $t^{\beta_{\mathrm{loc}}} l^H$, when the deposition time t is large or the size l of the region over which w is measured is small, and as $t^{\beta+\beta_{\mathrm{loc}}}$ when l is large or t is small. This is the first report of such anomalous scaling for an experimental (2 + 1)-dimensional system. When the deposition current density or Cu concentration is varied, only β_{loc} changes, while the other power law exponents H and β remain constant.

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Kinetic roughening is a process which takes place when material is added to or removed from a surface away from equilibrium. It is a complex phenomenon, which can depend on both local and nonlocal effects, and is of considerable practical importance in thin film growth and surface etching. Despite the complexity of the process, theoretical and experimental studies have shown that kinetic roughening often obeys simple scaling laws. In this Letter we show that kinetic roughening during Cu electrodeposition obeys an anomalous scaling law, whereby the *local* roughness exhibits a power law dependence on the deposition time. This is the first time that this type of scaling has been reported for an experimental (2 + 1)-dimensional system (two substrate dimensions plus one growth dimension). Remarkably, only the exponent describing the time evolution of the local roughness shows any dependence on deposition parameters such as the current density and electrolyte concentration.

Numerous models for surface roughening have been developed, many of which generate surfaces that are statistically self-affine for length scales within a bounded range [1]. Consequently, within this range the surface width w scales as l^H, where l is the size of the region over which w is measured, H is the Hurst exponent, and w is defined as

$$w(l) = \sqrt{\langle (h - \langle h \rangle)^2 \rangle}, \tag{1}$$

with h the surface height. For growth commencing from a smooth surface, w is frequently independent of the deposition time t for small l, and independent of l for large l, when it scales as t^β. The crossover between these types of behavior occurs at $l = l_c$, which gives the maximum extent of lateral correlations. l_c scales as $t^{1/z}$, and, for consistency, z must equal H/β. This is normal (Family-Vicsek) dynamic scaling, and may be represented by the scaling ansatz

$$w(l,t) = l^H f(t/l^z), \tag{2}$$

where the scaling function $f(x)$ is a constant for $x \gg 1$, and varies as x^β for $x \ll 1$ [2]. Examples of systems where normal dynamic scaling has been studied include unrestricted and restricted ballistic deposition models with 1- and 2- dimensional substrates [2,3], the Eden cell growth model [2,4], as well as models described by continuum equations [5].

More recently, a number of models have been studied in which the scaling of w must be represented by a different ansatz:

$$w(l,t) = l^H t^{\beta_{\mathrm{loc}}} f(t/l^z). \tag{3}$$

This differs from normal scaling because w is no longer independent of t for small l, but rather shows a power law dependence on both l and t. As before, w shows a power law dependence on t for large l, this time scaling as $t^{\beta+\beta_{\mathrm{loc}}}$. The crossover l_c continues to scale as $t^{1/z}$. However, the roughness exponent α, which describes the scaling of the maximum value of w with l_c is no longer equal to the Hurst exponent H, as it is for normal scaling, but rather to $H(1 + \beta_{\mathrm{loc}}/\beta)$ [1,6]. An ansatz equivalent to Eq. (3) [7,8] was first proposed to describe (1 + 1)-dimensional models incorporating surface diffusion [9–11], and was subsequently applied to other models, including the Wolf-Villain (WV) model in higher dimensions [12,13]. This work has played an important role in establishing limits to universality in dynamic scaling [13].

Previous experimental work on surface roughness scaling covered a wide range of systems. The (1 + 1)-dimensional systems studied include cultivated brain tumors [14] and cracks in stone and wood [15,16], while the (2 + 1)-dimensional systems include metal, insulator and semiconductor thin films grown by vapor deposition [17–20], sputtered films [21,22], and etched surfaces [23]. (1 + 1)-dimensional and (2 + 1)-dimensional films prepared by electrodeposition have also been studied, and have proved to be of interest because it is possible to access a wide range of experimental behaviors by varying the growth conditions. For example, different values of the scaling exponents H and β have been measured for deposition from Cu electrolytes with and without additives [24–26].

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Although in some (1 + 1)-dimensional systems the surface roughness has been found to scale according to Eq. (3) [14–16], evidence for such scaling in (2 + 1)-dimensional systems has remained elusive. Systems have been found where w depends on t for small l [19,22], and which therefore do not satisfy the normal scaling ansatz Eq. (2), but in these systems the dependence on t for small l is not given by a power law relationship. Instead, $w \sim l^{\alpha}\sqrt{\ln(t)}$ for small l, a relationship which has also been predicted theoretically [27]. Another form of scaling that has been reported for (2 + 1)-dimensional films is different from both Eqs. (2) and (3) because the power law exponent H in the scaling relationship $w \sim l^H$ takes more than one nonzero value depending on whether l is larger or smaller than the average grain size or other characteristic dimension [28, 29]. However, as we show here, Cu electrodeposition provides an experimental realization of a (2 + 1)-dimensional system which does scale according to Eq. (3).

We have studied the electrodeposition of Cu on 2 cm diameter sputtered Cu (25 nm)/Ti (5 nm)/glass or Au (25 nm)/Ti (5 nm)/glass substrates from an additive-free 0.3 M $CuSO_4$/1.2 M H_2SO_4 or 0.18 M $CuSO_4$/1.2 M H_2SO_4 electrolyte at room temperature [24]. Current densities between 4 and 24 mA cm^{-2} were used, corresponding to deposition rates from 5 to 30 μm h^{-1}, respectively. The substrates were held vertical during growth, and for our cell geometry the diffusion-limited current density associated with natural convection was measured as 26.7 ± 0.9 and 16.7 ± 0.9 mA cm^{-2} for the 0.3 and 0.18 M $CuSO_4$ electrolytes, respectively. Following growth, the surface topography near the center of each sample was measured in air using a molecular imaging PicoSPM atomic force microscope (AFM) for scan sizes up to 30 μm × 30 μm. Height data were obtained with a resolution of 256 × 256 pixels. A planar background was subtracted from the data to compensate for tilt of the sample relative to the scanning plane. Average values of the surface width $w(l)$ were calculated by applying Eq. (1) to all square regions of side l in a particular image. Only values of l corresponding to more than 3 times the dimension of a single image pixel were used. The results were checked for reproducibility by imaging several regions of the same sample, by changing the scan size, and by repeating the experiments with two different types of tip (silicon nitride and etched silicon).

Figure 1(a) shows $w(l,t)$ data for a series of films electrodeposited on Cu substrates from the 0.3 M $CuSO_4$ electrolyte at 24 mA cm^{-2} for a range of deposition times. Figure 1(b) is a typical AFM image of one of the films from which this data was obtained. For each film, w is approximately constant for large l and $\log w$ shows a linear dependence on $\log l$ for small l, indicating that w scales as l^H. H is constant for all films, within error (and quite close to results from earlier studies of Cu electrodeposition [24–26]), but $w(l,t)$ for small l increases with deposition time and, consequently, film thickness, which means that the kinetic roughening cannot be described by the normal scaling ansatz Eq. (2). It can, however, be described by the anomalous scaling ansatz Eq. (3), because, as Fig. 2 shows, $\log w$ varies linearly with $\log t$ in both the small l and large l regions.

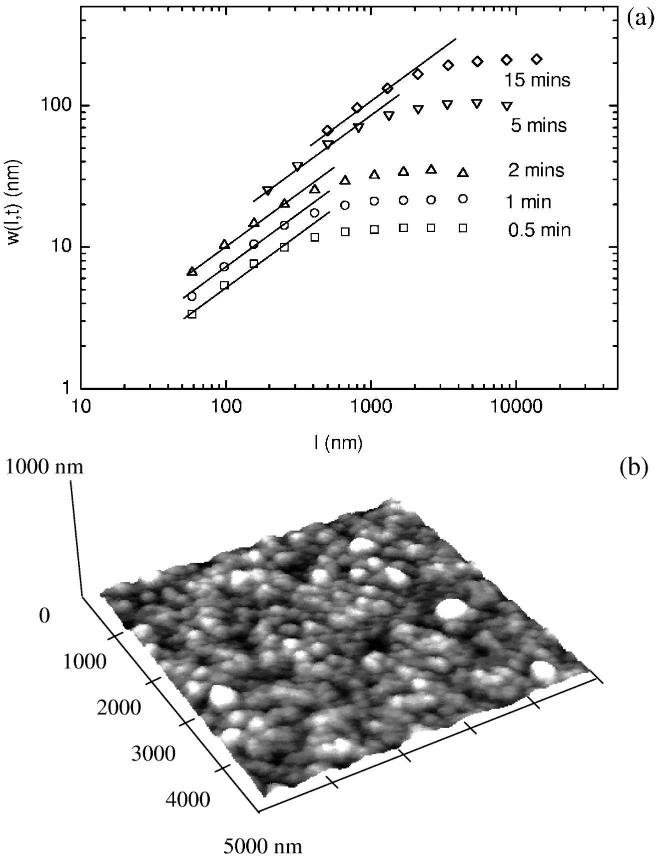

FIG. 1. (a) $w(l,t)$ (root-mean-square surface width) measured using an atomic force microscope over regions of size l for a series of electrodeposited films prepared from an additive-free 0.3 M $CuSO_4$/1.2 M H_2SO_4 electrolyte at room temperature. The current density was 24 mA cm^{-2} and the substrates were sputtered Cu (25 nm)/Ti (5 nm)/glass. Both axes are logarithmic. Each symbol corresponds to a film electrodeposited for a different time t (written in the figure). The solid lines are guides to the eye. Their gradient is equal to the average Hurst exponent H obtained from linear least squares fits to the data ($H = 0.75$). (b) AFM image of one of the films ($t = 1$ min) from which the data in (a) was obtained.

The range of t that can be studied is limited, because, when t is too small, $w(l,t)$ is dominated by the substrate, while when t is too large, the surface becomes too rough to measure reliably by AFM, and tip artifacts appear in the images. Nevertheless, as Fig. 2 shows, $w(l,t)$ scales over nearly 2 orders of magnitude of t. Anomalous scaling was also observed when the experiment was repeated using Au (25 nm)/Ti (5 nm)/glass substrates.

Our experiments further show that β_{loc} depends on the deposition current. Figure 3(a) shows $w(l,t)$ data for a series of films electrodeposited for different times t from the 0.3 M Cu electrolyte at a rather lower current density,

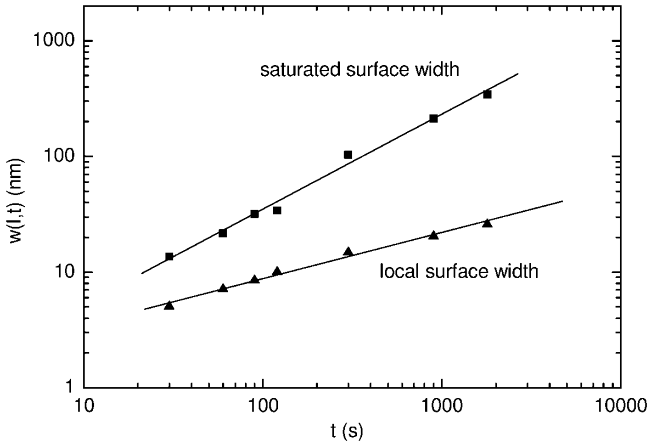

FIG. 2. Local surface width [$w(l,t)$ for $l = 100$ nm] and saturated surface width [$w(l,t)$ for $l > l_c$] for a series of Cu films deposited for different times t, calculated from the data of Fig. 1. Both axes are logarithmic. The lines through the local and saturated surface width data have slopes $\beta_{\mathrm{loc}} = 0.40$ and $\beta + \beta_{\mathrm{loc}} = 0.82$, respectively.

namely, 4 mA cm^{-2}. There are clear differences between this data and that of Fig. 1(a). For this current density, $w(l,t)$ does not appear to vary with t for small l, and β_{loc} is indistinguishable from zero. In other words, the scaling is normal, consistent with Eq. (2). A number of previous studies of Cu electrodeposition from additive-free sulphate electrolytes also used relatively low current densities, which presumably prevented the observation of anomalous scaling of the surface width [25,26]. Figure 2 of [24] suggests that, in one study where a higher current density was used, anomalous scaling was encountered but not recognized.

Increasing the current density will decrease the local concentration at the substrate and increase the overpotential driving electrocrystallization. The increase in overpotential could be the reason that higher current densities lead to a decrease in $w(l)$ for the thinnest films, since a higher overpotential increases the rate at which new grains are nucleated and can therefore lead to a finer-grained, smoother film. The decrease in roughness with increasing current density may be seen by comparing Figs. 1(b) and 3(b), which show films of the same thickness, but with the current density for Fig. 1(b) a factor of 6 higher. Since β_{loc} is larger for films electrodeposited at a higher current density, however, their $w(l)$ will increase more rapidly, so that films deposited for 15 min at 24 mA cm^{-2}, and for 90 min at 4 mA cm^{-2}, have very similar $w(l)$.

The increase in overpotential with increasing current density could also be responsible for the appearance of anomalous scaling, if it reduces the distance adatoms can move before being incorporated into the film. In 1-dimensional WV model simulations [7], a decrease in this distance causes β_{loc} to increase continuously from zero. However, the increase in overpotential is not the only important consequence of an increase in current density. Increasing the current density also brings it closer to its diffusion-limited value. Although the question of how (nonlocal) bulk diffusion effects influence anomalous scaling has not, to our knowledge, been treated theoretically, the following result suggests such effects could be important: when the current density was reduced from 24 to 15 mA cm^{-2}, and the solution concentration simultaneously reduced from 0.3 to 0.18 M CuSO$_4$ to keep the ratio of the current density i to its diffusion-limited value i_l the same, β_{loc} remained the same within experimental error despite the fact that the overpotential was expected to change. When the current density was reduced from 24 to 16 mA cm^{-2} without reducing the concentration, β_{loc} decreased significantly. While the evidence is not yet conclusive, the observed dependence of β_{loc} on i/i_l strongly suggests a link between anomalous scaling and bulk diffusion.

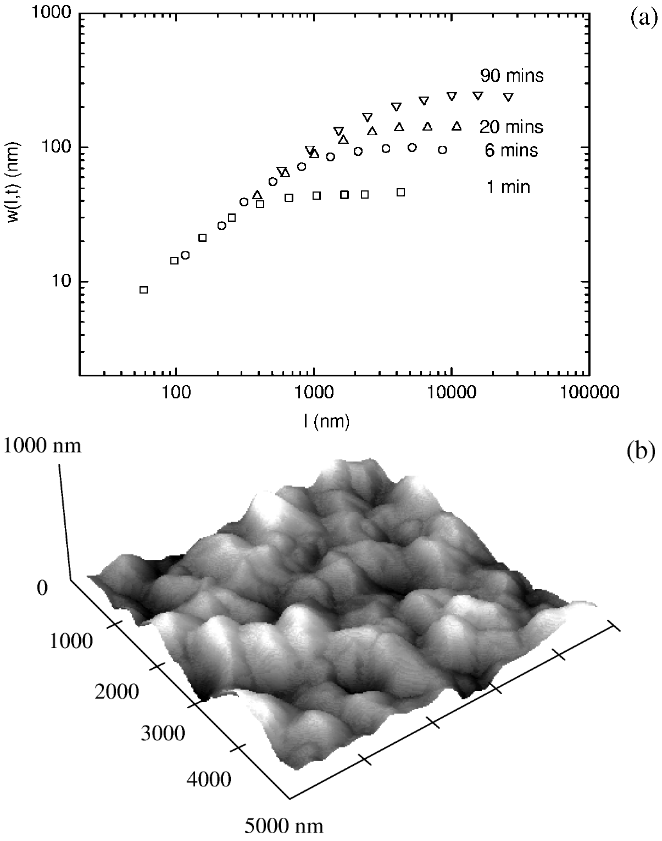

FIG. 3. (a) $w(l,t)$ (root-mean-square surface width) measured using an atomic force microscope over regions of size l for a series of electrodeposited films prepared as for Fig. 1 except that the current density was 4 mA cm−2. Both axes are logarithmic. Each symbol corresponds to a film electrodeposited for a different time t (written on the figure). (b) AFM image of one of the films ($t = 6$ min) from which the data in (a) was obtained

The results of these experiments are included in Table I, which shows values of the three independent scaling exponents H, β_{loc} and β measured for a series of samples electrodeposited using different current densities, different electrolyte concentrations, and different substrates. From Table I it is clear that β_{loc} can take a wide range of values,

TABLE I. Values of the 3 independent scaling exponents H, β_{loc} and β (see text) measured for series of samples electrodeposited using different current densities, different electrolyte concentrations and different substrates.

Electrolyte	Substrate	Current density (mA/cm^2)	$H(\pm 0.05)$	$\beta_{\mathrm{loc}}(\pm 0.03)$	$\beta(\pm 0.05)$
0.30 M $CuSO_4$/1.2 M H_2SO_4	Cu (25 nm)/Ti (5 nm)/glass	24	0.75	0.40	0.42
0.30 M $CuSO_4$/1.2 M H_2SO_4	Cu (25 nm)/Ti (5 nm)/glass	16	0.78	0.30	0.39
0.30 M $CuSO_4$/1.2 M H_2SO_4	Au (25 nm)/Ti (5 nm)/glass	6	0.79	0.00	0.35
0.30 M $CuSO_4$/1.2 M H_2SO_4	Cu (25 nm)/Ti (5 nm)/glass	4	0.75	0.00	0.37
0.18 M $CuSO_4$/1.2 M H_2SO_4	Cu (25 nm)/Ti (5 nm)/glass	15	0.75	0.44	0.41
0.18 M $CuSO_4$/1.2 M H_2SO_4	Au (25 nm)/Ti (5 nm)/glass	6	0.78	0.21	0.36
0.18 M $CuSO_4$/1.2 M H_2SO_4	Cu (25 nm)/Ti (5 nm)/glass	4	0.80	0.20	0.35

but note that, within error, H and β are constant. This reveals a remarkable hierarchy among the scaling exponents, with only β_{loc} affected by changes in the deposition parameters. It is interesting to compare our results with 1-dimensional numerical simulations [7], where β_{loc} was also found to vary with a small change in the model rules while H remained constant. In the simulations, however, β was not constant (in the notation of Ref. [7], z' was constant in the experiment, but z was constant in the simulations). It is also interesting that, for fracture surfaces in wood, H was found to be independent of material but α, which depends on β_{loc}, was not [16].

To summarize, we have provided evidence that kinetic roughening of Cu films electrodeposited from additive-free Cu electrolytes obeys the anomalous scaling ansatz Eq. (3). This is the first experimental $(2 + 1)$-dimensional system for which such scaling has been reported. Our work further illustrates the qualitative differences between the scaling exponents H, β, and β_{loc} by showing that only the last-mentioned shows any dependence on the experimental conditions (electrolyte concentration and applied current density). Under appropriate conditions, the anomalous scaling can even be reduced to normal.

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