Rough Growth and Morphological Instability of Compact Electrodeposits

J. M. Pastor and Miguel A. Rubio

*Departamento de Física Fundamental, Universidad Nacional de Educación a Distancia, C/ Senda del Rey s/n,
E-28040, Madrid, Spain*

We have investigated the initial stage of growth in electrochemical deposition at low constant currents in quasi-2D strip geometry. We used $0.5M$ aqueous solutions of $CuSO_4$, and current densities ranging between 20 and 100 $mA\,cm^{-2}$. We monitored the morphology of the growing interface and the electrical parameters of the system. We find two different growth regimes: at short times the interfaces show roughness scaling with a roughness exponent, $\alpha = 0.78 \pm 0.05$; at longer times a morphological instability develops whose characteristic time and length scales compare well with those expected from a Mullins-Sekerka instability.

PACS numbers: 61.43.Hv, 47.20.Hw, 47.54.+r, 81.15.Pq

Many industrial processes rely on the ability to control carefully the deposition of one material on top of a certain substrate. For instance, only in the semiconductor industry several techniques, such as electrodeposition, molecular beam epitaxy, chemical vapor deposition, or sputtering, are currently employed. One of the most striking facts in all of these processes is the possibility of the appearance of surface patterns that affect strongly the properties of the deposit. The understanding of these pattern formation problems is far from complete, although much effort has been dedicated to it in the recent past [1–3].

Several stochastic partial differential equation models have been devised to study rough compact growth from a planar surface close to equilibrium [3]. Models such as the Edwards-Wilkinson (EW) [4] and the Kardar-Parisi-Zhang (KPZ) [5] equations try to describe the spatiotemporal evolution of a surface profile $h(\mathbf{x}, t)$. The EW equation is a stochastic diffusion equation for the evolution of the surface profile, driven by white Gaussian noise. The KPZ equation is similar to the EW, supplemented with a nonlinear term, $(\nabla h)^2$, which favors growth in the direction of the local normal to the interface. The EW and KPZ are the simplest linear and nonlinear equations, respectively, that respect general symmetry requirements for equilibrium growth [3,6].

The main feature of these models is that they show rough compact profiles with roughness that behaves as a power law in both space and time. The scaling properties of rough interface profiles are studied by means of the scale dependent *roughness* $W(l, t)$ that measures the rms fluctuations of the interface about its local average value, measured on a certain length scale l. The scaling shows up as a functional dependence $W(l, t) \sim l^\alpha f(t/l^z)$, where $f(u) \approx u^\beta$, when $u \ll 1$, and $f(u)$ is constant, when $u \gg 1$. These relations imply also that $z = \alpha/\beta$. Usually α is called the *roughness* exponent, and β the *dynamical* exponent. If the noise is white and Gaussian, the values for the EW and KPZ equations in $1 + 1$ dimensions are $\alpha = 1/2$ for both equations, and $\beta_{EW} = 1/4$, and $\beta_{KPZ} = 1/3$.

Turning to the experimental aspects, electrochemical deposition is a good laboratory system to study interfacial growth phenomena, because it yields a wide variety of morphologies [7–9]. For instance, by changing the experimental parameters, diffusion-limited-aggregation-like [10,11], dense branching morphology [10,12], dendrites [8], or compact patterns [11] may appear.

In electrochemical deposition many experimental studies have been reported on ramified electrodeposits, but not much is known about compact rough growth. To our knowledge neither the EW nor KPZ equations have been derived from the equations for the electrodeposition problem. Nevertheless, some experimental results show roughness scaling properties although with different roughness exponents and temporal behavior. For instance, investigations [13] on copper electrodeposition in a thin cell at constant overpotential show a roughness exponent $\alpha = 0.55 \pm 0.06$. The exponent is obtained by computing the power spectra of the interfaces that show a power-law behavior $S(k) \propto 1/k^{1+2\alpha}$. However, the above-mentioned value may be affected by some problems related to the application of the power spectrum technique to columnarlike structures [14–16]. Independently of possible problems on the computation of α, Kahanda et al. remark that this exponent is obtained for interfaces after an instability of the Mullins-Sekerka type has developed, and, probably, models such as EW or KPZ do not apply.

Constant current electrodeposition experiments [17] have been performed in a stirred cell by means of atomic force microscopy. They show a roughness exponent $\alpha = 0.87 \pm 0.05$, and a dynamical exponent $\beta = 0.45 \pm 0.05$ in the 40–4000 nm range; both values disagree with those predicted for either EW or KPZ equations. In systems different from Cu, Vázquez et al. [18] have investigated the deposition of gold by means of scanning tunneling microscopy, in scales between 50 nm and 10 μm. They find two scaling regions separated by a crossover length that grows like $t^{1/4}$ and corresponds to the average columnar size. Below this crossover length the roughness exponent is 0.90 ± 0.07, while above it is 0.49 ± 0.07.

Here we report on new experimental results on Cu electrodeposition from aqueous CuSO$_4$ solutions. The experiments are carried out at constant current in a temperature-controlled quasi-2D cell. The use of a moderately high concentration (0.5M) allows us to have compact rough deposits that might develop branching at longer times. We show that the initial growth yields compact rough interfaces with $\alpha = 0.78 \pm 0.05$, in agreement with the results in Ref. [17] within the experimental uncertainty; at longer times a Mullins-Sekerka-type instability develops. The present results together with those in Refs. [13,17] allow us to draw a clearer picture of the slow growth regimes in compact Cu electrodeposition.

The experiment is run in a quasi-2D glass cell 10 μm deep, and in-between two high purity copper electrodes 3 cm long and placed 2 cm apart. The deposits are made out of 0.5M aqueous CuSO$_4$ (Aldrich, purity 99.999%) solutions in ultrapure water. The temperature of the cell is stabilized within ± 4 mK to avoid dimensional changes due to thermal dilations. We have performed all of the experiments reported here at $T = 315$ K. The imposed current is kept constant by means of a Radiometer PGP-201 galvanostat, and the nominal [19] range of current density, J, used in these experiments is between 20 and 100 mA cm^{-2}. We digitize, with 16 bit resolution, the electrical signals corresponding to the temperature, the current, and the externally applied voltage, V_{ext}.

We follow the evolution of the interface profile with a charge coupled device camera connected to an inverted microscope. The images are digitized in 768 $\times$ 512 squared pixels that allow for a maximal spatial resolution of 0.6 μm/pixel. We observe a field of about 0.5 mm in the central part of the electrode, and we verify after every experiment that the small observed "window" is representative of the whole deposit.

In Fig. 1 we plot a series of interfaces, grown at $J = 50$ mA cm^{-2}, separated by a time lapse of 100 min. The initial stages of growth show compact rough interfaces up to times of the order of 400 min (solid lines). The initially flat surface of the electrode grows at a rather constant speed, $v = 0.03$ μm/min, and no preferred length scale is apparent. This type of growth is accompanied by a monotonous increase in the external voltage needed to keep J constant. In this current range the initial value of V_{ext} is between 0.1 and 0.2 V, although its value cannot be selected externally in these experiments. The slow increase with time is probably due to a progressive depletion of cations in the area close to the cathode surface [20].

We have characterized the geometry of these interfaces by computing $W(l, t)$, as in [17]. A typical evolution of this function is shown in Fig. 2, where we plot $W(l, t)$ corresponding to the interfaces shown in Fig. 1. A power-law region appears for length scales below a certain crossover length l_c, and times above 200 min. Both the exponent of the power law and the crossover length increase with time until they saturate at values of $\alpha = 0.77 \pm 0.05$ and $l_c = 50$ μm, respectively. In Fig. 3 we show the roughness plot at five different nominal current densities, when saturation of the power law is attained, which occurs at times that decrease as the current density increases. The values of α obtained coincide within the experimental uncertainties and, therefore, α appears to be independent of the current density at which the experiment is performed. The average value is $\alpha = 0.78 \pm 0.05$ and agrees well with the value obtained by Iwamoto, Yoshinobu, and Iwasaki [17]. Figure 4 shows the temporal evolution of $W(l, t)$ at different length scales l corresponding to the interfaces shown in Fig. 1. For times less than ~650 min, the trend is roughly exponential at large l with a time constant of about 500 min. Therefore, no dynamical exponent may be defined for this interfacial growth.

This type of rough compact growth proceeds as far as V_{ext} remains roughly below 0.3 ± 0.05 V. Above this value the growth regime changes and the interface evolves
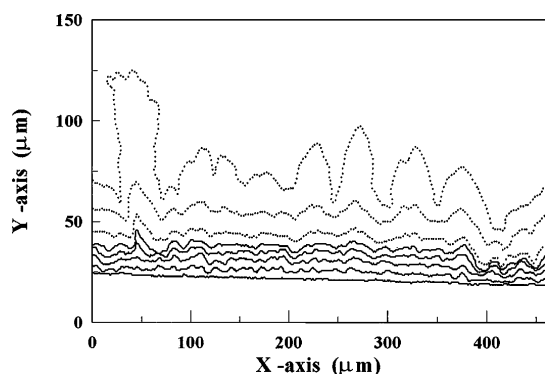

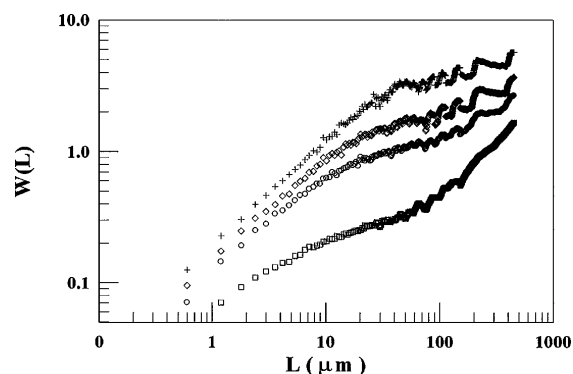FIG. 1. Time evolution of the interface profile at $J = 50$ mA cm^{-2}. The interfaces are separated by time intervals of 100 min (solid lines between $t = 0$ and 400 min; dotted lines between $t = 500$ and 700). Notice the change in growth speed and morphology between 400 and 500 min.

FIG. 2. Evolution of $W(L, t)$ for the interfaces shown in Fig. 1, at $t = 0$ min (squares), $t = 200$ min (circles), $t = 400$ min (diamonds), and $t = 600$ min (crosses). The power-law behavior at $L < 50$ μm is apparent. The value of the exponent is $\alpha = 0.77 \pm 0.05$.
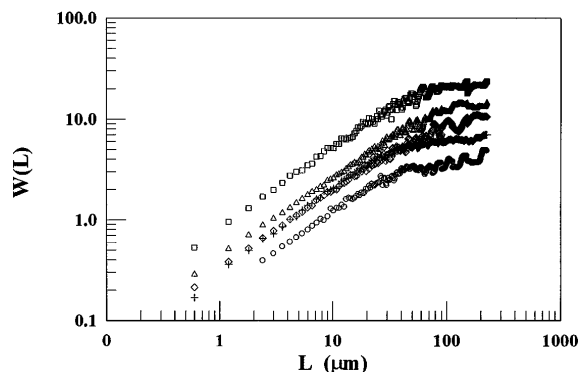
FIG. 3. Roughness plot at five different current densities: $J = 30$ mA cm^{-2} at $t = 800$ min (triangles), $J = 40$ mA cm^{-2} at $t = 800$ min (diamonds), $J = 50$ mA cm^{-2} at $t = 600$ min (circles), $J = 70$ mA cm^{-2} at $t = 400$ min (crosses), and $J = 90$ mA cm^{-2} at $t = 300$ min (squares). The average roughness exponent is $\alpha = 0.78 \pm 0.05$.

toward a fingered structure with somewhat faceted tips that we will call compact dendrites (CD). Usually this is also accompanied by a fast increase in V_{ext}. For instance, in Fig. 1 the initial growth is compact and rough during approximately 400 min. At later times a structure with a well-defined length scale of about 50 μm appears (dotted lines). The tips of the protrusions are slightly faceted, which reflects some anisotropy. Figure 5 shows the evolution of the average interface position and V_{ext} corresponding to the interfaces in Fig. 1. The evolution of $\overline{h}$ shows clearly an initial linear growth and a change in growth speed at about 450 min. This change in growth speed is accompanied by a sudden increase in V_{ext} that happens at a value of approximately 0.33 V. Note that this voltage value is not well defined; it may change from one experiment to another by ± 0.05 V. Computations of the spatial power spectra of the interfaces in the fingered regime show well-defined maxima at $k = 0.125$ μm^{-1}, i.e., $\lambda \approx 50$ μm. The time evolution of the most unstable
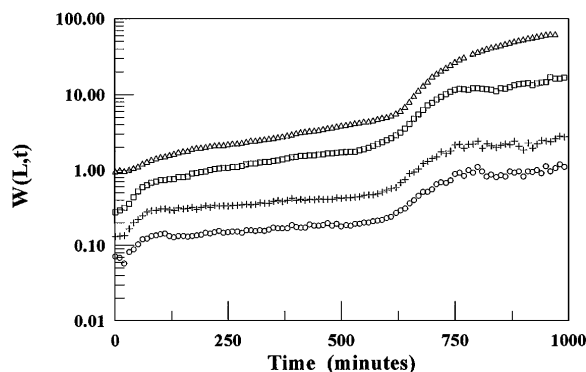
mode in this regime is exponential with a time constant of 120 min. These values of the typical wavelength and the exponential time constant agree well with the results of Kahanda et al. [13]. Figures 4 and 5 also indicate that at longer times (~ 650 min in this particular experiment) another instability develops that corresponds to a dendritic-dense branching transition. A detailed report on this instability will be published separately [21].

Following Ref. [13], we can compare the typical length scale of the CD structure with the one appearing in the Mullins-Sekerka instability. The dispersion relation for this instability is $\sigma(k) = v_0 k (1 - d_0 l_D k^2)$, where $\sigma(k)$ is the wave-number dependent growth rate, v_0 is the average interface velocity, d_0 is the capillary length, and l_D is the diffusion length. If we take as in [22] l_D as the interelectrode distance and $d_0 \approx 0.1$ nm, the wavelength of the most unstable wave vector is $\lambda = 2\pi\sqrt{3 d_0 l_D} \sim 16$ μm, which compares fairly well with the typical wavelength found. Substituting in the expression for $\sigma(k)$, the values of v_0 and k corresponding to Fig. 4, we obtain a growth rate of approximately 4×10^{-3} min^{-1}, which yields a time constant of about 250 min, which is within the order of magnitude of the experimental value.

The experimental facts concerning very slow compact Cu electrodeposition can be fitted in the following common scenario: experiments in Ref. [17] and ours show that at short times there is a compact rough growth, with a roughness exponent of about 0.8. Experiments in Ref. [13] and ours show that at longer times a morphological instability develops with characteristic time and length scales that are well explained by the Mullins-Sekerka instability.

The values of the roughness exponent we obtain are slightly below those obtained in Ref. [17]. The uncertainty intervals overlap, but there might be a reasonable explanation for the small discrepancy. The measurements performed by Iwamoto et al. are really 3D, while our values are obtained through 2D measurements. In this later case the real interface profile may differ from the digitized profile due to the depth of the cell. Even in very thin cells
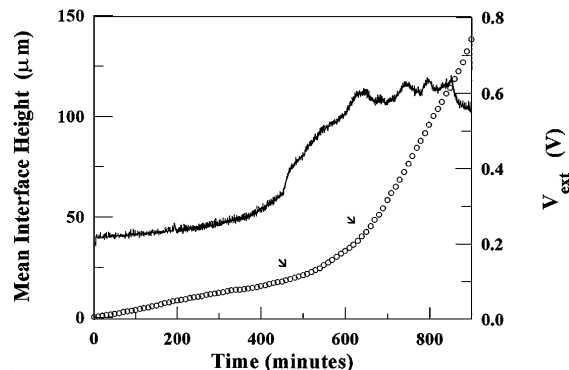

FIG. 4. Time evolution of $W(l,t)$ at different length scales: $L = 0.6$ μm (circles), $L = 3$ μm (crosses), $L = 30$ μm (squares), and $L = 230$ μm (triangles). An average exponential trend is apparent at large L, with time constant $\tau \approx 500$ min.

FIG. 5. Evolution of V_{ext} (solid line) and $\overline{h}$ (circles) corresponding to Fig. 1. Note the sudden increases coincident with the change in morphology.

like ours the actual digitized profile is a nonlinear super-position of the profiles occurring at different depths. This may increase the apparent roughness of the surface for length scales below the cell depth, and then yield a lower value for the roughness exponent.

The temporal evolution of the roughness in our experiments appears to be exponential, while in Ref. [17] it follows a power law. A possible explanation for this discrepancy is, for the moment, somewhat speculative. Kahanda *et al.* [13] first suggested that the present scenario might be described by a KPZ equation supplemented with some terms that would cause a morphological instability. A linear term ah with positive coefficient has been proposed in the context of chemical vapor deposition instabilities [23]. Numerical simulations of such a modified KPZ equation [24] suggest that at times $t \ll 1/a$ the influence of the linear term is small, the growth is dominated by the KPZ part, and the exponents obtained are the KPZ ones. At longer times, the morphological instability starts to develop and the roughness exponent grows with time. However, the time evolution of the roughness at large length scales is exponential with time constant $1/a$, and therefore no dynamical exponent may be defined. This phenomenology may explain the differences between our results and those in Ref. [17]. Actually Iwamoto *et al.* explore shorter time and length scales. Therefore, they may find saturated roughness scaling in the nanometer range while the system is still in the power-law temporal regime. Our experiments yield roughness scaling in the micrometer range; therefore, we need to wait until comparatively longer times for the roughness scaling to saturate at these length scales. Hence, temporal behavior of an exponential type might appear.

Finally, some comments are in order about the experimental procedure. Temperature stability appears to be an important requirement at these low voltages. Reference [2] gives a clue about how temperature enters into the problem. Kessler *et al.* have shown that, at vanishing overpotential, the electrodeposition problem may be mapped onto a diffusion-limited growth problem with a dimensionless supercooling given by

$$\Delta = \frac{q_c c_{c,\infty} v_c}{kT} V_{\text{ext}} ,$$

where q_c is the cation charge, and $c_{c,\infty}$ is the cation concentration in units in which the solid bulk concentration is unity. Straightforward calculations permit us to compare the effect that the noise in V_{ext} and T will have on the dimensionless supercooling. If one wants to perform a low noise experiment with $V_{\text{ext}} = 0.5$ V, voltage noise of the order of 0.5 mV, and at $T \sim 300$ K, one has to keep the temperature fluctuations well below 0.3 K.

We gratefully acknowledge useful discussions with F. Sagués, J. Claret, P. P. Trigueros, M. A. Plaza, E. Crespo del Arco, M. Llamas, P. Español, and J. M. R. Parrondo. J. M. P. has been supported by a fellowship from

[1] J. S. Langer, Rev. Mod. Phys. **52**, 1 (1980).

[2] D. A. Kessler, J. Koplik, and H. Levine, Adv. Phys. **37**, 255–339 (1988).

[3] A. L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, 1995).

[4] S. F. Edwards and D. R. Wilkinson, Proc. R. Soc. London, A **381**, 17 (1982).

[5] M. Kardar, G. Parisi, and Y. C. Zhang, Phys. Rev. Lett. **56**, 889 (1986).

[6] J. Krug, *Scale Invariance, Interfaces, and Non-Equilibrium Dynamics,* edited by A. McKane, M. Droz, J. Vannimenus, and D. Wolf, NATO ASI Series B (Plenum Press, New York, 1995), Vol. 344.

[7] R. M. Brady and R. C. Ball, Nature (London) **309**, 225 (1984).

[8] Y. Sawada, A. Dougherty, and J. P. Gollub, Phys. Rev. Lett. **56**, 1260 (1986).

[9] D. Grier, E. Ben-Jacob, R. Clarke, and L. M. Sander, Phys. Rev. Lett. **56**, 1264 (1986).

[10] F. Argoul, A. Arneodo, G. Grasseau, and H. L. Swinney, Phys. Rev. Lett. **61**, 2558 (1988).

[11] P. P. Trigueros, J. Claret, F. Más, and F. Sagués, J. Electroanal. Chem. **312**, 219 (1991).

[12] V. Fleury, M. Rosso, and J. N. Chazalviel, Phys. Rev. A **43**, 6908 (1991).

[13] G. L. M. K. S. Kahanda, X.-q. Zhou, R. Farrell, and P.-z. Wong, Phys. Rev. Lett. **68**, 3741 (1992).

[14] P. Keblinski, Phys. Rev. Lett. **71**, 805 (1993).

[15] G. L. M. K. S. Kahanda and P.-z. Wong, Phys. Rev. Lett. **71**, 806 (1993).

[16] Another possible disturbance not considered in [14] is the measurement window. If a rectangular window is used, the convolution of the signal transform with the rectangular window transform [a sinc(kx) function] will introduce again a $1/k^2$ trend.

[17] A. Iwamoto, T. Yoshinobu, and H. Iwasaki, Phys. Rev. Lett. **72**, 4025 (1994).

[18] L. Vázquez, R. C. Salvarezza, P. Ocón, P. Herrasti, J. M. Vara, and A. J. Arvia, Phys. Rev. E **49**, 1507 (1994).

[19] We cannot measure the actual current density passing through the observed growth surface. Growth occurs at all points in the cathode surface in contact with the solution, including interstitial regions between the cathode and the glass plates. As the experiments are run at constant current, this fact may also affect the measured voltage "threshold" values.

[20] J.-N. Chazalviel, Phys. Rev. A **42**, 7355 (1990).

[21] J. M. Pastor and M. A. Rubio, Physica D (to be published).

[22] R. M. Suter and P.-z. Wong, Phys. Rev. B **39**, 4536 (1989).

[23] G. S. Bales, A. C. Redfield, and A. Zangwill, Phys. Rev. Lett. **62**, 776 (1989).

[24] J. Buceta, J. M. Pastor, F. J. de la Rubia, and M. A. Rubio (to be published).