Interface dynamics for copper electrodeposition: The role of organic additives in the growth mode

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An atomistic model for Cu electrodeposition under nonequilibrium conditions is presented. Cu electrodeposition takes place with a height-dependent deposition rate that accounts for fluctuations in the local Cu^{2+} ions concentration at the interface, followed by surface diffusion. This model leads to an *unstable* interface with the development of protrusions and grooves. Subsequently the model is extended to account for the presence of organic additives, which compete with Cu^{2+} for adsorption at protrusions, leading to a *stable* interface with scaling exponents consistent with those of the Edwards-Wilkinson equation. The model reproduces the interface evolution experimentally observed for Cu electrodeposition in the absence and in the presence of organic additives.

The dynamics of growing interfaces has become of increasing interest for both theoretical and experimental work in order to understand the physical processes that determine film quality [1]. In the absence of morphological instabilities, the evolution of surfaces and interfaces, growing in out-of-equilibrium conditions, has been observed to lack characteristic time and length scales, producing rough self-affine morphologies. Rough surfaces can be conveniently described at time t by the value of its roughness, $w(t) = \sqrt{\langle [h(\mathbf{r},t) - \langle h(t) \rangle]^2 \rangle}$, i.e., the rms deviation of the surface height $h(\mathbf{r},t)$ around its mean value $\langle h(t) \rangle$, with $\mathbf{r}$ being a site of a substrate of lateral dimension L. For a flat initial condition, w increases as $w(t) \propto t^{\beta}$, with β the growth exponent. Surface features across the substrate, as measured by the characteristic lateral correlation length, ξ, also coarsen with time as $\xi \propto t^{1/z}$, where z is the dynamical exponent. Once ξ becomes of the order of L, the roughness saturates into a stationary value that scales as $w_s \propto L^{\alpha}$, where $\alpha = z\beta$ is the roughness exponent [2]. On the other hand, unstable interfaces are produced when Laplacian fields such as pressure, concentration gradients, or electric fields develop around the growing interface, or when step-edge energy barriers are present [1]. In this case the growth dynamics does not follow the scaling laws and the interface is no longer self-affine.

Electrodeposition (ED) is one of the methods most commonly used for metal film preparation in many technological processes. It is known that to prepare high quality micrometer thick films (smooth and bright deposits) at a reasonable high deposition rate, plating baths with a high concentration of metallic ions and small amounts of organic additives (OA) must be used [3]. In the absence of these additives, even in concentrated metallic-ion-containing solutions and under surface reaction control, the contribution of local fluctuations in concentration [4] and/or electric [5] fields could drive the interface to an unstable growth regime. In this case branched and low adherent deposits are formed.

Cu ED has been taken as a model system for interface evolution studies under nonequilibrium conditions [6]. Most of the experimental information has been reported in concentrated Cu^{2+} solutions (0.18–0.6M), at current densities 4 mA cm$^{-2} \leq j \leq 24$ mA cm^{-2}, corresponding to growth rates $5.5 \leq v \leq 33.3$ monolayer s^{-1} (ML s^{-1}). In these cases the growing interface is unstable with $\beta > 0.4$ [5,7,8]. On the other hand, when a small concentration of thiourea ([Tu]), $10^{-4}M \leq$ [Tu] $\leq 10^{-3}M$, is present in the plating bath the interface evolution changes from unstable to stable during a time interval t_i [7,9,10] before becoming unstable again.

Additive molecules form either ordered lattices or dilute two-dimensional (2D) gaslike adsorbates; they can either be buried into the bulk deposit, or float on the growing surface [11–13]. The understanding of the surface structure and dynamics of additives is a crucial point in controling the growth of smooth metal surfaces. In fact, the role of surfactants is important not only in ED, but also in other related techniques such as CVD (chemical vapor deposition).

Despite the importance of ED in technology, a model capable of accounting simultaneously for both, the unstable interface evolution of the system and the stable interface dynamics in the presence of an additive is still lacking. In this work we present, in a fairly simple fashion, an atomistic growth model for a micrometer thick Cu film deposition capable of describing those processes in a unified framework.

Cu ED was simulated in $1+1$ dimensions (1D) using lattices of length $8 \leq L \leq 2048$ lattice sites. Taking lattice sites of size ≈ 0.25 nm for Cu, the length scales of the simulations can be reported in nm. The attachment of Cu particles to the deposit is made at random with a site probability $P_s(t) \propto (h(\mathbf{r},t) - h_b(t))^{\delta_c}$ conveniently normalized. The height-dependent probability [site height $h(\mathbf{r},t)$ minus bottom height $h_b(t)$] accounts for fluctuations in the local Cu^{2+} ion concentration [14] or electric field [5] that could act around the growing interface. The exponent δ_c regulates the strength

FIG. 2. Logarithmic w vs t plots resulting from the analysis of profiles such as those shown in Fig. 1(a) (the slope of the solid line is 0.375). Inset: logarithmic w_s vs L results showing a slope $\alpha = 1.45 \pm 0.05$ (the slope of the solid line is 1.5).
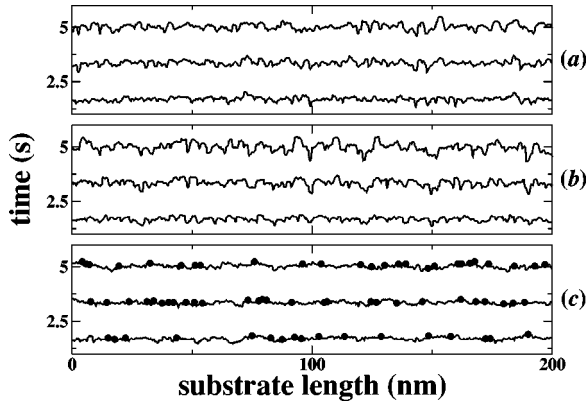
FIG. 1. Simulation snapshots showing the typical profiles' evolution for $v = 30$ ML s^{-1} and $t = 1.67$, 3.33, and 5 s for (a) surface diffusion conditions, (b) unstable growth, and (c) in the presence of an additive. Full circles indicate the position of additive molecules.

of such fluctuations. The deposition of a Cu monolayer was taken as the Monte Carlo time unit (MCs), i.e., for $v = 30$ ML s^{-1} a MCs is equivalent to $(30)^{-1}$ s. Thus, results from our simulations are presented in real time units (s). After deposition, attached Cu particles can diffuse a length l on the surface to increase the number of nearest-neighbors [15]. In fact, Cu adatoms exhibit non-negligible mobility in contact with electrolytes solutions at room temperature [16]. Recent experimental data [16] for Cu ED at a low rate (1.5 ML s^{-1}), that is, for negligible electric and concentration fields acting at the interface, indicate that the linear diffusion theory provides a good description for the interface dynamics. Thus, ξ, that in the experimental system corresponds to the average grain size, increases as $\xi = Kt^{1/4}$. Values of K ranging between 10^{-20} and 10^{-28} cm^4 s^{-1} have been reported for Cu and Au in contact with aqueous solutions [17,18]. Therefore, we have used in our surface diffusion process $K = 10^{-26}$ cm^4 s^{-1}.

Figure 1(a) and 1(b) shows configuration snapshots obtained at different growing times and using different values of δ_c. For $\delta_c = 0$ the interface becomes rougher [Fig. 1(a)] with $w(t) \propto t^\beta$, $\beta = 0.37 \pm 0.01$, and $w_s \propto L^\alpha$, $\alpha = 1.45 \pm 0.05$ (see also Fig. 2) as expected from the linear theory of surface diffusion in $1+1$ dimension [1]. This regime covers more than four decades in time, reaching the micrometer thickness range. On the other hand, for $\delta_c > 0.01$, steadily growing instabilities are formed [Fig. 1(b)] leading to $\beta \geq 0.4$ [Fig. 3(a)]. The w vs t plots reproduce the unstable behavior observed for Cu ED from acid baths in both $1+1$ and $2+1$ dimensions [5,8], and they reproduce the spatial and temporal scales experimentally observed [Fig. 3(a)] [7]. The β vs δ_c plot [Fig. 3(b)] shows that δ_c controls the strength of the unstable regime. In this figure we also have plotted experimental β values versus j/j_l (j_l is the limiting current density) taken from three different works [7–9]. For a given ED system the j/j_l ratio determines the kinetic control. Thus, when $j/j_l \to 0$ (low δ_c) the reaction is under surface reaction control, whereas when $j/j_l \to 1$ (high δ_c) the reaction is under mass transport control. At intermediate j/j_l mixed control is expected. The correspondence between δ_c
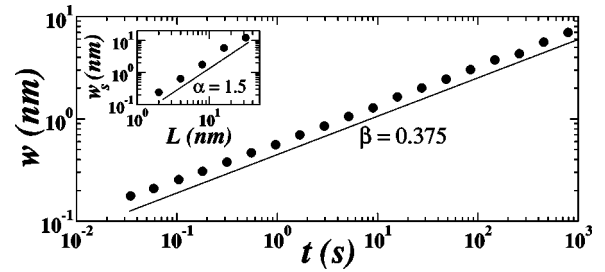
and j/j_l is clear. Note that our model predicts that even close to a complete surface reaction control the interface is unstable as observed in experimental systems [7–9].

The effect of the organic additive is introduced in our model through the adsorption probability (P_a) and two parameters (γ and c) that control the competition between OA and Cu^{2+} ions for the surface sites. Firstly, OA molecules are adsorbed at random with $P_a = (h(\mathbf{r},t) - h_b(t))^\gamma$. The phenomenological exponent γ controls the ability of protrusions to capture the arriving flux of OA in relation to other portions of the growing surface. As γ plays the same role for additive adsorption as δ_c does for Cu ED, we propose that its value is related to the j/j_l ratio for the electroadsorption reaction. Secondly, we define the parameter c that accounts for the Cu/(Cu+Tu) arriving molecule ratio. In the simulation $c = N/1000$, N being the average number of OA molecules for each 1000 molecules (Cu+Tu) that arrives to the surface. Besides, it is assumed that an additive molecule attached at a generic site $\mathbf{r}$, of height $h(\mathbf{r},t)$, completely inhibits Cu deposition within a protection zone of maximum length L_c, on the same terrace. The physical origin of the protected zone arises from the effective size of the additive molecule (0.4 nm) [20], which is larger than the substrate particle, and also due to its high mobility in the adsorbed state that has been described as a gaslike state [10]. Electrodesorption of Tu molecules should also be considered by the model because the S concentration (from Tu) into electrodeposited bulk Cu is negligible in relation to that expected from the surface
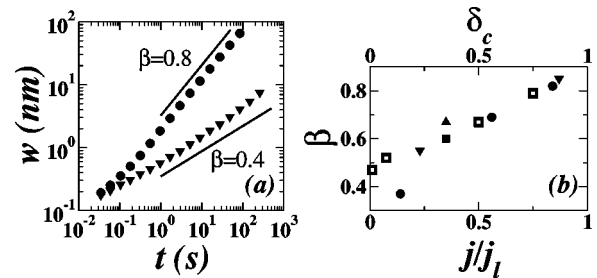

FIG. 3. (a) Logarithmic w vs t results for different values of δ_c: (▼) $\delta_c = 0.01$ and (●) $\delta_c = 0.75$. Note that β increases with δ_c (the slopes of the solid lines are 0.4 and 0.8, respectively); (b) β vs δ_c plot (□) and β vs j/j_l plots from different experimental data: (▲) [7], (●) [8], and (■) [9].

coverage by Tu (θ_{Tu}), estimated during Cu ED [10]. In our model this is achieved by additive particle detachment when the local surface of the deposit close to the protected zone equals or exceeds the height of this zone. This process effectively simulates the sharp electrodesorption of S-containing molecules with a small decrease in the electric potential [21] that should occur as a consequence of a curvature-dependent electric potential [22]. Therefore, no additive molecules are buried in the Cu deposit in our model.

The model allows us to explore a wide range of c values. However, in this paper we are interested in the range of concentrations used in real plating baths. In this case, Cu ED is made under galvanostatic conditions (constant j) so that the number of arriving Cu^{2+} ions is constant. Thus, the Tu/(Tu+Cu) ratio depends on the number of arriving Tu molecules. Under typical Cu ED conditions ($j = 20$ mA cm^{-2}, [Tu]$=10^{-3}$ M) the Tu surface coverage is $\theta_{Tu} \approx 0.03$, that is, much smaller than the saturation coverage $\theta_{Tu} \approx 0.7$ [10]. This means that Tu molecules arrive to the growing surface under mass transport control and the maximum electroadsorption current density can be estimated by Cottrell's equation,

$$j_l = \frac{zFD[\text{Tu}]}{\varepsilon}. \tag{1}$$

Taking in Eq. (1) the number of electron transferred $z=1$ [21], the Faraday's constant $F=96500$ C mol^{-1}, the surface diffusion coefficient in the electrolyte $D=10^{-5}$ cm^2 s^{-1}, [Tu]$=10^{-6}$ mol cm^{-3}, and the diffusion layer thickness $\varepsilon=0.02$ cm, it results $j_l=0.05$ mA cm^{-2}. Thus, the rate of Cu incorporation (at $j=20$ mA cm^{-2}) is 400 times greater than the maximum rate of Tu electroadsorption, i.e., 20 times greater for our 1D system. Therefore, values of c ranging from 0.01 to 0.5 are explored to cover the range of technological interest. Finally, the fact that the OA molecules arrive under mass transport control, that is, describing random walk [19] in the solution, implies that $j/j_l \rightarrow 1$ and γ should also be large.

Let us start with a $\delta_c = 0.075$, for which our model simulates an ED process under surface reaction control [Fig. 3(b)]. Configuration snapshots showing the effect of the additive, obtained for $\delta_c = 0.075$, $c=0.05$, $\gamma=1.1$, $L_c \approx 1$ nm, and different deposition times are presented in Fig. 1(c). Initially the interface becomes rougher with $w(t) \propto t^\beta$ and $\beta = 0.37 \pm 0.01$, as expected for the surface diffusion regime, then a crossover to $\beta = 0.25 \pm 0.01$ is observed before w becomes unstable again at t_i (Fig. 4). The values $\beta = 0.25 \pm 0.01$ and $\alpha = 0.50 \pm 0.01$ (Fig. 4 and inset) are consistent with the prediction of the Edwards-Wilkinson (EW) equation in $1+1$ dimension [23]. The positions occupied by the additive molecules for $t < t_i$ are also shown in Fig. 1(c), being the value of $\theta_{Tu} \approx 0.03$. The interface evolution shows that triggered instabilities cannot grow due to the preferential adsorption of the additive at protrusions [compare Fig. 1(b) with Fig. 1(c)]. Note that the initial surface diffusion regime that cross to the EW behavior at advanced stages reproduces the interface dynamics experimentally observed for Cu ED in the presence of OA [7,18]. For the typical c values used in
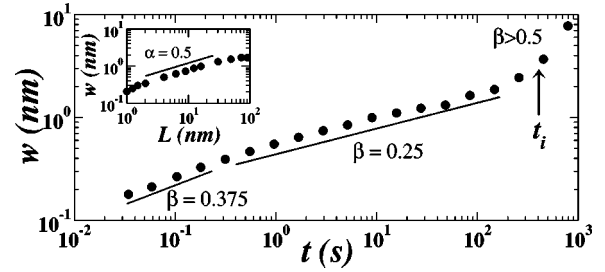
FIG. 4. Logarithmic w vs t plots resulting from the analysis of profiles as those shown in Fig. 1(c). The slopes of the solid lines are 0.375 and 0.25, respectively. The latter value is consistent with the EW growth mode. Inset: logarithmic w vs L from a characteristic profile within the EW range.

ED we observed that the OA is able to control instabilities only for low δ_c values, that corresponds to an ED process under surface reaction control ($j/j_l < 0.3$) [9]. In fact, as δ_c increases from 0.075 to 0.8, keeping constant both γ and c, a marked decrease and finally a complete elimination of the EW regime is observed.

Let us discuss the change in the ED regimes, from unstable to stable (EW), originated by the presence of OA. The amount of Cu (Tu) deposited at a site $\mathbf{r}$ is given by $F_{Cu} \propto [\text{Cu}]P_s(t)$ ($F_{Tu} \propto [\text{Tu}]P_a(t)$). As in real plating baths [Cu]$\gg$[Tu], Cu deposition can effectively be hindered only for $\gamma \gg \delta_c$. For the parameters used in Fig. 1(a), the concentration and $\Delta h = h(\mathbf{r},t) - h_b(t)$ dependence of both Cu deposition and Tu electroadsorption imply that for $\Delta h \rightarrow 0$ corresponds $F_{Cu} \gg F_{Tu}$, while for $\Delta h > 20$, $F_{Cu} < F_{Tu}$. Thus, while small Cu protrusions can grow practically free of Tu, these molecules cover the top of large protrusions, hindering further Cu deposition. Therefore, instabilities decay with time by the preferential Cu deposition at valleys. Finally, additive electrodesorption takes place due to the curvature dependence electric potential. Consequently a sort of feedback mechanism is established preventing the growth of instabilities, leading to stable interfaces. At a constant γ and for low c values, F_{Tu} is too small to hinder Cu deposition at
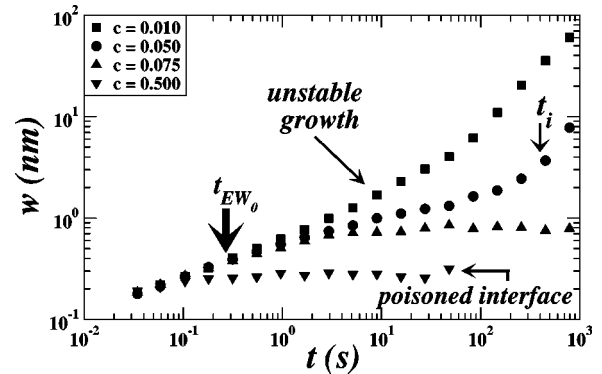
FIG. 5. Additive concentration influence in the model: logarithmic w vs t plots for different concentrations. The big arrow marked with t_{EW_0} indicates where the EW zone begins, while the thinner vertical arrow marked with t_i indicates the end of this regime for the corresponding concentration condition.

protrusions: unstable behavior is present (Fig. 5). At intermediate values of c, and after the short-time surface diffusion controlled regime, the interface exhibits the EW behavior within the interval $t_{EW_0} < t < t_i$. The value of t_i increases with c, reproducing experimental observations [7,9,10]. Finally, at high additive concentration, the interface rapidly reaches saturation becoming completely poisoned, i.e., Cu deposition is no longer allowed.

The behavior of the interface dynamics can also be described with continuous phenomenological (mesoscopic) equations [1]. In our case, a complete equation should contain the $-K\nabla^4 h$ term that accounts for the initial surface diffusion controlled regime, a Gh^δ term responsible of the unstable behavior, and the $\nu\nabla^2 h$ term that accounts for the EW behavior (a net flux of Cu from the protrusions—covered by the additive—to the valleys):

$$\frac{\partial h}{\partial t} = v - K\nabla^4 h + Gh^\delta + \nu\nabla^2 h + \eta. \qquad (2)$$

The last term in Eq. (2), η, represents the stochastic noise related to the growth process. Here we stressed the fact that the competition between the terms Gh^δ and $\nu\nabla^2 h$ determines the t_i value.

In conclusion, our model reproduces the experimentally determined interface dynamics of Cu ED in the absence [5–7,16] and in the presence of OA [5,9,18], providing a unified description of this complex system. In the frame of our model, the optimal conditions for stable interface dynamics can be explored working at low δ_c and high γ, and changing the additive concentration by tuning c. For electroplaters it means metal ED close to a complete surface reaction control, OA electroadsorption under mass transport control, and adequate metal ions/OA concentration ratio. Therefore, this model could be a powerful tool to predict the interface dynamics of other electrodeposition systems for which less information is available.

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