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TRANSITION OF GROWTH MODE IN ELECTROCHEMICAL DEPOSITION OF COPPER: ATOMIC FORCE MICROSCOPY ANALYSIS AND SIMULATION

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Abstract

The scaling behavior of roughness in electrochemical deposition of copper under stable growth conditions was studied by atomic force microscopy and numerical simulation. An abrupt transition in the growth mode was observed as the concentration of "brightener" (organic additive) in the plating solution was increased. The two growth modes are characterized by the roughness exponents $\alpha = 0.87$ and 0.63 for low and high concentrations of organic additive, respectively. The transition can be reproduced numerically via a Kardar-Parisi-Zhang (KPZ) -like equation with an additional term proportional to the surface height. The effect of current density on the transition is also investigated.

Key Words: Roughness, kinetic roughening, dynamic scaling, scaling exponent, electrochemical deposition, atomic force microscopy (AFM), Kardar-Parisi-Zhang (KPZ) model, copper.

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Introduction

Roughening in electrochemical deposition has been widely studied from both fundamental and technological points of view (Halsey, 1987; Barkey *et al*., 1989; Kahanda *et al*., 1992; Pritzker and Fahidy, 1992; Iwasaki and Yoshinobu, 1993; Iwamoto *et al*., 1994; Vazquez *et al*., 1994; Iwasaki *et al*., 1995; Iwasaki and Yoshinobu, 1995; Pastor and Rubio, 1996). Although fractal growth in the diffusion limited growth regime described below has been intensively studied, roughening in the stable growth mode, which is of technological importance, has scarcely been studied. Atomic force microscopy (AFM) is suitable for scaling analysis of surface roughness on mesoscopic scales, owing to its wide dynamic range of measurement in the horizontal direction (from nanometer to about 100 μm) and high sensitivity (subnanometer) in the vertical direction.

In electrochemical deposition, the concentration of cations (metal ions) in the boundary layer near the cathode is reduced with respect to the bulk concentration. Distribution of cations inside the boundary layer is determined by diffusion. Electromigration can be neglected in conductive solutions with supporting electrolyte. Air bubbling enhances convection and makes the boundary layer thinner. With increasing current density, the concentration of cations eventually becomes zero everywhere at the surface, and the current is limited by diffusion of cations. Thus, at higher current densities near the limiting current, the growth is governed by a diffusion-limited non-local mechanism, which produces rough morphology such as dense-branching and dendritic patterns (Halsey, 1987; Barkey *et al*., 1989).

At lower current densities where we performed experiments, as in the so called Tafel regime (Halsey, 1987), the growth instability is weak on length scales shorter than λ_c-D, where D is the thickness of the boundary layer, $\lambda_c = C_0 D/(C_0 - C_s)$, and C_0 and C_s are the respective concentrations of the cations outside the boundary layer and at the surface. C_0/λ_c gives the gradient of ion concentration in the boundary layer. The growth rate in the steady state is given by (Halsey, 1987)

$$\frac{\partial h(r,t)}{\partial t} \approx \frac{v}{(\lambda_c - D)}(h(r,t) - <h(r,t)> s) \qquad (1)$$

where h(**r**,t) is the height of the interface measured from the moving plane averaged over the whole area, which moves at a constant growth velocity v under the constant current condition. $<h(\mathbf{r},t)>_S$ means the average over the local area on a characteristic length scale S, which is of the order of D. Because of this averaging effect, the growth governed by Equation (1) exhibits non-local features, and the growth at higher (lower) positions is enhanced (suppressed).

Dynamic Scaling of Growing Films

Surface roughness of growing films on flat substrates has been shown to exhibit scaling behavior over large variations of length scales, and considerable interest has been directed to the physics of dynamic scaling (Krug and Spohn, 1990; Family and Vicsek, 1991). Theory (Kardar *et al.*, 1986; Family and Vicsek, 1991) predicts that the interface width W(L,t), defined as the mean surface height fluctuation on length scale L and at growth-time t, scales as

$$W(L,t) \propto L^{\alpha} \qquad \text{for } L << L_c \qquad (2)$$
$$W(L,t) = \Delta(t) \propto \mathbf{t}^{\beta} \qquad \text{for } L >> L_c \qquad (3)$$

where

$$L_c = \mathbf{t}^{1/z} \qquad (4)$$
$$Z = \alpha/\beta \qquad (5)$$

The scaling behavior is equivalent to scale invariance of the surface height, h(**r**,t): the statistical properties of h(**r**,t) are identical to those of $b^{-\alpha}h(b\mathbf{r},b^{z}t)$, where b is an arbitrary rescaling factor (Krug and Spohn, 1990).

In many growth processes, growth is determined solely by local conditions at the growing site such as sticking rates, surface relaxation rates and stochastic noise. In the model proposed by Kardar *et al.* (1986), the interface growth is described as

$$\frac{\partial h(r,t)}{\partial t} = \gamma \nabla^2 h(r,t) + \frac{\nu}{2}(\nabla h(r,t))^2 + \eta(r,t) \qquad (6)$$

The first term on the right-hand side describes relaxation of the interface by the surface tension γ. The second term is included to describe the growth normal to the local surface with a constant growth velocity ν.

To simulate electrochemical deposition, we start from the KPZ equation and add a non-local growth term corresponding to Equation (1), i.e.,

$$\frac{\partial h(r,t)}{\partial t} = \gamma \nabla^2 h(r,t) + \frac{\nu}{2}(\nabla h(r,t))^2 + \frac{\nu}{\lambda_c - D}(h(r,t) - <h(r,t)> s) \qquad (7)$$

A similar growth system was previously investigated by Honda and Toyoshima (1992) in 1+1 dimension.

Anisotropic crystal growth would affect surface morphology and the apparent scaling behavior (Barkey *et al.*, 1989). Because faceting is not observed in the present case of Cu deposit (see Fig. 1), we neglect the effect of anisotropic crystal growth on the scaling behavior of kinetic roughening.

Experimental and Simulation

We investigated the dynamic scaling behavior of copper growth in $CuSO_4$ solution at slow rates under stable growth conditions similar to those of standard electroplating. Copper was electrodeposited on copper plates in an acid copper sulfate solution under the same condition as that in our previous report (Iwamoto *et al.*, 1994). Some specimens were grown in solutions containing 0.5-10 ml/l of organic additive "Copper Gleam PCM", a sulfonium-alkane-sulfonate-type additive (LeaRonal, NY), as the brightener. The standard concentration recommended for practical use is 5-10 ml/l.

AFM was employed to measure the roughness of the copper surface. The AFM measurements were carried out in air with constant-force of 5.0 x 10^{-9} N. We performed measurements over a variety of areas, i.e., 5 x 5, 20 x 20, and 50 x 50 μm^2. In each measurement, the height data were acquired at a resolution of 256 x 256 or 512 x 512 pixels. The interface width W(L,t) was calculated from the numerical data obtained by AFM measurements (Yoshinobu *et al.*, 1994).

Deposits were also grown by computer simulation using the numerical method in 2 + 1 dimension. The equation of the form of Equation (7) was solved numerically for 256 x 256 lattice points using the difference equation (Amar and Family, 1990). The KPZ terms are rewritten as follows:

$$h_{\tau+\Delta\tau}(i,j) = h_\tau(i,j) \qquad (8)$$
$$+\Delta\tau(3[h_\tau(i,j+1)+h_\tau(i+1,j)+h_\tau(i-1,j)+h\tau(i,j-1)$$
$$-4h_\tau(i,j)]+(\varepsilon/4)\{[h_\tau(i,j+1-h_\tau(i,j-1)]^2$$
$$+[h_\tau(i+1,j)-h_\tau(i-1,j)]^2\})+\Delta\tau\xi(i,j;\tau)$$

(where ε is the nonlinearity parameter and ξ(i,j;τ) corresponds to independent Gaussian noise generated using the Box-Muller transformation. The additional term

is rewritten as

$$A\ X\ (\ h_\tau(i,j) - \sum_{i,j=1}^{256} h_\tau(i,j) / (256\ X\ 256)) \quad (9)$$

where A is a constant (Bales *et al.*, 1989; Iwasaki *et al.*, 1995; Yoshinobu *et al.*, 1995). We choose the same values of $\Delta\tau = 0.00025$ and $\varepsilon = 25$ as Amar and Family (1990). The parameter A was varied from 0 to 1.0. In the course of simulation, the interface width W(L,t) was calculated for the simulated surface.

Results and Discussion

Figures 1a and 1b show the AFM images of copper electrodeposits grown for one hour in solutions without and with 10 ml/l of the organic additive, respectively. The areas are 50 x 50 μm^2 for both images. It is clearly observed that the surface roughness is drastically reduced by addition of the organic additive in the plating solution. It should be noted that the vertical scale in Figure 1b is exaggerated by a factor of ~25 compared to that in Figure 1a.

Figure 2 shows the dependence of the interface width W(L,t) on the length scale L for copper electrodeposits grown for one hour at 24 mA/cm^2 with various concentrations of the organic additive. As shown in Figure 2, the copper electrodeposits exhibit two different scaling behaviors for higher and lower concentrations of the organic additive separated at 1 ml/l. The former has the smaller value of roughness exponent α, 0.63 ± 0.05, and the latter has the larger value, 0.87 ± 0.05. We call the two growth modes with higher and lower additive concentration as the smoother and the rougher modes, respectively, since the amplitude of roughness in the former mode is lower than that in the latter mode throughout the lengths scales investigated. It should be noted that the scaling behavior inside each mode is universal against variation of additive concentration.

Figure 3 summarizes the values of the roughness exponent α obtained for various current densities and the concentration of the organic additive in the plating solution. As shown in Figure 3, the two growth modes can be observed also at higher and lower current densities. At high current density of 48 mA/cm^2, however, the boundary between the two growth modes shifts toward high additive concentration, i.e., more of the organic additive is needed for the transition from the rougher mode to the smoother mode. At higher current density, a new growth mode is found for low concentration of organic additive, i.e., the surface morphology becomes unstable and bulk-fractal-like microstructures are formed. By increasing the amount of the organic additive, however, the morphology becomes stable and the two growth modes described above are observed again.

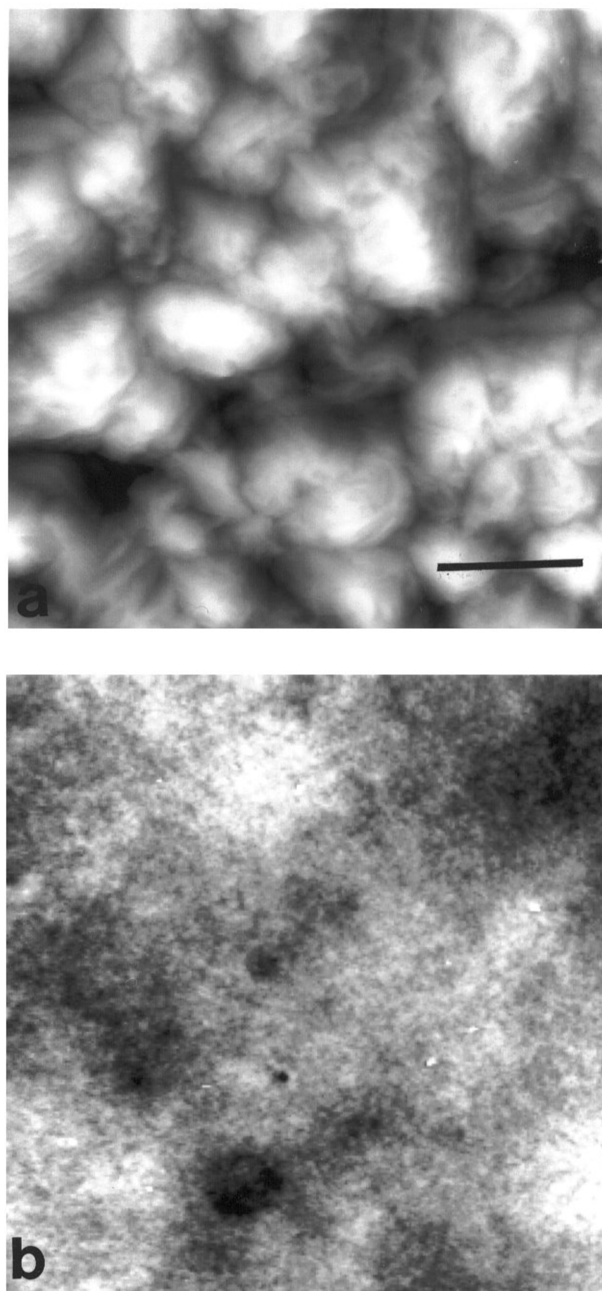

Figure 1. AFM images of the copper electrodeposits grown for 1 hour at 24 mA/cm^2: (**a**) without and (**b**) with 10 ml/l organic additives. The vertical scale is (a) 4000 nm and (b) 160 nm. Bar = μm.

Figure 4 shows surface roughness generated by computer simulation after 204800 steps for the parameter A of 0, 0.1, 0.5, and 1.0, respectively. Figure 4a corresponds to

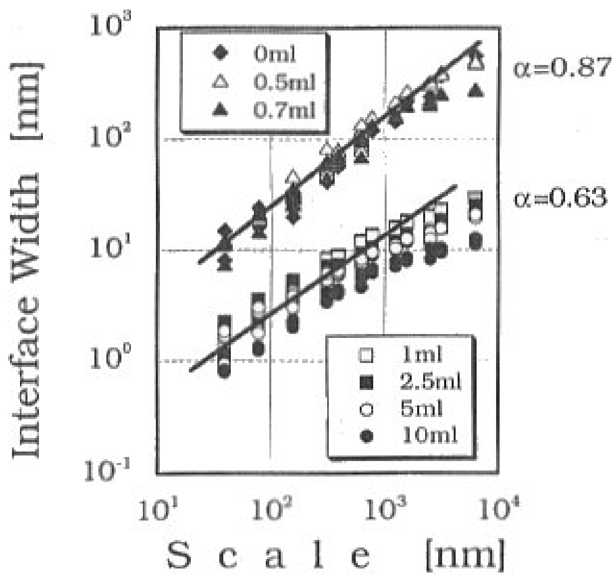

Figure 2. Interface width W in area L x L for samples grown for one hour at 24 mA/cm^2 with various concentrations of the organic additive. Solid lines with gradients 0.63 and 0.87 are drawn as guides to the eye.

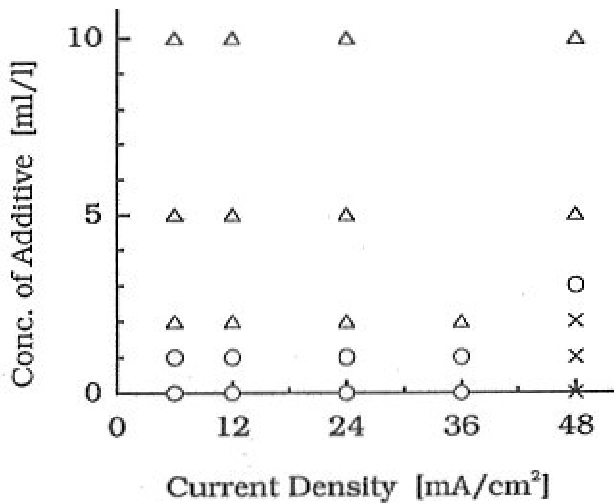

Figure 3: Growth mode phase diagram obtained from scaling analysis for various current densities and the concentrations of the organic additive: O and Δ represent the rougher growth mode (α = 0.87) and the smoother growth mode (α = 0.63), respectively. X represents the bulk fractal growth mode.

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the KPZ case. By increasing the contribution of the non-local effect, rounded protrusions become more obvious on the generated surface. In the case of A = 1.0, a surface similar to the one in the rougher growth mode (see Fig. 1a) is obtained.

Figure 5 shows the time-dependence (where the time is given by the number of integration steps) of the interface width W(L) for A = 1.0. In the early period, the effect of the non-local growth is little, and the W vs L plot is almost the same as that of the KPZ case, for which the value of α is known to be 0.4 (Krug and Spohn, 1990). As the growth advances, the value of α becomes larger and reaches the saturated value of 0.9. This behavior is observed for any value of A except for 0. The value of a increases faster for larger value of A.

Figure 6 shows the interface width W(L) of simulated surfaces for various values of A after 204800 integration steps. For A = 1.0, the roughness exponent a is 0.9, which approximately reproduces the rougher growth mode. For A = 0.1, the non-local effect is not strong at this stage of roughening and the roughness exponent a remains the same as that of the KPZ growth. For extended simulation steps, however, the roughness exponent a increases and eventually reaches the value of 0.9.

Though the smoother growth mode is closer to the KPZ growth, its roughness exponent 0.63 is still larger than that for the KPZ model, 0.4 in 2 + 1 dimension. The organic additive is considered to suppress the enhanced growth at protrusions, and/or to enhance relaxation of the surface, though the microscopic mechanism of the effect of additive is not known. Figure 3 suggests that the effect of the organic additive is competitive with the current density, and thus, with the growth rate. More study is necessary, however, to explain the transition of the growth mode in a quantitative manner.

Conclusion

We investigated the scaling behavior of surface roughness in copper electrochemical deposition under stable growth conditions by AFM and numerical simulation. A transition in the growth mode was observed, which depended on the concentrations of the organic additive in the plating solution. Two growth modes, characterized by roughness exponents 0.63 and 0.87, were found for high and low concentrations, respectively. The boundary between the two growth modes was a function of the current density, and shifted toward higher concentrations as the current density, and thus, the growth rate was increased. At higher current density, the bulk-fractal growth mode was found at lower concentrations of the organic additive. The rougher surface was reproduced by numerical solution of a KPZ-like equation with an additional growth term proportional to the height. Enhanced vertical growth of protrusions and successive lateral growth led to the characteristic humps of the rougher surface.

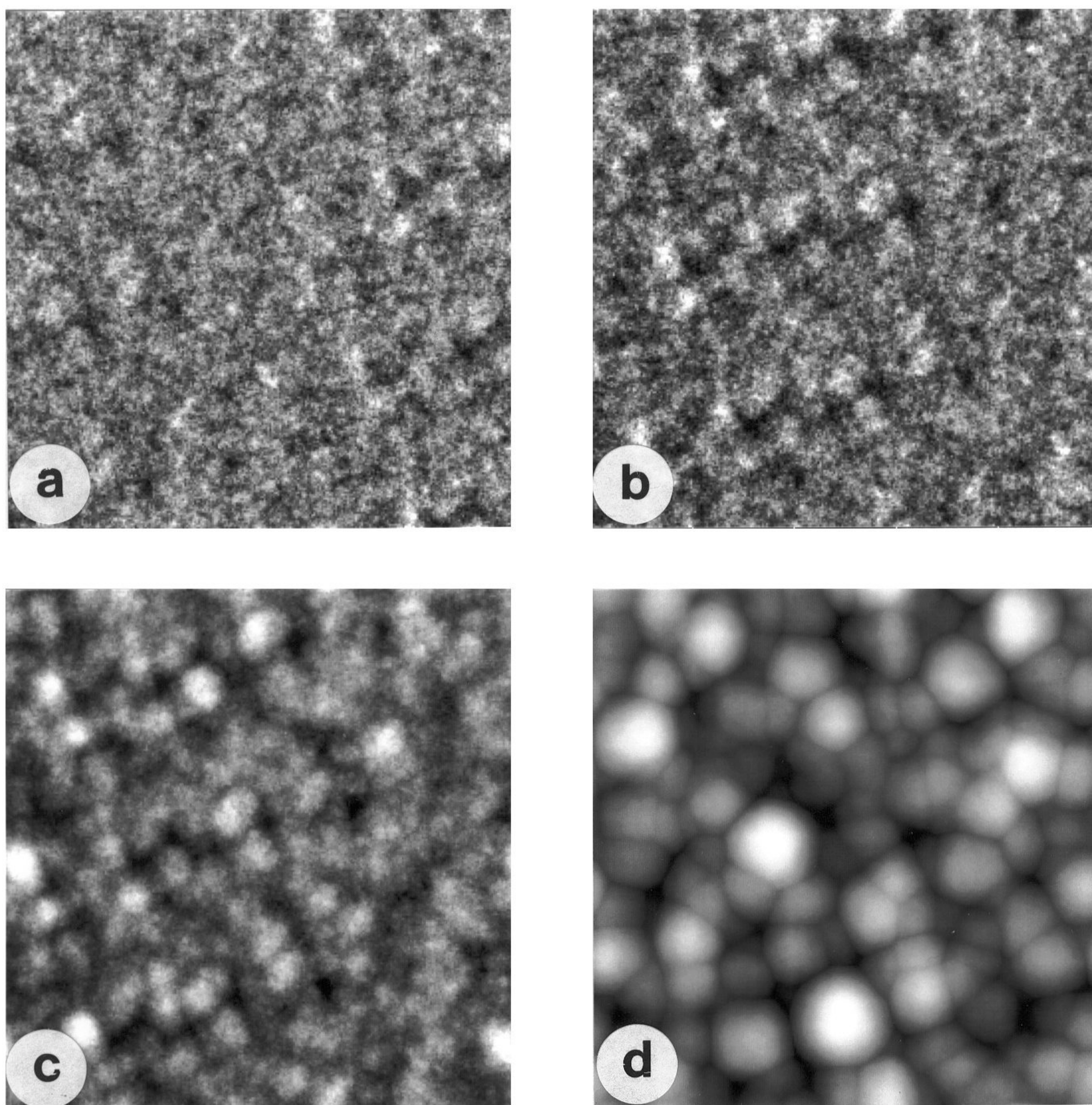

Figure 4. Simulated surfaces after 204800 steps for various values of A: (**a**) A = 0, (**b**) A = 0.1, (**c**) A = 0.5 and (**d**) A = 1.0.

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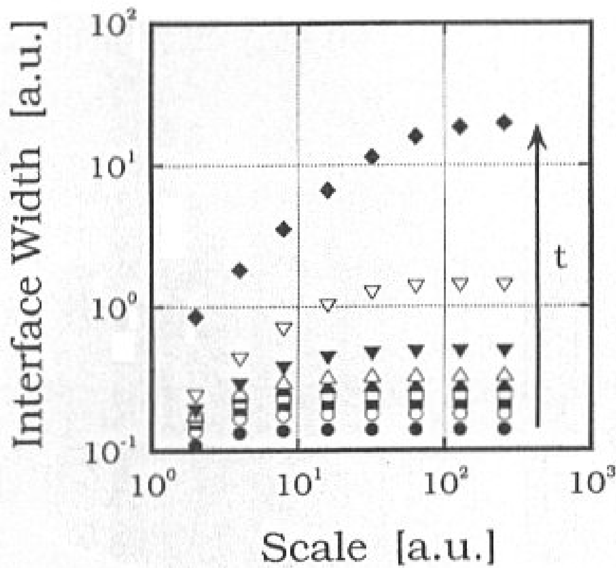

Figure 5. Time dependence of the interface width W(L) for A = 1.0: ● = 100, ○=200, ■ = 400, □ = 800, ▲ = 1600, Δ = 3200, ▼=6400, ∇=12800, ♦=25600 simulation steps. In the early stage of growth, the roughness exponent α is the same as that of the KPZ growth, i.e., 0.4. For extended simulation, α becomes larger and finally reaches the value of 0.9.

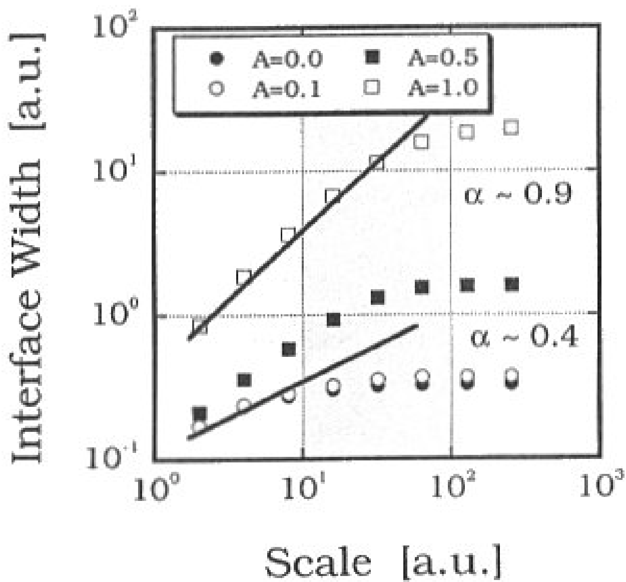

Figure 6. Interface width W(L) for the simulated surfaces in Figure 4. Solid lines with gradients 0.40 and 0.90 are drawn as guides to the eye.

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Discussion with Reviewers

J. Krim: While there appears to be an abrupt transition in the experimental data, the theoretical model appears to exhibit a very gradual, continuous transition. Could you please comment on this?
Authors: The simulation model discussed above only explains the large value of the roughness exponent under the existence of non-local effects. The origin of the abrupt transition in experiments is still under investigation.

Reviewer II: It might be of interest to study the dimensionality-dependence of α in the stable growth mode. In particular, what is the value of α in one dimension? Such an experiment might be possible if one starts out with a one-dimensional nanowire of Cu rather than a copper plate.
Authors: There are a few reports on quasi-(1 + 1)-dimensional electrochemical deposition (Kahanda *et al*., 1992; Pastor and Rubio, 1996). As for the interpretation of results, however, there seems to be a difference; Kahanda *et al*. (1992) compared their experimental value of a with the theoretical value in (1 + 1)-dimension, while Pastor and Rubio compared their experimental value with those in (2 + 1)-dimension. To realize one-dimensional growth, one would need a very thin wire in a very thin cell as mentioned by Reviewer II.