Stable Growth and Kinetic Roughening in Electrochemical Deposition

Atsushi Iwamoto, Tatsuo Yoshinobu, and Hiroshi Iwasaki
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567, Japan
(Received 21 January 1994)

We studied kinetic roughening of copper which was electrodeposited at slow rates. The surfaces showed a unique scaling. In the shorter length regime, the interface width scaled with the length scale L as L^{α} ($\alpha = 0.87 \pm 0.05$). In the longer length regime, the width scaled with the deposition time t as t^{β} ($\beta = 0.45 \pm 0.05$). The value of $\alpha + \alpha/\beta$, 2.8, is much larger than 2 predicted for the case where the growing direction is normal to the surface everywhere. The scaling behavior is interpreted as the result of enhanced growth of the protrusions owing to nonlocal Laplacian growth effect.

PACS numbers: 68.55.Jk, 05.70.Ln, 68.70.+w, 82.65.Dp

Surface roughness of growing films on flat substrates has been shown to exhibit scaling behavior over large variations of length scales, and thus considerable interest [1,2] has been recently directed to the physics of dynamic scaling. Theory [1,3] predicts that the interface width (the mean surface height fluctuation) $W(L,t)$ for length scale L and growth time t scales as

$$W(L,t) \propto L^{\alpha}, \quad \text{for } L \ll L_c, \tag{1}$$

$$W(L,t) = \Delta(t) \propto t^{\beta}, \quad \text{for } L \gg L_c, \tag{2}$$

where

$$L_c = t^{1/z}, \tag{3}$$

$$Z = \alpha/\beta. \tag{4}$$

The scaling behavior is equivalent to scale invariance of the surface height deviation from the average plane at point x and t, $\bar{h}(x,t)$: The statistical properties of $\bar{h}(x,t)$ coincides with those of $b^{-\alpha}\bar{h}(bx, b^z t)$, where b is an arbitrary rescaling factor [2].

In many growth processes, growth is determined solely by the local conditions at the growing site such as reaction rates, surface relaxation rates, and stochastic noise. Kardar, Parisi, and Zhang (KPZ) [3] studied such growing surfaces based on a nonlinear Langevin continuum equation using renormalization-group techniques. The ballistic deposition model [4,5] and Eden growth model [6] are believed to belong to the same universality class as the KPZ growth, and many theoretical and numerical simulation studies have been done [1,2]. For the KPZ type local growth model, the value of α is predicted to be 0.4 (Ref. [2]) for a planar substrate and the surface is compact and self-affine.

On the other hand, in a nonlocal growth process called Laplacian growth, the motion of the growing interface is controlled by a fieldlike quantity (e.g., concentration of a diffusing particle and electric potential) which satisfies the Laplace equation. In this case, deposition occurs preferentially on protrusions. This causes an instability, known as the Mullins-Sekerka instability [7], which can often lead to much rougher bulk-fractal (self-similar) structures where $\alpha \sim 1$. Surface growth in physical systems is likely to have both local and nonlocal growth effects.

Electrochemical deposition is an ideal system for studying the competition between these growth processes because the local and the nonlocal growth effects can be controlled by changing the growth conditions [8,9]. Deposition near the mass-transfer-limited current condition [10] corresponds to diffusion limited growth and leads to unstable morphologies such as fractal and dense-branching morphologies, which have been studied extensively [9,11,12]. At slow growth rates, the growth is controlled by both local effects and nonlocal effects such as diffusion and electromigration of the species in the electrolyte [13] and a planar electrode is morphologically stable. To study kinetic roughening, it is important to be able to investigate the time dependent scaling of the surface. There have been, however, very few experimental studies [9,14,15] of dynamic scaling. As we show below, such time dependent data can be readily obtained in electrodeposition experiments.

In this paper, we investigate dynamic scaling behavior of copper growth in a stirred $CuSO_4$ solution at slow rates under stable growth conditions. When the solution is stirred, the transport of the species is mainly caused by electromigration [16]. Copper was electrodeposited on copper plates in an acid copper sulfate plating solution ($0.30M$ $CuSO_4 \cdot 5H_2O/1.2M$ H_2SO_4). Electrodeposition was carried out for various time of deposition (1–60 min) at room temperature with several current densities (1.2–4.8 A/dm^2). The current density of 2.4 A/dm^2 corresponds to deposition rate of 0.5 μm/min. The copper plating bath was stirred with air bubbles during electrodeposition.

Atomic force microscopy (AFM) was employed to measure the roughness of the copper surface. AFM is not only capable of high-resolution observation of surfaces, but also capable of observation of wide areas, and thus, is suitable for scaling analysis: the dynamic range of length scale if 1 nm–100 μm. The AFM measurements were carried out in air using SFA300/SPI3600 from Seiko Instruments Inc., operated with a constant force of

0031-9007/94/72(25)/4025(4)$06.00

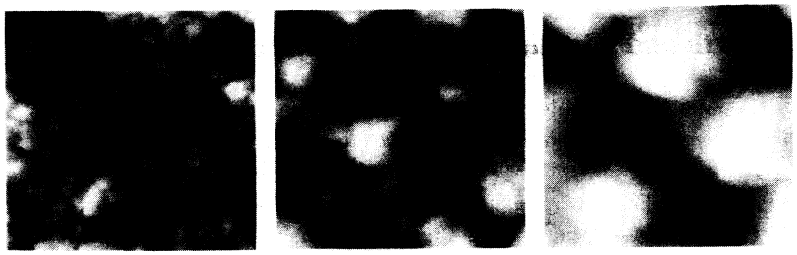

FIG. 1. AFM images of the copper surfaces electrodeposited in the acid sulfate solution with an electric current density of 2.4 A/dm^2 for electrodeposition times of (a) 5, (b) 30, and (c) 60 min. The area size is 20 × 20 μm^2 for all the images.

5.0×10^{-9} N. We performed measurements on a variety of area sizes, i.e., 5 × 5, 20 × 20, and 50 × 50 μm^2. In each measurement, the height data were acquired at a resolution of 256 × 256 pixels.

Figures 1(a), 1(b), and 1(c) show the AFM top-view images of copper surfaces of 20 × 20 μm^2 electrodeposited for 5, 30, and 60 min, respectively, with an electric current density of 2.4 A/dm^2. In Fig. 1, we observed protrusions (grains) of various sizes, and the maximum size of the protrusions becomes larger with increasing electrodeposition time. This indicates that the characteristic correlation length L_c becomes longer with increasing deposition time.

Figure 2 shows the interface width $W(L,t)$ of copper electrodeposited for 1–60 min under the same conditions as those in Fig. 1, calculated from several topographs of different sizes. The thickness varies from 0.5 to 30 μm corresponding to electrodeposition times ranging from 1 to 60 min. For each deposition time, the curve consists of two regimes separated by the correlation length L_c, i.e., the scale-dependent region and the saturated region. For $L < L_c$, W increases as a power of L, and the roughness exponent α is almost constant at 0.87 ± 0.05 for all the surfaces measured. Furthermore, Fig. 2 clearly shows that the scaling in the shorter length regime is indeed stationary after an initial growth of about 1 min. The interface width of the initial Cu substrate was smaller than those of Cu deposits by several orders of magnitudes for the measured length scales.

As shown in Fig. 3, the saturated value of the interface width, $\Delta(t)$ [$= W(L)$ for $L \gg L_c$] increases as the deposit grows thicker: $\Delta(t)$ depends on the deposition time t as t^{β} with the growth exponent β of 0.45 ± 0.05. Thus, Z is found to be 1.93, which is much larger than 1.6 expected for the KPZ model. The correlation length L_c increases in accordance with $t^{1/Z}$ although determination of L_c is somewhat ambiguous. For the present case, Z is smaller than but close to 2 and thus the temporal spread of surface fluctuations $L_c(t)$ is almost diffusive.

Figures 2 and 3 show clearly the two independent spatial and temporal scalings, shown by Eqs. (1)–(4) which was predicted by theory and simulation but until now lacked detailed experimental verification. Constant values of α and β also imply that the growth process is governed by a single process for length scales from ~ 50 nm to ~ 50 μm and deposition times from 5 to 60 min.

Figures 4(a), 4(b), and 4(c) show perspective view images of copper surfaces electrodeposited for 5, 30, and 60 min with anisotropically rescaled vertical and horizontal dimensions [(a) 14 × 14, (b) 28 × 28, and (c) 49 × 49 μm^2] in accordance with the spatial and the temporal scaling exponents derived above. As can be seen from Fig. 4, the morphologies of these three surfaces do indeed look like similar as expected.

The scaling behavior with $\alpha = 0.87$ was also observed for electrodeposition with conditions similar to those used for Fig. 1 but with a current density of 1.2 A/dm^2. In the case of current density of 4.8 A/dm^2, the morphology became unstable and bulk-fractal-like microstructures were formed for thicker films. Thus the scaling behavior is universal for stable copper electrochemical deposition. The same exponent of 0.87 was also observed for copper growth with a small amount of organic additives as reported in the previous paper [8]. More detailed experiments to investigate the effect of organic additives on the roughness exponent is in progress.

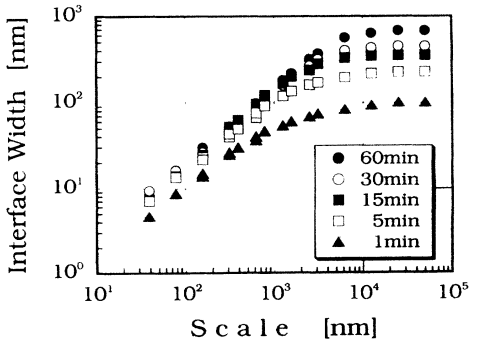

FIG. 2. The interface width of the copper electrodeposits $W(L,t)$ versus length scale L for electrodeposition times of 1, 5, 15, 30, and 60 min.

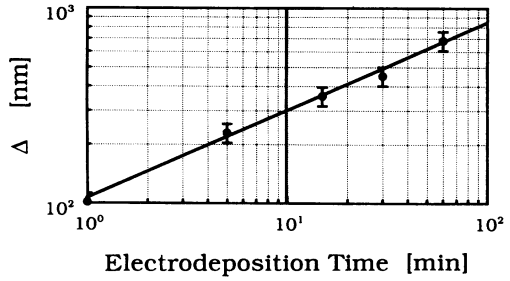

FIG. 3. The saturated value of surface width, Δ, for $L \gg L_c$ versus electrodeposition time.

Now, let us consider the scaling relation for $\alpha + Z$. The relation is derived from very general discussion how the largest protrusions evolve with time [2]. If we assume that the direction of growth is normal to the surface everywhere, as assumed in the KPZ growth model,

$$\frac{dL_c(t)}{dt} \sim \frac{\Delta(L_c(t))}{L_c} \sim L_c^{\alpha-1}, \tag{5}$$

where $\Delta(L_c(t))$ is the height of the largest protrusions at time t and the relation $\Delta(L_c) \sim L_c^{\alpha}$ is used. From the solution of this equation, $L_c(t) \sim t^{1/(2-\alpha)}$, we get $\alpha + Z = 2$. This scaling relation is universal because it is derived only on the assumption that the direction of growth coincides with the local surface normal. The obtained value of $\alpha + Z$, 2.8, is significantly larger than 2. We consider that, in electrochemical deposition under stable growth conditions, there is an electric field effect in addition to local growth effects. Kahanda *et al.* [9] also observed that $\alpha + Z$ is larger than 2 for electrodeposition at very slow rates where local growth effects compete with the nonlocal Laplacian effects. The electric field enhances vertical growth of protrusions but suppresses lateral growth. Both these effects make α and Z larger than those for KPZ growth, respectively as observed in the present study. The effects lead to inclination dependent growth: The local growth velocity v in the normal direction to the substrate is dependent on inclination of the surface u and when the leading nonlinear term is $\sim |u|^{\delta}$ ($\delta > 2$) [17],

$$\frac{dL_c(t)}{dt} \sim \left(\frac{\Delta(L_c)}{L_c}\right)^{\delta-1} \tag{6}$$

and thus $\alpha + Z = 2\alpha + \delta(1 - \alpha)$. The value of $\alpha + Z$ can be larger than 2 for large δ since $\alpha < 1$. It should be mentioned that the scaling relation $\alpha + Z > 2$ has been predicted by Villain: instabilities which are not of the Mullins-Sekerka type in growth by atomic beams result in the scaling relation $\alpha + Z = 4$ [18].

Further experimental study is needed to make clear effects of electrodeposition conditions such as electrolyte components and bubbling on the scaling behavior and to determine whether similar scaling behavior would be found in different systems. Theoretical and simulation studies are also necessary to explain why the scaling exponents α and β have the observed values for the stable electrochemical deposition.

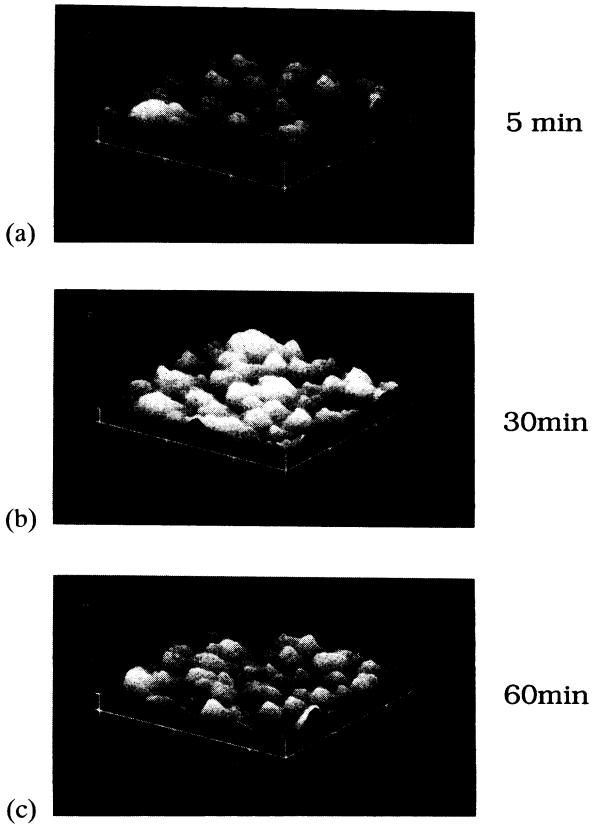

FIG. 4. Rescaled AFM images of those shown in Fig. 1: (a), (b), and (c) correspond to Figs. 1(a), 1(b), and 1(c), respectively. To show scaling behavior of the surface, the vertical and the horizontal dimensions are anisotropically scaled in accordance with the spatial and temporal scaling deduced from the quantitative analysis of the surface height correlations.

In summary, we investigated kinetic roughening of copper surfaces during electrochemical deposition. The interface width scaled with length scale L as $W \sim L^{\alpha}$ ($\alpha = 0.87 \pm 0.05$) for shorter length scales, and then saturated at a value, which scaled with time as t^{β} ($\beta = 0.45 \pm 0.05$). Finally, the scaling relation between the roughness exponent α and the dynamic exponent β indicates that the growth velocity has inclination dependent nonlinear $|u|^{\delta}$ ($\delta > 2$) term which reflects enhanced protrusion growth as expected for Laplacian growth. The fact that α and $\alpha + Z$ have the larger values than those expected for the KPZ growth indicates that the present Cu growth belongs to a new universality class which is the result of additional nonlocal growth effects in addition to local growth ones.

The authors acknowledge helpful discussions with E. D. Williams, N. Bartlet, T. Einstein, and N. Akutsu. We

gratefully acknowledge J. Sato, H. Matsuda, and A. Ikeda at Asahi Chemical Industry Co. Ltd. for helpful discussions on electrochemical deposition. This work was supported by a Grant-in-Aid for Scientific Research (Contract No. 04452092) from the Ministry of Education, Science and Culture.

[1] *Dynamics of Fractals Surfaces,* edited by F. Family and T. Vicsek (World Scientific, Singapore, 1991).

[2] J. Krug and H. Spohn, in *Solids Far From Equilibrium: Growth, Morphology, and Defects*, edited by C. Godreche (Cambridge University Press, Cambridge, England, 1990).

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

[4] P. Meakin, P. Ramanlal, L. M. Sander, and R. C. Ball, Phys. Rev. A **34**, 5091 (1986).

[5] J. Krug and P. Meakin, Phys. Rev. A **40**, 2064 (1989).

[6] M. Eden, in *Proceedings of the 4th Berkeley Symposium on Mathematical Statics and Probability*, edited by F. Neyman (University of California Press, Berkeley, 1961), Vol. 4.

[7] W. W. Mullins and R. F. Sekerka, J. Appl. Phys. **34**, 323 (1963); **35**, 444 (1964).

[8] H. Iwasaki and T. Yoshinobu, Phys. Rev. B **48**, 8282 (1993).

[9] G. L. M. K. S. Kahanda, X. Zou, R. Farrell, and P. Wong, Phys. Rev. Lett. **68**, 3741 (1992).

[10] D. P. Barkey, R. H. Muller, and C. W. Tobias, J. Electrochem. Soc. **136**, 2199 (1989).

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

[12] P. Garic, D. Barkey, E. B. Jacob, E. Bochner, N. Broxholm, B. Miller, B. Orr, and R. Zamir, Phys. Rev. Lett. **62**, 2703 (1989).

[13] M. D. Pritzker and T. Z. Fahidy, Electrochim. Acta **37**, 103 (1992).

[14] Y. L. He, H. N. Yang, T. M. Lu, and G. C. Wang, Phys. Rev. Lett. **69**, 3770 (1992).

[15] J. Krim, I. Heyvaert, C. V. Haesendonck, and Y. Bruynseraede, Phys. Rev. Lett. **70**, 57 (1993).

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

[17] For KPZ model, $\delta = 2$. As $|u| \to 0$, $v(u:\delta)$ for the case of $\delta > 2$ is smaller than that for $\delta = 2$. Thus growth of protrusions is enhanced for $v(u:\delta > 2)$.

[18] J. Villain, J. Phys. I (France) **1**, 19 (1991).

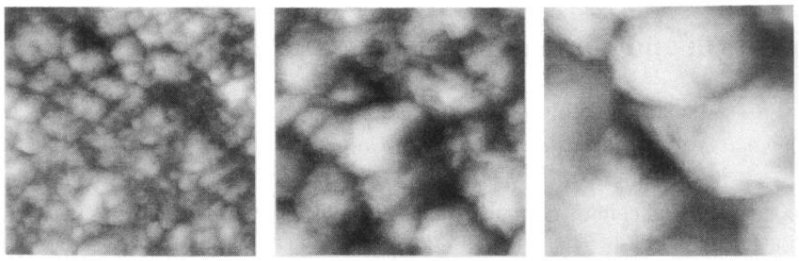

FIG. 1. AFM images of the copper surfaces electrodeposited in the acid sulfate solution with an electric current density of 2.4 A/dm^2 for electrodeposition times of (a) 5, (b) 30, and (c) 60 min. The area size is 20×20 μm^2 for all the images.

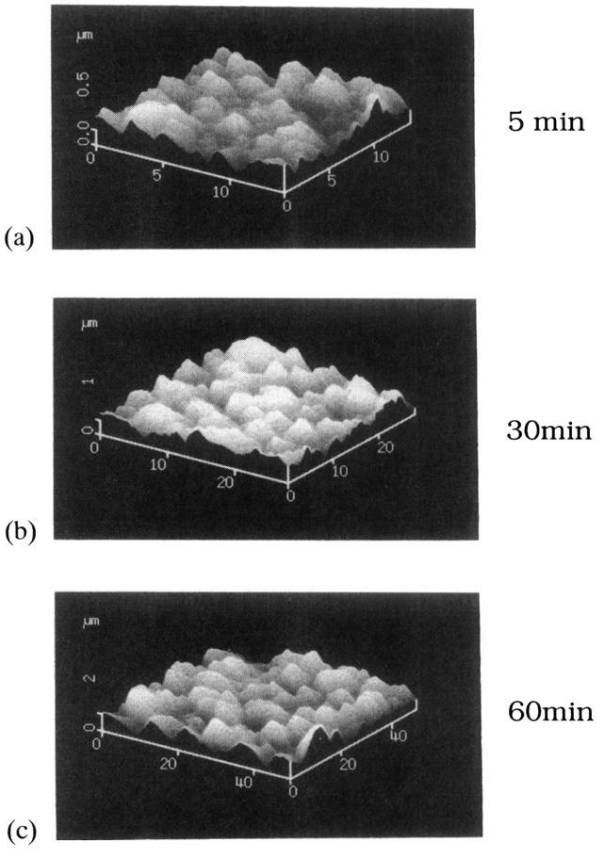

FIG. 4. Rescaled AFM images of those shown in Fig. 1: (a), (b), and (c) correspond to Figs. 1(a), 1(b), and 1(c), respectively. To show scaling behavior of the surface, the vertical and the horizontal dimensions are anisotropically scaled in accordance with the spatial and temporal scaling deduced from the quantitative analysis of the surface height correlations.