

## Kinetic roughening in electrodisolution of copper

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(Received 18 May 1998)

We studied kinetic roughening of copper surfaces electrochemically dissolved at constant current densities by atomic force microscopy. The surface was found to roughen with time and the surface width increased with the length scale with the roughness exponent  $\alpha$  of  $0.73 \pm 0.05$  in the stationary state. This value is different from that in electrochemical deposition, 0.87, under the stable growth condition [A. Iwamoto *et al.*, Phys. Rev. Lett. **72**, 4025 (1994)]. The observed roughening in the dissolution process is discussed in terms of nonlocal effects. [S1063-651X(99)11305-9]

PACS number(s): 05.40.-a

### INTRODUCTION

Surface roughening of growing/dissolving surfaces is of great interest from industrial and physical points of view. For example, a variety of deposition/etching techniques is employed in many semiconductor device processes, and the surface/interface roughness is known to affect the device performance such as carrier mobility. To control the roughness, it is important to investigate its statistical behavior and to clarify its origin.

Various types of growth have been studied on the basis of the concept of fractals introduced by Mandelbrot [1]. It is known that in compact rough growths, surface roughness shows the self-affine fractal property, i.e., power-law dependence on the length scale with an exponent smaller than 1. In terms of dynamic scaling theory [2,3], it is expected that the interface width  $W(L,t)$ , which is the mean fluctuation of the surface height on length scale  $L$  at growth time  $t$ , shows the spatiotemporal scaling behavior;  $W \sim L^\alpha$  for  $L \ll L_c$  and  $W \sim t^\beta$  for  $L \gg L_c$ . The correlation length  $L_c$  grows with  $t$  as  $t^{1/Z}$ , where  $Z = \alpha/\beta$ . These scaling exponents of  $\alpha$ ,  $\beta$ , and  $Z$  are called the roughness exponent, the growth exponent, and the dynamic exponent, respectively. The growth mode can be characterized with these exponents.

Surface growth in physical systems is likely to have both local and nonlocal growth effects. For the local growth model, accretion of materials is solely determined by local conditions at the growing site. Kardar, Parisi, and Zhang (KPZ) [4] studied such growing surfaces based on a nonlinear Langevin continuum equation using renormalization-group techniques. For KPZ-type growth, the growth direction is normal to the local surface, the surface is compact, and the value of  $\alpha$  is predicted to be 0.4 for a planar substrate [2]. There is a nonlocal growth process called Laplacian

growth, in which accretion of materials is limited by nonlocal processes such as diffusion and electric potential. This causes an instability, known as the Mullins-Sekerka instability [5], which often leads to much rougher bulk-fractal (self-similar) structures with  $\alpha \sim 1$ .

In an electrochemical system, deposition and dissolution usually occur simultaneously at the cathode and anode surfaces, respectively. As for the electrochemical deposition, which is the cathodic reaction, a lot of studies have been done. It is known that growth morphology changes from compact rough morphology to dendritic morphology with an increase of nonlocal growth effects [6–11]. In our previous papers [6,8–11], we reported on kinetic roughening of copper surfaces during electrochemical deposition, where deposited surfaces showed self-affine fractal growth with exponents  $\alpha = 0.87 \pm 0.05$  and  $\beta = 0.45 \pm 0.05$  under the stable growth condition. We also found that adding organic additives as the “brightener” in the plating solution, the surface morphology became smoother with  $\alpha = 0.63$ . This change of growth mode was considered to result from the decrease of the contribution of the nonlocal growth effect.

Compared to electrodeposition, there have been few studies on evolution of the topography of a solid under dissolution [12]. Recently, Pritzker and Fahidy [13] studied morphological stability of a planar metal electrode during electrodeposition and electrodisolution. Surface energy effects always tend to restore the planar interface in order to minimize the surface area. The concentration of metal ions in proximity of the surface is highest at the leading points both during deposition and dissolution. This causes the concentration overpotential to shift positively, and thus results in a destabilizing effect during deposition, but a stabilizing effect during dissolution. Pritzker and Fahidy pointed out that instability may arise even in the case of electrodisolution owing to the kinetic effect by which the current density increases with the concentration of metal ions on the surface [13].

In this study, we investigated kinetic roughening of electrochemically dissolved surfaces at constant current densities. The experimental conditions were kept the same as in the electrochemical deposition processes we reported in our previous papers, except for the direction of the current. To study the kinetic roughening not only in the electrochemi-

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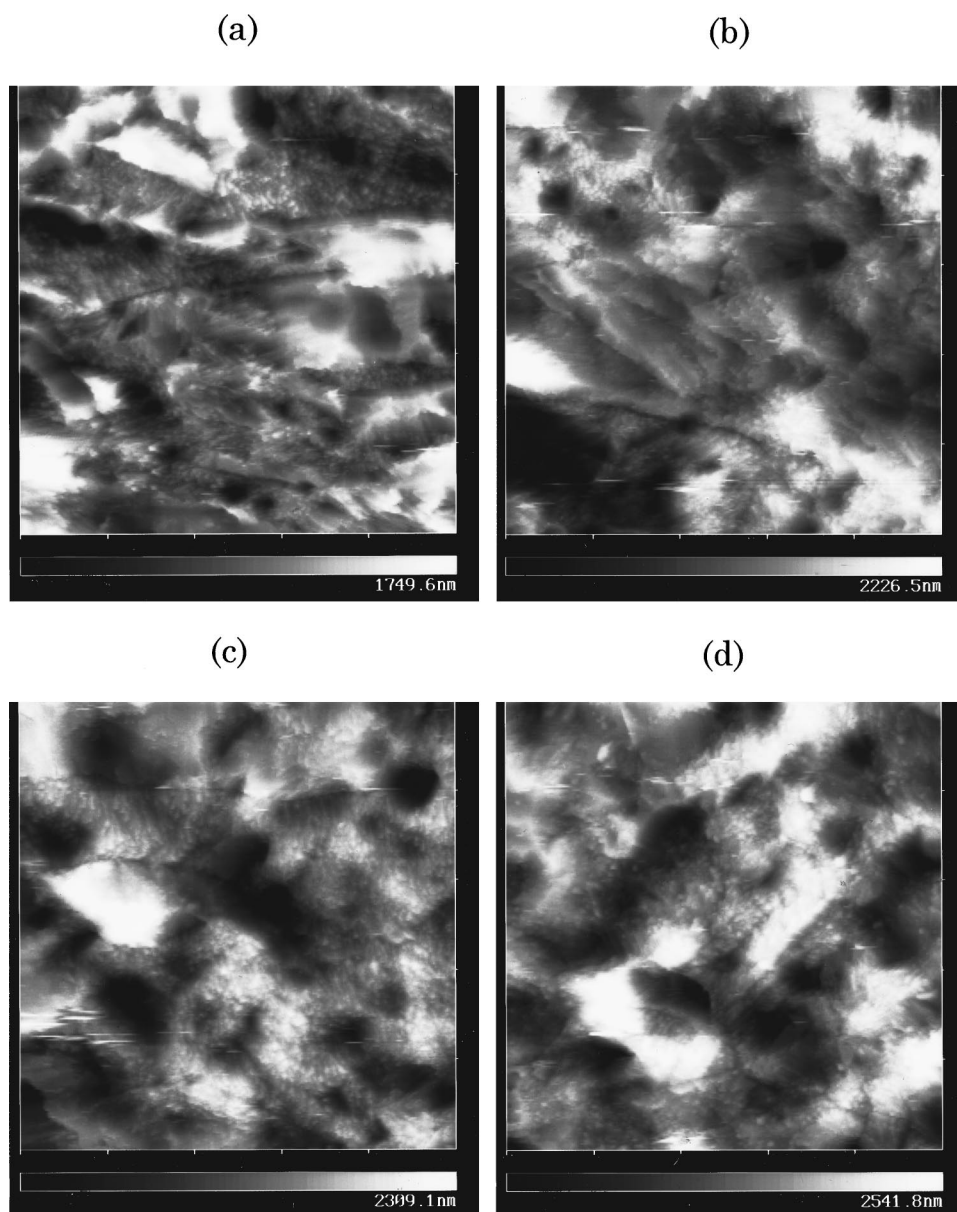


FIG. 1. AFM images of the copper surfaces electrodissolved in the acid sulfate solution with an electric current density of  $30 \text{ A/m}^2$  for electrodisso- lution times of (a) 10, (b) 20, (c) 30, and (d) 50 min. The area size is  $50 \times 50 \mu\text{m}^2$  for all the images.

caldeposition but also in the dissolution seems to be useful to understand the electrochemical processes.

### EXPERIMENT

The anodic copper plate was electrochemically dissolved in an acid copper sulfate plating solution ( $0.30 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O}/1.2 \text{ M H}_2\text{SO}_4$ ). The current densities were chosen to be similar to those at which electrochemical deposition was stable and the surface was self-affine. Some specimens were dissolved in solutions containing organic additive ‘‘copper gleam PCM’’ (a sulfonium-alkane-sulfonate-type additive, LeaRonal, NY) which works as the brightener in electrodeposition. The standard concentration recommended for practical electroplating is 5–10 ml/l. Electrodis- solution was carried out at several current densities ( $30\text{--}120 \text{ A/m}^2$ ) at room temperature and for various times (5–50 min). The current density of  $30 \text{ A/m}^2$  corresponds to a dissolution rate of  $0.06 \mu\text{m}/\text{min}$ . The copper plating bath was stirred with air bubbles during dis- solution.

Atomic force microscopy (AFM) was employed to mea- sure the roughness of the copper surface. AFM is not only capable of a high-resolution observation of surfaces, but it is also capable of the observation of wide areas, and thus it is suitable for scaling analysis: the dynamic range of length scale is 1 nm to  $100 \mu\text{m}$ . The AFM measurements were carried out in air using SFA300/SPI3700 from Seiko Instru- ments Inc. operated with a constant force of  $5.0 \times 10^{-9} \text{ N}$ . We performed measurements on a variety of area sizes, i.e.,  $5 \times 5$ ,  $20 \times 20$ , and  $50 \times 50 \mu\text{m}^2$ . In each measurement, the height data were acquired at a resolution of  $256 \times 256$  pixels. The interface width  $W(L, t)$  was calculated from the numerical data obtained by AFM measurements [11].

### RESULTS AND DISCUSSIONS

Figures 1(a)–1(d) show typical AFM topographies of copper surfaces electrochemically dissolved with an electric current density of  $30 \text{ A/m}^2$  without organic additives in the plating solution for dissolution times of 10, 20, 30, and 50

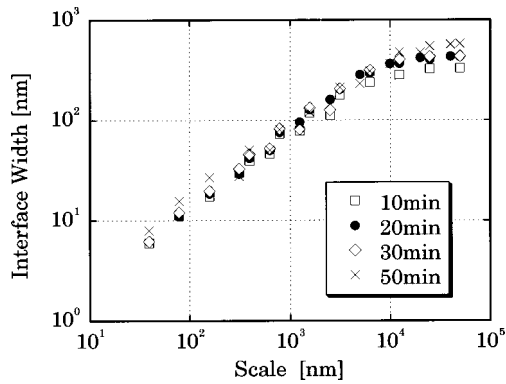


FIG. 2. The interface width of the copper electrodissoved surface  $W(L,t)$  vs length scale  $L$  for electrodissoved times of 10, 20, 30, and 50 min.

min, respectively. As shown in Fig. 1, various sizes of pits are observed, and the maximum size of the pits becomes larger with increasing dissolution time. This indicates that the characteristic correlation length  $L_c$  becomes longer with increasing dissolution time. Figure 2 shows examples of the interface width  $W(L,t)$  of copper surfaces dissolved for 10–50 min under the same conditions as those in Fig. 1.  $W(L,t)$  was calculated from several AFM images of different sizes. The interface width of the initial copper substrate was smaller by several orders of magnitude than those of the dissolved surfaces for the measured length scales. For each dissolution time, the  $W(L,t)$  curve consists of a scale-dependent region and a saturated region separated by the correlation length  $L_c$  around  $10^4$  nm. For  $L$  shorter than  $L_c$ ,  $W$  increases as a power of  $L$  with a roughness exponent  $\alpha = 0.73 \pm 0.05$  for all the surfaces measured. As shown in Fig. 3, the saturated value of the interface width  $W [= \Delta(t)]$  increased as the dissolution time  $t$  as  $t^\beta$ . The value of the growth exponent  $\beta = 0.22$ .

Then we also investigated the spatial scaling behavior for various electric current densities of 60, 90, and  $120 \text{ A/m}^2$  for a dissolution time of 5 min. In the case of  $120 \text{ A/m}^2$ , we also added 10 ml/l of organic additives in the solution to study the effect of the organic additives in the dissolution process. Figure 4 shows examples of the  $W$  versus  $L$  plots under each condition. The slope in the scale-dependent region was calculated and averaged for several  $W(L,t)$  curves at each dissolution time. In Table I, we collect the values of roughness exponents obtained through the present study. The roughness exponent  $\alpha$  is  $0.73 \pm 0.05$ , which is smaller than that in electrochemical deposition ( $\alpha = 0.87 \pm 0.05$ ). These results show that the roughness exponent is independent of the electric

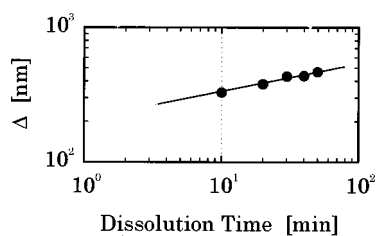


FIG. 3. The saturated value of surface width,  $\Delta$ , for  $L \gg L_c$  vs electrodissoved time.

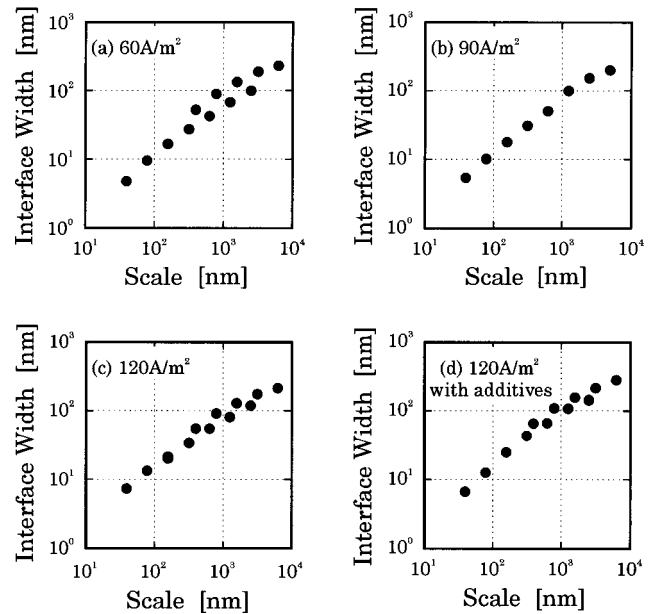


FIG. 4. The interface width of the copper electrodissoved surface  $W(L,t)$  versus length scale for dissolution time of 5 min with a variety of electric current density of (a) 60, (b) 90, and (c) and (d)  $120 \text{ A/m}^2$ : in the case of (d), the solution contains 10 ml/l of organic additives.

current density, and the correlation length increases with dissolution.

It is also found that the organic additives in the solution do not affect the roughening of the anodic surface during dissolution. In the case of deposition on the cathode, addition of organic additives resulted in reduction of the roughness by an order of magnitude and transition of the roughness exponent from 0.87 to 0.63, suggesting a transition of the growth mode [9,10]. We consider that the smoothing effect is the result of adsorption of organic additives on the surface: it suppresses the surface reaction and thus changes the diffusion-limited electrodeposition process to surface reaction limited growth [9,10]. The present results suggest that adsorbed organic additives do not affect the surface reaction during the electrodissoved process.

Now we consider the similarity between dissolution and deposition. Figure 5(a) shows the upside-down (height-inverted) representation of an AFM image of a copper surface after 60 min of electrochemical deposition at an electric

TABLE I. The obtained values of roughness exponent  $\alpha$  for various experimental conditions.

Current density ( $\text{A/m}^2$ )	Dissolution time (min)	$\alpha$
30	10	0.73
30	20	0.74
30	30	0.76
30	40	0.71
30	50	0.71
60	5	0.73
90	5	0.76
120	5	0.71
120 (with additive)	5	0.72

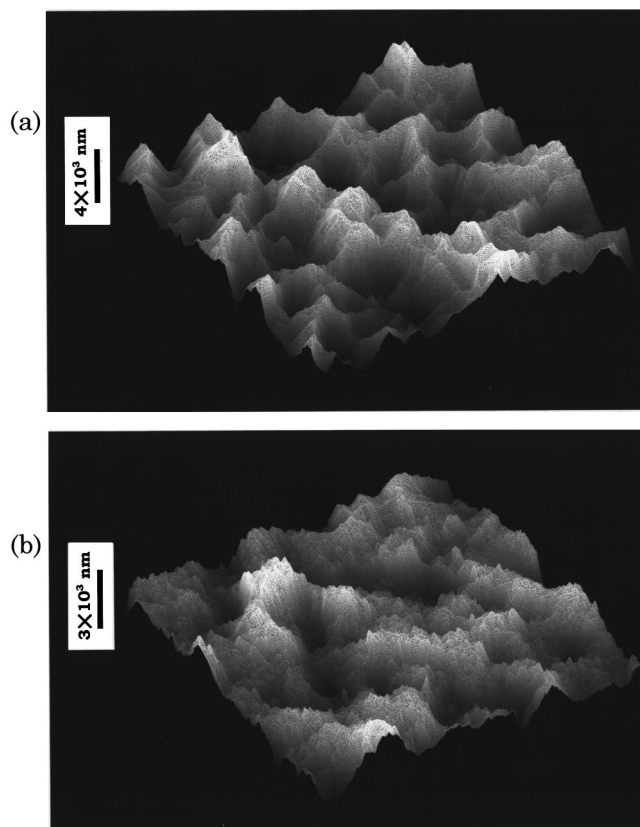


FIG. 5. (a) The  $50 \times 50 \mu\text{m}^2$  upside-down AFM image of the copper surface electrodeposited in the same solution for 60 min with an electric current density of  $240 \text{ A/m}^2$ . (b) Bird's-eye view of electrodissolved surface shown in Fig. 1(d).

current density of  $240 \text{ A/m}^2$ . The inverted geometry resembles those of dissolved surfaces that consist of concave paraboloids and ridges as shown in Fig. 5(b), suggesting that evolution of the surface roughness in dissolution should be described by a model similar to that for deposition.

In our previous study [9,10], we proposed a model to describe the roughening of a surface in electrodeposition in which a growth term proportional to the local height was added to the KPZ equation to take account of nonlocal effects:

$$\frac{\partial h(\mathbf{r},t)}{\partial t} = \gamma \nabla^2 h(\mathbf{r},t) + \frac{\nu}{2} (\nabla h(\mathbf{r},t))^2 + \eta(\mathbf{r},t) + k[h(\mathbf{r},t) - \langle h(\mathbf{r},t) \rangle_s], \quad (1)$$

where the height  $h(r,t)$  is measured from the average growing plane,  $\gamma$  is the surface tension,  $\nu$  is the growth rate normal to the surface, and  $\eta(r,t)$  is the random noise. The term  $\langle h(r,t) \rangle_s$  denotes the average height within a certain area of  $S$ , to which extent topographical effects have an influence on the diffusion of ions, and the parameter  $k$  represents the contribution of the nonlocal effects. In the case of dissolution,  $h(r,t)$  should be measured downward, and the stability of growth is determined by the sign of the parameter  $k$ . As was discussed by Pritzker and Fahidy [13], instability may arise even in the case of electro-dissolution. If the kinetic effect dominates the stabilizing effects owing to concentration overpotential, the parameter  $k$  in Eq. (1) becomes positive.

Further experimental and theoretical studies are needed to clarify more detailed dynamical behavior of the dissolution process and the difference between dissolution and deposition.

## CONCLUSION

We investigated kinetic roughening in electrochemical dissolution. On shorter length scales, the interface width  $W$  was stationary and scaled with length scale  $L$  as  $L^\alpha$  ( $\alpha = 0.73 \pm 0.05$ ). The growth exponent  $\beta$  was 0.22. The value of  $\alpha$  was larger than that of the KPZ local growth model. The geometry of a dissolved surface resembles the inverted geometry of the deposited surfaces. Thus it is probable that, in the electrochemical dissolution case also, the growth of roughness was controlled not only by the local effect but also by the nonlocal effect in the similar way to electrodeposition.

## ACKNOWLEDGMENTS

The authors acknowledge helpful discussions with K. Sudoh. This work was supported by a Grant-in-Aid for Scientific Research (Contract No. 04452092) from the Ministry of Education, Science, Sports and Culture.

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