# Self-affine growth of copper electrodeposits

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(Received 14 June 1993)

We have studied the static surface roughness of 50-$\mu$m-thick copper electrodeposits on length scales between 5 and $10^4$ nm using scanning tunneling and atomic force microscopy. The surface roughness depends strongly on the concentration of organic additives in the plating solution. Both the surface width and power spectra scale as a power of the system size. Self-affine surfaces became more fractal-like with decreased additives. The scaling exponent of the self-affine surface ($\frac{1}{2}$) is slightly larger than the simulation results for local growth models.

Growth processes often result in rough surfaces (interfaces) that exhibit special scaling behavior depending on the microscopic details of the growth. Many growth processes involve an accretion of material which is limited by diffusion. In these cases deposition occurs preferentially on any protuberances. This causes an instability, known as the Mullins-Sekerka instability, which can often lead to self-similar (fractal) structures.[1] The growth process is governed by a spatial distribution of a fieldlike quantity which is inherently *nonlocal* and satisfies Laplace's equation.[1] In other cases, irreversible nonequilibrium growth phenomena result in compact but nonsmooth surfaces which can be well approximated by a single-valued function (no overhangs). The scaling properties of such surfaces are direction dependent and thus are self-affine.[1] Kardar, Parisi, and Zhang (KPZ) (Ref. 2) studied growing self-affine interfaces theoretically based on the nonlinear Langevin equation using renormalization-group techniques; the interface grows *locally* along the normal to the interface and relaxes due to surface tension at protrusions in the presence of position and time-dependent fluctuations. The ballistic deposition model[1] and Eden[3] growth model are believed to belong to the same universality class as KPZ growth. Many theoretical and numerical simulation studies have been done to obtain a more complete picture of possible universality classes of growing interfaces.[1-9] However, more experimental studies of this problem are necessary to establish the validity of the models as descriptions of real growth.

In this paper, we study the growth of copper electrodeposits by analyzing the surfaces using a scanning tunneling microscope (STM) and an atomic force microscope (AFM). STM has been used before in a similar manner to probe the equilibrium properties of rough surfaces.[10] In simple electrodeposition conditions, the growth is considered to be diffusion limited;[1] the reaction is limited by ion diffusion or Ohmic resistance where the fieldlike variable is the ion concentration or the electric potential. Several observations of fractal growth of electrodeposits have been reported.[11,12] In the commercial process of copper electrodeposition, the solution is stirred and the reaction is considered to be limited by Ohmic resistance. To make the grown surface specularly bright, organic additives are added to the solution. We find that surfaces prepared with certain concentrations of the organic additives destroyed the previously observed fractal nature of the bulk electrodeposit. Instead, we find surfaces which are self-affine: that is, a crossover from a fractal-type structure to a less disordered self-affine geometry occurs when a parameter of the growth condition changes.

Copper was electrodeposited on copper plates in an acid copper sulfate plating solution designed for fine print circuits. The solution contained the organic additive "Copper Gleam PCM" (a sulfonium-alkane-sulfonate-type additive,[13] LeaRonal, NY). Deposits of 50-$\mu$m thickness were made at room temperature with a constant current of 6 A / dm$^2$. The copper plating bath was stirred with air bubbles during electrodeposition. The samples are called $A$ and $B$ according to whether the concentration of the additive is 1 (standard concentration) or 0.5 wt. %, respectively. The STM and AFM used are models STE-330 and SFA-300 from Seiko Instruments Inc. Scanning electron microscopy (SEM) observation indicated no overhangs for the surfaces of both samples $A$ and $B$.

Figures 1(a) and 1(b) show $50\times50$ $\mu$m$^2$ AFM topographs of the copper electrodeposits for samples $A$ and $B$, respectively. It is clear that the surface roughness depends strongly on the concentration of organic additives; note that the vertical scale of Fig. 1(a) is expanded by about 10 times that of Fig. 1(b).

Figure 2 shows the dependence of the surface width $w$ on the size of the surface $r$ for sample $A$ (solid marks) and $B$ (open marks) calculated for several measured topographs of different size.

$$w(r)=\left\{[1/N_s(r)]\sum_{i=1}^{N_s(r)}[h_i-h_{\rm av}(r)]^2\right\}^{1/2},$$

where $N_s(r)$ is the total number of surface sites of a surface of size $r$, $h_i$ is the distance of the $i$th surface site from the substrate, and

$$h_{\rm av}(r)=[1/N_s(r)]\sum_{i=1}^{N_s(r)}h_i .$$

For each measurement, we canceled the "sample mounting error" by choosing the substrate parallel to the

 

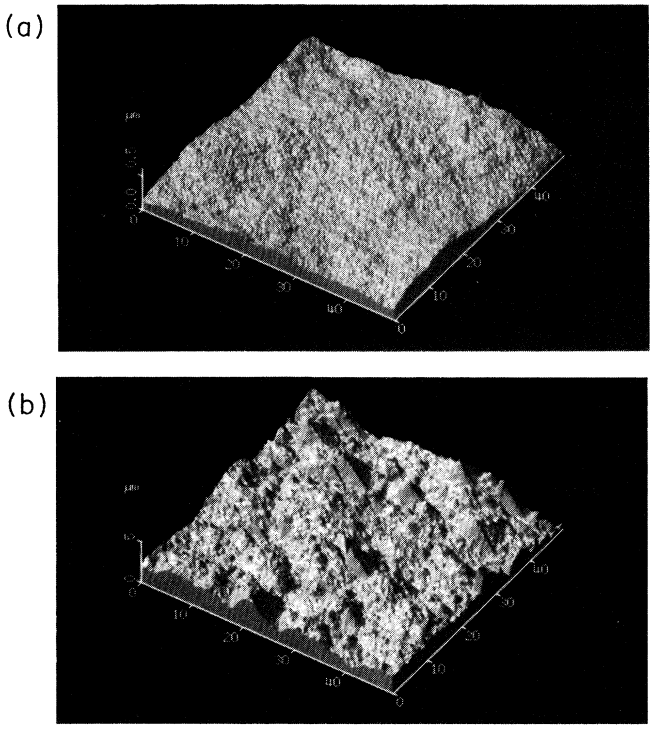


FIG. 1. AFM topographs of the copper electrodeposits of 50-$\mu$m thickness: (a) for sample $A$ and (b) for sample $B$. The vertical scale is greatly expanded in (a). All lengths are in $\mu$m.

"least-square-fit plane" to the whole area of size $L_w \times L_w$. A series of $w(L_w/2^n)$ ($n$ is an integer) are calculated for the $4^n$ divided surfaces of the whole surface for each data set [$w(L_w/2^n)$ for $n \sim 1-3$ are omitted because we suspect that the widths may be underestimated by the error canceling procedure]. Three of the symbols in Fig. 2 refer to AFM data: the areas of dimension $50\times50$ (squares), $20\times20$ (triangles), and $5\times5$ (circles) $\mu m^2$. Each of these areas had a common central point. The $0.8\times0.8$ $\mu m^2$ region (diamonds) was obtained using STM on the same sample. As the surface of sample $B$ was too rough, STM measurement could not be done for it. The plots for the $50\times50$ $\mu m^2$ region are calculated from the same topographs shown in Fig. 1. The measured heights are calibrated by the standards of the microscopes and no translation of each plot along the vertical axis was done for the display of Fig. 2. We have made measurements of several other surface regions for both samples and obtained plots which are very close to Fig. 2.

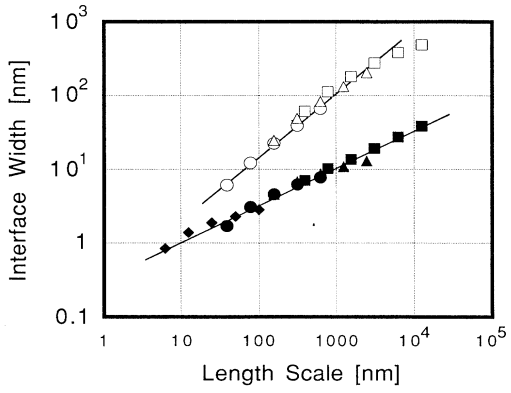


FIG. 2. Interface width $w$ vs surface-size $r$ plot for the surface $A$ (solid marks) and $B$ (open marks). The plots are for $50\times50$ (squares), $20\times20$ (triangles), and $5\times5$ (circles) $\mu m^2$ measured areas for the same central point by AFM and for $0.8\times0.8$ (diamonds) $\mu m^2$ by STM for the same sample. Solid lines of slopes $\frac{1}{2}$ and 0.87 are drawn as guides to the eye.

We concentrate on the scaling behavior for $h_{av}(r)/r^z \gg 1$ [$h_{av}(r)$ is about 50 $\mu$m] where $w$ is expected to depend on $r$ as $r^\alpha$; $\alpha$ and $z$ are called stationary and dynamic scaling exponents, respectively, and theoretically $\alpha+z=2$.[1,4] In Fig. 2, we see an approximate power-law dependence as predicted by the scaling theory.[1,2] The exponent $\alpha$ can be extracted and is found to be $0.50\pm0.02$ for the curve $A$. The surface for which $w \sim r^\alpha$ and $\alpha < 1$ is described as self-affine;[14] the surface area of a surface of size $r$, measured on a length scale $l$, diverges as $l^{\alpha-1}$ for $l \ll b$ but converges to $r^2$ for $l \gg b$, where $b$ is the crossover length for which $w$ is comparable to $l$. The crossover length $b$ is several Å for the curve $A$ if the above power-law dependence is extrapolated to small $l$. For the sample $B$, grown with less organic additives (curve $B$ in Fig. 2), the width is much wider and increases as $\sim r^{0.84\pm0.03}$ with increase of $r$ for $r < 5\times10^3$ nm and the increase appears to saturate above $5\times10^3$ nm. If $\alpha > 1$, the surface area is $r^{1+\alpha}$ for large $r$, and since the exponent is greater than 2, the surface would correspond to the surface of a fractal.[14] As it is well known empirically that black dendritic (fractal) growths of bulk copper are electrodeposited when the density of organic additives is small, we believe that the surface $B$ is in the transition region from a state in which the bulk electrodeposit is fractal to one in which the bulk is not fractal, but the surface is self-affine.

Figure 3 shows the log-log power spectral density plots for the same data used in Fig. 2. As in Fig. 2, no translation of each plot along the vertical axis was done. Roughly speaking, both curves are linear for a wide range of wavelengths, as one would expect for surfaces which are self-similar or self-affine. The slopes of curves $A$ and $B$ are about 2 and $\frac{5}{2}$, respectively. Using the relation[15] $D=(7-\text{slope})/2$, one can deduce the surface "fractal dimension" $D$ to be 2.5 and 2.25, respectively. These values are in good agreement with those estimated from the $w$ vs $r$ dependence; the local fractal dimension $D$ is given by $3-\alpha$, which is 2.5 (2.16) for the surface $A$ ($B$). It should be noted that, from the power spectrum plots alone, one cannot tell whether the surface is self-similar or self-affine.

A self-affine surface is rough and scales as fractal structure only at a lower scale length than the crossover length and looks smooth above a certain length scale; it has local fractal and global dimensions for the former and the latter regimes.[1] Here we introduce an exponent $\delta$ which quantifies, for the upper length scale, the roughness of the self-affine surface for which $w \sim r^\alpha$; [(the area

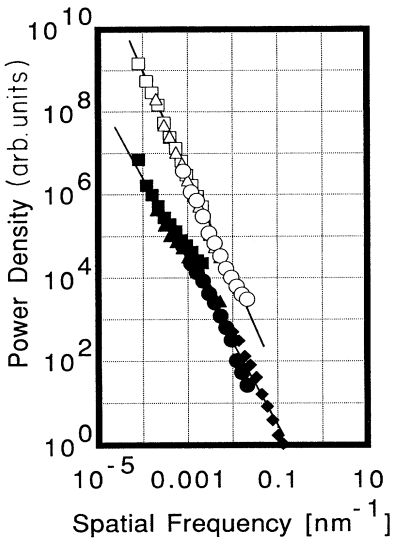


FIG. 3. Surface power spectral density vs spatial frequency for the same surface topographs used in Fig. 2. Solid lines of slopes 2 and 2.5 are drawn as guides to the eye.

of a surface of size $r$)$-r^2$] varies as $r^{1+\alpha}$ for large $r$ even $\alpha<1$ (see Ref. 14). In addition, we define the exponent $(1+\alpha)$ as $\delta$ ($<2$). Thus, a self-affine surface has excess surface area compared to a plane of the same size. This excess diverges as $r^{\delta}$, although it is negligibly smaller compared with the area of the plane. The $\delta$ value for the surface $A$ ($B$) is 1.50 (1.84). Thus we can say that the surface $B$ is rougher than the surface $A$ from the scaling behavior ($\delta$ is larger) and also from the interface width and the power spectral densities which are larger for the surface $B$ than for the surface $A$ for the surface sizes studied.

Additional agents in the plating solutions probably adsorb on faster-growing sites, permitting the microscopic recessed regions to catch up. This process affects the growth process in a similar way as the surface tension does; faster-growing protrusions tend to disappear under the influence of the smoothing effect of surface tension. It is not clear at present, however, why the more pronounced fractal behavior of the Cu electrodeposits changes to growth that forms a self-affine surface by adding chemical additives.

We compare the scaling exponent $\alpha=\frac{1}{2}$ for sample $A$ with the KPZ scaling exponent. Although the two-dimensional growth is theoretically well understood ($\alpha=\frac{1}{2}$, $z=\frac{3}{2}$), no theoretically predicted exact values are available in higher dimensions ($d\geq 3, d$ is the embedding dimension).[8] Simulation results obtained from a variety of growth models were summarized by Krug and Spohn.[8] Using the Eden growth model, Wolf and Kertesz[6] conjectured that $\alpha=1/d$ ($\frac{1}{3}$ for $d=3$). Kim and Kosterlitz[7] proposed lately that $\alpha=2/(d+2)$ (0.4 for $d=3$) based on a restricted solid-on-solid model simulation. More recently, using a modified ballistic deposition model, Yan, Kessler, and Sander[9] showed $\alpha=0.4$ and 0.2 for strong and weak coupling (i.e., large and small noise) regimes, respectively. According to these conjectures and the other recent results in the summary of Krug and Spohn, one may consider that there is now a consensus that the exponent $\alpha$ is about 0.40 in $d=3$. The exponent $\alpha=\frac{1}{2}$ obtained in the present measurement is slightly but significantly larger than $\frac{2}{5}$. It should be noted that curve $A$ may result from some transition region since the scaling in $B$, which is attributed to a transition region to a bulk fractal, is described by a power law. Further experimental studies such as growth at various growth rates are needed to clarify how universal the observed scaling behavior is.[16]

In summary, with increasing organic adsorbents, electrodeposited copper surfaces become less rough. The exponent governing the interface width divergence with surface size for the typical electrodeposition condition ($\alpha=\frac{1}{2}$) appears to be slightly but significantly larger than the exponents found for KPZ growth models. Further studies are needed to see whether the Cu electrodeposition is described by a KPZ type of growth.

The authors acknowledge helpful discussions with E. D. Williams, N. Bartelt, T. Einstein, and N. Akutsu. We gratefully acknowledge J. Sato, H. Matsuda, and A. Ikeda at Asahi Kasei Co. Ltd. for preparation of the samples and helpful discussions.

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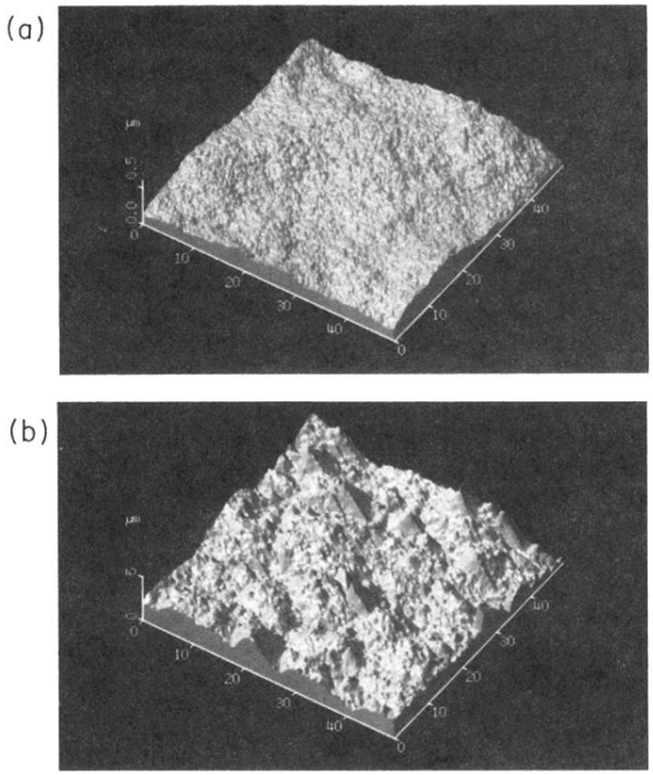
[16]We also studied the general $q$th moments of the width $w_q$,

$$\left\{[1/N_s(r)]\sum_{i=1}^{N_s(r)}[h_i-h_{\rm av}(r)]^q\right\}^{1/q},$$

which is closely related to the $q$th moment of the height-height correlation function introduced by Barabasi and Vicsek [Phys. Rev. A **44**, 2730 (1991)]. The third moment, for example, showed quite similar scaling to the second moment shown in Fig. 2 for both samples $A$ and $B$. $w_q$ varies as $r^{Hq}$ for $0.5<q<4$ and $Hq$ increases very slowly from 0.49 (0.84) to 0.52 (0.89) for sample $A$ ($B$) with an increase of $q$ from 0.5 to 4. These results provide additional information about the scaling properties of the surfaces of the Cu electrodeposits [see A.-L. Barabasi, R. Bourbonnais, M. Jensen, J. Kertesz, T. Vicsek, and Y.-C. Zhang, Phys. Rev. A **45**, R6951 (1992)].

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