

ANALYZING STM IMAGES OF Cu(110) IN DILUTE HYDROCHLORIC ACID USING THE DYNAMIC SCALING METHOD

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Studies of a Cu(110) single crystal surface in 10 mM HCl electrolyte using STM investigations were carried out. Changes of surface topography on a larger scale that depend on the applied potential were investigated using the dynamic scaling method. Dynamic parameters were computed in order to determine the universality class of the reconstruction process.

INTRODUCTION

A systematic formalism for studying the non-equilibrium processes is difficult; statistical mechanics approximations are not suitable, but analyzing the scaling properties of characteristic quantities is possible and has led to the development of a general scaling approach¹. This formalism, based on the general concepts of scale-invariance and fractals^{2,3} is a useful tool for studying interface growth.

Simulations studies leading to the same scaling exponents as measured in experiments allow to separate the essential processes and quantities that really determine the morphology, from the unnecessary details. Moreover, simulations will help us to design materials with better properties and to understand better the physical and chemical surface processes.

The dynamic scaling approach is an important tool for describing the time evolution of surface topography. It computes the dynamic scaling parameters α and β that characterize surface and time correlations.^{1,4,5}

The purpose of our work is to compute the dynamic scaling parameters of surface reconstruction on a larger scale of Cu(110) surface in 10 mM HCl electrolyte at different potentials using STM images analysis.

THEORY

1. The dynamic Scaling Method

A surface embedded in a d-dimensional Euclidian space which grows in a well-defined direction in time can be easily described by the function $h(\mathbf{x},t)$ which gives the maximum height of the interface position given by \mathbf{x} at the moment t . This function fluctuates, so one can define the average height.⁶

$$\langle h \rangle = \frac{\sum h(\mathbf{x},t)}{L^{d-1}} \quad (1)$$

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where L is the characteristic surface size perpendicular to the growth direction and the summation is over all \mathbf{x} . The surface width, $w(L,t)$, is one of the quantities which scales, so it is very important in this formalism. It can be defined as the root mean square of the height fluctuations:

$$w(L,t) = \left(\langle h^2 \rangle - \langle h \rangle^2 \right)^{1/2} \quad (2)$$

Family and Vicsek¹ proved that, in the absence of any characteristic length scale, the width is expected to be a power function of time. The exponent describes correlations with time along the growth direction:

$$w(L,t) \propto t^\beta \quad (3)$$

The time evolution of the surface follows the algorithm: first, the surface width increases with time according to Eq.(3) and after a characteristic time τ the correlations do not grow anymore; the surface reaches a steady-state, and the surface width is a power function of L :

$$w(L,t \rightarrow \infty) \approx L^\alpha \quad (4)$$

In Eq.(4), α is the roughness exponent (also called the Hurst exponent). In the steady state the surface is a self-affine fractal; the Hurst exponent is a fundamental parameter for describing the roughness of a self-affine fractal. In addition to the roughness exponent α , it is possible to associate a fractal dimension D with a self-affine function. On very short length scales, there is a relation between fractal dimension and roughness exponent: $D=d-\alpha$ (for an object embedded in a d -dimensional Euclidean space).

The exponents α and β can be easily computed using correlations functions. For a profile, the correlation function can be described with the aid of the height difference function:

$$G(r,t) \equiv \langle C(r,t) \rangle \quad (5)$$

where $\langle h(t) \rangle$ that depends x and T ; $\langle h(t) \rangle$ denotes the average height at time t . The height correlation function $C(r,t)$ is:

$$C(r,t) = \left\{ \left[h(x,T) - \langle h(T) \rangle \right] - \left[h(x+r,T+t) - \langle h(T+t) \rangle \right] \right\}^2 \quad (6)$$

In the above, the symbol $\langle \dots \rangle$ denotes an average over x and T .

The dynamic scaling approach leads to the following scaling relations:¹

$$\begin{aligned} G(r,0) &\propto r^{2\alpha}, r \ll L, \\ G(0,t) &\propto t^{2\beta}, t \ll \tau. \end{aligned} \quad (7)$$

Equations (7) are used here to compute the characteristic parameters α and β from STM images.

2. Larger scale reconstruction

The cyclic voltammogram (CV) of the Cu(110)/Cl⁻ system is presented in Fig. 1. The CV is characterised by a quasi-reversible redox peak pair which is attributed to the chloride desorption/adsorption process. In the domain of the most positive potentials, there are two different phenomena taking place: dissolution at anodic potentials and surface redeposition at cathodic potentials.

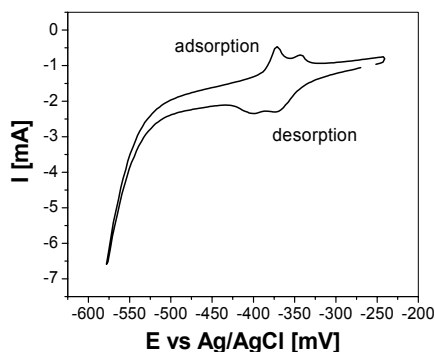


Fig. 1 – Typical CV of a Cu(110) single crystal surface in 10 mM HCl electrolyte; $dE/dt = 10$ mV/s.

Investigations of STM images show that the reconstruction process involves the removal and the adding of complete rows along the [001] direction, the surface becoming extremely furrowed. During this process, the surface will be rougher and rougher.

Surface redeposition occurs at cathodic potentials. The deposition process will take place in the sense of reconstruction of the single crystal surface.

RESULTS AND DISCUSSION

Fig. 2 shows the potential dependent change of the surface topography on a larger scale. The picture series begins with the adsorbate free copper surface (a); at anodic potentials dissolution processes take place (b), ending with surface reconstruction at cathodic potentials (c-d). To compute the scaling parameters α and β , different images time-series were analyzed. In Table 1 are presented scaling parameters α and β , from 27 STM images displayed at potentials indicated below.

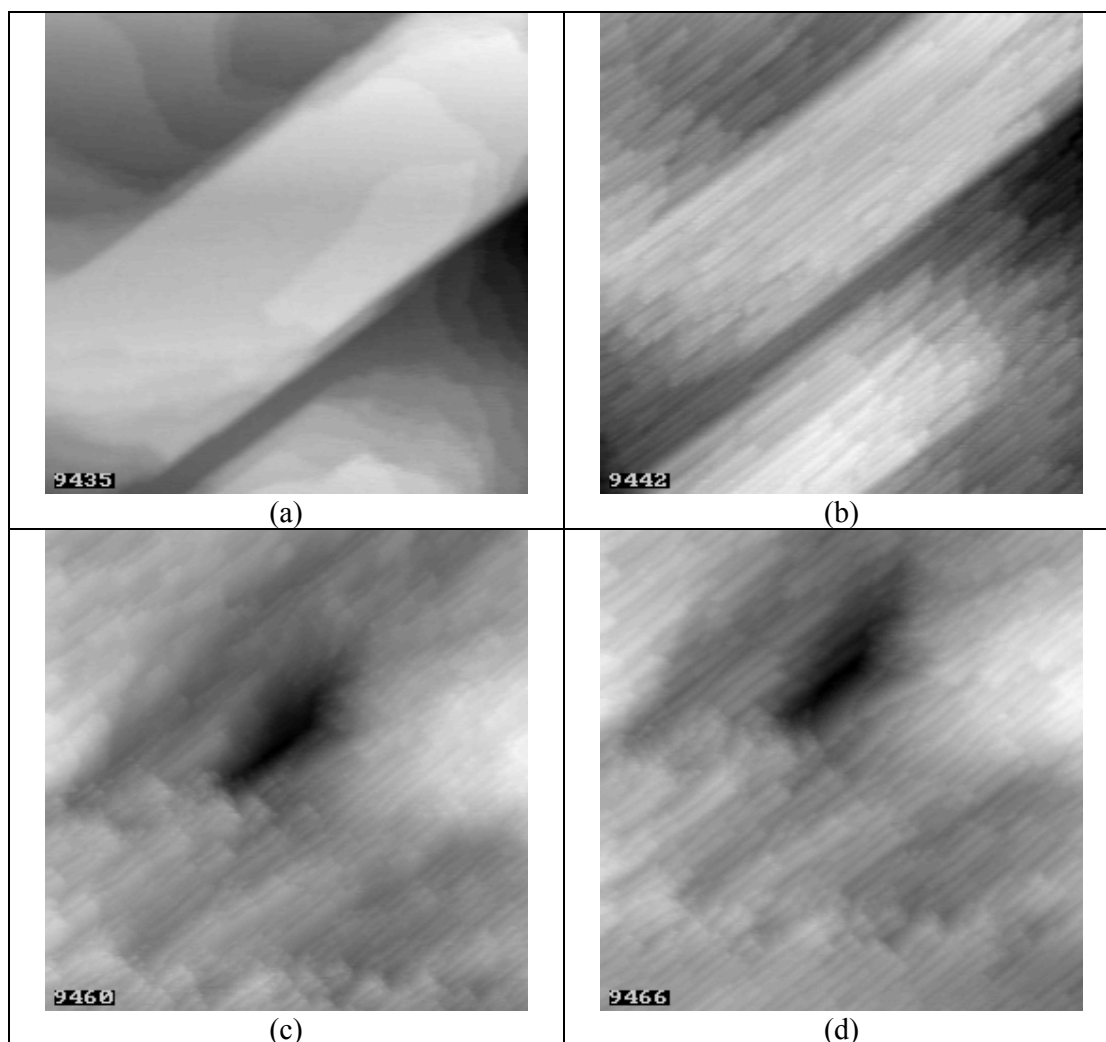


Fig. 2 – a) Adsorbate free copper surface 119nm \times 119nm; b) STM image of Cu(110) surface topography at anodic potential -370mV; c) STM image of Cu(110) surface topography at the cathodic potential -190mV; d) STM image of Cu(110) surface topography at the cathodic potential -300mV.

In Table 1, all scaling parameters α and β were computed using equations (7) described above. In results presented at nos.1-7, dissolution occurs at anodic potentials; dynamic parameters α and β were computed as $\alpha = 0.59$ (average value) and $\beta = 0.6$. At nos.7-12, the constant potential of -200mV will lead to other values for α and β . While β has a constant value of 0.53, α has a slow decrease from 0.59 to 0.54, meaning that one can assign to this roughness parameter a fractal dimension increasing from

2.41 to 2.46. Although this variation is not significant, it indicates the global shift for the roughness parameter from 0.59 to 0.50, for the next domain (nos.13-17), when the potential is constant at -170 mV. The values obtained for images nos.7-17, $\beta > 0.5$, suggest that there is an instability in the system, corresponding to the development of the diffusion-bias generated by the Schwoebel barrier. This observation is consistent with other experimental data from molecular beam epitaxy.⁷ In that case, during the deposition of Cu on Cu(100), the interface was observed to evolve into a state characterized by pyramid-like structures and the Schwoebel barrier will lead to values for β greater than 0.5.

So, while the potential is constant, diffusion will be responsible for surface roughening and the effect of the Schwoebel barrier will determine the final morphology of the surface, leading to formation of large mounds on the surface.

The size of the Schwoebel barrier determines the transient time, during which the scaling laws are obeyed, continuum equations dominate, and one can observe signs of the kinetic roughening process.

Table 1

The dynamic scaling parameter

STM image no.	E(mV)	$\alpha (\pm 0.02)$	$\beta (\pm 0.02)$
1.	-422	0.60	0.60
2.	-397	0.59	
3.	-397	0.58	
4.	-370	0.59	
5.	-302	0.59	
6.	-250	0.59	
7.	-200	0.59	
8.	-200	0.58	0.53
9.	-200	0.59	
10.	-200	0.58	
11.	-200	0.56	
12.	-200	0.54	
13.	-170	0.50	0.51
14.	-170	0.50	
15.	-170	0.51	
16.	-170	0.50	
17.	-170	0.49	
18.	-180	0.50	0.50
19.	-190	0.57	
20.	-200	0.61	
21.	-210	0.63	
22.	-220	0.63	
23.	-230	0.63	
24.	-240	0.63	
25.	-250	0.62	
26.	-270	0.62	
27.	-300	0.60	

A lower Schwoebel barrier will determine a very long transient time for mounds to develop. In our case, the value of $\beta > 0.5$, indicates the influence of diffusion-bias on the dissolution process.

However, when the potential increases (nos.1-7), although $\beta = 0.60$, we assume that this is the effect of correlated noise and not of the diffusion-bias and Schwoebel barrier, the dissolution process being the determinant one.

When the potential moves to more negative values (nos.17-27), the surface is reconstructed and the scaling parameters were computed as $\alpha = 0.62$ and $\beta = 0.50$.

Figs. 3 and 4 present α and β computation from STM images analysis, using equations (7).

We obtained three classes of universality: first, for the dissolution region, at anodic potentials, $\alpha = 0.59$ and $\beta = 0.60$; second, for constant potentials, the temporal scaling parameter $\beta > 0.5$; this behavior can be assigned to diffusion-bias, meanwhile the value of α , leading to 0.50 is an argument that in the system correlated noise is important; third, at cathodic potentials, $\alpha = 0.62$ and $\beta = 0.50$, a new universality class is defined for surface restructuring, random deposition with correlated noise.

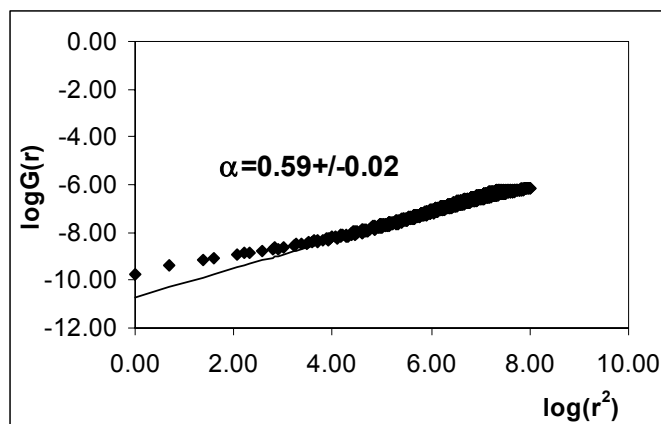


Fig. 3 – Computation of the roughness parameter from the STM image analysis for the anodic potential $E=-250\text{mV}$.

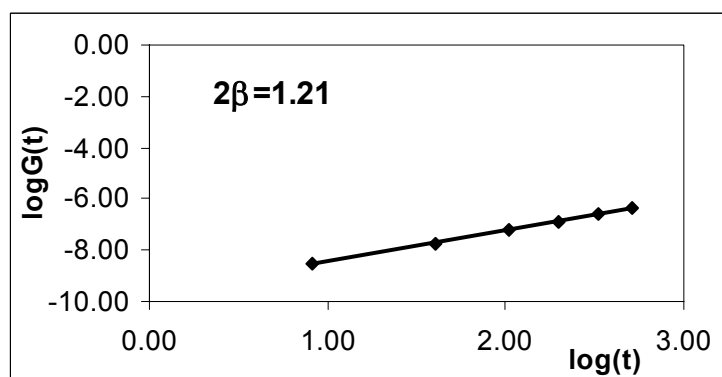


Fig. 4 – Computation of the temporal scaling parameter for dissolution at anodic potentials; the slope is 2β .

CONCLUSIONS

Surface reconstruction on a larger scale of Cu(110) in dilute hydrochloric acid was studied using the dynamic scaling approach; both parameters α and β were computed using STM images analysis; the existence of the scaling rough parameter α proved that surfaces are self-affine.

We obtained three classes of universality: first, for the dissolution region, at anodic potentials, $\alpha = 0.59$ and $\beta = 0.60$; second, for constant potentials, the temporal scaling parameter $\beta > 0.5$, as in the case of diffusion-bias, and α , leading to 0.50, implying that a new universality class noise correlated is created. Third, at cathodic potentials, $\alpha = 0.62$ and $\beta = 0.50$, a new universality class is defined for surface restructuring, random deposition with correlated noise.

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