Substrate effects and diffusion dominated roughening in Cu$_2$O electrodeposition

I. S. Brandt$^1$, V. C. Zoldan$^1$, V. Stenger$^1$, C. C. Plá Cid$^1$, A. A. Pasa$^{1,(a)}$, T. J. Oliveira$^{2,(b)}$ and F. D. A. Aarão Reis$^{3,(c)}$

$^1$ Departamento de Física, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, SC, Brazil
$^2$ Departamento de Física, Universidade Federal de Viçosa, 36570-000, Viçosa, MG, Brazil
$^3$ Instituto de Física, Universidade Federal Fluminense, Avenida Litorânea s/n, 24210-340 Niterói RJ, Brazil

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Cuprous oxide (Cu$_2$O) films from 25 nm to 1500 nm were electrodeposited on n-Si(100) and Ni/n-Si(100) substrates from aqueous solution at room temperature. X-ray diffraction and transmission electron microscopy imaging show that the Cu$_2$O structure and morphology is strongly affected by the substrate choice, with V shape and U shape columnar growth on n-Si(100) and Ni/n-Si(100), respectively. Atomic force microscopy reveals the presence of rounded grains at the surface in both cases. Anomalous and normal roughening are observed in films grown on n-Si and Ni, respectively, but estimates of scaling exponents are not conclusive. On the other hand, the distributions of local heights, roughness, and extremal heights show good agreement with those of the fourth order nonlinear stochastic equation of Mullins and Herring (MH). Thus, surface dynamics in both systems is dominated by diffusion of adsorbed molecules, with no large scale effect of possible inhomogeneities in mass flux from the solution or in reaction and adsorption rates. In growth on n-Si substrates, the noise amplitude of the MH equation increases in time as $t^0.8$, while the coefficient of the curvature-related term is time-independent. Step edge energy barriers restrict the mass flux across grain boundaries, thus a broad size distribution of initial grains leads to coarsening of the larger ones. This explains their V shape in the thickest films and establishes a connection with the anomalous roughening. These effects are reduced in films grown on Ni/n-Si, which initially have much larger grains with narrower size distributions and, consequently, smaller fluctuations in coarse grained growth rates. Thus, despite the relevance of electrochemical conditions for Cu$_2$O films to grow and their influence on crystallographic orientation, large scale surface features are determined by physical properties of the material and its interactions with the substrate, with a universal microscopic dynamics similar to vapor deposition.

I. INTRODUCTION

Cu$_2$O (cuprous oxide) is a p-type semiconductor that has recently attracted the attention of experimental and theoretical groups due to its potential for application in metal base transistors [1], spintronic [2], photocathode for water splitting [3], electrochemical supercapacitors [4] and catalysts [5], and for light harvesting [6]. The deposition of Cu$_2$O layers has been achieved by different techniques, such as pulsed laser deposition [7], magnetron sputtering [8], copper oxidation [9], radical oxidation [10], and electrodeposition [11]. Electrodeposition is a very versatile technique, allowing to modify many structural, optical, and electrical properties by the control of the deposition parameters [12-13]. Moreover, electrodeposition appears as a cost effective method to the preparation of metal and semiconductor thin films for device applications. When compared with physical deposition processes, such as sputtering, electrodeposition has the particular feature of diffusive mass transport of species from the electrolyte to the growing surface [16].

A comprehensive understanding of the electrochemical growth mechanisms, taking into account the mass transport at the electrode surface, plays a vital role to the production of films with the desired properties. One example is the technological requirement for mesoscopic layers to be used in photocathode applications, in which the grain shape and the exposed crystalline faces need to be controlled to improve stability and efficiency [17]. On the other hand, the study of surface topography of deposited layers helps to discriminate the basic mechanisms of growth dynamics from the particular features of each set of physico-chemical deposition conditions [18-22]. A crucial condition may be the substrate, which affects the early stages of island formation and growth and, possibly, the subsequent film dynamics.

Bearing in mind the above mentioned arguments, the present work aims to investigate the structure of electrochemically grown Cu$_2$O films on top of a semiconducting and monocrystalline substrate and on top of a metallic and polycrystalline substrate, viz. n-Si(100) and Ni evaporated on n-Si(100). Recently, our group showed that these two substrates are suitable for morphological, structural and optical studies on Cu$_2$O [13]. Moreover, the Cu$_2$O/Ni structure may be employed on photochemical [23] and spin transport [24] investigations.
Raman spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM) measurements are carried out to characterize film composition and structure. Atomic force microscopy (AFM) images are used to study kinetic roughening of the film surface, thus helping to disclose the main mechanisms of the growth dynamics. Films directly grown on the semiconductor substrate have a V shape columnar structure, preferential growth in [100] direction, and show anomalous roughening, while those grown on the Ni layer present an U shape columnar structure, change the dominant crystallographic orientation during the growth, and have normal roughening. A deeper analysis of surface morphology shows that the dominant mechanism in the Cu$_2$O growth is surface diffusion of adsorbed molecules, with uniform incoming flux. Step edge energy barriers explain the anomaly of the former films, connecting this feature to the grain shape. The universal coarse-grained growth dynamics is similar to what is observed in many vapor deposited films, despite the relevance of electrochemical conditions to local reaction and adsorption processes. On the other hand, the interaction between the film and the substrate, which is frequently restricted to island nucleation and growth, here is shown to have drastic consequences to the structure of the thickest Cu$_2$O films.

The rest of this work is organized as follows. In Sec. II the experimental procedure for growth and characterization of the Cu$_2$O films is described. In Sec. III the experimental results are presented and analyzed in the light of kinetic roughening concepts. Section IV presents a discussion of the results and our conclusions.

II. EXPERIMENTAL

Cu$_2$O films were deposited on (100) monocrystalline n-type silicon (resistivities in the range of 6 - 9 Ω·cm) without and with a cap layer of 50 nm of evaporated Ni. Before Cu$_2$O electrodeposition or Ni deposition, the silicon substrates were immersed in HF 5% for 20s to remove silicon native oxide from the surface. The roughnesses of the n-Si substrate and of the Ni layer surface are respectively 0.2 nm and 1.3 nm. Ni thin films deposited on Si(100) had preferential growth in the [111] direction, which was checked by XRD measurements.

The electrochemical experiments were conducted in a conventional three electrode cell connected to a potentiostat Autolab PGSTAT30. The counter electrode was a Pt foil and the reference electrode was a Saturated Calomel Electrode (SCE). The electrolyte, prepared from analytical grade reagents and deionized water (resistivity of 18 M Ω·cm), contains 0.4 M CuSO$_4$ and 3.0 M lactic acid, with the pH adjusted to 10.00 by adding a solution of 5.0 M NaOH [11].

The deposits were obtained via potentiostatic experiments. Samples were deposited at 25 °C for a deposition potential of −0.5 V vs SCE, where the only varied parameter was the thickness $H$ of the samples for the 2 different substrates, n-Si(100) and Ni/n-Si(100).

The efficiency of the Cu$_2$O electrodeposition process was checked by Rutherford backscattering in a previous work and values of 90% were obtained [25]. The samples were characterized by various techniques including Raman spectroscopy (inVia, Renishaw), XRD (XPERT, Philips), TEM (JEM-2100, JEOL) and AFM (Pico-SPM, Molecular Imaging Corporation). Raman spectra were obtained from 514.5 nm wavelength excitation (argon ion laser). The AFM images were acquired in contact mode in air at room temperature and the values of the root mean-square deviation of the local surface height, $W(l, H)$, are representative of at least three images of different regions of the surface. Three different regions for sample were measured with scan sizes of 1 × 1, 2 × 2 and 5 × 5 µm for each region and number of pixels per line ranging from 256 to 1024, respectively. From these measurements we have concluded that for 2 × 2µm image size the $W(l, H)$ reaches the saturation value. In addition, before starting measurements on Cu$_2$O samples, the performance of the AFM tip was checked by imaging Au thin films with known surface.

III. RESULTS

A. Characterization of film composition and structure

The copper oxide phase formed in the electrodeposited thin films was analyzed by Raman spectroscopy and XRD. The measurements were done on layers with thickness between 150 and 1500 nm deposited on n-Si(100) and Ni/n-Si(100).

Raman spectroscopy results of films with thickness 1250 nm are shown in Fig. [1k]. The predominance of Cu$_2$O phase is evident. Contributions of Cu$_4$O$_3$ and possibly CuO phases are also observed. The peaks in Fig. [1k] were addressed to the respective phase and Raman vibration mode based on Ref. [26]. Despite the observation of Cu$_4$O$_3$ and CuO Raman peaks, these phases are not present in XRD Bragg-Brentano patterns of the same films, shown in Fig. [1b], probably due to the higher surface sensitivity of Raman measurements. Cu$_4$O$_3$ and CuO phases are likely to be formed by oxidation of Cu$_2$O top layers. Since the layers are mostly of Cu$_2$O, this work will be concerned to the description of the electrochemical growth of this phase.

Fig. [1b] also shows the XRD patterns of Cu$_2$O films with 1250 nm of thickness deposited on Ni/n-Si(100). The peaks are also in the expected positions for the Cu$_2$O crystal. Cu$_2$O/n-Si(100) samples display strong preferential growth in [100] direction, following the orientation of the substrate. On the other hand, Cu$_2$O film grown on top of Ni/n-Si(100) substrate is composed by grains oriented in [100], [110], [111], and [311] directions.

The evolution of Cu$_2$O growth on Ni/n-Si(100) is explained by Ref. [13] as follows: (i) the Cu$_2$O films...
show initial [111] growth due to a better coupling of the Cu$_2$O(111)/Ni(111) interface compared to the Cu$_2$O(100)/Ni(111) one: (ii) at electrolyte pH of 10.00 the [100] growth is favored, the initial [111] growth starts to be suppressed by the [100] one and at a specific thickness a major part of the Cu$_2$O deposit will be composed by [100] grains.

These growth steps are confirmed by the inset of Fig. 1, which shows the fraction of the material growing in [100] and [111] directions as a function of film thickness. While Cu$_2$O on n-Si(100) is, independently of film thickness, oriented in [100] direction, Cu$_2$O on Ni/n-Si(100) grows up to 750 nm with ~60% of its grains oriented in [111] direction, but only ~30% remain with this orientation in larger thicknesses. The initial growth of Cu$_2$O on Ni(111) is thermodynamically controlled by the Cu$_2$O(111)/Ni(111) coupling, likewise as previously reported for Cu$_2$O(111)/Au(111) and Cu$_2$O(100)/Au(100) interfaces [12]. However, the crystallographic orientation transition at 750 nm is related to the oxygen concentration in electrolyte at pH 10.00, which favors the [100] growth [13].

The structure of Cu$_2$O films was checked by cross section TEM images. Figure 2 shows an image obtained from electrodeposited Cu$_2$O film on n-Si(100). A high density columnar microstructure without voids is observed. These columns have a V shape as stressed by discontinuous red lines, exhibiting a grain width increase as a function of film thickness. On the other hand, as seen in Fig. 2(b), Cu$_2$O films deposited on the Ni layer under same conditions (solution, temperature and deposition potential) displayed a columnar microstructure with U shape, as indicated in Fig. 2(b), and grain width roughly constant as a function of growth time.

Figure 3 shows 2 × 2µm$^2$ AFM images of the films...
FIG. 3. (Color online) 2\(\mu\)m \(\times\) 2\(\mu\)m AFM images of the surface morphology of Cu\(_2\)O layers electrodeposited on: a), b) n-Si; and c), d) Ni/n-Si. Upper row is for thickness of 250 nm, while lower row is for 1500 nm. Bright areas are elevations and dark ones are deep regions.

with thicknesses of 250 and 1500 nm. A common feature in both substrates is that the film surface presents a granular aspect. In films deposited on n-Si, there is a remarkable increase of the grain size from the thinnest to the thickest film. The columnar structure with V shape shown in TEM images and this increase in grain size suggest a coarsening process, with part of the initial columns growing and enlarging up to 1500 nm at the expenses of neighboring ones. On the other hand, a mild increase of grain size is observed in the films grown on Ni/n-Si, which is in agreement with TEM images showing columns in U shape.

B. Dynamic scaling of surface roughness

The surface roughness \(W\) is the most used quantity to characterize height fluctuations. For a given surface under a process of kinetic roughening, \(W\) depends on the lengthscale in which fluctuations are measured. Moreover, given a scanning box with lateral size \(l\), the fluctuation in film height inside the box also depends on the box position.

For these reasons, the box roughness is defined as the root-mean-square (rms) fluctuation of the film height \(\langle h \rangle\) inside a box at a given position, i.e., \(w = \sqrt{\langle h^2 \rangle - \langle h \rangle^2}\). The average local roughness \(W(l, H) = \langle w \rangle\) of a film of thickness \(H\) in the lengthscale \(l\) is the average of the box roughness \(w\) among all possible box positions. \(W(l, H)\) is hereafter simply called roughness.

Using the heights from AFM images, \(W(l, H)\) is calculated for Cu\(_2\)O layers grown on both substrates. The results are shown in Figs. 4a and 4b for a range of thicknesses \(H\) varying from 25 to 1500 nm. The structural changes induced by substrates n-Si and Ni/n-Si are reflected in topographic differences in the growing surface of the films, confirming the visual inspection of AFM images.

The roughness \(W(l, H)\) of films grown on Ni/n-Si show normal dynamic scaling because it is approximately time-independent for small box size \(l\) and saturates at values increasing with the thickness \(H\). Deviations for the thinner samples (25 to 75 nm) are characteristic of the initial island growth and coalescence, indicating that an extended film is formed between 75 nm and 150 nm of thickness. For this reason, only results for \(H \geq 150\) nm will be analyzed below.

On the other hand, the oxide layers grown on n-Si have anomalous scaling, since the roughness in small boxes shift to larger values with increasing thicknesses [27–30]. The presence of a single dominant orientation during the growth (shown by XRD) and the coarsening of growing columns from the smallest to the largest thicknesses.
FIG. 5. (Color online) a) Local roughness for box size $l = 40$ nm ($W^*$) and b) global roughness ($W_s$) as functions of the film thickness $H$. Rescaled correlation functions $\Gamma(l)/\Gamma(0)$ against the length $l$ for c) n-Si and e) Ni/n-Si substrates. Their first minima (the correlation length $\xi$) are shown in d) and f) as functions of $H$. Continuous lines are power law fits of the data and dashed lines have the slopes indicated.

(suggested by TEM and AFM images) indicate that the scaling anomaly is an intrinsic feature of the surface dynamics in this system. The data presented in Fig. 4 for the thickest films with $l \lesssim 100$ nm were fit to the relation $W \sim l^{\alpha_l}$. It gives estimates of the local roughness exponents $\alpha_l = 0.90$ and 0.91 in n-Si and Ni/n-Si substrates, respectively. These values are consistent with the interpretation of granular effects in Refs. [31] and [32], which predict an exponent near 1 if the maximal box size is smaller than the grain size. Inspection of the AFM images (Fig. 3) supports this hypothesis. These estimates of $\alpha_l$ must not be interpreted as true exponents of dynamic scaling, but as exponents representing the grain shapes [32]. The local roughness $W^* \equiv W(l^*, H)$ is measured for a fixed small box size $l^* = 40$ nm. It is shown in Fig. 5a as a function of the thickness $H$. For films deposited on Ni, $W^*$ fluctuates around a constant value as the thickness increases, from small values to the largest ones. This is consistent with normal scaling. On the other hand, for films deposited on n-Si, $W^*$ shows a power law increase from small thicknesses ($H = 150$ nm) to the largest ones ($H = 1500$ nm). This is the main evidence of anomalous scaling in these films. The fit of the data in Fig. 5a by the scaling relation $W^* \sim H^{\kappa}$ [27] gives an anomaly exponent $\kappa = 0.49$ ($\kappa$ is also called local slope exponent in theoretical works and local growth exponent $\beta_{loc}$ in experimental works [29, 30]).

The saturation values of the roughness in Fig. 4 give the global roughness $W_s$, which characterize fluctuations...
of the whole surface at a given thickness. In Fig. 5b, $W_s$ is shown as a function of $H$ for both films. The fits to the scaling relation $W_s \sim H^\beta$ for $H \geq 150$ give the growth exponents $\beta = 0.84$ and $\beta = 0.33$ for films deposited on n-Si and Ni/n-Si substrates, respectively.

Since the growth on Ni/n-Si substrates has normal scaling, we search for a model of local stochastic growth equation, which may disclose the main mechanisms of the surface dynamics [19, 20]. The above estimate of $\beta$ is larger than the values provided by the equations of second and fourth orders, which are in the range $[0, 0.25]$ [19]. However, Fig. 5b shows that a slope close to $\beta = 0.25$ cannot be discarded for large thicknesses.

This is close to the exponents of the Kardar-Parisi-Zhang (KPZ) class [33], $\beta \approx 0.24$ [34, 35], and of the Mullins-Herring (MH) class [36], $\beta = 0.25$.

Information on surface correlations can be obtained from the spatial correlation function $\Gamma(x,t) \equiv \langle \hat{h}(x,t)\hat{h}(x,0) \rangle$ at time $t$, with $\hat{h} = h - \langle h \rangle$. The rescaled functions $\Gamma(l,t)$ of the oxide films respectively grown on n-Si and Ni/n-Si substrates are shown in Figs. 5c and 5d as a function of the distance $l$, for several thicknesses. A reliable estimate of the correlation length $\xi$ is the minima of $\Gamma(l,t)$, which is shown in Figs. 5e and 5f as a function of the thickness $H$.

The estimates of $\xi$ are close to those obtained by intersection of straight line fits of the roughness in the growth and saturation regimes, which is a usual method in the analysis of experimental data. Ref. [39] shows that this method leads to estimates of $\xi$ of the same order of the average grain size estimated by inspection of microscopy images [39]. However, an accurate calculation of the average grain size is more complicated and not performed here.

The scaling $\xi \sim t^{1/z} \sim H^{1/z}$ is expected for large thicknesses [19, 20]. Linear fits of the data for $H \geq 500$ nm give estimates $1/z = 0.32$ and 0.21 (dynamic exponents $z = 3.1$ and 4.7) for growth on n-Si and Ni/n-Si substrates, respectively. These exponents are very different from the KPZ value $z = 1.6$ [34, 40]. On the other hand, the Figs. 5b and 5c show that the slopes of the log $\xi \times \log H$ plots for the largest thicknesses are close to the MH value $1/z = 0.25$ (the corresponding slope of KPZ scaling $1/z = 0.625$ is also shown for comparison).

The EH equation is a model for growth dominated by surface diffusion of adsorbed species [36]:

$$\frac{\partial h}{\partial t} = -K\nabla^4 h + \eta(x,t),$$

where $h(x,t)$ is the interface height at substrate position $x$ and time $t$, $K$ is a constant, and $\eta$ is a Gaussian (non-conservative) noise with covariance amplitude $D$ [19, 36]. A constant external flux was omitted from Eq. (1), which corresponds to a spatially uniform and time-independent adsorption rate. Thus, the local growth rate of the MH model is not affected by diffusion in solution, for instance due to the presence of diffusive layers, shadowing effects etc.

On the other hand, the KPZ equation is a model for interface growth dominated by surface tension and by a nonlinear effect of the local slope [33]:

$$\frac{\partial h}{\partial t} = \nu\nabla^2 h + \frac{\lambda}{2}(\nabla h)^2 + \eta(x,t),$$

where $\nu$ and $\lambda$ are constants. Distinguishing these possibilities is an important step to understand the microscopic growth dynamics of the oxide films. The KPZ model also assumes spatially uniform and time-independent adsorption rate, with no effect of diffusion in solution to the local growth rate.

C. Scaling of distributions

We now turn to the analysis of distributions of heights and of local quantities, which was recently shown to be a more powerful tool to the study of kinetic roughening of thin films [37, 41, 42].

The height distribution $P(h)$ is defined as the probability density of the height $h$, so that $P(h)dh$ gives the probability of finding a height in the range $[h, h+dh]$. Figures 6c and 6e, and 6d and 6f show the scaled height distributions of the oxide films grown on both substrates, respectively. They are compared with distributions of the KPZ and MH classes in the growth regimes. The KPZ distribution was numerically calculated in Refs. [33] and [44]. For the MH class, the distribution is Gaussian, which was confirmed by direct integration of the MH equation [Eq. 1] and by simulation of the large curvature model (LCM) [45].

The experimental data in Figs. 6a and 6c: since the scaled height distributions are the same for films deposited on both substrates, the main physico-chemical processes responsible for their roughening are the same.

The distribution $P(w_2)$ of the squared box roughness $w_2 = \sigma^2$ is defined so that $P(w_2)dw_2$ is the probability that the squared roughness in a given box is in the range $[w_2, w_2+dw_2]$ [40, 47]. Figures 7a and 7b compares the scaled roughness distributions of the oxide films grown on both substrates and that of the MH class in the growth regime ($\sigma_{w_2}$ is the rms fluctuation of $w_2$). The size of the box in which $w_2$ is measured ranges from 100 nm to 300 nm. The MH curve is calculated by integration of the MH equation in the growth regime.

In Figs. 7a and 7c, the collapse of the scaled distributions for films grown in different substrates is clear, which is additional support to the proposal that their
FIG. 6. (Color online) Scaled height distributions for a) and c) n-Si, and b) and d) Ni/n-Si substrates. In a) and b) the data are presented in semi-log scale and in c) and d) in linear scale. The skewness $S$ and kurtosis $Q$ of the height distributions as functions of the thickness $H$ are shown in e) and f) for n-Si and Ni/n-Si, respectively.

FIG. 6. (Color online) Scaled height distributions for a) and c) n-Si, and b) and d) Ni/n-Si substrates. In a) and b) the data are presented in semi-log scale and in c) and d) in linear scale. The skewness $S$ and kurtosis $Q$ of the height distributions as functions of the thickness $H$ are shown in e) and f) for n-Si and Ni/n-Si, respectively.

roughening is governed by the same physico-chemical processes (despite the very different structures of those films). Good agreement with the MH curve reinforces the proposal that diffusion of adsorbed species is the main mechanism of the surface dynamics.

We also analyzed the distribution $P(m)$ of the maximal relative height $m \equiv h_m - \langle h \rangle$ in the growth regime. Here, $h_m$ and $\langle h \rangle$ are, respectively, the maximal and the average heights measured inside each box position. The distributions for both films are shown in Figs. 7b and 7d, showing good data collapse among them and with the MH curve.

Following the procedure described in Ref. [48], we also calculated the local surface slope $\theta$ using the AFM images. The local slope images corresponding to the height images shown in Fig. 5 are displayed in Fig. 8. They clearly show that larger values for $\theta$ are obtained in intergranular regions, while small $\theta$ are related to flat areas near the top of CuO grains.

The distributions of local slopes are shown in Figs. 8e and 8f for CuO/n-Si and CuO/Ni films, respectively. The position $\bar{\theta}$ of the peaks of those distributions are displayed in Fig. 8g as a function of thickness. For films grown on n-Si, the distribution significantly changes as the thickness increases, with an increase in $\bar{\theta}$. This is typical of anomalous scaling [27, 28] and is qualitatively consistent with the local roughness increase shown in Fig. 5a. On the other hand, for films grown on Ni/n-Si, average local slopes decrease with the thickness, saturating in the thicker films. This is consistent with normal scaling. Comparison of local slope distributions with those of theoretical models is not possible because there are
significant thickness effects and the present concept of local slope differs from the definitions in integrated growth equations or in lattice models.

The MH scaling was formerly observed in electrochemically deposited Prussian Blue films [49]. In that case, the anomalous roughening was generated by time increasing adsorption rates.

**D. Extended analysis of MH scaling**

The exact solution of the MH equation [20, 50] allows an extension of the interpretation of the experimental data, particularly those of films grown on n-Si substrates.

The MH roughness $W(l, H)$ is expected to scale similarly to the height-height correlation function; in terms of box size $l$ and time $t$ we have [20]

$$W^2(l, t) \sim \frac{D}{K} l^2 \ln (\xi/l) F(l/\xi),$$

where $F$ is a scaling function [$F(x) \approx \text{const}$ for small $x$] and

$$\xi = (2Kt)^{1/4}. \quad \text{(4)}$$

Recall that $H$ is proportional to the time $t$.

The long time (large thickness) scaling of the correlation length gives exponent $z$ near the MH value ($1/z \sim 1/4$). Thus, Eq. (4) indicates that $K$ is approximately time-independent. The coefficient $K$ in Eq. (1) represents the relation between surface diffusion coefficients and local surface geometry of a given material. This relation is not expected to change in the course of the (constant temperature) deposition.

For $l \ll \xi$, Eq. (3) suggests that the local roughness $W^*$ (measured for fixed $l^* = 40$ nm; Sec. III B) scales as $W^{*2} \sim D/\ln H$. Figure 9 shows $W^{*2}/\ln H$ versus $H$ for both films. The approximately constant value of $W^{*2}/\ln H$ for the films grown on Ni/n-Si indicates that $D$ is also time-independent in that case. However, the scaling in films grown on n-Si and the time-independence of $K$ gives $D \sim t^{0.8}$. Since $D$ is the amplitude of time and spatial fluctuations of deposition rate, this means that those fluctuations increase in time in the films grown on n-Si. This leads to the anomalous scaling in those films. The above increase of $D$ is sufficiently slow, thus the original solution of the MH equation can be consistently used with the time-dependent form of that parameter [20, 50]. This feature was already illustrated in other continuous and lattice models with time dependent couplings [51, 52] showing anomalous scaling.

**IV. DISCUSSION AND CONCLUSION**

The scaling of distributions of local heights, maximal heights, and roughness provide strong evidence that the roughening in electrodeposited Cu$_2$O films is governed by the MH equation [1]. The noise amplitude increases in
FIG. 8. (Color online) Slope images of Cu$_2$O films on n-Si, a) and b), and Ni/n-Si, c) and d), evaluated from height images shown in Fig. 3. In the first and second row Cu$_2$O films have 250 and 1500 nm of thickness, respectively. The color bar indicates the surface slope $\theta$, which can vary from 0 to 90°. Slope histograms for e) Cu$_2$O/n-Si and f) Cu$_2$O/Ni structures, and g) mean surface slope as a function of the film thickness.

FIG. 9. (Color online) $W^{*-2}/\ln H$ as a function of the thickness $H$ for films grown on n-Si (triangles) and on Ni/n-Si (squares). The solid line, with slope 0.8, is a least squares fit of the large thickness data for films grown on n-Si.

The MH equation was proposed for roughening in molecular beam epitaxy [19], in which a crystalline film slowly grows by random adsorption of atoms/molecules from vapor and surface adatoms diffuse and preferentially bind to high coordination (low energy) sites. Thus, in the electrochemical deposition of Cu$_2$O films, those results indicate that this interplay of surface diffusion and deposition noise is also the main ingredient for roughening under the present growth conditions.

The MH equation considers that adsorption rates are spatially uniform and do not depend on time. This suggests that electrochemical conditions do not determine the main dynamic mechanisms for roughening, although they probably affect the values of the parameters in the associated MH equation. Since the same electrochemical conditions were used for growth of films on both substrates, we are led to the conclusion that their different structures are consequence of the substrate-film interaction. The different interactions in different substrates determine the island nucleation and growth and has consequences in the thickest films, despite the universal MH dynamics.

The connections between the microscopic dynamics and the structure of the growing films can be derived from our results, as follows.

In systems with diffusion-dominated dynamics, molecules at a surface grain randomly move, with rates depending on local energy barriers. At first approximation, those barriers depend on coordination numbers and increase at step edges. For an adatom or ad-molecule to go down a step, the additional activation energy, known time in the equation associated to the films grown on n-Si substrates, corresponding to the scaling anomaly. This analysis clearly advance over the calculation of scaling exponents, which however are also compatible with the MH ones.
as Ehrlich-Schwoebel (ES) barrier [53–54], reduces the downward flux near the step edge, favoring nucleation of new atomic terraces over the ones previously formed [21]. The effect of ES barriers is enhanced at grain boundaries, constraining the mass flux between the grains if height differences are large. These features are observed in films of several materials grown by vapor methods. The above results strongly suggest to extend this interpretation to Cu$_2$O electrodeposition.

Figure 5 shows that films grown on n-Si substrates have an initially small average grain size, but with a broad size distribution. This is confirmed quantitatively by the small values of the correlation length in Fig. 5 (ξ ≈ 80 nm in 75 nm thick films). Thus, the islands nucleating at that substrate also had large size fluctuations. This may be a consequence of large spatial fluctuations of the adsorption rate during the first stages of the growth.

When an extended film is formed, the local adsorption rates may become uniform, particularly if the dominant crystallographic orientation does not change, as shown in Sec. III A; see also inset of Fig. 1b. However, larger grains have larger numbers of terraces and steps, consequently the mass flux from their tops to their boundaries is small. With restricted mass exchange in grain boundaries, the large grains increase in width and cover the smaller ones. From a coarse grained point of view, the fluctuations in the adsorption rate continue to increase, which qualitatively explains the time increase of the parameter $D$ in the corresponding hydrodynamic model (the MH equation).

Figure 8e shows that the shape of the slope distribution is the same while its average value moves to the right during the film growth. This means that local slopes increase inside the grains and at their boundaries, consistently with the above interpretation.

On the other hand, Fig. 9 shows that films grown on Ni/n-Si substrates have larger initial grains with a much narrower size distribution (see also insets of Figs. 5 and 8). This is related to small fluctuations in local adsorption rates, a feature that is maintained during the growth and leads to normal roughening.

AFM images also reveal that the grain top surfaces are similar in the films grown in both substrates, thus the local (microscopic) adsorption rates at those surfaces are expected to be the same. In growth on n-Si substrates, the difference in the net growth rate of individual grains have to be explained by the restricted mass flux across grain boundaries, not by intra-grain features. If some grains with large slopes are initially formed, they may grow faster at the expenses of the neighboring ones. This establishes a connection between the V-shaped grains and the anomalous roughening.

Unusual scaling features are frequently found in diffusion-dominated growth in the presence of step energy barriers [21]. For instance, a small barrier in Fe/Fe(100) epitaxy leads to mound formation at the film surface, with skewed height distribution and β = 0.2 [54], which are characteristics of the non-linear molecular beam epitaxy equation [55–57]. Moreover, mound steepening in Ag/Ag(100) epitaxy at room temperature occurs with an effective exponent β much larger than 0.5 in thicknesses ranging from 100 to 1000 monolayers [56] ($β = 0.5$ is a feature of completely uncorrelated growth [19]).

We conclude that, although control of electrochemical conditions is essential to enable growth of Cu$_2$O films and to determine the crystallographic orientation, our results show that large scale surface features are determined by physical properties of the material and the substrate, with consequences on the internal film structure. Roughening is governed by the interplay of deposition and ad-species surface diffusion, similarly to vapor deposition, with no significant influence of inhomogeneous mass flux from the solution (if it exists). However, substrate-film interactions have a strong effect on island nucleation and growth, thus the structure of the thickest films is drastically affected by these initial conditions, despite the universal (MH) roughening dynamics.

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