Pattern preserving deposition: Experimental results and modeling

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In this work we discuss pattern-preserving growth during metal deposition from the vapor on micro/nano-structured metal substrates. Experimental results for Cu deposition on patterned Cu substrates show pattern preserving growth or pattern destruction depending on the incident angle. We introduce a mesoscopic 1+1 dimensional model including deposition flow (directed and isotropic), surface diffusion and shadowing effects that account for the experimental growth data. Moreover, simulations on post-deposition annealing, for high aspect-ratio patterns show departures from the predictions of the linear theory for surface diffusion. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2053368]

Structured surfaces play a major role in modern technologies, attracting the attention of the research community from theoretical physicists to materials scientists. The reason for this ever-growing interest lies on the wide range of technological applications of structured surfaces, including solar cells, distributed feedback lasers or microelectromechanical systems.

Traditionally, the fabrication of structured or patterned surfaces involves the use of hard lithography or, more recently, the use of alternative lithographic techniques like nanoimprint or step and flash lithography.[1] However, a different, interesting and less frequent approach consists in the preservation (translation) of the surface pattern during multilayer deposition.[2] This strategy is successfully used to build up sophisticated optoelectronic devices where the preservation of the grating period and height along multilayer deposition on submicron gratings is mandatory.[3]

There are different physical processes that render the making of nano/micropatterns using this procedure difficult. One of them is related to the thermal instability of the deposited material (bulk+surface diffusion). The second one is related to the pattern destruction due to the leveling of the growing interface (surface diffusion+isotropic growth). The third issue is related to pattern destruction due to the triggering of instabilities resulting from nonlocal effects (shadowing+mass transport effects).

In Fig. 1 we show an example of self-preserving growth and pattern destruction for a simple experimental system that is suitable for modeling. We analyze the growth of Cu on submicrometer patterned Cu substrates by physical vapor deposition (PVD) because the deposit structure and the surface mobility of Cu at different temperatures are well known and the growth conditions in PVD are fairly understood. However, the conclusions of this paper can be extended to other materials and deposition techniques.

We have deposited Cu at different incident angles on a Cu template with a periodic array on its surface [Fig. 1(a)]. Cu was deposited at a pressure of 10^{-5} Pa with the substrate kept at 298 K. Figure 1(b) also shows Cu surfaces after depositing a 400 nm thick copper film at $\theta=0°$ (θ is the angle between the incidence direction and the substrate normal). The cross-section analysis reveals that the template pattern has been entirely translated to the Cu films without distortions along the deposition of micrometer thick film, i.e., self-preserving growth takes place.

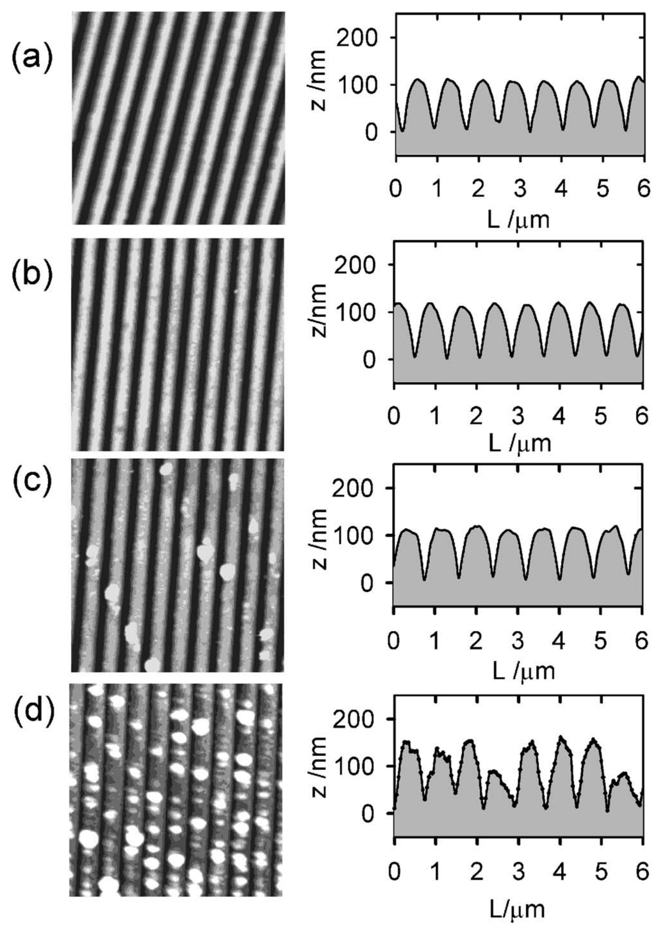

FIG. 1. Atomic force microscopy images with their respective cross sections. (a) Initial patterned Cu substrate. Patterned Cu substrate after depositing a Cu film of: (b) 400 nm thick at $\theta=0°$; (c) 346 nm thick at $\theta=30°$, (d) 200 nm at $\theta=60°$.

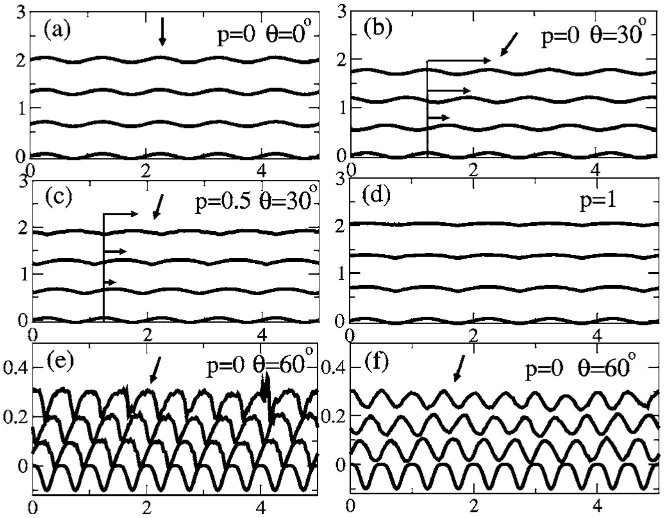

FIG. 2. (a) and (b) Pattern preserving with normal and oblique incidence, for directed flow at 400 K (arrows are visual guides). (c) Partial pattern destruction by cavity filling due to isotropic flow at 400 K. (d) Fast pattern destruction by pure isotropic flow at 400 K. (e) Development of instabilities due to shadowing at 300 K. (f) Growth at 600 K. All the simulations were performed with $F=2$ and the total growth time was 1000 s in (a), (b), (c), (d) and 300 s in (e) and (f). Units are μm in both axes.

Similar results were observed for Cu films deposited at $\theta=30°$ [Fig. 1(c)], although the triggering of a few instabilities on top of the periodic array can be observed. Conversely, for $\theta=60°$, shadowing originates a larger number of instabilities that destroy the periodic array [Fig. 1(d)].

Here, we propose a continuous mesoscopic 1+1 dimensional model for the growth of solid films from the vapor on nano/micro-structured substrates. The model includes: directed and isotropic deposition flow, surface diffusion, and shadowing effects. There are many models focused particularly on re-emission processes,[4,5] surface diffusion,[6] and shadowing effects.[7] In contrast, in our model those processes have room in a unified picture and it contains the main variables present in the experiments: the mean free path, incident angle, and temperature.

Let us consider an incident beam of particles (with an average size σ) collimated in the direction of the flow vector $-J_d\vec{d}$ travelling across an inert vapor and impinging onto a substrate. Particles in the incident beam are scattered by the vapor molecules and by the growing surface, through reemission processes due to a nonperfect sticking. We take into account scattered particles by considering an isotropic flow: the overall flow J is made from the contributions of a fraction p of isotropic flow and a fraction $1-p$ of directed flow. Physically, the fraction p depends on the sticking coefficient and on the relation between the mean free path of the particles and the source-substrate distance. We describe the interface at time t as a parametric curve $\vec{r}(s,t)$, where s is the arc length parameter.

The growth at a segment ΔS_i of the interface proceeds following the local outward normal $\vec{n}_i(\|\vec{n}_i\|=1)$. While the isotropic flow makes a constant contribution to the local rate on the complete interface, the directed fraction of the beam has a cross section that depends on the cosine of the angle γ_i between the local normal $\vec{n}_i$ and the opposite direction to the incident beam, given by $\vec{d}=(\sin\theta,\cos\theta)$.[7]

As it is usual[8] the surface diffusion current is assumed to be proportional to the local curvature gradient. The most relevant contribution to the fluctuations in deposition and diffusion flows, come from the Poisson process representing the arrival of particles approaching at a constant rate to the surface. Following firmly established knowledge in population dynamics[9] and considering that only the arrival of a very large number of small particles will modify the surface, the noise terms respond to spatially uncorrelated stochastic variables normally distributed with variance equal to the flow arriving to the surface element. Thus, naturally emerges the mesoscopic character of model: the length of the discretization segments ΔS_i must be *small* enough so that the interface can be approximated locally in a small region of size ΔS_i by the tangent plane within a reasonable tolerance, and must be *large* enough to justify the use of the law of large numbers.

A surface element of length ΔS_i centered at s, will be translated by the processes considered in a (macroscopically) small time interval dt in the form

$$\delta\vec{r}(s,t) = \Bigg\{ \Bigg[\Bigg(Fp + F(1-p)\cos(\gamma)\epsilon(s) - K\frac{\partial^2 \mathcal{C}}{\partial s^2}\Bigg)\Bigg] dt + \sqrt{[Fp + F(1-p)\cos(\gamma)\epsilon(s)]\frac{\sigma dt}{\Delta S_i}}\,\eta + \sqrt{\frac{2K\sigma}{(\Delta S_i)^2}\left|\frac{\partial \mathcal{C}}{\partial s}\right| dt}\,\xi \Bigg\}\vec{n}, \qquad (1)$$

where F is the local rate of the interface, K is proportional to the surface diffusion coefficient D_s,[8,10] $\mathcal{C}$ is the local curvature, while η and ξ are independent random variables with standard normal distributions. The function $\epsilon(s)$ takes values 0 or 1 depending if the element ΔS_i is shadowed or not, respectively.

Equation (1) is a stochastic, state-dependent, vectorial equation that provides a general framework for modeling film solid growth from vapor deposition. A detailed discussion of this model will be reported elsewhere.[11] Equation (1) will be investigated by Monte Carlo simulations, but previously it is interesting to study the deterministic limit, obtained in the "unphysical" limit when the particles size $\sigma \to 0$: if there is neither shadowing nor overhangs, under the small slopes approximation, we can solve analytically the resulting (linear) equation. The result is that a Fourier mode of the initial pattern $A\sin(kx)$ evolves at time t into

$$Ft\cos\theta + A\exp(-Kk^4 t)\sin[k(x - Ft\sin\theta)], \qquad (2)$$

meaning that the wave undergoes a rigid translation (origin of the pattern preserving) in the direction of the $\vec{d}$ vector plus an exponential decay in amplitude due to surface diffusion.

In terms of the complete equation (1), Figs. 2(a) and 2(b) show how the pattern preserving phenomenon is observed after the deposit of a few micrometers thick film. Figures 2(c) and 2(d) show how the pattern destruction phenomenon occurs because of cavities filling through isotropic flow. Moreover, Fig. 2(e) shows instabilities at the top of the structures spontaneously formed due to shadowing coupled with the interface fluctuations generated by deposition noise. By increasing the temperature these fluctuations are smoothed by surface diffusion (f). The temperature enters the simulations because of the temperature dependence of the copper surface diffusion coefficient reported in Ref. 10.

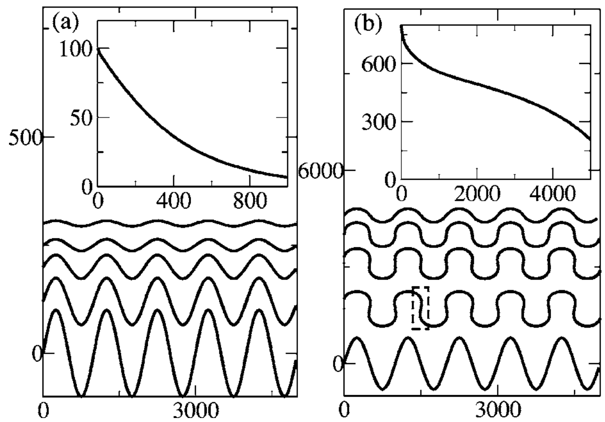

FIG. 3. (a) and (b) Annealing snapshots (at 800 K) for sin waves with initial amplitudes 100 nm and 1000 nm, respectively, and zero incident flow ($F=0$). Curves are offset for clarity (all must have zero mean). Box in (b) stress the overhangs formation. Insets: Amplitudes (in nm) vs time (in s.).

Annealing of metallic films is used to manipulate physical properties such as electrical conductivity or mechanical resistance. A key question is the stability of micro/nanostructured films with temperature. Recently, we showed that Cu patterns similar to those shown in Fig. 1 survive for annealing temperatures as high as 800 K.[10] In Fig. 3 results from our model for the annealing of an initial sinusoidal pattern at 800 K are reported; snap-shots at several times for a small aspect ratio wave are shown (a) with the corresponding wave amplitude time evolution (inset). A smooth exponential decay following the linear diffusion theory is observed. Surprisingly for larger aspect ratio patterns, i.e., far from the small slopes approximation, we found an interesting deviation from linear theory predictions accompanied with a spontaneous development of overhangs [Fig. 3(b)]. The wave decay exhibits a clear departure from the exponential decay [Fig. 3(b) inset]. It means that depending on the aspect ratio the annealing process can also be used not only to modify the physical properties but also to manipulate the shape of the patterns under post-deposition conditions.

Summarizing, we have introduced a mesoscopic model suitable to study the pattern preserving growth, pattern destruction, and pattern manipulation for a wide range of experimental conditions.

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