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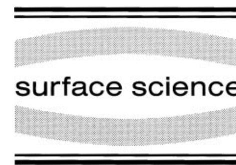

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Pulsed sputtering during homoepitaxial surface growth: layer-by-layer forever

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Abstract

The homoepitaxial growth of initially flat surfaces has so far always led to surfaces which become rougher and rougher as the number of layers increases: even in systems exhibiting "layer-by-layer" growth the registry of the layers is gradually lost. We propose that pulsed glancing-angle sputtering, once per monolayer, can in principle lead to layer-by-layer growth that continues indefinitely, if one additional parameter is controlled. We illustrate our suggestion with a fairly realistic simulation of the growth of a Pt(111) surface, coupled with a simplified model for the sputtering process. © 1998 Published by Elsevier Science B.V. All rights reserved.

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When depositing atoms on a surface, one often wants control of the growth morphology. At the most primitive level, when depositing atom X on a low-index, flat surface of the X crystal, it would be nice to be able to ensure that the resulting surface remained flat!

This simple goal has often been difficult to achieve in practice, especially in metals [1]. At low temperatures, one observes three-dimensional growth: interlayer mobility is low, and the second layer starts growing as soon as the first layer gains any substantial coverage. At intermediate temperatures, one observes what is called two-dimensional or layer-by-layer growth. Layer-by-layer is used to describe systems with oscillations in some measured property (antiphase scattering of He [2], RHEED [3], low-energy electrons [4], or X-rays [5]), decaying slowly as the number of layers increases. For a few materials under special conditions, this decay can be quite slow {2200 periods in silicon [6], 150 oscillations for platinum (111) [7–9] at much higher temperatures than those simulated in this paper}. Under most circumstances, however, it decays over a few tens of layers. At higher temperatures, for slightly miscut surfaces, one can have a step-flow regime which typically exhibits quite stable layered growth.

In this paper, we consider the question of how one might achieve indefinite layer-by-layer growth: a mode-locked state [10,11] where the surface irregularities due to the growth process would remain bounded and oscillations in the properties would continue forever. Such long-range order

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despite the noise (random fluctuations in deposition, nucleation, and growth) would be separated from the traditional decaying layer-by-layer growth by a phase transition. The key is to periodically force the system, pulsing in synchrony with the deposition of each monolayer (keeping in phase by using one of the real-time oscillatory measurements described above). Pulsing the temperature, pulsing the deposition rate, and pulsing with an ion-assisted anneal have been used to good effect experimentally [2]. We argue that pulsing these quantities cannot lead to indefinite flat growth, but that pulsed sputtering can yield layer-by-layer growth forever.

Indeed, pulsed sputtering has been used to enhance layer-by-layer growth [12]. Sputtering was used to roughen the surface at each maximum (where the surface is flattest), to roughen the surface and enhance island nucleation. We propose glancing-angle sputtering to flatten the surface. In principle, unpulsed glancing-angle sputtering could also yield flat growth.

This decaying layered growth is usually described by theories focusing on the nucleation and growth of islands on the surface. Atoms deposited on top of existing islands can either nucleate into new islands (leading to three-dimensional growth) or can attach to the edge of the island (after crossing the Ehrlich–Schwoebel energy barrier at the perimeter). Competition between these two rates leads to a transition between layered and three-dimensional growth, with island density and island size being important parameters [13]. Most of the pulsed attempts to improve the stability of layered growth [2] have been motivated by the nucleation and growth theories, and have deliberately increased the nucleation rate at the onset of a new layer (where depositing on top of existing islands is not a concern), while reducing it thereafter.

The dashed line in Fig. 1 shows a typical thermal growth on a surface. It is a numerical simulation of Pt/Pt(111) at 130 K, grown at one monolayer/second, with parameters determined using effective medium theory and available experimental information as described in [14,15]. The figure shows $I=[\Sigma_{i=0}^{\infty}(-1)^i(\theta_{i+1}-\theta_i)]^2$ as a function of time, where θ_i is the fractional coverage in the ith layer;

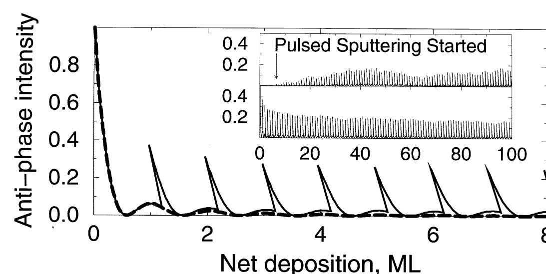

Fig. 1. Layer-by-layer growth, with and without pulsed sputtering. The main plot shows the simulated antiphase intensity I; the oscillations with a traditional thermal deposition (dashed line) decay rapidly. Pulsed sputtering of $\lambda=25\%$ of a monolayer is done after each deposition of 1.25 monolayers, yielding sharp jumps in the curves. (Here the sputtering phase $\mu=0.20$.) The lower curve in the inset shows the peaks of the jumps for the first 100 monolayers deposited: we expect the layers to stay flat indefinitely, for the correct choice of μ. The upper inset curve is the signal from an initially rough sample prepared by first depositing several layers without sputtering. When the sputter–deposit sequence is started, we observe that the surface regains a flat interface.

this measure corresponds closely to what is measured in antiphase scattering probes used in the experimental systems. Notice that the signal vanishes whenever the number of atoms in odd and even layers becomes equal. Notice that the peaks decay as more layers are deposited: as the surface begins to span several layers, the surface morphologies at integer and non-integer monolayer coverages become indistinguishable. One must note that, for the parameters we simulate, the surface does not grow wildly rough even for thermal deposition, where we observe four oscillations in I.

There is another school of theoretical models, which focus not on individual islands but rather on the effect of fluctuations in the deposition rate and the role of diffusion within a continuum description for the height of the surface. These models predict that the random fluctuations in deposition will always overwhelm the available diffusive mechanisms for retaining a flat interface, on sufficiently long length and time scales. Decompose the height $h(\boldsymbol{x})$ in Fourier space $h_{\boldsymbol{k}}$. The random noise introduced by depositing a monolayer will increase the mean square of each Fourier component $\langle h_k^2 \rangle$ by the same amount η (the Fourier transform of random noise is flat).

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On the other hand, the various diffusion processes on the surface will tend to flatten the surface. For example, above the roughening transition an initial sinusoidal perturbation will decay exponentially with a rate given by the inverse fourth power of the wavelength [16,17]. This result has been seen below the roughening transition [18–20], perhaps because of small miscuts or perhaps because of crossover effects. Thus in this regime $\mathrm{d}\langle h_k^2\rangle/\mathrm{d}t \propto -k^4\langle h_k^2\rangle + \eta$, yielding a stationary state whose roughness grows as the wavevector shrinks, as k^{-4}.

There are several mechanisms and models [21–25] for this diffusive smoothing of surfaces, but they all predict that the surfaces will eventually become rough: the noise is independent of wavelength, and the diffusion becomes feeble at long wavelengths. However unlikely it is to nucleate on top of an existing island, diffusion cannot transport the extra atoms from one region of the surface to another fast enough: eventually the extra atoms in one region will nucleate extra layers. Pulsing the temperature, pulsing the deposition rate, or pulsed annealing with an ion beam only changes the effective diffusion rates on the surface, and does not fundamentally alter this conclusion: we need a non-diffusive mechanism.

How can we smooth the surface in a more effective way? Atomic beams incident at glancing angles to the surface are a known way of generating flat surfaces [26–29]: the beam preferentially sputters atoms off the mountains and hills. Especially for groups using energetic beams for growing surfaces [5], it would seem natural to try to use a pulsed sputtering mechanism. We envision beams of relatively low energy (50–100 eV) or at glancing angles, where only single adatoms and atoms at step edges would typically be disturbed in a collision. Consider starting with a flat surface with an initial deposition of $1+\mu$ monolayers. We then repeatedly sputter off λ and deposit $1+\lambda$ monolayers, so as to always start the sputtering at an integer plus μ monolayers coverage. If a surplus of atoms is deposited onto a region of the flat surface, there will be a surplus of adatoms at the time of sputtering, and thus the sputtering will remove extra mass from the region. This non-diffusive mechanism, being independent of wavelength, should in principle be able to produce indefinite layered growth.

We decided to test these ideas with a simple model. Building on our well-characterized [14,15], physically realistic solid-on-solid kinetic Monte Carlo model for thermal deposition and growth on Pt(111), we implemented a primitive, simplistic model for glancing-angle rotating-beam sputtering. (We got grooves when sputtering from one direction only.) We wanted atoms in an intact layer to be immune from sputtering, solitary atoms and edges of small islands to be sputtered at high rates, and pit edges to be at least partially shielded. We sputter equally from each of the six directions lying along atomic rows. An atom is immune from sputtering from a given direction if it is shadowed by another atom upwind in the same row and the same monolayer, within a distance $L=5$ interatomic distances. Fig. 1 shows that this model can produce smooth growth, seemingly forever.

This sputtering model we imagine might correspond roughly to a beam at an angle $\arctan(1/L)=11°$. Our model is likely over-optimistic in that intact monolayers and shadowed atoms are protected completely. It is using a pessimistic angle of attack: angles from 1° to 15° have been used for smoothing rough surfaces [26–29], and a more glancing angle in our simulation would produce much smoother surfaces. This kind of simplistic model is particularly useful in studies of the qualitative features and feasibility of a new method, and indeed it immediately uncovered an important issue neglected in our discussions so far.

Fig. 2 shows a surface grown with our sputtering schedule with a different value of μ, after growing 41 monolayers. Notice the pit. Up until this point in the simulation, we saw excellent layer-by-layer growth, similar to that shown in Fig. 1; subsequent to this frame the oscillations die away. We interpret this behavior as the nucleation of a critical pit, analogous to critical droplets at first-order phase transitions [30,31].

Consider what happens to a pit of radius R_n under a cycle of depositing $1+\lambda$ monolayers and sputtering off λ. During the deposition, atoms falling on the upper layer will typically nucleate new islands, which grow and merge to raise the height by one. Atoms landing inside the pit will stick to its outer edges; the pit will fill in (given a

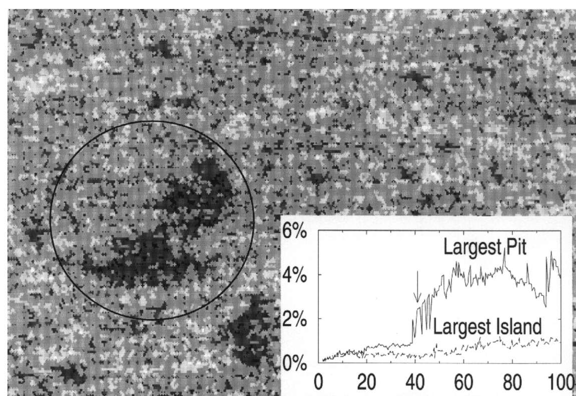

Fig. 2. Critical pit. This is a snapshot of our simulation with $\lambda=0.25$, and $\mu=0.1$, after 41 layers have been deposited. Lower layers are darker grey (pits). The inset shows a plot of the percentage of the system size occupied by the largest island and largest pit, as a function of how many monolayers have been deposited. The arrow in the inset shows the time of the snapshot. Until 39 layers, all we see are small pits and islands which appear and disappear. At this point, we see a large pit form (circled), which grows irregularly thereafter. The oscillations in the antiphase intensity (as in Fig. 1) die out slowly after the pit nucleates.

large Ehrlich–Schwoebel barrier) at about the time a whole monolayer is deposited. However, the region of the former pit will remain depressed, since new islands start nucleating and growing only after it fills in. As a zeroth approximation, a new pit one level higher of the same radius will exist after one cycle of deposition and sputtering:

$$R_{n+1} \sim R_n.$$

Consider a flat step on the surface – interpretable either as a pit or an island of infinite radius. Under one cycle of deposition and sputtering, there is no reason to expect that the attachment at the step edge will balance the sputtering. (That is, our model has no symmetry between pits and islands.) One expects the step edge to move by a distance Δ, where we define positive Δ to represent the growth of the pit (lower terrace). To a first approximation for large radius, we expect the pit area after one cycle on average to change:

$$R_{n+1} = R_n + \Delta.$$

Now, since the edges of small pits are partially shielded, and islands are more exposed to the sputtering, the net effect after one cycle is to remove less material in existing pits, and more near existing islands. The smaller the pit radius R_n, the more protected is the pit, and the higher is the net deposition after the entire cycle. To a second approximation, we expect that the pit will be reformed at a new radius $R_{n+1} = R_n + \Delta - \Sigma/R_n$. The term $-\Sigma/R_n$ represents the physics of the self-shielding for small pits which tends to make them shrink; it also makes small islands shrink (negative radius). This is the term found for detachment-limited coarsening for islands on surfaces [32,33], is the first term in a Taylor series in the curvature of the edge, and can be derived with a simple geometrical argument based on shielded sites.

Finally, there is the stochastic fluctuation in the pit radius. We expected that the dominant source of fluctuations would be the fluctuations in the number of atoms deposited within the area of the pit, which should scale as the square root of its area; hence the radius fluctuations will be independent of radius:

$$R_{n+1} = R_n + \Delta - \Sigma/R_n + \Omega\xi_n. \tag{1}$$

$\Omega\xi_n$ in Eq. (1) is the noise term: ξ_n is a random variable with mean zero and standard deviation one, and Ω gives the strength of the noise. Measuring these fluctuations directly, in the interesting range $0<\mu<0.2$, we have verified that they are indeed roughly independent of R and of width $\Omega \sim 0.65a$. Fig. 3 shows the results of a fit of the average shrinking and growing of pits, using Eq. (1) without noise ($\Omega=0$).

The layer-by-layer growth in our model ends when the fluctuating noise produces a pit of the critical size

$$\langle R_c \rangle = \Sigma/\Delta, \tag{2}$$

after which the pit grows by itself to macroscopic size. Our Eq. (1) can be thought of as a thermal random-walk in radius, with step size Ω, temperature $T=2\Omega^2$, and potential $\Sigma \log(R) - (R-1)\Delta$: the critical radius is the local maximum $V_{\max}$ in the potential. The effective noise is much higher for our non-equilibrium islands than it is for thermal pits: hence power laws rather than exponentials in Eq. (3). One can solve a continuum approximation to Eq. (1) for the rate of formation

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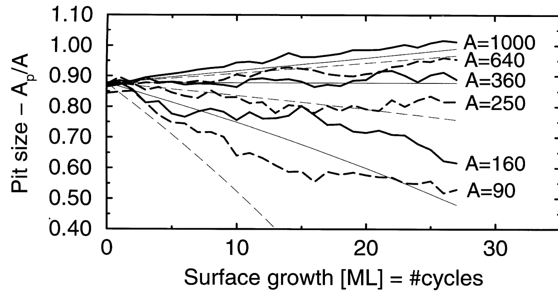

Fig. 3. Large pits grow, small pits decay, for $\lambda=0.25$, and $\mu=0.15$. Shown is the evolution of the area A_p of a pit for six different initial pit sizes A, each 10% of the initial area of the simulation, averaged over 100 runs each (except for size 100, with 85 runs). We follow the evolution of the pit by measuring its size every time there is an integer number of monolayers down. The thin curves are Eq. (1) fit to the data (if a is the lattice spacing, then $\Delta\sim 0.09a$, and $\Sigma\sim 0.9a^2$, with an initial shrinkage of the island radius of about 6%.) The critical pit size R_c is estimated to be 280 ± 60 in area, or about 10 lattice constants in radius.

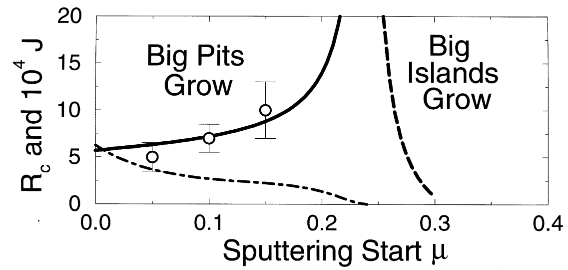

Fig. 4. Critical pit size R_c (in units of the lattice constant a) and large pit formation rate J (in units of nucleated large pits per monolayer per vacancy) as a function of sputtering phase μ. The points with error bars are eyeball estimates from plots like Fig. 3. The upper curves are from Eq. (2) with sinusoidal fits to $\Delta(\mu)$ and $\Sigma(\mu)$. Because Δ changes sign at $\mu_c\sim 0.24$, the critical pit size diverges there; for $\mu<\mu_c$ large pits are unstable (solid curve), and for $\mu>\mu_c$ large islands become unstable (dashed curve). When the critical pit size diverges, the rate of large pit formation J goes to zero (dot-dashed curve).

of large pits, per density of pits of size $R=1$:

$$J=\Delta(2\Delta/\Omega^2)^{2\Sigma/\Omega^2}/\Gamma[1+2\Sigma/\Omega^2,\,2\Delta/\Omega^2]$$
$$=\Delta\{[2\Sigma/(e\Omega^2)]^{2\Sigma/\Omega^2}/\Gamma[1+2\Sigma/\Omega^2,\,2\Delta/\Omega^2]\}e^{-V_{\max}/T} \quad (3)$$

where Γ is the incomplete gamma function.

The last Eq. (3) shows the connection with traditional critical droplet theory [30–33]. Here the term in curly brackets is a prefactor, Δ is a bound on the velocity at which one could cross the barrier, and $e^{-V_{\max}/T}$ is the Boltzmann probability of sitting at the critical radius.

How can we grow layer-by-layer forever? Clearly, we wish to set Δ to zero, imposing a long-wavelength symmetry between islands and pits, sending the nucleation rate J to zero. All three constants Δ, Σ, and Ω in Eq. (1) will depend on temperature, deposition rate, sputtering angle, other adsorbates on the surface, the fraction λ sputtered, and the point μ during the deposition of a monolayer that the sputtering occurs. If by varying any of these parameters we can set $\Delta=0$ without making $\Sigma<0$, we ought to suppress the nucleation altogether, and sustain layered growth indefinitely.

Fitting to simulations like those shown above in Fig. 3, we have measured the critical pit size R_c, Δ, and Σ as functions of μ. We find Δ, Σ, and an initial island shrinkage all fit well to the form $a\sin(2\pi\mu+\phi)+b$. Direct measurements of the critical pit size show a divergence where our sinusoidal interpolation for Δ changes sign (Fig. 4). (Above about $\mu=0.3$, $\Sigma<0$; our theory no longer applies.) Above μ_c, where $\Delta<0$, we expect all pits to be stable and large islands to be unstable. Our exploration of this region does indeed show islands substantially larger than the corresponding pits, and we qualitatively saw large island clusters nucleate and destroy the flatness. The large shadowing length L led to diffuse islands whose sizes were hard to measure.

Can we show that the surfaces remain flat near μ_c? The sputtered simulation shown in Fig. 1 was done at $\mu=0.20$ (near $\mu_c=0.24$ where the lifetime of flat growth diverges); the inset shows that the oscillations are persisting as long as we have simulated. Eq. (3) predicts the rate of formation of large pits $J(\mu=0.20)$ to be 1.4×10^{-4} times the density of pits of size one. For values of μ far from μ_c the oscillations decay rapidly: at $\mu=0.7$ the oscillations die roughly as they do for a thermal growth without sputtering (although the r.m.s. roughness for the sputtered surface is much smaller than that for a thermally grown, unsputtered surface even away from μ_c). Fig. 4 also shows our

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prediction of the nucleation rate J for large pits: proportional to the inverse of the lifetime for flat growth.

Finally, in perhaps the most convincing demonstration that our method is working, note back in Fig. 1 the second plot in the inset. It shows a rough surface becoming flat once we start our pulsed sputtering schedule!

In trying to grow flat layers, why not go for perfection? We argue that the methods used heretofore to grow flat surfaces (pulsing temperature, deposition rate, ion-assisted diffusion, etc.) cannot compete in the end with the stochastic noise in the deposition rate. We claim that pulsed sputtering, smoothing once per deposited monolayer, can in principle yield layer-by-layer growth oscillations that last forever, provided that one parameter is tuned to a critical value.

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