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2008 J. Phys.: Condens. Matter 20 395001

(http://iopscience.iop.org/0953-8984/20/39/395001)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 395001 (8pp) doi:10.1088/0953-8984/20/39/395001

Synthesis of pans and mesas using a beam of self-ions

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Received 27 May 2008, in final form 21 July 2008
Published 19 August 2008
Online at stacks.iop.org/JPhysCM/20/395001

Abstract

We report the synthesis of pans and mesas ∼10 μm in diameter on Pt(111), in ultra-high vacuum, using a beam of Pt^- ions as the processing tool, and a low energy electron microscope to observe the surface microtopography. Mesas are perfect terraces surrounded by a bunch of outward pointing steps; an ion beam of low energy was used to create excess adatoms that accrete to expand that terrace and increase the height of the step bunch. Pans are similar, but with reversed steps, and a beam of high energy ions was used to sputter the surface, creating advacancies that expand the pan terrace. The critical constraint that leads to successful synthesis is preventing new steps from nucleating on the terrace, by gradually reducing the driving force of the ion beam as time progresses. A model of this process is presented on the basis of a recent theoretical description that models the flow as a quasistatic process with negligible Gibbs–Thompson forces, so that the evolution is reversible, as observed. The model successfully reproduces the main features of the observations.

1. Introduction

Many important surface processes are effectively local in character. These include island nucleation, the evolution of island size, the behavior of threading screw dislocations, Bardeen–Herring sources and other intrinsic nanostructures. Other nanostructures localized on terraces involve chemical impurities, and may be as simple as adsorbate islands or as complex as the capabilities of the synthesizer permits. When, in practice, the evolution of such structures is examined, it is invariably the case that the behavior is influenced by the surrounding surface structure. A simple example is the nucleation of new islands by an excess of adatoms or advacancies on the surface. The nucleation events are keyed [1] to the local chemical potential μ^*, and μ^* is determined in turn by a solution of the diffusion equation that depends on the local distribution of sinks, typically in the form of step edges. In short, the nucleation event is responsive to the local surface topography fixed by the exterior structures. Many other local processes on surfaces share this sensitivity to neighboring structure.

Experiments that attempt to study such local behavior can clearly benefit from procedures that isolate the locality from more remote surface structure. Suitable structures are pans and mesas that contain the particular region of concern on a perfect terrace surrounded by a step bunch of considerable height. This paper describes the procedures by which pans and mesas of dimensions up to ∼10 μm can be created on the surfaces of metallic crystals by irradiation with self-ions [2, 3]. Methods have been reported earlier for making very large free terraces on Si surfaces using lithographic methods, followed by sublimation [4, 5].

One can readily appreciate why a surrounding step bunch isolates a terrace from external perturbation. Diffusion currents, driven by the gradients of chemical potential caused by neighboring non-equilibrium structure, are carried over surfaces by mobile thermal point defects in the forms of adatoms and advacancies. It is a direct consequence of detailed balance for equilibrium that the diffusion fields these defects create satisfy boundary condition at defect sources and sinks, such as step edges. The boundary condition at free sinks is that the concentrations there always take the particular values appropriate for thermal equilibrium of the terrace at the given temperature, regardless of applied forces that may cause excess defect creation, and at both sides of a step edge (i.e. uphill or downhill) [1, 6]. Detailed balance assures that any process and its time-reversed anti-process occurs with equal frequencies at equilibrium. Owing to this broad constraint, non-equilibrium

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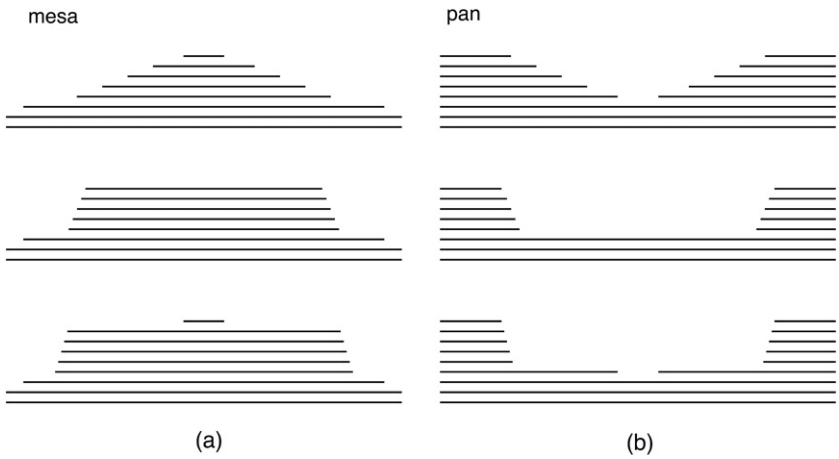

Figure 1. Cartoons illustrating structure of mesas (left, middle) and pans (right, middle). Lines indicate atomic planes near the surface. A pan is a terrace surrounded by a bunch of inward pointing steps while for a mesa the steps point outwards, as shown. Vertical sequences indicate growth from pre-existing surface extremum using appropriate ion beam of low energy (left) or high energy (right). The lowest cartoons indicate the critical steps of nucleating new islands, which must be *avoided* for successful growth.

structures *outside* a perimeter formed by a step bunch can no longer affect diffusion fields *inside* the perimeter [1]. In this way, localized processes on the terrace are well isolated from all structure outside the step bunch that surrounds the pan or mesa, and any fluxes caused by such processes are subject to the boundary condition of equilibrium concentration at the step bunch. Here we call the structures *pans* if the step edges are oriented downhill *inwards* to create a terrace sheltered below the level of the remaining surface, and *mesas* if the they point *outward* to create a central terrace raised above its surroundings. Cartoons that illustrate these structures are provided in figure 1.

The surface evolution that creates large pans and mesas, as reported here, was observed during experiments in which clean Pt(111) was irradiated using a beam of Pt^- ions [2, 3, 7]. Pans and mesas evolved from pre-existing local minima and maxima on the as-prepared surface. It is shown elsewhere how a beam of low energy ions creates excess adatoms on the Pt surface, while a beam of high energy (>250 eV) creates instead an excess of advacancies by sputtering atoms off the surface into vacuum [2]. The two cases cause opposite flow of the step edges that absorb the excess antidefects from the terraces. We have been able to reproduce the main effects of pan and mesa growth accurately, using a theory sufficiently general as to leave little doubt that similar behavior should be observable on other surfaces of Pt, and on surfaces of other materials. The use of a beam of self-ions is valuable because it maintains surface cleanliness and avoids chemical effects inherent in the use of foreign ions. It nevertheless appears certain that mesas could be grown by these means during ordinary molecular beam epitaxy, and it is likely that clean pans can be grown by irradiation with rare gas ions with energy chosen to avoid deeply implanted contaminants [8, 9]. Consequently these methods, while reported here only for Pt(111), may have application much more widely to a variety of alternative materials and surfaces.

The equipment needed to tailor pans and mesas by these methods comprises a focused ion beam in UHV combined with an instrument capable of viewing atomic steps on surfaces during irradiation [10]. In the present research this technically challenging combination took the form of a low energy electron microscope (LEEM) [11] that had been fitted with the necessary ion source [12]. The LEEM makes individual atomic steps visible by interference contrast at a lateral resolution of about 10 nm. In the tandem instrument employed here, the ion beam was relayed to a focus near the sample surface, to provide intense beams of selectable negative ions with energies in the required range. Pt^- self-ions were used to irradiate Pt(111) to avoid the complications of mixed chemical species on the surface. Further details of equipment design and the experimental results are given in section 2 below.

We have been able to successfully model the observed behavior by a theoretical description of the diffusion fields [1] by which the mobile adatoms and advacancies, created by self-ion irradiation, are transported to step edge sinks. This model is discussed in the appendix and included in the discussion of results in section 3. The predictions of the model treatment compare favorably with the observations presented in section 2.

2. Experiments

A LEEM designed by Tromp at IBM, Yorktown Heights [11], was fitted post-manufacture with a SNICS II source of negative ions [12] purchased from National Electrostatics Corp., Madison Wisconsin. The beam was relayed to a focus near the sample surface by a spherical mirror analyzer, to provide ion beam flux densities up to almost 0.1 monolayers per second for Pt^- ions. The ion beam and LEEM electron beam occupy the same area of sample surface such that the surface topography, as defined by the step structure, could be monitored during actual irradiation. A full description of the equipment has been published [10]. For the present purposes the main additional capabilities were that single crystal samples could be investigated at temperatures up to 1400 K with the vacuum maintained at 10^{-10} Torr or below.

No contamination associated with the beam of self-ions was detected.

A Pt crystal 9 mm in diameter and 1 mm thick, cut within 0.2° of the (111) plane, was employed in these experiments. The cleaning procedures using sputtering, elevated temperatures, and O_2 exposure, are described in detail elsewhere [13]. From observations by LEED, LEEM, and PEEM using capabilities of the microscope, and by *in situ* Auger analysis, no trace of signals caused by contamination was visible after cleaning.

We turn now to the driven evolution of pans and mesas that constitutes the central topic of this paper. The Pt(111) surface when cleaned was found to possess a mean miscut, roughly along $[11\bar{2}]$, with mostly straights steps, at a spacing consistent with the miscut. It is an important matter that the surface topography exhibited additional structure on a length scale typically $\sim$20 μm, without evident directional preference, that created shallow maxima and minima by chance at points spaced over the surface by many tens of μm. The main point of interest here is the response of the crystal near these extrema to ion irradiation with beams of differing energies.

On a cleaned and annealed surface, the step edges near a local maximum of surface height are generally found to meander around that maximum in closed loops that resemble contour lines on a map. It is easy to understand that an 'adatom self-ion beam', with low enough energy as to add net atoms to the surface, generally causes the contours around a maximum to expand. By the time that all added atoms have attached to the steps, the areas swept out by the steps moving away from the maximum must sum to precisely the number of added atoms times the area A per atom. On the other hand, an 'advacancy beam', with ion energy high enough to sputter a net excess of atoms from the surface, causes the step edge loops to contract towards the maximum. We have created pans by irradiating local minima with an advacancy beam, thereby expanding the contours about the minimum, and have made mesas by irradiation of a maximum by an adatom beam, again expanding the step edge contours.

Figure 2(a) shows the surface structure near a maximum of the surface height, as described, after cleaning and annealing but before processing with a beam of self-ions. Successive images (a)–(d) illustrate the way the step-loops initially all expand. Two features warrant immediate comment. First, the central island expands faster than the second, third loop, etc. The result is that the central step eventually catches up with the second step and merges with it to form an embryonic step bunch. Because the islands are neither circular nor exactly concentric, various point on the steps make contact at generally differing times. What happens next is that the step bunch expands to meet the next step, and the process repeats without apparent limit. In this way, a central terrace surrounded by a step bunch of progressively greater height gradually evolves. The reason for identifying the result a step bunch rather than a multistep will emerge below.

The second point for comment is the single most critical factor in the selective synthesis of a mesa. Specifically, the beam intensity must be reduced (or ambient temperature increased) with lapsed time to prevent the nucleation of a new island near the middle of the original central island (see lowest cartoons in figure 1). If this necessity is neglected, the result is that the expansion of existing loops and nucleation of new central islands will together approximately reproduce the original local maximum on a surface of ever-increasing average height. This is easily explained because the normal consequence of uniform deposition is a uniform increase of height everywhere. Given that nucleation is suppressed while growth continues, however, the original central island evolves into the terrace on top of a mesa, surrounded by a collar formed by a deep perimeter step bunch. Some quantitative comments about the reductions of beam flux are offered below in section 3.

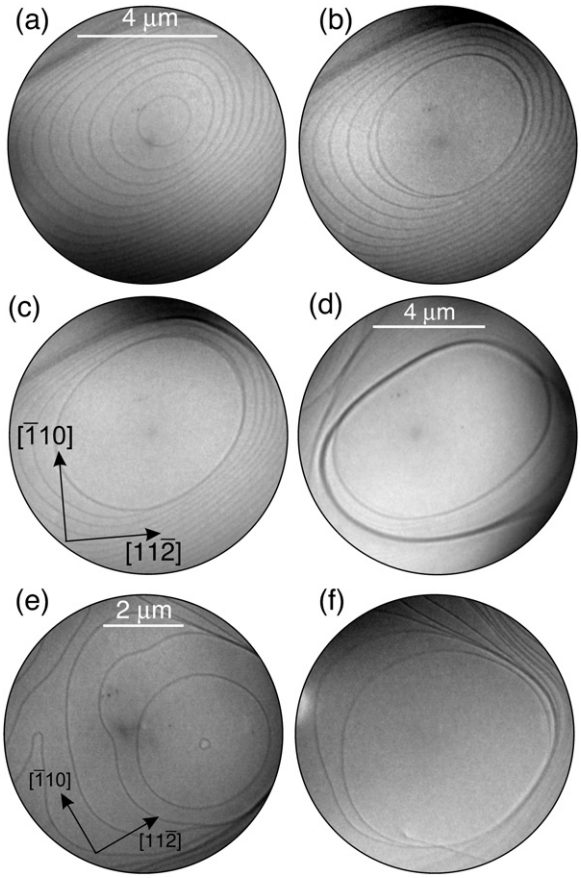

Figure 2. Parts (a)–(d) show the formation at 1190 K of a mesa, of diameter $\sim$6 μm on Pt(111), from a pre-existing local hillock on a well-annealed surface. The lines are step edges pointing outwards that behave like contour lines. With irradiation by a Pt-adatom beam, the surface evolves in (a)–(d) to form a mesa consisting of a perfect terrace surrounded by a step bunch. A 65 eV ion beam was used with a flux density 4.6 μA cm^{-2}. (e)–(f) A pan, surrounded by an inward pointing step bunch, similarly formed at about 1100 K from a local minimum of surface height by an advacancy beam of Pt^- ions with 515 eV energy at a flux of 1.0 μA cm^{-2}. A screw dislocation has slipped into the image (bottom left in (f)). A LEEM impact energy of 17 eV was used for imaging.

An advacancy beam that sputters atoms from the locality of a pre-existing local minimum on a clean surface creates a similar evolution for a pan. Figures 2(e) and (f) shows a pan formed in this way much as illustrated in detail by figures (a)–(d) for mesas. While figures 2(d) and (f) appear similar, they

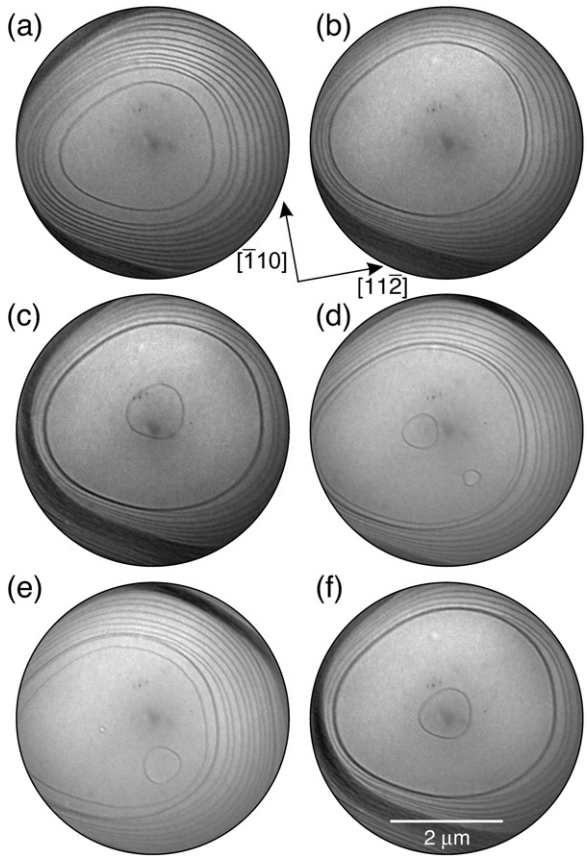

Figure 3. Driven attachment and detachment of steps from step bunch. In (a)–(c) steps driven by an adatom (65 eV) beam of 3.7 μA cm^{-2} expand to form a mesa with a peripheral step bunch three steps high, as the surface is cooled from 1240 K through 1125 to 1075 K, where the central adatom island in (c) nucleates and grows. (d) and (e) show the subsequent results of an advacancy beam of 415 eV, flux 3.7 μA cm^{-2}, in peeling and shrinking one step from the inside of the bunch. Also, the adatom island shrinks and a new advacancy island nucleates and grows. A restored adatom beam in (f) replaces the step in the bunch, regrows the adatom island and eliminates the advacancy island.

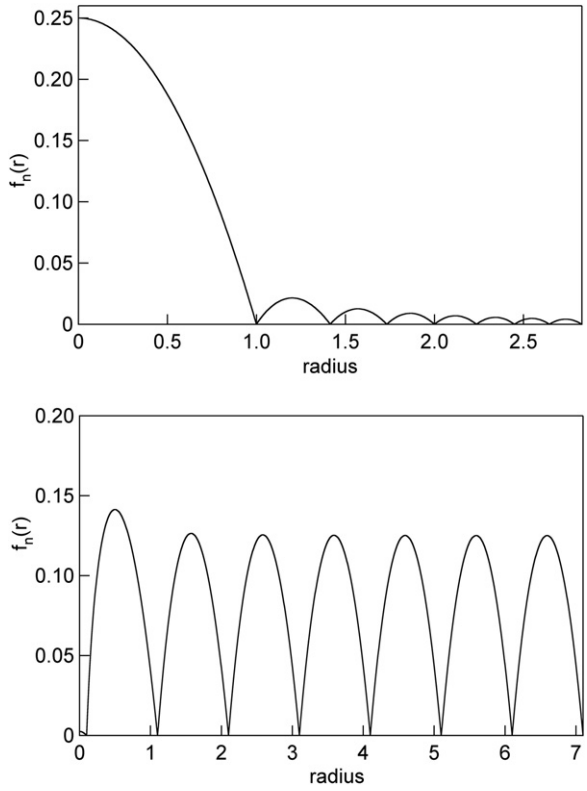

Figure 4. The quasistatic variation of defect density with radius for a series of concentric circular steps driven by an ion beam, obtained using equations (4) for the assumed radii shown, for two cases described in the text. (a) Radii $R_n = n^{1/2}$, forming a rounded maximum. (b) Radii $R_n = n - 0.9$, forming a cone. When driven by an ion beam these configurations evolve differently, as illustrated in figures 5 and 6.

differ in that the latter contains an *inward*-facing step bunch, as shown in figure 1(b).

At the time of writing only a limited quantity of information is available about the distinctions between multisteps and step bunches. One possible distinction seems to be that the motions of stable multisteps do not cause the component steps to dissociate. This has made it possible, for example, to determine for Pt(111) the stiffnesses of multisteps having various heights, using step fluctuation spectroscopy [14]. The component steps of a step bunch are, in contrast, bound together more weakly, such that the steps can relax apart to some degree [15].

The relevance of these distinctions to the present research is clarified in figure 3. There, panels (a) through (c) show a low mesa forming under an adatom (65 eV) beam as the surface is cooled from 1240 K (a) through 1125 K (b), to 1075 K in (c). The beam of 3.7 μA cm^{-2} is large enough for the central adatom island to nucleate and grow to the size shown at the final temperature. Then ion beam is changed to an advacancy beam of 3.7 μA cm^{-2} at 415 eV that shrinks the central adatom island and nucleates an advacancy island (figure 4(d)) where the chemical potential is lowest. These processes of shrinkage and growth continue through figure 4(e) (note the opposite threefold shapes of the two types of island). The main point of the figure is to show the step edge peeling off the inside of the peripheral step bunch that forms the mesa, and shrinking inwards under the advacancy beam (which also shrinks the central adatom island and grows the off-center advacancy island). Finally under a restored adatom beam, in (e), the step grows out to rejoin the step bunch, while the central adatom island regrows, and the off-center advacancy island shrinks until it is eliminated. The important point demonstrated here is the reversible addition, (b) and (f), and loss (d) of steps from the inside of the step bunch, depending on the perturbing beam employed.

We invariably observe for mesas that an advacancy beam causes the last step to detach from the step bunch, such that the last phases of evolution that took place under an advacancy beam are simply reversed. Precisely the complementary behavior is observed when the advacancy beam that has creating a pan is followed by an adatom beam. Specifically, the evolution is reversed and the last step to be attached detaches by shrinking away from the step bunch. We infer from this

evidence that the steps in a bunch are weakly bound together and are easily separated.

3. Driven diffusion to step edge sinks

3.1. Theoretical description

Our main purpose here is to develop a theoretical model that explains the observed behavior, and offers insight into changes that may arise in differing circumstances. Any such theory must start from the way the ion beam creates mobile thermal defects that diffuse to step edge sinks. There they annihilate with consequent flow of the surface steps. The task is therefore to determine the concentrations $c_1(\mathbf{r}, t)$ of adatoms and $c_2(\mathbf{r}, t)$ of advacancies on the terraces, and to find from these values the fluxes $J_i = -D_i \nabla c_i$. Here $i = 1, 2$, an index distinguishing between the two antidefects, with hopping diffusion coefficients D_i. From the fluxes at the steps, the step flow rate is readily predicted as

$$\dot{\rho} = A(J_1 - J_2) = A[D_1 \nabla c_1 - D_2 \nabla c_2]_\rho, \tag{1}$$

A is the area per atom on the surface terrace, and the gradients are evaluated, as indicated, at the step edge, ρ. An important feature of the solution is that the diffusion fields assign to the mobile defects specific concentrations at the sink locus ρ, equal to the values for thermal equilibrium on the terrace, namely $\bar{c}_1$ and $\bar{c}_2$, as explained above [1].

Much is known about the diffusion fluxes from earlier experiments. It is established that (a) the response remains linear in ion beam intensity [2]; (b) that the behavior is reaction limited at these temperatures on Pt(111) [13]; and (c) that the evolution of the concentration distribution is quasistatic [3, 7]. Reaction limited means that the antidefect (adatoms and vacancies) lifetimes are determined by pair reactions rather than processes at sinks (step edges). Quasistatic means that the fluxes caused by the concentration distribution are much larger that those arising from time derivative terms $\partial c_i / \partial t$. Processes of this type follow a reversed evolution when the driving force changes sign. The closely related growth problem of isolated islands growing on large terraces has been shown to have universal behavior associated with quasistatic evolution [7]. Thus we interpret the shrinkage of the last step from the peripheral step bunch under an ion beam of reversed sign, shown in figure 3, as a sign of quasistatic evolution. In terms of excess defect densities $s_1 = c_1 - \bar{c}_1$; $s_2 = c_2 - \bar{c}_2$, the reaction limited condition makes

$$s_1/\bar{c}_1 = s_2/\bar{c}_2. \tag{2}$$

This is the law of mass action for the reacting thermal point defects.

A theory that incorporates these necessary features has been presented elsewhere [1] and is reprised in the appendix. Its predictions have been successful in describing quantitatively the nucleation of new islands on terraces [3], and both the functional form and the absolute rates of driven island growth on terraces [7]. For these reasons a similar treatment here of contour evolution in driven growth may be approached with some confidence. For a uniform field of irradiation that creates K_1 adatoms per surface site per second and K_2 advacancies per second, the net atomic current in the steady state, combining adatom and advacancy flow, is

$$J(r) = -D_1 \nabla s_1 + D_2 \nabla s_2 = (K_1 - K_2) \nabla f(\mathbf{r}). \tag{3}$$

Here, $f(\mathbf{r})$ is the solution of the Poisson equation $\nabla^2 f = 1$ with the boundary condition $f = 0$ for the step edge sinks that occupy the surface [1].

Suppose then that in the case of present interest, the inner step is initially circular with radius R_1, and successive further steps are at radii R_2, R_3, R_n, etc. For $r < R_1$, the Poisson equation yields

$$f_0(r) = (R_1^2 - r^2)/4, \tag{4a}$$

while for each of the successive annuli $R_n < r < R_{n+1}$, the result is

$$f_n(r) = \frac{R_{n+1}^2 - r^2}{4} - \frac{(R_{n+1}^2 - R_n^2)\ln(r/R_{n+1})}{4\ln(R_n/R_{n+1})}. \tag{4b}$$

It is readily verified that these satisfy the required equation and boundary conditions.

Figure 4(a) shows by way of example the variation of $f(r)$ with r through a circular region covered by steps with radii $R_n = n^{1/2}$, $1 \leqslant n \leqslant 8$ (solid line). This is the case of an initial rounded maximum, relevant to pans and mesas, as described below. The step radii increase with time because of the defects fluxes that flow to steps down the gradients of f, evident in figure 4. Precise examples of this behavior are detailed in section 3.2 below. Also shown, in figure 4(b), is a second profile appropriate to the comparison case of a conical initial profile. with steps initially at $R_n = n - 0.9$, which is discussed further below.

The rates at which the step radii change with time may now be predicted for any chosen example by combining equations (1) and (3), and then inserting the result for $f(r)$. For each step, say step n, the flow from inside and from outside R_n must be combined to obtain the net rate of radius change. This prescription gives, for the first step,

$$\frac{\mathrm{d}R_1}{\mathrm{d}t} = \frac{\Delta K (R_2^2 - R_1^2)}{4R_1 \ln(R_2/R_1)}, \tag{5a}$$

in which $\Delta K = K_1 - K_2$. For $n > 1$ the comparable result is

$$\frac{\mathrm{d}R_n}{\mathrm{d}t} = \frac{\Delta K}{4R_n}\left[\frac{(R_{n+1}^2 - R_n^2)}{\ln(R_{n+1}/R_n)} - \frac{(R_n^2 - R_{n-1}^2)}{\ln(R_n/R_{n-1})}\right], \qquad n > 1. \tag{5b}$$

We note the important fact that the magnitude of the diffusion coefficient does not enter into the predicted rates. This curious result is a consequence of the steady state conditions, in which the defect concentrations caused by irradiation simply build up until the flow to the steps exactly cancels the creation rates, everywhere. The flow thus matches the creation rate regardless of the specific value of the diffusion coefficient, and the step motions simply reflect the defect formation rate ΔK per site. A similar conclusion has been reached earlier in connection with driven island growth [7].

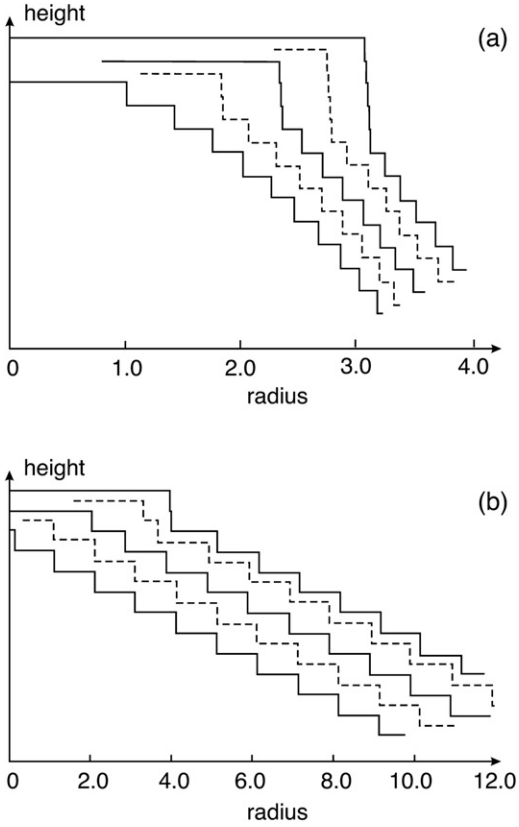

Figure 5. (a) A rounded maximum with step radii given by $R_n = n^{1/2}$ is employed to model the evolution of a mesa driven by an adatom beam, using the iteration method presented in the text. The profile is also shown for four later times (with small vertical offsets for clarity) as the mesa and surrounding step bunch grow in size. (b) The evolution of an initially conical maximum with $R_n = n - 0.9$, obtained by similar methods.

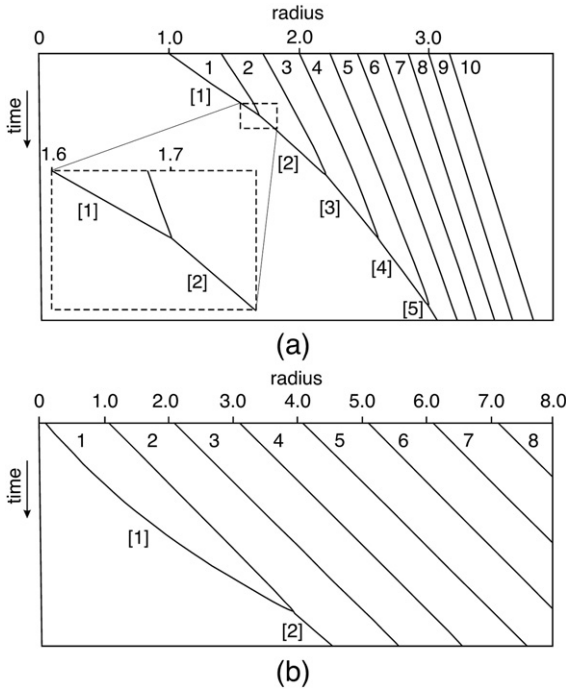

Figure 6. (a) The growth of a mesa driven by an ion beam. The line indicate the calculated time evolution of step radii. The inner steps grow fastest and successively merge into a surrounding step bunch of increasing height that forms a collar around the perfect central terrace, much as observed experimentally. Inset shows on an expanded scale the smooth behavior as the first step merges with the second step. (b) In the different evolution of a conical initial configuration, the merging of the inner steps to form a step bunch is delayed to much longer times.

3.2. Illustrative cases

Equations (5) provide a set of simultaneous equations that may be iterated to obtain self-consistent values of the radii as they develop together in time under the influence of net defect creation ΔK. As the equations are interdependent, the time dependence of any one radius depends on all the remainder. However, the behavior for R small, near the origin, on which our immediate interest focuses, is not sensitive to the precise time evolution of radii at large n. A self-consistent iteration of the set may therefore be achieved by establishing a convenient boundary condition at a chosen, finite, value $\bar{n}$ of n, for which the exact evolution is $R_{\bar{n}}(t)$. For our present interest in $n < \bar{n}$ it suffices to simply extrapolate $R_{\bar{n}}(t)$ from the calculated values of $R_n(t)$ for $n < \bar{n}$ (which require the values for $R_{\bar{n}}(t)$ obtained from the extrapolation). This allows the evolution of the radii to be iterated from any chosen set of starting radii, Results for two cases of interest are now described.

3.2.1. Surface extremum. In the case of central interest in this paper, the starting configuration consists of steps that form a rounded extremum of surface height, which under irradiation evolves into a pan or mesa. To follow the evolution of the extremum when nucleation of new steps is not permitted we choose as the set of initial radii $R_n(0) = n^{1/2}$. This describes a parabolic extremum, drawn as a maximum in figure 5(a). The quasistatic defect profile for this case is shown as the solid line in figure 4(a). From this starting point equations (5) were iterated at equal intervals of defect creation, as described above. The radii thus derived evolve self-consistently as shown in figures 5(a) and 6(a). We find that the first step expands most rapidly. Accordingly, it eventually encounters the second step to form a step bunch at $R \sim 1.7$. An expanded view of the process, shown inset in figure 6(a), indicates that the growth rate of the second step slows prior to the encounter.

It is not known at this time how steps bond into a step bunch. For this reason there is some ambiguity in the way the freshly formed bunch of two steps should be treated inside the present model. For the purpose of the present calculations we have noted that the steps remain together and so, in some way, defects that precipitate must be shared appropriately between the two steps. Thus the combined steps after the bunching change radius at the average of the rates of the two steps, separately, before they meet. In the calculations reported in figures 5 and 6 the same logic has been extended to step bunches of height 3, 4, 5 steps and so on.

With this procedure for step bunches, the calculations were iterated with results reproduced in figures 5(a) and 6(a). There it can be seen that the calculations qualitatively reproduce the experimental observations quite well. The

step bunch continues to expand faster than the outer steps, and gradually increases height step by step as new steps are absorbed. In this way a local maximum evolves into a mesa provided that the nucleation of new central islands is inhibited. It is easy to understand from the model that precisely the analogous behavior is obtained when similar calculations are carried out for pans, and using ΔK negative, so that inward pointing steps then grow in diameter. Only the signs of the terms distinguishes the two cases in the calculations.

In figure 5(a) the surface profile is shown (with small vertical offsets for clarity) at five distinct times as the mesa evolves. A useful way to view the results is that, in the absence of constraints, a surface with a uniform coverage processes must increase in height by the same average amount everywhere, which would result in step configurations that reproduce cyclically each added monolayer. The constraint in the present case is that nucleation on the central plateau is prevented, so that the surface height there remains fixed. The excess material freed up by this constraint evidently deposits as close by as possible, and finishes up as a collar around the edge of the constrained terrace, thereby creating a step bunch.

3.2.2. A conical surface. It is useful to contrast the case of a smooth height extremum with a second example in which the initial shape of the local surface is conical. The surface chosen here initially has step edges of radii $R_n(0) = n - 0.9$, to form the cone with equally spaced steps shown in figure 5(b). The calculation proceeds exactly as above, with step radii iterated at uniform time intervals, and with an extrapolation of evolution at smaller n that provides the boundary condition at a suitable large $\bar{n}$.

In figure 6(b) the self-consistent radii of steps forming the cone are shown evolving with time. The main result is that, for some extended time, the structure remains almost exactly conical except near the center itself. This is clearly apparent also in the surface profiles shown for several elapsed times in figure 5(b). Near the peak of the cone, however, the central island grows fastest, and eventually overtakes the second step when they both reach a radius $R_1 \sim 3$. These changes can once more be explained by the tendency for the surface height to increase uniformly everywhere. The deviation near the center again arises because nucleation of new islands there is deliberately prevented. The result is a growing cone of unchanged angle, but with a flat top surrounded by a step bunch, both caused by the constraint on nucleation. The mesa on top evolves more slowly for the cone than for the rounded extremum because more mass is required to create the shape change for a cone.

4. Summary

In the work reported above we describe the way pans and mesas can be created on clean metal surfaces by using a beam of self-ions. Starting from rounded extrema of the surface nanotopography, the synthesis proceeds automatically under uniform irradiation provided that the driving effect of the ion beam is reduced with passage of time to prevent new islands from nucleating. An ion beam of energy less than the neutral energy is needed to grow mesas from local hillocks, in order to provide the required excess of adatoms. Conversely, a beam of energy greater than the neutral energy is needed to grow pans from local depressions, in order that excess advacancies are supplied. By observing step edge motion using LEEM for a Pt(111) surface driven by Pt^- ions we have successfully followed the evolution of numerous pans and mesas. These follow a common form with the central island overtaking successive steps and forming a step bunch that increases progressively with height.

It has proved possible to model the observed processes with reasonable fidelity by means of a robust theory that includes reactions among the thermal point defects created by the ion beam. The main approximation of this treatment is to consider the evolution as quasistatic, to the neglect of flux explicitly associated with the time derivatives $\partial c/\partial t$ of defect densities. This approximation has, however, been tested and confirmed by earlier studies of universality in island growth [7]. The calculated evolutions of pans and mesas closely resemble those observed. It is possible to understand how the constraint preventing nucleation of new central islands directly causes the collar of material around the peak that forms the step bunch.

One feature of the behavior that remains imperfectly explained is the detailed structures and mechanisms of the step bunches themselves. Because they remain compact during the absorption of steady fluxes of defects it is apparent that absorbed defects are shared evenly among the component steps. An interesting and important observation that lacks detailed explanation is that a reversed ion beam (creating excess advacancies in a mesa, for example) causes the last step to peel off the step bunch and contract, reversing the earlier process by which excess adatoms caused the island to merge into the step bunch. Evidently these processes are reversible to a degree that has not yet been explored fully in our research.

It remains to be affirmed that the pans and mesas created by the processes studied here can play valuable roles in studies of other local nanostructures. The presence of a step bunch surrounding a perfect terrace has the effect of shielding processes on the terrace from the influence of unwanted external structures that affect diffusion fields or the local chemical potential. Their efficacy has been demonstrated in investigations of island nucleation [3] and universal island growth [7] reported elsewhere. We expect that pans and mesas synthesized by ion irradiation will find similarly useful applications in a variety of other contexts in the future.

Acknowledgments

This research was supported in part by DOE under grant DEFG02-02-ER46011. The LEEM was maintained in the Center for Microanalysis of Materials in the Materials Research Laboratory, supported by DOE grant DEFG02-91-ER45439.

Appendix. Defect fluxes in a driven assembly of reacting thermal point defects

Here the goal is to predict the time evolution of island size on a terrace that has its thermal defect population driven by a uniform flux density J of ions. Suppose that the beam creates adatoms at a rate K_1 per surface site per second, and advacancies at a rate K_2, such that the equilibrium concentrations $\bar{c}_1, \bar{c}_2$, per site, of adatoms and advacancies are modified to values $c_1(\mathbf{r}, t)$, $c_2(\mathbf{r}, t)$. These depend on time t and position $\mathbf{r}$ on the terrace. The desired result is achieved by solving, for the particular case of interest here, equations that are given explicitly in an earlier publication [6]. The boundary condition [5, 6] at fixed sinks such as step edges requires that the concentrations there take their equilibrium values: $c_i(\mathbf{r}, t) = \bar{c}_i, i = 1, 2$. This choice ensures that the step edges at those locations create thermal defects at rates that correspond to thermal equilibrium. We must calculate the $c_i(\mathbf{r}, t)$ to find the chemical potential $\mu^*(\mathbf{r}, t)$ that is consistent with the boundary conditions, for the uniform defect production defined by K_1, K_2, above.

The theory includes reactions between antidefects, such that the c_i obeys

$$\begin{aligned} \dot{c}_1 - D_1\nabla^2(c_1 - \bar{c}_1) - K_{12}(\bar{c}_1\bar{c}_2 - c_1c_2) &= K_1(\mathbf{r}, t); \\ \dot{c}_2 - D_2\nabla^2(c_2 - \bar{c}_2) - K_{12}(\bar{c}_1\bar{c}_2 - c_1c_2) &= K_2(\mathbf{r}, t). \end{aligned} \tag{A.1}$$

Here, K_{12} is the rate constant for antidefect reaction, with $K_{12}\bar{c}_1\bar{c}_2$ the rate per lattice site at which pairs are created, and $K_{12}c_1c_2$ the annihilation rate. D_1 and D_2 are the hopping diffusion coefficients of the two species, so that the first two terms of equations (A.1) comprise the diffusion equation for a species in the absence of reactions and driving terms.

When the nonlinear equations (A.1) are linearized by writing $c_1 = \bar{c}_1 + s_1$; $c_2 = \bar{c}_2 + s_2$, and solved simultaneously for the steady state with K_1, K_2, constant, the general solutions are

$$\begin{aligned} D_1s_1 &= \frac{D_1\bar{c}_1(K_2 - K_1)}{D_1\bar{c}_1 + D_2\bar{c}_2} f(\mathbf{r}) + \frac{\mathbf{A}}{\kappa^2}\left[\frac{g_\kappa(\mathbf{r})}{g_\kappa(\rho)} - 1\right] \\ D_2s_2 &= \frac{D_2\bar{c}_2(K_1 - K_2)}{D_1\bar{c}_1 + D_2\bar{c}_2} f(\mathbf{r}) + \frac{\mathbf{A}}{\kappa^2}\left[\frac{g_\kappa(\mathbf{r})}{g_\kappa(\rho)} - 1\right] \end{aligned} \tag{A.2}$$

in which A is a constant, $f(\mathbf{r})$ is the solution of the Poisson equation $\nabla^2 f = 1$ that has $f(\mathbf{r}) = 0$ for the fixed sinks at $\mathbf{r} = \boldsymbol{\rho}$, and $(\nabla^2 - \kappa^2)g(\mathbf{r}) = 0$, with $g = 1$ at fixed sinks. Owing to the form of equation (2), the second term in these equations makes no net contribution to the atomic flux, leaving the simple final result

$$J(\mathbf{r}) = -D_1\nabla s_1 + D_2\nabla s_2 = (K_1 - K_2)\nabla f(\mathbf{r}). \tag{A.3}$$

We now adapt this result to the particular geometry of interest in the experiments reported in the text. In an idealized description, a circular island of radius a is concentric with a circular terrace surrounded by a step bunch at radius R. Therefore the constraints on the solutions $s(\mathbf{r})$ are circular symmetry and $s_i = 0$ at $r = R_n n = 1, 2, \ldots$. The required solution for $r < R_1$ is

$$f_0(r) = (R_1^2 - r^2)/4, \tag{A.4a}$$

while for each of the successive annuli $R_n < r < R_{n+1}$, the result is

$$f_n(r) = \frac{R_{n+1}^2 - r^2}{4} - \frac{(R_{n+1}^2 - R_n^2)\ln(r/R_{n+1})}{4\ln(R_n/R_{n+1})}. \tag{A.4b}$$

The second term on the left of equation (A.4*b*) is a solution of Laplace's equation $\nabla^2 g(r) = 0$. It is then quickly verified that the functions in equations (A4) solve the Poisson equation and satisfy the stated boundary conditions. The form of these solutions is illustrated in figure 4.

The results are employed in section 3 to obtain the rate surface evolution on Pt(111) caused by irradiation with a beam of Pt^- ions.

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