Kinetics of mesa overlayer growth: Climbing of adatoms onto the mesa top

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We have calculated the energy barriers for an adatom climbing up onto a Pb mesa top either over a facet-facet edge or through a facet-step joint, using a modified embedded atom method. We found that the second process is not only thermodynamically more favorable than the first one but also much faster with a diminishing barrier. Our results provide a plausible explanation for the experimentally observed intriguing growth behavior of a Pb mesa. The underlying mechanisms can be generally applicable to other systems. © *2008 American Institute of Physics*.
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Adatom diffusion is the most important kinetic process involved in the epitaxial growth of thin films. To grow a multilayer film or a stepped island [three-dimensional (3D) mound], in addition to surface diffusion, which controls intralayer mass transport, another rate-limiting kinetic process is for an adatom to cross over a step, which controls interlayer mass transport. The extra energy barrier for an adatom diffusing over a step edge, compared to diffusing on surface, is referred to as the Ehrlich-Schwoebel (ES) barrier.[1,2] Furthermore, if the growing 3D islands are faceted with sharp edges (in contrast to "continuous" 3D mound), it has been shown that two forms of adatom diffusion processes, i.e., diffusing over a facet-facet edge [a 3D analog of two-dimensional (2D) ES barrier][3] or through a facet-step joint,[4,5] may become the dominant kinetic process controlling the faceted island growth. Here, we investigate how these two adatom diffusion processes will affect the kinetics of overlayer growth on a faceted mesa top.

Our theoretical studies are motivated by a recent experiment as shown in Fig. 1. The experimental details have been reported elsewhere.[6–9] Briefly, Pb mesas are first grown on Si(111) substrate. Then, nucleation and growth of a 2D island in the middle of mesa top was triggered by applying a scanning tunneling microscopy (STM) pulse through the "Coulomb sink" charging effect.[10,11] The 2D island continues to grow until a complete overlayer is formed on the top. One interesting observation is that the rate of overlayer growth undergoes three different stages. First, the 2D island expands slowly in the middle of the mesa top until it touches the edge of the mesa top, as shown from points *O* to *P* of the island areal growth curve in Fig. 1. Second, as soon as the island touches the edge, it grows rapidly along the edge to form a closed annular ring around the mesa top, as shown from points *P* to *Q* in Fig. 1. Last, the annular ring grows inward again slowly until it closes to form a complete overlayer, as shown from points *Q* to *R* in Fig. 1. The growth rate of stage 2 is several orders of magnitude higher than that of stages 1 and 3, and the stage 3 is slightly slower than the stage 1.

In order to understand the intriguing kinetics of Pb mesa overlayer growth, we postulate that the rate-limiting step for the growth is the process of adatom climbing over the mesa top from the sidewalls, i.e., diffusing from the side facets to the top facet. Specifically, in stage 1, the rate-limiting step is for adatom diffusion over a facet-facet edge; in stage 2, it is over a facet-step joint; in stage 3, it is again over a facet-facet edge like in stage 1, but plus an additional step-edge ES barrier because after the adatom climbing over the mesa top it has to also jump over a step edge for the annular island ring to grow inward. To test this idea, we have calculated the energy barriers for each of the above processes, using the second nearest-neighbor modified embedded atom method (2NN MEAM).[12] Indeed, our calculations show that the

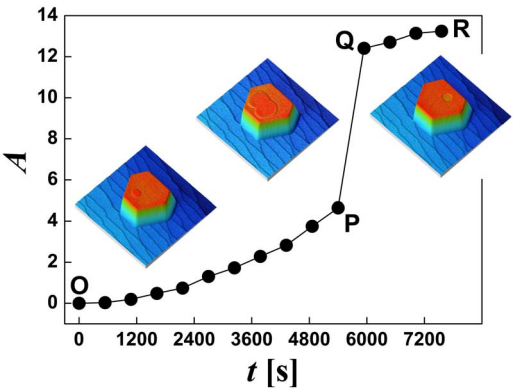

FIG. 1. (Color online) The area (A, in unit of 10^4 nm^3) of the adatom island as a function of time (t) in the overlayer growth of a Pb mesa, showing three different growth stages. The insets show the STM images (720×720 nm^2) recorded at the different stages. *O* is the starting point of growth (see left inset). At *P*, the adatom island touches the mesa top edge (middle inset), and it grow quickly along the mesa top edge to form a closed annular ring at *Q* (right inset). From *Q* to *R*, the annular ring grows slowly inward until forming a complete overlayer.

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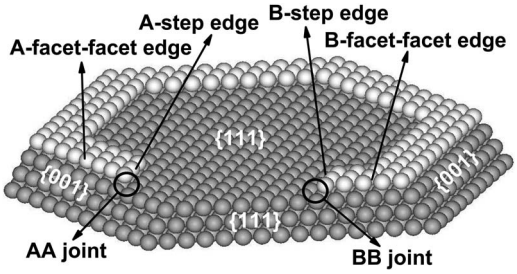

FIG. 2. Schematics of an incomplete ring along the Pb mesa top edge, showing the mesa top morphology with different types of step edges, facet-facet edges, and facet-step joints.

facet-step joint process is both thermodynamically more favorable and having a much smaller kinetic barrier than the facet-facet process, providing a plausible explanation for the experimental observation.

To facilitate our discussion, Fig. 2 shows the schematics of an incomplete ring formed along the Pb mesa top edge, illustrating the mesa top morphology consisting of different types of step edges, facet-facet edges, and facet-step joints. The mesa top is known to be {111} facet,[13] but the mesa sidewall facets are less clear from experiments. Based on our MEAM calculations, which show that the two Pb facets having the lowest surface energies are the {111} and {001} planes, we assume the mesa sidewalls are made of both the {111} and {001} facets as shown in Fig. 2. Consequently, when an adatom climbs from the sidewall to the mesa top by crossing over a facet-facet edge, it may cross either a {001}-{111} or {111}-{111} edge, which are denoted as *A*- and *B*-facet edges, respectively. When an adatom climbs through a facet-step joint, it may go through four possible joints, which are denoted as *AA* joint (from {001} facet to *A* step), *AB* joint (from {001} facet to *B* step), *BA* joint (from {111} facet to *A* step), and *BB* joint (from {111} facet to *B* step), respectively.

For adatom to cross over either an *A*- or *B*-facet edge, we find that the exchange mechanism[14] is always energetically more favorable over the direct hopping mechanism. Figures 3(a) and 3(b) show the calculated energy curves along the most favorable diffusion path for an adatom crossing the *A*- and *B*-facet edges, respectively, via the exchange mechanism. From Fig. 3(a), we see that there is no additional energy barrier for adatom to cross the A-edge from the (001) sidewall facet to (111) top facet. However, the adatom chemical potential on the (001) mesa sidewall (with a much stronger binding) is about 203 meV lower than that on the (111) mesa top. Thus, the adatom is thermodynamically prevented from climbing onto the mesa top from the (001) sidewalls. The adatom chemical potential is the same on the (111) sidewall and (111) top, but Fig. 3(b) shows that there is an additional 38 meV energy barrier for adatom to cross the B-edge from the (111) sidewall to (111) top. Thus, the adatom is kinetically hindered from climbing onto the mesa top from the (111) sidewalls.

The above results indicate that normally the adatom concentration must be very low on the mesa top because it is difficulty for adatoms to climb onto the mesa top either thermodynamically from the (001) sidewalls or kinetically from the (111) sidewalls. This is consistent with the experimental observation that flat-top Pb(111) mesas are extremely stable staying intact for days, and island nucleation and overgrowth

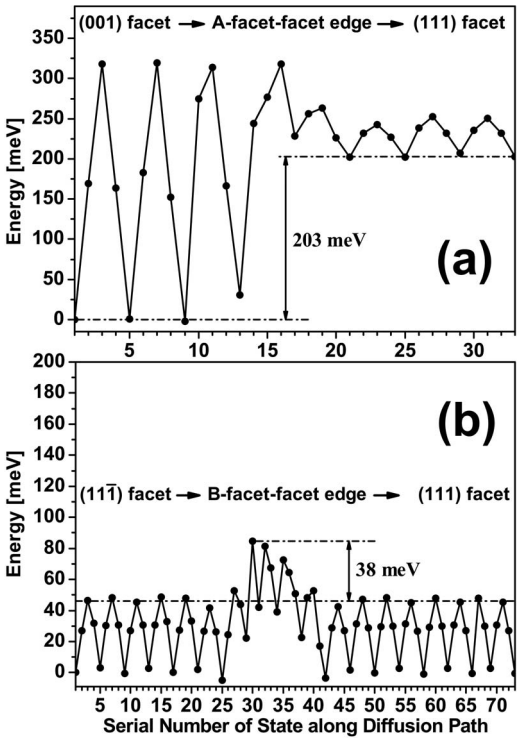

FIG. 3. Calculated energy curve along diffusion path of an adatom crossing: (a) an A facet-facet edge from (001) sidewall facet to (111) top facet, and (b) a *B*-facet-facet edge from (11$\bar{1}$) sidewall facet to (111) top facet.

on the mesa top can only be triggered by an external perturbation using STM pulse,[10] as shown in Fig. 1. For this very same reason, the initial growth of 2D island, after its nucleation being triggered by STM, is very slow as shown from points *O* to *P* in Fig. 1, because adatoms have to cross over either an *A*- or *B*-facet edge to climb onto the mesa top to facilitate the growth.

When the 2D island touches the mesa edge (see the middle inset in Fig. 1, the adatom can now climb onto the mesa top going through a facet-step joint instead of going over a facet-facet edge. We have calculated the potential-energy surfaces for an adatom to cross all four possible *AA*, *AB*, *BA*, and *BB* facet-step joints. In all the cases, the exchange mechanism gives the lowest energy barrier with similar potential-energy profiles. For example, Fig. 4 shows the calculated energy curves for an adatom going through an *AA* and *BB* joint, respectively. One thing drawing immediate attention is that both processes are thermodynamically very favorable. Upon climbing onto the mesa top through a facet-step joint, the adatom will bind to the step edge and consequently its chemical potential becomes much lower (with higher coordination bonding at the edge) than on the sidewall facets by 100 and 281 meV, as shown in Figs. 4(a) and 4(b), respectively. This provides an extra thermodynamic driving force for adatoms to climb onto the mesa top. In other words, the step edge serves as adatom sink to promote a step-flow type of growth around the mesa edge to form the annular ring. Also, the kinetic energy barrier for adatoms crossing the facet-step joint is very low, to be, respectively, 0 and 18 meV at the *AA* and *BB* joints, as shown in Fig. 4. Thus, the second-stage growth of annular ring is very fast until the ring closes, as shown from points *P* to *Q* in Fig. 1.

Once the annular ring is closed, the facet-step joints disappear so that adatoms have to again go over the facet-facet

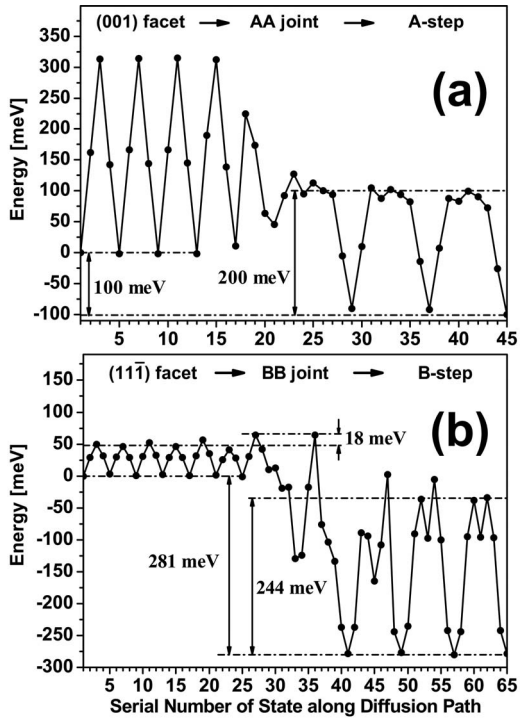

FIG. 4. Calculated energy curve along the diffusion path of an adatom crossing (a) an *AA* joint from (001) sidewall facet to *A*-step edge on the mesa top and (b) a *BB* joint from (11$\bar{1}$) sidewall facet to *B*-step edge on the mesa top.

edge in order to climb onto the mesa top. Consequently, the inward growth of annular ring in stage 3 is slowed down again like the initial outward growth of 2D island in stage 1. However, during the inward growth of annular ring, the adatoms must also overcome an additional step-edge ES barrier[8] to fall inside the annular ring after climbing onto the mesa top. This additional ES barrier makes stage 3 slightly slower than the stage 1, as as shown from points *Q* to *R*, in comparison to from points *O* to *P*, in Fig. 1.

In conclusion, we have studied the kinetic processes involved in the overlayer growth on top of a faceted Pb mesa, by calculating the energy barriers for an adatom climbing up onto the mesa top which is identified as the rate-limiting step. We found that adatoms can easily climb onto the mesa top through a facet-step joint, whose process is both thermodynamically more favorable and kinetically faster than the process of adatom diffusing over a facet-facet edge. Our finding gives a good explanation for the three different stages of growth rate occurred during the overlayer growth on a Pb mesa as observed experimentally. The physical mechanisms we reveal here can be generally applicable to many other systems.

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