Adatom Ascending at Step Edges and Faceting on fcc Metal (110) Surfaces

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Using first-principles total-energy calculations, we show that an adatom can easily climb up at monatomic-layer-high steps on several representative fcc metal (110) surfaces via a place exchange mechanism. Inclusion of such novel adatom ascending processes in kinetic Monte Carlo simulations of Al(110) homoepitaxy as a prototypical model system can lead to the existence of an intriguing faceting instability, whose dynamical evolution and kinetic nature are explored in comparison with experimental observations.

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Atomic-scale understanding of the microscopic mechanisms involved in film growth and nanocluster formation remains an active area of research in materials science, particularly in nanoscale phenomena. In recent studies, it has been well recognized that the selection of a specific growth mode in a given system is often the outcome of the interplay between growth kinetics, characterized by a set of atomic rate processes, and thermodynamics, measured by the system's overall tendency towards lower free energy configurations. Of all the atomic rate processes that have been established so far, one that has received perhaps the most attention is the step-down or descending process of an adatom at the edge of a monatomic-layerhigh step. Typically, such a descending adatom will encounter an additional potential energy barrier, known as the Ehrlich-Schwoebel (ES) barrier [1,2], whose effect is to hinder interlayer atom transport, resulting in the formation of three-dimensional (3D) islands [3]. Interesting extensions of the ES barrier concept have also been made recently to both lower and higher dimensions [4,5], but all these existing efforts have been focused primarily on step-down processes, characterized by an atom descending at the outer corner, edge, or ridge of an elemental defect feature on a surface.

In this Letter, we use first-principles total-energy calculations within density functional theory (DFT) and kinetic Monte Carlo (KMC) simulations to establish the importance of a new type of atomic rate process in homoepitaxial growth on the (110) surfaces of a few representative fcc metal systems. First, we show that, contrary to traditional belief, an adatom can easily climb up at a monatomic-layer-high step in such a system via a place exchange mechanism, valid for Al, Ag, Cu, and Pb. We further demonstrate that the inclusion of such novel adatom ascending processes in KMC simulations of Al(110) homoepitaxy as a prototypical model system can lead to the existence of an intriguing faceting instability. This faceting instability is characterized by the formation of hut-shaped islands with precise slope selections, and its dynamical evolution and kinetic nature are explored in comparison with experimental observations. The adatom ascending process established here is likely to be important for other related metal epitaxial growth systems as well. Furthermore, it may not be limited to metal systems alone, as shown previously for adatom ascent on stepped Si(100) surfaces without [6] or with [7] hydrogen termination.

The DFT results reported here are based on the Perdew-Wang 1991 version of the generalized gradient approximation (PW91-GGA) [8] and are obtained using the efficient and accurate total-energy and moleculardynamics package, VASP (Vienna ab initio simulation package) [9,10]. Default plane-wave cutoffs from the GGA ultrasoft-pseudopotential database [11] are used in the calculations-specifically, 9.50, 6.50, 17.18, and 13.28 Ry for Al, Pb, Cu, and Ag, respectively. The Monkhorst-Pack scheme [12] is used for Brillouin zone sampling. These treatments produce the bulk lattice constants of 4.04, 5.04, 3.64, and 4.17 Å for Al, Pb, Cu, and Ag, respectively. To accelerate electronic relaxation, we use the Fermi-level smearing approach of Methfessel and Paxton [13] with proper parameters. Optimized atomic geometries are achieved until the forces on all unconstrained atoms are smaller than 0.01 eV/Å. The "nudged elastic band" method [14] is applied to locate transition state geometries.

To study the mobility of adatom at a step edge on an fcc (110) surface, we compute the total energies of appropriate vicinal surfaces, with an adatom placed in appropriate locations. There are two principal diffusion directions on an fcc (110) surface. For diffusion along the $\langle 1\overline{10} \rangle$ or inchannel direction, we use the (650) vicinal surface consisting of (110) terraces, which are six atoms wide. For Al and Pb, the slab contains ten atomic layers, or 165 atoms per supercell, and the atoms within the top five layers are allowed to optimize their positions. For Cu and Ag,

TABLE I.Adatom ascending barriers at a monatomic-layer-
high step on (110) surfaces (in eV).

	Al	Pb	Cu	Ag
Upward in channel	0.60	0.46	0.84	0.68
Downward in channel	0.43	0.37	0.54	0.54
Upward cross channel	0.67	0.43	0.75	0.62
Downward cross channel	0.71	0.43	0.82	0.62

considering computational cost and the relatively larger plane-wave cutoffs, we reduce the slab to six atomic layers, containing 102 atoms per supercell, and the atoms within the top three layers are allowed to relax. For diffusion along the $\langle 001 \rangle$, or cross channel, direction, we use the (991) vicinal surface, which is five atoms wide. For A1 and Pb, the slab again contains ten atomic layers, but with 180 atoms, and the top five layers are permitted to relax. For Cu and Ag, a six-layer slab is used, containing 128 atoms, with the top three layers fully relaxed. The *k*-point sampling in the total-energy calculations uses a $3 \times 3 \times 1$ mesh for the C650 surface and $4 \times 4 \times 1$ mesh for the S991 surface for A1 and Pb, and a $2 \times 3 \times 1$ mesh for Cu and Ag.

The calculated diffusion barriers are summarized in Table I, and the atomic geometries of the exchange process and corresponding energy profiles for Pb are shown in Figs. 1(a) and 1(b). Here the most surprising finding is that the upward diffusion process for an adatom at a step edge along the cross-channel direction is as easy as downward diffusion, preferably via a reversible place exchange process [15]. This is true for all four representative elements considered. In fact, for Al and Cu, upward diffusion is even slightly easier than downward diffusion. For the in-channel direction, both the upward and downward diffusion processes are again via a reversible place exchange mechanism, but the upward diffusion barriers are higher than the downward diffusion barriers. Most importantly, the upward diffusion barriers along both the in-channel and cross-channel directions, of a few tenths of eV in magnitude, are substantially lower than the



FIG. 1. Illustrations of the atomic geometry, energy profile, and activation barriers for adatom ascent via place exchange at a monatomic-layer-high step on an fcc metal (110) surface, along the in-channel (a) and cross-channel directions (b), respectively.

corresponding barriers for adatom ascent at monatomic steps on fcc metal (111) and (100) surfaces which are typically well over 1 eV [16–19]. Therefore, whereas upward diffusion processes have typically been ignored in modeling epitaxial growth on fcc (111) and (100) surfaces, they must be considered in describing epitaxial growth on fcc (110) surfaces. In particular, inclusion of such adatom ascending processes should further enhance the traditional ES barrier effect for kinetic roughening. It may also result in new types of growth instabilities, such as faceting [15].

The possibility of the adatom ascending processes in inducing faceting can be explored in KMC simulations of growth, but before doing so, we must first address another adatom ascending process, which can be regarded as an extension of the above process to multi-atomic-layer steps. The specific atomic configurations are shown in Fig. 2. Here, the (111) or the (100) facets can be viewed as being formed by the edge atoms of a multilayer step along the cross-channel or in-channel direction, respectively, and the activation energy for upward hopping of an adatom located at a site along the inner ridge between a given facet and the (110) surface can be calculated. In these calculations, we use two supercells as shown in Fig. 2, containing 229 and 233 atoms along the inchannel and cross-channel directions, respectively. The results for both Al and Pb are given in Table II, showing again the generic trend of the activation energies for fcc metal (110) systems. In these large supercell calculations, we used a $3 \times 5 \times 1$ mesh for Brillouin zone sampling. Qualitatively, the activation energy for adatom departing from an inner-ridge site onto a (111) or (100) facet is higher than the corresponding barrier for adatom ascent at a monatomic-layer-high step, a trend similar to that established for adatom crossing at an outer ridge [5]. One subtle aspect is the orientation dependence of the specific atomistic mechanisms involved. Along the in-channel



FIG. 2. Illustrations of the facets and ridges along the inchannel (a) and cross-channel (b) directions.

TABLE II. Adatom diffusion barriers for ridge crossing processes on (110) surfaces (in eV).

	Al		Pb		
	In channel	Cross channel	In channel	Cross channel	
$A \longrightarrow B$	0.18	0.03	0.19	0.03	
$B \longrightarrow A$	0.69	0.70	0.47	0.55	
$B \longrightarrow E$	0.65	0.36	0.33	0.42	
$E \rightarrow B$	0.40	0.38	0.24	0.37	
$C \longrightarrow D$	0.33	0.69	0.34	0.43	
$D \rightarrow C$	0.13	0.04	0.11	0.03	

direction, it is still energetically favorable for an adatom to climb up onto the (100) facet via the place exchange mechanism, but along the cross-channel direction the preferred diffusion pathway for an adatom to climb up onto the (111) facet is via adatom direct hopping. These different mechanisms are consistent with what have been shown for Al self-diffusion on flat (100) and (111) surfaces, via place exchange [20] and direct hopping [21], respectively. For completeness, we have also calculated the activation energy barriers for an adatom crossing the outer ridge between a (100) or a (111) facet and the atop (110) surface, as well as the barriers for adatom departing from an inner-ridge site onto the (110) surface, as summarized in Table II. Here we note that place exchange as a preferred diffusion mechanism is a norm rather than an exception: In the last four rows of activation energies, only the $B \leftrightarrow E$ processes along the in-channel direction are via direct hopping, with all the rest via place exchange.

With these activation barriers presented in Tables I and II, as well as those for adatom self-diffusion on (110), (111), and (100) surfaces [15], we now carry out KMC simulations of Al(110) homoepitaxy to establish the crucial role of adatom ascending at monatomic-layer-high steps in inducing the faceting instability. Complete 3D simulations of the growth involving on the order of 10^7 atoms would be needed to fully explore the faceting instability, a task still beyond the reach of our present computing power. Fortunately, the faceting instability can already be elucidated in (1 + 1)-dimensional [(1 + 1)D] simulations, with the substrate direction along the in-channel and cross-channel directions. In these KMC simulations, the diffusion rate of an adatom is given by $R_i = \nu \exp(-V_i/k_B T)$, where V_i is the activation energy for process *i*, k_B is the Boltzmann constant, and *T* is the temperature. The attempt frequency is chosen as $\nu =$ $k_B T/h = 4.2 \times 10^{10}$ T, with h Planck's constant, and T given in degrees Kelvin. We start with a flat substrate having periodic boundary conditions and a width of 1000 sites. Aluminum atoms are deposited onto the surface randomly and are sequentially placed in a cubic grid, with no desorption and no overhang allowed. When the terminating atoms of two or more atomic layers are separated by precisely one atom between two neighboring layers, we identify the local atomic geometry with the formation of a mini-(100) or (111) facet.

The dynamical evolution of the faceting instability, as illustrated by the coverage dependence of the surface morphology obtained at a constant deposition rate of five monolayers (ML) per second and a constant growth temperature of 400 K, is shown in Fig. 3(a) for KMC simulations along the in-channel direction. Several distinct features become clear from these simulations. First, the growth is relatively flat up to about ten atomic layers, with only minimal mounds scattered across the growth front. But as the total coverage exceeds 10 ML, a faceting instability is triggered, characterized by the formation of a pyramidal island with well-defined slopes on both sides. Amazingly, this faceting evolution takes place within only one layer of deposition. Furthermore, this and other emerging faceted islands collect essentially all the atoms deposited subsequently.

To determine the slope of the faceted islands, we have monitored the number of atoms which can be identified as belonging to the (100) facets in the growth front. The result establishes a clear one-to-one correspondence between the emergence of faceted island(s) and the onset of (100) facet formation. The existence of a critical thickness on the order of ten layers for faceting is further confirmed



FIG. 3. (a) Dynamical evolution of the surface morphology obtained from KMC simulations along the in-channel direction (growth temperature: 400 K; deposition rate: 5 ML/s). (b) Surface morphologies obtained from KMC simulations at different growth temperatures but with the same deposition rate of 5 ML/s.

in independent KMC simulations with different random numbers for the deposition but at identical growth conditions. The physical origin for the existence of a critical thickness for faceting can be understood if comparing the asymmetric processes for adatom transport between the Cand D sites shown in Fig. 2(a) and those shown in Fig. 1(a). Initially it is easier for an adatom to descend at the singleheight step. But as soon as the step evolves into being part of a (100) minifacet, it becomes much easier for an adatom to leave the minifacet and climb up to the top of the faceted island. In order for the mini-(100) facet to develop, the absolute roughness in the growth front has to be sufficiently large, thereby demanding the existence of a critical thickness.

Here we stress that the faceted islands observed in these simulations cannot be obtained if the adatom ascending processes at monatomic-layer-high steps shown in Fig. 1(a) are forbidden. On the other hand, if the processes shown in Fig. 1(a) are active, but not those $B \rightarrow A$ processes shown in Fig. 2(a), sizable faceted islands can still be formed in the KMC simulations. These tests further establish the central role of the adatom ascending processes at monatomic-layer-high steps in inducing the faceting instability observed in Al(110) homoepitaxy [15].

The kinetic nature of the faceting instability is reflected in its temperature dependence. As shown in Fig. 3(b), at the low temperature of 300 K or high temperature of 450 K, no sizable faceted islands are formed, even though the total coverage is as high as 20 ML. These results suggest that the pyramidal islands can form only within a proper growth temperature window around 400 K. This feature is qualitatively and semiquantitatively consistent with experimental observations [15].

Finally, we have also carried out (1 + 1)D simulations along the cross-channel direction, and qualitatively similar results are obtained. On a quantitative level, the nanocrystals with (111) facets are even taller, partly because the critical thickness for triggering faceting is much smaller along this direction (on the order of 1 ML). Detailed comparisons between the simulation results along the two directions will be reported elsewhere.

In summary, we have used first-principles total-energy calculations to show that, contrary to traditional belief, an adatom can easily climb up at a monatomic-layer-high step via a reversible exchange mechanism on the (110) surfaces of a few representative fcc metals. We have further demonstrated via KMC simulations of Al(110) homoepitaxy as a prototypical model system that the inclusion of such novel adatom ascending processes can lead to the existence of an intriguing faceting instability, which is kinetic in nature, and characterized by the formation of hut-shaped islands with precise slope selections. The adatom ascending processes established here and the corresponding faceting instability are expected to find applicability in many other related homo- and heteroepitaxial growth systems as well.

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