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Epitaxial growth and erosion on (001) crystal surfaces: Far-from-equilibrium transitions, intermediary states, and vertical asymmetry

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General phenomenology of multilayer epitaxial growth and erosion on square symmetry crystal surfaces is discussed within a unified model. We elucidate recently observed 45° rotation transitions between pyramidal states on (001) surfaces. We predict and characterize novel intermediary states of many-sided pyramids *ubiquitously* intervening in these transitions and causing an enhanced roughening. We elucidate the actual effects of the elusive vertical (pyramid-pit) growth asymmetry on the multitude of states on (001) crystal surfaces.

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Growing surface nanostructures induced by the Ehrlich-Schwoebel-Villain instability,[1] are often observed in molecular-beam epitaxy growth and erosion of various crystal surfaces. This is documented by numerous experiments and simulations on (001), (111), and (110) crystal surfaces.[2–14] On square symmetry surfaces, nearly periodic (defected) checkerboard arrangements of alternating four-sided pyramids and pits (inverted pyramids) frequently develop, with sizes growing in time as $t^{1/4}$, as exemplified by the Cu(001) growth.[2] This coarsening law has been understood only recently, in terms of the dynamics of topological defects (dislocations) of the regular checkerboard structure.[3,4] However, other structures have been recently inferred on (001) surfaces.[10–14] Moreover, a far-from-equilibrium phase transition between two kinds of pyramidal states has been very recently seen in the growth on Ag(001), by de Mongeot *et al.*[10] They report a 45° rotation of pyramid facets at a low $T \approx 100$ K, and attribute it to deactivation of corner crossing processes.[5] Coincidentally, at significantly higher temperatures, in erosion on Cu(001), a similar transition has been seen, and, at the same time, disputed.[11] There is a lack of deep qualitative understanding of these recent findings, whereas some long-standing basic questions remain unresolved, even for the common (001) surfaces. How does the well known vertical (pyramid-pit) asymmetry affect interface coarsening dynamics? What is the generic multitude of interfacial morphologies possible to occur on (001), and what is the real nature of the surface nanostructures involved in the recently revealed far-from-equilibrium transitions seen on (001)? Here, we answer these questions, both recent and long-standing.

We will elucidate the epitaxial growth and erosion on (001) crystal surfaces by considering the general phenomenological model,[1,6] expressing dynamics of the interface profile $h(x_1,x_2,t)$ as the conservation law involving the surface current $\mathbf{J}=(J_1,J_2)$,

$$\partial_t h = -\nabla \mathbf{J}, \quad \mathbf{J} = \mathbf{J}^{(\mathrm{NE})}(\mathbf{M}) + \mathbf{J}^{(\mathrm{curv})}. \tag{1}$$

Here, $\mathbf{J}^{(\mathrm{NE})}$ is the surface nonequilibrium current being a function of the local interface slope vector $\mathbf{M}=(M_1,M_2)=\nabla h$. In Eq. (1), $\mathbf{J}^{(\mathrm{curv})}$ includes other, curvature currents that vanish on flat interfaces (facets), such as the usual surface diffusion Mullins current $\sim\nabla(\nabla)^2 h$, and the *vertical asymmetry* Villain current $\sim\nabla(\nabla h)^2$ breaking the vertical reflection symmetry $h\rightarrow -h$.[1,6] (001) surface has square symmetry imposing a few ubiquitous properties of $\mathbf{J}^{(\mathrm{NE})}(\mathbf{M})=(J_1^{(\mathrm{NE})}(\mathbf{M}),J_2^{(\mathrm{NE})}(\mathbf{M}))$. It must transform in the same way the slope vector $\mathbf{M}$ transforms under symmetry transformations of (001). Thus, under the simple square reflections: $(M_1,M_2)\rightarrow(-M_1,M_2)$, $(J_1^{(\mathrm{NE})},J_2^{(\mathrm{NE})})\rightarrow(-J_1^{(\mathrm{NE})},J_2^{(\mathrm{NE})})$, and $(M_1,M_2)\rightarrow(M_1,-M_2)$, $(J_1^{(\mathrm{NE})},J_2^{(\mathrm{NE})})\rightarrow(J_1^{(\mathrm{NE})},-J_2^{(\mathrm{NE})})$. Also, the square diagonal reflection symmetry $(M_1,M_2)\rightarrow(M_2,M_1)$ implies $J_1(M_1,M_2)=J_2(M_2,M_1)$. Commonly, the solutions (zeros) of $\mathbf{J}^{(\mathrm{NE})}(\mathbf{M})=\mathbf{0}$ are related to the preferred slopes $\mathbf{M}$ of the facets that develop across the growing interface and organize themselves into pyramidal structures.[3,4] By the square symmetry of (001), there are *three* possible kinds of these preferred slope vectors $\mathbf{M}=(|\mathbf{M}|\cos(\theta),|\mathbf{M}|\sin(\theta))$: (i) *singlet*, at $|\mathbf{M}|=0$; (ii) *quartet* of four equivalent (symmetry related) slope vectors. There are two *nonequivalent* types of quartets: type I quartet, along square diagonals, $\theta=45°+90°(n-1)$, $n=1,2,3,4$, and type II quartet, along square sides, $\theta=90°(n-1)$, $n=1,2,3,4$. Importantly for the following, the two quartets are *not* equivalent to each other because the 45° rotation is not a symmetry of (001); (iii) *octet* of eight equivalent slope vectors pointing along the *eight* polar angles: $\theta=90°(n-1)\pm\phi$, where ϕ is an angle in the range $-45°<\phi<+45°$, and $n=1,2,3,4$. In the unstable epitaxial growth, the singlet at $\mathbf{M}=\mathbf{0}$ is unstable, and preferred facets may thus correspond to the quartets or to an octet. Thus, the stable type I quartet may give rise to the checkerboard Phase I (P I) pyramidal structure, see Fig. 1. Likewise, stable type II quartet may give rise to the checkerboard Phase II (P II) pyramidal structure in Fig. 1. The states P I and P II *both* enter Fig. 1 which gives our unified far-from-equilibrium phase diagram for the epitaxial growth and erosion phenomena on (001) surfaces, derived in the following. Type I and type II facets are geometrically related by the 45° rotation. Our phase diagram thus reproduces the recently observed 45° facet rotation transition on Ag(001).[10] Moreover, we find that the uncommon octet zeros give rise to a novel interface state, seen in Fig. 1(a) from our simulations. There, this state intervenes between P I and P II, and its signature is the interface slope distribution (SD) function in

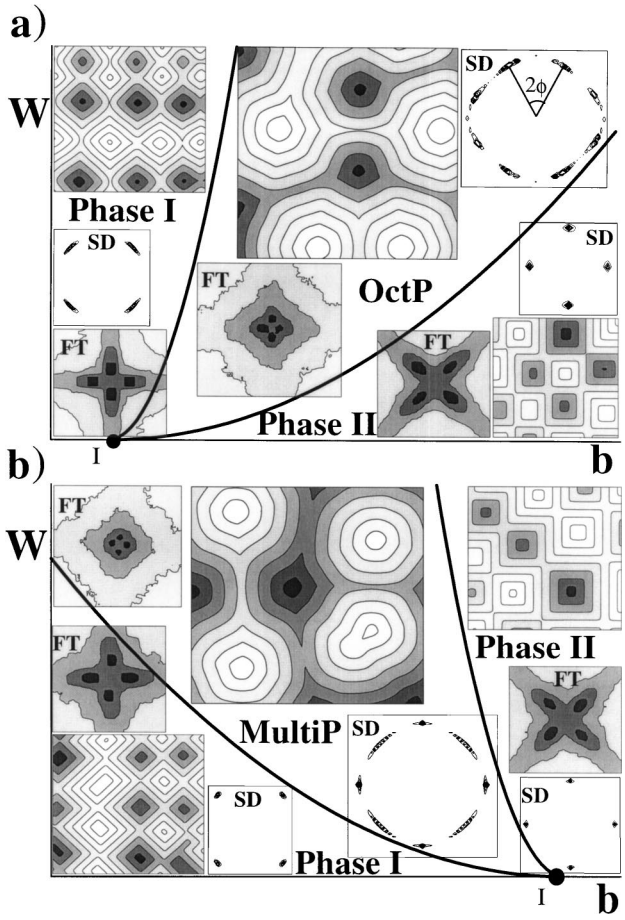

FIG. 1. The kinetic phase diagram of the interface model with $\mathbf{J}^{\mathrm{NE}}(\mathbf{M})$ in Eq. (2). We depict it in the $(b, W=wu^2/r)$ plane for fixed c and d. The point I is at $b=1$, $W=0$. In (a) the case $(d-1)(c-d-1)<0$, with OctP is realized. In (b) the case $(d-1)(c-d-1)>0$, with MultiP is realized. We give interface height contour plots, height FTs (yielding in-phase diffraction patterns), and SD functions (yielding out-of-phase diffraction patterns), from our simulations. The OctP angle ϕ in (a) changes from 0 (at the transition to P II) to 45° (at the transition to P I). For all data here, VA=0.

Fig. 1(a), with eight peaks forming an octagon in the **M** plane, at the eight polar vectors $\theta=90°(n-1)\pm\phi$, $n=1,2,3,4$. Thus, we call it the *octagonal pyramid* (OctP) state. From simulations, we find that OctP corresponds to a structure with pyramids having *up to* eight facets, see Fig. 2(a). Notably, the SD of our OctP, with eight peaks positioned as in Fig. 1(a), is the same as the SD of the intermediary state revealed in the 45° rotation transition on Cu(001); see the eight lobe out-of-phase diffraction patterns in Ref. 11. It has been however suggested that the 45° rotation transition on Cu(001) (erosion) is an effect of posterosion annealing.[11] On the other hand, for the Ag(001) growth, such postgrowth annealing effects are carefully eliminated at the low $T \approx 100$ K, where the transition occurs.[10] It can be thus addressed as a far-from-equilibrium growth transition.

We proceed to expose general phenomenology of the epitaxial growth and erosion on common (001) surfaces, by considering the kinetic model Eq. (1) with generic form of the nonequilibrium current $\mathbf{J}^{(\mathrm{NE})}(\mathbf{M})$. It can be obtained as an

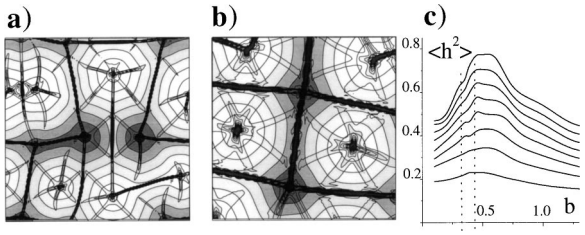

FIG. 2. (a) OctP state: a superposition of its interface height contour plots and facet edges plots (contour plots of the interface curvature magnitude). Note sharp (dark) edges at pyramid bases, and blunt (faint) edges emerging from pyramid tops. (b) MultiP state pyramids, formed out of both type I and type II facets: Note that the spatial arrangement of MultiP pyramids is as in phase I [see also Figs. 1(b) and 3(b) right panel]. For all data here, VA=0. (c) Square of interface width, $\langle h^2 \rangle$ versus b for a fixed W for several times, increasing from bottom to top: Note the enhanced roughening in the proximity of the intermediary state (here, MultiP) between the dashed lines.

expansion in powers of **M** respecting the stringent restrictions imposed by the square symmetry of (001). By the inversion symmetry of (001), this expansion must contain only odd powers of **M**. By respecting the square reflection symmetries, we arrive at the general expansion of the form,

$$J_1^{(\mathrm{NE})} = M_1[r - u(M_1^2 + bM_2^2) - w(M_1^4 + cM_1^2M_2^2 + dM_2^4) + \cdots],$$

$$J_2^{(\mathrm{NE})} = M_2[r - u(M_2^2 + bM_1^2) - w(M_2^4 + cM_2^2M_1^2 + dM_1^4) + \cdots]. \quad (2)$$

The ubiquitous fifth order in **M**, i.e., the w-terms in Eq. (2) are essential for the correct qualitative understanding of the 45° rotation transition on *realistic* (001) surfaces.[15] These terms are directly responsible for our novel, ubiquitously present intermediary states OctP and MultiP (see below), seen for $w \neq 0$ in the kinetic phase diagram in Fig. 1. Thus, for typical situations with small selected $|\mathbf{M}|$, the minimal, basic growth model for (001) is actually obtained by truncating out the higher order terms in the ellipses in Eq. (2). In this limit, we model $\mathbf{J}^{(\mathrm{curv})}$ as described below Eq. (1). Thus, through the Villain current, we *do* include the effects of the vertical asymmetry (VA). The kinetic phase diagram in Fig. 1 is deduced by stability analysis of the facets corresponding to the zeros of $\mathbf{J}^{(\mathrm{NE})}(\mathbf{M})$ in Eq. (2), and further corroborated by numerical simulations of the model in Eqs. (1) and (2). The model yields the 45° rotation transition between P I and P II in Fig. 1. There we see also our intermediary OctP state which occupies in Fig. 1(a) a region in which neither type I nor type II facets are stable. Interestingly, though many sided, OctP pyramids have the same coordination (spatial arrangement), and thus yield qualitatively the same Fourier transforms (FT), i.e., in-phase-diffraction pattern, as the four sided pyramids of a nearby checkerboard state, see Fig. 1(a).

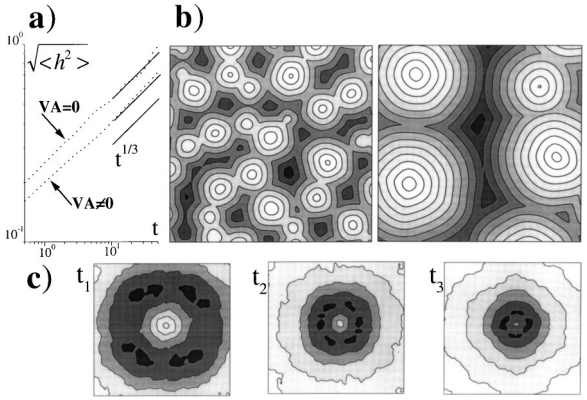

FIG. 3. VA effects on the MultiP intermediary state. (a) Interface width $\langle h^2\rangle^{1/2} \sim t^{1/3}$, both with and without VA. (b) Due to VA $\neq 0$, at early times (left panel) the pyramids form with the spatial arrangement of phase II. However, at later times (the right panel), the spatial pyramid arrangement turns into that of phase I. This spatial rearrangement is illustrated also by the time sequence of FTs in (c), at $t_1 < t_2 < t_3$.

There is one more, qualitatively different intermediary state called as MultiP in Fig. 1(b): There, the 45° rotation transition goes through a *multistable region* in which type I and type II quartet facets are *both* stable. In this region, SD (thus, also the out-of-phase-diffraction) also has eight peaks [see Fig. 1(b)]. However, in contrast to the SD of OctP in Fig. 1(a), the eight SD peaks of the MultiP in Fig. 1(b) are not equivalent to each other: Note that SD of MultiP structures as a superposition of the nearby P I and P II SD peak patterns, with strong sharp peaks along type II facets directions, and broad weaker peaks along type I facets directions. Corresponding to this are multisided pyramids (with *up to* eight sides) with prominent type II facets (like in the P II state) see Figs. 1(b), 2(b), and 3(b). However, this state has spatial arrangement of pyramids which is the same as that of the P I state [see interface plots and their FTs in Figs. 1(b), 2(b), and 3]. Thus, the MultiP is a *hybrid* state—it is neither P I nor P II state. For VA=0, MultiP has the pyramid spatial arrangement of P I *already* at early times. For VA $\neq$ 0, MultiP pyramids form initially with the spatial arrangement of P II, see Fig. 3(b) left panel. Eventually, however, the pyramid lattice rearranges, and spatial arrangement becomes the same as that of P I, see Fig. 3(b) right panel. This striking spatial rearrangement of MultiP is documented also by the time sequence of FTs in Fig. 3(c). Interestingly, there are no such dramatic transient VA effects on the other, OctP state.

The pyramid sizes in MultiP and OctP states grow as $t^{1/3}$, *both with and without* VA, see Fig. 3(a). We find that both intermediary states coarsen via local pyramid (or pit) coalescence. These numerical results evidence striking robustness of the $t^{1/3}$ law for the growth via local pyramid coalescence.[16] Away from the intermediary states in Fig. 1, pyramid sizes in checkerboard states P I and P II grow as $t^{1/4}$, *both with and without* VA, see Fig. 4(a). This growth proceeds via topological defects (dislocations) of the checkerboard,[3] see Figs. 4(b) and 4(c): Note that VA introduces two kinds of pyramid facet edges, sharp and blunt. However, this decoration of the edges mesh does not affect

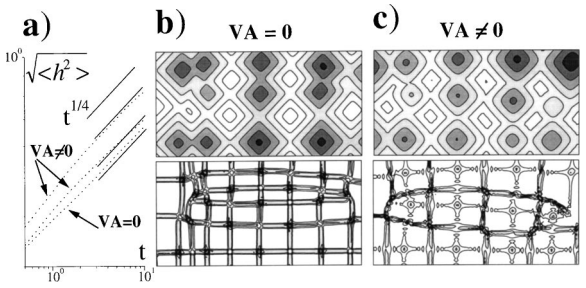

FIG. 4. VA effects on checkerboard structure (away from intermediary states regions). (a) Interface width for three different strengths of VA (increasing from zero, from bottom to top): $\langle h^2\rangle^{1/2} \sim t^{1/4}$ both with and without VA. Surface without [in (b)] and with VA [in (c)]. In (c), note blunt (faint) facet edges emerging from pyramid tops, and sharp (dark) edges emerging from the pits.

the topology of the *defected* checkerboard. In accord with the experiments,[2] these results for the first time explain the striking insensitivity of the (zero VA) checkerboard $t^{1/4}$ growth law,[3] to the presence of VA. Both with and without VA, in the *proximity* of the intermediary states, the coarsening mechanism changes into coalescence yielding the *enhanced roughening* manifested through the $t^{1/3}$ growth at long times and, also, a faster growth at short times *as well*, see Fig. 2(c). It is enlightening to elucidate various recent experiments on Ag(001) growth by using these findings of our theory. Indeed, our enhanced roughening has been seen by Stoldt *et al.*[12] in the proximity of the temperature $\approx$100 K, *exactly* where de Mongeot *et al.*[10] report the 45° rotation transition. Thus, within a unified framework, our theory ties together previously disconnected findings on Ag(001) growth. By the above discussions, we predict that either MultiP or OctP state ubiquitously develops on Ag(001) and intervenes in the 45° rotation transition. We note that, in contrast to our model, the previous KMC models of Ag(001) in Refs. 12–14 (by construction) do not exhibit the facet rotation transition seen in the experiments, Ref. 10.

In summary, by a consistent physical account of the square symmetry, our model is the first one to exhibit the *generic* multitude of interfacial states and transitions in the epitaxial growth and erosion on *any* (001) crystal surface. We have revealed that the 45° rotation phenomenon on realistic (001) surfaces is ubiquitously a sequence of two transitions. Between them, our intermediary states ubiquitously develop and cause an enhanced interface roughening. Our results for out-of-phase (SD) and in-phase (FT) diffraction patterns can be used to reveal our intermediary states in future experiments and numerical studies. And, for the first time we have elucidated the actual effects of the elusive vertical growth asymmetry on the multitude of states on (001) crystal surfaces.

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[15] For $w \sim W = 0$, the 45° rotation transition occurs at the *single* point I at $(b=1, W=0)$ in Fig. 1. There, $\mathbf{J}^{(\mathrm{NE})}(\mathbf{M})=0$ on the circle $|\mathbf{M}|^2 = r/u$. This vanishing of crystal anisotropy is unphysical and *in general* excluded on (001). Thus, the ubiquitous *w*-terms in Eq. (2), breaking this artificial symmetry, *must* be included to discuss the transition.
[16] For $W=0$, $b=1$, at the isotropic transition point I in Fig. 1, pyramids form with randomly oriented facets and grow as $t^{1/3}$ via local pyramid coalescence (see Ref. 3, Secs. IV, VI, and IX). For realistic (001) surfaces, $w \sim W \neq 0$, and the transition ubiquitously goes through the intermediary states in Fig. 1, with pyramid facets oriented by (001) anisotropy. However, they still grow as $t^{1/3}$ via local coalescence, as revealed by our simulations here.
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