Kinetics of two-dimensional island nucleation on reconstructed surfaces

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Nucleation of two-dimensional (2D) islands on reconstructed surfaces might involve formation of metastable nonepitaxial clusters as precursors for 2D islands. Being a thermally activated process the transformation of nonepitaxial clusters to epitaxial 2D islands might become a rate limiting step of the nucleation process at low deposition temperatures leading to substantial accumulation of the depositing atoms in nonepitaxial clusters. In the present paper, we study how slow cluster transformation influences the nucleation kinetics. For a simple model case of metastable nonepitaxial dimers and irreversible adatom incorporation into the epitaxial 2D islands, we analyze possible nucleation regimes and derive scaling relations for the density of stable 2D islands. We show that the 2D island density depends strongly on the cluster transformation rate as well as on the atomic mechanism of the dimer transformation. In particular, a steady-state nucleation regime different from the standard diffusion-mediated aggregation is possible if the transformation of a nonepitaxial dimer to the smallest epitaxial 2D island is triggered by attachment of an additional adatom. In this regime, the 2D island density obeys a nonstandard scaling $N \sim (F/D)^{1/4}$. Deposition conditions where this nonstandard scaling could be observed are determined.

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I. INTRODUCTION

It is well known that the surface reconstruction might have a great impact on the mechanisms and kinetics of epitaxial growth. For instance, the presence of the surface reconstruction might induce anisotropy of adatom diffusion[1] and incorporation[2] and lead to kinetic step instabilities in the step flow growth such as kinetic step bunching[3,4] and step "rotation."[5,6] Additionally, the surface reconstruction might determine the shape of 2D islands[7,8] and influence their growth kinetics.[9–11] Some of these reconstruction related phenomena can be understood in terms of standard growth models properly parameterized by taking into account the effect of the surface reconstruction on the kinetic parameters of the surface processes. However, in a general case, the standard models might fall because the surface reconstruction not only changes the growth parameters, but also brings a new fundamental growth process into play. Indeed, in order to grow an epitaxial layer on a reconstructed surface, one has to destroy the reconstruction and build it up again on top of the growing layer. If, for some reasons, the local reconstruction removal by the growing layer becomes slow, formation of metastable nonepitaxial structures is expected. This situation is typical for deposition of metals on reconstructed semiconductor surfaces where the formation of surface magic clusters, i.e., clusters with enhanced stability at certain sizes, is frequently observed.[12]

In semiconductor growth, two relevant examples could be found in molecular beam epitaxy of Si and Ge on Si(111)-7 × 7 and Si(001)-2 × 1 surfaces. So, experiments have shown that the growth of epitaxial 2D Si and Ge islands on the 7 × 7 reconstructed Si(111) surface is accompanied by the formation of small nonepitaxial clusters occupying the half unit cells of the surface reconstruction.[13–16] On Si(100)-2 × 1 surface, the formation of dimers and longer chains of Si (or Ge) atoms in nonepitaxial adsorption positions have been observed.[17–19] Such clusters are relatively stable both against dissociation and against transformation to epitaxial 2D islands. Therefore one may expect that at relatively low deposition temperatures the formation of 2D islands would represent a multistage process involving the formation of metastable nonepitaxial clusters and their subsequent transformation to stable crystalline nuclei having proper structure of the new epitaxial layer.[20–24]

A classical approach to the nucleation kinetics is based on the mean-field rate equations describing the temporal evolution of the adatom density and density of stable 2D islands[25,26] (for a recent review, see Ref. 27). A theoretical analysis of the 2D island nucleation via an intermediate metastable cluster was performed in Ref. 29 using the standard rate equations model of Ref. 25. It has been shown that the steady-state density of 2D islands N obeys the classical power-law dependence $N \sim (F/D)^{\chi}$ on the ratio between the deposition flux F and the surface diffusion rate D with $\chi = i/(i+2)$, where $i+1$ stands for the size of the smallest stable cluster. All clusters consisting of $i+1$ and more atoms, including the metastable clusters, were considered in Ref. 29 as 2D islands. So, the formation of metastable nonepitaxial clusters, which are structurally distinct from the epitaxial 2D islands, was not taken into account.

A generalized rate equations model taking into account the multistage character of the nucleation process on the Si(111)-7 × 7 surface has been proposed in Ref. 24. It has been shown that the presence of an extra barrier for the transformation of nonepitaxial clusters to epitaxial 2D islands may lead to accumulation of nonepitaxial clusters on the surface and result in an unusual flux dependence of the 2D island density.[24] Similar to Ref. 29, it was assumed in Ref. 24 that the nucleation takes place in the steady-state regime, where atoms adsorbing on the surfaces are mainly captured by the already existing islands. However, if the activation barrier for the transformation of nonepitaxial clusters to epitaxial 2D islands is high, the very existence of the steady-state nucleation regime is not obvious. For instance, in the limit of an extremely high transformation barrier, atoms adsorbed on the surface will rather accumulate into nonepitaxial clusters than form any epitaxial 2D islands.

In the present work, we theoretically investigate kinetics of the 2D nucleation and growth on reconstructed surfaces considering two alternative mechanisms of the transformation of a metastable nonepitaxial cluster to the smallest epitaxial 2D island. For a simple case of metastable nonepitaxial dimers and irreversible adatom incorporation into the epitaxial 2D islands, we analyze possible nucleation regimes and derive scaling relations for the density of stable 2D islands. Using kinetic Monte Carlo simulations, we study how the 2D island density depends on the transformation barrier and deposition conditions. Simulation results are compared with predictions of the developed analytical models. We show that the 2D island density behavior depends strongly on the value of the transformation barrier as well as on the atomic mechanism of the dimer transformation. In particular, a steady-state nucleation regime, different from the standard diffusion-mediated aggregation,[25,26] is possible if the transformation of a nonepitaxial dimer to the smallest epitaxial 2D island is triggered by attachment of an additional adatom. In this regime, the 2D island density obeys a nonstandard scaling: $N \sim (F/D)^{1/4}$. Deposition conditions where this nonstandard scaling could be observed are determined.

II. MODEL

In the standard growth model, atoms arrive at a surface with a flux F and diffuse on the surface with a temperature-dependent diffusion rate $D = \nu \exp(-E_s/k_BT)$, where E_s is the surface diffusion barrier, ν is the attempt frequency, k_B is Boltzmann constant, and T is the substrate temperature. When two diffusing atoms meet, they form a cluster on the surface. The cluster can either grow to larger sizes by capturing diffusing adatoms or dissociate by breaking bonds between the atoms. In the simplest case, no bond breaking between atoms occurs on the time scale of the experiment, and a cluster of two atoms (dimer) represents the smallest stable 2D island [see Fig. 1(a)]. The density of adatoms n_1 and the total density of stable 2D islands N satisfy in this case the following rate equations:[25–27]

$$\frac{dn_1}{dt} = F - 2\sigma_1 D n_1^2 - \sigma_{\text{av}} D n_1 N, \quad (1)$$

$$\frac{dN}{dt} = \sigma_1 D n_1^2. \quad (2)$$

Here, σ_1 is the capture number of adatoms, and $\sigma_{\text{av}} = \sum_{s=2} \sigma_s N_s/N$ is the average capture number of 2D islands (N_s is the density of 2D islands consisting of $s = 2,3,\ldots$ atoms and σ_s is the capture number of a 2D island of size s). It should be noted that Eqs. (1) and (2) describe the nucleation kinetics for a submonolayer stage of growth when the total surface coverage $\theta = Ft$ is sufficiently small to neglect coalescence of 2D islands. Usually, it is assumed that the activation barrier for adatom attachment to a 2D island is equal to the diffusion barrier E_s.[28]

It follows from Eqs. (1) and (2) that there are two distinct nucleation regimes. In the initial or transient nucleation regime, which takes place at the very beginning of the deposition process, adatom losses for nucleation and incorporation are negligible and $dn_1/dt \approx F$. In this case, $n_1 \approx Ft = \theta$ and $N \sim (D/F)\theta^3$. When the density of stable islands becomes appreciable, the system enters the steady-state growth regime, where nucleation events are rare and most of the depositing adatoms join the existing islands. In this regime, the adatom density n_1 remains nearly constant because the deposition flux is completely balanced by the incorporation of adatoms into the islands $dn_1/dt \approx F - \sigma_{\text{av}} D n_1 N \approx 0$. Applying this condition to Eqs. (1) and (2) one comes to the standard scaling relations for the steady-state density of adatoms, $n_1 \sim (F/D)^{2/3}$, and 2D islands, $N \sim (F/D)^{1/3}$. Duration of the transient nucleation stage and the corresponding surface coverage $\theta^* \sim (F/D)^{1/2}$ could be determined by the matching of the transient and steady-state solutions.[27] Since under typical MBE conditions $F/D \ll 1$, the transient regime is very short ($\theta^* \ll 1$) and the majority of 2D islands nucleate in the steady-state regime.

Now, let us extend this standard model assuming that atoms in the smallest stable clusters (dimers) do not occupy proper epitaxial positions and that such nonepitaxial clusters cannot grow further unless they take a proper epitaxial structure. In the following, we will consider two different mechanisms of the transformation of a nonepitaxial dimer to the smallest epitaxial 2D island.

By the first mechanism, the transformation of a nonepitaxial dimer to the epitaxial one occurs by a thermally activated irreversible lifting of the surface reconstruction beneath the dimer [see Fig. 1(b)]. An energy barrier E_{nuc} has to be surmounted to launch the transformation process and no additional atoms may attach to the dimer prior to the transformation. Hereafter, we will refer to the model describing this direct transformation (DT) mechanism as the DT model.

By the second mechanism, reconstruction removal is triggered by attachment of an additional adatom to a nonepitaxial dimer with an activation energy E_{nuc} [see Fig. 1(c)]. The attachment barrier E_{nuc} is assumed to be higher than the surface diffusion barrier, since an extra energy has to be spent to rearrange atoms in the dimer to epitaxial positions. Thereby the attachment barrier to epitaxial islands is assumed to be equal

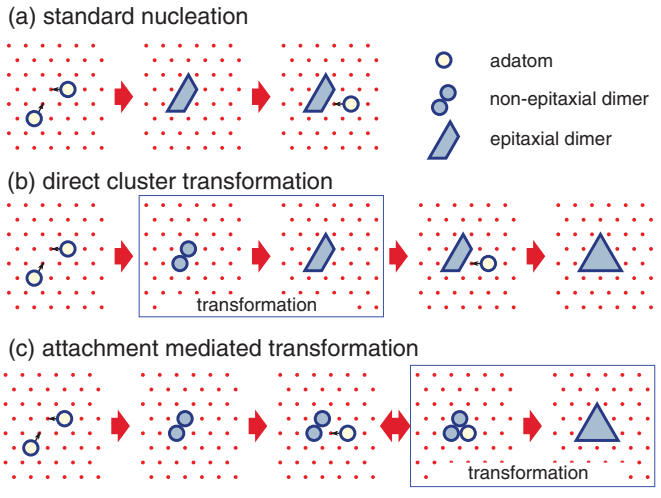

FIG. 1. (Color online) Different nucleation mechanisms: (a) standard nucleation, (b) direct cluster transformation, and (c) attachment mediated cluster transformation.

to the surface diffusion barrier. We will refer to the model describing this attachment mediated transformation (AMT) mechanism as the AMT model.

The major difference between these two mechanisms is that for DT the rate of transformation of nonepitaxial clusters to epitaxial 2D islands does not depend on any other surface processes, whereas for AMT, the transformation rate is proportional to adatom concentration. As will be shown in the following, this subtle difference in the nucleation kinetics greatly influences the flux and temperature dependence of the 2D island density.

The density of adatoms n_1, nonepitaxial dimers N_2^*, and epitaxial 2D islands in our extended nucleation models obey the following rate equations:

$$\frac{dn_1}{dt} = F - 2\sigma_1 D n_1^2 - G_{\rm inc}, \tag{3}$$

$$\frac{dN_2^*}{dt} = \sigma_1 D n_1^2 - G_{\rm tr}, \tag{4}$$

$$\frac{dN}{dt} = G_{\rm tr}, \tag{5}$$

where $G_{\rm inc}$ is the flux of adatoms irreversibly incorporating into the clusters and 2D islands of size $s \geqslant 2$ and $G_{\rm tr}$ is the rate of transformation of nonepitaxial dimers to epitaxial 2D islands (the number of transformation events per unit area per unit time). The quantities N, $G_{\rm inc}$, and $G_{\rm tr}$ in Eqs. (3)–(5) are determined in a different way for DT and AMT mechanisms as explained below.

In the DT model, the minimal 2D island is an epitaxial dimer. Therefore the 2D islands density includes the density of the transformed dimers: $N = \sum_{s=2} N_s$. Thereby the incorporation flux is given by $G_{\rm inc} = \sigma_{\rm av} D n_1 N$. The transformation rate $G_{\rm tr}$ for this mechanism can be written as $G_{\rm tr} = K_{\rm tr} N_2^*$, where $K_{\rm tr} = \nu \exp(-E_{\rm nuc}/k_B T)$ is the transformation frequency of a dimer.

In the AMT model, the transformation requires attachment of an additional adatom to the dimer. That is the minimal epitaxial 2D island consists of three atoms and the sizes of epitaxial 2D islands in this model start from $s = 3$. For this model $N = \sum_{s=3} N_s$, $G_{\rm inc} = G_{\rm tr} + \sigma_{\rm av} D n_1 N$ ($\sigma_{\rm av} = \sum_{s=3} \sigma_s N_s / N$), and $G_{\rm tr} = \sigma_2 K_{\rm tr} n_1 N_2^*$. It should be noted that the AMT model is reduced to the standard nucleation model if one puts $K_{\rm tr} = D$ and sums up Eqs. (4) and (5).

Let us now analyze the nucleation regimes that might be realized in the DT and AMT models. Evidently, the transient nucleation regime takes place at $\theta < \theta^*$ independent on the presence of the barrier $E_{\rm nuc}$ for the transformation of a dimer to the epitaxial 2D island. However, the possibility of transition to the steady-state nucleation regime depends both on the detailed transformation mechanism (DT or AMT) and on the value of the activation barrier $E_{\rm nuc}$. Thereby there might be new nucleation regimes absent in the standard nucleation model.

A. Direct transformation

Transformation of nonepitaxial dimers to epitaxial 2D islands might be hindered by a substantial transformation barrier $E_{\rm nuc}$. In this case, the density of nonepitaxial dimers N_2^* might become much higher than the density of epitaxial 2D islands N. If, additionally, the 2D island density N will stay lower than the density of adatoms n_1, the dimer formation rate $\sigma_1 D n_1^2$ will exceed the incorporation flux $\sigma_{\rm av} D n_1 N$ and adatoms will predominately accumulate into the nonepitaxial dimers. Applying the slow transformation condition $\sigma_1 D n_1^2 \gg K_{\rm tr} N_2^*$ together with the weak incorporation condition $2\sigma_1 D n_1^2 \gg \sigma_{\rm av} D n_1 N$ to Eqs. (3)–(5), one gets

$$\frac{dn_1}{dt} \approx F - 2\sigma_1 D n_1^2 \approx 0, \tag{6}$$

$$\frac{dN_2^*}{dt} \approx \sigma_1 D n_1^2, \tag{7}$$

$$\frac{dN}{dt} = K_{\rm tr} N_2^*, \tag{8}$$

It follows from Eqs. (6)–(8) that in the dimer accumulation regime,

$$n_1 \sim \left(\frac{F}{D}\right)^{1/2}, \quad N_2^* \approx \frac{\theta}{2}, \quad N \sim \frac{K_{\rm tr}}{F}\theta^2. \tag{9}$$

As can be seen, in this regime, the 2D island density decreases with increasing deposition flux and increases with increasing deposition temperature. The physics behind such an unusual behavior is simple: higher temperatures facilitate the dimer transformation, whereas lower deposition fluxes provide more time for the dimers to transform.

To proceed, let us rewrite the transformation frequency as $K_{\rm tr} = D P_{\rm tr}$, with $P_{\rm tr} = \exp(-\Delta E/k_B T)$ and $\Delta E = E_{\rm nuc} - E_s$. The introduced quantity $P_{\rm tr}$ has a meaning of the probability of the cluster transformation on the time scale of a single diffusion jump of an adatom and ΔE represents an excess of the cluster transformation barrier over the surface diffusion barrier E_s. If a dimer transforms to an epitaxial island before it is visited by a migrating adatom, the transformation kinetics is irrelevant. Therefore the accumulation of adatoms in nonepitaxial dimers could only be observed if the transformation frequency $K_{\rm tr}$ is smaller than the frequency of attempts of adatom attachment to the dimer $\sigma_2 D n_1 \sim (DF)^{1/2}$. This sets up an upper bound for the transformation probability in the dimer accumulation regime: $P_{\rm tr} < (F/D)^{1/2}$.

A lower bound for $P_{\rm tr}$ is determined by the characteristic surface coverage $\theta_{\rm DT} = (F/D)^{3/4} P_{\rm tr}^{-1/2}$ at which the density of 2D islands N becomes equal to the density of adatoms n_1. Above $\theta_{\rm DT}$, the weak incorporation condition $2\sigma_1 D n_1^2 \gg \sigma_{\rm av} D n_1 N$ is violated and the dimer accumulation regime ends up. If $\theta_{\rm DT} > 1$, i.e., $P_{\rm tr} \leqslant (F/D)^{3/2}$ the majority of adatoms of the first deposited layer will go to nonepitaxial dimers, so only a minor fraction of the monolayer will have the proper epitaxial structure.

Note that accomplishment of the weak incorporation condition implies also accomplishment of the slow transformation condition $\sigma_1 D n_1^2 \gg K_{\rm tr} N_2^*$. Indeed, the latter inequality is fulfilled if the surface coverage does not exceed $F/(D P_{\rm tr})$, which is larger than $\theta_{\rm DT}$ when $P_{\rm tr} < (F/D)^{1/2}$.

Thus depending on the transformation probability, $P_{\rm tr}$, the following nucleation regimes might be identified [see Fig. 2(a)]: (1) dimer accumulation regime at $P_{\rm tr} \leqslant (F/D)^{3/2}$ and (2) regime of rapid cluster transformation at $P_{\rm tr} \gg (F/D)^{1/2}$. At $(F/D)^{1/2} > P_{\rm tr} \gg (F/D)^{3/2}$, one has an intermediate case where dimer accumulation occurs at early stages of growth (at $\theta < \theta_{\rm DT}$). In the rapid dimer transformation

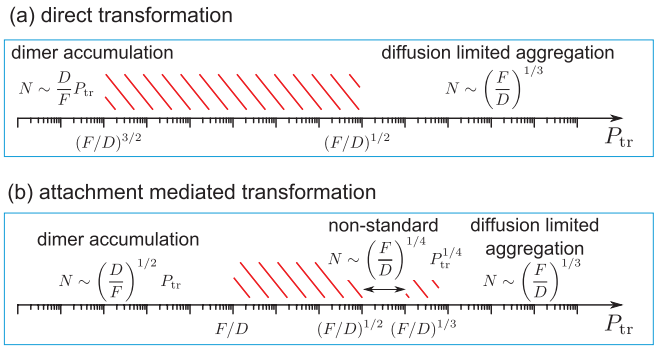

FIG. 2. (Color online) Nucleation regimes for different mechanisms of transformation of nonepitaxial clusters (dimers) to epitaxial 2D islands: (a) direct dimer transformation and (b) attachment mediated dimer transformation.

regime, the density of epitaxial 2D islands follows the standard scaling relation $N \sim (F/D)^{1/3}$, whereas in the dimer accumulation regime a nonstandard scaling $N \sim DP_{tr}/F$ should be observed.

B. Attachment mediated transformation

In the AMT model, attachment of an additional adatom to a dimer is required to launch the dimer transformation, so that the dimer transformation rate is given by $\sigma_2 K_{tr} n_1 N_2^*$. In the case of slow dimer transformation, $\sigma_1 D n_1^2 \gg \sigma_2 K_{tr} n_1 N_2^*$, and weak incorporation into 2D islands, $2\sigma_1 D n_1^2 \gg \sigma_{av} D n_1 N$, one has

$$\frac{dn_1}{dt} \approx F - 2\sigma_1 D n_1^2 \approx 0, \tag{10}$$

$$\frac{dN_2^*}{dt} \approx \sigma_1 D n_1^2, \tag{11}$$

$$\frac{dN}{dt} = \sigma_2 K_{tr} n_1 N_2^*. \tag{12}$$

From Eqs. (10)–(12), one obtains the following scaling relations for the dimer accumulation regime of the AMT model:

$$n_1 \sim \left(\frac{F}{D}\right)^{1/2}, \quad N_2^* \approx \frac{\theta}{2}, \quad N \sim \left(\frac{D}{F}\right)^{1/2} P_{tr}\theta^2. \tag{13}$$

Since the transformation of a dimer is conditioned by attachment of an additional adatom, the transformation cannot occur before the dimer is visited by a migrating adatom. Therefore the transformation frequency $\sigma_2 K_{tr} n_1$ is, by definition, smaller than the frequency of adatom attachment to the dimer $\sigma_2 D n_1$ if there is a nonzero extra barrier ΔE_{nuc}. An upper bound for the transformation probability P_{tr} corresponds here to a natural condition $P_{tr} < 1$.

Characteristic surface coverage, above which the weak incorporation condition $2\sigma_1 D n_1^2 \gg \sigma_{av} D n_1 N$ is violated, is given in the AMT model by $\theta_{AMT} = (F/D)^{1/2} P_{tr}^{-1/2}$. Hence the dimer accumulation regime ($\theta_{AMT} \geqslant 1$) takes place at $P_{tr} \leqslant F/D$. Similar to the DT model, the accomplishment of the weak incorporation condition implies also the accomplishment of the slow transformation condition.

When the density of 2D islands becomes appreciable, the adatom capture by growing 2D islands reduces the adatom density on the surface and slows down the formation of new dimers. However, in the AMT model, the decreased adatom density also reduces the transformation rate of the already existing dimers to 2D islands. Therefore a new steady-state nucleation regime different from the steady-state aggregation regime of the standard nucleation model could be realized. In this regime, adatoms attach mainly to the already existing 2D islands, whereby formation of new 2D islands is hindered by slow transformation of dimers. If $\sigma_1 D n_1^2 \geqslant \sigma_2 K_{tr} n_1 N_2^*$ (slow dimer transformation) and $\sigma_{av} D n_1 N \gg 2\sigma_1 D n_1^2$ (predominant adatom incorporation to the 2D islands), then Eqs. (3)–(5) could be written as follows:

$$\begin{aligned} \frac{dn_1}{dt} &\approx F - \sigma_{av} D n_1 N \approx 0, \\ \frac{dN_2^*}{dt} &\approx \sigma_1 D n_1^2, \\ \frac{dN}{dt} &= \sigma_2 D P_{tr} n_1 N_2^*. \end{aligned} \tag{14}$$

Assuming that the coverage dependence of the capture numbers of 2D islands does not affect the flux and temperature dependencies of n_1, N_2^*, and N,[14] one finds from Eq. (14) the following scaling relations for the nonstandard steady-state nucleation regime:

$$n_1 \sim \left(\frac{F}{D}\right)^{\frac{3}{4}} P_{tr}^{-\frac{1}{4}}, \quad N_2^* \sim \left(\frac{F}{D}\right)^{\frac{1}{2}} P_{tr}^{-\frac{1}{2}}, \quad N \sim \left(\frac{F}{D}\right)^{\frac{1}{4}} P_{tr}^{\frac{1}{4}}. \tag{15}$$

As can be seen, the flux dependence of the 2D island density is expected here to be somewhat weaker than in the classical steady-state regime predicted by the standard nucleation model.

An upper bound for the transformation probability P_{tr} in the nonstandard steady-state nucleation regime is given by the slow transformation condition $\sigma_1 D n_1^2 \geqslant \sigma_2 D P_{tr} n_1 N_2^*$ that fulfills when $P_{tr} \leqslant (F/D)^{1/3}$. A lower bound for P_{tr} follows from the requirement that the dimers formed at early stages of the deposition process (in the regime of dimer accumulation) will transform to 2D islands during time substantially less than the deposition time of one monolayer. Otherwise, nucleation of 2D islands will occur in an intermediate regime characterized by substantial accumulation of adatoms in nonepitaxial clusters. The condition above fulfills at $P_{tr} \gg (F/D)^{1/2}$. The later inequality means that the transformation frequency $K_{tr} = DP_{tr}$ of a "dimer + adatom" cluster is higher than the frequency $\sigma_2 D n_1 \sim (DF)^{1/2}$ of adatom attachment to a dimer at an early stage of growth.

Thus the nonstandard steady-state nucleation regime could be observed at $(F/D)^{1/3} \geqslant P_{tr} \gg (F/D)^{1/2}$. When $P_{tr} \gg (F/D)^{1/3}$, the nucleation kinetics is the same as in the standard model. All possible nucleation regimes in the AMT model are sketched in Fig. 2(b).

III. MONTE CARLO SIMULATIONS

Kinetic Monte Carlo (KMC) simulations were performed on a 2000×1000 triangular lattice. In the KMC model, atoms are deposited randomly onto the lattice with a frequency F and allowed to perform random hops to nearest-

neighbor sites with a temperature-dependent hopping rate $D = \nu \exp(-Es/k_BT)$. The activation energy for adatom diffusion was set to $E_s = 1.1$ eV, which is close to the estimated value for Si surface diffusion on Si(111)-7 × 7 surface.[24,30,31] The activation energy for adatom migration along the step edge was assumed to be equal to the surface diffusion energy. To mimic the analytical models of Sec. II, detachment of adatoms from the edges of epitaxial 2D islands as well as migration of clusters of any size were prohibited. Transformation of a dimer to the epitaxial 2D island according to the DT and AMT mechanisms was considered as an individual kinetic process in the KMC scheme. A common attempt frequency $\nu = 10^{13}$ s^{-1} was used for all the kinetic processes in the model.

Figure 3(a) shows flux dependencies of the 2D island density for the case of the direct transformation of dimers

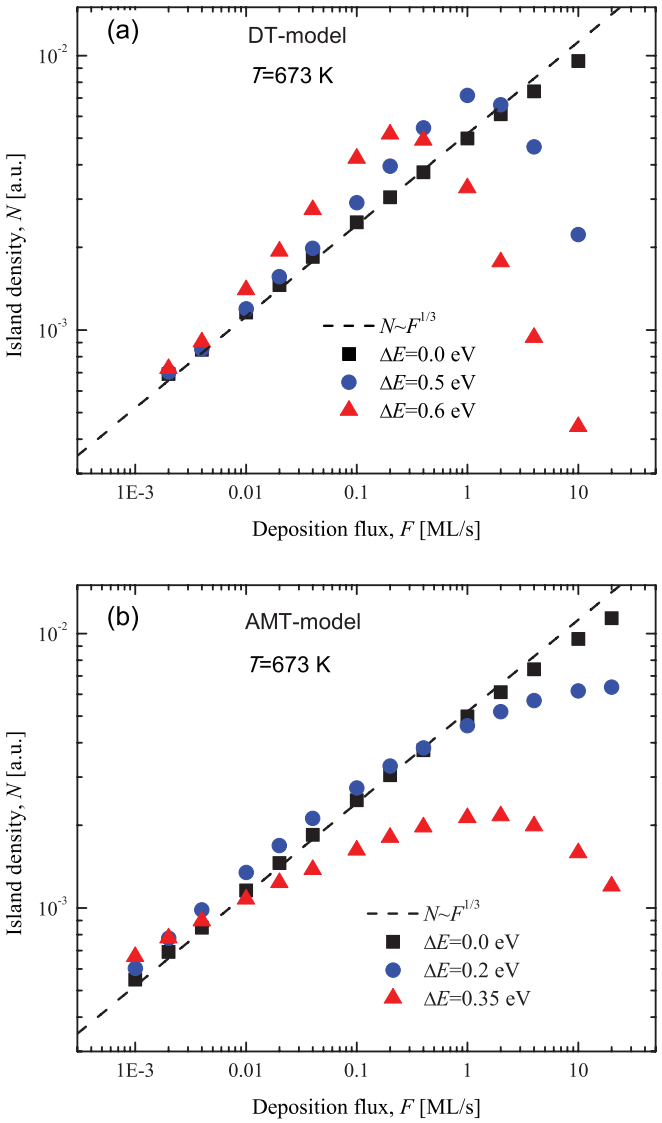

FIG. 3. (Color online) Flux dependencies of the 2D island density at different values of the transformation barrier ΔE and different mechanisms of the cluster transformation: (a) direct cluster transformation and (b) attachment mediated cluster transformation. Dashed line shows the $N \sim F^{1/3}$ dependence, predicted by the standard nucleation theory.

(DT model) to 2D islands at $T = 673$ K, $\theta = 0.2$ monolayer (ML) and different values of the extra transformation barrier ΔE. As expected, at $\Delta E = 0$, the simulated 2D island density follows the classical scaling law $N \sim F^{1/3}$ shown as a dashed line in Fig. 3(a). Only at high F, simulated points slightly depart from the theoretical line, which is explained by a too small ratio D/F at the given simulation parameters.[27]

The deviation of the 2D island density from the standard scaling dependence becomes appreciable at $\Delta E > 0.3$ eV. Already at $\Delta E = 0.5$ eV and $F = 0.2$ ML/s, the density of 2D islands is 1.5 times higher than that predicted by the standard model. At given values of T and ΔE, the transformation probability $P_{tr} \approx 2 \times 10^{-4}$ falls between the values $F/D \approx 3 \times 10^{-6}$ and $(F/D)^{1/2} \approx 2 \times 10^{-3}$, which, according to the analytical model of Sec. II, corresponds to an intermediate nucleation regime [hatched area in Fig. 2(a)]. At small fluxes $F < 0.005$ ML/s, the simulated dependence $N(F)$ coincides with the classical one, and at high fluxes $F > 2$ ML/s one observes a decreasing $N(F)$ dependence, characteristic for the regime of accumulation of adatoms into nonepitaxial dimers. An increase of the transformation barrier shifts the parameters window for the dimer accumulation regime toward smaller F. Thus predictions of the analytical model for the direct transformation mechanism of nonepitaxial dimers to 2D islands are in good agreement with results of kinetic Monte Carlo simulations.

In the case of attachment mediated transformation of dimers (AMT model), deviation of the flux dependence of the 2D island density from the classical scaling $N \sim F^{1/3}$ occurs at smaller values of ΔE and F than in the case of the direct transformation mechanism [see Fig. 3(b)]. This is related to more strict limitations on the values of the transformation probability at which the standard steady-state nucleation regime might be observed [$P_{tr} \gg (F/D)^{1/3}$ in the AMT model versus $P_{tr} \gg (F/D)^{1/2}$ in the DT model]. Similar to the DT mechanism, deviation from the classical dependence becomes stronger at higher transformation barriers ΔE. At high F, a transition to the $N \sim 1/F$ dependence, characteristic for the dimer accumulation regime, is observed.

For the AMT mechanism, in agreement with the analytical model, KMC simulations reveal a nonstandard scaling relation $N \sim F^{1/4}$ in a certain range of deposition conditions. Linear segments of the $N(F)$ curves (in double logarithmic scale) corresponding to the nonstandard steady-state nucleation regime discussed in Sec. II are shown in Fig. 4. Simulations were performed at $\Delta E = 0.2$ and 0.3 eV for two different surface coverages ($\theta = 0.15$ and 0.2 ML). All the values of the deposition flux in Fig. 5 satisfy the conditions $(F/D)^{1/3} \geqslant P_{tr} \geqslant (F/D)^{1/2}$. A linear fit of the simulated data points yields scaling exponents that are very close to the theoretically predicted value $\chi = 0.25$.

Temperature dependence of the 2D island density also shows markedly different behavior for the DT and AMT mechanisms, as can be seen in Fig. 5. In the case of direct transformation of the dimers, the simulated dependence $N(T)$, obtained at $\Delta E = 0.2$ eV, follows the classical dependence $N \sim D^{-1/3}$ in a wide temperature range down to temperatures as low as ~300 °C. At the same simulation parameters, the dependence $N(T)$ obtained for the case of attachment mediated transformation shows considerable deviation from

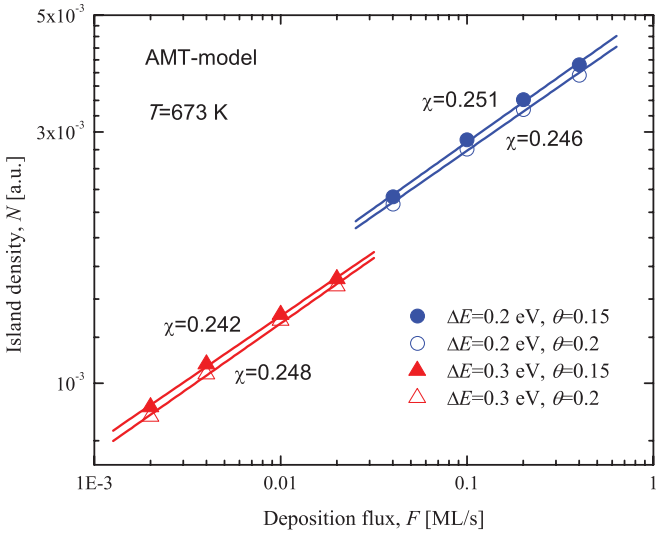

FIG. 4. (Color online) Flux dependencies of the 2D island density in a nonstandard steady-state nucleation regime of the AMT model.

the classical one, falling to the classical curve only in the limit of high T. In a range of deposition temperatures satisfying the inequality $(F/D)^{1/3} \geqslant P_{\rm tr} \geqslant (F/D)^{1/2}$, KMC simulations reproduce the relation $N \sim (P_{\rm tr}/D)^{1/4}$ characteristic for the nonstandard steady-state nucleation regime of the AMT model.

IV. LARGER NONEPITAXIAL CLUSTERS

So far, we have been discussing the nucleation kinetics on reconstructed surfaces assuming that nonepitaxial dimers cannot dissolve and cannot grow further unless they are transformed to epitaxial 2D islands. This is the simplest case where the magic cluster size, i.e., the size, which is reached

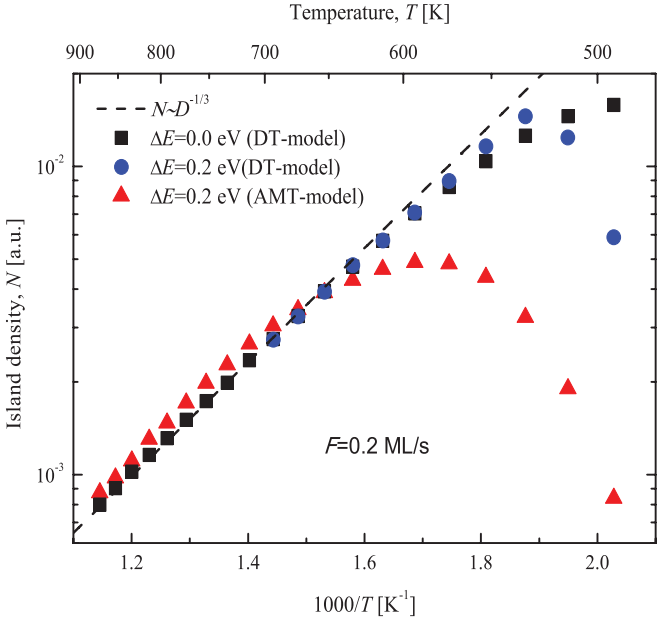

FIG. 5. (Color online) Temperature dependencies of the 2D island density at different values of the transformation barrier ΔE and different mechanisms of the cluster transformation.

by a nonepitaxial cluster before it stops to grow, coincides with the size $i+1$ of the smallest stable nucleus. However, experiments show that the size of magic clusters varies in a wide range depending on the depositing material and surface reconstruction.[12,15] So, in general, the magic cluster size can be larger than the size of the stable nucleus.

Let us assume that, as earlier, the dimer is stable against dissociation (the size of the critical nucleus $i = 1$) but the magic size of the cluster is larger than two atoms. To generalize the developed model to larger magic sizes, one should replace the factor of two in the nucleation term on the right-hand side of Eq. (3) by the actual number of atoms that constitute the magic cluster. Such a substitution extends the regime of adatom accumulation in nonepitaxial clusters to somewhat higher surface coverages, however, it does not affect the scaling relations derived in Sec. II. Therefore the major conclusions of the developed model are directly applicable not only to the systems with nonepitaxial dimers, but also to the systems with larger nonepitaxial clusters, provided that all other assumptions of the model (e.g., the size of the critical nucleus $i = 1$) are fulfilled.

An important example in that respect is provided by low-temperature Si growth on Si(111)-7 × 7 surfaces. Experiments show that the size of nonepitaxial Si clusters on Si(111)-7 × 7 is about eight atoms,[15] but at relatively low deposition temperatures the critical nucleus for the nonepitaxial cluster is just one atom.[24] That is, whenever two adatoms meet within a Si(111)-7 × 7 half unit cell, they irreversibly form a nonepitaxial cluster that rapidly grows up to about eight atoms. An unusually weak flux dependence, $N \sim F^{0.24}$, of the submonolayer density of 2D Si islands on Si(111)-7 × 7 experimentally measured at 673 K (see Ref. 24) is very close to the $N \sim F^{1/4}$ dependence, predicted for a nonstandard steady-state nucleation regime of the AMT model of Sec. II.

The developed model can be further generalized to account for larger sizes of the critical nucleus. This is done by the substitution of the dimer nucleation term $\sigma_1 D n_1^2$ in the rate equations of Sec. II by $\sigma_i D n_1^{i+1} \exp(E_i/k_B T)$, with σ_i being the capture number of the critical nuclei of size i, and E_i is the dissociation energy of the critical nucleus into i adatoms.[25,26] The scaling relations for the density of adatoms n_1, nonepitaxial clusters N^*_{i+1}, and epitaxial 2D islands at different nucleation regimes are then found by integration of the modified rate equations.

In particular, for the nonstandard steady-state regime of the AMT model one finds

$$N \sim \left(\frac{F}{D}\right)^{\frac{i}{i+3}} \exp\left[\frac{E_i}{(i+3)k_B T}\right] P_{\rm tr}^{\frac{1}{i+3}}. \qquad (16)$$

As can be seen, a somewhat weaker flux dependence of the 2D island density is predicted for the nonstandard steady-state nucleation regime, as compared to that predicted by the standard atomistic nucleation theory.[25,26] However, already at $i \geqslant 2$, the nonstandard scaling exponent $\chi = i/(i+3)$ falls into the limits of the standard nucleation theory ($1/3 \leqslant \chi < 1$), therefore predictions of these two models become experimentally indistinguishable.

The size of the critical nucleus influences also the deposition conditions under which the nonstandard scaling

behavior could be observed. Applying the slow-transformation condition $\sigma_i D n_1^{i+1} \exp(E_i/k_BT) \geqslant \sigma_{i+1} D P_{\rm tr} n_1 N_{i+1}^*$ and requesting that the nonepitaxial clusters formed at early stages of the deposition process transform to epitaxial 2D islands during time substantially less than the deposition time of one monolayer, one finds that the nonstandard steady-state regime of the AMT model could be realized if $B^{i/(i+2)} \geqslant P_{\rm tr} \gg B^{i/(i+1)}$, where $B = (F/D)\exp(E_i/ik_BT)$. As can be seen, larger critical nuclei act in favor of standard nucleation kinetics reducing the interval of $P_{\rm tr}$ were the nonstandard steady-state regime described by Eq. (16) could be observed. The physical reason for the transition to the standard nucleation kinetics at larger i is increasing (due to dissociation of unstable subcritical clusters) adatom density, which facilitates the transformation of nonepitaxial clusters to 2D islands by the AMT mechanism.

V. CONCLUSIONS

Kinetics of 2D island nucleation on reconstructed surfaces has been studied analytically and with kinetic Monte Carlo simulations. The formation of a minimal epitaxial island was considered as a multistage process involving the formation of a metastable nonepitaxial cluster and transformation of the cluster to an epitaxial 2D island. Two mechanisms of the cluster transformation have been considered: thermally activated direct transformation of the cluster to epitaxial 2D island and transformation mediated by attachment of an additional adatom to the metastable nonepitaxial cluster.

It is shown that independent on the transformation mechanism at small deposition fluxes F or/and high deposition temperatures T, the nucleation takes place in the standard steady-state nucleation regime at which the flux and temperature dependencies of the 2D island density obey the standard scaling relation $N \sim (F/D)^{1/3}$. At high F (low T), the formation of 2D islands occurs in the regime of accumulation of adatoms into the nonepitaxial clusters. In this cluster accumulation regime, the DT-model predicts $N \sim (D/F)P_{\rm tr}$, i.e., the 2D island density decreases with increasing flux F and increases with decreasing growth temperature T. A similar trend, although with somewhat weaker flux dependence of the 2D island density $N \sim (D/F)^{1/2}P_{\rm tr}$ is predicted by the ATM model. In general, nonmonotonous dependencies of the 2D island density on F and T are expected.

In the case of the AMT mechanism, a nonstandard steady-state nucleation regime could be observed at $(F/D)^{1/3} \geqslant P_{\rm tr} \gg (F/D)^{1/2}$. The unusually weak flux dependence $N \sim F^{1/4}$ predicted for this regime is very close to the experimental dependence $N \sim F^{0.24}$ of the submonolayer density of 2D Si islands on Si(111)-7 × 7 reconstructed surface at a relatively low deposition temperature of 673 K.[24] This shows that the present model captures the essential physics of the nucleation process on Si(111)-7 × 7 surface. Due to its simplicity, the model has allowed not only to reproduce the scaling relation for the 2D island density but also to clear up the conditions under which the nucleation may proceed in the nonstandard steady-state regime.

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