Phase-field modeling of submonolayer growth with the modulated nucleation regime

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A B S T R A C T

In this letter, we perform the phase-field simulations to investigate nucleation regime of submonolayer growth via a quantified nucleation term. Results show that the nucleation related kinetic coefficients have changed the density of islands and critical sizes to modulate the nucleation regime. The scaling behavior of the island density can be agreed with the classical theory only when effects of modulations have been quantified. We expect to produce the quantitative descriptions of nucleation for submonolayer growth in phase-field models.

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1. Introduction & model descriptions

Submonolayer growth, due to its fundamental regime in the initial nucleation and the later influence on the surface morphology, has been seen as an intensive topic for studies of epitaxial growth [1–3]. A "step flow" model to describe epitaxial growth was first proposed by Burton, Cabrera and Frank [4], who suggest that atoms adsorbed on surfaces (called "adatoms") diffuse along the terrace until they are attached to a step or are desorbed from the terrace. This step flow model can be extended to the growth of submonolayer islands by treating island boundaries as steps [5].

In the submonolayer regime, rate equations with [1–3] can be straightforward to describe the classical nucleation theory as well as estimating the size distribution of islands. The average densities of monomers n and the stable islands N in submonolayer growth can be determined by [6]

$$dn/dt = F - (1 + \delta_{s,1})\sigma_s Dnn_s - \bar{\sigma} DnN, \qquad (1)$$

$$dN/dt = \Gamma_s n^{s+1}, \qquad (2)$$

where F is the deposition rate, s is the critical size of clusters, n_s is the average density of islands for s clusters, σ_s are capture numbers associated with the attachment of diffusing monomers to clusters, $\bar{\sigma} = \sum_{j=s+1}^{\infty} \sigma_j n_j / N$ is the average capture number, D is

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the surface diffusion coefficient, and Γ_s is the capture related coefficient written by $\Gamma_s = D^s \prod_{j=2}^{s} \sigma_{j-1}/K_j$, where K_j are defined as the rates of detachment of monomers from j clusters. Equations (1) and (2) offer the specific kinetic motions for submonolayer nucleation, yielding the classical scaling law in a quasi-stationary approximation [1,2,6],

$$N \simeq \eta(\theta, s) \left(\frac{F}{D}\right)^\chi \exp\left[\frac{E_s}{(s+2)k_B T}\right], \qquad (3)$$

where θ denotes the coverage for growing film, η is a kinetic related prefactor that has been specified in Ref. [6] and E_s represents the binding energy with s cluster. $\chi = s/(s+2)$ is called the scaling law that describes the general regime of nucleation during complete condensation of two-dimensional islands. This was originated from the quasi-stationary solution of rate equations by Venables [1] with the systematical deduction. The scaling behavior of the island density was extended from the "saturation regime" into the "initial time regime" by Einax et al. [6], in the condition $n \ll N$. It always remains valid in the submonolayer growth with the low coverage θ or the high values of D/F.

Although many theoretical efforts [1–3,7–11] have been made to understand the kinetics or obtain appropriate analytical formulae for the submonolayer growth, it still remains a challenging problem in quantitatively connecting theoretical models with experimental observations due to the different ranges of length and time scales spanning several orders of magnitude during the growth processes. In mean-field rate theory [12], it is effective in describing the average density or distributions of islands but

does not give the local information on motions of adatoms. In simulations, kinetic Monte Carlo method (KMC) [13–15] successfully predicted the possibilities of atomistic kinetic processes, but this method usually focuses on the length and time scales of single atoms, so predicting growth morphologies on larger scales for device applications is not always feasible. The level-set method [16–20] is a general technique for simulating the motion of moving boundaries in continuum modeling. It has been well applied to the descriptions of epitaxial growth, island dynamics, submonolayer growth with defects, and edge diffusion on vicinal surfaces. Yet, it appears to be inefficient in handling the larger scale problems with amounts of boundaries or islands.

The phase-field method, based on the Ginzberg–Landau theory of phase transitions, is known as a new technology for describing step motions, exploring epitaxial processes and investigating the submonolayer regime of islands [21–26]. The phase-field model is very similar to the level-set method. Actually, they adopt the same technique for simulating the motion of moving boundaries. The instinct difference is that the evolution of islands in the level-set method is only based on the mathematic operation of ϕ without the physical significance, except for $\phi = 0$ regarded as the boundaries of islands. In the phase-field model, however, the height of monolayers is quantified via an order parameter ϕ (it is an integer on terraces but a decimal at steps), which evolves based on the thermodynamic consistent principle. It means that the level-set method directly deals with sharp interfaces in the atomic scales while the phase-field model deals with diffused interfaces in a larger simulated scale. Attributed to this treatment, the complex interface conditions can be changed into the free boundary problems without front tracking at steps. Furthermore, according to the systematic asymptotic analysis, Karma and Plapp (KP) [26] established quantitative relations between simulated scales and kinetic coefficients in epitaxial growth. This promotes the phase-field model not only to deal with kinetics for local information with atomic scales, but also to enable the more precise description of surface morphologies with considerable range of length and time scales in mesoscopic fields. Recently, Kharchenko et al. [27–29] developed the model by introducing the interactions of adatoms and the detailed fluctuation. Their generalized model has given an overview in the effects of interaction strength and noise intensity on pyramidal islands growth, which is valuable for studies of elastic tensions and temperature oscillations in stochastic films. Furthermore, pattern formation with monolayer mechanisms has been investigated in an overdamped stochastic reaction-Cattaneo model. Yet, phase-field modeling of the submonolayer regime still remains a challenging aspect when nucleation has been taken into account due to the lack of quantification of kinetic coefficients considering nucleation.

According to Equation (2), Yu et al. [30] introduced a similar form of nucleation term into the KP model for investigating islands growth, step meandering and bunching, as well as epitaxial surfaces. In this model, the height of monolayers was quantified via a variable order parameter, ϕ, with the values of 0, 1, 2...n corresponding to the substrate, the first, the second ... and the nth monolayer, respectively. The evolution equations for atom motions and layers are governed by:

$$\frac{\partial u}{\partial t} = D\nabla^2 u - \frac{u}{\tau_s} - \frac{\partial \phi}{\partial t} + F + \delta(r - r')\delta(t - t'), \tag{4}$$

$$\frac{\partial \phi}{\partial t} = \frac{1}{\tau}\left[W^2\nabla^2\phi - 2\sin 2\pi\phi - \lambda u(2\cos 2\pi\phi - 2)\right] + \lambda' u^{i+1}, \tag{5}$$

where u is the local density of atoms, τ_s is the time constant as a description of desorbing from terraces, which is infinite when

desorption is considered to be negligible in our present epitaxial growth, τ is the characteristic time of the kinetic attachment, W is related to the length scale of the step width, and λ is defined as a dimensionless coupling coefficient. Moreover, the last term of Equation (5) introduces nucleation, where a nucleation related coefficient λ' and a preset critical size i were introduced to represent Γ_s and s of classical nucleation theory. In simulations, nucleation was introduced with fluctuations by adding into the right hand of Equation (4) a random term $\delta(r - r')\delta(t - t')$, which works by setting the density of u to be 1 at times $t = t'$ and positions of $r = r'$. This yields the local supersaturation that will induce the remarkable evolution of ϕ and lead to the formation of initial islands at the certain times and positions. Note that the evolution term $\partial\phi/\partial t$ is regarded as the loss term that must be added into Equation (4) to quantify the loss of density due to nucleation. It is a possible way to give a quantitative description of nucleation in phase-field model. Ming et al. [31] have performed systematical investigations on the island size distribution by the phase-field model. In their suggestions, the phase-field results can agree very well with KMC and level-set simulations for submonolayer island growth. Furthermore, they have studied the agreed scaling curves of island size distribution for different simulated scales. It is suggested that the phase-field model can predict the rationalized nucleation regime that is in the quantitative or at least the semi-quantitative agreement with other simulations for the different simulated scales. Yet, limitations of comparisons of kinetic coefficients with the classical nucleation theory were involved in the previous work, which presents a promising issue for the future developments of the quantified phase-field simulations. In this work, we mainly focus on the quantification of the nucleation term in phase-field models to propose a quantitative link of the simulated results with the classical nucleation theory.

2. Implementation

We start phase-field simulations by performing submonolayer growth of perovskite films. Equations (4) and (5) were discretized in a square domain with the area of $N_m W \Delta x \times N_m W \Delta x$. The parameters used in simulations are: $a = 0.390$ nm, $d_0 = 0.06$ nm, $D = 2.2 \times 10^3 a^2/s$, $W = 20a$, $\tau = 4.16$ s, $N_m = 256$, $\Delta x = 0.5$, $\Delta t = 4.7 \times 10^{-4}$, $\lambda' = 1.0$ s^{-1} and $i = 1$. Fig. 1 illustrates the simulated morphologies with the coverage of 0.1 monolayers (ML) with the varied rate of deposition ($D/F = 10^4 \sim 10^6$). It demonstrates that a larger rate of deposition makes clusters more difficult in coarsening or coalescing, thus leading to the increase of the number of islands and the decreased average size of islands. It should be noted that because the present phase-field model is lacking of quantitative links of coefficients with the nucleation kinetics, both λ' and the critical sizes i are preset in the simulations. We expect the quantifications of these parameters with the purpose of modulating the nucleation regime of submonolayer islands to be agreed with the classical nucleation theory.

In order to estimate that consistency, the predicted results from phase-field simulations should be compared with the scaling law in Equation (3). In particular, a study of the island density as a function of deposition rate has enabled the determination of the critical island sizes for simulations in a variety of systems. Fig. 2(a) shows the total island density as a function of F/D with coverage of 0.1 ML. The deposition rate F enlarges the density of islands for different values of i. The linear fitting curves indicate that the densities of the initial islands exponentially depend on deposition, as described by Equation (3), with the scaling exponents χ^s of 0.50366, 0.66222, 0.6712, 0.68119, and 0.69437 for $i = 1, 2, 3, 4$ and 5, respectively. Note that the real critical sizes s are calculated from the scaling law $\chi^s = s/(s + 2)$, which are remarkably different from the preset values of i, as shown in Fig. 2(b). We at-