Mean-field theory of nucleation and growth on strained surfaces

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Mean-field nucleation and growth modeling is important for understanding various adsorbate-substrate systems, particularly in the context of epitaxial growth. Conventional mean-field theory does not take into account nonlocal interactions, but adparticles may interact with strained islands via long range elastic interactions mediated by the substrate. We show that recent extensions of mean-field theory to deal with nonlocal interactions do not describe such processes faithfully. Here, we derive a generally applicable mean-field theory of adparticle dynamics on strained surfaces, when interdiffusion is neglected. This approach enables us to determine the transport coefficients from the microscopic physics; in particular, we find explicit expressions for the diffusion coefficient and drift velocity at all positions relative to an arbitrarily strained island. We demonstrate the role of strain on island growth, using island strain fields that are dynamically updated, for Ge/Si(001) parameters. This approach has important applications in the modeling of nucleation and growth of many nanostructures, such as metal nanoclusters, semiconductor hut clusters, and silicide nanowires.

Over the past few years, it has become clear that capture of adparticles (atoms, molecules, and/or small clusters) on surfaces cannot always be treated in the diffusion-controlled limit and that adparticle interactions are often important in forming nanostructures. For example, repulsive interactions are thought to play an important role in the nucleation and growth of metal nanoclusters, hut clusters, and nanowires. Recent papers on the early stages of (epitaxial) growth, in which repulsive fields may be important, are given by Fichthorn and Scheffler,[1] Merrick *et al.*,[2] Ovesson,[3] Venables and Brune,[4] and Niu *et al.*[5] This field has been reviewed by Ratsch and Venables.[6]

Consider adparticles on a solid substrate, which are initially deposited at a rate determined by the flux. In the early stages, diffusive movement leads to the formation of island nuclei which dissociate or grow depending on whether their size is below or above a critical value. As time progresses, these adparticles are more likely to be captured by already formed nuclei rather than forming new ones; the interplay of short and long range interactions between adparticles together with diffusive movement leads to the growth of various nanostructures.

The time evolution of the adparticle concentration $c_i(t)$ at site i is described via an equation of the type

$$\frac{\partial c_i(t)}{\partial t} = F - F_{des} - F_{cap} + F_{rel} + \sum_j \left[W_{j \to i} c_j(t) - W_{i \to j} c_i(t) \right],$$

$$(1)$$

where the first two terms denote deposition and desorption fluxes, the next two terms account for the capture and release of adparticles from islands, and the sum over nearest neighbors of site i represents hopping to and from site i with hopping rates $W_{j \to i}$ and $W_{i \to j}$, respectively. These transition rates are modified by adsorbate interactions or the application of an external field.

Conventional mean-field theory (MFT) typically ignores adsorbate interactions during diffusion and capture. Ovesson[3] made a first attempt to include such interactions. Here, we analyze the assumptions behind Ovesson's approach and show that they are inapplicable to the case of strain fields. We then construct an extension of MFT which correctly describes nucleation and growth in the presence of strain fields and apply this theory to calculate island growth quantities of interest.

As mentioned by Ovesson,[3] the challenge to deriving a continuum mean-field description from Eq. (1) stems from calculating the sum. Hence, we shall focus solely on this sum and ignore the other terms. According to transition-state theory, the hopping rate between two sites i and j take the general form,

$$W_{i \to j} = W^0_{i \to j} e^{-\beta E_{i \to j}},$$

$$(2)$$

where $E_{i \to j}$ is the energy barrier jump from site i to j and $\beta = (k_b T)^{-1}$. In the absence of an external field, the diffusion barrier is given by $E_{i \to j} = E_s - E_i$, where E_i and E_s are the adparticle energies at site i and at the saddle point between sites i and j, respectively. This energy difference is usually denoted as the diffusion energy E_d.[3,4] Here, we use E_d for the zero-strain value.

The application of an external field V changes the diffusion barrier to $E_{i \to j} = E_s + V_s - E_i - V_i$. Assuming that the change of saddle-point energy in an external field equals the average changes at the binding sites, i.e., $V_s = (V_i + V_j)/2$, we get

$$E_{i \to j} = E_d + \frac{V_j - V_i}{2}.$$

$$(3)$$

Note that this is exactly the expression used by Ovesson[3] in the derivation of his nonlocal MFT. Thus, we stress that an implicit assumption is that the change of saddle-point energy in an external field equals the average changes at the binding sites. This assumption may perhaps work well in a particular

situation, e.g., Ref. 1; however, we show here that it is not generally satisfied, for the important case of fields due to strain. We illustrate this flaw using an analytic one-dimensional (1D) model.

Consider a 1D substrate in which substrate atoms are periodically placed with a lattice spacing a. The interactions between an adatom and substrate atoms and between the substrate atoms themselves are via a Lennard-Jones (LJ) 6-12 potential: $V(r)=4\gamma[(\sigma/r)^{12}-(\sigma/r)^6]$. The equilibrium spacing between the substrate atoms is $a_0=2^{1/6}\sigma$, but since the spacing is kept fixed at a value a, this implies that the surface is under a strain given by $\epsilon=(a-a_0)/a_0=2^{-1/6}\sigma^{-1}a-1$. This model was considered by Shu and Gong[7] in the context of carbon nanotubes, in which case, it was solved numerically. We are interested in deriving explicit expressions for the changes in potential energy at the binding sites and at the saddle points as a function of strain; thus, we can assess directly whether the assumption discussed in previous paragraphs holds or not for the cases of compressive and tensile strain fields. Note that the substrate is "frozen;" i.e., once the spacing a (and thus the strain) is changed to a new value, the substrate atoms are not allowed to relax back to the equilibrium spacing but remain in a stressed state with the new spacing a. Positive values of ϵ correspond to strain due to a tensile stress and negative values to compressive strain.

The binding sites and the saddle points in this model naturally correspond to the hollow and the atop sites. To a first approximation, the adatom will adopt a configuration such that the distance to its nearest neighbors is equal to a_0 (see Ref. 8 for a general discussion of this point). Then, it is easily shown that the potential energy of the adatom including interactions up to next-next nearest neighbors, at a binding site (V_1) and at a saddle point (V_2), is given by

$$V_1 = 2\gamma\{4[(\sigma/r_1)^{12}-(\sigma/r_1)^6]+4[(\sigma/r_2)^{12}-(\sigma/r_2)^6]-1\},$$
(4)

$$V_2 = \gamma\{8[(\sigma/r_3)^{12}-(\sigma/r_3)^6]+8[(\sigma/r_4)^{12}-(\sigma/r_4)^6]-1\},$$
(5)

where distances are given by $r_1^2=a_0^2+2a^2$, $r_2^2=a_0^2+6a^2$, $r_3^2=a_0^2+a^2$, and $r_4^2=a_0^2+4a^2$. Using the previously stated relation between a and ϵ, one can Taylor expand these equations in the strain to obtain

$$V_1 = -\gamma(2.16-0.63\epsilon)+O(\epsilon^2),$$
(6)

$$V_2 = -\gamma(1.50-1.47\epsilon)+O(\epsilon^2).$$
(7)

Using the notation introduced in the prelude to Eq. (3), the changes in saddle-point energy and binding energy due to the strain field are $V_s=1.47\gamma\epsilon$ and $V_i=0.63\gamma\epsilon$. This explicitly shows that the assumption that the saddle-point energy is an average of the neighboring binding site energies is incorrect when a small strain field is applied to a given surface. Since the barrier energy will vary with strain, then the local diffusion coefficient D must also depend on the local magnitude of the strain; this feature is missing from Ovesson's extended version of conventional MFT. These results can also be obtained from a two-dimensional (2D) analog of our model; in

this more general case, the saddle-point and binding energies (and hence values of D) at a site are linear combinations of the local strain tensor components.

We note that the dependence of the diffusion barrier on the strain is also known from first-principles calculations of adatom diffusion on Si(001) surfaces.[9,10] In line with the predictions of these more detailed models, we find that D generally increases with the application of compressive strain (negative ϵ) and decreases for tensile strain (positive ϵ). First-principles calculations show that these effects are still present when the substrate is allowed to relax due to the adatom[9] and that quantitative differences between this case and the frozen substrate case are small,[8] at least for the LJ potential.

We now develop the continuum mean-field theory of adparticle dynamics on strained surfaces. Generally, the strain at a given point on the surface will be due to nonlocal islands or other nanostructures. The general case is that of an inhomogeneously strained surface such that the strain is given by some function of space and time $\epsilon=\epsilon(x,y,t)$. We will use the results previously derived for homogenously strained surfaces locally; the use of the results for homogeneous fields to understand the case of heterogeneous fields has been previously verified to yield qualitatively correct predictions using microscopic simulations.[8]

We shall assume that the adparticles move on a 2D square lattice of substrate atoms. Let the strain at lattice site i be ϵ_i; then, the extra potential at binding site i due to the application of a strain field is $V_i=\alpha_1\epsilon_i$. Similarly, the change in the saddle-point potential $V_s=\alpha_2(\epsilon_i+\epsilon_j)/2$. The values of these two parameters depend on the specific type of adparticles, surfaces, and interactions under consideration. Note that since α_1, α_2, and ϵ are generally tensors (and functions of position), a summation convention is implied in our equations for the potential energies, e.g., $\alpha_1\epsilon=\alpha_{1xx}\epsilon_{xx}+\alpha_{1yy}\epsilon_{yy}\ldots$. In the spirit of mean-field approximation, we assume that the strain is slowly varying between neighboring lattice points. Thus, the equation for the energy barrier takes the form

$$E_{i\to j}=E_d+V_s-V_i=E_d+\frac{\alpha_2}{2}(\epsilon_i+\epsilon_j)-\alpha_1\epsilon_i,$$
(8)

which leads to transition rates of the form

$$W_{i\to j}=W_{i\to j}^0 e^{-\beta E_d}e^{-(1/2)\beta\alpha_2\epsilon_j}e^{-\beta[(1/2)\alpha_2-\alpha_1]\epsilon_i}.$$
(9)

The factor $W_{i\to j}^0 e^{-\beta E_d}$ has units of inverse time and so can be expressed as D_1/h^2, where D_1 is the diffusion coefficient of the adparticles in the absence of external fields and h is the lattice spacing. Hence, the previous expression can be rewritten in the convenient form

$$W_{i\to j}=f_j g_i/h^2,$$
(10)

where

$$f_j=\sqrt{D_1}e^{-(1/2)\beta\alpha_2\epsilon_j},$$
(11)

$$g_i=\sqrt{D_1}e^{-\beta[(1/2)\alpha_2-\alpha_1]\epsilon_i}.$$
(12)

In a separate but related development, Grima and

Newman[11] showed that advection-diffusion equations of the general form

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \nabla \cdot (c\mathbf{v}), \tag{13}$$

where $D = fg$ and $\mathbf{v} = g \nabla f - f \nabla g$ are the continuum limit of discrete master equations of the form

$$\frac{\partial c_i}{\partial t} = \sum_j [W_{j \rightarrow i} c_j - W_{i \rightarrow j} c_i], \tag{14}$$

where the sum is over nearest neighbors of site i and the transition rates are of the form of Eq. (10). Note that f and g are some functions of space and time and f_j represents the value of the function f at site j on a regular lattice of step size h. This result is valid in all dimensions; it is useful in the context of this Brief Report in that it enables us to immediately construct the macroscopic dynamical equation from the underlying microscopic equations since our rate equations are exactly of the above form. Substituting the forms of f and g which we previously derived, Eqs. (11) and (12), into the expressions for the macroscopic diffusion and drift velocity following Eq. (13),

$$D(x,y) = D_1 e^{-\beta(\alpha_2 - \alpha_1)\epsilon(x,y)}, \tag{15}$$

$$\mathbf{v}(x,y) = -\beta D(x,y) \left(\frac{\partial(\alpha_1 \epsilon)}{\partial x} \hat{x} + \frac{\partial(\alpha_1 \epsilon)}{\partial y} \hat{y} \right). \tag{16}$$

Hence, the continuum mean-field description of adparticle diffusion on homogeneously or inhomogeneously strained surfaces is given by Eq. (13) with Eqs. (15) and (16).

We now use these equations to investigate adatom kinetics near an island. This shall be done in two distinctive ways: first, by means of an analytical approach to distill the main features of adparticle movement in the neighborhood of an island and second, by direct numerical integration of the mean-field equations for the specific case of Ge islands on Si(001).

The calculation of the strain field around an island is the subject of ongoing research. However, it is well known that for a relatively flat island in a one-dimensional space, an approximative expression is given by[12,13]

$$\epsilon(x) = \epsilon_0 + 2\epsilon_0 \tan(\theta) \frac{1+\nu}{\pi}$$

$$\times \ln \left| \frac{[x - H\cot(\theta) + L_2][x + H\cot(\theta) - L_2]}{(x + L_2)(x - L_2)} \right|, \tag{17}$$

where θ is the angle of the island facets, H is the height, ϵ_0 is the misfit strain, ν is the Poisson ratio, and L_2 is half the base length L. Here, the edges are at $x = \pm L_2$. This approximation is valid for a relatively flat island satisfying $H/L \ll 1$; this has been verified by molecular dynamics simulations of Ge on Si(001).[13] A two-dimensional (1+1) model of this type also captures the main features of the strain field close to a 2D island edge, though it neglects corner effects (see Zinovyev et al.[13] and references therein).

Using the above expression and Eq. (15), one can easily get an expression for D as a function of distance from the island. Close to the island, this expression reduces to $D(x) \propto (x - L_2)^\omega$ in the range $x > L_2$, where the proportionality constant is positive and $\omega = 2\beta\epsilon_0 \tan(\theta)(\alpha_2 - \alpha_1)(1+\nu)/\pi$. Using Eq. (16), one can similarly calculate $\mathbf{v}$ in the vicinity of the island, finding that the leading term is $v(x) \propto \alpha_1 \epsilon_0 (x - L_2)^{\omega-1}$. It is difficult to generalize beyond this point because the exact behavior depends on the signs of α_1 and $\alpha_2 - \alpha_1$. If we consider the case of Ge on Si, α_1 and $\alpha_2 - \alpha_1$ are known from Refs. 9 and 10 to be negative in the case of α_1 and positive in the case of $\alpha_2 - \alpha_1$. Since ϵ_0 is also negative for this case,[13] then it follows that the drift velocity is away from the island on each side. The diffusion coefficient increases monotonically as the island is approached from either side. Note that these predictions are different than those from Ovesson's theory;[3] the latter corresponds to the special case $\omega = 0$ in our theory which implies a constant diffusion coefficient and a drift velocity which decays artificially slowly with distance from the island.

Now, we consider the case of monolayer (ML) thick islands of Ge on Si(001), which we study by direct numerical integration of the mean-field equations. The case of anisotropic but spatially constant D has already been studied.[14] Here, we extend this by a brief study of the effect of strain on island growth, with a more detailed study to follow.[15] The adparticle dynamics follows the continuum equation [Eq. (13)] with the diffusion coefficient and drift velocity given by Eqs. (15) and (16) and with the strain field given by Eq. (17). This equation is integrated using the master equation discretization approach;[11] the stability analysis is given in Ref. 16.

We study the case of an island with $H = 1$ in the 128×1 periodic simulation space, the facet angle $\theta = 45°$, and initial length $L = 11$ units, at $T = 450 °C$. We use $\epsilon_0 = -0.042$, $\nu = 0.26$, $\alpha_1 = -1.75$ eV, and $(\alpha_2 - \alpha_1) = 0.75$ eV; all values are appropriate for Ge on Si.[9,10,13] Illustrative results are given in Figs. 1 and 2.

Figure 1 shows the plots of diffusion coefficient, drift velocity, and strain as a function of distance from the island center. The deposited dose Ft at $t = 400$ is 0.4 ML in units of H; the initial adparticle concentration is 0.005 ML.[17] The zero-strain values of $D_1 = 5$ and $\Delta t = 0.03$ are chosen such that stability is assured for all strains encountered. The data are for the end of a run in which the island size and strain field are updated when the amount of material added to each side of the island has increased by one lattice constant. Time-lapse movies have been made to visualize the growth processes, as MATLAB movies (mov) and video clips (avi).[14,15]

The diffusion constant D and strain are both symmetric in position x, whereas the drift velocity $\mathbf{v}$ is antisymmetric; the case of $\alpha_2 - \alpha_1 = 0.75$ eV is highlighted, with the $\alpha_2 = \alpha_1$ case shown by the dotted line for comparison. Note that strain causes a 60% increase in the diffusion constant far away from the island and a much larger enhancement close to the island edges.

Figure 2 shows the corresponding adparticle concentration profiles and final island sizes. We see directly that $\alpha_2 = \alpha_1$, curve (a), leads to incorrect predictions of island growth rates. In our case [$\epsilon < 0$ and $\alpha_2 > \alpha_1$, curves (b) and
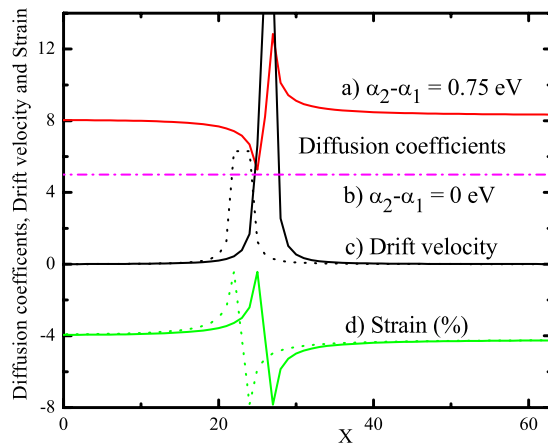
FIG. 1. (Color online) [(a) and (b)] Diffusion coefficient, (c) drift velocity, and (d) strain as a function of distance from the island center. The dotted and dash-dotted lines are for $\alpha_2=\alpha_1=-1.75$ eV. The solid (red/gray, black, and green/light gray) lines are for $\alpha_2-\alpha_1=0.75$ eV, with $\alpha_1=-1.75$ eV.
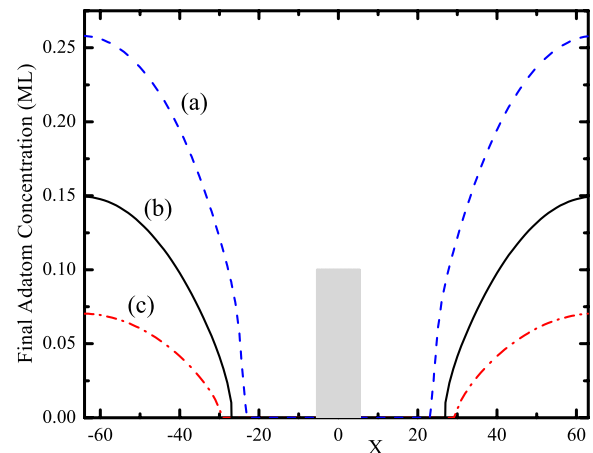

FIG. 2. (Color online) Final concentration profiles around an island; the initial island width=11, as shown by the shaded region. The parameter $\alpha_2-\alpha_1$ equals (a) 0 eV (dash blue line), (b) 0.75 eV (full black line), and (c) 1.5 eV (dashed-dotted red line). In all cases $\alpha_1=-1.75$ eV. See text for discussion.

(c)], the concentrations are lower, and the island width is larger, than those predicted by nonlocal MFT[3] based on the $\alpha_2=\alpha_1$ assumption. This occurs because for the ϵ and α parameter values illustrated here, strain-enhanced diffusion is able to overcome the general trend of drift away from the island. More cases are considered elsewhere.[15]

To summarize, we have introduced a quantitative treatment of nucleation and growth on a lattice, in which the transport coefficients are directly deduced from the microscopic dynamics for the case of strain. For specific systems, such as Ge/Si(001), this may limit application to relatively low temperatures, where interdiffusion is unimportant. Epitaxial growth in such systems at high temperatures is complex[18] and is specific to all the (nonlinear) processes, such as reconstruction and nucleation[5] that need to be considered. Our general approach allows such processes to be added one at a time to study particular regimes in any specific system.

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