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Elastic interactions and kinetics during reversible submonolayer growth: Monte Carlo simulations

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The reversible submonolayer heteroepitaxial growth is studied by means of kinetic Monte Carlo simulations of a simple model with short- and long-range interactions. The Green function of a film on a deformable substrate allows a fast computation of elastic energy barriers and the investigation of the islands statistical properties as functions of strain and the diffusion to deposition flux ratio. We find an unexpected decrease of the island density due to elastic interactions which can be understood as a decrease of the effective adatom binding energy coupled to kinetic effects. The island size distribution satisfies the usual scaling and does not significantly depend on elasticity.

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Aggregation phenomena are ubiquitous in physics, chemistry, or biology. A paradigm arising in surface science deals with island formation during molecular beam epitaxy, which involves adatom deposition and diffusion, island nucleation, growth, and coalescence. In heteroepitaxial systems, elasticity is an extra crucial effect which can lead to a transition between two- (2D) and three- (3D) dimensional islands and quantum dot formation.[1] The progress in experimental techniques for surface scanning, together with application for electronic devices fabrication has shed some new light on this field.[2–4] The understanding of the density, mean size, and size dispersion of submonolayer strained islands is then of significant importance as they are templates for the subsequent surface evolution. Moreover, beyond aggregation mechanisms, the submonolayer regime may be used to measure adatom diffusion coefficients otherwise hard to measure.[5,6]

To tackle this far-from-equilibrium many-body problem, different approaches are available without elasticity in the irreversible case where adatoms never detach from islands.[7,8] Scaling analysis[9,10] first predict that the number N_s of islands with s atoms is merely

$$N_s = (\Theta/\langle s\rangle^2) f(s/\langle s\rangle), \tag{1}$$

given by the scaling function f and the only characteristic island size $\langle s\rangle$. They depend solely on the ratio of the adatom diffusion constant D to the deposition flux F, and $\langle s\rangle = \Theta^z (D/F)^\chi$, where Θ is the deposited coverage $\Theta = Ft$, and z and χ—two scaling exponents. More detailed information are then found from rate equations which treat the system in a mean-field way[11–14] and compare favorably with kinetic Monte Carlo (KMC) simulations. However, even if the irreversible hypothesis is well suited for metallic materials at low temperatures, it fails for semiconductors or at high temperatures when E_N, the atom binding energy to islands, is no longer large compared to the thermal energy k_BT. A simple solid-on-solid (SOS) model accounting for reversible aggregation[15] reveals that the system depends both on D/F and E_N, and exhibits a different regime where the island density saturates before coalescence occurs. In another description, islands with more than the critical nucleus i atoms do not loose matter and are characterized by both i and D/F (see Ref. 13 and 16).

For strained systems with a misfit ε between the film and substrate, the extra nonlocal elastic interactions are long range and differ qualitatively from the short-range effects previously described. One may first expect that the weak long-range elastic repulsions favor adatoms to drift away from other adatoms[17,18] and existing islands.[19] They should also favor atom detachment from islands.[20] Most studies of these effects focused on the irreversible growth,[17,18,21] but little is known about the statistical properties of submonolayer strained islands during reversible growth. To answer this, we display a simple model devised for studying the interplay between short- and long-range interactions and between kinetics and thermodynamics. This model is studied by means of KMC simulations including the elastic chemical potential in energy barriers. The latter is computed using a discrete form of the continuum Green function of a film on a deformable substrate and includes in a fast computation the aforementioned elastic effects. We find that, contrarily to the irreversible case, the elastic interactions first favor a decrease (increase) in the island density (mean size) for a given D/F ratio. These variations result from the interplay of kinetics and an effective decrease in adatoms binding energy. We did not consider a stress-dependent adatom diffusion, which is a microscopic one-body effect which could be embedded in the diffusion constant. Hence, we characterize the island density as function of D/F and ε separately. In addition, we find that the scaling law [Eq. (1)] is still fulfilled even with elasticity with f not depending significantly on strain.

We consider a SOS model on a cubic lattice where the surface is characterized by its height $h(\mathbf{r})$ on a square of sites $\mathbf{r}$ in unit of the substrate lattice parameter a. Atoms can diffuse to the four in-plane nearest-neighbors (nn) sites with possible jumps on the upper or lower terraces. This diffusion is described by an activation barrier E_S with the underneath layer while atoms interact with a binding energy E_N with their in-plane nn.[15] In order to disentangle different mechanisms, we do not consider wetting nor Erlich-Schwoebel effects. To study the system dynamics with KMC simulations, the energy barrier ΔE_i for the move of an atom at site i with n_i in-plane nn reads $\Delta E_i = E_S + n_i E_N - \Delta E_i^{\mathrm{el}}$. The long-range contribution $\Delta E_i^{\mathrm{el}} = a^3 \mu^{\mathrm{el}}(\mathbf{r}_i)$ is the elastic energy difference between the configurations with and without the atom at $\mathbf{r}_i$ (see Ref. 22): $\Delta E_i^{\mathrm{el}} = \mathrm{F}^{\mathrm{el}}[h(\mathbf{r}_i), h(\mathbf{r}')] - \mathrm{F}^{\mathrm{el}}[h(\mathbf{r}_i)-1, h(\mathbf{r}')]$, with $\mathbf{r}'$ the positions different from $\mathbf{r}_i$. The elastic contribution ΔE_i^{el} is usually positive and thence lowers the activation barrier ΔE_i. Different computations of elasticity are available for KMC simulations, considering either spring models,[22–25] Lennard-Jones interactions[26,27] or $1/r^3$ elastic repulsions,[17,18,21] effective barrier reduction,[28] or Green function with edge relaxation.[29] Here, we consider the total energy of a thin film with lattice parameter $a(1+\varepsilon)$ in coherent epitaxy with a substrate with *a priori* different elastic properties, computed from the continuum linear elasticity and discretized on the SOS lattice,

$$\mathrm{F}^{\mathrm{el}} = \mathcal{E}^0 a^3 \sum\nolimits_{\mathbf{r}} h(\mathbf{r})[1 - (\omega_1/2)\mathcal{H}_{ii}(h)]. \tag{2}$$

The parameters $\mathcal{E}^0$ and ω_1 depend on the isotropic film (f) and substrate (s) Poisson ratios ν and Young modulus E via $\mathcal{E}^0 = E^f \varepsilon^2/(1-\nu_f)$ and $\omega_1 = 2E^f(1-\nu_s^2)/E^s(1-\nu_f)$, see Ref. 30. The nonlocal operator $\mathcal{H}_{ii}$ is given in Fourier space by $\mathcal{H}_{ii}[h] = \mathcal{F}^{-1}\{|\mathbf{k}|\mathcal{F}[h]\}$. We consider periodic boundary conditions with $\mathbf{r}_\alpha$ ($\alpha=1,2$) integers between 0 and $N-1$, and Fourier series given by

$$\mathcal{F}[h](\mathbf{k}) = (1/N^2)\sum\nolimits_{\mathbf{r}_1,\mathbf{r}_2=0}^{N-1} h(\mathbf{r}) e^{-2i\pi\mathbf{k}.\mathbf{r}/N}. \tag{3}$$

This method allows a fast computation of the elastic problem at each KMC test. Indeed, the elastic contribution is merely the convolution

$$\mu^{\mathrm{el}}(\mathbf{r}) = -\,\omega_1 \mathcal{E}^0 \sum\nolimits_{r'} h(\mathbf{r}') G(\mathbf{r}-\mathbf{r}'), \tag{4}$$

with the $(2N-1)^2$ Green function matrix computed once

$$G(\mathbf{r}) = \frac{2\pi}{N^3} \sum_{\mathbf{k}_1,\mathbf{k}_2=-N/2+1}^{N/2} |\mathbf{k}| \cos(2\pi\mathbf{k}\,.\,\mathbf{r}/N). \tag{5}$$

In Eq. (4), we drop the constant contribution $\mathcal{E}^0 a^3$, which is a one-body effect linked to the diffusion of a single adatom on a plane substrate.[26] The latter could be better estimated by microscopic studies such as *ab-initio* calculations, which reveal a complex strain dependence of the adatom surface diffusion depending on the material under scrutiny.[31] In a continuum description,[30] the barrier ΔE_i^{el} is linked to the usual surface chemical potential, $\mu^{\mathrm{el}} = \delta \mathrm{F}^{\mathrm{el}}/\delta h(\mathbf{r})$. For infinite systems, using the distribution identity, $\int d\mathbf{k} |\mathbf{k}| e^{i\mathbf{k}.\mathbf{r}} = -2\pi/|\mathbf{r}|^3$, one would get

$$\mu^{\mathrm{el}}(\mathbf{r}) = \frac{\omega_1 \mathcal{E}^0}{2\pi} \int d\mathbf{r}' \frac{h(\mathbf{r}') - \langle h \rangle}{|\mathbf{r}-\mathbf{r}'|^3}. \tag{6}$$

This result corresponds to the argument of Ref. 7 stating that elasticity could be described in heteroepitaxy by dipolar interactions with dipoles proportional to $h(\mathbf{r}) - \langle h \rangle$. Consistently, we checked numerically that in our description, two adatoms have a repulsive $U^{\mathrm{el}}/|\mathbf{r}-\mathbf{r}'|^3$ interaction at large separations, where $U^{\mathrm{el}} = \omega_1 \mathcal{E}^0 a^3/2\pi$ is proportional to ε^2.

The simulation parameters are aimed to mimic typical semiconductors, $E_N = 0.3$ eV and $E_S = 0.8$ eV. Once a KMC move is succeeded, an atom can go equally to its four nn sites but we forbid all jumps greater than one layer in the vertical direction. The working temperature is $T = 500$ K if not explicitly mentioned. At this temperature, we checked that KMC moves of atoms with three or four nn have a negligible acceptance rate even with elasticity and consequently forbid them. The diffusion constant is $D = \frac{1}{4} a^2 \nu_0 \exp(-E_S/k_B T)$ with the bare KMC attempt frequency $\nu_0 = k_B T/h = 10^{13}$ s^{-1}. The substrate and film elastic properties are chosen to describe Si and Si$_{1-x}$Ge$_x$ materials. Hence, $a = 0.27$ nm of an equivalent cubic lattice, the misfit $\varepsilon = 0.04x$ so that $U^{\mathrm{el}} = 5$ meV and $U^{\mathrm{el}}/k_B T = 0.1$ for $x=1$. The statistical properties are obtained for each parameters with 100 different runs of systems with $N = 128$.

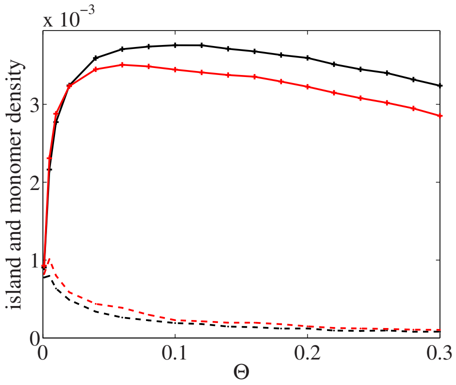

FIG. 1. (Color online) Time evolution of the total island density (full line) and monomer density (dashed) for $F = 0.1$ ML/s with vs without elasticity, red (dark gray) vs black line.

The typical time evolution of the monomer ($s=1$) and island ($s \geq 2$) density per lattice site is then depicted in Fig. 1 with and without elasticity for $F = 0.1$ monolayer per second (ML/s). After a short nucleation regime, the island density ρ saturates and slightly decreases as usual in reversible growth[15] due mainly to dimer breaking into monomers and some coalescence. However, for the *same* D/F ratio, we find that elasticity *decreases* ρ while it *increases* the mean island size $\langle s \rangle$ (see Fig. 2). The difference in island density is more important for large D/F (see Fig. 3), and was also checked at higher temperatures, $T = 600$ K and 700 K but with smaller amplitudes.

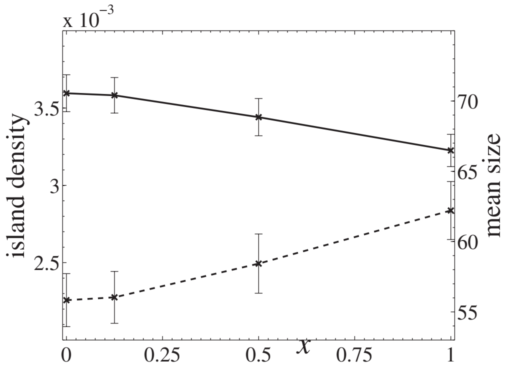

FIG. 2. Island density (full) and mean size (dashed) at $\Theta = 0.2$ as function of elasticity parametrized by x for $F = 0.1$ ML/s.

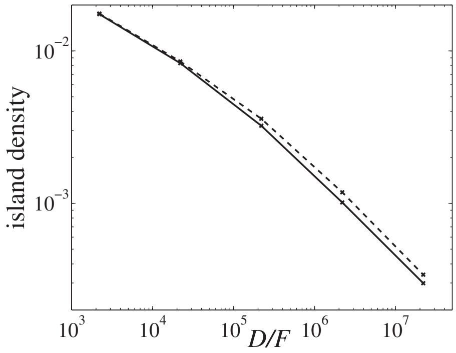

FIG. 3. Island density as function of the diffusion to deposition flux ratio with (without) $x=1$ elasticity, full (dashed) line at $\Theta=0.2$.

To explain these tendencies, we find that the repulsive elastic interactions favor atom detachment from islands and thence induce an increase in $\langle s\rangle$. This puzzling effect is analogous to the results of Ref. 32 in which the authors investigated reversible growth without elasticity and found that the island density decreases when E_N decreases. Indeed atom detachment favors the exploration of a larger phase space and therefore more stable, larger, thence less dense, islands. Hence, KMC simulations without elasticity but with a decreasing binding energy E_N (however not too small) lead to an increase in $\langle s\rangle$ and a consistent decrease in ρ at a given coverage Θ (see Fig. 4).

To estimate semiquantitatively the influence of elasticity in the reversible case, we consider a model without elasticity but where the binding energy E_N is decreased by an effective elastic barrier reduction $\Delta E_N^{\mathrm{el}}(s)$. The latter is computed using Eq. (4) at the border of a square island of size s (see Fig. 5). The saturation of ΔE_N^{el} for large s is to be expected for $1/r^3$ interactions integrated on a surface.[7]

Considering the typical island size $s\simeq 60$ for $F=0.1$ ML/s at $\Theta=0.2$, one gets a 20% decrease in ρ for $x=1$ relative to $x=0$, which compares favorably with the KMC 10% diminution for the same values. This comparison is all the more instructive as the elastic reduction $-\Delta E_N^{\mathrm{el}}$, valid for $n=1$, overestimates an effective decrease in the binding energy E_N. Moreover, this estimate does not account for the adatom repulsion from islands which favor smaller and denser islands because adatoms drift away from islands due to the elastic chemical potential gradient.[19]

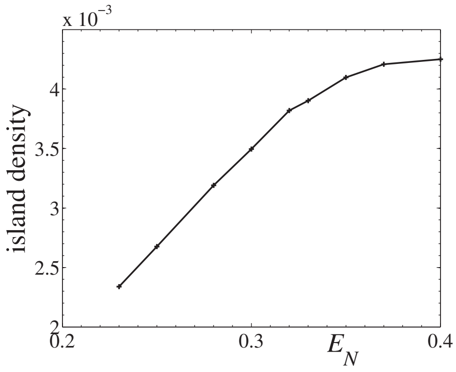

FIG. 4. Dependence of the island density on binding energy E_N without elasticity for $F=0.1$ ML/s and $\Theta=0.2$.

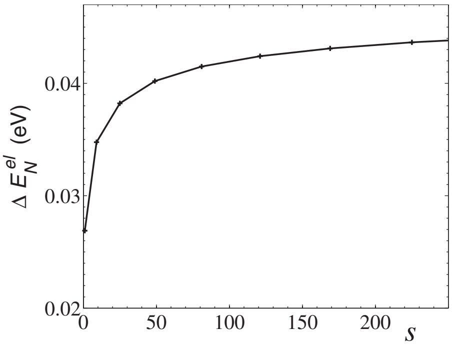

FIG. 5. Elastic reduction barrier near an island of size s.

In the irreversible case, the island density was found to increase with elasticity because the adatom repulsion effect is alone at stake.[17,18] We note also here that the reversible study of the 2D/3D transition of Ref. 20, where elasticity was treated by effective reductions in binding energies, lead to denser islands. However we checked here that the concentration of atoms on the second layer is negligible for the parameters investigated, $\varepsilon\leq 0.04$.

Finally, another quantity relevant for both experiments and theories is the island size distribution N_s. Scaling arguments predict form (1) which is parametrized by D/F and E_N/k_BT in the reversible case.[15,28] We find that Eq. (1) is indeed valid with (and without) elasticity on the whole range of the saturation regime $0.1\leq\Theta\leq 0.25$. This validity is not *a priori* evident as elasticity introduces a length scale, l_0

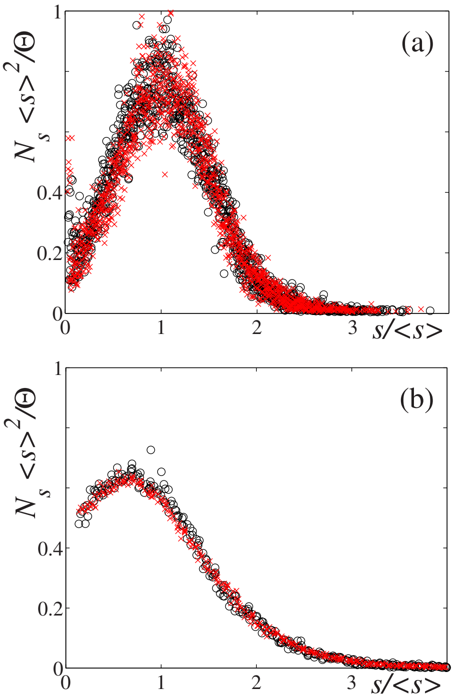

FIG. 6. (Color online) Rescaled probability distribution function with ($x=1$, red/dark gray crosses) and without (black circles) elasticity for (a) $F=0.1$ ML/s ($D/F=2\ 10^5$), and (b) $F=10$ ML/s ($D/F=2\ 10^3$), and Θ between 0.1 and 0.24.

$=E_N/\mathcal{E}^0a^2$, the Asaro-Tiller-Grinfel'd length. However, one gets here $l_0/a\simeq 10^3$ for $x=1$, which is too large to be significant for the systems under scrutiny. Consistently, we did not find any relevant dependence of the scaling function f on elasticity for both $D/F=2\times 10^3$ and 2×10^5 (see Fig. 6). Nevertheless, elasticity has an influence on $\langle s\rangle$ and therefore leads to different nonrescaled N_s distributions. Finally, note that the size distribution depends on the ratio D/F and is less dispersed in the low flux regime.

The results of KMC simulations can be used to estimate diffusion barriers otherwise hard to measure.[5,6] Indeed, when the dependence between island densities and adatom diffusion is known from KMC simulations, the measure of the former indirectly reveals the surface diffusion activation barriers. The decrease of the island density with elasticity here is obtained at D/F and E_N fixed. However, it is well known that strain also influences adatoms surface diffusion so that E_S also varies with ε, as shown by first-principles calculations.[31] Hence, a measure of the island density variation with and without elasticity, together with the island density as function of D/F as in Fig. 3, should display the variation in E_S due to strain. These measures should be done and all the other parameters kept fixed (flux, temperature, composition, surface reconstruction, etc.).[6] Note that we find here a scaling exponent $\chi=0.51$ for large D/F, very slightly decreasing with elasticity. For a given material, a strain dependent diffusion could also be introduced prior to simulations with given energies $E_S(\varepsilon)$ and $E_N(\varepsilon)$. Other effects such as surface stress, elastic anisotropy, and diffusion anisotropy were not considered but could also be implemented within the present framework.

As a conclusion, we studied island aggregation during the reversible submonolayer growth of a strained film by means of KMC simulations. Thanks to a fast calculation based on elastic interactions between every lattice sites computed via a Green function, we compute the island statistical properties and find that they crucially depend on strain. The island density (mean size) decreases (increases) with the misfit ε for fixed D/F, binding energy E_N, and temperature T. This effect is rationalized as a decrease in the effective binding energy leading to a kinetically allowed increase of the island size. In addition, the island size distribution still fulfills the usual scaling form and is not affected by elasticity for the values of the misfit that we studied. This model is well suited for the analysis of the subsequent surface evolution beyond the submonolayer regime where the 2D/3D transition should occur[1] and which will be presented in a forthcoming work.

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