Simulation of wetting-layer and island formation in heteroepitaxial growth

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Abstract

We investigate various phenomena of strained heteroepitaxial growth. To this end we study a model in $1+1$ dimension by means of off–lattice Kinetic Monte Carlo simulations. We observe the appearance of strain induced mounds upon a wetting layer, *i.e.* Stranski–Krastanov growth. The transition from 2d to 3d islands occurs at a critical layer thickness and its dependence on the growth parameters is studied quantitatively. We find that for large enough deposition rates the layer thickness as well as the size and density of islands depend on the misfit between substrate and adsorbate, only.

1 Introduction

In recent years the importance of semiconductor and opto-electronic devices fabricated in strained layer epitaxy has increased continuously. As a consequence, heteroepitaxial growth has been a matter of significant interest in, both, experimental and theoretical studies (see *e.g.* [2, 3] for an overview). In particular, the strain induced formation of self-assembled three-dimensional (3d) islands offers a promising route to the fabrication of *quantum dots*.

In this Letter, we address scenarios of heteroepitaxial growth where the deposited material has the same crystal structure as the substrate, but with a slightly different lattice constant. This mismatch between substrate and adsorbate causes strain in the growing film which can be relieved by two possible mechanisms: the introduction of misfit dislocations or the formation of dislocation-free self-assembled islands. In the frequently observed Stranski-Krastanov (SK) growth mode, see *e.g.* [4], these structures emerge on top of an adsorbate film of several monolayers (ML). Such a wetting layer is absent in the so-called Vollmer-Weber growth, where the islands form in the first adsorbate layer already.

In this work we will focus on the SK growth mode and investigate the formation of islands as well as their evolution into mound like structures, *i.e.* the so-called 2d-3d transition. To this end we adapt and advance an off-lattice Kinetic Monte Carlo (KMC) method for simulations of heteroepitaxial growth in $d = 1+1$ dimensions, which was introduced in [10, 5, 6].

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Key questions we address in this Letter are: Under which conditions does a wetting layer of adsorbate form and persist; how does its thickness depend on the growth conditions? Which microscopic processes trigger and control the aggregation of islands and their later 2d-3d transition? How do the sizes of islands and their spatial distribution depend on the parameters of the growth process?

As a step towards a theoretical understanding of these fundamental questions, we follow previous studies [7, 8, 9, 10] and choose a pair potential ansatz to model the interactions between the particles in our system. In contrast to earlier investigations of so-called *ball and spring* models, see *e.g.* [11, 12] for the simulation of heteroepitaxial growth, we do not implement strain effects in a predefined lattice structure but consider interacting particles with unrestricted continuous positions in space. As we address rather general aspects and qualitative features of heteroepitaxial growth, here, we consider a fairly simple *Lennard-Jones* (LJ) system.

In spite of its conceptual simplicity and the small number of free parameters our model describes various phenomena observed in different heterostructure systems. As demonstrated in the following we observe, for instance, a kinetically controlled wetting layer thickness as reported for heteroepitaxial growth on GaAs, *e.g.* [13, 14, 15, 16]. We also find a narrow distribution of island sizes and a density of islands which depend on growth rates, temperature and the lattice mismatch as observed in experiments, qualitatively.

2 Method

In our off-lattice model, two particles i and j are separated by a *continuous* distance r_{ij}. Pairwise interactions are given by LJ potentials of the form

$$U_{ij}\left(U_0,\sigma\right) = 4U_0\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]. \tag{1}$$

The choice of U_0 and σ characterizes the different material properties in our simulations: The interaction between two substrate particles is given by $U_{ij}\left(U_s,\sigma_s\right)$, adsorbate particles interact via $U_{ij}\left(U_a,\sigma_a\right)$. In principle, an independent pair of quantities U_0,σ could specify the substrate-adsorbate potential. For the sake of simplicity, aiming at a low number of free parameters, we will use $U_{ij}\left(\sqrt{U_sU_a},\left(\sigma_s+\sigma_a\right)/2\right)$ for the interaction between the two species of particles.

As the equilibrium distance r_0 between two LJ-particles is proportional to σ the lattice misfit ε becomes $\varepsilon = \left(\sigma_a - \sigma_s\right)/\sigma_s$. In order to save computer time the potential U_{ij} is cut off at a distance $r_{ij} > 3r_0$ where the interaction strength is less than 1% of the value at the equilibrium distance.

Given eq. (1) the activation barrier $E_{a,i}$ for a hopping diffusion step i is calculated for a frozen crystal, see [5, 6]. Note that in LJ systems exchange diffusion and other concerted moves can be neglected [10]. As demonstrated in a forthcoming publication, this simplifications are justified for small misfits ε. The rate R_i for a diffusion event i is given by an Arrhenius law

$$R_i\left(E_{a,i},T\right) = \nu_0 e^{-\frac{E_{a,i}}{k_BT}} \tag{2}$$

where T is the simulation temperature. For simplicity, we assume that the attempt frequency ν_0 is the same for all relevant processes. Numerical values given in the following correspond to the choice $\nu_0 = 10^{12}s^{-1}$.

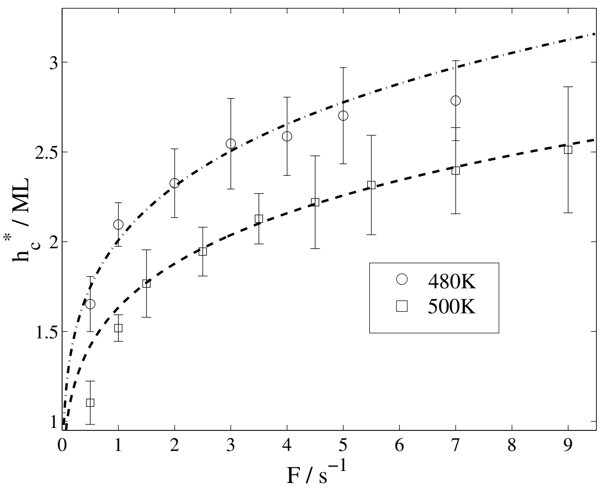


Figure 1: Kinetic critical thickness h_c^* vs. the deposition flux F for two temperatures. Both curves correspond to eq. 3, with h_o and γ obtained from the data for $T = 500K$, only.

In order to enhance layer-by-layer growth the additional Ehrlich-Schwoebel (ES) barrier for inter-layer diffusion is suppressed by hand in our simulations. One motivation for this is that LJ-systems in $d = 1 + 1$ display a much stronger ES effect than more realistic 2+1 dimensional models. More importantly, we wish to investigate the role of strain in mound formation without interference of the ES instability.

The rate R_d for the deposition of new adsorbate particles is given by $R_d = LF$, where L is the system size and F is the deposition flux. The obtained rates for deposition and diffusion processes of adsorbate particles are used in a rejection free KMC simulation [17] where in every simulation step an event j with rate R_j is drawn according to its probability $R_j/(R_d + \sum_i R_i)$.

In order to consider the deformation of the crystal, after each microscopic event (diffusion or deposition) the total potential energy of all n adsorbate and substrate particles within a circle of radius $3r_0$ around the locus of the event is minimized. This is done using a conjugate gradient descent [18] with respect to the coordinates of the n particles. To avoid the accumulation of strain caused by this local relaxation of the crystal, after a distinct number [5] of microscopic events a minimization of E_{tot} under variation of all particle coordinates in the system is performed. We would like to stress that both types of relaxation do not lead to a substantial rearrangement of the crystal in our simulations. Coordinates and activation energies of the affected particles are changed only slightly in order to accommodate with the new configuration of the crystal.

In our model growth takes place on six atomic layers of substrate with a fixed bottom layer and periodic boundary conditions in horizontal direction. The system size L (number of particles per substrate layer) is set to $L = 800$ in the following. Earlier simulations of smaller system sizes ($L = 400, 600$) revealed no significant L-dependence of the results presented here. In each simulation run $4ML$ of adsorbate are deposited with rates R_d in the range $0.5MLs^{-1} \leq R_d \leq 9.0MLs^{-1}$. After deposition of particles is finished, an additional number of about 10^7 diffusion steps is performed. In most of the simulation runs the lattice misfit is set to $\varepsilon = +4\%$ - a

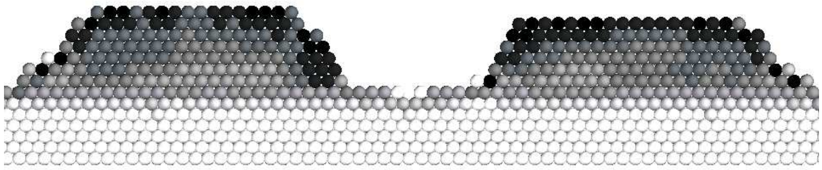


Figure 2: Section of a simulated crystal for $R_d = 7.0 MLs^{-1}$, $T = 500K$. The six bottom layers correspond to the substrate. The darker the grey level of a particle, the bigger is the average distance to its nearest neighbors.

typical value for heterostructures which grow in SK mode. As we have demonstrated in [5], strain relaxation through dislocations is not expected for such a small misfit within the first few ML. All results presented in the following were obtained by averaging over at least 15 independent simulation runs for each data point.

3 Results and Discussion

During deposition, we observe in our simulations layer-by-layer growth up to a kinetic critical thickness of the adsorbate film h_c^*. At this thickness monolayer islands located on the wetting layer undergo a rather rapid transition to bilayer islands [1]. We identify this transition as the 2d-3d transition (see *e.g.* [19]). Further growth of islands is fed both by capturing newly deposited adsorbate particles and the decomposition of the adsorbate layer. After the transition, the thickness of the wetting layer decreases to a stationary value denoted by h_c. This process can extend well into the relaxation phase after deposition is switched off.

The precise value of h_c depends on the substrate-adsorbate interaction strength $U_{sa} = \sqrt{U_s U_a}$. For $U_{sa} \leq U_a$ the adsorbate layer thickness decreases from h_c^* to $h_c = 0$ with the adsorbate islands located directly on the substrate, eventually. For $U_{sa} > U_a$ a stable *wetting-layer* thickness $h_c > 0$ persists. If we set $U_a = 0.74eV$, for instance, the choice $U_{sa} = 2.72eV$ leads to a layer thickness $h_c \approx 2ML$, whereas for $U_{sa} = 0.86eV$ a single ML of adsorbate forms the stationary wetting layer. In the following we will use the latter set of parameters and restrict ourselves to $h_c = 1ML$ as a prototype SK scenario. However, the results presented in this work should not depend on the precise value of h_c, qualitatively.

The deeper reason for the stable layer formation is the difference of activation barriers for diffusion on successive layers ΔE_a. Our choice $U_a = 0.74eV$ and $U_{sa} = 0.86eV$ leads to an activation barrier for adsorbate diffusion on the empty substrate of $E_a^{sub} \approx 0.55eV$ and $E_a^{ad} \approx 0.45eV$ for the faster diffusion on the first adsorbate layer. We find that an increase of ΔE_a by roughly $0.1eV$ results in the formation of one additional stable adsorbate layer. Our choice of parameters corresponds to a fairly realistic situation: Note, for instance, that in [20] barriers $E_a^{sub} \approx 0.64eV$ and $E_a^{ad} \approx 0.40eV$ are reported for the growth of Ge on Si(001), resulting in a wetting layer thickness of about $3ML$.

We will now focus on the kinetic critical thickness h_c^* at which the 2d-3d transition is observed during growth. Figure 1 shows h_c^* as a function of the deposition flux F for two temperatures. Increasing values of h_c^* are observed with increasing flux and decreasing temperature. Qualitatively the same dependence of the kinetic critical thickness on F and T was reported in [16] for InP/GaAs heteroepitaxial growth.

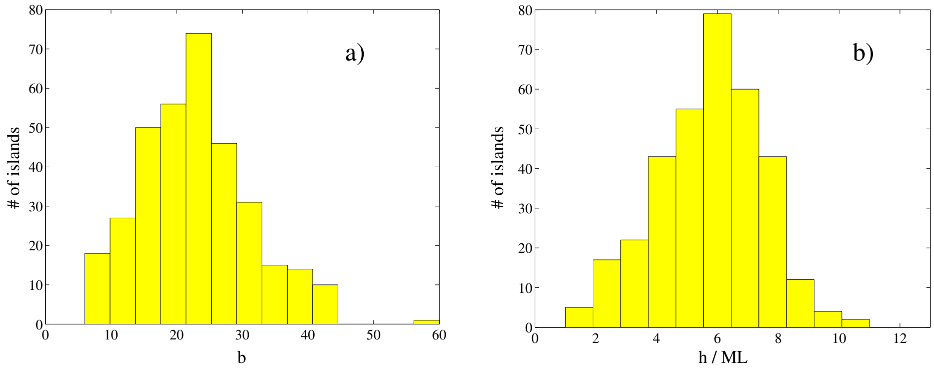


Figure 3: Base size b and height h distribution of islands for $R_d = 7.0MLs^{-1}$, $T = 500K$.

This behavior of h_c^* can be understood within our model: We consider fairly low diffusion barriers at high temperatures and suppress the ES effect explicitly. As a consequence, layer-by-layer growth is favored and second layer nucleation will play a minor role in the formation of mounds. The limiting effect which sets the characteristic time for the 2d-3d transition is the upward diffusion of particles at the edge of existing islands. Clearly, the rate for this process will decrease drastically with decreasing temperature, because a high activation barrier E_{up} has to be overcome. This rate is to be compared with the time scale set by the incoming flux. A high flux F will fill the layer before particles can perform an upward hop, and hence it will delay the 2d-3d transition.

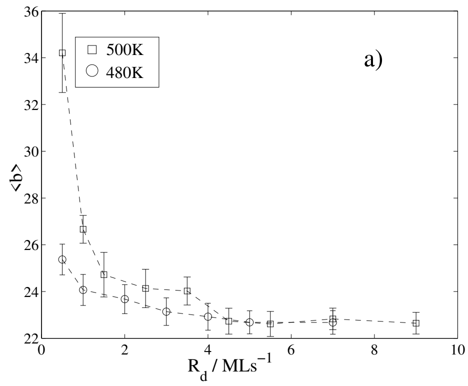
These considerations, together with the results of [16], suggest a functional dependence of h_c^* on F and T of the form

$$h_c^* = h_0 \left(\frac{F}{R_{up}} \right)^{\gamma} \tag{3}$$

where R_{up} is the diffusion rate computed from E_{up} according to eq. (2). Eq. (3) is not expected to hold for very low fluxes or high temperatures where h_c^* nearly coincides with the stationary value h_c [16].

In our simulations we observe at the 2d-3d transition a typical value of $E_{up} \approx 1.0eV$ for upward hops. Using this value we have performed a non-linear fit according to Eq. (3) with the data for $T = 500K$. It yields very good agreement for $h_o \approx 3ML, \gamma \approx 0.2$, cf. Fig. 1 (dashed lower curve). Setting the temperature to $T = 480K$ in eq. (3) with otherwise unchanged parameters yields the dashed-dotted upper curve in fig. 1. The good agreement with the simulation data strongly supports our assumptions. Note that γ is expected to vary strongly between materials systems. However a positive value of γ captures the essential F and T dependencies of h_c^* like observed in [16]. Preliminary simulation results suggest a strong dependence of h_c^* on the misfit ε. This feature will be examined in detail in a forthcoming publication.

The driving force for the formation of islands is the reduction of strain energy in the adsorbate layer. To examine this more closely we compute for each particle of the system the average distance $\overline{a}$ to its nearest neighbors. Figure 2 shows a typical section of a crystal obtained in our simulations. The islands are located on top of the stable adsorbate wetting layer which is formed on the substrate. The darker the grey level of a particle the closer is $\overline{a}$ to the lattice constant of bulk adsorbate a_a. The upper row of the substrate is slightly



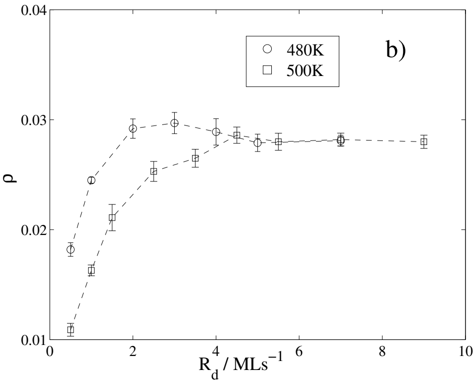


Figure 4: Average base size $< b >$ (a) of of multilayer islands and the density of multilayer islands ρ (b) vs. the deposition rate R_d for two temperatures.

affected by the adsorbate as indicated by the darker grey level. Adsorbate particles reach the preferred lattice constant at best on top and at the side faces of the islands. But also particles in the island centers may relax to some degree.

In order to characterize the islands we measure their base b given by the number of particles in the island bottom layer and their height h in monolayers. Figure 3 shows base size and height distribution for $R_d = 7.0 MLs^{-1}$ at $500K$. For this case the mean base size is 23 particles and the mean height is $5.7ML$. As one can further conclude from fig. 4(a) the mean base size first decreases with increasing R_d but becomes constant and independent of the temperature for higher values of the deposition rate. All results shown here are obtained at the end of the relaxation period with $R_d = 0$. Whereas the mean values do not change significantly, fluctuations decrease with time in this phase.

From several simulation runs for values of the misfit $2\% \leq \varepsilon \leq 4\%$ at $R_d = 4.5MLs^{-1}$ we deduce that the base size at high deposition rates is mainly determined by the misfit and decreases with increasing misfit like $b = 0.91\varepsilon^{-1}$. In misfit heteroepitaxy due to the incompatibility of the substrate and the adsorbate lattice ε^{-1} is the relevant length scale (see *e.g.* [5]). We believe that the observed dependence of the base size on the misfit for high growth rates is reminiscent of this fact. High growth rates lead therefore to a narrow size distribution around a self-limiting, strain dependent island size. Note that in situations close to equilibrium one would expect an ε-dependence $b \propto \varepsilon^{-2}$, see *e.g.* [2]. In principle, this regime should be attained within our model in the limit $R_d \to 0$ where the observed size b and island height increases drastically, indeed. Forthcoming publications will discuss the misfit and flux dependence of island formation in greater detail.

As a last aspect we consider here the density ρ of multilayer islands, *i.e.* their total number per particle in a substrate layer. Fig. 4(b) shows ρ as a function of deposition rate and temperature. For low deposition rates the density rises with increasing R_d while it decreases for increasing temperature (fig. 4). At higher values of the deposition rate the island density becomes constant. A similar behavior of the island density as a function of R_d and T was reported for InP/GaAs heteroepitaxial growth [15, 16]. The constant, temperature independent region of the density is reminiscent of the behavior of the base size for high fluxes. We also observe a dependence of ρ on ε: the island density decreases with decreasing misfit.

4 Conclusion and Outlook

In conclusion we have presented a model for simulation of heteroepitaxial growth which is capable of reproducing various important phenomena observed in strained heteroepitaxial growth. We demonstrate that the appearance of a kinetic critical wetting layer thickness can be explained on the basis of very few assumptions within the model. The formation of islands is traced back to the relaxation of strain in the adsorbate layer. We show that for large deposition rates the island size and density become independent of the temperature and are determined by the misfit between substrate and adsorbate only.

Our investigations open many new directions in which to extend these studies. We will, among other aspects, examine more closely the statistics of island sizes and island density. The aim should be a theoretical understanding of how a regular spatial ordering of islands and a very narrow distribution of their sizes can be obtained. One interesting aspect of this question is the temporal evolution of existing islands in the relaxation phase after deposition which we will study in greater detail. Another key issue is the influence of the deposition rate as it relates to the competition between equilibrium and kinetic effects in island formation. Ultimatively, we plan to extend our model to the more realistic case of $d = 2 + 1$ and to material specific pair potentials.

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References

[1] e-mail: *much@physik.uni-wuerzburg.de*, mpeg movies of the simulations are available at the web page *http://theorie.physik.uni-wuerzburg.de/~much/*

[2] P. Politi, G. Grenet , A. Marty, A. Ponchet and J. Villain, Phys. Rep. **324**, 271 (2000).

[3] W.K. Liu and M.B. Santos *Thin Films: Heteroepitaxial Systems*, (World Scientific, 1999).

[4] W. Seifert, N. Carlsson, M. Miller , M.-E. Pistol, L. Samuelson and L.R. Wallenberg, Prog. Crystal Growth Charact. **33**, 423 (1996).

[5] F. Much, M. Ahr, M. Biehl and W. Kinzel, Europhys. Lett.**56**(6), 791 (2001).

[6] F. Much, M. Ahr, M. Biehl and W. Kinzel, Computer Physics Communications **147**, 226 (2002).

[7] D.A. Faux , G. Gaynor, C.L. Carson, C.K. Hall and J. Bernholc, Phys. Rev. B **42**, 2914 (1990).

[8] W.M. Plotz, K. Hingerl and H. Sitter, Phys. Rev. B **45**, 12122 (1992).

[9] J. Kew, M.R. Wilby and D.D. Vvedensky, J. Crystal Growth **127**, 508 (1993).

[10] A. Schindler, (Dissertation, Duisburg, 1999).

[11] B.G. Orr, D.A. Kessler, C.W. Snyder, and L.M. Sander, Europhys. Lett. **19**, 33 (1992).

[12] K.E. Khor and S. Das Sarma, Phys. Rev. B **62**, 16657 (2000).

[13] C.W. Snyder, B.G. Orr, D. Kessler and L.M. Sander, Phys. Rev. Lett. **66**, 3032 (1991).

[14] D. Leonard, K. Pond and P.M. Petroff, Phys. Rev. B **50**, 11687 (1994).

[15] H.T. Dobbs, D.D. Vvedensky, A. Zangwill, J. Johansson, N. Carlsson and W. Seifert, Phys. Rev. Lett. **79**, 897 (1997).

[16] J. Johansson and W. Seifert , J. Crystal Growth **234**, 132 (2002).

[17] M.E.J. Newman and G. T. Barkema, *Monte Carlo Methods in Statistical Physics, Oxford University Press, 1999.*

[18] Press W.H., Teukolsky S. A., Vetterling W. T. and Flannery B. P., Numerical Recipes in C, Cambridge University Press, 1992

[19] E. Korutcheva, A.M. Turiel and I. Markov, Phys. Rev. B **61**, *16890 (2000).*

[20] C. Roland and G.H. Gilmer, Phys. Rev. **B 47**, *16286 (1993).*