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Various phase-field approximations for Epitaxial Growth

Andreas Rätz, Axel Voigt*

Crystal Growth Group, Research Center Caesar, Ludwig-Erhard-Allee 2, D-53175 Bonn, Germany

Abstract

We present diffuse interface approximations for a step flow model in epitaxial growth. In this model, the motion of step edges of discrete atomic layers is determined by the time evolution of an introduced phase-field variable. In order to incorporate the attachment–detachment kinetics at step edges into the phase-field model a degenerate mobility-function is established. The model is used to simulate the evolution of a step train.

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1. Introduction

Thin film epitaxy is a modern technology of growing single crystals that inherit atomic structures from substrates. It produces almost defect-free, high-quality materials that have a wide range of device applications. One of the most typical and important examples of thin film epitaxy is molecular beam epitaxy(MBE). The deposition material is thermally evaporated from a source and forms a directed beam of neutral atoms inside the chamber. Due to chemical bonding, such atoms in the vapor arrive at a given substrate or crystal surface. The adsorbed atoms—adatoms—can desorb with a limited probability into the vapor phase, but most likely they remain on the surface in diffusive motion, probing for the energetically most favorable position. Adatoms can interact with each other and form adatom clusters and islands that grow due to further sticking of diffusing adatoms to their boundaries. The morphology of the vapor–solid interface, i.e., the thin film surface, consists therefore of terraces, step edges, and kinks, and is determined by the interplay between the microscopic processes such as adsorption, desorption, island nucleation, diffusion, attachment and detachment to and from island boundaries, and island coalescence [1–3].

Burton, Cabrera and Frank [4] first developed a systematic and detailed model—BCF model—to describe the adatom density and the motion of step edges or island boundaries in epitaxial growth of thin films. In this model, the adatom density solves a diffusion equation with an equilibrium boundary condition, and step edges or island boundaries move at a velocity determined by a two-sided diffusive flux of adatoms to the edges or boundaries. Modifications of the BCF model have been made in Refs. [2,5,6] to incorporate into the boundary conditions additional effects such as the line tension and in particular the Ehrlich–Schwoebel barrier–a

*Corresponding author. Tel.: +49-228-9656236; fax: +49-228-9656187.
E-mail addresses: raetz@caesar.de (A. Rätz), voigt@caesar.de (A. Voigt).

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higher energy barrier that must be overcome by an adatom in order for it to stick to the boundary from upper terrace [7–9].

Recently, level-set based finite difference methods have been developed for the simulation of island dynamics in epitaxial growth [10–14]. Such a method is particularly efficient in handling topological changes. Phase-field models for island dynamics proposed in Refs. [15–18,21] are also able to handle topological changes, but besides [18,21] were until now not able to handle the attachment–detachment kinetics in epitaxial growth. Front-tracking finite element methods such as in Refs. [19,20] on the other side are unable to treat topological changes but can incorporate surface effects, such as edge diffusion of edge-adatoms along the steps much more naturally.

Here we will concentrate on phase-field models. Phase-field models for diffusion limited situations of epitaxial growth without the Ehrlich–Schwoebel barrier where already used in Refs. [15,16], without showing the formal justification of the model. In Ref. [15] the motion of a 1d step train is analyzed, whereas in Ref. [16] the growth of a spiral is simulated. In Ref. [17] formal matched asymptotic expansion is used to determine the asymptotic limit of vanishing interfacial thickness and show the reduction to the Burton–Cabrera–Frank model in this situation. In order to incorporate the attachment–detachment kinetics into the phase-field model a degenerate mobility-function has to be introduced. In this case the formal justification by reducing to the Burton–Cabrera–Frank model was given in Ref. [18] and for a quasi-stationary approximation of the Burton–Cabrera–Frank equation without desorption in Ref. [21].

After introducing the models, a numerical approach by adaptive finite elements is described and finally the algorithm is applied to study the evolution of a two-dimensional step train.

2. Problem description and diffuse interface approximation

We denote by $\Omega \subset \mathbb{R}^2$ the projected domain of the film surface in a two-dimensional Cartesian coordinate system, and assume that Ω is independent of time t. We denote also by $\Omega_0 = \Omega_0(t) \subset \mathbb{R}^2$ the projected domain of the substrate, and by $\Omega_i = \Omega_i(t) \subset \mathbb{R}^2$, $i = 1, \ldots, N$, that of the terraces of height i at time t, respectively. Thus, $N+1$ is the total number of layers that are exposed on the film surface. The corresponding steps are denoted by $\Gamma_i(t) = \overline{\Omega_i(t)} \cap \overline{\Omega_{i-1}(t)}$, $i = 1, \ldots, N$. Denote by $\rho_i = \rho_i(x,t)$ the adatom density on terrace $\Omega_i(t)$ ($i = 0, \ldots, N$) at time t.

In the framework of a BCF type or island dynamics model, the dynamics of the steps can be described by the diffusion equation for the adatom density $\rho_i = \rho_i(x,t)$, with $x = (x_1, x_2)$, on the surface except the step edges $\Gamma_i(t)$, the boundary condition for ρ_i on the step edges $\Gamma_i(t)$ and the normal velocity v_i of the step edges $\Gamma_i(t)$. The diffusion equation is

$$\partial_t \rho_i - D\Delta\rho_i = F - \tau^{-1}\rho_i \qquad \text{in } \Omega_i(t), \tag{1}$$

where D is the diffusion constant, F the deposition flux rate, and τ^{-1} the desorption rate. There are mainly two classes of boundary conditions. *Thermodynamic boundary conditions*:

$$\rho = \rho_{i-1} = \rho_i = \rho^*(1 + \mu\kappa_i) \qquad \text{on } \Gamma_i(t), \tag{2}$$

where ρ^* is a thermodynamic equilibrium value of the adatom density at straight steps, μ represents the step stiffness, and κ_i is the curvature of the step edge $\Gamma_i(t)$. We adopt the convention that $\kappa_i > 0$ for a convex curve such as a circle.

Kinetic boundary conditions:

$$\begin{aligned} &-D\nabla\rho_i \cdot \vec{n}_i = k_+(\rho_i - \rho^*(1 + \mu\kappa_i)) \\ &\text{on } \Gamma_i(t), \\ &D\nabla\rho_{i-1} \cdot \vec{n}_i = k_-(\rho_{i-1} - \rho^*(1 + \mu\kappa_i)) \end{aligned} \tag{3}$$

where $\vec{n}_i$ is the unit normal of the boundary $\Gamma_i(t)$ pointing from the upper into lower terrace, k_+ and k_- are the attachment rates of adatoms to the boundary $\Gamma_i(t)$ from upper and lower terraces, respectively. In general, we have $k_+ \leqslant k_-$ with our notation. The strict inequality models the Ehrlich–Schwoebel effect. Setting $k_- = k_+ = \infty$ in Eqs. (3), we obtain Eq. (2).

We assume the following laws for the normal velocity v_i of the island boundary $\Gamma_i(t)$ determined by the two-sided flux

$$v_i = -D\nabla\rho_i \cdot \vec{n}_i + D\nabla\rho_{i-1} \cdot \vec{n}_i, \tag{4}$$

where we neglect the diffusion of edge-adatoms along step edges.

We now introduce phase-field models as a diffuse interface approach for this set of equations. By a diffuse-interface approximation we understand an approximation, where the discrete height function which counts the atomic monolayers, is smeared out on a length scale $\varepsilon \ll 1$.

$$\begin{aligned} &M_2(\phi^\varepsilon,\varepsilon)\partial_t\rho^\varepsilon - \nabla\cdot(M_1(\phi^\varepsilon,\varepsilon)\nabla\rho^\varepsilon) \\ &\quad = F - \tau^{-1}\rho^\varepsilon - \partial_t\phi^\varepsilon, \\ &\alpha\varepsilon^2\partial_t\Delta\phi^\varepsilon = \varepsilon^2\Delta\phi^\varepsilon - \frac{\partial G(\phi^\varepsilon)}{\partial\phi^\varepsilon} + \frac{\varepsilon}{\rho^*\mu}(\rho^\varepsilon - \rho^*) \end{aligned} \tag{5}$$

with the approximated adatom density $\rho^\varepsilon = \rho^\varepsilon(x,y,t;\varepsilon)$ and the phase-field variable $\phi^\varepsilon = \phi^\varepsilon(x,y,t;\varepsilon)$. α is a constant and $G(\phi^\varepsilon)$ is a multiwell potential. Each minimum of the potential corresponds to a phase (terrace height) of the system. The potential can be chosen as $G(\phi^\varepsilon) = c(\phi^\varepsilon - i)^2(i+1-\phi^\varepsilon)^2$, $\phi^\varepsilon \in [i, i+1]$, $i = 0,\ldots,N-1$. The mobility function $M_1(\phi^\varepsilon,\varepsilon)$ is chosen in a way to account for the asymmetry in the attachment–detachment kinetics at the steps: the Ehrlich–Schwoebel barrier is thereby modeled by reducing the mobility of adatoms approaching the step from the upper terrace. For that purpose $M_1(\phi^\varepsilon,\varepsilon)$ is defined as $M_1(\phi^\varepsilon,\varepsilon) = D\varepsilon/(\varepsilon + f(\phi^\varepsilon)G(\phi^\varepsilon))$ with some bounded asymmetric function $f(\phi^\varepsilon)$. The function $M_2(\phi^\varepsilon,\varepsilon)$ drives the adatom density towards the equilibrium value close to the step edge and is defined as $M_2(\phi^\varepsilon,\varepsilon) = \varepsilon/(\varepsilon + G(\phi^\varepsilon))$; cf. Fig. 1. In these approximations, the phase-field variable ϕ^ε can be seen as a continuous height function. As shown by matched asymptotic expansions in Ref. [18] for $\varepsilon \to 0$ and an appropriate choice of α Eq. (5) reduce to the classical Burton–Cabrera–Frank model with kinetic boundary conditions. For $M_1 = 1, M_2 = D$ and $\varepsilon, \alpha \to 0$, Eq. (5) reduce to the classical Burton–Cabrera–Frank model with thermodynamic boundary conditions, as shown in Ref. [17]. The diffuse interface approximation introduced in Ref. [21] is a viscous Cahn-Hilliard equation with a degenerate mobility function

$$\begin{aligned} &-\nabla\cdot(M_1(\phi^\varepsilon,\varepsilon)\nabla\rho^\varepsilon) = F - \partial_t\phi^\varepsilon, \\ &\varepsilon^2\zeta_1(\phi^\varepsilon)\partial_t\phi^\varepsilon = \varepsilon^2\Delta\phi^\varepsilon - \frac{\partial G(\phi^\varepsilon)}{\partial\phi^\varepsilon} + \frac{\varepsilon}{\rho^*\mu}(\rho^\varepsilon - \rho^*). \end{aligned} \tag{6}$$

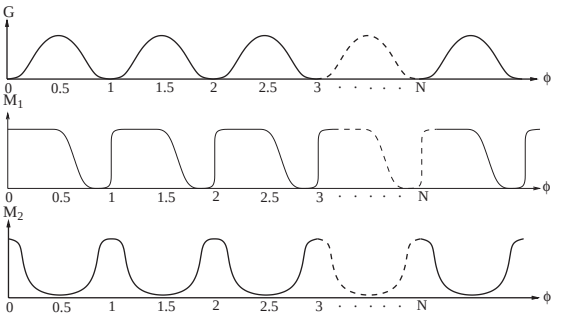

Fig. 1. Potential $G(\phi)$, mobility function $M_1(\phi)$ and function $M_2(\phi)$.

It was shown to reduce to the quasi-stationary Burton–Cabrera–Frank model without desorption. Here ζ_1 is chosen as a periodic function in ϕ. Also in this model by an appropriate choice of M_1 and ζ_1 arbitrary combinations of k_+ and k_- can be obtained. In the following, we concentrate on Eq. (5) and will drop the dependence on ε in the nomenclature and use ρ and ϕ also for the phase-field model.

3. Numerical scheme and results

A numerical scheme for the phase-field approximations is obtained by multiplying Eq. (5) with test functions ψ, integrating by parts and using a semi-implicit time-discretization scheme which can be iteratively solved starting with Eq. (8)

$$\begin{aligned} &\int_\Omega M_2(\phi^{m+1})\frac{\rho^{m+1}-\rho^m}{\Delta t_m}\psi + \int_\Omega M_1(\phi^{m+1})\nabla\rho^{m+1}\cdot\nabla\psi \\ &\quad = \int_\Omega F\psi - \int_\Omega \tau^{-1}\rho^{m+1}\psi - \int_\Omega \frac{\phi^{m+1}-\phi^m}{\Delta t_m}\psi, \end{aligned} \tag{7}$$

$$\begin{aligned} &\int_\Omega \alpha\varepsilon^2\frac{\phi^{m+1}-\phi^m}{\Delta t_m}\psi + \int_\Omega \varepsilon^2\nabla\phi^{m+1}\cdot\nabla\psi \\ &\quad = -\int_\Omega \frac{\partial G(\phi^m)}{\partial\phi}\psi + \int_\Omega \frac{\varepsilon}{\rho^*\mu}(\rho^m - \rho^*)\psi. \end{aligned} \tag{8}$$

This system can now be discretized by finite elements. We use an adaptive strategy for mesh refinement and coarsening in order to account for the high spacial resolution needed at the step edges. The algorithm is applied to study the

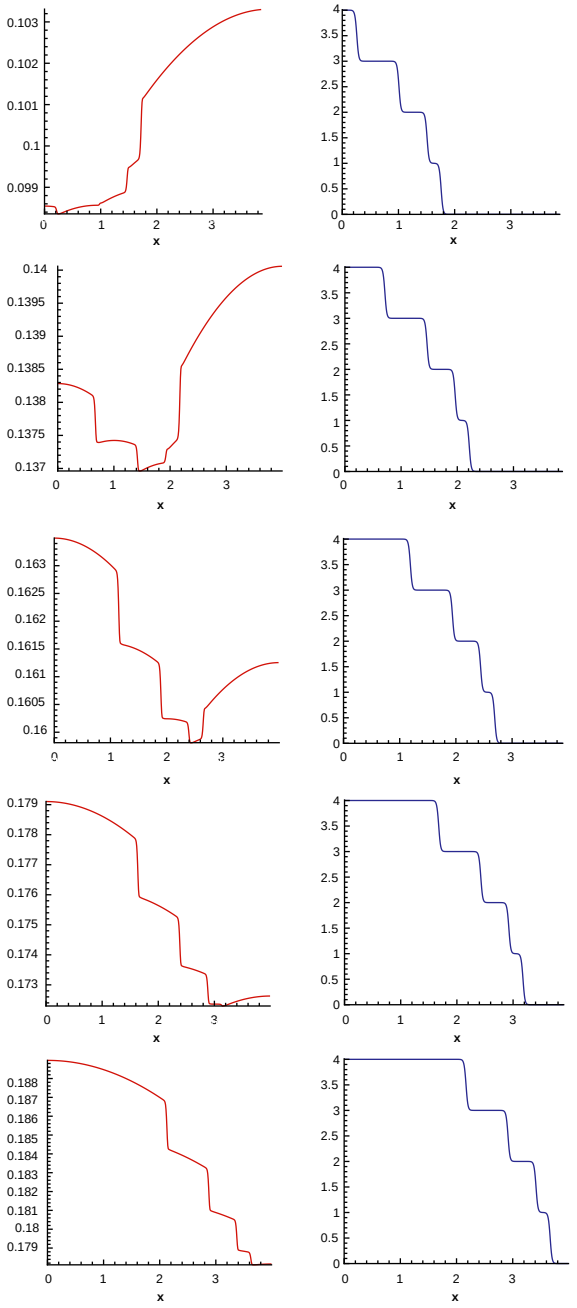

Fig. 2. Phase-field variable (right) and adatom density (left) at various times, $t_1 = 1.0 \times 10^{-3}$, $t_2 = 2.0 \times 10^{-3}$, $t_3 = 3.0 \times 10^{-3}$, $t_4 = 4.0 \times 10^{-3}$, $t_5 = 5.0 \times 10^{-3}$.

evolution of a step train. The parameter used are chosen to model a strong Ehrlich–Schwoebel barrier: $G(\phi) = 18\phi^2(1-\phi)^2$, $D = 1000$, $f(\phi) = 200\phi^{20}$, $\rho^* = 0.1$, $\mu = 1.0$ and $\alpha = 1.0$. In the first example, a one-dimensional step train consisting of 4 steps with different terrace width is considered. No-flux boundary conditions are applied. Fig. 2 shows the phase-field variable, indicating the height of film, and the adatom density.

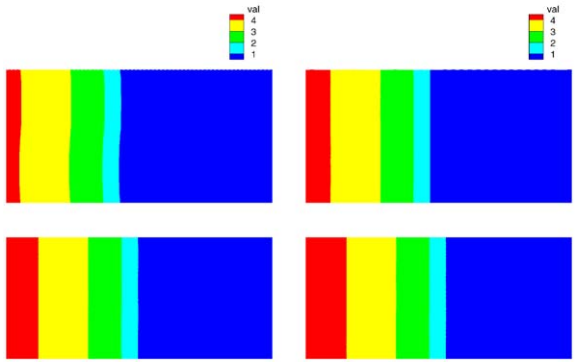

Fig. 3. Phase-field variable at various times, $t_1 = 0.5 \times 10^{-3}$, $t_2 = 1.0 \times 10^{-3}$, $t_3 = 1.5 \times 10^{-3}$, $t_4 = 2.0 \times 10^{-3}$.

The jump in the adatom density is clearly observed. The height and the direction of the jump depend on the size of the terraces. Due to the no-flux boundary conditions the highest and lowest terrace have a strong influence on the adatom density profile. The initial condition is set to be a superposition of tanh-functions for ϕ and the equilibrium value for ρ.

The second example shows a two-dimensional step train consisting of 4 slightly perturbed steps in a domain of length 4. The perturbation is a sinqfunction with amplitude 0.2 and wavenumber 1. Again no-flux boundary conditions are applied at left and right. Up and down periodic boundary conditions are set. Fig. 3 shows the phase-field variable.

The small perturbation is smoothed out due to the strong curvature effects resulting from the parameter $\mu = 1.0$. Only at the first time instant the perturbation can be observed. For $t \geqslant 1.0 \times 10^{-3}$ the steps are straight lines.

4. Conclusions

Phase-field models for epitaxial growth were described. These models can be seen as a diffuse

interface approximation for step-flow models of Burton–Cabrera–Frank type. Approximations for both thermodynamic (diffusion limited) and kinetic (attachment limited) boundary conditions are shown. Due to the use of asymmetric degenerate mobility function the Ehrlich–Schwoebel barrier can be modeled.

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References

[1] A.-L. Barabási, H.E. Stanley, Fractal Concepts in Surface Growth, Cambridge University Press, Cambridge, 1995.
[2] J. Krug, Physica A 318 (2002) 47.
[3] A. Pimpinelli, J. Villain, Physics of Crystal Growth, Cambridge University Press, Cambridge, 1998.
[4] W.K. Burton, N. Cabrera, F.C. Frank, Phil. Trans. Roy. Soc. London Ser. A 243 (866) (1951) 299.
[5] G. S. Bales, A. Zangwill, Phys. Rev. B 41 (9) (1990) 5500.
[6] R. Ghez, S.S. Iyer, IBM J. Res. Develop. 32 (1988) 804.
[7] G. Ehrlich, F.G. Hudda, J. Chem. Phys. 44 (1966) 1036.
[8] R.L. Schwoebel, J. Appl. Phys. 40 (1969) 614.
[9] R.L. Schwoebel, E.J. Shipsey, J. Appl. Phys. 37 (1966) 3682.
[10] R.E. Caflisch, M.F. Gyure, B. Merriman, S. Osher, C. Ratsch, D. Vvedensky, J. Zink, Appl. Math Lett. 12 (1999) 13.
[11] S. Chen, B. Merriman, M. Kang, R.E. Caflisch, C. Ratsch, L.-T. Cheng, M. Gyure, R.P. Fedkiw, C. Anderson, S. Osher, J. Comput. Phys. 167 (2001) 475.
[12] M.F. Gyure, C. Ratsch, B. Merriman, R.E. Caflisch, S. Osher, J. Zinck, D. Vvedensky, Phys. Rev. E 58 (1998) R6931.
[13] M. Peterson, C. Ratsch, R.E. Caflisch, A. Zangwill, Phys. Rev. E 64 (2001) 061602.
[14] C. Ratsch, M.F. Gyure, R.E. Caflisch, F. Gibou, M. Peterson, M. Kang, J. Garcia, D.D. Vvedensky, Phys. Rev. B 65 (2002) 195403.
[15] F. Liu, H. Metiu, Phys. Rev. E 49 (1997) 2601.
[16] A. Karma, M. Plapp, Phys. Rev. Lett. 81 (1998) 4444.
[17] A. Rätz, A. Voigt, Appl. Anal. 2004, to appear.
[18] A. Rätz, A. Voigt, Euro. J. Appl. Math. 2004, to appear.
[19] E. Bänsch, F. Haußer, O. Lakkis, B. Li, A. Voigt, J. Comput. Phys. 194 (2004) 409.
[20] E. Bänsch, F. Haußer, A. Voigt, Technical Report 36, Research Center Caesar, 2003.
[21] F. Otto, P. Penzler, A. Rätz, T. Rump, A. Voigt, Technical Report 35, Research Center Caesar 17 (2004) 477.