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EPITAXIAL CRYSTAL GROWTH

HUNG HOANG DIEU *

Abstract. This article deals with a numerical simulation of the spiral growth using a phase-field formulation of the Burton-Cabrera-Frank model. The numerical scheme developed for the simulation is based on a finite difference method. We investigate the influence of numerical parameters to the growth and results are presented.

Key words. free boundary problem, phase field model, epitaxial growth, FDM

AMS subject classifications. 35K55, 35R35, 80A20, 80M40

1. Introduction. Crystallization is the process where solid crystals are formed from melt, solution or vapour phase. There are two major stages involved in the crystallization process - nucleation and crystal growth. Nucleation is the stage where crystal forming units (atoms, ions or molecules) gather into clusters which are unstable until they reach a critical size. Stable clusters are called nuclei which have three-dimensional formation. Because the workings of three-dimensional nucleation are analogous to those for two-dimensional nucleation, we will only consider the latter one. After nuclei are created, crystal growth begins. It is the stage where new crystal forming units are incorporated into the crystal lattice. In this article the term atom is used for the crystal forming unit.

Seed crystals are used to bypass the nucleation stage; thus, the growth can start immediately. In this article we deal with phenomenon of growth of a crystal over the substrate which acts as a seed crystal. Such phenomenon is called epitaxy.

The history of crystal growth goes back to the seventeenth century when the Danish anatomist Nicolas Steno introduced law of the constancy of interfacial angles. Later in the nineteenth century crystals were classified into seven crystal systems due to their symmetry. Study of crystal growth at atomic level has started since the 1930s by Volmer, Kossel, and Stranski who have developed the theory of growth of perfect crystals. Burton, Cabrera, and Frank continued their works and developed the theory of real crystals in 1951 [6]. Mullins and Sekerka developed the theory of morphological stability in 1963. The dynamics of spiral ridge formation in the BCF model has been investigated in the work of Karma-Plapp [5] where quantitive predictions for the selected step spacing as a function of the deposition flux have been made.

2. The Model. There are two fundamental models of crystal growth mechanism: two-dimensional nucleation growth of perfect crystals and spiral growth of real crystals.

Recently, crystal growth has been investigated from a mathematical point of view. For more details, we refer the reader to the works of Guo-Nakamura-Ogiwara-Tsai [11] and Ohtsuka [12].

* Department of Mathematics, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, Prague, Czech Rupublic.

2.1. Two-dimensional growth. Classically epitaxial crystal growth is modeled using Burton-Cabrera-Frank (BCF) theory. According to that theory atoms are first adsorbed to the crystalline surface. Such atoms are called adatoms. Then they diffuse freely along the surface and they can either desorb from the surface with a probability $1/\tau_S$ per unit time, or they are incorporated into the crystal at one of the three sites: ledge site, step site or kink site. Incorporation at a kink site will be the most energetically favorable. Two-dimensional growth occurs only at relatively higher super-saturation when random nuclei are generated on existing flat surface.

2.2. Spiral growth. Real crystals are not perfect, they contain dislocations which are crystallographic defects in the structure of the crystal lattice as depicted in Fig. 2.1. The presence of dislocations influences the mechanism of crystal growth. If dislocations are present in the crystal lattice of the substrate, they provide a way of controlling the growth as they are a source of new steps where adatoms are incorporated to. Hence, the growth can proceed at lower temperatures and supersaturations. Steps wind around the dislocation and produce spirals or closed loops. Let l be the final steady-state spacing between successive steps and $x_S = \sqrt{D_S \tau_S}$ the diffusion length, where D_S is the surface diffusion constant. Then there are two different growth regimes depended on the ratio of l and x_S. When desorption is fast $(x_S << l)$, only adatoms which are deposited near a step can be incorporated. In contrast, when desorption is negligible all deposited atoms reach a step. This regime refers to step-flow growth at temperatures.

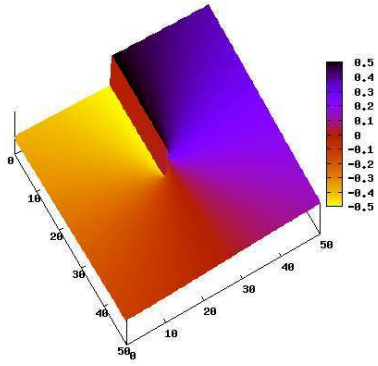


Fig. 2.1: Single screw dislocation

The BCF model consists of a diffusion equation for the concentration of adatoms, as well as two boundary conditions at the growing steps:

$$\partial_t c^S = D_S \Delta c^S - \frac{1}{\tau_S} c^S + F \tag{2.1}$$

in the domain S and

$$c^S = c^S_{eq}(1 + \kappa\Omega\gamma/k_B T) \tag{2.2}$$

$$v_n = D_S \Omega [\frac{\partial c^S}{\partial n+} - \frac{\partial c^S}{\partial n-}] \tag{2.3}$$

on the interface $\Gamma(t)$. Here, c^S is the density of adatoms on the surface S, D_S is the surface diffusion coefficient, τ_S is the mean time for the desorption of adatoms from to the solution, F is the deposition rate, c^S_{eq} is the equilibrium concentration for a straight step, κ is the curvature of step $\Gamma(t)$, Ω is the area of a single atom, γ is the step stiffness, k_BT describes the thermal energy for a fixed temperature T and v_n is the normal velocity of the step and $\frac{\partial u}{\partial n\pm}$ is the normal concentration gradient on the lower $(+)$ and upper $(-)$ side of the step.

Direct numerical simulations of the sharp-interface problem $(2.1) - (2.3)$ are difficult, since the position of the step has to be tracked explicitly [3]. The BCF model described above can be replaced by a phase field model where a higher-dimensional order parameter function $\Phi(x, y, t)$ is introduced whose values indicates the phase at a given position. In our case, the phase field $\Phi(x, y, t)$ describes the height of the epitaxial solid by the number of monoatomar layers. The phase-field model was previously used by Liu and Metiu [7] for one-dimensional step train, then enhanced by Karma and Plapp [5]. This model, which represents a system of parabolic partial differential equations, has the form

$$\partial_t c^S = D_S \Delta c^S - \frac{c^S}{\tau_S} + F - \Omega^{-1}\partial_t \Phi \tag{2.4}$$

$$\alpha\partial_t \Phi = \xi^2 \Delta\Phi + sin(2\pi(\Phi - \Phi_S)) + \lambda c^S(1 + cos(2\pi(\Phi - \Phi_S))) \tag{2.5}$$

in the domain S, where α is the time relaxation parameter, ξ is the width of steps between terraces, Φ_S is the height of the initial substrate surface and λ is the coupling constant.

The boundary conditions are given by

$$\frac{\partial c^S}{\partial n}(t, x) = \frac{\partial \Phi}{\partial n}(t, x) = 0, t \in (0, T), x \in \partial S \tag{2.6}$$

The initial conditions are given by

$$c^S(0, x) = 0, x \in S \tag{2.7}$$

$$\Phi(0, x) = \Phi_S(x), x \in S \tag{2.8}$$

3. Numerical scheme. For solving the free boundary problem of epitaxial crystal growth we use an explicit scheme of a finite difference method which is easy to develop. Using a finite difference method, one must first discretize the problem's domain, then derivative expressions are replaced with equivalent finite differences.

We consider S to be a rectangular domain $(0, L_1) \times (0, L_2)$ which is to be discretized. We introduce this notation: $h_1 = \frac{L_1}{N_1}, h_2 = \frac{L_2}{N_2}$ are the mesh sizes on the surface S and $\omega^S_h = \{(ih_1, jh_2)|i = 1, ..., N_1 - 1, j = 1, ..., N_2 - 1\}$ are the grids of internal nodes. We discretize the time interval $[0, T] : T_\tau = \{k\tau|k = 0, ..., N_T\}$ where $\tau = \frac{T}{N_T}$ is the time step. Then we can use a grid function $u : T_\tau \times \omega^S_h \to \mathbb{R}$ for which $u^k_{ij} = u(ih_1, jh_2, k\tau)$.

Time derivative are approximated by forward difference

$$\partial_t u^k = \frac{u^{k+1} - u^k}{\tau}$$

and the space derivatives are approximated by second-order central differences:

$$\partial_x^2 u_{ij}^k = \frac{u_{i+1,j}^k - 2u_{ij}^k + u_{i-1,j}^k}{h_1^2}$$
$$\partial_y^2 u_{ij}^k = \frac{u_{i,j+1}^k - 2u_{ij}^k + u_{i,j-1}^k}{h_2^2}.$$

The Laplace operator in two dimensions is given by $\Delta_h u^k = \partial_x^2 u_{ij}^k + \partial_y^2 u_{ij}^k$.
The explicit schema has the form

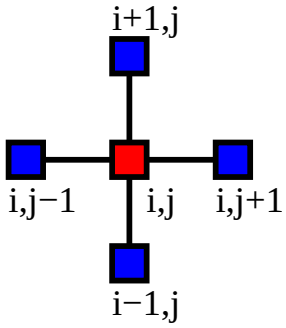
$$\begin{aligned}\alpha\frac{\Phi_{ij}^{k+1} - \Phi_{ij}^k}{\tau} &= \xi^2 \Delta_h \Phi_{ij}^k + sin(2\pi(\Phi_{ij}^k - \Phi_{S_{ij}}^k)) \\ &\quad + \lambda c_{ij}^{S^k}(1 + cos(2\pi(\Phi_{ij}^k - \Phi_{S_{ij}}^k))) \\ \frac{c_{ij}^{S^{k+1}} - c_{ij}^{S^k}}{\tau} &= D_S \Delta_h c_{ij}^{S^k} - \frac{c_{ij}^{S^k}}{\tau_S} + F - \Omega^{-1}\frac{\Phi_{ij}^{k+1} - \Phi_{ij}^k}{\tau}\end{aligned}$$

for $i = 1, ..., N_1 - 1, j = 1, ..., N_2 - 1, k = 0, ..., N_T$.
Finally we express Φ and c^S

$$\begin{aligned}\Phi_{ij}^{k+1} &= \Phi_{ij}^k + \frac{\tau\xi^2}{\alpha}\Delta\Phi_{ij}^k + \frac{\tau}{\alpha}sin(2\pi(\Phi_{ij}^k - \Phi_{S_{ij}}^k)) \\ &\quad + \frac{\tau\lambda}{\alpha}c_{ij}^{S^k}(1 + cos(2\pi(\Phi_{ij}^k - \Phi_{S_{ij}}^k))) \qquad (3.1)\end{aligned}$$

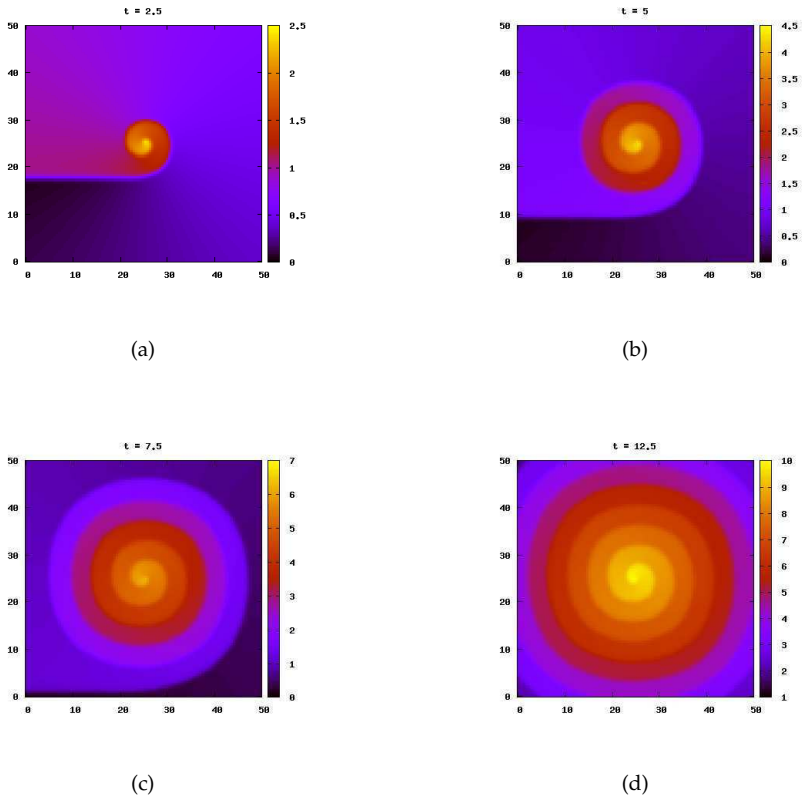
$$c_{ij}^{S^{k+1}} = c_{ij}^{S^k} + \tau D_S \Delta c_{ij}^{S^k} - \frac{\tau}{\tau_S}c_{ij}^{S^k} + \tau F - \frac{\Phi_{ij}^{k+1} - \Phi_{ij}^k}{\Omega_1} \qquad (3.2)$$

for $i = 1, ..., N_1 - 1, j = 1, ..., N_2 - 1, k = 0, ..., N_T$. That means we can obtain the values at time $k + 1$ from the corresponding ones at time k which can be illustrated using five-point stencil as follows



For $h = h_1 = h_2$ this explicit method is known to be numerically stable and convergent whenever $\frac{\xi^2\tau}{\alpha h^2} < \frac{1}{4}$ and $\frac{D_S\tau}{h^2} < \frac{1}{4}$.
The boundary conditions are treated by mirroring the values in the inner nodes across the boundary.

4. Numerical results. In the numerical experiments the parameters are set up as follows: $\Omega = 2.0$, $\alpha = 1.0$, $\xi = 1.0$, $\lambda = 10.0$, $D_S = 2.0$, $F = 3.0$, $\tau = 0.00025$, $N_T = 100000$, so that $T = 25$. The dimensions of ω_h^S are 100×100 and the spatial step size is set to $50/99$. The initial height of the substrate Φ_S is formed by $\frac{arctan(y/x)}{2\pi}$ for the dislocation. We investigated the influence of the parameter τ_S to the spiral



(a) (b)

(c) (d)

Fig. 4.1: Spiral ridge at different times t for $\tau_S = 0.1$

growth. The numerical simulations show that for small τ_S the spiral finds its final step spacing l essentially after a single rotation which is demonstrated in Fig. 4.1. In contrast, for very large τ_S the transient spiral ridge evolves slowly towards a spiral with a constant l. This surface evolution is demonstrated in Fig. 4.2.

From these numerical simulations we conclude that step spacing is dependent on desorption time. The larger desorption time is, the smaller the step spacing is. In the future works, we would consider elastic deformation of the solid generated by the misfit strain between atoms in the epitaxial layer and the substrate and include it to the model [2-3].

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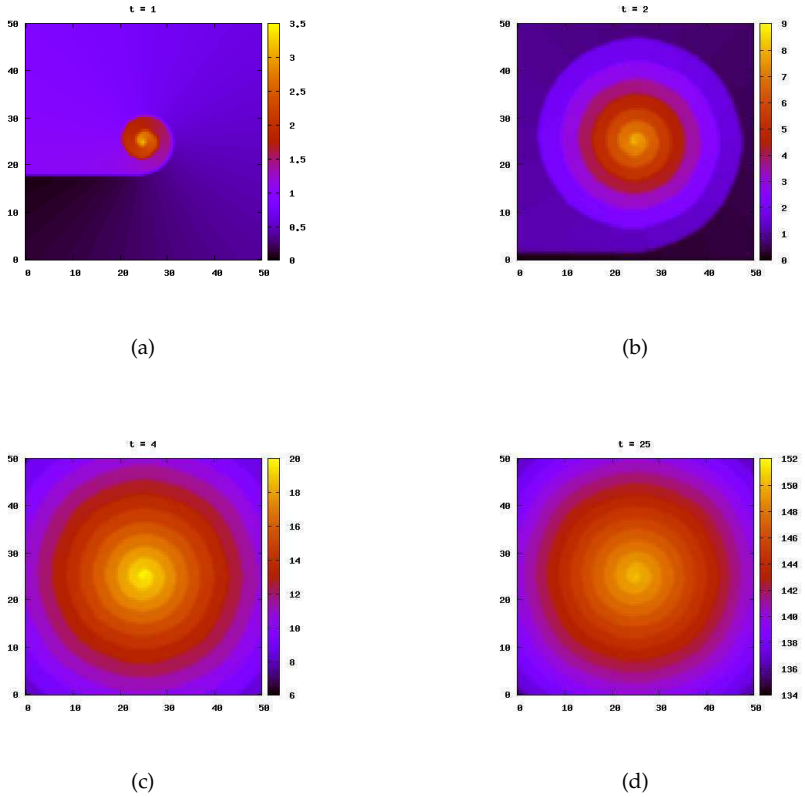

(a) (b)

(c) (d)

Fig. 4.2: Spiral ridge at different times t for $\tau_S = 1 \times 10^{200}$

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