Spiral growth of a crystal due to chemical reaction

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Abstract. The article is devoted to the study of crystal growth due to chemical reactions in multicomponent media via terrace-kink-step mechanism. The theory of Burton, Cabrera and Frank is developed and applied to multicomponent case. Equations are obtained for speed of movement of single step, group of steps at certain interstep distance. Growth spirals caused by screw dislocations are considered. Growth rate of the crystal is found. Impact of partial pressures of reaction products on diffusion length of adatoms and growth rate is analyzed.

1. Introduction
Nowadays crystals, thin films and methods for their growth are in great demand in industry and there is a significant amount of work devoted to theoretical aspects of crystal growth via different mechanisms: crystallization, nucleation, sublimation and many others. One of the mechanisms playing key role during the growth at low supersaturation is growth due to terrace-kink-step mechanism, at which atoms adsorbed to the surface diffuse one-by-one towards steps and kinks and then incorporate into crystalline lattice. This mechanism was described in the classical works of Burton, Cabrera, and Frank (BCF) and related generalizations in numerous reviews and books [1-2]. A theory has been proposed for describing the growth of single-component crystals via this mechanism. The theory made it possible to predict the dependence of the crystal growth rate on various growth conditions, and to explain why the crystals grow even at very low supersaturations (<1%), when nucleation of nanoislands on the surface is impossible, and therefore growth by the mechanism of nucleation is suppressed. It should be noted that the theory was refined and modified many times, and attempts were made to apply it to multicomponent crystals growing due to chemical reactions, in particular, gallium nitride [3]. However, in general, the theory was developed mainly with respect to single-component crystals growing from its own saturated vapors [1], atomic fluxes or solutions, and as far as we know, there is no generalization of the theory for multicomponent systems with chemical reactions, which would allow one to fully describe the growth of arbitrary single-component or multicomponent crystal from multicomponent media due to chemical reaction. In fact, many modern methods of thin films growth involving chemical reactions are widely used in industry, in particular, semiconductor (thin films of AIII-BV, AII-BIV semiconductors). HVPE (hydride vapor phase epitaxy), MOCVD (metal-organic chemical vapor deposition) and MBE (molecular beam epitaxy) should be mentioned, the growth during which occurs at the presence of flows of various chemical components towards the surface. The processes and surface structures, which are
observed during such multicomponent growth [4], a very similar to ones observed during the growth in single-component system. One can notice steps, terraces, growth spirals. That’s why we suppose that all of the mechanisms described by BCF theory are also valid for the growth of multicomponent crystals. The main goal of this work is to extend mathematical apparatus of this theory on multicomponent systems.

To extend existing BCF theory a series of particular problems should be understood and solved. Namely these problems are: 1) growth of single-component crystal due to chemical reaction from multicomponent media (e.g. Si epitaxy in atmosphere of SiH\textsubscript{4} and H\textsubscript{2}) It should be noted that the formation of molecular crystals also may belong to this case; 2) growth of multicomponent crystal from the atmosphere of vapors of its individual components (e.g. growth of GaN via MBE, which involve individual fluxes of Ga and N). After solving these problems one could combine solutions to describe growth of arbitrary multicomponent crystal when the individual components are being delivered to its surface due to chemical reaction (e.g. growth of GaN via HVPE, when Ga and N arrive in the form of reagents GaCl and NH\textsubscript{3}, which react near the surface).

This work is the first in a series of papers devoted to extension of BCF theory to multicomponent systems and it considers the first abovementioned problem, namely, growth of single-component crystal due to chemical reaction in multicomponent media via terrace-step-kink and spiral mechanisms.

2. Growth of single-component crystal due to chemical reaction

Let us consider a crystal growing from a multicomponent medium as a result of a chemical reaction. In general, the reaction can be written as:

\[
v_1A_1(g) + v_2A_2(g) + \cdots + v_NA_N(g) \rightarrow S(s) + v'_1B_1(g) + \cdots + v'_NB_N(g) \quad (1)
\]

where \(A_i(g)\) are the initial chemical reagents in liquid or gas state, \(B_i(g)\) are reaction products, \(S(s)\) is a solid crystalline phase; \(v_i\) are the stoichiometric coefficients. As a result of this reaction, \(S(s)\) adatoms are delivered to the surface of the crystal. We believe that the growth of a crystal having terraces-steps-kinks is caused by the following factors: the exchange between the vapor and the adsorption layer due to chemical reaction, diffusion of the atoms of the adsorption layer along the steps, their subsequent diffusion along steps to kinks, and incorporation into crystalline lattice which ensures movement of the step. The mathematical formulation of the problem is completely analogous to that presented in the works of Burton, Cabrera, and Frank [1], except for the fact that in this paper we consider the growth of a crystal in a multicomponent system. The main difference is that in a multicomponent system different substances are present in the gas phase and on the surface. For simplicity, we assume that the average distance between kinks is significantly less than the diffusion length of the adatoms, i.e. concentration of kinks at the step is sufficiently high and step can be considered as continuous drain, due to reasoning similar to those given in [1].

In general, the crystal \(S(s)\) can consist of atoms of one type, for example, silicon (Si), or from atoms of several types, such as gallium nitride (GaN). We will consider the first case, the second will
be considered in subsequent papers. It is also believed that only adatoms in adsorbed state participate in the reverse chemical reaction, since much more energy is needed to remove atoms incorporated into lattice (and thus having a large number of bonds). We assume that the reaction of formation of the solid phase occurs directly on the surface, and there is no reaction in the gas phase, which is true for many growth processes.

Figure 1. Mechanism of crystal growth due to chemical reaction. Flux of chemical reagents and formation of $S_{(s)}$ adatoms on the surface (upper insets), and their subsequent diffusion and incorporation in steps (lower inset). Evaporation is the process inverse to upper figure.

For comprehensive description of the dependence of the growth rate of the crystal on the conditions, it is necessary to solve a number of individual tasks, as was done in the classical work of Barton, Cabrera, and Frank [1], namely, to find the speed of movement of a single step, the speed of a series of parallel steps, and the speed of movement of a spiral step formed due to screw dislocation.

Firstly, we should find the speed of single step. Using the principle of detailed equilibrium, it is easy to find in a general form the fluxes of atoms moving from the gas phase to the adsorbed state on the surface $j_{v↓}$ and back to gas $j_{v↑}$ and their difference $j_v$:

$$j_v = j_{v\downarrow} - j_{v\uparrow} = k_d \prod_{i=1}^{N} C_{A_i}^{v_i} - k_r n_z \prod_{i=1}^{M} C_{B_i}^{v_i} =$$

$$= \left( \frac{K}{K_{eq}} - \frac{n_s}{n_{s0}} \right) k_r n_{s0} \prod_{i=1}^{M} C_{B_i}^{v_i}$$

(2)

where $k_d$ is the rate constant of the direct chemical reaction, $k_r n_{s0}$ is the rate constant of the reverse reaction, $K = \prod_{i=1}^{N} C_{A_i}^{v_i} / \prod_{i=1}^{M} C_{B_i}^{v_i}$, $K_{eq} = k_r n_{s0} / k_d$ is the equilibrium constant of chemical reaction (1), $C_{B_i}$ and $C_{A_i}$ are concentrations of reagents, $n_s$ and $n_{s0}$ are the true and equilibrium concentrations of adsorbed atoms, respectively. Comparing formula (2) and the equation for the flux from the gas phase obtained in [1] for crystal growth from own vapors, it is not difficult to see that the role of supersaturation in the multicomponent case is played by the ratio $K / K_{eq}$, and the role of the evaporation time of adatoms from the surface is $1 / k_r \prod_{i=1}^{M} C_{B_i}^{v_i}$. It should be noted that in general case...
during the growth direct evaporation of adatoms from the surface is also possible and expression (2) on the right-hand side should have the term $-n_s/\tau_s$, where $\tau_s$ is the true lifetime of adatoms in the absence of a chemical reaction. However, we believe that $\tau_s \gg 1/k_r \prod_i^M c_{B_i}^{V_l}$, evaporation is extremely slow compared to the rate of reverse chemical reaction, and therefore we neglect it. In further papers we will consider effects which may arise due to competition of fluxes caused by own vapors and by chemical reaction.

To find the speed of movement of an individual step, we introduce the following variables, using the notation of [1]:

$$\sigma = \alpha - 1$$
$$\sigma_s = \alpha_s - 1$$

where $\sigma$ is the supersaturation in the gas phase, $\alpha = \frac{K}{K_{eq}}$, $\sigma_s$ is the supersaturation of the adatoms on the surface, $\alpha_s = n_s/n_{s0}$. In general, $n_s$ depends on the distance to the step, whereas $K$ and the concentrations of the components are assumed to be independent from this distance. Further mathematical calculations are very close to that ones obtained in [1]. To find the diffusion flux of adatoms over the surface $j_s$ by analogy with [1] one can write the following equation:

$$j_s = -D \nabla n_s = Dn_{s0} \nabla \varphi$$

where $\varphi = \sigma - \sigma_s$ is determined by supersaturation in the gas phase and on the surface. The flux of the adatoms from the gas to the surface $j_v$, using this notation, can be written as follows:

$$j_v = (\alpha - \alpha_s) k_r n_{s0} \prod_i^M c_{B_i}^{V_l} = \varphi k_r n_{s0} \prod_i^M c_{B_i}^{V_l}$$

If the supersaturation is sufficiently small, then the growth rate of the crystal and, correspondingly, the movement of the steps can also be neglected. In this case, when solving the problem of diffusion of adatoms towards the step, it can be considered immobile, so that the solution becomes stationary. Under these conditions, the value of $\varphi$ must satisfy the continuity condition:

$$\nabla \cdot j_s = j_v$$

Substituting $j_s$ (3) and $j_v$ (4), as it was done in [1], we obtain equation for function $\varphi$:

$$\lambda_s^2 \nabla^2 \varphi = \varphi$$

where the mean free path of the adatom of crystalline phase is introduced $\lambda_s^2 = \frac{D}{k_r \prod_i^M c_{B_i}^{V_l}}$. Note that in our case, unlike [1] it is not a constant and depends on the rate of reverse chemical reaction and concentrations of reaction products.

The coordinate system is chosen so that the step lies on the x-axis. The y coordinate determines the distance from the step. As boundary conditions at infinity, we choose $\varphi|_{y=\infty} = 0$ ($\sigma = \sigma_s$). We will slightly complicate the task for generality and assume that directly at the step the flux of the component, will depend not only on diffusion, but also on the incorporation rate $\beta$ of adatom into step:
\[-D \frac{dn_s}{dx} = \beta V (n_s - n_{s0}) \bigg|_{y=0}\]

where V is the volume of the adatom. Then by making a replacement one can obtain:

\[D \frac{d\varphi}{dx} = \beta V (\sigma - \varphi) \bigg|_{y=0}\]

The solution of this diffusion problem, as it can be easily shown, is \(\varphi = C \exp(\pm \frac{\gamma}{\lambda_s})\), where

\[C = \sigma(1 + \frac{D}{\lambda_s \beta V})^{-1}\]

The plus sign refers to the lower half-plane \((y < 0)\), the minus sign is for the upper half-plane \((y > 0)\). The flux of adatoms to the step can be calculated using equation (1):

\[j_s \big|_{y=0} = \frac{D \beta V n_{s0}}{\beta V \lambda_s + D} \sigma\]

The speed of movement of the single step \(\vartheta_\infty\), in this case, according to [1] will be equal to:

\[\vartheta_\infty = 2j_s/n_0 = 2\left(\frac{D \beta V}{\lambda_s \beta V + D}\right) \sigma\]

The factor 2 in (6) is due to the fact that the flux of adatoms arrives from both sides of the step. In extreme cases the expression coincides with the one obtained by Burton, Cabrera and Frank [1].

Let us calculate the speed of movement of group of steps with interstep distance of \(y_0\). The first step is at position \(-y_0/2\), the second one is at \(y_0/2\), etc. In this case we should solve equation (5) with the following boundary conditions \(\varphi'(0) = 0, D \frac{d\varphi}{dx} = \beta V (\sigma - \varphi) \bigg|_{y=y_0/2}\)

The solution is:

\[\varphi = \sigma \frac{\beta V \lambda_s ch(y_0)}{D \ sh(y_0 \frac{2}{\lambda_s}) + \beta V \lambda_s ch(y_0 \frac{2}{\lambda_s})}\]

Now we can calculate the flux towards each step and speed of movement of group of steps \(\vartheta_\infty^{gr}\):

\[\vartheta_\infty^{gr} = \frac{2j_{sl}}{n_0} = 2\sigma \frac{D \beta V}{D \ th(y_0 \frac{2}{\lambda_s}) + \beta V \lambda_s \ th(y_0 \frac{2}{\lambda_s})}\]

Next step is the calculation of vertical growth rate \(R\) of the spiral step caused by exit of screw dislocation (and therefore growth rate of the crystal). By substituting \(\vartheta_\infty^{gr}\) to equation for \(R\) and taking into account distance between steps \(y_0 = 4\pi \rho_c\) [1], one can obtain:

\[R = \frac{n_0 V \vartheta_\infty^{gr}}{4\pi \rho_c} = \frac{n_0 V}{2\pi \rho_c} \frac{D \beta V \ th(\frac{4\pi \rho_c}{2\lambda_s})}{D \ th(\frac{4\pi \rho_c}{2\lambda_s}) + \beta V \lambda_s \ th(\frac{4\pi \rho_c}{2\lambda_s})} \left(\frac{K}{K_{eq}} - 1\right)\]

where \(n_0 V\) – is a height of a step, \(\rho_c\) is a half of 2D-critical nucleus size.
One can see, that in case of diffusion growth limit \((\beta V \lambda_s \gg D \, th(\frac{\lambda_s}{2})\)) growth rate is determined by expression:

\[
R = \frac{n_0 \beta V D}{2 \pi \rho_c \lambda_s} \, th\left(\frac{\lambda_s}{2}\right) \left(\frac{K}{K_{eq}} - 1\right)
\]  

(8)

In case of incorporation limit \((\beta V \lambda_s \ll D \, th\left(\frac{\lambda_s}{2}\right)\)) the growth rate is:

\[
R = \frac{n_0 \beta V}{2 \pi \rho_c} \beta \left(\frac{K}{K_{eq}} - 1\right)
\]  

(9)

and not dependent on interstep distance as expected. One should note that equations (7-9) are correct in case that partial pressure of own vapors is small enough to neglect flux of adatoms from vapor phase, and lifetime of adatoms is determined not by evaporation, but only by reverse chemical reaction rate.

3. Conclusions

The growth of a crystal from multicomponent media due to chemical reaction is considered. The model of growth is proposed based on classical Burton, Cabrera and Frank theory. The model is very similar to classical one, and the main difference is that the ratio of \(K/K_{eq}\) plays a role of supersaturation, and the lifetime of adatoms is not constant, but is determined by the rate of reverse chemical reaction and concentration of products of the reaction, which can be pumped out of the growth chamber. It opens up new possibilities in controlling of crystal growth mechanism because one can vary both supersaturation and diffusion length whereas during growth from own vapors one can vary only supersaturation.

References

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