Nucleation of nano-islands of pure components during growth of a multicomponent crystal via step-flow mode

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Abstract. The work is devoted to an analysis of the processes taking place at the surface of the multicomponent crystal during its growth via step-flow mode. It is shown, that at certain conditions nucleation of pure components in a form of nanoislands can take place at the terraces between the steps. The mechanism of formation of such islands is discussed. The criterion for the conditions at which such nucleation takes place is derived.

1. Introduction
Nowadays, multicomponent crystals and thin films are increasingly being used in modern electronics, optics, and many other directions of technology, instead of single-components ones (like classical semiconductors: silicon and germanium). Such materials as widebandgap semiconductors (GaN,AlN,SiC) found applications in optoelectronic devices and high electron mobility transistors. In order to make a device of high efficiency, it is necessary to produce its basement – crystalline thin films of high quality. In this regard, a detailed understanding of the crystal growth mechanisms and their theoretical description is one of the high priority tasks. The theory of growth of single-component crystals is well-developed, however, there are still some white spaces in the multicomponent crystal growth. One of the important questions is the criteria of the transition from step-flow to 2D-nucleation growth regime. In single-component crystals [1] which demonstrate such behaviour during for example molecular beam epitaxy process, this phenomenon was studied extensively because of the great impact of the growth mechanism (step-flow or 2D-nucleation) on the crystalline quality of the film. The effect was described firstly in [2], where the authors found appearance of oscillations in RHEED patterns in situ during growth of a crystal at certain conditions, and addressed them to the formation of 2D islands, whereas during step-flow growth no oscillations should appear, as the surface is atomically smooth.

Since then many papers were published on the study of both single-component or compound semiconductors like GaAs [3-5]. However, the main question, which was investigated therein, was the transition of the film growth from step-flow mode to 2D-nucleation mode in a single-component sense (eg. growth of GaAs film due to movement of steps, or due to nucleation of whole GaAs islands), despite the fact that the multicomponent system can demonstrate other effects. For example, crystal as a whole can grow in step-flow mode, whereas some pure components may nucleate into islands on the surface [6]. Indeed, during the growth of some materials, for example gallium nitride in excess of gallium [7], one can observe in certain cases nucleation of pure Ga islands at the terraces[8]. Since nucleation of nanoislands greatly affects distribution of adatoms at the terrace, it also influences the advancement of steps and the overall crystal growth process.
We note that the other assumption made in papers [3-5] is that there is no evaporation of adatoms from the terrace to gas phase (which is indeed fair in certain MBE growth conditions) and that supersaturation is very high and a critical nuclei consist of only 1 atom (that is when two atoms meet each other, they form a stable cluster). Thus, there are only two sinks for adatoms: steps and nucleation of dimers. These assumptions lead to natural criteria: if the mean free path of the adatom before collision with the other adatoms and forming dimers ($\lambda_c$) is less, then the half of the interstep distance $y_0/2$, then the nucleation of dimers (and then larger clusters) is possible and likely will take place [3].

However, as far as we know, there is no model, which could describe this criteria at the surface of an arbitrary N-component crystal without these assumptions, i.e. when desorption of different components is also possible and critical radius of the nucleating component is larger, then single atom (i.e. supersaturation is quite low). We note that the problems of growth of nanosized islands on heterogeneous stepped surface itself and its different stages (nucleation, coagulation, dissolution) were studied in detail for example in papers [9,10], however, the steps on the surface were treated in [9,10] as immobile, since they were not participating in the growth process. This is not the case in multicomponent growth, at which one can control the movement of steps via adjusting fluxes of different components (independently on one, which is under consideration), thus increasing or decreasing the rate of advance of such a multi-component step. This problem itself was studied in detail in [6], where the existing theory of crystal growth via step-flow mode (Burton-Cabrera-Frank mode [11]) was extended to multicomponent case. Further we will use the notation and the main equations, describing growth rate and distribution of adatoms of different components near the step, which were presented in [6].

The main goal of this work is to combine ideas from [9,10,12,13] on heterogeneous nucleation of islands of some component on the terraces between the steps, and from [6] on the advancement of multicomponent steps, and thus to find a criterion, at which conditions the formation of nanosized islands of pure components at the terraces between the steps take place during multicomponent crystal step-flow growth. We also note, that right after the nucleation different effects involving islands and moving steps are also possible which were well described in [14], such as interaction of the formed islands with the stepped surface itself and its different stages (nucleation, coagulation, dissolution) were studied in detail in [6], where the existing theory of crystal growth via step-flow mode (Burton-Cabrera-Frank mode [11]) was extended to multicomponent case. Further we will use the notation and the main equations, describing growth rate and distribution of adatoms of different components near the step, which were presented in [6].

2. Nucleation mechanism

As in [6] let us consider a multicomponent crystal, growing from its vapors according to the reaction:

$$A_1 + A_2 + \ldots + A_n \leftrightarrow C_{(s)}$$

where $A_i$ are the initial components, $C_{(s)}$ is the crystalline phase. This chemical reaction is in equilibrium when $\prod_{i=1}^n P_i = K_{eq}$, that is the product of partial pressures $P_i$ of all components (which can be also expressed via corresponding fluxes $J_i = P_i/\sqrt{2\pi n m k_b T}$) equals to equilibrium constant $K_{eq}$ and thus evaporation of adatoms of all components is stabilized with fluxes from vapor to surface. If $\prod_{i=1}^n P_i < K_{eq}$ the crystal starts to evaporate, whereas if $\prod_{i=1}^n P_i > K_{eq}$ it grows. If supersaturation is very low

$$\xi = \frac{\prod_{i=1}^n P_i}{K_{eq}} - 1 \ll 1$$

the preferable mechanism of growth is step-flow growth which was considered in detail in [11,6]. The rate of advancement $\vartheta_{co}^r$ of the group of equidistant steps in this case is determined by:

$$\vartheta_{co}^r = \frac{2L}{n_c \beta_0 \beta_{os} \delta_{os} n_l^0}$$

Here, according to [6], $1/n_c$ is the area occupied by the molecule/unit cell of $C_{(s)}$, $D_{os}$ is the generalized diffusion coefficient, $\delta_{os}$ is the generalized incorporation rate (see [6] for details), $\beta_{os} = \left(\sum_{i=1}^n \frac{1}{\beta_i V_i n_l^0}\right)^{-1}$ is the generalized diffusion coefficient, specific incorporation rate, atomic volume and equilibrium surface concentration of the i-th component before evaporation, $D_i, \beta_i, V_i, n_l^0$ are diffusion coefficient, specific incorporation rate, atomic volume and equilibrium surface concentration of the i-th component. We note that since the crystal in such multicomponent system may be in equilibrium with different sets of pressures $(P_1, P_2, \ldots, P_n)$ or fluxes $(J_1, J_2, \ldots, J_n)$, the surface concentrations $(n_1^0, n_2^0, \ldots, n_3^0)$ at each set will also may vary significantly. At
each set $D_{os}$ and $\beta_{os}$ have different values. Physical meaning of the equation (2) is quite simple. When some small supersaturation $\xi$ is applied, and the crystal is slightly moved from its equilibrium set of fluxes, its growth can be described in the same way as a single component crystal [11], having effective diffusion coefficient $D_{os}$ and incorporation rate $\beta_{os}$, which are determined by the surface concentrations and properties of individual components. Thus, by choosing different ratios of the fluxes and surface concentrations $n_i^0$ one can significantly affect the crystal growth rate even at fixed supersaturation $\xi$.

One should take into account, that each of $n$ components is considered above in multicomponent growth process sense. On the other hand, the deposition of the $i$-th component on the surface may be also treated as a single-component heterogeneous epitaxy [9,10] and thus can demonstrate all of its features: nucleation, decoration on steps and defects on the surface etc. Equilibrium concentration in the sense of single-component heteroepitaxy in general case is different from $n_i^0$. Let’s denote it as $n_i^{0,\text{crit}}$.

If we slightly move the crystal from multicomponent equilibrium, step-flow growth begins, and as it was shown in [6], the surface concentrations of each component will change and become maximal at the terrace between the steps. Let’s denote actual concentration of the $i$-th component at the surface between the steps as $n_i$ which is higher than $n_i^0$. If during growth concentration $n_i$ of some component will exceed single-component equilibrium concentration $n_i^{0,\text{crit}}$, the nucleation of nanoislands of that component may begin. We note, that in this paper we consider a very narrow range of concentrations in which the described phenomena may occur. This is caused by the following conditions:

1) in multicomponent system step-flow takes place only at low supersaturation, that is $\xi \ll 1$ and thus $\frac{n_i}{n_i^0} - 1 \ll 1$;

2) “multicomponent” equilibrium concentration $n_i^0$ of the considered component should be less then “single-component” equilibrium concentration $n_i^{0,\text{crit}}$, otherwise nucleation will begin even at zero multicomponent supersaturation, and equation (2) will become inapplicable ($n_i^0 < n_i^{0,\text{crit}}$);

3) maximal concentration between the steps must be higher, then “single-component” equilibrium concentration $n_i > n_i^{0,\text{crit}}$, otherwise nucleation is not possible at all. So, once these conditions are satisfied, our goal is to calculate whether nucleation will begin or not.

Schematic representation of the described process and growth modes for two-component AB crystal is shown on Figure 1.

![Figure 1. Schematic representation of the growth modes of two-component AB crystal depending on the fluxes of the individual components $J_A$, $J_B$ (a). At different ratios of the fluxes nucleation of A or B component is possible.](image-url)
(nAcrit or nBcrit) and nucleation of the corresponding component begins, and eq. (2) will not describe growth process correctly. Figure 2 demonstrates a relation between (nA, nB, nA_crit, nB_crit) and shows the resulting formed nanoislands at the terraces at three cases, marked in Figure 1.

Let us evaluate the criterion for the formation of these nanoislands in general way for n-component crystal. Note that since the nucleation rate is very sharply dependent on the supersaturation, even a slight decrease in the surface concentration leads to suppression of nucleation, and therefore we believe that nucleation is possible only in the region where the concentration is maximal, i.e., on the area of the terrace of width $l_i = y_0 - 2\lambda_i$ (see Figure 2). Here we consider the case, when $2\lambda_i \ll y_0$, otherwise the maximal concentration of the component at the center of the terrace will be even less, and nucleation is less probable. To assess whether the formation of at least one nanoisland at the terrace will take place, it is necessary to compare its nucleation time $\tau_{ni}^i$ at a given surface concentration of the $i$-th component $n_i$, and time $\tau_s$, which is necessary for the step to cover a distance equal to $l_i$, and thereby to lower concentration back to $n_i^0$ and “restart” the process.

For the characteristic rate of island formation per unit area, one can write [15,16]:

$$I_0^i = 2\pi \rho_{ct}^i \sin \theta \frac{l_i^2 a}{v} \Gamma_i \exp \left( \frac{2E_{des}^i - E_{sd}^i}{kT} \right) \exp \left( \frac{-\Delta G_{ct}^i}{kT} \right)$$

where $2\pi \rho_{ct}^i \sin \theta$ is the perimeter of the island of the $i$-th component of critical radius $\rho_{ct}^i = \frac{2\gamma_i \nu_i}{kT \xi_i}$, $\theta_i$ is the contact angle, $J_i$ is the flux of the $i$-th component, $a$ is the lattice parameter, $\nu$ is the characteristic frequency of atomic vibrations, $\gamma_i$ is the surface energy of the nucleus of the $i$-th component. $\Gamma_i = \frac{\Delta \mu_i^2}{8\pi \nu_i^2 \phi_i (\theta) kT}$ is the Zeldovich factor, $\phi_i (\theta)$ is the wetting function, which is determined by the ratio of the surface energies of solid phases (Cs, i) and gas phase. $E_{des}^i$ is the desorption activation energy, $E_{sd}^i$ is the diffusion activation energy of the $i$-th component. $\Delta G_{ct}^i = \frac{16\gamma_i^3 \nu_i^2 \phi_i (\theta)}{3\Delta \mu_i^2}$ is the work of formation of the nuclei of critical radius. $\Delta \mu_i = kT \ln \left[ \frac{n_i}{n_{i, crit}} \right]$ is the difference in chemical potentials of

![Figure 2. Distribution of adatom surface concentrations nA and nB at the terrace at the modes, marked with 1, 2 and 3 on figure 1 and formed nanoislands of different pure components.](image-url)
the \(i\)-th component in the nucleus and in the adsorbed state on the surface. Here we suppose, that critical radius \(\rho_{cc}^{i}\) of the forming island is significantly less, than \(l_{i}\), otherwise the nucleation will be also impossible.

We note that the rate \(I_{0}^{i}\) characterizes the number of islands of the \(i\)-th component formed per unit time per unit area. Then, the characteristic time of formation of at least one nanoisland of the \(i\)-th pure component in the area between the steps, referred to a unit length of step, is inversely proportional to the distance \(l_{i} = y_{0} - 2\lambda_{i}\) and nucleation rate \(I_{0}^{i}\):

\[
\tau_{n}^{i} = \frac{1}{l_{i}I_{0}^{i}}
\]

On the other hand, according to (2), the time \(\tau_{y}\) which step takes to cover distance \(l\) and “restart” the process of nucleation equals to:

\[
\tau_{y} \sim \frac{l_{i}}{\rho_{cc0}^{gr}} = \frac{l_{i}n_{C0}}{2\xi} \left( \frac{D_{os}^{gr} + \beta_{os}}{D_{os}^{gr} \rho_{os}} \right)
\]

So, if \(\tau_{n}^{i} < \tau_{y}\), then at least one island will have time to nucleate between the steps. If, on the contrary, \(\tau_{n}^{i} > \tau_{y}\) then, nucleation is impossible, and crystal growth will occur according to the multicomponent BCF mechanism [11,6]. The final criteria can be written as follows:

\[
\frac{\tau_{n}^{i}}{\tau_{y}} = \frac{2\xi}{l_{i}n_{C0}l_{i}^{2} \left( \frac{D_{os}^{gr} \beta_{os}}{D_{os}^{gr} \rho_{os} + \beta_{os}} \right)} < 1
\]  

(4)

If this condition is met for at least one of the components during multicomponent growth, then nucleation of islands of the \(i\)-th component is possible. The nascent islands significantly reduce surface concentration of the \(i\)-th component and total multicomponent supersaturation \(\xi\). Thus, the crystal growth rate may also decrease, and will be no longer described by equation (2), since the deposited \(i\)-th flux will be also spent on nanoisland growth, but not only on the incorporation into the step.

We note that criterion (4) includes the distance between the steps \(y_{0}\), which, at spiral growth, is proportional to the critical radius \(y_{0} = 19 \rho_{c}\) [17] (where \(\rho_{c}\) is treated in “multicomponent” sense), determined itself by multicomponent supersaturation \(\xi\). So in the spiral growth and \(y_{0} \gg \lambda_{i}\) it can be seen, that supersaturation \(\xi\) is included in criterion (4) powered by 3, and the larger it is, the less is the probability (with a fixed supersaturation of the \(i\)-th component) that islands of the \(i\)-th component will nucleate. It has a simple physical explanation. The greater the multicomponent supersaturation, the less is the distance between the steps on the surface of the crystal, and the higher is the rate of their advancement. The steps pass through a given point on the surface significantly more often, reduce the local concentration and “restart” the nucleation process. Therefore, the \(i\)-th component have significantly less time and area for nucleation.

3. Conclusions
The formation of islands of pure components at the terraces during multicomponent crystal growth via step-flow mode is considered. A criterion is found for the regimes at which nucleation of pure components takes place. It is shown, that by increasing multicomponent supersaturation and thus increasing the rate of advance of the steps on the surface of a multicomponent crystal, one can suppress the nucleation of nanoislands of pure components. The results can be used to choose crystal growth conditions at which growth proceeds via classical step-flow mode or in mixed mode, when along with classical step-flow growth some components are being nucleated in a form of nanoislands.

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