ARTICLE

Supplementary materials for:

Theoretical aspects of the growth of a non-Kossel crystal from vapours: role of advacancies

Alexey Redkov and Sergey Kukuhskin

Solution for the distribution function of vacancies and adatoms ψ_i, φ_i.

We will solve the system of equations (Eq. 4) in the following way. First, we express the function $\psi(x)$ from the second equation in the system in terms of the function $\varphi(x)$:

$$\psi = \frac{-\varphi + Kn_v^0\tau_a(-1 + \alpha_a\alpha_v - \alpha_v\varphi) + D_a\tau_a\frac{\partial^2\varphi}{\partial x^2}}{Kn_v^0\alpha_a\tau_a}$$

Substituting it into the first equation of the system, we obtain the differential equation for $\varphi(x)$ of the 4st order. Solving the equation gives:

$$\phi(x) = B_1\mathrm{e}^{-x/\lambda'} + C_1\mathrm{e}^{x/\lambda'} + D_1\mathrm{e}^{-x/\lambda''} + E_1\mathrm{e}^{x/\lambda''} - n_{\mathrm{v0}}\tau_a\frac{\mathrm{K}(\alpha_a\alpha_v - 1)}{1 + \mathrm{K}n_{\mathrm{v0}}\alpha_v\tau_a + \mathrm{K}n_{\mathrm{a0}}\alpha_a\tau_v}$$

where

$$\frac{1}{\lambda'^2} = \frac{\frac{1}{\lambda^2} - \frac{1}{\lambda^2}\sqrt{1 - 4\lambda^4(\frac{1}{\lambda_v^{r\,2}\lambda_a^{e\,2}} + \frac{1}{\lambda_a^{r\,2}\lambda_v^{e\,2}} + \frac{1}{\lambda_v^{e\,2}\lambda_a^{e\,2}})}}{2}$$

$$\frac{1}{\lambda''^2} = \frac{\frac{1}{\lambda^2} + \frac{1}{\lambda^2}\sqrt{1 - 4\lambda^4(\frac{1}{\lambda_v^{r\,2}\lambda_a^{e\,2}} + \frac{1}{\lambda_a^{r\,2}\lambda_v^{e\,2}} + \frac{1}{\lambda_v^{e\,2}\lambda_a^{e\,2}})}}{2}$$

depend on the diffusion lengths of adatoms and vacancies in different processes. Here, $D_a\tau_a = \lambda_a^{e\,2}$ is the squared diffusion length of adatoms due to evaporation (superscript 'e'); $D_v\tau_v = \lambda_v^{e\,2}$ is the same value for vacancies; and $D_v/\mathrm{K}n_a^0\alpha_a = \lambda_v^{r\,2}$ and $D_a/\mathrm{K}n_v^0\alpha_v = \lambda_a^{r\,2}$ are the squared diffusion lengths of adatoms and vacancies due to recombination (superscript 'r'). For simplicity, we also introduced λ, which is the generalised diffusion length that depends on all the diffusion lengths presented in the system.

$$\lambda^2 = (\tfrac{1}{\lambda_a^{e\,2}} + \tfrac{1}{\lambda_v^{e\,2}} + \tfrac{1}{\lambda_a^{r\,2}} + \tfrac{1}{\lambda_v^{r\,2}})^{-1} \qquad (A1)$$

Note that λ according to Eq. A1 is determined by the smallest diffusion length ($\lambda \approx min(\lambda_a^e, \lambda_v^e, \lambda_a^r, \lambda_v^r)$. If the smallest diffusion length is significantly smaller than the others, then we can estimate $\lambda' \approx 0$, and $\lambda'' = \lambda$. In the article, we will use the non-zero solution $\lambda'' = \lambda$.

We note that for simplicity above, we omitted subscript *i*, but the final solution for each component is obviously dependent on the corresponding diffusion coefficients and lifetimes (e.g., $D_{ai}, K_i\ n_{\mathrm{vi0}},\ \tau_{ai}$…) of this component. Thus, the final solution of the system of equations is as follows:

$$\begin{cases} \varphi_i(x) = \xi_{ai}\dfrac{\mathrm{ch}(x/\lambda_i)}{\mathrm{ch}\left(\frac{l}{2\lambda_i}\right)} + I_i n_{vi}^0\tau_{ai}\left(1 - \dfrac{\mathrm{ch}(x/\lambda_i)}{\mathrm{ch}\left(\frac{l}{2\lambda_i}\right)}\right) \\ \psi_i(x) = \xi_{vi}\dfrac{\mathrm{ch}(x/\lambda_i)}{\mathrm{ch}\left(\frac{l}{2\lambda_i}\right)} + I_i n_{ai}^0\tau_{vi}\left(1 - \dfrac{\mathrm{ch}(x/\lambda_i)}{\mathrm{ch}\left(\frac{l}{2\lambda_i}\right)}\right) \end{cases}$$

where $I_i = \frac{\mathrm{K}_i(\alpha_{ai}\alpha_{vi}-1)}{1+\mathrm{K}_i n_{vi}^0\alpha_{vi}\tau_{ai}+\mathrm{K}_i n_{ai}^0\alpha_{ai}\tau_{vi}}$

The solution for the total surface flux toward the step considering the stoichiometric relationship of the fluxes of individual components and vacancies.

First, let us express the supersaturations in terms of surface fluxes[32] $j_{ai\leftarrow}, j_{vi\leftarrow}$:

$$\begin{cases} \dfrac{j_{ai\leftarrow}\lambda_i}{D_{ai}n_{ai}^0 th\left(\frac{l}{2\lambda_i}\right)} = \xi_{ai} - I_i n_{\mathrm{vi0}}\tau_{ai} \\ \dfrac{j_{vi\leftarrow}\lambda_i}{D_{vi}n_{vi}^0 th\left(\frac{l}{2\lambda_i}\right)} = \xi_{vi} - I_i n_{\mathrm{ai0}}\tau_{vi} \end{cases}$$

Then we multiply each of the equations by the corresponding stoichiometric coefficient and sum all the equations for all L components:

$$\begin{cases} \sum_{i=1}^{L}\dfrac{j_{ai\leftarrow}\nu_i\lambda_i}{D_{ai}n_{ai}^0 th\left(\frac{l}{2\lambda_i}\right)} = \sum_{i=1}^{L}\nu_i\xi_{ai} - \sum_{i=1}^{L}I_i\nu_i n_{vi}^0\tau_{ai} \\ \sum_{i=1}^{L}\dfrac{j_{vi\leftarrow}\nu_i\lambda_i}{D_{vi}n_{vi}^0\ th\left(\frac{k_i l}{2}\right)} = \sum_{i=1}^{L}\nu_i\xi_{vi} - \sum_{i=1}^{L}I_i\nu_i n_{ai}^0\tau_{vi} \end{cases}$$

Then, keeping in mind that all flows of all components to the step must be stoichiometric, that is, $j_{ai\leftarrow}/\nu_i = j_{aj\leftarrow}/\nu_j = j_{a\leftarrow}$,

$j_{vi\leftarrow}/\nu_i = j_{vj\leftarrow}/\nu_j = j_{v\leftarrow}$and taking these values out of the bracket, we have:

$$\begin{cases} \frac{j_{a\leftarrow}}{D_a{}^{os}} = \xi_a - \sum_{i=1}^{L} I_i \nu_i n_{vi}^0 \tau_{ai} \\ \frac{j_{v\leftarrow}}{D_v{}^{os}} = \xi_v - \sum_{i=1}^{L} I_i \nu_i n_{ai}^0 \tau_{vi} \end{cases}$$

The following generalised diffusion coefficients are dependent on the properties of each component:

$$D_a{}^{os} = \left(\sum_{i=1}^{L} \frac{\nu_i{}^2 \lambda_i}{D_{ai} n_{ai}^0 \mathrm{th}\left(\frac{l}{2\lambda_i}\right)} \right)^{-1} \quad D_v{}^{os} = \left(\sum_{i=1}^{L} \frac{\nu_i{}^2 \lambda_i}{D_{vi} n_{vi}^0 \mathrm{th}\left(\frac{l}{2\lambda_i}\right)} \right)^{-1}$$

$\xi_a = \sum_{i=1}^{N} \nu_i \xi_{ai}$ and $\xi_v = \sum_{i=1}^{L} \nu_i \xi_{vi}$ are generalised supersaturations of adatoms and advacancies, respectively. Substituting $I_a = \sum_{i=1}^{L} I_i \nu_i n_{vi}^0 \tau_{ai}$, and $I_v = \sum_{i=1}^{L} I_i \nu_i n_{ai}^0 \tau_{vi}$ we immediately have:

$$\begin{cases} j_{a\leftarrow} = D_a{}^{os}(\xi_a - I_a) \\ j_{v\leftarrow} = D_v{}^{os}(\xi_v - I_v) \end{cases}$$

The case of growth of GaN via HVPE (decomposition on subreactions and components).

The typical HVPE reaction of GaN growth can be written as follows[60]:

$$\mathrm{GaCl} + \mathrm{NH_3} \leftrightarrow \mathrm{GaN_{(s)}} + \mathrm{HCl} + \mathrm{H_2}$$

If we formally decompose this reaction onto subreactions that deliver different types of adatoms toward the surface ($\mathrm{Ga_{(ads)}}$ and $\mathrm{N_{(ads)}}$), we have the following:

$$\begin{cases} GaCl + \frac{1}{2} H_2 \leftrightarrow Ga_{(ads)} + HCl & (A2) \\ NH_3 \leftrightarrow N_{(ads)} + \frac{3}{2} H_2 & (A3) \end{cases}$$

Using the kinetic coefficients of these reactions, we may write the following:

1) The mean lifetimes of the adatoms on the surface and their diffusion length before leaving the surface due to a chemical reaction:

$$\tau_{Ga} = \frac{1}{k_{r1} P_{HCl}} \qquad \tau_N = \frac{1}{k_{r2} P_{H_2}{}^{\frac{3}{2}}}$$
$$\lambda_{Ga}^2 = \frac{D_{Ga}}{k_{r1} P_{HCl}} \qquad \lambda_N^2 = \frac{D_N}{k_{r2} P_{H_2}{}^{\frac{3}{2}}}$$

where $k_{r1} n_{aGa}^0$ and $k_{r2} n_{aN}^0$ are the kinetic rates of reverse chemical reactions of (A2) and (A3), respectively.

2) Supersaturations of Ga and N adatoms that can be expressed via pressures of components in the gas phase $P_{GaCl}, P_{HCl}, P_{H_2}, P_{NH_3}$ and their equilibrium values:

$$\xi_{Ga} = \frac{K_{Ga}}{K_{Ga}^0} - 1 = \frac{P_{GaCl} * P_{H_2}{}^{\frac{1}{2}}}{P_{HCl}} / \left(\frac{P_{GaCl}^0 * P_{H_2}^0{}^{\frac{1}{2}}}{P_{HCl}^0}\right) - 1,$$

$$\xi_N = \frac{K_N}{K_N^0} - 1 = \frac{P_{NH_3}}{P_{H_2}{}^{\frac{3}{2}}} / \left(\frac{P_{NH_3}^0}{P_{H_2}^0{}^{\frac{3}{2}}}\right) - 1$$

Substituting these values into the formula in Section 3.1 yields the final expression for the dependence of the growth rate of the GaN crystal on the applied pressures via the mechanism considered, considering the effect of advacancies.

Equation for multicomponent supersaturation in the presence of stress.

Guided by the considerations provided in Refs. 27 and 29 and Section 3.1, let us find the equilibrium vapour pressure of the *i*-th component in the presence of the elastic stress σ. The vapour pressure increases proportionally to the component's volume ω_i as $P_{i0}(1 + \sigma\omega_i/k_B T)$. Thus, the dependence of the supersaturations on the applied stress should be

$$\xi_{ai}(\sigma) = \frac{P_i}{P_{i0}\left(1 + \frac{\sigma\omega_i}{k_B T}\right)} - 1 \approx \frac{P_i}{P_{i0}}\left(1 - \frac{\sigma\omega_i}{k_B T}\right) - 1 = \xi_{ai}(0) - \frac{\sigma\omega_i}{k_B T}.$$

Using this formula, we find for generalised supersaturation $\xi_a(\sigma)$:

$$\xi_a(\sigma) = \sum_{i=1}^{L} \nu_i \xi_{ai}(\sigma) = \sum_{i=1}^{L} \nu_i \xi_{ai}(0) - \frac{\sigma \sum_{i=1}^{L} \nu_i \omega_i}{k_B T} = \xi_a(0) - \frac{\sigma\omega}{k_B T}$$