

Surface defects formation on strained thin films growing via chemical reaction: a model

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Abstract. We investigated in a general way evolution of the elastic flat surface of the crystal during its growth from multicomponent media. The morphological instability caused by mechanical stress has been demonstrated and conditions under which a multicomponent thin film retains its shape have been found. As an example, we have analyzed growth of GaN on different substrates and discussed the impact of III/V ratio on the stability of the GaN epitaxial film growing by HVPE.

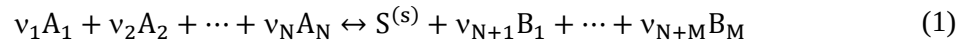
1. Introduction

The study of growth processes of epitaxial thin films is of great interest of science and industry, since almost all electronic components are being made using thin-film technology. One of the main goals is to find the reasons of formation of different defects in the film during growth and to eliminate them. For example, common type of defects are so-called V-defects [1], which affect dramatically the quality of the heterostructures. In this paper, we assume that one of the possible causes of the development of surface defects can be local fluctuations of stress and concentrations of the components in strained areas of the film, leading to the further development of the instability of the growth front by mechanism of Mullins and Sekerka [2]. The choice of the ratio of III / V components may affect the growth rate of the instability. Generally, there are a lot of studies, devoted to stability of the growing crystals, in which authors considered various systems, differing in geometry, the cause of instability, and the factors affecting the development of the instability [3,4]. For example, in [5] authors discussed the stability of one-component strained epitaxial film commending the contribution of vacancies. Most studies, however, are devoted to one-component systems, whereas many of the modern technologies for growing GaN epitaxial layers often include chemical reaction in a multicomponent medium, for example, MOCVD [6] or HVPE [7].



2. The model

Let us consider a flat surface of the crystal of phase S growing from multicomponent medium in the reactor. Near the surface there is always boundary hydrodynamic layer of thickness l because of viscosity, where components move due to diffusion. The flow of the reactants from the atmosphere into the hydrodynamic layer is constant (see. Fig. 1a). Components can diffuse along the surface and react chemically (1) forming substance S, which incorporates directly into the surface and increase the height at that point.



Hereinafter stoichiometric coefficients of reaction products will be redenoted as negative for convenience.

Initial reactants as well as reaction products can also leave the hydrodynamic layer. Let's imagine some defects below the surface like dislocations, pores, or substrate with a lattice parameter different from the growing phase S, or other defects that create stress field σ , which in general may change with height of the film ($\partial\sigma_0/\partial z \neq 0$ [8]).

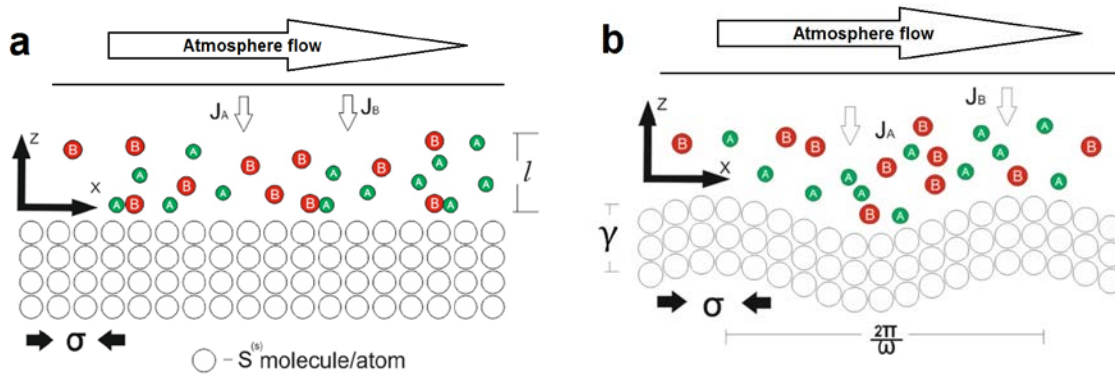


Figure 1. Illustration of the unperturbed (a) and perturbed (b) surfaces of thin film, growing via reaction of the type $A + B \leftrightarrow S$. In general, the chemical reaction in the valleys and on the tops can occur with different rates.

During steady growth the system of equations describing the concentrations of all components in hydrodynamic layer can be written as (2):

$$\begin{cases} 0 = D_i \frac{\partial^2 C_i}{\partial x^2} + J_i - K_p v_i \prod_{k=1}^N C_k^{v_k} + K_o v_i \prod_{k=N+1}^M C_k^{-v_k} - \frac{C_i}{\tau_i}, & i = A_1 \dots B_M \\ \rho_s \frac{dz}{dt} = K_p \prod_{k=1}^N C_k^{v_k} - K_o \prod_{k=N+1}^M C_k^{-v_k} \end{cases} \quad (2)$$

Here C_i - the concentration of component i in the hydrodynamic layer, which changes due to incident flux J_i , diffusion, chemical reaction and flying back to the reactor. D_i - diffusion coefficient of substance i in gas, K_p - the rate of direct chemical reaction of S formation, K_o - the rate of reverse chemical reaction. τ_i - the lifetime of the component i in hydrodynamic layer, dz/dt - growth rate of the surface, ρ_s - concentration of molecules in solid phase S. We can estimate the time τ_i for each component as $\tau_i \sim l^2/D_i$, where l can be an order of 0.5-1mm [9].

Now we should make a small sinusoidal perturbation of surface Z with amplitude γ :

$$Z = z + \gamma \sin(\omega x)$$

Due to the change of surface geometry local stresses will also change according to [5,10]:

$$\sigma|_{z+\gamma\sin(\omega x)} = \sigma_0 + \left(\frac{\partial\sigma_0}{\partial z} - 2\sigma_0\omega\right)\gamma\sin(\omega x) \quad (3)$$

This will affect the rate of a chemical reaction, since the stress variation contributes to the energy of the reaction product S. Additional elastic energy density ΔU , which is caused by the perturbation of the surface can be expressed by modified equation from [10]:

$$\Delta U(x) = U\gamma\sin(\omega x) = \frac{\sigma_0^2}{\bar{M}} \left[\frac{1}{\sigma_0} \frac{\partial\sigma_0}{\partial z} - 2(1+\nu)\omega \right] \gamma\sin(\omega x)$$

Where $\bar{M} = E/(1-\nu)$ is biaxial elastic modulus, E is Young's modulus of the film, ν - Poisson ratio [10]. Therefore the local chemical potential and thus equilibrium constant will change and reaction rates can be described by the formula:

$$\left. \frac{K_0}{K_p} \right|_{z+\gamma\sin(\omega x)} = \frac{K_0}{K_p} \left(1 + \left[\frac{\theta V_s}{kT} \omega^2 + \frac{UV_s}{kT} \right] \gamma\sin(\omega x) \right) \quad (4)$$

Here $V_s = \sum_{i=1}^M v_i V_i / \sum_{i=1}^M |v_i|$, V_i - volume of i component, and θ - surface tension coefficient. Fluctuations of reaction rate (4) in its turn will lead to a corresponding change in the concentrations and growth rates of the surface.

$$C_k|_{z+\gamma\sin(\omega x)} = C_k^0(1 + \delta_k \sin(\omega x)), \quad k = A_1..B_M \quad (5)$$

$$\dot{Z} = \frac{dz}{dt} + \frac{dy}{dt} \sin(\omega x)$$

Taking into account expressions (4) and (5), substitute them into the system of equations (2). Then we should apply a similar chain of mathematics as in [11], taking into account the first order in γ , and we can obtain the formula for the rate of growth of perturbations in case of small multicomponent oversaturation.

$$\frac{\rho_s}{\gamma} \frac{dy}{dt} = - \frac{\mu_o^{os} \mu_p^{os}}{\mu_o^{os} + \mu_p^{os}} \left(\frac{UV_s}{kT} + \frac{\theta V_s}{kT} \omega^2 \right) \quad (6)$$

Where μ_o^{os} , μ_p^{os} are generalized coefficients:

$$\mu_p^{os} = \left(\sum_{k=1}^N \left(\frac{v_k^2 \tau_k^0}{C_k^0(\tau_k^0 D_k \omega^2 + 1)} \right) \right)^{-1}, \quad \mu_o^{os} = \left(\sum_{k=N+1}^M \frac{v_k^2 \tau_k^0}{C_k^0(\tau_k^0 D_k \omega^2 + 1)} \right)^{-1} \quad (7)$$

It can be seen that the perturbation will not grow if the right side of (6) is zero or negative, i.e., the inequality is satisfied

$$\frac{\rho_s}{\gamma} \frac{dy}{dt} \sim \frac{\sigma_0^2}{M} \left[\left(2(1+\nu)\omega - \frac{1}{\sigma_0} \frac{\partial\sigma_0}{\partial z} \right) \right] - \theta\omega^2 \leq 0$$

The stability criterion fully corresponds to the formula obtained in [10] for one-component film, but the growth rate of perturbation depends on properties of all components. Also, from (6) it can be concluded that for any harmonic there is a critical stress at which the perturbation will increase with time. If the stress gradient is absent or small $\sigma_0\omega \gg \frac{1}{2} \frac{\partial\sigma_0}{\partial z}$, then the surface is stable at frequencies satisfying the inequality:

$$\frac{2\sigma_0^2}{\theta E} < \omega \quad (8)$$

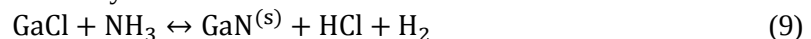
Where $\bar{E}$ is the plain strain modulus. If the main contribution comes from the stress gradient, the critical frequency can be defined as

$$\sqrt{\left| \frac{\sigma_0}{2\bar{E}\theta} \frac{\partial\sigma_0}{\partial z} \right|} \leq \omega$$

One should note, that stability criterion (8) doesn't itself contain individual properties of components, because in such formulation of the problem stress affects each component indirectly, only through the chemical reaction rate. If we considered growth of perturbation via surface diffusion of adatoms, stress could affect differently adsorption-desorption processes of each component.

3. Stability of GaN film

Let us consider as an example the growth of GaN by methods involving chemical reaction e.g. HVPE (9) and make some estimates of film stability on different substrates.



We suppose that the gradient of the stress along z axis is absent ($\partial\sigma_0/\partial z = 0$). Thus the dependence of the critical size of perturbation $\lambda_{cr} = 2\pi/\omega$, at which the surface becomes unstable, can be found from the formula (8). Knowing the type of substrate on which GaN grows, we can estimate the characteristic dimensions of the perturbations and defects that may appear on the surface of the film via considered mechanism (see Fig.2).

The surface tension of GaN $\theta \approx 2 \text{ J/m}^2$ [12], Young's modulus $E \approx 301 \text{ GPa}$ [12]. We also should estimate stresses in the film during growth process (see Table 1).

Table 1. Stress (tensile if negative) in $\sim 1 \mu\text{m}$ -thick GaN film on different substrates.

Substrate	Stress at growth temperature (estimation), GPa
Sapphire(Al_2O_3)	-0.3 [14,15]
Si with AlN-buffer	-0.25 [16]
SiC	-0.1 [17] (in this work GaN was Si-doped)

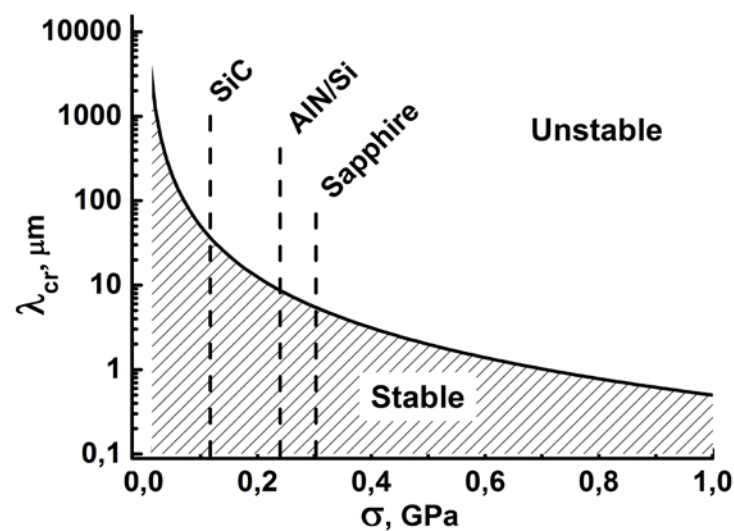


Figure 2. Dependence of the critical wavelength on stress for GaN film. Estimates for common substrates are shown on the graph. The shaded area corresponds to stable growth.

4. Impact of III/V ratio on surface stability

We have shown, that growth rate of perturbation via abovementioned mechanism depends dramatically on the generalized coefficients μ_p^{os} , μ_o^{os} , which are determined by diffusion coefficients and concentrations of components. We should analyze how the ratio of III/V affects HVPE (9) growth process. Let's fix chemical reaction rate:

$$C_{GaCl}C_{NH_3} \approx \text{const}$$

One can see that coefficient before parenthesis in (6) is maximal when concentrations of III/V components obey the rule $C_{NH_3} = (D_{GaCl}/D_{NH_3}) C_{GaCl}$ (for case $D_i\omega^2 \gg 1$). Thus, for stable frequencies maximal "stabilizing force" via considered mechanism will be achieved if $\frac{C_{NH_3}}{C_{GaCl}} \sim 0.4$ (see Table 2). We should note, that unstable harmonics will also grow with maximal rate in such conditions. We emphasize that this condition involve concentrations in hydrodynamic layer, not in reactor atmosphere. For calculation of them one should take into account growth rate and lifetimes of components in particular growth process and solve (2).

Table 2. Diffusion coefficients of components involved in HVPE reaction in gaseous phase [18].

	GaCl	NH ₃	HCl	H ₂
D, 10 ⁻⁴ m ² /s (at 1000K)	1.08	2.68	1.83	7.82

5. Conclusions

We have studied the morphological stability of epitaxial strained film, growing via chemical reaction in multicomponent system. A criterion of stability connecting the stress in the film and the critical wavelength of the perturbation from which the surface becomes unstable is derived and applied to growth of GaN films via HVPE method which involves chemical reaction. Under standard growth stresses of 0.1-0.5 GPa on different substrates the critical wavelength for this mechanism of instability corresponds to tens or hundreds of microns.

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