Impact of metalorganic vapor phase epitaxy growth conditions on compressive strain relaxation in polar III-nitride heterostructures

Mikhail E. Rudinsky, Anna V. Lobanova, Sergey Yu. Karpov, and Roman A. Talalaev

STR Group—Soft-Impact, Ltd., 64 Bolshoi Sampsonievski Ave., Bld. ‘E’, 194044 St. Petersburg, Russia

E-mail: sergey.karpov@str-soft.com

Received December 14, 2018; revised January 14, 2019; accepted January 19, 2019; published online May 8, 2019

A novel approach to estimating the critical thicknesses (CTs) of compressively strained III-nitride layers is suggested, based on a quasi-thermodynamic growth model and accounted for the effect of material decomposition during dislocation half-loop formation on the CT value. The approach provides good qualitative agreement with available data on CTs of MOVPE-grown InGaN/GaN and AlGaN/AlN epilayers. The extremely large CTs observed for high Al-content AlGaN alloys grown on bulk AlN substrates may be attributed, in particular, to the dominant AlGaN decomposition mechanism, producing group-III metallic liquid and gaseous nitrogen. The suggested approach may also be helpful for analysis of threading dislocation inclination in compressively strained layers and applicable to studying point defect formation in semiconductors and its dependence on growth conditions. © 2019 The Japan Society of Applied Physics

1. Introduction

III-nitride alloys are materials with high lattice constant mismatch between binary constituents, GaN, InN, and AlN. In the case of epitaxy on a binary substrate, the mismatch results in plastic stress relaxation via dislocation formation, limiting the crystal quality of the relaxed epitaxial layers. This limitation is very critical for III-nitride optoelectronic devices, leading to considerable reduction of their emission efficiency because of enhanced non-radiative electron and hole recombination at the generated dislocations. Therefore, knowledge of the critical thicknesses (CTs) of various epitaxial layers used in device structures, and understanding of the factors affecting the thicknesses is extremely important for fabrication technology of the devices.

In conventional zinc-blende III–V semiconductors, the principal relaxation mechanism is gliding of misfit dislocations (MDs). The 60° dislocations glide in the (111) plane of the crystals normally grown on the (001) surfaces. Therefore, there always exists a non-zero component of the shear stress inducing the dislocation gliding. The CT of strained epitaxial layers, corresponding to the onset of plastic relaxation, can be accurately predicted for cubic III–V compounds by the Matthews–Blakeslee (MB) model. That is not the case in polar III-nitride heterostructures, however, where dominant α-type basal-plane dislocations tend to glide in the basal (0001) plane. Here, the resolved shear stress vanishes but the length of the gliding path tends to infinity, resulting in a finite work of mismatch stress during MD formation. In spite of this fact, application of the MB model accounting for anisotropic elastic properties of III-nitrides to polar InGaN/GaN and AlGaN/AlN layers provides CTs one to two orders of magnitude smaller than are obtained experimentally. Possible reasons for this are a rather low resolved shear stress, which may be insufficient for overcoming the Peierls barrier in the basal plane, and a too large gliding path, on which the MDs may be pinned by defects and impurities, suppressing the gliding. Therefore, other mechanisms of stress relaxation may become dominant in the polar structures.

Recently, an alternative mechanism of plastic stress relaxation in (0001) InGaN/GaN layers has been suggested invoking generation of V-shaped dislocation half-loops (DHLs) on the growth surface followed by their penetration to the lower interface of the strained epilayer. The importance of the mechanism was supported by numerous observations of the DHLs—see, in particular, the review of experiments reported in Ref. 4. The mechanical model of CT extended to the case of DHLs predicted CTs much more accurately than the MB model. Nevertheless, the experimental CTs were still noticeably larger than the corresponding theoretical predictions (see Fig. 2 from Ref. 4).

A well-established mechanism of stress relaxation in (0001) AlGaN/AlN layers is inclination of threading dislocations (TDs). This mechanism is dominant, however, at a high density of TDs. If AlGaN is grown on a bulk AlN with extremely low TD density (TDD), typically of 10−1−10 cm−2, inclination of existing TDs becomes insufficient for effective stress relaxation and DHLs are observed in such epilayers similarly to as in the case of InGaN/GaN. However, our attempts to predict CTs for DHLs in AlGaN/AlN layers using the model of Ref. 4 failed to reproduce the available data, the experimental CTs were much larger than the theoretical ones. This fact highlights the insufficient understanding of the relaxation processes occurring in AlGaN grown on bulk AlN.

In polar III-nitride structures, TDs forming “arms” of DHLs are inclined with respect to the basal plane that is normal to the Peierls vector of the dislocations (the Burgers vector) plane, i.e. is normal to both dislocation lines. This means that such dislocations are formed by climbing rather than by gliding. Therefore, their formation in compressively strained layers should be accompanied by release of the material confined between the dislocation “arms”. The release occurs by decomposition of the material (see Fig. 1). So, it is naturally expected that the CTs of such epilayers become dependent not only on the mechanical (elastic) properties of dislocations and mismatch strain but also on the thermodynamic properties of the solid alloys (InGaN or AlGaN) and...
the products of their decomposition during dislocation formation.

The goals of this study are: (i) to assess the importance of the thermodynamic aspect for stress relaxation in InGaN/GaN and AlGaN/AlN layers grown by metalorganic vapor phase epitaxy (MOVPE) and (ii) to provide a more accurate estimation of CTs by accounting for this aspect.

2. Modified model of CT

2.1. Criterion for dislocation formation

A dislocation may be generated in an epitaxial layer by gliding, if the work of the lattice-mismatch stress $W$ exceeds the elastic energy of the dislocation $E_{\text{dis}}$. For dislocations formed by climbing, which is accompanied by either material release (in compressively strained layers) or material consumption (in the layers under tensile strain), the criteria of dislocation formation should include additionally the chemical energy $E_{\text{ch}}$ related to the difference in chemical potentials of the released/consumed material in the final and initial states. The latter is valid if the kinetics of the dislocation formation is not the limiting stage of the process, i.e. if the dislocations are formed faster, for example, than growth of the epitaxial layer occurs and if the nucleation of DHLs on the growth surface does not limit their overall rate of formation. In this case, plastic relaxation of the mismatch stress is expected when $E_{\text{dis}} + E_{\text{ch}} < W$ where $W = S(n \cdot \hat{\sigma} \cdot b)$, $n$ and $S$ are the normal to the plane of the DHL and the loop area, respectively, $\hat{\sigma}$ is the mismatch stress tensor, and $b$ is the Burgers vector of the dislocation.

Here, we consider a-type edge dislocations with the Burgers vector $b = \frac{a}{2}(11\bar{2}0)$ that are formed in compressively strained polar epilayers. We will distinguish between two types of dislocation: (i) MDs with length $L$ much longer than the thickness $h$ of an epitaxial layer and (ii) DHLs with the dislocation “arms” inclined to the hexagonal axis of the wurtzite crystal by the angle $\alpha$ (at $\alpha \rightarrow 90^\circ$ both types become equivalent to each other). In the former case, the elastic energy of dislocation can be approximated by the expression

$$E_{\text{dis}} = \frac{b^2 K(\theta) L}{4\pi} \log \left( \frac{2h}{R_0} \right),$$

where $K(\theta)$ is the energy factor depending on the angle $\theta$ between the dislocation line and the Burgers vector and $R_0$ is the dislocation core radius. In the case of DHLs, the energy $E_{\text{dis}}$ should be computed numerically by integrating the elastic fields of infinitesimal prismatic dislocation loops, known in analytical form, over the total DHL area.

Fig. 1. (Color online) Schematic view of a DHL in a strained InGaN/GaN layer with its Burgers vector and atomic release. Open and solid circles schematically show group-III and N atoms, respectively.

Fig. 2. (Color online) Maps of $\sigma_{yy}$ stress component around a DHL formed in In$_{0.1}$Ga$_{0.9}$N: (a) top view ($xy$ plane, $z = b$, where $b$ is the Burgers vector length), and (b) side view ($xz$ plane; $y = 160b$). All the coordinates are given in lengths of the Burgers vector. Stress is normalized by the shear modulus of the alloy, and the Poisson ratio $\nu = 0.24$. The black line in (b) indicates the dislocation core.
We assume that material release during dislocation formation under compressive strain occurs via decomposition of the strained material followed by a fast removal of the decomposition products from the area confined by the dislocation lines. If \( \Delta \mu \) is the difference in the chemical potentials of the decomposition products and the initial solid phase, corresponding to 1 mol of the material, then the chemical energy \( E_{\text{ch}} \) can be calculated by the expression:

\[
E_{\text{ch}} = \Delta \mu (bS/\Omega) \quad \text{where} \quad \Omega_a \text{ is the molar volume of the solid phase.}
\]

For dislocations considered here, the normal \( \mathbf{n} \) and the Burgers vector \( \mathbf{b} \) are parallel to each other and oppositely directed. Then the resolved mismatch stress \( \sigma_{\text{m}} = (\mathbf{n} \cdot \mathbf{\hat{b}}) (\mathbf{b} / b = M \eta / \pi M) \) where \( \mathbf{b} \) is a specific elastic modulus, \( \eta = 1 - a_{\text{eq}} / a \) is the lattice mismatch, and \( a \) and \( a_{\text{eq}} \) are the unstrained lattice constants of the epitaxial layer and of the template on which the epilayer is grown, respectively. Using the above expression and assuming that dislocations start to form at \( E_{\text{dis}} + E_{\text{ch}} = W \), one can obtain a general equation for the CT, \( h_c \):

\[
\left( 4h_c / b \right) \frac{K(\theta)}{4 \pi M} \cdot F \left( \frac{h_c}{b}, \alpha \right) = \eta - \eta_{\text{ch}}, \quad \eta_{\text{ch}} = \frac{\Delta \mu}{M \Omega_a}
\]

(2)

where the function

\[
F \left( \frac{h_c}{b}, \alpha \right) = \log \left( \frac{4h_c}{b} \right) \quad \text{for} \quad \alpha = \frac{\pi}{2} \text{(MDs)}.
\]

For \( \alpha < \pi/2 \) (DHLs), the function \( F \) can be found numerically by integrating the elastic energy density over the space. In Eqs. (2)–(3), we used the relationship \( S/L = h \sin \alpha \), valid for both types of dislocation under consideration, and assumed that \( R_b = b / 2 \). A solution to Eq. (2) exists, if

\( \eta > \eta_{\text{ch}} \).

In the case of polar III-nitride structures, \( M = C_{11} + C_{12} - 2C_{13} / C_{33} \) with \( C_{ij} \) being the stiffness constants of epitaxial materials, whereas the energy factor \( K \) can be calculated using the method\(^{12} \) for \( \theta = 90^\circ \). In isotropic elasticity theory, \( M = 2G(1 + \nu) / (1 - \nu) \) and \( K = G / (1 - \nu) \) where \( G \) is the shear modulus and \( \nu \) is the Poisson ratio.

### 2.2. Chemical potentials

In order to calculate the CT \( h_c \) from Eq. (2), one needs to evaluate the difference in the chemical potentials of the decomposition products and the initial solid material, which is either InGaN or AlGaN in our study. The chemical potential \( \mu^s \) of the initial solid phase can be straightforwardly calculated. In particular, for In,Ga,N/In,Ga,N alloys

\[
\mu_{\text{In,Ga,N}}^s = \mu_{\text{In}}^0 + \mu_{\text{Ga}}^0 + \mu_{\text{N}}^0 (1 - x) + RT \left[ x \log x + (1 - x) \log(1 - x) \right] + H_{\text{mix}} + H_{\text{el}}.
\]

Here, \( \mu_{\text{In}}^0 \) and \( \mu_{\text{Ga}}^0 \) are tabulated standard chemical potentials of pure InN and GaN, respectively.\(^{13} \) \( R \) is the universal gas constant, \( T \) is the temperature, \( x \) is the molar fraction of InN in InGaN, \( H_{\text{mix}} = W_x (1 - x) \) is the enthalpy of mixing of InN and GaN in the InGaN alloy, \( W \) is the interaction energy, and \( H_{\text{el}} = M \Omega_a \bar{u}^2 \) is the elastic energy of the strained alloy. The molar volume of the alloy is found from those of the binary compounds using Vegard’s rule

\( \Omega_k = \Omega_{\text{InN}} + \Omega_{\text{GaN}} (1 - x) \) where \( \Omega_k = m_k / p_k \) (\( k = \text{InN,GaN} \)) and \( m_k \) and \( p_k \) are the molar mass and density of the binaries, respectively. Similarly, the elastic modulus \( M \) of the alloy is estimated. Equation (4) is derived for InGaN alloys; in the case of other ternary compounds, e. g. AlGaN, the chemical potential of the solid phase is estimated in the same manner.

Evaluation of the chemical potentials of the crystal-decomposition products is a more complicated task. It is closely related to the “thermodynamic reservoir” problem normally introduced for calculating the formation energies of dopants and point defects.\(^{14,15} \) Here, thermodynamic properties of the reaction products are assumed to be the same as in the equilibrated reservoir with which atoms/molecules are being exchanged. Normally, thermodynamic potentials of species in the reservoir are considered in two limiting cases: the so-called metal-rich and nitrogen-rich conditions. In the former case, the chemical potentials of group-III metals are assumed to be equal to that of the solid metal; in the latter case, the chemical potential of nitrogen corresponds to that of molecular nitrogen (\( \text{N}_2 \)) in the gas phase. Both cases are weakly relevant to the real growth conditions used for growth of III-nitride heterostructures by different techniques. In addition, growth of nitride compounds occurs under strong influence of \( \text{N}_2 \) adsorption/desorption kinetics originating from a high kinetic barrier for \( \text{N}_2 \) dissociation preceding the adsorption stage.\(^{16} \) The kinetic effect modifies considerably the properties of \( \text{N}_2 \) outgoing from the growth surfaces of nitride compounds, which should be accounted for in the choice of an appropriate “thermodynamic reservoir”. In any case, such a choice should correlate with a particular growth technique and growth conditions used for fabrication of nitride heterostructures.

Earlier, we developed a quasi-thermodynamic (QT) model of III-nitride compound growth by MOVPE with \( \text{N}_2 \) adsorption/desorption kinetics taken into consideration.\(^{17} \) Accounting for atomic conservation on the growth surface, the model relates the flux \( J_k \) of the \( k \)-species at a certain point on the wafer with the partial pressure \( p_k \) of the species at this point via the expression: \( J_k = \alpha_k \beta_k (p_k - p_k^0) \) where \( \alpha_k \) and \( \beta_k = N_k / (2m_k RT)^{1/2} \) are the sticking coefficient and the Hertz–Knudsen factor of the \( k \)-species, respectively, and \( N_k \) is Avogadro’s number. In this expression, \( p_k^0 \) is the so-called thermodynamic pressure of the \( k \)-species. The thermodynamic pressures are related to the chemical potentials of the species via mass-action law equations written for all independent chemical reactions involved in growth. At known \( p_k \), the mass-action law equations together with the atomic conservation equations represent a full system for finding all \( p_k^0 \) and the composition of the growing alloy, and its growth rate.\(^{18} \) In turn, \( p_k \) can be found from the species’ partial pressures \( p_k^{\text{inlet}} \) at the reactor inlet, maintained according to the growth recipe by either numerical simulations,\(^{19} \) or an approximate expression derived for a horizontal reactor:

\[
J_k = B_k (p_{k, \text{inlet}} - p_k),
\]

\[
B_k = 2.68 \exp \left( \frac{-2.84 D_k z}{H V_p} \right),
\]

where \( B_k \) and \( D_k \) are the diffusion conductivity and diffusion coefficient of the \( k \)-species in the gas phase, respectively, \( H \) is the reactor height, \( V_p \) is the mean gas flow velocity over the wafer, and \( z \) is the local lateral coordinate counted downstream from the beginning of the growth zone.
Excluding $p_k$ from the Hertz–Knudsen representation of the species fluxes and Eq. (5), one can obtain

$$J_k = \frac{\alpha_k \beta_k B_k}{B_k + \alpha_k \beta_k} (p_k^\text{in} - p_k^0).$$

(6)

If the sticking coefficient $\alpha_k$ is close to unity, then normally $\alpha_k \beta_k > B_k$ and the expression (6) for the species flux is reduced to $J_k \approx B_k (p_k^\text{in} - p_k^0)$. In contrast, at very small $\alpha_k$ ($\alpha_k \beta_k \ll B_k$), the species flux $J_k \approx \alpha_k \beta_k (p_k^\text{in} - p_k^0)$.

The QT-model of MOVPE growth is derived under the assumption that atoms in the adsorption layer are nearly in equilibrium with the growing crystal. Since the $\alpha_k \beta_k p_k^\text{in}$ product represents the flux of the k species desorbing from the growth surface to the gas phase, it is reasonable to choose $p_k^0$ as the pressure characterizing the thermodynamic properties of the k species in the “thermodynamic reservoir”. In this case, the chemical potential of the gaseous species is:

$$\mu_k^0 = \mu_k^0 + RT \log p_k^0$$

where $\mu_k^0$ is the standard chemical potential of the gaseous k species.

### 2.3. Decomposition routes

Dislocations considered in this study are assumed to nucleate on the growth surface by fluctuations. Therefore, there may be various routes of their formation depending on the particular way of the solid phase decomposition. The most natural way of decomposition is product release to the gas phase by the reverse reactions of those producing crystal growth. In MOVPE of InGaN, these decomposition reactions may be

\begin{align*}
\text{InN(s)} + \frac{3}{2} \text{H}_2(g) & \rightarrow \text{In(g)} + \text{NH}_3(g), \\
\text{GaN(s)} + \frac{3}{2} \text{H}_2(g) & \rightarrow \text{Ga(g)} + \text{NH}_3(g)
\end{align*}

where s and g denote solid phase and gas phase, respectively. An alternative set of the decomposition reactions is

\begin{align*}
\text{InN(s)} & \rightarrow \text{In(g)} + \frac{1}{2} \text{N}_2(g), \\
\text{GaN(s)} & \rightarrow \text{Ga(g)} + \frac{1}{2} \text{N}_2(g).
\end{align*}

It is an intrinsic feature of the QT-model that the difference in the chemical potentials of the initial crystal and its decomposition product does not depend on the particular choice of decomposition reactions. This fact can be checked by using the above expressions for the chemical potentials of solid and gaseous species along with the mass-action law equations relating the thermodynamic pressures $p_k^0$. Another important feature of the QT-model is that in the case of decomposition reactions reverse to those producing crystal growth, $\Delta \mu = 0$ for decomposition products released to the gas phase. This follows from direct calculation of $\Delta \mu = \frac{1}{2} \mu_{\text{N}_2}^0 + \mu_{\text{In}}^0 + (1 - x) \mu_{\text{Ga}}^0 - \mu_{\text{InGaN}}^0$ corresponding, e.g. to the latter of the above sets of decomposition reactions and mass-action law equations derived for MOVPE growth of InGaN. From a physical point of view, $\Delta \mu = 0$ is the consequence of quasi-equilibrium between the species in the adsorption layer and bulk of the growing crystal assumed in the QT-model. So, in the case of the decomposition products release into the gas phase, there is no predicted impact of chemical factor on the CT of strained InGaN/GaN. The same conclusion is valid also for AlGaN/AlN alloys.

However, there is an alternative route of decomposition where group-III atoms are released into the liquid phase on the growth surface while nitrogen comes to the gas phase in the form of diatomic molecules. Assuming the liquid-phase compositions, $x_\text{In}^0$ and $x_{\text{Ga}}^0$, to be nearly equal to the group-III composition of the ternary alloy, i.e. $x_\text{In}^0 \approx x$ and $x_{\text{Ga}}^0 \approx 1 - x$, and neglecting the energy of In and Ga mixing in the liquid phase, one can calculate the chemical potential of the liquid phase as

$$\mu_{\text{In}}^0 + \mu_{\text{Ga}}^0 = \mu_{\text{In}}^0 + \mu_{\text{Ga}}^0 (1 - x) + RT \left[ x \log x + (1 - x) \log (1 - x) \right].$$

(7)

Here, $\mu_{\text{In}}^0$ and $\mu_{\text{Ga}}^0$ are the standard chemical potentials of liquid In and Ga, respectively. Then the chemical potential difference

$$\Delta \mu = \mu_{\text{In}}^0 + \frac{1}{2} \mu_{\text{N}_2}^0 - \mu_{\text{InGaN}}^0$$

(8)

$$= \mu_{\text{R}} - H_{\text{mix}} - H_{\text{d}} + RT \log p_{\text{N}_2}^0,$$

where $\mu_{\text{R}} = x (\mu_{\text{In}}^0 + \frac{1}{2} \mu_{\text{N}_2}^0 - \mu_{\text{InGaN}}^0) + (1 - x) (\mu_{\text{Ga}}^0 + \frac{1}{2} \mu_{\text{N}_2}^0 - \mu_{\text{InGaN}}^0)$ can be calculated from tabulated chemical potentials of the relevant solid, liquid, and gaseous species. In contrast to the decomposition product release into the gas phase, $\Delta \mu$ is not equal to zero here, as the liquid phase is not in equilibrium with the bulk of growing crystal. A similar consideration can also be applied to AlGaN alloys. In order to estimate the value of $\Delta \mu$, it is necessary to evaluate $p_{\text{N}_2}^0$. This can be done with the QT-model of MOVPE growth of InGaN by considering the reaction of NH₃ decomposition on the growth surface: NH₃(g) $\rightarrow \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{H}_2(g)$. Using Eq. (5) for the species fluxes, assuming the relationship $\alpha_{\text{N}_2} \beta_{\text{NH}_3} \ll B_{\text{NH}_3}$, and neglecting the contribution of group-III metalorganic species to NH₃ decomposition, one can obtain the following equations of the QT-model:

\begin{align*}
B_{\text{NH}_3}(p_{\text{NH}_3}^\text{in} - p_{\text{NH}_3}^0) &= \frac{1}{2} \alpha_{\text{N}_2} \beta_{\text{NH}_3} p_{\text{N}_2}^0, \\
B_{\text{NH}_3}(p_{\text{NH}_3}^\text{in} - p_{\text{NH}_3}^0) &= \frac{3}{2} B_{\text{H}_2}(p_{\text{N}_2}^\text{in} - p_{\text{H}_2}^\text{in}), \\
p_{\text{NH}_3}^0 &= K_d (p_{\text{N}_2}^\text{in})^{1/2} (p_{\text{H}_2}^\text{in})^{3/2}, \\
K_d &= \exp \left[ \frac{1}{2} \frac{\mu_{\text{N}_2}^0 - \frac{3}{2} \mu_{\text{H}_2}^0 - \mu_{\text{NH}_3}^0}{RT} \right].
\end{align*}

(9)

The first two equations of Eq. (9) account for the conservation of N and H atoms on the growth surface, whereas the third one is the mass-action law equation for the reaction of NH₃ decomposition, having the reaction constant $K_d$. To account for the fact that InGaN MOVPE uses N₂ as the carrier gas, one should set in Eq. (9) $p_{\text{H}_2}^\text{in} = 0$. In contrast to InGaN, MOVPE of AlGaN is normally carried out using H₂ as the carrier gas. In this case, $p_{\text{H}_2}^\text{in} = 0$. At the known partial pressures of species at the reactor inlet, numerical solution of Eq. (9) provides the thermodynamic pressures necessary for calculating $\Delta \mu$.

### 3. Results and discussion

#### 3.1. Dislocations in InGaN/GaN heterostructures

First of all, the modified model of CT has been applied to MOVPE-grown InGaN/GaN heterostructures. Normally, the
InGaN composition is controlled in MOVPE by variation of InGaN growth temperature. In order to find a relationship between the InGaN composition and its growth temperature, we used data from both experimental and theoretical studies on InGaN/GaN growth in the horizontal AIX 200/4 RF-S reactor \((H = 3 \text{ cm})\).\(^{20}\) The growth was carried out at a pressure of 200 mbar in a \(N_2\) atmosphere and an \(NH_3\) molar fraction at the reactor inlet of 0.352 \((p_{NH_3} = 7040 \text{ Pa})\). Growth temperature variation from 700 °C to 940 °C provided a decrease of InN molar fraction in InGaN from \(x = 0.36\) to \(x = 0.02\); the detailed dependence of the InGaN composition on growth temperature was reported earlier in Ref. 20. The gas flow velocity in the reactor \(V_f\) was about 0.5 m s\(^{-1}\), weakly depending on the growth temperature.

The diffusion conductivities of the species were calculated analytically using Eq. (5) for the center of a two inch wafer \((z = 2.54 \text{ cm})\), using diffusion coefficients estimated from conventional molecular-kinetics theory.\(^{21}\) Thermodynamic properties of all the species were borrowed from Ref. 13 except for the enthalpy of InN formation, for which the value of 53 kJ mol\(^{-1}\) was chosen, providing good agreement between numerical simulations and experiment.\(^{20}\) The interaction energy \(W\) and its dependence on the InGaN composition was taken from Ref. 22. The sticking coefficient \(\alpha_{\text{InN}}\) of \(N_2\) on the InGaN growth surface was interpolated between those of pure GaN and InN as follows:

\[
\log \alpha_{\text{N}_2} = x \log \alpha_{\text{N}_2}^{\text{GaN}} + (1 - x) \log \alpha_{\text{N}_2}^{\text{InN}}. \tag{10}
\]

The sticking coefficients of \(N_2\) at the surfaces of the binary compounds, \(\alpha_{\text{N}_2}^{\text{GaN}}\) and \(\alpha_{\text{N}_2}^{\text{InN}}\), were determined from analysis of temperature-dependent Langmuir evaporation of GaN and growth of InGaN by MBE.

The chemical potential difference \(\Delta\mu\) calculated by Eq. (8) and Eq. (9) for a wide range of growth temperatures, corresponding to the group-III atom release into liquid phase, varied from 34.3 kJ mol\(^{-1}\) at 655 °C to 59.7 kJ mol\(^{-1}\) at 885 °C.

The inclination angle of DHLs in \(In_{\text{Ga}_{1-x}}N/GaN\) heterostructures measured by high-resolution transmission electron microscopy is about 20° at \(x = 0.23–0.28\), corresponding to the [0113] and [1103] directions.\(^{23}\) As there is a lack of reliable data on dislocation inclination at other InGaN compositions, we have chosen this value for the whole range of the alloy compositions.

Figure 3 shows the CT calculated when accounting for the above \(\Delta\mu\) (solid line) and with \(\Delta\mu = 0\) (dash-dotted line). One can see that non-zero \(\Delta\mu\) increases the CT, especially at low InGaN compositions where \(\Delta\mu\) is high. Moreover, in the case of InGaN decomposition accompanied by liquid phase formation \((\Delta\mu \neq 0)\), the CT tends to infinity at \(x \approx 0.05\), i.e. there is no stress relaxation via DHLs at smaller \(x\). Symbols in Fig. 3 show the experimental data on CT collected earlier\(^{24–32}\) and borrowed additionally from Ref. 33. One can see that the theoretical curves calculated for \(\Delta\mu = 0\) and \(\Delta\mu \neq 0\) represent nearly the lower and upper boundaries for the array of experimental points, respectively. This may be explained by competition between the InGaN decomposition mechanisms, with the product release entirely to the gas phase \((\Delta\mu = 0)\) and that involving liquid phase formation \((\Delta\mu \neq 0)\). It should be noted, however, that there exists an alternative interpretation for the observed large scatter of the data on CT, which is especially large at low InGaN compositions. In the case of a relatively high density of TDs, one more relaxation mechanism may come into play, reducing the CT: inclination of TDs in the strained epilayer.\(^{5,6}\) Indirect evidence for this is provided by the data\(^{53}\) demonstrating dependence of InGaN/GaN CT on the TDD controlled by using either sapphire or bulk GaN substrate for MOVPE growth (the data are shown in Fig. 3 by half-filled pentagons and stars, respectively). Unfortunately, this study did not report detailed investigation into particular relaxation mechanisms of stress relaxation in high-TDD and low-TDD InGaN/GaN epilayers. So, further efforts are needed to identify the dominant routes of stress relaxation in such structures in a wide range of InGaN compositions. Besides, InGaN layers with similar compositions can be grown under significantly different growth conditions, which may also contribute to scatter of experimental CT values.

### 3.2. Dislocations in AlGaN/AIN heterostructures

MOVPE of the layers is normally carried out using \(H_2\) carrier gas. Here, we consider AlGaN/AIN layers grown by MOVPE at 1100 °C, a reactor pressure of 100 mbar, and an \(NH_3\) molar fraction at the reactor inlet of 0.01 \((p_{NH_3} = 100 \text{ Pa})\). Growth was assumed to be performed in the same AIX 200/4 RF-S reactor with Al\(_{1-x}\)Ga\(_x\)N composition controlled by adjusting flow rates of metallicorganic species.

The diffusion conductivities of the gaseous species were calculated in a manner similar to that discussed in Sect. 3.1. The thermodynamic properties of all the species and interaction energy \(W\) of AlGaN were taken from Ref. 13 and Ref. 22, respectively. The \(N_2\) sticking coefficient on the AlGaN growth surface was obtained from Eq. (10) with \(\alpha_{\text{AlN}}\) instead of \(\alpha_{\text{N}_2}\) where the sticking coefficient \(\alpha_{\text{AlN}}\) was found from analysis of temperature-dependent Langmuir evaporation of AlN.

The chemical potential of the Al–Ga liquid phase \(\mu_{\text{Al–Ga}}\) was found using Eq. (7) with the standard chemical potential \(\mu_{\text{Al}}\) of liquid Al instead of \(\mu_{\text{In}}\) on the right-hand side. The chemical potential difference \(\Delta\mu\) calculated for the growth temperature of 1100 °C using Eq. (8) with \(\mu_{\text{Al–Ga}}\) instead of \(\mu_{\text{In–Ga}}\) and Eq. (9) varied from 11.0 kJ mol\(^{-1}\) at \(x = 0\) (pure
GaN to 226.0 kJ mol\(^{-1}\) at \(x = 0.97\). At 1250 °C, \(\Delta \mu\) varied from \(-7.6 \text{ kJ mol}^{-1}\) at \(x = 0\) to 194.9 \text{ kJ mol}^{-1}\) at \(x = 0.97\). The negative value of \(\Delta \mu\) points to the fact that GaN decomposition into liquid Ga and gaseous \(\text{N}_2\) becomes thermodynamically more favorable under the chosen conditions than growth of GaN. The addition of Al results in a dramatic rise in \(\Delta \mu\) due to the high enthalpy of liquid Al formation.

Little is known about the inclination angle \(\alpha\) of DHLs in AlGaN/AlN layers. To our knowledge, there is only one paper\(^{34}\) reporting on DHL formation in an AlGaN-based structure grown on bulk AlN. In that study, the inclination angle of dislocation lines forming half-loops was found to vary from 20° to 60°. Unfortunately, stress relaxation was initiated in that study by inserting a 10-period \(\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}/\text{AlN}\) superlattice between the main \(\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}\) layer and the AlN. Therefore, the data on the inclination angle cannot be regarded as highly reliable. On the other hand, the CT of GaN layers grown on AlN by \(\text{NH}_3\) MBE at 900 °C was reported to be nearly that of three monolayers, i.e. 0.78 nm,\(^{34}\) which is close to the value predicted by the MB model. Since the MB model deals with conventional MDs, the above correspondence implies \(\alpha \approx 90°\) for GaN/AlN layers.

Given the lack of reliable information on the inclination angle of DHLs, we have decided to use instead the data on composition-dependent inclination of TDs. Figure 4 summarizes available data\(^{5-7,35}\) on the inclination angle observed in AlGaN/AlN layers as a function of AlGaN composition. Despite the data scatter, there is a distinct trend of inclination angle decrease with the AlN molar fraction in AlGaN. Approximation of the data with the smooth curve shown in Fig. 4 (see appendix) was then regarded in this study as the composition dependence of inclination angle for new DHLs.

Figure 5 compares the CTs of AlGaN/AlN epilayers estimated for the cases of \(\Delta \mu = 0\) and \(\Delta \mu \neq 0\). In the latter case, calculations were carried out for two growth temperatures: 1100 °C (dotted line in Fig. 5) and 1250 °C (solid line in Fig. 5). One can see that CT rises dramatically if the DHL formation occurs with group-III atoms releasing to the liquid phase. Moreover, at the same flow rates of metallicorganic species at the reactor inlet, the CT depends noticeably on the growth temperature: a lower temperature provides a larger CT. In the case of \(\Delta \mu \neq 0\), no plastic relaxation via DHL formation is predicted for \(x > 0.6\) at 1250 °C and for \(x > 0.55\) at 1100 °C. In contrast, the CT predicted for \(\Delta \mu = 0\) varies from 1 nm at \(x = 0\) to 84 nm at \(x = 0.80\) and 1012 nm at \(x = 0.93\).

There is a lack of reported data on the CTs of AlGaN/AlN layers to compare with our theory. Two points are obtained for \(x = 0.6\) and \(x = 0.7\) by extrapolating the data\(^{34}\) on relaxation degrees of various AlGaN layers grown on bulk AlN substrates to zero relaxation level (filled diamonds in Fig. 5). These points are close to the CT predicted for \(\Delta \mu \neq 0\), exceeding that corresponding to \(\Delta \mu = 0\) by about two orders of magnitude. This may be evidence for the dominant route of stress relaxation via DHL formation involving liquid phase for group-III atomic release. The quantitative discrepancy between the experimental points and theoretical curve for \(\Delta \mu = 0\) may be explained by differences in the growth conditions used in Ref. 8 and those assumed in our simulations. There are also data\(^{9}\) on the growth of relaxation-free AlGaN on bulk AlN, which are shown in Fig. 5 by open squares. Two of the three points lie above the theoretical curve corresponding to \(\Delta \mu = 0\), supporting the above conclusion on the possible mechanism of stress relaxation in AlGaN/AlN.

To our knowledge, there are no data in the literature on the CT of MOVPE-grown Al\(_{x}\)Ga\(_{1-x}\)N/AlN layers with small \(x\), including GaN/AlN. In order to understand how stress relaxation occurs in such epilayers, we include the data on the CT of GaN on AlN grown at 900 °C by \(\text{NH}_3\) MBE\(^{34}\) (filled pentagon in Fig. 5). According to Ref. 34, CT at this temperature is not affected by the type of substrate used for growth, either AlN/sapphire template or AlN bulk crystal. One can see from Fig. 5 that all the theoretical curves tend to merge at \(x \to 0\), becoming weakly dependent on the particular growth technique and being close to the above experimental point.

### 3.3. Growth parameters affecting CT

Our simulations discussed in the previous sections show that growth temperature is the primary factor affecting the CT of grown epilayers in the case of atomic release with group-III liquid formation. In all the cases considered in this study, a
Figure 6. (Color online) CT of GaN layers grown by MOVPE on relaxed Al$_{0.21}$Ga$_{0.79}$N buffers at various reactor pressures calculated for $\Delta \mu \neq 0$ as a function of growth temperature.

The critical thickness of GaN layers grown by MOVPE on relaxed Al$_{0.21}$Ga$_{0.79}$N buffers at various reactor pressures (200 mbar, 2000 mbar) is shown in the diagram. The critical thickness increases with decreasing growth temperature and decreases with increasing reactor pressure. This behavior is due to the change in chemical potential $\Delta \mu$ with temperature and pressure.

4. Conclusions

As the Burgers vector of DHLs formed in strained InGaN/GaN or AlGaN/AlN epilayers is normal to the inclination plane, formation of such dislocations should be accompanied by atomic release from the area confined by the dislocation “arms”. During the release, solid alloy, InGaN or AlGaN, decomposes, so that the difference of chemical potentials between the decomposition products and the initial alloy contribute to the energy balance, controlling the CT of the epilayers. Since the chemical potential difference depends generally on the growth conditions, CTs of the strained layers become dependent on the growth conditions as well. In order to estimate the impact of the chemical factor on the CT value, we have suggested using the QT-model of MOVPE growth of III-nitride materials, accounting for the kinetic effects of N$_2$ adsorption/desorption. Considering the effect of the growth conditions on the energetics of dislocation formation, such an approach may also be helpful for analysis of TD inclination in compressively strained epilayers, and applicable to studying point defect generation in semiconductors.

The chemical factor is found to be negligible, if the products of InGaN or AlGaN decomposition are released to the gas phase. In contrast, if the alloys decompose into group-III metallic liquid and gaseous nitrogen, the chemical factor becomes important, generally increasing the CT. In the case of InGaN/GaN layers, the above two decomposition routes provide nearly the lower and upper boundaries for experimental data on the CTs of the alloys, which is explained by competition of the decomposition mechanisms. An alternative explanation invokes inclination of TDs in the InGaN layer as a competitive mechanism of stress relaxation. For AlGaN/AIN, the large CTs predicted for AlGaN decomposition with group-III liquid phase formation and nitrogen release into gas phase agree well with the few experimental data points available for these materials. The dominance of such a decomposition route may explain the fact that AlGaN/AIN alloys with AIN fraction exceeding 60% can be grown without plastic relaxation up to thicknesses as large as 0.5–1.0 μm.

Our approach to the estimation of CTs of the compressively strained polar epilayers is based on the assumption that the kinetics of the atomic release and nucleation of DHLs at the growth surface are not limiting stages of dislocation formation. Accounting for the kinetic effects in future studies may improve further our understanding of stress relaxation in III-nitride heterostructures.

Appendix

Inclination of $\alpha$-type TDs is a well-known mechanism of stress relaxation in compressively strained AlGaN/AIN and of build-up of tensile stress in AlGaN:Si layers. In order to understand how the inclination angle $\alpha$ depends on the alloy composition in AlGaN/AIN layers, we, following Refs. 37, 38, assume that TD inclination occurs via outgoing atoms from the dislocation core crossing the growth surface. The inclination is considered as a kinetic process, mainly determined by a relation between the chemical potential variation during decomposition of the material and mismatch energy release due to dislocation inclination. Therefore, the inclination angle depends on growth conditions, layer composition and stress in the epilayer.

Since AlN has a much higher binding energy than GaN, Al atoms hardly abandon the dislocation core, as compared to Ga atoms. Therefore, the inclination angle $\alpha$ of TDs in AlGaN layers is expected to rise monotonically with the GaN content in the alloy. If the inclination is primarily controlled by outgoing Ga atoms only, then, at a certain stress, Ga atomic release becomes insufficient for the process, thus involving Al atoms. Under these conditions, the rise in $\alpha$ with compressive stress is stopped. After that, the inclination angle turns out to be constant in a certain range of stresses, until the mismatch energy release due to additional inclination becomes comparable with the chemical potential variation due to AlN decomposition. Associating the angle, corresponding to the maximal inclination produced by Ga atoms only, with the inclination angle $\alpha$ we can estimate its value as a function of AlGaN composition.
To obtain the dependence, we supposed that only Ga atoms go out from the dislocation at its edge on the growth surface, leaving the TD core to consist of Al atoms. By using a cross-sectional view of an AlGaN layer showing the (2110) half-plane related to an inclined TD, the equation for the maximal angle of TD inclination can be easily obtained:

$$\alpha = \tan^{-1}\left[\sqrt{a(x)} \frac{1 - x}{c(x)} \cdot x\right].$$  (11)

Here, $a(x)$ and $c(x)$ are the composition-dependent lattice constants of Al$_{x}$Ga$_{1-x}$N. The analytical expression (11) is shown in Fig. 4 by a line, approximating well the available data.

Equation (11) can be used, as a first approximation, for the inclination angle of DHLs while predicting their nucleation. Indeed, the nucleation of new dislocations is likely to occur via outgoing material and generation of new dislocations usually occurs at a stress level which is high enough to meet the conditions of maximal inclination discussed above.

It should be noted that for pure GaN Eq. (11) predicts $\alpha = 90^\circ$, which corresponds to the transformation of TDs into MDs lying in the basal plane. The prediction can be indirectly verified by the fact that the experimentally measured CT for a GaN layer grown on AlN, agrees well with the value obtained by the Matthews–Blakeslee approach for a long MD (see Sect. 3.2).

ORCID iDs
Sergey Yu. Karpov https://orcid.org/0000-0001-5593-4167

1) J. Tsao, Materials Fundamentals of Molecular Beam Epitaxy (Academic, New York, 1993), Chap. 5.
2) J. W. Matthews and A. E. Blakeslee, J. Cryst. Growth 27, 118 (1974).
3) A. M. Smirnov, E. C. Young, V. E. Bougrov, J. S. Speck, and A. E. Romanov, APL Mater. 4, 016105 (2016).
4) A. V. Lobanova, A. L. Kolesnikova, A. E. Romanov, S. Yu. Karpov, M. E. Rudinsky, and E. V. Yakovlev, Appl. Phys. Lett. 103, 152106 (2013).
5) D. M. Follstaedt, S. R. Lee, P. P. Provencio, A. A. Allerman, J. A. Floro, and M. H. Crawford, Appl. Phys. Lett. 87, 121112 (2005).
6) D. M. Follstaedt, S. R. Lee, A. A. Allerman, and J. A. Floro, Appl. Phys. Lett. 105, 085307 (2009).
7) Z. Ren et al., Appl. Phys. Lett. 91, 051116 (2007).
8) J. R. Grandusky, J. A. Smart, M. C. Mendrick, L. J. Schowalter, K. X. Chen, and E. F. Schubert, J. Cryst. Growth 311, 2864 (2009).
9) R. Dalmau et al., ECS Trans. 33, 43 (2010).
10) M. Zhu, S. You, T. Detchprohm, T. Paskova, E. A. Preble, D. Hanser, and C. Wetzel, Phys. Rev. B 81, 125325 (2010).
11) L. B. Freund, J. Appl. Mech. 54, 554 (1987).
12) L. J. Teutonico, Mater. Sci. Eng. 6, 27 (1970).
13) I. N. Przhevalskii, S. Y. Karpov, and Y. N. Makarov, MRS Internet J. Nitride Semicond. Res. 3, 30 (1998).
14) C. G. Van de Walle and J. Neugebauer, J. Appl. Phys. 95, 3851 (2004).
15) J. L. Lyons and C. G. Van de Walle, npj Comput. Mater. 3, 12 (2017).
16) M. V. Aver'yanova, S. Y. Karpov, Y. N. Makarov, I. N. Przhevalskii, M. S. Ramm, and R. A. Talalaev, MRS Internet J. Nitride Semicond. Res. I, 31 (1996).
17) S. Y. Karpov, V. G. Prokofyev, E. V. Yakovlev, R. A. Talalaev, and Y. N. Makarov, MRS Internet J. Nitride Semicond. Res. 4, 4 (1999).
18) S. Y. Karpov, J. Cryst. Growth 248, 1 (2003).
19) W. G. J. H. M. van Sark, G. Janssen, M. H. J. M. de Croon, and L. J. Giling, Semicond. Sci. Technol. 5, 16 (1990).
20) E. V. Yakovlev, R. A. Talalaev, R. W. Martin, C. Jeynes, N. Peng, C. J. Deatcher, and I. M. Watson, Phys. Status Solidi C 3, 1620 (2006).
21) C. R. Klein, in Computational Modeling in Semiconductor Processing, ed. M. Meyyapan, (Artech House Publishers, Boston, 1995), Chap. 4.
22) S. Y. Karpov, N. I. Podolskiy, I. A. Zhmakin, and A. I. Zhmakin, Phys. Rev. B 70, 235203 (2004).
23) N. Cherkashin, CEMES-CNRS and Université de Toulouse, France, private communication.
24) K. Pantras, G. Patriarche, G. Orai, S. Gautier, T. Moudakir, M. Abid, V. Gorge, Z. Djebbour, P. L. Voss, and A. Ougazzaden, Phys. Status Solidi A 209, 25 (2012).
25) M. Müller, G. D. W. Smith, B. Gault, and C. R. M. Grovenor, Acta Mater. 60, 4277 (2012).
26) M. Leyron, J. Stellmack, C. Meissner, M. Pistorussek, and M. Kneissl, J. Cryst. Growth 310, 2591 (2008).
27) Z. Liliental-Weber, K. M. Yu, M. Hawkrigde, S. Bedair, A. E. Berman, A. Emara, D. R. Khanal, J. Wu, J. Domagala, and J. Bak-Misiuk, Phys. Status Solidi C 6, 2626 (2009).
28) H. Wang, D. S. Jiang, U. Jahn, J. J. Zhu, D. G. Zhao, S. S. Liu, S. M. Zhang, Y. X. Gu, and H. Yang, Physica B 405, 4668 (2010).
29) P. M. F. J. Costa, R. Datta, M. J. Kappers, M. E. Vickers, C. J. Humphreys, D. M. Graham, P. Dawson, M. J. Godfrey, E. J. Trush, and J. T. Mullins, Phys. Status Solidi A 203, 1729 (2006).
30) D. Holoc, Y. Zhang, D. V. Siddhara Rao, M. J. Kappers, C. McAleese, and C. J. Humphreys, J. Appl. Phys. 104, 125314 (2008).
31) A. V. Sakharov et al., Semiconductors 43, 812 (2009).
32) M. J. Reed, N. A. El-Masry, C. A. Parker, J. C. Roberts, and S. M. Bedair, Phys. Status Solidi C 7, 3 (2010).
33) S. P. DenBaars, and J. S. Speck, Appl. Phys. Lett. 77, 4212 (2000).
34) G. Ju, M. Tabuchi, Y. Takeda, and H. Amano, Appl. Phys. Lett. 110, 262105 (2017).
35) P. Sohl, D. Martin, and N. Grandjean, Semicond. Sci. Technol. 32, 075010 (2017).
36) Z. Wu, K. Nonaka, Y. Kawai, T. Asai, F. A. Ponce, C. Chen, M. Iwaya, S. Kamiyama, H. Amano, and I. Akasaki, Appl. Phys. Express 3, 111003 (2010).
37) P. Cantu, F. Wu, P. Walterite, S. Keller, A. E. Romanov, U. K. Mishra, S. P. DenBaars, and J. S. Speck, Appl. Phys. Lett. 83, 674 (2003).
38) S. Raghavan, Phys. Rev. B 83, 052102 (2011).
39) S. Raghavan, I. C. Manning, X. Weng, and J. M. Redwing, J. Cryst. Growth 359, 35 (2012).