Elastic constants, composition, and piezoelectric polarization in $\text{In}_x\text{Al}_{1-x}\text{N}$: From ab initio calculations to experimental implications for the applicability of Vegards rule

Mengyao Xie, Ferenc Tasnadi, Igor Abrikosov, Lars Hultman and Vanya Darakchieva

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Mengyao Xie, Ferenc Tasnadi, Igor Abrikosov, Lars Hultman and Vanya Darakchieva, Elastic constants, composition, and piezoelectric polarization in $\text{In}_x\text{Al}_{1-x}\text{N}$: From ab initio calculations to experimental implications for the applicability of Vegards rule, 2012, Physical Review B. Condensed Matter and Materials Physics, (86), 15, 155310.

<http://dx.doi.org/10.1103/PhysRevB.86.155310>

Copyright: American Physical Society

<http://www.aps.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-85295>

Elastic constants, composition, and piezoelectric polarization in $\text{In}_x\text{Al}_{1-x}\text{N}$: From *ab initio* calculations to experimental implications for the applicability of Vegard's rule

M.-Y. Xie, F. Tasnádi, I. A. Abrikosov, L. Hultman, and V. Darakchieva*

IFM, Linköping University, SE-581 83 Linköping, Sweden

(Received 4 August 2012; published 12 October 2012)

We present a theoretical analysis on the applicability of Vegard's linear rule in $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys in relation to strain related elastic and piezoelectric properties. We derive the elastic stiffness constants and biaxial coefficients, as well as the respective deviations from linearity (Vegard's rule) by using *ab initio* calculations. The stress-strain relationships to extract composition from the lattice parameters are derived in different coordinate systems for $\text{In}_x\text{Al}_{1-x}\text{N}$ with an arbitrary surface orientation. The error made in the composition extracted from the lattice parameters if the deviations from linearity are not taken into account is discussed for different surface orientations, compositions and degrees of strain in the $\text{In}_x\text{Al}_{1-x}\text{N}$ films. The strain induced piezoelectric polarization is analyzed for $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys grown pseudomorphically on GaN. The polarization values are compared with those obtained from our experimental data for the lattice parameters. We establish the importance of the deviation from linearity to correctly determine the piezoelectric polarization and also a smooth, not particular piezoelectric response at GaN lattice matched conditions.

DOI: [10.1103/PhysRevB.86.155310](https://doi.org/10.1103/PhysRevB.86.155310)

PACS number(s): 62.20.de, 68.60.Bs, 78.66.Fd

I. INTRODUCTION

Strained semiconducting thin films and low-dimensional structures are the building blocks of contemporary and future electronic and optoelectronic devices, and present test systems to study a variety of physical phenomena. Strain has a profound effect on materials fundamental parameters and properties as it may change the crystal symmetry and the electronic band structure. For instance, the optical, polarization, and vibrational properties of heteroepitaxial thin films and heterostructures are affected by the unintentional strain present in such systems. Often, strain is intentionally introduced in semiconducting thin films in order to modify the device performance, e.g., in laser diodes and light-emitting diodes or to create new functionalities, e.g., generation of two-dimensional electron gas (2DEG) in high electron mobility transistors (HEMTs) and large in-plane optical polarization anisotropy for data storage devices, sensors, and biophotonics. Studying the effect of strain on the fundamental material properties requires the knowledge of elastic constants, which describe the response to an applied macroscopic stress.

Group-III nitrides, InN, GaN, AlN, and their alloys, attract substantial research interest due to their unique properties and importance for optoelectronic and electronic devices.¹⁻⁶ Strain effects are particularly important for group-III nitrides because of the lack of native substrates. The growth on foreign substrates typically leads to the presence of built-in strain in heteroepitaxial nitride layers due to the difference in lattice parameters and thermal expansion coefficients between layers and substrates.

$\text{In}_x\text{Al}_{1-x}\text{N}$ alloys cover the widest wavelength region among the III-nitride ternaries (or any other semiconductor system) with band gaps ranging from 0.6 eV (InN) to 6.2 eV (AlN). This makes the $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys promising candidates for light emitting diodes and laser diodes in the range from far infrared to deep ultraviolet, as well as for solar cells applications. $\text{In}_x\text{Al}_{1-x}\text{N}$ thin films with In content $x = 0.17$ – 0.20 allow lattice-matching to GaN and are extensively studied in

relation to their application for Bragg reflectors, microcavities, polariton emission, HEMTs, in selective etching, etc.⁷⁻⁹ Furthermore, strain adjusted $\text{In}_x\text{Al}_{1-x}\text{N}$ films were proposed for solar-blind photodiode application by considering the piezoelectric polarization.¹⁰ Despite the intense research in the field, many of the alloy properties remain unexplored or controversial. For instance, the compositional dependencies of the band gap bowing parameters,¹¹⁻¹³ lattice parameters, and applicability of Vegard's rule to the lattice parameters are debated.¹⁴⁻¹⁷ The alloy stiffness constants and strain effects on many of the fundamental properties are still not conclusively established.¹⁸⁻²⁰

Furthermore, the precise control of $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy composition, which is mandatory for device design and fabrication, remains an issue. A widely employed method is to extract composition of ternary alloys from the lattice parameters measured by x-ray diffraction (XRD). Usually, validity of Vegard's rule is assumed, i.e., the *relaxed* lattice parameters of the ternary are calculated from a linear interpolation between the relaxed lattice parameters of the respective binaries. Recently, we have shown by *ab initio* calculations that the $\text{In}_x\text{Al}_{1-x}\text{N}$ lattice parameters slightly deviate from Vegard's rule.¹⁷ Although small, these deviations are important to account for in order to determine the alloy composition correctly. In addition, in order to extract alloy composition from XRD measurements, the strain should be considered and therefore the stiffness constants of the $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy need to be known.¹⁶ The alloy stiffness constants are also required for establishing the compositional dependence of the piezoelectric polarization in $\text{In}_x\text{Al}_{1-x}\text{N}$ heterostructures. However, the experimental determination of the stiffness constants is hampered by the lack of good quality thick $\text{In}_x\text{Al}_{1-x}\text{N}$ films covering the whole compositional range, and no experimental values for the stiffness constants exist in the literature. Therefore, theoretical calculations are an alternative to study the compositional dependence of the stiffness constants and to provide useful insights on the strain effects on the composition of the $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys.

TABLE I. Optimized short-range order parameters of the applied $(4 \times 2 \times 4)$ sized SQS supercells for the studied compositions x .

In content, x	Shell order						
	#1	#2	#3	#4	#5	#6	#7
0.125	0	0	0	0	0.02	0	0
0.1875	0.01	0.01	0.01	-0.03	0.03	0.01	-0.01
0.2031	0	0	0	0.04	0	0	-0.01
0.3906	0.02	-0.01	-0.01	0.02	-0.02	-0.01	0.02
0.5937	-0.02	0.01	0.01	-0.04	0	0.01	0.01
0.75	0	0	0	0	0	0	0

In this work we report the compositional dependencies of the stiffness constants and biaxial coefficients of $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys. We discuss the deviations of the elastic constants from Vegard's rule and present a comprehensive study on their effect on the extraction of composition and piezoelectric polarization in $\text{In}_x\text{Al}_{1-x}\text{N}$ films with different surface orientations.

II. THEORY AND BACKGROUND

A. First principle calculations

We applied the special quasirandom structure²¹ (SQS) method to model effects of substitutional disorder in $\text{In}_x\text{Al}_{1-x}\text{N}$. This approach introduces a supercell with vanishing short-range order (SRO) parameters, which describes completely random alloy. The applied approximate SQS supercells have been generated by optimizing the Warren-Cowley pair short-range order parameters^{22,23} up to seven shells of nearest neighbors. The optimizations were performed by using the Metropolis-type simulated annealing algorithm²⁴ with a cost-function built from the properly weighted pair SRO parameters. Substitutional alloys have been considered, where the In atoms can occupy sites only on the Al sublattice. Accordingly, the SRO parameters were calculated only on the Al sublattice. Among the several generated SQS supercells, the one with size of $(4 \times 2 \times 4)$ turned out to be a very good model along the entire composition range because of showing almost vanishing Warren-Cowley SRO parameters up to the seventh neighboring shells. It has 128 atoms, and its SRO parameters for each composition studied here are given in Table I.

The elastic stiffness constants were derived from the second order Taylor-expansion coefficients of the total energy,

$$C_{ij} = \frac{1}{V} \frac{\partial^2 E(\varepsilon_1 \cdots \varepsilon_6)}{\partial \varepsilon_i \partial \varepsilon_j}, \quad (1)$$

where Voigt's notation was used to describe the strain tensor. In the calculations we applied 1% and 2% deformations to the supercells and used the simple finite difference technique to obtain the stiffness constants. Total-energy calculations were performed by the first-principles density-functional theory (DFT) using the projector augmented wave (PAW) approach²⁵ as implemented in the Vienna Ab-initio Simulation Package (VASP).²⁶ The detailed study by Stampfl *et al.*²⁷ has shown that the thermodynamic properties of both components, the wurtzite AlN and InN, are well described by the generalized gradient approximation (GGA). Accordingly, we used the Perdew-Burke-Ernzerhof (PBE) GGA²⁸ for the exchange-

correlation energy functional. We used the plane-wave basis set expansion up to 400 eV and a $4 \times 2 \times 4$ grid of special k points for the integrations over the supercells Brillouin zone. The $4d$ orbitals of In were treated as valence electrons. Both the unit cell lattice parameters (a , a/c) and the internal atomic positions were fully relaxed. During these structural relaxations the hexagonal symmetry of the underlying crystal lattice was conserved.

B. Strain in epitaxial films with wurtzite crystal structure and arbitrary orientation

Sapphire and SiC are among the most often used substrates to grow group-III nitrides, and typically growth is realized on the basal (0001) c -plane of the substrates (see Fig. 1). In such instances the nitride films grow along the [0001] direction. The sixfold symmetry of the basal planes of the wurtzite (nitrides, SiC) and rhombohedral (sapphire) crystal structures dictates their isotropy in the basal plane and hence the thermal expansion coefficients, piezoelectric, and elastic properties should be the same for any direction within the c -plane. As a consequence the films grown on c -plane substrates experience isotropic biaxial in-plane strain. Recently, there has been a strong research interest in growing group III-nitrides with nonpolar and semipolar orientations (with the c -plane inclined with respect to sample surface) in order to avoid or minimize

FIG. 1. (Color online) Schematic presentation of the wurtzite crystal structure of group-III nitrides and the most common substrates (sapphire and SiC). Hatched areas indicate the most often used planes for epitaxial growth: the polar c -plane (0001), the nonpolar a -plane (11 $\bar{2}$ 0) and m -plane (1 $\bar{1}$ 00), and the semipolar r -plane (1 $\bar{1}$ 02) and (10 $\bar{1}$ 1).

the effects of the polarization fields in device heterostructures and enable efficient green and white light emitting diodes.²⁹ To enable nonpolar and semipolar growth substrate surfaces different from the conventional c -plane are typically employed (Fig. 1). Whenever growth is realized on non- c -plane oriented sapphire and SiC surfaces (Fig. 1) the nitride films will be under anisotropic biaxial strain (independently of the film orientation) as a consequence of the anisotropy of the growth

surfaces. For instance, a -plane $\text{In}_x\text{Al}_{1-x}\text{N}$ films grown on r -plane sapphire are expected to experience anisotropic strain in the basal plane because of the difference in thermal expansion coefficients between substrate and film, and the different lattice mismatches along the two main in-plane directions.³⁰

In linear elasticity theory the relation between the stress σ and strain ϵ tensors in films with wurtzite crystal structure is given by

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2(C_{11} - C_{12}) \end{pmatrix} \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ 2\epsilon_{yz} \\ 2\epsilon_{xz} \\ 2\epsilon_{xy} \end{pmatrix}, \quad (2)$$

where C_{ij} are the elastic stiffness constants and the x , y , and z axes are chosen along the $[11\bar{2}0]$, $[1\bar{1}00]$, and $[0001]$ directions, respectively. The strains along the main crystallographic directions can be experimentally determined by

$$\epsilon_{xx} = \frac{a - a_0}{a_0}, \quad \epsilon_{yy} = \frac{m - m_0}{m_0}, \quad \epsilon_{zz} = \frac{c - c_0}{c_0}, \quad (3)$$

where a_0 and c_0 are the strain-free lattice parameters, a and c are the measured lattice parameters, and $m_0(m) = \frac{2}{\sqrt{3}}a_0(a)$.

The stress along the growth direction of epitaxial films vanishes because their surfaces are free to expand or contract. In other words, $\sigma_{zz} = 0$, $\sigma_{xx} = 0$, and $\sigma_{yy} = 0$ for films with c , a , and m -plane surface orientations, respectively. It follows then from Eq. (2) that the strain along the growth direction can be expressed by the two in-plane strain components. For c -plane films, it has the following form:

$$\epsilon_{zz} = -\frac{C_{13}}{C_{33}}(\epsilon_{xx} + \epsilon_{yy}). \quad (4)$$

Since in this case the in-plane strain is isotropic $\epsilon_{xx} = \epsilon_{yy}$, the out-of-plane strain can be expressed as

$$\epsilon_{zz} = -R_{c\text{-plane}}^B \epsilon_{xx}, \quad (5)$$

with $R_{c\text{-plane}}^B = 2\frac{C_{13}}{C_{33}}$ being the biaxial relaxation coefficient.

For nonpolar a - and m -plane $\text{In}_x\text{Al}_{1-x}\text{N}$ films, the strain in the basal plane is no longer isotropic $\epsilon_{xx} \neq \epsilon_{yy}$ and the

out-of-plane strains are related to the in-plane components via

$$\epsilon_{xx} = -R_{\text{nonpolar}}^B \begin{pmatrix} \epsilon_{yy} \\ \epsilon_{zz} \end{pmatrix} \quad (6)$$

and

$$\epsilon_{yy} = -R_{\text{nonpolar}}^B \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{zz} \end{pmatrix}, \quad (7)$$

for the a - and m -plane, respectively, with a biaxial coefficient, which has a vector form due to the anisotropy of the in-plane strain:

$$R_{a\text{-plane}}^B = R_{m\text{-plane}}^B = R_{\text{nonpolar}}^B = \begin{pmatrix} \frac{C_{12}}{C_{11}} \\ \frac{C_{13}}{C_{11}} \end{pmatrix}. \quad (8)$$

In order to deduce the strain relationships in the case of a nitride film with an arbitrary surface orientation let us consider two coordinate systems as illustrated in Fig. 2. The normal coordinate system is described by the three principal axes of the wurtzite crystal structure as discussed above: $x \parallel [11\bar{2}0]$, $y \parallel [1\bar{1}00]$, and $z \parallel [0001]$, while the prime coordinate system is related to the arbitrary surface. The prime coordinate system is obtained by a rotation of the normal coordinate system by an angle θ with respect to x , so that z' is parallel to the growth direction. The relationship between the two coordinate systems in terms of strain and stress is given by

$$\begin{pmatrix} \eta_{x'x'} \\ \eta_{y'y'} \\ \eta_{z'z'} \\ \eta_{y'z'} \\ \eta_{x'z'} \\ \eta_{y'y'} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \cos^2 \theta & \sin^2 \theta & -\sin^2 \theta & 0 & 0 \\ 0 & \sin^2 \theta & \cos^2 \theta & \sin^2 \theta & 0 & 0 \\ 0 & \frac{1}{2} \sin 2\theta & -\frac{1}{2} \sin 2\theta & \cos 2\theta & 0 & 0 \\ 0 & 0 & 0 & 0 & \cos \theta & \sin \theta \\ 0 & 0 & 0 & 0 & -\sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \eta_{xx} \\ \eta_{yy} \\ \eta_{zz} \\ \eta_{yz} \\ \eta_{xz} \\ \eta_{xy} \end{pmatrix}, \quad (9)$$

where η_{ij} and $\eta_{i'j'}$ are the stress (strain) components in the normal and prime coordinate systems, respectively.

FIG. 2. (Color online) Schematic representation of wurtzite group-III nitride crystal with an arbitrary crystal orientation. The normal coordinate system (x, y, z) has its main axes along the principal crystallographic axes: $x \parallel [11\bar{2}0]$, $y \parallel [1\bar{1}00]$, $z \parallel [0001]$, and the prime coordinate system (x', y', z') is rotated with respect to the normal coordinate system by an angle θ , so that z' is parallel to the growth direction.

The stress along the growth direction z' of a nitride film with an arbitrary surface orientation (see Fig. 2), $\sigma_{z'z'}$, is zero. In addition, the shear stresses, $\sigma_{y'z'}$ and $\sigma_{x'z'}$, are also zero. It follows from Eq. (9) that

$$\begin{aligned}\sigma_{z'z'} &= \sigma_{yy} \sin^2 \theta + \sigma_{zz} \cos^2 \theta + \sigma_{yz} \sin 2\theta = 0, \\ \sigma_{y'z'} &= \frac{\sigma_{yy} - \sigma_{zz}}{2} \sin \theta + \sigma_{yz} \cos 2\theta = 0.\end{aligned}\quad (10)$$

Since it is straightforward to measure the lattice spacings along the main crystallographic directions of $\text{In}_x\text{Al}_{1-x}\text{N}$ with an arbitrary surface orientation, we will deduce the strain-stress relationship for the determination of the composition in the normal coordinate system. This is done by substituting the expressions for the stress components along the main axes in the normal coordinate system from Eq. (2) in the above equations for $\sigma_{z'z'}$ and $\sigma_{y'z'}$ [Eq. (10)]. It results in

$$A_z \epsilon_{zz} = A_x \epsilon_{xx} + A_y \epsilon_{yy}, \quad (11)$$

where

$$\begin{aligned}A_x &= C_{12} - C_{13} - (C_{12} + C_{13}) \cos 2\theta, \\ A_y &= C_{11} - C_{13} - (C_{11} + C_{13}) \cos 2\theta, \\ A_z &= C_{33} - C_{13} + (C_{13} + C_{33}) \cos 2\theta\end{aligned}$$

are the biaxial relaxation coefficients.

We also derived the alternative stress-strain relationship in the prime coordinate system as detailed in the Appendix.

C. Piezoelectric polarization in epitaxial films with wurtzite crystal structure and arbitrary orientation

Due to the lack of inversion symmetry, wurtzite crystals exhibit a spontaneous electrical polarization along the polar $[0001]$ direction. Under strain, epitaxial nitride films also exhibit piezoelectric polarization, P_{PZ} . In the normal coordinate system P_{PZ} is related to the strain components via

$$P_{PZ} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ \epsilon_{yz} \\ \epsilon_{xz} \\ \epsilon_{xy} \end{pmatrix}. \quad (12)$$

FIG. 3. (Color online) Lattice parameters of $\text{In}_x\text{Al}_{1-x}\text{N}$.

For a nitride epitaxial film with an arbitrary surface orientation, the piezoelectric polarization along the growth direction, z' , $P_{PZ}^{z'}$, can be expressed by the projection of P_{PZ} along the y axis, (P_{PZ}^y) , and z axis (P_{PZ}^z) :

$$\begin{aligned}P_{PZ}^{z'} &= P_{PZ}^y \sin \theta + P_{PZ}^z \cos \theta \\ &= e_{15} \epsilon_{yz} \sin \theta + e_{31} (\epsilon_{xx} + \epsilon_{yy}) \cos \theta + e_{33} \epsilon_{zz} \cos \theta.\end{aligned}\quad (13)$$

Alternatively, using Eq. (9) the piezoelectric polarization along the growth direction can be expressed via the strain components in the prime system:

$$\begin{aligned}P_{PZ}^{z'} &= e_{15} \cos \theta \epsilon_{x'x'} + [e_{31} \cos^3 \theta + (e_{33} - e_{15}) \theta \sin^2 \theta] \epsilon_{y'y'} \\ &\quad + [e_{33} \cos^3 \theta + (e_{31} + e_{15}) \cos \theta \sin^2 \theta] \epsilon_{z'z'} \\ &\quad + [e_{15} \cos 2\theta \sin \theta + (e_{31} - e_{33}) \cos \theta \sin 2\theta] \epsilon_{y'z'}.\end{aligned}\quad (14)$$

III. RESULTS AND DISCUSSION

A. Lattice parameters and elastic constants of $\text{In}_x\text{Al}_{1-x}\text{N}$

The calculated relaxed lattice parameters, a and c , the stiffness constants, C_{ij} , and bulk modulus, B , of $\text{In}_x\text{Al}_{1-x}\text{N}$ as a function of the In composition, x , are shown in Figs. 3 and 4, and summarized in Table II. The linear dependencies according to Vegard's rule and the parabolic fits to the data according to Eq. (15) are also given in Figs. 3 and 4:

$$\xi(x) = x \xi^{\text{InN}} + (1-x) \xi^{\text{AlN}} - \delta_\xi x(1-x), \quad \xi = a, c, C_{ij}, B. \quad (15)$$

The bowing parameters δ_ξ describe the deviations from Vegard's rule in the lattice parameters and elastic constants. The values of δ_ξ obtained from the fits are listed in Table II. It is seen from Fig. 3 and Table II that the lattice parameters of $\text{In}_x\text{Al}_{1-x}\text{N}$ show very small deviations from linearity, $\delta_a = 0.0412 \pm 0.0039$ Å and $\delta_c = -0.060 \pm 0.010$ Å.¹⁷ C_{11} , C_{44} , and B exhibit larger deviations from Vegard's rule with $\delta_{C_{11}} = 98.6$ GPa, $\delta_{C_{44}} = 47.3$ GPa, and $\delta_B = 71.3$ GPa, while C_{13} , C_{13} , and C_{13} exhibit essentially linear dependences with composition (Table II and Fig. 4). $R_{c\text{-plane}}^B$ [see Eq. (5)] changes from 0.55 (AlN) to 0.76 (InN) with a substantial bowing of 0.07. The biaxial coefficients for the nonpolar planes [see Eq. (8)] vary from 0.34 (AlN) to 0.47 (InN) for C_{12}/C_{11} , and

FIG. 4. (Color online) Stiffness constants and bulk modulus of $\text{In}_x\text{Al}_{1-x}\text{N}$.

from 0.26 (AlN) to 0.39 (InN) for C_{13}/C_{11} , showing smaller but still appreciable deviations from Vegard's rule of 0.03 and -0.05 , respectively. For arbitrary surface orientations, the biaxial coefficients A_x/A_z and A_y/A_z [see Eq. (11)] do not show any systematic trend with the angle of inclination θ . Apart from the (10 $\bar{1}$ 3), the rest of the planes show significant bowing parameters of the biaxial coefficients.

Our GGA stiffness constants (Table II) are somewhat lower than recent results obtained using LDA calculations based on 32-atom supercell.¹⁹ In general, LDA is overbinding, which results in higher elastic constants. We note here that our 128-atom supercell provides not only a more realistic description of a random alloy, but also ensures a more accurate prediction of the elastic constants³¹ compared to the previous calculations based on 32-atom supercell.¹⁹ Recently, we have shown that the elastic constants of nitride alloys obtained from supercell calculations can depend on both the size and the atomic configuration of the cell.³¹ The dependence becomes weaker with increased supercell size³¹ and, accordingly, larger supercells ensure more solid results and a better convergence. It is worth mentioning that our elastic constants of the binary AlN and InN agree well with previous calculations in the GGA approximation.³²

B. Determination of composition in $\text{In}_x\text{Al}_{1-x}\text{N}$

The composition of ternary nitride alloys is often extracted from the lattice parameters measured by XRD. In general, the

lattice parameters in nitride layers (strain-free, under isotropic or anisotropic strain) can be measured in high-resolution mode with a high precision of 0.0001 Å.^{30,33,34} However, additional errors in the composition arise from the unknown behavior of the alloy lattice parameters and stiffness constants with composition. A typical approach is to assume linear relationship between the two binaries forming the alloy.^{14–16,35} However, our results show that both lattice parameters and stiffness constants deviate from Vegard's rule (Fig. 4 and Table II). In order to perform analysis on the effect of strain and deviations from linearity in the stiffness and lattice constants on composition, x , and piezoelectric polarization, P_{PZ} , in $\text{In}_x\text{Al}_{1-x}\text{N}$ we have estimated the respective errors, Δx and ΔP_{PZ} .

1. Strain-free material

Let us first consider strain-free $\text{In}_x\text{Al}_{1-x}\text{N}$, such as one-dimensional structures for advanced optoelectronic applications.^{36,37} The error in the In composition if the deviations from Vegard's rule in the lattice parameters of strain-free $\text{In}_x\text{Al}_{1-x}\text{N}$ material are not accounted for, Δx_{SF} , is estimated as $\Delta x_{\text{SF}} = x - x'_L$. x'_L is the composition extracted from the lattice parameters of InN and AlN according to our first principle calculations (Table II), but assuming linear dependence of the lattice parameters on composition and x is the actual composition. The results are shown in Fig. 5. The dashed lines mark 1% of error in the composition, typically quoted for XRD experiments.^{14,16} It is seen that the error in the

TABLE II. Lattice parameters, a , c , elastic constants, C_{ij} , bulk modulus, B , and respective deviations from Vegard's rule, δ_ξ , for the different In compositions, x , studied.

x	a (Å)	c (Å)	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)	B (GPa)
0	3.13	5.01	376	126	98	356	116	204
0.125	3.19	5.12	338	116	94	338	98	195
0.1875	3.21	5.17	327	114	93	322	93	191
0.2031	3.22	5.19	323	113	94	319	91	178
0.3906	3.30	5.33	280	108	91	293	77	152
0.5937	3.39	5.49	245	101	86	267	65	144
0.75	3.47	5.60	229	97	81	236	58	136
1	3.59	5.79	197	93	76	201	48	127
δ_ξ	0.0412	-0.06	98.6	22.7	-4.4	6.3	47.3	71.3

FIG. 5. (Color online) Error in the composition, Δx_{SF} , if the deviations from Vegard's rule in the lattice parameters of strain-free $\text{In}_x\text{Al}_{1-x}\text{N}$ are not accounted for.

composition exceeds 1% for $x > 0.6$ if the lattice parameter c is used to extract the composition. An overestimation of about 2% can be expected for the lattice-matched composition of ≈ 0.18 . The error in the composition could reach 3% if the a lattice parameter is used (Fig. 5). These results show that although small the deviations from Vegard's rule, δ_a and δ_c , will lead to measurable errors in the composition of strain-free $\text{In}_x\text{Al}_{1-x}\text{N}$ structures.

2. Epitaxial films under strain

Most often $\text{In}_x\text{Al}_{1-x}\text{N}$ is grown in the form of thin layers, which experience different degrees of biaxial strain depending on composition, thickness, structures, growth method, etc.^{14–16} To evaluate the effect of biaxial strain on the composition extracted from the lattice parameters, we applied different in-plane strains, ϵ_{xx} , to the supercell and estimated the errors in the composition if the strain is not taken into account. Both tensile and compressive in-plane strain of 1% and 2% are considered. The error in the composition in this case is estimated as $\Delta x_S = \Delta x - \Delta x_{SF}$, where Δx_{SF} is the error in the composition of strain-free $\text{In}_x\text{Al}_{1-x}\text{N}$, if the deviation from Vegard's rule in the lattice parameters are not taken into account (as shown in Fig. 5); and Δx is the total error in the composition extracted from the c lattice parameter of c -plane $\text{In}_x\text{Al}_{1-x}\text{N}$ under different degrees of strain. Therefore, Δx_S represents the error in composition caused by the strain applied to $\text{In}_x\text{Al}_{1-x}\text{N}$ alone. The results showing a monotonic increase of Δx_S with composition for a given strain are presented in Fig. 6(a). The error in the composition due to the pure effect of strain is from $\pm 3\%$ to $\pm 5\%$ in the entire compositional range for 1% of in-plane strain, for example. Similarly, for a given composition, e.g., $x = 0.20$, the error in the composition linearly increases with strain if the strain is not taken into account [Fig. 6(b)]. The further the In composition deviates from the lattice matched value the more important the effect of strain. We note that it is difficult to know *ad hoc* what is the precise lattice match composition. The GaN films may have different lattice parameters due to the heteroepitaxial nature of the growth and depending on the growth conditions even if they are grown with similar thicknesses. As a result the lattice-match conditions occur at different compositions and

FIG. 6. (Color online) Error in the composition of $\text{In}_x\text{Al}_{1-x}\text{N}$, Δx_S , if the strain is not accounted for (a) as a function of composition and fixed strain indicated above the respective lines and (b) as a function of strain for a given composition of $x = 0.2$.

thin $\text{In}_x\text{Al}_{1-x}\text{N}$ films even with intended compositions close to the lattice matched value for GaN may still be strained.¹⁶

Thus the influence of strain and composition on the lattice parameters must be separated in order to obtain the *correct* In content in the $\text{In}_x\text{Al}_{1-x}\text{N}$ films from the lattice parameters.^{16,35} This can be achieved by taking into account the fact that the $\text{In}_x\text{Al}_{1-x}\text{N}$ films are under biaxial strain and thus according to elasticity theory out-of-plane and in-plane strain obey the relationship described by Eq. (11) for an arbitrary surface orientation. In the simplest case of c -plane oriented films it has the form

$$\frac{c_{\text{In}_x\text{Al}_{1-x}\text{N}} - c_0(x)}{c_0(x)} = -\frac{2C_{13}(x) a_{\text{In}_x\text{Al}_{1-x}\text{N}} - a_0(x)}{C_{33}(x) a_0(x)}, \quad (16)$$

where $c_{\text{In}_x\text{Al}_{1-x}\text{N}}$ and $a_{\text{In}_x\text{Al}_{1-x}\text{N}}$ are the measured alloy lattice parameters, c_0 and a_0 are the relaxed parameters, and C_{ij} are the alloy stiffness constants. The *correct* In content may then be obtained by solving Eq. (16). Similar equations, which involve all three strain components, can also be solved for the cases of nonpolar or arbitrary surface orientations of the $\text{In}_x\text{Al}_{1-x}\text{N}$ films.

3. Effect of the deviations from Vegard's rule on the composition of $\text{In}_x\text{Al}_{1-x}\text{N}$

In order to evaluate the effect of strain on the accuracy of the determination of $\text{In}_x\text{Al}_{1-x}\text{N}$ composition we estimated

the respective error Δx as follows. First the composition of $\text{In}_x\text{Al}_{1-x}\text{N}$ is extracted from the lattice parameters according to Eq. (11) and assuming linear dependence of the alloy stiffness constants and lattice parameters on the composition, x^L . For this purpose, we consider several cases for $\text{In}_x\text{Al}_{1-x}\text{N}$ grown on a GaN template: (i) pseudomorphic growth valid for thin films; (ii) 50% and (iii) 95% strain relaxation from the pseudomorphic growth, valid for relatively thick films and compositions away from the lattice matched value; (iv) certain value for ϵ_{xx} . In all instances the following lattice parameters of GaN (as measured for strain-free material) were considered: $a = 3.1893 \text{ \AA}$ and $c = 5.8151 \text{ \AA}$.³⁴ The error in the composition, Δx is then given by $\Delta x = x - x^L$, where x is the true composition as listed in Table II.

In the simplest situation of c -plane orientated films and pseudomorphic growth, the a -lattice parameter of $\text{In}_x\text{Al}_{1-x}\text{N}$ for a given composition is assumed to be equal to the a -lattice parameter of GaN. Then the respective c -lattice parameter of $\text{In}_x\text{Al}_{1-x}\text{N}$ is calculated from Eq. (5) taking into account the deviations from Vegard's rule δ_ξ (Table II). From these a and c values the composition x^L assuming linearity in lattice parameters and stiffness constants is obtained by solving Eq. (16).

In the case of nonpolar surface orientations and pseudomorphic growth both $a(m)$ - and c -lattice parameters of $\text{In}_x\text{Al}_{1-x}\text{N}$ are assumed to be equal to the respective parameters of GaN. Equation (7) is then used to extract the out-of-plane lattice parameter, $m(a)$, taking into account all δ_ξ . The as-obtained lattice parameters are then used to estimate x^L assuming linear dependence of the lattice parameters and stiffness constants from Eq. (11), which has the following form for a -plane orientation:

$$\frac{a_{\text{In}_x\text{Al}_{1-x}\text{N}} - a_0(x)}{a_0(x)} = -\frac{2C_{12}(x)}{C_{11}(x)} \frac{m_{\text{In}_x\text{Al}_{1-x}\text{N}} - m_0(x)}{m_0(x)} - \frac{2C_{13}(x)}{C_{11}(x)} \frac{c_{\text{In}_x\text{Al}_{1-x}\text{N}} - c_0(x)}{c_0(x)}. \quad (17)$$

For an $\text{In}_x\text{Al}_{1-x}\text{N}$ film with an arbitrary surface orientation (Fig. 2) grown pseudomorphically on a GaN template, the in-plane spacings of the template and layer should be equal. Along the y' axis $OB_{\text{GaN}} = OB_{\text{AlInN}}$ and along the x' axis $a_{\text{AlInN}} = a_{\text{GaN}}$ (see Fig. 2). For angles of inclination of the arbitrary plane with respect to the c -plane $0^\circ \leq \theta \leq 43^\circ$,

$$m_{\text{AlInN}}(x, \theta) = \frac{m_{\text{GaN}} \cos \theta_{\text{AlInN}}(x)}{\cos \theta_{\text{GaN}}}, \quad (18)$$

where $OA = m$ and $OB = \frac{m}{\cos \theta}$. Then Eq. (11) is used to obtain the c -lattice parameters taking into account all deviations δ_ξ . For angles of inclination of $43^\circ < \theta \leq 90^\circ$,

$$c_{\text{AlInN}}(x, \theta) = \frac{c_{\text{GaN}} \cos[90 - \theta_{\text{AlInN}}(x)]}{\cos(90 - \theta_{\text{GaN}})}, \quad (19)$$

and the m -lattice spacing is obtained from Eq. (11) using all δ_ξ . The set of lattice parameters is then used to derive x^L from Eq. (11) assuming linear dependence of the lattice parameters and stiffness constants on composition.

Similarly, the errors are estimated for the cases of different degree of strain or relaxation from the pseudomorphic growth. For 50% relaxation, for example, the lattice parameters of $\text{In}_x\text{Al}_{1-x}\text{N}$ for given composition follow from the assumption

that the pseudomorphic strain components in the two orthogonal in-plane directions have relaxed by 50%. In other words for the polar and nonpolar orientations a (c) are assumed to be equal to $0.5[a_{\text{GaN}}(c_{\text{GaN}}) + a_0(x)(c_0(x))]$.

Equation (11) exhibits a singularity for angles of inclination between 41° and 45° depending on the composition. This singularity is related to the fact that at $\theta = 41^\circ - 45^\circ$ the two normal strains ϵ_{yy} and ϵ_{zz} are equal, and the biaxial coefficient A_x tends to zero. This renders the two sides of Eq. (11) infinitely small resulting in the observed singularity. Figure 7 shows the evolution of the strain components in the normal and prime coordinate systems with the angle of inclination for three different values of the $\text{In}_x\text{Al}_{1-x}\text{N}$ composition (details can be found in the Appendix). It is seen that ϵ_{yy} and ϵ_{zz} cross at about $41^\circ - 45^\circ$ depending on the composition. Similar crossing of the normal strains at about 45° has been previously reported for InGaIn and AlGaIn with 80% and 60% of Ga, respectively.³⁸ This effect is a direct consequence from the wurtzite crystal structure of group-III nitrides. Due to the singularity we have excluded the planes with $41^\circ < \theta < 47^\circ$, e.g., $(10\bar{1}2)$ and $(1\bar{1}23)$, from the analysis of the errors in the normal coordinate system, as the errors become infinitely large.

Figure 8 shows the error in the composition of $\text{In}_x\text{Al}_{1-x}\text{N}$ films with different surface orientations if the deviations from Vegard's rule, δ_ξ (Table II), have not been accounted for. Results for pseudomorphic (0% relaxation), 50%, and 95% relaxed films are presented in Figs. 8(a) and 8(b). Note that under the consideration of constant relaxation the films with different compositions exhibit different degrees and types of strain. For instance, the films with $x < 0.1875$ are under tensile strain, while those with $x \geq 0.1875$ are under compressive strain which increases with increasing In content.

The errors in the composition for pseudomorphic c - and a -plane films are relatively small and remain below 1% for the whole compositional range (see Fig. 8). A similar result is obtained for the m -plane $\text{In}_x\text{Al}_{1-x}\text{N}$ (not shown here). On the other hand, the pseudomorphic $\text{In}_x\text{Al}_{1-x}\text{N}$ films with semipolar orientations exhibit larger errors in composition that can reach 4% in absolute value for intermediate x . Strain relaxation does not lead to significant changes in the error for polar and nonpolar material, while for semipolar planes it can alter substantially the error [Fig. 8(b)]. When the strain relaxation increases from 0% to 95% the In composition for a certain surface orientation becomes more underestimated. As a result, with increasing the degree of relaxation the absolute value of the error decreases for positive errors and increases for negative errors [Fig. 8(b)]. Thus the error in the In composition of $\text{In}_x\text{Al}_{1-x}\text{N}$ films with their surface plane inclined by $0^\circ \leq \theta \leq 41^\circ$ with respect to the c axis will be significantly reduced with strain relaxation. For example, the error for $(10\bar{1}3)$ oriented films with high In content, which are expected to be relaxed when grown on GaN, will be close to 0 for high degree of strain relaxation. On the contrary, the error for $\text{In}_x\text{Al}_{1-x}\text{N}$ films with their surface plane inclined by $47^\circ \leq \theta \leq 90^\circ$ increases with increasing the degree of strain relaxation. In all cases the absolute error and effect of strain relaxation become greater as the angles of inclination of the respective plane approaches the critical angle of $41^\circ - 45^\circ$.

FIG. 7. (Color online) Strain components in the normal, ϵ_{ij} [(a)–(c)], and prime coordinate system, ϵ'_{ij} [(d)–(f)], for $\text{In}_x\text{Al}_{1-x}\text{N}$ films grown pseudomorphically on GaN as a function of the inclination angle between the c axis and the surface plane.

For the sake of completeness, we also investigated the evolution of the errors as a function of composition for a given degree of strain. Results for three different values of the compressive in-plane strain and for the same planes as those shown in Fig. 8(b) are presented in Fig. 8(c). Since we consider only compressive in-plane strain the composition below the lattice-matched value is omitted. It is seen that for the polar (0001) plane the errors do not change significantly with strain and remain below $\pm 1\%$ even for relatively high degree of strain of -6% . Similar results are obtained also for the two nonpolar planes. For the semipolar planes with $0^\circ \leq \theta \leq 41^\circ$ and In compositions between 0.2 and 0.6, the errors do not show a pronounced trend with composition for a given strain. On the other hand, for high In compositions ($x = 0.8$) the errors are reduced more than two times for the same degree of strain. For the semipolar planes with $47^\circ \leq \theta \leq 90^\circ$, no clear trend in the evolution of the errors with composition can be seen for a specific strain.

It should be mentioned that the strain-stress relationship to extract composition in the prime system (see for details the Appendix),

$$(C'_{34}{}^2 - C'_{33}C'_{44})\epsilon_{z'z'} = (C'_{13}C'_{44} - C'_{14}C'_{34})\epsilon_{x'x'} + (C'_{23}C'_{44} - C'_{24}C'_{34})\epsilon_{y'y'}, \quad (20)$$

does not exhibit the singularity at $41^\circ - 45^\circ$ due to the fact that none of the strains in the prime system cross each other with varying θ (Fig. 7). If the strains in the prime coordinate system can be measured they can be used for the determination of the composition as detailed in the Appendix. In this case for all compositions and angles of inclination the error in composition remains close to or below 1%.

To appreciate the effect of the uncertainties in the stiffness constants on the $\text{In}_x\text{Al}_{1-x}\text{N}$ composition, we also estimated the composition for the different planes and degrees of relaxation but using the stiffness constants reported in Ref. 19. We

FIG. 8. (Color online) Error in the composition Δx of $\text{In}_x\text{Al}_{1-x}\text{N}$ films with different surface orientations if the deviations from Vegard's rule, δ_ξ , are not taken into account: (a) pseudomorphic growth, (b) different degree of strain relaxation, and (c) different degrees of strain.

considered only the normal coordinate system. The use of the stiffness constants from Ref. 19 leads to an underestimation of the composition for pseudomorphically grown $\text{In}_x\text{Al}_{1-x}\text{N}$ under compressive strain independently of the surface orientation. The absolute values of the differences in the composition estimated by the two sets of stiffness constants increase in a linear manner with composition and change between $\approx 0\%$ and -2% for the (0001), -2.2% for the (1120), -2.7% for the (1122) and (1011), and -4.5% for the (1013). Strain relaxation in the films leads to a slight decrease in the differences, but they still remain appreciable. In general, these differences will

add to the errors introduced by neglecting the deviations from Vegard's rule discussed above.

C. Piezoelectric polarization

The piezoelectric polarization along the growth direction P_{PZ}^z in $\text{In}_x\text{Al}_{1-x}\text{N}$ epitaxial films grown pseudomorphically on GaN were calculated as a function of the composition and angle of inclination between the surface and the c axis using Eq. (13). The piezoelectric coefficients of InN and AlN from Refs. 38 and 39 were used, respectively, and a linear dependence of e_{ij} on composition is assumed. Equation (11) was used to estimate ϵ_{zz} for $0^\circ \leq \theta \leq 45^\circ$ and ϵ_{yy} for $45^\circ < \theta < 90^\circ$, respectively, and taking into account all deviations from Vegard's rule in the lattice parameters and stiffness constants. The results are shown in Figs. 9(a) and 9(b). The piezoelectric polarization assuming linear dependence of the stiffness constants and lattice parameters, $P_{\text{PZ},L}^z$, was also calculated and the difference $\Delta P_{\text{PZ}}^z = P_{\text{PZ}}^z - P_{\text{PZ},L}^z$ is presented in Fig. 9(c).

The piezoelectric polarization for a given composition changes its sign at an angle of inclination of 45° [see Fig. 9(a)]. The vanishing P_{PZ}^z at $\theta = 41^\circ - 45^\circ$ is a direct consequence of the hexagonal symmetry of $\text{In}_x\text{Al}_{1-x}\text{N}$ and the fact that the normal strain components cross each other at this point [see Figs. 7(a)–7(c)]. Because the normal strains have the same sign at $\theta = 41^\circ - 45^\circ$ depending on the composition, together with the opposite sign of the piezoelectric coefficients e_{31} and e_{33} , this will lead to the zero crossover in the piezoelectric polarization dependence on the inclination angle [Fig. 9(a)]. The variation of the normal strain components with the angle of inclination also provides explanation why the piezoelectric polarization for some semipolar planes will be vanishing, e.g., (1012) and (1123), independent of the In composition.

Alternatively, we can inspect the dependence of P_{PZ}^z of a particular plane with In composition [Fig. 9(b)]. The piezoelectric polarization changes sign at In composition of 13%–20%, which is the range of GaN lattice-matched values depending on the specific plane orientation. This spread in compositions, for which the crossover occurs, is related to the fact that the lattice-matched conditions are fulfilled at different values for $a = 3.1893 \text{ \AA}$ ($x \sim 13\%$) and $c = 5.1850 \text{ \AA}$ ($x \sim 20\%$) (see Table II). For angles of inclination $0^\circ \leq \theta \leq 43^\circ$, i.e., for the (0001) and (1013) planes, P_{PZ}^z changes from negative to positive following the changes in the strain components [see Eq. (13) and Figs. 7 and 9]. The opposite trend is observed for $47^\circ \leq \theta < 90^\circ$, for which P_{PZ}^z switches from positive to negative at the respective GaN lattice-matched compositions of In. As mentioned above, the piezoelectric polarization becomes very small for planes with an angle of inclination of $\theta \sim 45^\circ$.

The difference in the piezoelectric polarization introduced by using Vegard's rule for the lattice parameters and stiffness constants decreases when approaching the critical angles between 41° and 45° depending on the composition [Fig. 9(c)]. The largest differences in P_{PZ}^z are estimated for the polar surface orientation and ΔP_{PZ}^z increases with increasing In content up to 59% following the trend of P_{PZ}^z [see Fig. 9(b)]

FIG. 9. (Color online) Piezoelectric polarization $P_{PZ}^{z'}$ as a function of the inclination angle (a) and composition (b). Differences in piezoelectric polarization $\Delta P_{PZ}^{z'}$ introduced by assuming validity of Vegard's rule for the lattice parameters and stiffness constants (c).

and 9(c)]. As a result, the relative errors $\Delta P_{PZ}^{z'}/P_{PZ}^{z'}$ for $\text{In}_x\text{Al}_{1-x}\text{N}$ films with (0001) orientation is estimated to be as high as 6–7% for intermediate In compositions [see Fig. 9(c)]. The relative errors $\Delta P_{PZ}^{z'}/P_{PZ}^{z'}$ become very important around the lattice-match compositions where $P_{PZ}^{z'}$ tends to zero. For example, $\Delta P_{PZ}^{z'}/P_{PZ}^{z'}$ reaches -67% and -56% for the (0001) and the (1013) planes.

It is interesting to compare the $P_{PZ}^{z'}$ for a set of 15-nm-thick $\text{In}_x\text{Al}_{1-x}\text{N}$ films with $0.07 \leq x \leq 0.21$ and (0001) orientation estimated from the experimentally measured a - and c -lattice parameters, $P_{PZ,\text{exp}}^{z'}$ and those estimated from the a -lattice parameter, but assuming Vegard's rule for the stiffness constants $P_{PZ,L}^{z'}$ (Fig. 10). Details about the film properties and

FIG. 10. Piezoelectric polarization $P_{PZ}^{z'}$ for c -plane $\text{In}_x\text{Al}_{1-x}\text{N}$ films grown pseudomorphically on GaN estimated from the measured c - and a -lattice parameters (full symbols), and from the a -lattice parameter assuming linearity (open symbols). The line shows the piezoelectric polarization calculated with an a -lattice parameter of $3.1826 \text{ \AA}$. The inset shows the resulting relative error $\Delta P_{PZ}^{z'}/P_{PZ}^{z'}$.

lattice parameters measurements can be found in Refs. 16 and 40. Note that in all calculation the In composition measured by RBS, which is independent on the degree of strain,¹⁶ is used. The resulting relative error, $\Delta P_{PZ}^{z'}/P_{PZ,\text{exp}}^{z'}$, where $\Delta P_{PZ}^{z'} = P_{PZ,\text{exp}}^{z'} - P_{PZ,L}^{z'}$ is shown in the inset of Fig. 10. For the films with x close to the lattice-match In composition, the values of $P_{PZ,\text{exp}}^{z'}$ estimated from the experimental strains (filled symbols in Fig. 10) lie on the line, calculated for pseudomorphic growth on a GaN buffer layer accounting for the deviations in Vegard's rule and with a -lattice parameter of $3.1826 \text{ \AA}$, measured by XRD.¹⁶ On the other hand, assuming linearity leads to upshift of $P_{PZ}^{z'}$ (open symbols in Fig. 10). The resulting relative error, $\Delta P_{PZ}^{z'}/P_{PZ}^{z'}$, is in the range of -39% to 94% around the lattice-matched composition, which is in a good agreement with our predictions from first-principle calculations. These results further indicate the correctness of our C_{ij} and the importance of accounting for δ_ξ in order to determine correctly $P_{PZ}^{z'}$.

For the semipolar planes with angles of inclination $47^\circ \leq \theta \leq 90^\circ$, the relative error is extremely large around the lattice-matched composition, as the differences $\Delta P_{PZ}^{z'}$ become larger by orders of magnitude than the values of the piezoelectric polarization itself [see Figs. 9(b) and 9(c)]. The relative errors $\Delta P_{PZ}^{z'}/P_{PZ}^{z'}$ for these planes and intermediate compositions are in the range from 1% to -13% . The differences $\Delta P_{PZ}^{z'}$ for $\text{In}_x\text{Al}_{1-x}\text{N}$ films with semipolar surface orientations with θ close to the critical angles of $41^\circ - 45^\circ$ do not change significantly for In composition between 39% and 75% remaining close to zero. In these instances, the relative errors $\Delta P_{PZ}^{z'}/P_{PZ}^{z'}$ are between -4% and 4% for the (1012), and between -4% and 14% for the (1123), respectively. For In compositions lower than 39% the relative error increases significantly reaching values as high as 63%.

Our results clearly show that accounting for the deviations from the linear behavior of the stiffness constants and lattice parameters has a very strong impact on the proper determination of the piezoelectric polarization in $\text{In}_x\text{Al}_{1-x}\text{N}$. This is

particularly important around the lattice-match composition. We note that for a variety of devices $\text{In}_x\text{Al}_{1-x}\text{N}$ films are grown very thin, which renders determination of their a -lattice parameters from HRXRD difficult. It is often assumed that in such cases $\text{In}_x\text{Al}_{1-x}\text{N}$ grows pseudomorphically on GaN (the situation we consider above). Thus to avoid erroneous P_{PZ}^z all deviations from Vegard's rule need to be accounted for.

IV. CONCLUSIONS

We obtained the elastic stiffness constants, biaxial coefficients, and the respective deviations from Vegard's rule of $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys by using *ab initio* calculations. Equations to extract the In composition from the lattice parameters of $\text{In}_x\text{Al}_{1-x}\text{N}$ films with an arbitrary surface orientation are derived in both the normal coordinate system associated with the principle crystallographic axes and in the prime coordinate system related to the arbitrary orientation. A detailed discussion on the errors in the composition and piezoelectric polarization associated with the deviations from Vegard's rule in the lattice parameters and stiffness constant is presented. The effect of composition, surface orientation, and degree of strain relaxation on these errors are substantially discussed. Our results show that whenever the normal strains (along $[11\bar{2}0]$, $[1\bar{1}00]$, and $[0001]$) are used to extract alloy composition the deviations from Vegard's rule need to be accounted for. This is particularly important for semipolar planes with an angle of inclination with respect to the c axis $32^\circ \leq \theta < 41^\circ$ and $47^\circ < \theta \leq 72^\circ$. Strain relaxation leads to increase underestimation of the composition if the deviations from Vegard's rule are not taken into account. The error in composition Δx becomes infinitely high in the normal coordinate system when the angle of inclination approaches $41^\circ - 45^\circ$. This is due to a singularity in the stress-strain relationships stemming from the wurtzite crystal structure. An alternative approach is to estimate the composition from the strains in the prime coordinate system related to the specific arbitrary orientation. In such instances, Δx associated with the deviations from Vegard's rule remains close to or below 1% in absolute value independently of orientation, composition, and strain in the films. We found that, apart from the nonpolar surfaces, $\text{In}_x\text{Al}_{1-x}\text{N}$ with $(10\bar{1}2)$ and $(11\bar{2}3)$ surface orientations exhibit vanishingly small piezoelectric polarization for all composition as a result of the zero crossover in P_{PZ}^z at an angle of inclination close to $41^\circ - 45^\circ$. Again, this observation is tightly bound to the hexagonal symmetry of the alloy. Our results further suggest that for thin $\text{In}_x\text{Al}_{1-x}\text{N}$ grown pseudomorphically on GaN it is vital to account for the deviations from Vegard's rule in order to correctly determine P_{PZ}^z for $\text{In}_x\text{Al}_{1-x}\text{N}$ with different surface orientations and x in the vicinity of the lattice-matched composition. The detailed discussions in the paper provide guidance to experimentalists on the appropriate approaches to estimate composition and piezoelectric polarization for $\text{In}_x\text{Al}_{1-x}\text{N}$ with different compositions, surface orientations, and degrees of strain. The derived stress-strain relationships for $\text{In}_x\text{Al}_{1-x}\text{N}$ film with an arbitrary surface orientation are applicable to wurtzite group-III nitride and IIb oxide epitaxial ternary alloys and can be used to extract composition in such films in different coordinate systems depending on the specific measurement and sample conditions.

ACKNOWLEDGMENTS

We acknowledge support from the Swedish Research Council (VR) under Grant No. 2010-3848, the Swedish Governmental Agency for Innovation Systems (VINNOVA) under the VINNMER international qualification program, Grant No. 2011-03486, and FCT Portugal under Contract No. PTDC/FIS/100448/2008 and program Ciência 2007. The financial support by the Linköping Linnaeus Initiative on Nanoscale Functional Materials (LiLiNFM) supported by the Swedish Research Council (VR) is gratefully acknowledged. The simulations were carried out using supercomputer resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Center.

APPENDIX

Hooke's law in the prime coordinate system, related to the sample (see Fig. 2), is $\sigma_{i'j'} = C_{i'j'k'm'}\epsilon_{k'm'}$ or

$$\begin{pmatrix} \sigma_{x'x'} \\ \sigma_{y'y'} \\ \sigma_{z'z'} \\ \sigma_{y'z'} \\ \sigma_{x'z'} \\ \sigma_{x'y'} \end{pmatrix} = \begin{pmatrix} C'_{11} & C'_{12} & C'_{13} & C'_{14} & 0 & 0 \\ C'_{12} & C'_{22} & C'_{23} & C'_{24} & 0 & 0 \\ C'_{13} & C'_{23} & C'_{33} & C'_{34} & 0 & 0 \\ C'_{14} & C'_{24} & C'_{34} & C'_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C'_{55} & C'_{65} \\ 0 & 0 & 0 & 0 & C'_{56} & C'_{66} \end{pmatrix} \begin{pmatrix} \epsilon_{x'x'} \\ \epsilon_{y'y'} \\ \epsilon_{z'z'} \\ 2\epsilon_{y'z'} \\ 2\epsilon_{x'z'} \\ 2\epsilon_{x'y'} \end{pmatrix}, \quad (\text{A1})$$

FIG. 11. (Color online) Error in the composition extracted in the prime coordinate system Δx of $\text{In}_x\text{Al}_{1-x}\text{N}$ films with different surface orientations if the deviations from Vegard's rule, δ_ξ , are not taken into account: (a) pseudomorphic growth and (b) different degrees of strain relaxation.

where $C_{i'j'k'm'} = TC_{ijkm}JT^{-1}J^{-1}$ according to Eqs. (2) and (9). The elements for $C_{i'j'k'm'}$ are defined as

$$\begin{aligned}
 C'_{11} &= C_{11}, \\
 C'_{12} &= C_{12} \cos^2 \theta + C_{13} \sin^2 \theta, \\
 C'_{13} &= C_{13} \cos^2 \theta + C_{12} \sin^2 \theta, \\
 C'_{14} &= \frac{(C_{12} - C_{13})}{2} \sin 2\theta, \\
 C'_{22} &= C_{11} \cos^4 \theta + C_{33} \sin^4 \theta + \frac{C_{13} + 2C_{44}}{2} \sin^2 2\theta, \\
 C'_{23} &= C_{13} + \frac{C_{11} + C_{33} - 2C_{13} - 4C_{44}}{4} \sin^2 2\theta, \quad (A2) \\
 C'_{24} &= \frac{\sin 2\theta}{2} [(C_{11} - C_{33}) \cos^2 \theta \\
 &\quad + (C_{13} - C_{33}) \sin^2 \theta] - \frac{C_{44}}{2} \sin 4\theta, \\
 C'_{33} &= C_{11} \sin^4 \theta + C_{33} \cos^4 \theta + \frac{C_{13} + 2C_{44}}{2} \sin^2 2\theta, \\
 C'_{34} &= \frac{\sin 2\theta}{2} [(C_{11} - C_{33}) \sin^2 \theta \\
 &\quad + (C_{13} - C_{33}) \cos^2 \theta] + \frac{C_{44}}{2} \sin 4\theta, \\
 C'_{44} &= \frac{C_{11} + C_{33} - 2C_{13}}{4} \sin^2 2\theta + C_{44} \cos^2 2\theta.
 \end{aligned}$$

The out-of-plane stress $\sigma_{z'z'}$ is zero since the surface is free to expand or contract. The shear stress $\sigma_{y'z'}$ is also zero due to constraints to preserve the Miller indexes of the specific plane. According to Eq. (A1) $\epsilon_{z'z'}$ and $\epsilon_{y'z'}$ can be expressed as functions of the two in-plane strains $\epsilon_{x'x'}$ and $\epsilon_{y'y'}$ as

$$\epsilon_{z'z'} = \frac{(C'_{13}C'_{44} - C'_{14}C'_{34})\epsilon_{x'x'} + (C'_{23}C'_{44} - C'_{24}C'_{34})\epsilon_{y'y'}}{C'^2_{34} - C'^2_{33}C'_{44}}, \quad (A3)$$

$$\epsilon_{y'z'} = \frac{(C'_{14}C'_{33} - C'_{13}C'_{34})\epsilon_{x'x'} + (C'_{24}C'_{33} - C'_{23}C'_{34})\epsilon_{y'y'}}{2C'^2_{34} - 2C'_{33}C'_{44}}.$$

The two in-plane strains are

$$\epsilon_{x'x'} = \frac{a_{\text{InAlN}} - a_0}{a_0}, \quad (A4)$$

$$\epsilon_{y'y'} = \frac{OB_{\text{InAlN}} - OB_0}{OB_0}, \quad (A5)$$

where $OB_0 = m_0 / \cos \theta$ is strain free value for the planes with angle of inclination with respect to the c -axis $0^\circ \leq \theta \leq 45^\circ$ (the situation presented in Fig. 2), and $OB_0 = c_0 / \sin \theta$ for $45^\circ \leq \theta \leq 90^\circ$.

The strains in the normal coordinate system (see Fig. 2) can be obtained from the two in-plane strains in the prime coordinate system using Eq. (9):

$$\begin{aligned}
 \epsilon_{xx} &= \epsilon_{x'x'}, \\
 \epsilon_{yy} &= \frac{1}{2C'_{33}C'_{44} - 2C'^2_{34}} \left\{ [2 \sin^2 \theta (C'_{14}C'_{34} - C'_{13}C'_{44}) + \sin 2\theta (C'_{14}C'_{33} - C'_{13}C'_{34})] \epsilon_{x'x'} \right. \\
 &\quad \left. + [2 \cos^2 \theta (C'_{33}C'_{44} - C'^2_{34}) + 2 \sin^2 \theta (C'_{24}C'_{34} - C'_{23}C'_{44}) + \sin 2\theta (C'_{24}C'_{33} - C'_{23}C'_{34})] \epsilon_{y'y'} \right\}, \\
 \epsilon_{zz} &= \frac{1}{2C'_{33}C'_{44} - 2C'^2_{34}} \left\{ [2 \cos^2 \theta (C'_{14}C'_{34} - C'_{13}C'_{44}) - \sin 2\theta (C'_{14}C'_{33} - C'_{13}C'_{34})] \epsilon_{x'x'} \right. \\
 &\quad \left. + [2 \sin^2 \theta (C'_{33}C'_{44} - C'^2_{34}) + 2 \cos^2 \theta (C'_{24}C'_{34} - C'_{23}C'_{44}) - \sin 2\theta (C'_{24}C'_{33} - C'_{23}C'_{34})] \epsilon_{y'y'} \right\}, \\
 \epsilon_{yz} &= \frac{1}{2C'_{33}C'_{44} - 2C'^2_{34}} \left\{ [\sin 2\theta (C'_{13}C'_{44} - C'_{14}C'_{34}) + \cos 2\theta (C'_{13}C'_{34} - C'_{14}C'_{33})] \epsilon_{x'x'} \right. \\
 &\quad \left. + [\sin 2\theta (C'_{33}C'_{44} - C'^2_{34} + C'_{23}C'_{44} - C'_{24}C'_{34}) + \cos 2\theta (C'_{23}C'_{34} - C'_{24}C'_{33})] \epsilon_{y'y'} \right\}. \quad (A6)
 \end{aligned}$$

The composition in the prime coordinate system can be derived from Eq. (A1) and $\sigma_{z'z'} = 0$:

$$(C'^2_{34} - C'_{33}C'_{44})\epsilon_{z'z'} = (C'_{13}C'_{44} - C'_{14}C'_{34})\epsilon_{x'x'} + (C'_{23}C'_{44} - C'_{24}C'_{34})\epsilon_{y'y'}. \quad (A7)$$

The errors in the composition of $\text{In}_x\text{Al}_{1-x}\text{N}$ pseudomorphically grown on GaN, extracted from the strains in the prime coordinate system, remain below 1% for all planes and different degrees of relaxation. (See Fig. 11.)

*vanya@ifm.liu.se

¹H. Morkoç and S. N. Mohammad, *Science* **267**, 51 (1995).

²F. A. Ponce and D. P. Bour, *Nature (London)* **386**, 351 (1997).

³K. Okamoto, I. Niki, A. Shvarts, Y. Narukawa, T. Mukai, and A. Scherer, *Nat. Mater.* **3**, 601 (2004).

⁴F. Qian, Y. Li, S. Gradeak, H. G. Park, Y. Dong, Y. Ding, Z. L. Wang, and C. M. Lieber, *Nat. Mater.* **7**, 701 (2008).

⁵Y. Taniyasu, M. Kasu, and T. Makimoto, *Nature (London)* **441**, 325 (2008).

⁶J. W. Schwede, I. Bargatin, D. C. Riley, B. E. Hardin, S. J. Rosenthal, Y. Sun, F. Schmitt, P. Pianetta, R. T. Howe, Z. X. Shen *et al.*, *Nat. Mater.* **9**, 762 (2010).

⁷A. Dadgar, F. Schulze, J. Blasing, A. Diez, A. Krost, M. Neuburger, E. Kohn, I. Daumiller, and M. Kunze, *Appl. Phys. Lett.* **85**, 5400 (2004).

- ⁸R. Butté, J.-F. Carlin, E. Feltin, M. Gonschorek, S. Nicolay, G. Christmann, D. Simeonov, A. Castiglia, J. Dorsaz, H. J. Buehlmann *et al.*, *J. Phys. D: Appl. Phys.* **40**, 6328 (2007).
- ⁹G. Christmann, R. Butté, E. Feltin, A. Mouti, P. A. Stadelmann, A. Castiglia, J.-F. Carlin, and N. Grandjean, *Phys. Rev. B* **77**, 085310 (2008).
- ¹⁰Z. T. Chen, Y. Sakai, J. C. Zhang, T. Egawa, J. J. Wu, H. Miyake, and K. Hiramatsu, *Appl. Phys. Lett.* **95**, 083504 (2009).
- ¹¹M. Ferhat and F. Bechstedt, *Phys. Rev. B* **65**, 075213 (2002).
- ¹²E. Iliopoulos, A. Adikimenakis, C. Giesen, M. Heuken, and A. Georgakilas, *Appl. Phys. Lett.* **92**, 191907 (2008).
- ¹³R. E. Jones, R. Broesler, K. M. Yu, J. W. Ager, E. E. Haller, W. Walukiewicz, X. Chen, and W. J. Schaff, *J. Appl. Phys.* **96**, 123501 (2008).
- ¹⁴K. Lorenz, N. Franco, E. Alves, I. M. Watson, R. W. Martin, and K. P. O'Donnell, *Phys. Rev. Lett.* **97**, 085501 (2006).
- ¹⁵T. Seppänen, L. Hultman, J. Birch, M. Beckers, and U. Kreissig, *J. Appl. Phys.* **101**, 043519 (2007).
- ¹⁶V. Darakchieva, M. Beckers, M.-Y. Xie, L. Hultman, B. Monemar, J.-F. Carlin, E. Feltin, M. Gonschorek, and N. Grandjean, *J. Appl. Phys.* **103**, 103513 (2008).
- ¹⁷V. Darakchieva, M.-Y. Xie, F. Tasnádi, I. A. Abrikosov, L. Hultman, B. Monemar, J. Kamimura, and K. Kishino, *Appl. Phys. Lett.* **93**, 261908 (2008).
- ¹⁸J. Wu, *J. Appl. Phys.* **106**, 011101 (2009).
- ¹⁹S. P. Lepkowski and I. Gorczyca, *Phys. Rev. B* **83**, 203201 (2011).
- ²⁰I. Gorczyca, T. Suski, N. E. Christensen, and A. Svane, *Phys. Rev. B* **83**, 153301 (2011).
- ²¹A. Zunger, S. H. Wei, L. G. Ferreira, and J. E. Bernard, *Phys. Rev. Lett.* **65**, 353 (1990).
- ²²J. M. Cowley, *Phys. Rev.* **77**, 669 (1950).
- ²³A. V. Ruban and I. A. Abrikosov, *Rep. Prog. Phys.* **71**, 046501 (2008).
- ²⁴N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Phys. Chem.* **21**, 1087 (1953).
- ²⁵P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ²⁶G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ²⁷C. Stampfl and C. G. Van de Walle, *Phys. Rev. B* **59**, 5521 (1999).
- ²⁸J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²⁹J. S. Speck, *Mater. Res. Soc. Bull.* **34**, 309 (2009).
- ³⁰V. Darakchieva, T. Paskova, M. Schubert, H. Arwin, P. P. Paskov, B. Monemar, D. Hommel, M. Heuken, J. Off, F. Scholz *et al.*, *Phys. Rev. B* **75**, 195217 (2007).
- ³¹F. Tasnádi, M. Odén, and I. A. Abrikosov, *Phys. Rev. B* **85**, 144112 (2012).
- ³²A. Zoroddu, F. Bernardini, P. Ruggerone, and V. Fiorentini, *Phys. Rev. B* **64**, 045208 (2001).
- ³³V. Darakchieva, P. Paskov, T. Paskova, E. Valcheva, B. Monemar, and M. Heuken, *Appl. Phys. Lett.* **82**, 703 (2003).
- ³⁴V. Darakchieva, B. Monemar, and A. Usui, *Appl. Phys. Lett.* **91**, 031911 (2007).
- ³⁵S. Pereira, M. Correia, E. Pereira, K. O'Donnell, E. Alves, A. Sequeira, N. Franco, I. Watson, and C. Deatcher, *Appl. Phys. Lett.* **80**, 3913 (2002).
- ³⁶K. Kishino, J. Kamimura, and A. Kikuchi, *Appl. Phys. Express* **5**, 031001 (2012).
- ³⁷J. Kamimura, K. Kishino, and A. Kikuchi, *Phys. Status Solidi RRL* **6**, 123 (2012).
- ³⁸A. E. Romanov, T. J. Baker, S. Nakamura, and J. S. Speck, *J. Appl. Phys.* **100**, 023522 (2006).
- ³⁹J. G. Gualtieri, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **4**, 53 (1994).
- ⁴⁰M. Gonschorek, J.-F. Carlin, E. Feltin, M. A. Py, N. Grandjean, V. Darakchieva, B. Monemar, M. Lorenz, and G. Ramm, *J. Appl. Phys.* **103**, 093714 (2008).