Macroscopic Polarization Effect on Bowing Constant of Thermal Parameters of $\text{In}_x\text{Ga}_{1-x}\text{N}$

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In this work, we have investigated theoretically the effect of macroscopic polarization [sum of spontaneous (SP) and piezoelectric (PZ) polarization] on various physical parameters of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy. The macroscopic polarization contributes to the effective elastic constants of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy. This modifies the phonon group velocity, Debye temperature, and Debye frequency of the alloy. These thermal parameters are estimated as a function of In composition. Our calculation shows that these material parameters are enhanced and vary nonlinearly with In composition, i.e., show bowing. The cause of bowing is the nonlinear dependence of the spontaneous and piezoelectric polarization on composition. The bowing constant of each material parameter (with and without polarization) is also theoretically predicted by the best-fit method. The results show that the polarization mechanism not only enhances the parameters but also contributes significantly to the bowing constant. The macroscopic polarization contributes more than 25% to the bowing constant. The obtained results can be used to predict the effect of the polarization mechanism on the thermoelectric properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy.

Key words: $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy, macroscopic polarization, thermal parameters, bowing constant

INTRODUCTION

One of the important methods of controlling properties of III–V nitrides relies on alloying instead of employing pure binaries such as InN, GaN, etc.¹ By adjusting the composition, one can tune selected material parameters such as the bandgap, lattice constant or polarization to the desired optimal value. The wide-bandgap semiconductor InGaN is a key technological material for fabrication of light-emitting diodes (LEDs) and laser diodes.² The wavelength of the radiation emitted from InGaN can be tuned over a wide range from visible red (~610 nm) to ultraviolet (~365 nm) by changing the alloy composition and forming heterostructures such as quantum wells (QWs).³ The material has a larger peak electron velocity, larger saturation velocity, higher breakdown voltage, and thermal stability, making it highly suitable for use

as a channel material in microwave power devices.^{4,5} Applications of InGaN include LEDs, laser diodes,^{6–8} solar cells,^{9–11} and photodetectors. Much interest has been focused on InGaN/GaN multi quantum wells (MQWs) because of their utility as the active layer in high-brightness III-nitride LEDs and continuous-wave (CW) blue–green laser diodes (LDs).

Understanding the optical and thermal properties of InGaN/GaN MQWs is important for fabrication of light-emitting devices. Because of the large lattice mismatch (11%) between InN and GaN, growth of InGaN/GaN MQWs is strongly related to the strain distributions of their well and barrier layers. The built-in macroscopic polarization field consists of spontaneous polarization and the strain-induced piezoelectric polarization field. These fields are a common feature of nitride heterostructures and have a profound impact on the nitride's optical, thermal, and electrical properties. The existence of these fields in III–V nitrides has been confirmed by

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both first-principles calculations and experiments.^{12–21} Calculated and experimental results show that two-dimensional electron gases (2DEGs) are generated by spontaneous and piezoelectric polarization effects with sheet resistivity suitable for high-electron-mobility transistors without doping of the barrier layer.²² These fields significantly influence the distribution and lifetime of excess carriers in InGaN QWs and can have an important impact on the performance of InGaN/GaN-based optoelectronic devices.²³ The presence of a large piezoelectric field in the InGaN/GaN wells leads to a quantum confined Stark effect, which has been considered to play an important role in the emission mechanism of InGaN/GaN heterostructures. Recently, the effect of the polarization mechanism on the efficiency of LEDs and laser diodes was reported.^{24–27} The reported results show that the efficiency drop is caused by several internal physical mechanisms including the built-in electrostatic field induced by the spontaneous and piezoelectric polarization. The effect of polarization has also been studied in the context of solar cell performance.^{28–33} That study showed that polarization charges produce large band bending, leading to a dead layer in the intrinsic region of the solar cell. The valence-band discontinuity across the heterojunction interface also gives rise to a small barrier for hole transport. Both factors are responsible for the small output photocurrent. Thus, the performance is significantly controlled by the polarization mechanism. Although some of these devices are expected to achieve outstanding performance, further improvements of the design and efficiency seem to be possible only on the basis of more detailed understanding of the polarization in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy nanostructures.

In our earlier works,^{34,35} we investigated the effect of macroscopic polarization on various physical parameters and thermal properties of binary nitrides. On the basis of these results, one can expect equivalent enhancement in various material parameters and the thermal conductivity of nitride alloys due to the polarization mechanism also. It was established that, similar to the behavior of the spontaneous and piezoelectric polarizations in $\text{In}_x\text{Ga}_{1-x}\text{N}$,^{14,16,17} the bandgap of these alloys depends on the In content.³⁶ To describe the effect of strain in the framework of continuum elasticity theory, knowledge of the lattice parameters and elastic constants of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys is needed.^{37,38} Therefore, description of elastic and polarization-related properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys can have a decisive influence on the design criteria for nitride nanostructures. Theoretical calculations show that, in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys, both the lattice parameters and bandgap energy deviate from Vegard's law, i.e., depend nonlinearly on composition.³⁶ The composition dependence of the elastic constants of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy was studied using first-principles calculations.^{37–42} That study predicted a finite

degree of bowing (composition-dependent nonlinear nature) in these parameters. This first-principles calculation prediction has been validated by measuring the surface acoustic wave velocity in InGaN alloy by means of high-resolution Brillouin spectroscopy.⁴¹ To the best of the authors' knowledge, the macroscopic polarization effect on various physical parameters of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy, particularly on the elastic constant and thermal parameters, has not been investigated. For accurate prediction of optical and thermal properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy, the bowing parameters of the elastic constant, phonon velocity, and Debye temperature are required.^{41,42} High-resolution Brillouin spectroscopy experiments reported the composition dependence of the surface acoustic velocity of InGaN.⁴¹ The bowing constant value of thermal parameters such as the Debye temperature and Debye frequency are yet to be investigated. The significance is that, once the bowing constant is known, the physical parameter, in principle, can be predicted for all In compositions. As thermal conduction controls the design, performance, and lifetime of a device, study of the polarization effect on thermal parameters and on their bowing nature deserves attention. The obtained results will be useful to study the effect of the macroscopic polarization mechanism on the thermoelectric properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy.^{43,44} Recently, Wang and group performed a number of pioneering studies on the potential of the piezoelectric polarization mechanism.^{45–47} Their study pointed out that the polarization mechanism can offer a new concept for increasing the efficiency of photodetectors and organic LEDs, and has great potential for a wide variety of high-performance flexible optoelectronic devices.

This paper is organized in the following manner: The model and thermal parameters are discussed in Sect. 2. The results and discussion are presented in Sect. 3. Conclusions are given in Sect. 4.

MODEL

The macroscopic polarization field P is composed of two fields: (i) the spontaneous polarization field P^{sp} , and (ii) the piezoelectric polarization field P^{pz} . The field P^{sp} is an intrinsic electric field of the material, but during growth of nitrides on a substrate, strain is generated due to the lattice mismatch and external stress. This strain produces the piezoelectric polarization field P^{pz} in the material. Both the polarization fields and elastic constants of nitride materials are composition-dependent properties, depending nonlinearly on the In composition.^{14,16,17,37–41} Due to the macroscopic polarization, the coupling between the elastic strain and electric field induces an additional electric polarization.^{37,38,41,48} This contributes to the effective elastic constant of the alloy material.⁴¹ The effective elastic constant of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy can be written as^{34,35,49}

$$\bar{C}_{44}^{\text{InGaN}} = C_{44}^{\text{InGaN}} + [(e_{15}^2 + e_{31}^2 + e_{33}^2 + p_{\text{sp}}^2)/\varepsilon_0\varepsilon]^{\text{InGaN}}, \quad (1)$$

where $\bar{C}_{44}^{\text{InGaN}}$ is the elastic constant of $\text{In}_x\text{Ga}_{1-x}\text{N}$ with the polarization effect, which we denote as $C_{44,p}^{\text{InGaN}}$; and C_{44}^{InGaN} is the elastic constant without polarization. e_{15} , e_{31} , and e_{33} are the piezoelectric constants, and p^{sp} is the spontaneous polarization constant of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy. ε_0 is the vacuum permittivity, and ε is the dielectric constant of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy. The elastic constant C_{44}^{InGaN} is calculated as

$$C_{44}^{\text{InGaN}} = xC_{44}^{\text{InN}} + (1-x)C_{44}^{\text{GaN}} + b_{44}x(1-x), \quad (2)$$

where $b_{44} = -16$ GPa is the bowing constant of C_{44}^{InGaN} .³⁹⁻⁴¹ The piezoelectric constants of $\text{In}_x\text{Ga}_{1-x}\text{N}$ were estimated using Vegard's formula^{14,17}

$$e_{ij}^{\text{InGaN}} = xe_{ij}^{\text{InN}} + (1-x)e_{ij}^{\text{GaN}}. \quad (3)$$

The constants e_{15} , e_{31} , and e_{33} show linear variation with the In composition,¹⁶ whereas $p^{\text{sp InGaN}}$ varies nonlinearly with the composition as^{14,17}

$$p^{\text{sp InGaN}}(x) = -0.042x - 0.034(1-x) + 0.037x(1-x). \quad (4)$$

The dielectric constant also shows linear variation and is given by¹⁴

$$\varepsilon^{\text{InGaN}}(x) = x\varepsilon^{\text{InN}} + (1-x)\varepsilon^{\text{GaN}}. \quad (5)$$

In nitride crystals, the phonon velocity v depends on the direction and magnitude of the phonon wavevector. The phonon velocities along the two transverse directions are the same and can be calculated as $v_{\text{t}}^{\text{InGaN}} = (C_{44}^{\text{InGaN}}/\rho^{\text{InGaN}})^{1/2}$. According to Callaway's formulation, the average velocity v along a specified direction is⁵⁰

$$(v^{\text{InGaN}})^{-1} = \frac{1}{3}[(v_{\text{t}}^{-1} + v_{\text{t}}^{-1} + v_{\text{l}}^{-1})], \quad (6)$$

where $v_{\text{l}} = \sqrt{C_{33}^{\text{InGaN}}/\rho^{\text{InGaN}}}$ is the phonon velocity along the longitudinal direction. C_{33}^{InGaN} is calculated as

$$C_{33}^{\text{InGaN}} = xC_{33}^{\text{InN}} + (1-x)C_{33}^{\text{GaN}} + b_{33}x(1-x), \quad (7)$$

where $b_{33} = -71$ GPa is the bowing constant of C_{33}^{InGaN} .³⁹⁻⁴¹ The material density ρ^{InGaN} is calculated as $\rho^{\text{InGaN}}(x) = x\rho^{\text{InN}} + (1-x)\rho^{\text{GaN}}$.⁴¹ Now, due to the inclusion of the macroscopic polarization, the transverse velocity becomes $v_{\text{t,p}}^{\text{InGaN}} = (C_{44,p}^{\text{InGaN}}/\rho^{\text{InGaN}})^{1/2}$. It should be noted that the longitudinal velocity does not change due to the polarization effect. The average

velocity v_p^{InGaN} including the polarization effect along a specified direction can be written as

$$(v_p^{\text{InGaN}})^{-1} = \frac{1}{3}[(v_{\text{t,p}}^{-1} + v_{\text{t,p}}^{-1} + v_{\text{l}}^{-1})]. \quad (8)$$

The other two thermal parameters which are very important for the calculation of the thermal conductivity and thermoelectric properties are the Debye frequency and Debye temperature. The Debye frequency is calculated from the relation $\omega_{\text{D}} = v(3N/4\pi V_0)^{1/3}$, where N is the number of atoms per unit cell, V_0 is the unit cell volume of the crystal, and v is the average phonon velocity. The Debye temperature θ_{D} is defined as $\theta_{\text{D}} = \hbar\omega_{\text{D}}/k_{\text{B}}$, where $\hbar$ is Planck's constant and k_{B} is Boltzmann's constant. The Debye frequency and Debye temperature depend directly on the phonon velocity, so these parameters are revised due to the macroscopic polarization effect.

RESULTS AND DISCUSSION

We first discuss the applicability of and deviation from Vegard's rule. The physical properties of ternary alloys are usually investigated using Vegard's law, i.e., assuming that the lattice constants of the ternary compound can be expressed as a linear combination of the lattice constants of the two forming binary compounds. The validity of this approach is recognized among researchers.⁵¹ For $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy, Vegard's law can be written as

$$P^{\text{InGaN}}(x) = xP^{\text{InN}} + (1-x)P^{\text{GaN}}, \quad (9)$$

where P stands for a physical parameter of $\text{In}_x\text{Ga}_{1-x}\text{N}$. The application of Vegard's law to the lattice and elastic constants of binaries has proved to be a useful tool for understanding the elastic behavior and compositional nature of ternary and quaternary III-N semiconductor alloys.⁴² In Ref. 51, this theoretical concept is supported by a solid experimental dataset. However, there are serious indications that deviations from this simple rule should be expected for lattice constants, bandgap energy, and elastic properties,³⁶⁻⁴² similar to the nonlinear dependence on composition predicted for the spontaneous and piezoelectric properties of III-V nitride alloys.¹⁷ This prediction has been supported by experiments.^{14,15,41} This nonlinearity is attributed essentially to sources such as (i) chemical effects due to the different cation electronegativity of the components, (ii) internal strain effects due to varying cation-anion bond lengths, and (iii) disorder effects due to the random distribution of chemical elements on the cation sites.¹⁷ Thus, a necessary condition to apply Vegard's law is high-quality homogeneity of the structure and composition of ternary and quaternary alloys.⁵¹ As internal

strains and chemical and disorder effects are always present in alloys, deviation from Vegard's law is certain. Hence, determination of the deviation from Vegard's rule, i.e., the nonlinear behavior (bowing constant), is essential for accurate prediction of optical and thermal properties of ternary alloys.^{41,42} Once the bowing constant is known, the physical parameter value can be predicted for any In composition. To explore the polarization effect on physical parameters and on their bowing, we calculated physical parameters of $\text{In}_x\text{Ga}_{1-x}\text{N}$ with and without consideration of the polarization property. First the elastic constant $C_{44}^{\text{InGa}}^{\text{N}}$ of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy was calculated using Eq. 2, which takes bowing into account. The recommended values of C_{44}^{InN} and $C_{44}^{\text{Ga}}^{\text{N}}$ ⁵² and the bowing constant $b_{44} = -16 \text{ GPa}$ ⁴¹ were used in the calculation. The elastic constant $C_{44}^{\text{InGa}}^{\text{N}}$ as a function of the In composition is shown in Fig. 1 by curve c-1. For clear visualization of the deviation, the elastic constant $C_{44}^{\text{InGa}}^{\text{N}}$ of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy was also calculated by Vegard's rule using Eq. 9. Curve c-2 shows the elastic constant $C_{44}^{\text{InGa}}^{\text{N}}$ (obtained by Vegard's rule) as a function of the In composition (Fig. 1). From the curves c-1 and c-2 one can clearly observe a noticeable deviation from Vegard's rule, noting that Vegard's rule overestimates $C_{44}^{\text{InGa}}^{\text{N}}$.⁴¹ However, what happens when the polarization effect of the material is taken into account?

The elastic constant $C_{44,p}^{\text{InGa}}^{\text{N}}$ of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy, which is known as the elastic constant with polarization, can be calculated from Eq. 1 as a function of the In composition. The polarization property of $\text{In}_x\text{Ga}_{1-x}\text{N}$ contributes to its elastic constant. First, the polarization constants of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy were

calculated. The piezoelectric constants e_{15} , e_{31} , and e_{33} , and the spontaneous polarization p^{sp} of $\text{In}_x\text{Ga}_{1-x}\text{N}$ were calculated from Eqs. 3 and 4, respectively. The dielectric constant was calculated from Eq. 5. The values of the polarization constants e_{15} , e_{31} , and e_{33} for binary InN and GaN were taken from Refs. 14,53. The variation of $C_{44,p}^{\text{InGa}}^{\text{N}}$ as a function of the In composition is shown in Fig. 1 by curve c-3. To proceed with the analysis of the amount of deviation from Vegard's law in the case of polarization, the elastic constant $C_{44,p}^{\text{InGa}}^{\text{N}}$ was calculated through Vegard's rule $C_{44,p}^{\text{InGa}}^{\text{N}} = xC_{44,p}^{\text{InN}} + (1-x)C_{44,p}^{\text{Ga}}^{\text{N}}$. Here, the elastic constant of binaries with the polarization effect from Ref. 35 was used in the calculation. This is represented by curve c-4 in Fig. 1. One can see from curves c-3 and c-4 that Vegard's rule overestimates the value of $C_{44,p}^{\text{InGa}}^{\text{N}}$. Also, it can be observed that curve c-3 exhibits a significant degree of bowing. The bowing constant of $C_{44,p}^{\text{InGa}}^{\text{N}}$ can be calculated by applying the curve-fitting method available in Origin 6.1 software. The calculation was done in the following way: Curve c-3 can be approximated by the following formula:³⁹⁻⁴²

$$C_{44,p}^{\text{InGa}}^{\text{N}} = xC_{44,p}^{\text{InN}} + (1-x)C_{44,p}^{\text{Ga}}^{\text{N}} + b_{44,p}x(1-x). \quad (10)$$

$C_{44,p}^{\text{InN}}$ and $C_{44,p}^{\text{Ga}}^{\text{N}}$ are the elastic constants of binary InN and GaN where the polarization effect has been taken into account, and $b_{44,p}$ is the bowing constant of $C_{44,p}^{\text{InGa}}^{\text{N}}$. The bowing parameter accounts for the nonlinear dependence on composition, x . If we best-fit curve c-3 in Fig. 1 using Origin 6.1 software (up to second order), we obtain

Fig. 1. Elastic constant C_{44} of $\text{In}_x\text{Ga}_{1-x}\text{N}$ as a function of In composition.

Fig. 2. Phonon velocity in $\text{In}_x\text{Ga}_{1-x}\text{N}$ as a function of In composition.

$$C_{44,p}^{\text{InGaN}} = [1.2457 \times 10^{11} - (8.26593 \times 10^{10})x + (1.96561 \times 10^{10})x^2]. \quad (11)$$

Now, using the values of $C_{44,p}^{\text{InN}}$ and $C_{44,p}^{\text{GaN}}$ from Ref. 35 in Eq. 10 and comparing the coefficients of x and x^2 in Eqs. 10 and 11, we obtain the bowing constant as $b_{44,p} = -19.65$ GPa. This can be taken as the minimum bowing of $C_{44,p}^{\text{InGaN}}$, as only the bowing factor for spontaneous polarization is taken into consideration in the calculation while the piezoelectric constants were computed by applying Vegard's rule $C_{44,p}^{\text{InGaN}} = xC_{44,p}^{\text{InN}} + (1-x)C_{44,p}^{\text{GaN}}$. It can be pointed out that curve c-4 does not exhibit bowing even if polarization is considered in the binary materials. Comparing b_{44} and $b_{44,p}$, one can find that the elastic constant with polarization shows more nonlinear behavior than the elastic constant without polarization. The finite bowing b_{44} of the elastic constant C_{44}^{InGaN} has been validated by measuring the surface acoustic wave velocity in InGaN alloy by means of high-resolution Brillouin spectroscopy.⁴¹ The cause of the greater bowing in $C_{44,p}^{\text{InGaN}}$ is the spontaneous and piezoelectric polarization effect. It can be argued that the nonlinear behavior would be more pronounced if the bowing of the piezoelectric constants were also known. From the above discussion, it can be accepted that the polarization not only enhances the elastic constant $C_{44,p}^{\text{InGaN}}$ but also significantly contributes to its bowing constant. The elastic constant of $\text{In}_x\text{Ga}_{1-x}\text{N}$ without and with polarization using its bowing constant can now be written as follows:

$$C_{44}^{\text{InGaN}} = xC_{44}^{\text{InN}} + (1-x)C_{44}^{\text{GaN}} - 16x(1-x) \text{ GPa}, \quad (2a)$$

$$C_{44,p}^{\text{InGaN}} = xC_{44,p}^{\text{InN}} + (1-x)C_{44,p}^{\text{GaN}} - 19.65x(1-x) \text{ GPa}. \quad (10a)$$

The phonon velocity v of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was computed as a function of the In composition with and without consideration of polarization using Eqs. 8 and 6, respectively. The transverse velocity v_t of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was calculated from $v_t = \sqrt{C_{44}^{\text{InGaN}} / \rho^{\text{InGaN}}}$.

C_{44}^{InGaN} is given by Eq. (2a), and the material density ρ^{InGaN} is calculated by Vegard's rule.⁴¹ Then, the longitudinal velocity v_l of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was calculated from $v_l = \sqrt{C_{33}^{\text{InGaN}} / \rho^{\text{InGaN}}}$. C_{33}^{InGaN} was calculated by Eq. 7. The phonon velocity v^{InGaN} was finally estimated from Eq. 6. The phonon velocity v^{InGaN} as a function of the In composition is shown in Fig. 2 by curve c-1. To visualize the deviation from Vegard's rule, the phonon velocity v^{InGaN} was also estimated as $v^{\text{InGaN}} = xv^{\text{InN}} + (1-x)v^{\text{GaN}}$, where v^{InN} and v^{GaN} are the phonon velocities without the polarization effect, taken from Refs. 34,35. The phonon velocity v^{InGaN} (obtained by Vegard's rule) as a function of the In composition is represented by curve c-2 in Fig. 2.

It can be observed from Fig. 2 that curve c-1 exhibits a finite degree of bowing. This bowing is the deviation from Vegard's rule and can be calculated

by the best-fit method. Curve c-1 can be approximated by the following formula:^{39–42}

$$v^{\text{InGaN}} = xv^{\text{InN}} + (1-x)v^{\text{GaN}} + b_v x(1-x), \quad (12)$$

where b_v is the bowing constant of the phonon velocity. Now, using the Origin software's curve-fitting method, the polynomial equation representing curve c-1 of Fig. 2 is

$$v^{\text{InGaN}} = (4933.160 - 1958.300x + 256.994x^2) \text{ m s}^{-1}. \quad (13)$$

Now, using the values of v^{InN} and v^{GaN} from Ref. 35 in Eq. 12 and comparing the coefficients of x and x^2 in Eqs. 12 with 13, we obtain the bowing constant as $b_v = -258 \text{ m/s}$. From curves c-1 and c-2, one can draw the conclusion that Vegard's rule overestimates the phonon velocity. Now, what happens to the phonon velocity when the polarization effect is taken into account? The transverse velocity with polarization $v_{t,p}^{\text{InGaN}}$ is calculated as

$v_{t,p}^{\text{InGaN}} = \sqrt{C_{44,p}^{\text{InGaN}} / \rho^{\text{InGaN}}}$. Now, Eq. 10a can be applied to estimate $C_{44,p}^{\text{InGaN}}$. The longitudinal velocity v_l is not affected by the polarization mechanism.^{35,48,49} The phonon velocity with polarization v_p^{InGaN} was estimated from Eq. 8. The phonon velocity v_p^{InGaN} as a function of the In composition is depicted by curve c-3 in Fig. 2. To visualize the deviation from Vegard's rule, the phonon velocity v_p^{InGaN} was also calculated as $v_p^{\text{InGaN}} = xv_p^{\text{InN}} + (1-x)v_p^{\text{GaN}}$, where v_p^{InN} and v_p^{GaN} are the phonon velocities of the binaries (with polarization), taken from Ref. 35. The phonon velocity v_p^{InGaN} (obtained by Vegard's rule) as a function of the In composition is shown by curve c-4 in Fig. 2. From Fig. 2, it can be seen that curve c-3 exhibits a significant degree of bowing. This bowing was calculated in the following way: Curve c-3 can be approximated by the following formula:^{39–42}

$$v_p^{\text{InGaN}} = xv_p^{\text{InN}} + (1-x)v_p^{\text{GaN}} + b_{v,p} x(1-x), \quad (14)$$

where $b_{v,p}$ is the bowing constant of the phonon velocity (with polarization). If we best-fit curve c-3 of Fig. 2 using Eq. 14, we obtain the bowing constant of the phonon velocity (with polarization) as $b_{v,p} = -328 \text{ m/s}$. Comparing the two bowing constants for velocity (with and without polarization), one finds that the bowing is higher in the case with polarization. This suggests that the bowing constant depends on the macroscopic polarization. The percentage increase in the bowing constant due to polarization is around 27.15%. The composition dependence of the surface acoustic velocity of InGaN has been validated by means of high-resolution Brillouin scattering experiments.⁴¹ The

phonon velocity of $\text{In}_x\text{Ga}_{1-x}\text{N}$ without and with the polarization mechanism can now be summarized as follows:

$$v^{\text{InGaN}} = xv^{\text{InN}} + (1-x)v^{\text{GaN}} - 258x(1-x) \text{ m/s}, \quad (12a)$$

$$v_p^{\text{InGaN}} = xv_p^{\text{InN}} + (1-x)v_p^{\text{GaN}} - 328x(1-x) \text{ m/s}. \quad (14a)$$

The Debye frequency of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was estimated as a function of the In composition with and without consideration of polarization. The Debye frequency ω_D^{InGaN} of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was calculated using the phonon velocity Eq. 12a. This is plotted as a function of the In composition by curve c-1 in Fig. 3. To visualize the deviation, the Debye frequency ω_D^{InGaN} was also calculated by Vegard's rule using the Debye frequencies of the individual binaries.³⁵ Curve c-2 of Fig. 3 shows a plot of the Debye frequency as a function of the In composition as obtained by Vegard's rule. It can be observed from Fig. 3 that curve c-1 shows a finite degree of bowing. The bowing constant of the Debye frequency can be predicted by applying the curve-fitting method. Curve c-1 can be approximated by the following formula:^{39–42}

$$\omega_D^{\text{InGaN}} = x\omega_D^{\text{InN}} + (1-x)\omega_D^{\text{GaN}} + b_\omega x(1-x), \quad (15)$$

where b_ω is the bowing constant of the Debye frequency. If we best-fit curve c-1 of Fig. 3 using Eq. 15, we obtain the bowing constant of the Debye frequency as $b_\omega = -7.055 \times 10^{12} \text{ rad/s}$.

To explore the polarization effect, the Debye frequency with polarization was calculated using Eq. 14a. The Debye frequency $\omega_{D,p}^{\text{InGaN}}$ as a function of the In composition is shown by curve c-3 in Fig. 3. Also, to visualize the deviation in the figure, the Debye frequency $\omega_{D,p}^{\text{InGaN}}$ was also calculated using Vegard's rule from the Debye frequencies of the individual binaries (with polarization).³⁵ This is shown by curve c-4 in Fig. 3. To proceed with the analysis of the amount of deviation from Vegard's law, curve c-3 can be approximated by the following formula:^{39–42}

$$\omega_{D,p}^{\text{InGaN}} = x\omega_{D,p}^{\text{InN}} + (1-x)\omega_{D,p}^{\text{GaN}} + b_{\omega,p} x(1-x), \quad (16)$$

where $\omega_{D,p}^{\text{InN}}$ and $\omega_{D,p}^{\text{GaN}}$ are the Debye frequency of InN and GaN with polarization, and $b_{\omega,p}$ is the bowing constant of the Debye frequency (with the polarization effect). If we best-fit curve c-3 of Fig. 3 using Eq. 16, we obtain the bowing constant of the Debye frequency (with polarization) as $b_{\omega,p} = -8.997 \times 10^{12} \text{ rad/s}$. Comparing the two bowing constants of the Debye frequency (with and without polarization), one observes that the bowing is higher in the case with polarization. This suggests that the bowing constant of the Debye frequency depends on the macroscopic polarization.

Fig. 3. Debye frequency of $\text{In}_x\text{Ga}_{1-x}\text{N}$ as a function of In composition.

The percentage increase in the bowing constant due to polarization is around 27.05%. The Debye frequency without and with polarization can now be expressed as follows:

$$\omega_{\text{D}}^{\text{InGa}} = x\omega_{\text{D}}^{\text{In}} + (1-x)\omega_{\text{D}}^{\text{Ga}} - 7.055 \times 10^{12}x(1-x) \text{ rad/s}, \quad (15a)$$

$$\omega_{\text{D,p}}^{\text{InGa}} = x\omega_{\text{D,p}}^{\text{In}} + (1-x)\omega_{\text{D,p}}^{\text{Ga}} - 9.05 \times 10^{12}x(1-x) \text{ rad/s}. \quad (16a)$$

Using the Debye frequency, the Debye temperature of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was estimated as a function of the In composition with and without consideration of the polarization effect. The Debye temperature $\theta_{\text{D}}^{\text{InGa}}$ of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was calculated using the Debye frequency Eq. 15a. This is plotted as a function of the In composition by curve c-1 in Fig. 4. Also, the Debye temperature of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was calculated by Vegard's rule using the individual Debye temperatures of the binaries. Curve c-2 of Fig. 3 shows the plot of the Debye temperature (obtained by Vegard's rule) as a function of the In composition. It can be observed from Fig. 4 that curve c-1 shows a finite degree of bowing. The bowing constant of the Debye temperature can be predicted by the curve-fitting method. Curve c-1 can be approximated by the following formula:³⁹⁻⁴²

$$\theta_{\text{D}}^{\text{InGa}} = x\theta_{\text{D}}^{\text{In}} + (1-x)\theta_{\text{D}}^{\text{Ga}} + b_{\theta}x(1-x), \quad (17)$$

where $\theta_{\text{D}}^{\text{In}}$ and $\theta_{\text{D}}^{\text{Ga}}$ are the Debye temperature of InN and GaN, and b_{θ} is the bowing constant of the Debye temperature.

If we best-fit curve c-1 of Fig. 4 using Eq. 17, we obtain the bowing constant of the Debye temperature as $b_{\theta} = -54.15$ K. To explore the polarization effect, the Debye temperature (with polarization) was calculated from Eq. 16a. The Debye temperature $\theta_{\text{D,p}}^{\text{InGa}}$ as a function of the In composition is shown by curve c-3 in Fig. 4. To visualize the deviation graphically, the Debye temperature $\theta_{\text{D,p}}^{\text{InGa}}$ was also calculated using Vegard's rule. This is shown by curve c-4 in Fig. 4. To proceed with the analysis of the amount of deviation from Vegard's rule due to the polarization effect, curve c-3 can be approximated by the following formula:³⁹⁻⁴²

$$\theta_{\text{D,p}}^{\text{InGa}} = x\theta_{\text{D,p}}^{\text{In}} + (1-x)\theta_{\text{D,p}}^{\text{Ga}} + b_{\theta,p}x(1-x), \quad (18)$$

where $\theta_{\text{D,p}}^{\text{In}}$ and $\theta_{\text{D,p}}^{\text{Ga}}$ are the Debye temperature of InN and GaN (with polarization), and $b_{\theta,p}$ is the bowing constant of the Debye temperature (with the polarization effect). If we best-fit curve c-3 of Fig. 4 using Eq. 18, we obtain the bowing constant of the Debye temperature (with polarization) as $b_{\theta,p} = -68.80$ K. Comparing the two bowing constants of the Debye temperature (with and without polarization), one observes that the bowing is higher in the case with polarization. This suggests that the bowing constant of the Debye temperature depends on the macroscopic polarization. The percentage increase in the bowing constant due to the polarization is around 27.58%. The importance of the bowing constant b in this case is that the Debye temperature of $\text{In}_x\text{Ga}_{1-x}\text{N}$ can be predicted for the whole range of In composition. The Debye temperature of $\text{In}_x\text{Ga}_{1-x}\text{N}$ without and with polarization finally can be expressed as follows:

Fig. 4. Debye temperature of $\text{In}_x\text{Ga}_{1-x}\text{N}$ as a function of In composition.

Table I. Calculated bowing constants of $\text{In}_x\text{Ga}_{1-x}\text{N}$

Parameter	Without polarization bowing (b)	With polarization bowing (b_p)	Increase (%)
C_{44} (GPa)	-16	-19.65	22.81
v (m/s)	-258	-328	27.15
ω_D (rad/s)	-7.055×10^{12}	-9.05×10^{12}	28.36
θ_D (K)	-54.15	-68.80	27.05

$$\theta_D^{\text{InGa}} = x\theta_D^{\text{In}} + (1-x)\theta_D^{\text{Ga}} - 54.15x(1-x) \text{ K}, \quad (19)$$

$$\theta_{D,p}^{\text{InGa}} = x\theta_{D,p}^{\text{In}} + (1-x)\theta_{D,p}^{\text{Ga}} - 68.80x(1-x) \text{ K}. \quad (20)$$

The computation of these parameters such as the phonon velocity, Debye temperature, and Debye frequency with and without the polarization mechanism has been performed from knowledge of the elastic constant with and without polarization. All these parameters (with the polarization effect) show a higher degree of bowing due to the effect of the spontaneous and piezoelectric polarization. The calculation considers bowing in the spontaneous polarization, whereas the piezoelectric polarization constants of $\text{In}_x\text{Ga}_{1-x}\text{N}$ were obtained by linear interpolation of the polarization constants of the binaries. It can be argued that the nonlinear nature would be more pronounced if the bowing of the piezoelectric constants were also known. Table I

presents the calculated values of the bowing constants and their percentage increase due to the polarization mechanism.

CONCLUSIONS

We investigated theoretically the effect of the macroscopic polarization on various physical parameters of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy. The spontaneous (SP) and piezoelectric (PZ) polarizations are composition-dependent properties in nitride materials. The elastic constants are also composition-dependent parameters. Due to the macroscopic polarization, the coupling between the elastic strain and electric field induces an additional electric polarization. This contributes to the effective elastic constant of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy. From the knowledge of the elastic constant, various physical parameters of $\text{In}_x\text{Ga}_{1-x}\text{N}$ such as the phonon group velocity, Debye frequency, and Debye temperature with and without the polarization effect were estimated as a function of the In composition. Our calculations show that these parameters are enhanced and vary nonlinearly with the In composition, i.e., show bowing. The bowing constant for each parameter with

and without the polarization mechanism were also theoretically predicted by the method of best fit up to second order. The results show that the polarization mechanism not only enhances the physical parameters but also contributes significantly to their bowing constants, i.e., to the nonlinear nature. The macroscopic polarization contributes more than 25% to the bowing constant. It is argued that the nonlinear effect would be more pronounced if the bowing constant of the piezoelectric constants were also known. Future first-principles calculations and experiments should address the macroscopic polarization to confirm this predicted result. The obtained results can be used to study the effect of the macroscopic polarization mechanism on the optical, electrical, and thermoelectric properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy to optimize the design and performance of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy optoelectronic devices.

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