

Piezoelectric Polarization Effect on Phonon Relaxation Rates in Nitride Wurtzites

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(Received December 22, 2011)

Abstract: We have reported the effect of piezoelectric polarization on phonon group velocity in wurtzite nitrides. The phonon group velocity, Debye frequency and Debye temperature of wurtzite nitrides are modified due to piezoelectric polarization. The modified parameters are calculated for binary nitrides (GaN , AlN and InN) and ternary nitrides ($Al_xGa_{(1-x)}N$, $In_xGa_{(1-x)}N$ and $In_xAl_{(1-x)}N$). The variation of these parameters with concentration x are also obtained. The obtained results can be used to calculate the effect of piezoelectric polarization on phonon relaxation rates and thermal conductivity which can give some insight about the large difference between theoretical and experimental value of thermal conductivity of wurtzite nitrides particularly of GaN films.

Keywords: piezoelectric polarization, wurtzite nitrides, phonon group velocity, Debye frequency and Debye temperature.

1. Introduction

The wurtzite nitride semiconductors (GaN , AlN , InN and their alloys) are promising materials for the next generation of high-power optoelectronics devices^{1,2}. One of the important issues in further development of wurtzite nitrides is self-heating. Self-heating strongly affects the performance of the device^{3,4}. Recently, wurtzite nitride LEDs suffer from the problem of efficiency droop which is resulted from the piezoelectric effect⁵. The material in the active layer and the substrate

material generally determine the thermal resistance of the device structure. Thus, it is important to know the accurate value of the thermal conductivity (k) of corresponding material.

Several groups have reported investigation of the thermal conductivity value in wurtzite nitride films⁶⁻⁹. The thermal conductivity for *GaN* films grown by hydride vapour phase epitaxy (HVPE) is about $1.3 W/cm K$ at room temperature⁶. Florescu et al.⁸ have determined thermal conductivity of *GaN* films fabricated by lateral epitaxial overgrowth is about $1.7-1.8 W/cm K$ using the scanning thermal microscopy technique. Adachi has reported the k value $1.95 W/cm K$ for *GaN* films¹⁰. For some samples with lower dislocation density the thermal conductivity value reaches $k = 2.1 W/cm.K$. The theoretical studies of the thermal conductivity of bulk *GaN*, conducted by Zou and co-workers^{11,12}, on the basis of the Callaway - Klemens approach^{13,14}, have reported k value from 3.36 to $5.40 W/cm K$ by taking two sets of material parameters for *GaN*. The relatively large difference between these two values of the thermal conductivity is entirely due to ambiguity in the values of material parameters of *GaN*. In the same work they have also demonstrated the effect of impurities and dislocations on thermal conductivity. The piezoelectric polarization effect on thermal conductivity, so far in our knowledge has not been considered. As nitride wurtzites are strong piezoelectric polarized materials, the effect should be taken to study the change in the thermal conductivity. We expect the effect may bring experimental and theoretical values of thermal conductivity very close to each other and can play a key role in determining the thermal budget at the active region of the nitride devices. In this work, we have calculated the group velocity of the phonons by taking piezoelectric polarization property. Using modified phonon group velocity, calculation has been done for Debye temperature and frequency for both binary and ternary wurtzite nitrides. Due to modification in the phonon group velocity and frequency, the phonon relaxation rates also get modified.

The paper is organized in the following manner. In the next section a brief introduction about spontaneous and piezoelectric polarization phenomenon in wurtzite nitrides has been discussed. The modified phonon group velocity due to polarization effect is presented in section 3. In section 4, the modified phonon group velocity, Debye frequency and Debye temperature are calculated for binary and ternary wurtzite nitrides and their variation with concentration is presented. Conclusions are given in section 5.

2. Spontaneous and Piezoelectric Polarization

A unique feature of the wurtzite nitrides is strong polarization effect¹⁵. It has been theoretically calculated and experimentally confirmed. Both spontaneous polarization (SP) and piezoelectric polarization (PZ) present in the wurtzite nitrides influence the optical, electrical and thermal properties and thus, significant consequence on device design¹⁶. Polarization induces sheet charges and electric fields values as high as $1\text{MV}/\text{cm}$ ^{17, 18} in these materials. The effect can be used constructively in device design to enhance carrier collection, ohmic resistance reduction and bending bands to reduce surface recombination. Polarization is defined by the equation $D = \epsilon_0 \epsilon_r E + P$, where D is electric flux density (C/m^2), E is electric field (V/m), P is net polarization (C/m^2), ϵ_0 is vacuum permittivity, ϵ_r is relative permittivity. The net polarization is composed of two parts: (i) spontaneous, which is intrinsic to a material, and (ii) piezoelectric, which is strain-induced, $P = P_{SP} + P_{PZ}$, here P_{SP} is spontaneous polarization (C/m^2) and P_{PZ} is piezoelectric polarization (C/m^2). The spontaneous polarization along the z (or c) axis of the wurtzite crystal is $\vec{P}_{SP} = P_{SP} \hat{z}$. The piezoelectric polarization can be calculated by $P_{PZ} = \epsilon_x e_{31} + \epsilon_y e_{32} + \epsilon_z e_{33}$, where $\epsilon_x, \epsilon_y, \epsilon_z$ are strain components in the x, y, z directions, and e_{31}, e_{32}, e_{33} are piezoelectric constants. The strain along the z -axis is $\epsilon_z = \frac{(c - c_0)}{c_0}$ and in-plane strain $\epsilon_x = \epsilon_y = \frac{(a - a_0)}{a_0}$ is assumed to be isotropic. Table 1²⁰ shows the equilibrium values of the lattice parameters a_0, c_0 of wurtzite nitrides (GaN etc.). The relation between ϵ_x and ϵ_z is $\epsilon_z = -2 \left(\frac{C_{13}}{C_{33}} \right) \epsilon_x$, where C_{13}, C_{33} are elastic constants. Table 2^{17,18} shows the values of elastic constants of wurtzite nitrides (GaN etc.). Using the relation ϵ_x and ϵ_z , the piezoelectric polarization in the direction of the c - axis becomes

$$P_{PZ} = 2 \frac{(a - a_0)}{a_0 \left[e_{31} - e_{33} \left(\frac{C_{13}}{C_{33}} \right) \right]}. \quad \text{Table 3}^{17,18} \text{ shows the spontaneous and}$$

piezoelectric polarization values of wurtzite nitrides.

3. Modified Phonon Velocity

The coupling between the elastic strain and electric field is characterized by the third rank piezoelectric tensor $e_{\alpha\beta\gamma}$, according to the relation²¹

$$(3.1) \quad \sigma_{\alpha\beta} = \sum_{\gamma\delta} C_{\alpha\beta\gamma\delta} \frac{\partial u_\gamma}{\partial x_\delta} - \sum_\gamma e_{\gamma\alpha\beta} E_\gamma$$

where $\sigma_{\alpha\beta}$ is the stress tensor, $C_{\alpha\beta\gamma\delta}$ is the fourth-rank elastic modulus tensor, u_γ is the particle displacement, and E_γ is the electric field. The equations of motion take the form

$$(3.2) \quad \begin{aligned} \rho \frac{\partial^2 u_\alpha}{\partial t^2} &= \sum_\beta \frac{\partial \sigma_{\alpha\beta}}{\partial x_\beta} \\ &= \sum_{\beta\gamma\delta} C_{\alpha\beta\gamma\delta} \frac{\partial^2 u_\gamma}{\partial x_\beta \partial x_\delta} - \sum_{\beta\gamma} e_{\gamma\alpha\beta} \frac{\partial E_\gamma}{\partial x_\beta} \end{aligned}$$

The constitutive relation involving the electric displacement D_α and the dielectric tensor $\epsilon_{\alpha\beta}$ when piezoelectricity is present, is

$$(3.3) \quad D_\alpha = \sum_{\alpha\beta} e_{\alpha\beta\gamma} \frac{\partial u_\beta}{\partial x_\gamma} + \epsilon_0 \sum_\beta \epsilon_{\alpha\beta} E_\beta.$$

Combining this relation with the Maxwell's equation

$$(3.4) \quad \vec{\nabla} \cdot \vec{D} = 0$$

gives the equation,

$$(3.5) \quad \sum_{\alpha\beta\gamma} e_{\alpha\beta\gamma} \frac{\partial^2 u_\beta}{\partial x_\alpha \partial x_\gamma} + \sum_{\alpha\beta} \epsilon_0 \epsilon_{\alpha\beta} \frac{\partial E_\beta}{\partial x_\alpha} = 0,$$

which is to be solved simultaneously with Eq. (3). As a specific example, let us consider the wurtzite form of nitrides (GaN, AlN, InN) with its six fold axis parallel to the z -direction. For elastic waves polarized in the z -direction and propagating in the x -direction, there is a single element of the piezoelectric tensor to be considered, conventionally designated by e_{15} and a single element of the dielectric tensor ϵ_{xx} . The equations of motion and the Maxwell's equation reduce to

$$(3.6) \quad \rho \frac{\partial^2 u_z}{\partial t^2} = C_{44} \frac{\partial^2 u_z}{\partial x^2} - e_{15} \frac{\partial E_x}{\partial x},$$

$$(3.7) \quad 0 = e_{15} \frac{\partial^2 u_z}{\partial x^2} + \epsilon_0 \epsilon_{xx} \frac{\partial E_x}{\partial x},$$

where C_{44} is the appropriate elastic modulus in the Voigt notation. Eliminating the electric field from the equation of motion, we obtain the wave equation

$$(3.8) \quad \rho \frac{\partial^2 u_z}{\partial t^2} = \bar{C}_{44} \frac{\partial^2 u_z}{\partial x^2},$$

with $\bar{C}_{44}$ the effective elastic modulus specified by

$$(3.9) \quad \bar{C}_{44} = C_{44} + \left[\frac{e_{15}^2}{(\epsilon_0 \epsilon_{11})} \right].$$

The dispersion relation is $\omega \left[\frac{\bar{C}_{44}}{\rho} \right]^{\frac{1}{2}} q = v q$ here v is the speed of the wave.

It is clear that the speed is enhanced by the piezoelectric polarization effect²¹. Without piezoelectric polarization effect the transverse velocity of

phonon is $v_T = \left[\frac{C_{44}}{\rho} \right]^{\frac{1}{2}}$. When piezoelectric effect is considered the

transverse velocity becomes $v_{T,P} = \sqrt{\left[C_{44} + \left(\frac{e_{15}^2}{\epsilon_0 \epsilon_{11}} \right) \right] / \rho}$. In real crystals,

the sound velocity $v(q)$ depends on the direction and magnitude of the phonon wave vector q and is specific to a given phonon polarization type. According to Callaway's formulation^{13, 14}, a single-branch polarization-averaged velocity v along a specified crystallographic direction is

$$(3.10) \quad v = \left[\frac{1}{3} \left(\frac{1}{v_{T,1}} + \frac{1}{v_{T,2}} + \frac{1}{v_L} \right) \right]^{-1}$$

where v_L and $v_{T,1,2}$ are the longitudinal and transverse sound velocities, respectively. Along [0001] direction, two transverse branches are degenerate and have the same velocity given by $v_{T,1} = v_{T,2} = v_T = (\bar{C}_{44} / \rho)^{1/2}$; where

$\bar{C}_{44} = C_{44} + \left(\frac{e_{15}^2}{\epsilon_0 \epsilon_{11}} \right)$ the extra term is due to piezoelectric polarization

effect, the longitudinal velocity is defined as $v_L = \left(\frac{C_{33}}{\rho} \right)^{\frac{1}{2}}$. Here C_{ij} are the

elastic constants of the crystal. It should be noted that longitudinal velocity does not change due to polarization effect while transverse velocity is affected.

4. Result and Discussion

Modified Phonon group velocity along different directions for binary wurtzite nitrides (GaN, AlN, InN) are calculated using values of elastic constants from Table 2 (calculated values) and polarization constants from Table 3. The values of modified velocities are noted in Table 4. Using Vegard's law^{17,18}, $v_{AlGaN} = x.v_{AlN} + (1-x).v_{GaN}$ modified phonon group velocity for ternary wurtzite nitride $Al_xGa_{(1-x)}N$ is computed and its variation with concentration x is shown in Fig.1(a) considering with and

without piezoelectric effect. From Fig. 1(a) it is observed that relative difference between the two velocities (velocity without piezoelectric effect and with piezoelectric effect) increases as the concentration of *Al* increases. This difference is prominent when $x=1$. The variation of phonon group velocity with concentration x in case of $In_xGa_{(1-x)}N$ is shown in Fig. 1(b). Here, it can be seen that as *In* concentration increases the difference between the two lines increases and when $x=1$ the difference becomes maximum. Fig. 1(c) shows the variation of phonon group velocity of $In_xAl_{(1-x)}N$ with concentration x . From this graph, it can be observed that the relative difference between the phonon group velocities without piezoelectric effect and with piezoelectric effect is uniform as the concentration of *In* increases. Thus, piezoelectric polarization effect enhances the phonon group velocity²¹. The enhancement of phonon group velocity is prominent in *InGaN* among the three ternary wurtzite nitrides.

The Debye frequency is defined by the relation $\nu_D = \nu \left(\frac{3N}{4\pi V} \right)^{\frac{1}{3}}$. Here,

N is the number of atoms present in volume V of the crystal and ν is phonon group velocity. Table 5 shows the Debye frequency of *GaN*, *AlN* and *InN* with and without piezoelectric effect. Using Vegard's law, $\nu_{AlGaN} = x.\nu_{AlN} + (1-x).\nu_{GaN}$ Debye frequency for $Al_xGa_{(1-x)}N$ has been computed and variation of ν_D with *Al* concentration x is shown in Fig. 2(a) taking with and without piezoelectric polarization effect. The two lines are separate showing that frequency is enhanced by piezoelectric polarization effect. Fig. 2(b) shows the variation of Debye frequency in case of $In_xGa_{(1-x)}N$ with *In* concentration x while for $In_xAl_{(1-x)}N$, the variation of Debye frequency is shown in Fig. 2(c).

The Debye temperature θ_D is defined as $\theta_D = h\nu_D / k_B$, where ν_D is the Debye frequency, h is planck's constant and k_B is Boltzmann's constant. The Debye temperature for binary wurtzite nitrides *GaN*, *AlN* and *InN* without piezoelectric effect are 600, 1150 and 660 K respectively taken from reference²². The modified Debye temperatures with piezoelectric effect are calculated and shown in Table 6. Using Vegard's law $\theta_{AlGaN} = x.\theta_{AlN} + (1-x).\theta_{GaN}$ Debye temperature of

$Al_xGa_{(1-x)}N$ with and without piezoelectric polarization effect is calculated. The variation of θ_D with Al concentration x is shown in Fig. 3(a). Figure clearly shows that due to piezoelectric effect, the Debye temperature is increased and the increment is more when the concentration of Al is high. Fig. 3(b) shows the variation of Debye temperature for $In_xGa_{(1-x)}N$ with In concentration x while for $In_xAl_{(1-x)}N$, the variation of Debye temperature is shown in Fig. 3(c).

For wurtzite nitrides the important relaxation processes are Umklapp scattering (τ_U), point defect scattering (τ_p), scattering on dislocations (τ_{DC}), boundary scattering (τ_B) and phonon– electron scattering (τ_{ph-e}). The relaxation rates for three phonon Umklapp scattering is

$$(4.1) \quad \frac{1}{\tau_U} = 2\gamma^2 \frac{K_B T \omega^2}{\mu V_0 \omega_D},$$

where γ is the Gruneissen anharmonicity parameter, μ is shear modulus, V_0 is the volume per atom and ω_D is the Debye frequency. The relaxation rates for point defects is

$$(4.2) \quad \frac{1}{\tau_p} = \frac{V_0 \Gamma \omega^4}{4\pi v^3},$$

where Γ is the measure of strength of point defect scattering. The phonon scattering rate at the core of the dislocation is proportional to the cube of the phonon frequency,

$$(4.3) \quad \frac{1}{\tau_{DC}} = \eta N_D \frac{V_0^{\frac{4}{3}}}{v^2} \omega^3,$$

where N_D is the density of dislocation lines. The boundary scattering relaxation rates is given by

$$(4.4) \quad \frac{1}{\tau_B} = \frac{v}{L},$$

where L is the dimension of the sample.
The phonon-electron scattering relaxation rates is

$$(4.5) \quad \frac{1}{\tau_{ph-e}} = \frac{n_e \varepsilon_1^2 \omega}{\rho v^2 K_B T} \sqrt{\frac{\pi m^* v^2}{2 K_B T}} \exp\left(-\frac{m^* v^2}{2 K_B T}\right),$$

where n_e is the concentration of conduction electrons, ε_1 is the deformation potential, ρ is the mass density and m^* is the effective mass of electron.

Table 1. Lattice constants of wurtzite nitrides GaN, AlN and InN²⁰

Parameters	GaN	AlN	InN
a_0 (in Å)	3.189	3.112	3.54
c_0 (in Å)	5.185	4.982	3.54

Table 2. Measured and calculated elastic constant (in GPa) of wurtzite nitrides GaN, AlN and InN^{17, 18}

Elastic Constant	GaN		AlN		InN	
(in GPa)	Exp.	Cal.	Exp.	cal	Exp.	Cal.
C_{11}	374	367	190	223	345	396
C_{12}	106	135	104	115	125	137
C_{13}	70	103	121	92	120	108
C_{33}	379	405	182	224	395	373
C_{44}	101	95	10	48	118	116

Table 3. Spontaneous polarization, piezoelectric polarization and dielectric constants of GaN, AlN and InN^{17, 18}

Parameters	GaN	AlN	InN
$P_{sp}(C/m^2)$	-0.029	-0.081	-0.032
$e_{33} (C / m^2)$	0.73	1.55	0.73
$e_{31} (C / m^2)$	-0.49	-0.58	-0.49
$e_{15} (C / m^2)$	-0.40	-0.48	-0.40
$\varepsilon_{11} (= \varepsilon_{xx})$	9.5	9.0	15.3
ε_{33}	10.4	10.7	-

Table 4. Phonon group velocities (m/sec) in wurtzite nitrides GaN, AlN and InN

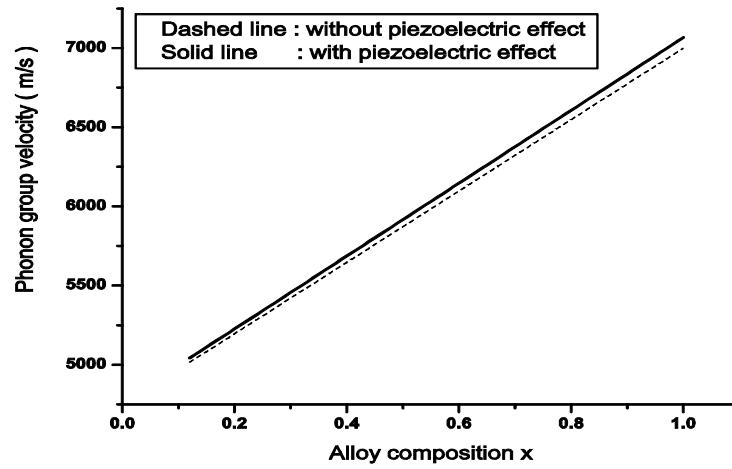
Materials Wurtzite	Without PZ effect	With PZ effect	% change
GaN	4746.11	4784.10	0.80
AlN	6999.90	7067.60	0.96
InN	3233.85	3265.88	0.99

Table 5. Debye frequencies (rad/sec) in wurtzite nitrides GaN, AlN and InN

Materials	Without PZ effect	With PZ effect	% change
GaN	1.249623×10^{13}	1.259625×10^{13}	0.80
AlN	2.395110×10^{13}	2.418245×10^{13}	0.96
InN	1.374585×10^{13}	1.388203×10^{13}	0.99

Table 6. Debye temperatures (K) in wurtzite nitrides GaN, AlN and InN

Materials	Without PZ effect	With PZ effect	% change
GaN	600.00	604.80	0.80
AlN	1150.00	1161.10	0.96
InN	660.00	666.53	0.99

Fig. 1(a) Comparison of phonon group velocities (without piezoelectric effect and with piezoelectric effect) in $\text{Al}_x\text{Ga}_{(1-x)}\text{N}$.

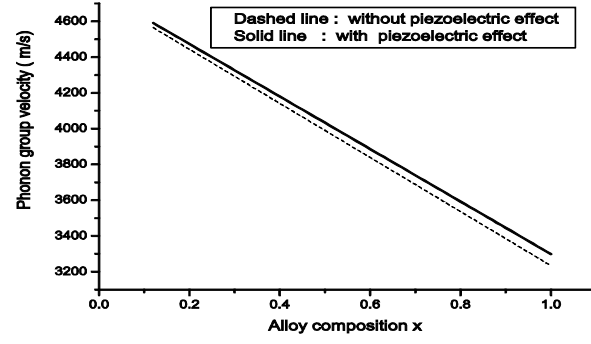


Fig. 1(b) Comparison of phonon group velocities in $\text{In}_x \text{Ga}_{(1-x)} \text{N}$.

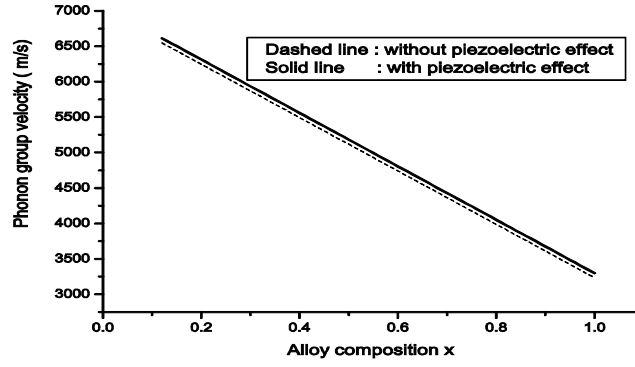


Fig. 1(c) Comparison of phonon group velocities in $\text{In}_x \text{Al}_{(1-x)} \text{N}$.

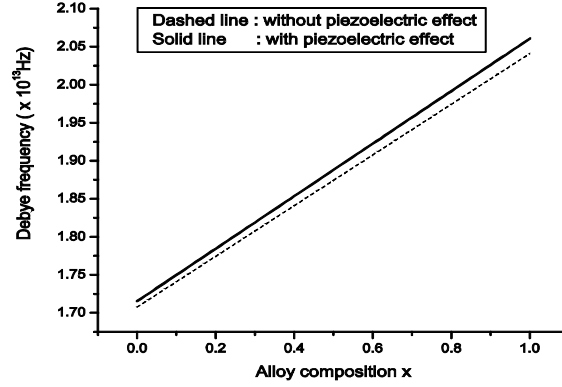


Fig. 2(a) Comparison of Debye frequencies (without piezoelectric effect and with piezoelectric effect) in $\text{Al}_x \text{Ga}_{(1-x)} \text{N}$

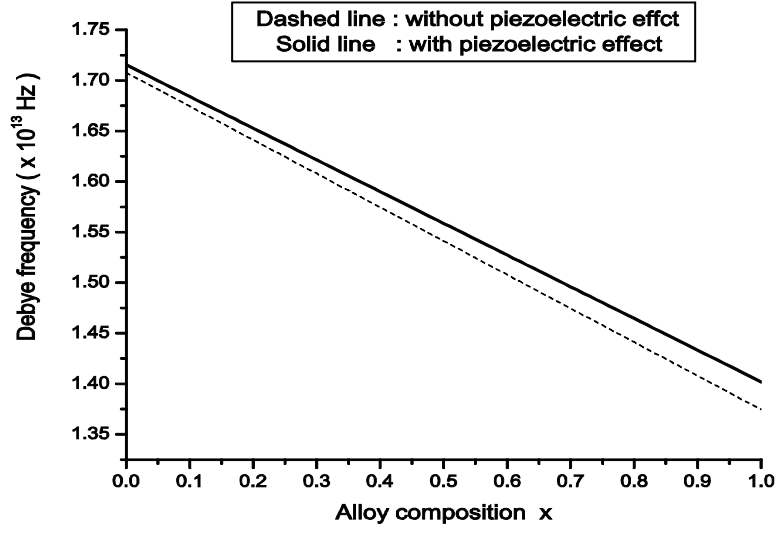


Fig. 2(b) Comparison of Debye frequencies in $\text{In}_x \text{Ga}_{(1-x)}\text{N}$.

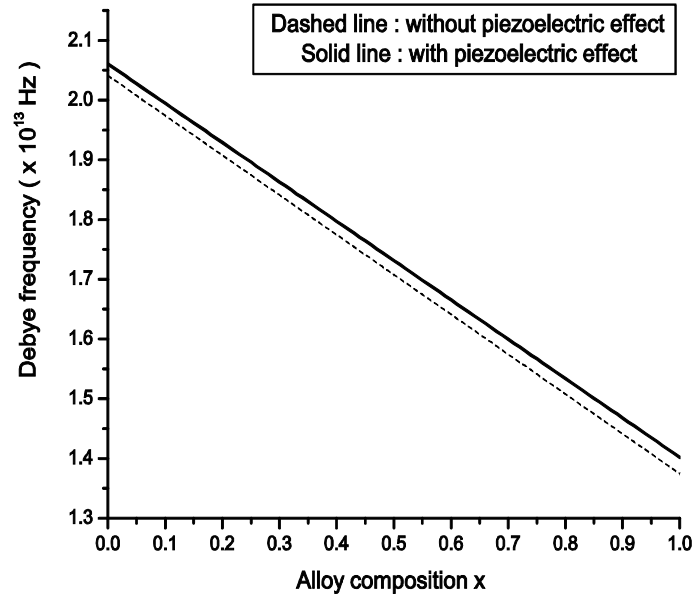


Fig. 2(c) Comparison of Debye frequencies in $\text{In}_x \text{Al}_{(1-x)}\text{N}$.

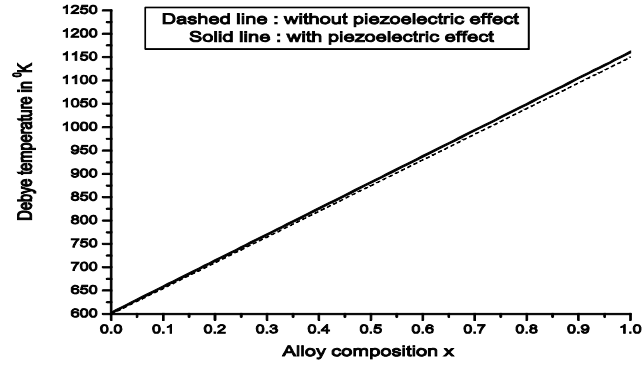


Fig. 3(a) Comparison of Debye temperatures (without piezoelectric effect and with piezoelectric effect) in $\text{Al}_x \text{Ga}_{(1-x)} \text{N}$.

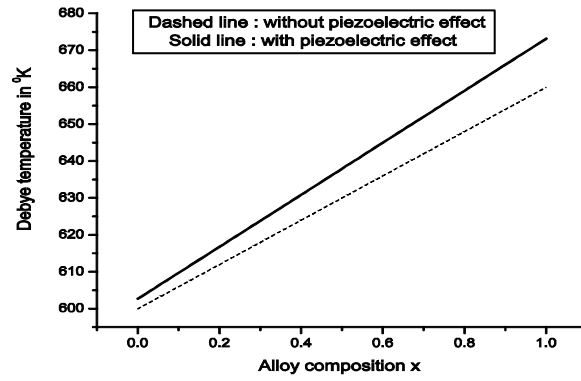


Fig. 3(b) Comparison of Debye temperatures in $\text{In}_x \text{Ga}_{(1-x)} \text{N}$.

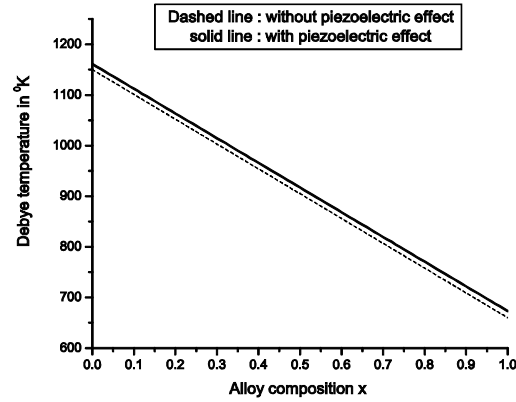


Fig. 3(c) Comparison of Debye temperatures in $\text{In}_x \text{Al}_{(1-x)} \text{N}$.

5. Conclusion

We have calculated modified phonon group velocity by considering piezoelectric polarization effect in wurtzite binary and ternary nitrides. The piezoelectric polarization effect increases the velocity of the phonon and hence changes the Debye frequency, Debye temperature and phonon relaxation rates of wurtzite nitrides. The enhancement of phonon relaxation rate affects the thermal conductivity of wurtzite nitrides.

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