High-T Thermodynamics of GaN: A Comparative Study using Mean-Field Theory and Quasiharmonic Debye Model

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***Abstract** – The thermodynamic properties of wide-bandgap semiconductor GaN have been investigated systematically using the concept of mean-field potential (MFP) approach and quasiharmonic Debye-model. These properties including volume thermal expansion, isothermal bulk modulus, Grüneisen parameter, constant pressure and volume specific heats and anharmonic contribution to ionic specific heat at constant volume are calculated in a wide range of temperatures (0–2500 K) for cubic zinc-blende (ZB) structure. We have employed nearest-neighbour tight-binding second-moment approximation (TB-SMA) to evaluate ambient condition cohesive properties of GaN. The parameters of the TB-SMA model are derived from the full-potential linearized augmented plane-wave (FP-LAPW) DFT-approach, obtained within the generalized gradient condition (GGA). The obtained structural and thermodynamic parameters under normal condition are found to be in good agreement with the existing experimental and other theoretical results. Meanwhile, the detailed comparison between the quasiharmonic approximation (QHA) and anharmonic-MFP models gives insight to the anharmonicity at elevated temperature. This detailed knowledge of thermodynamic behavior at high–T condition is of fundamental importance for device applications of GaN.*

***Keywords:** GaN; thermodynamics; mean-field potential; Debye model.*

I. Introduction

In the last two decades, there is an increasing rise of performance-enhancing electronics, due largely to the availability of capable microelectronics coupled with the ever-growing demand for improved ICs performance. However, the presence of high-temperatures, well beyond the limits of conventional electronics, pause inherent limitation to the operation of many of these systems. These difficulties stand as major hindrances toward expanded use of electronics to directly improve hot-environment system performance [1]. To dispose of the problem wide-bandgap semiconductors are used for high-T electronics applications, which cannot be met by readily available Si-semiconductor technology. In this regard, gallium nitride (GaN) and other group-III nitrides are important materials for the fabrication of various semiconductor devices. Since GaN is also a promising semiconductor material that exhibit many outstanding physical and chemical properties in high-T optoelectronics and high-power, high-frequency devices [1]-[2]; its thermal characterization at high-T seems inevitable. From a crystallography point of view, under ambient conditions GaN crystallizes in the hcp wurtzite structure. However, it was noticed that the cubic zinc-blende (ZB) structure has technological advantages than wurtzite structure [3]. Despite such technological developments of GaN, many fundamental problems such as high-T thermodynamics still remain unsolved [4]-[6].

Our immediate aim is therefore to examine the effect of thermal expansion due to the anharmonicity of the interatomic potential and can be related to the intrinsic energy of the solid similar to the specific heat and the thermal conductivity. In the case of epitaxial layers of GaN grown on foreign substrates (e.g., sapphire or SiC), the difference in thermal expansion coefficients between the layer material and the substrate material governs the strain induced in the layer during cool down from growth to room temperature. Because the strain determines various important parameters like bandgap energy, internal electric field, and the onset of plastic deformation of lattice, the accurate knowledge of the thermal expansion and other vibrational properties are essential not only from a physical point of view but also for device engineering.

From this perspective, we have studied several high-T (0–2500 K) thermodynamic properties of cubic-ZB GaN using the conventional quasiharmonic Debye model and anharmonic mean-field potential approach. Results for various thermal properties are compared with other first principles and molecular dynamics (MD) findings to estimate the effect of anharmonicity.

II. Computational Scheme

The total Helmholtz free energy is written as,

$$F(V,T) = E_C(V) + F_{ion}(V,T), \tag{1}$$

where $E_C(V)$ represent cohesive energy at T = 0 K and $F_{ion}(V,T)$ denotes the vibrational free energy of ions. In the present calculation, cold energy $E_C(V)$ was obtained using the energy functional within the tight-binding second-moment approximation (TB-SMA) up to nearest-neighbour interaction [7].

$$E_C(V) = AZe^{-p x} - \xi \sqrt{Z} e^{-q x} \quad \text{with} \quad x = \left[\left(\frac{V}{V_0} \right)^{\frac{1}{3}} - 1 \right]. \tag{2}$$

Here, Z is the number of nearest neighbours. The model Parameters A, ξ, p, q were determined from all-electron calculations of Daoudi *et al.* [8]. These authors have reported ground state properties of group-III nitrides XN (X=Al, Gn, In) using full-potential linearized-augmented plane-wave (FP-LAPW) approach within both the generalized gradient approximation (GGA) and the local density approximation (LDA). However, as expected, GGA results are in closer agreement to experiment than the LDA ones, and we have used their GGA motivated results as input to our calculations.

For vibrational free energy, we have deployed quasiharmonic (QH) Debye model [9] and anharmonic mean-field potential (MFP) approach [10]-[12].

II.1. MFP Approach: Model-1

In this approach (we call it Model-1: M-1), in which, in the classical limit (i.e., T > θ_D; the Debye temperature), the wonderer atom is assumed to move in the mean-potential produced by surrounding atoms. Under this assumption, $F_{ion}(V,T)$ can be calculated in terms of $E_C(V)$ as follows [10]-[11].

$$F_{ion}(V,T) = -k_B T \left[\frac{3}{2} \ln \left(\frac{m k_B T}{2 \pi \hbar^2} \right) + \ln(v_f(V,T)) \right], \tag{3}$$

with $\quad v_f(V,T) = 4\pi \int \exp \left\{ -\frac{g(s,V)}{k_B T} \right\} s^2 ds.$

$$g(s,V) = \frac{1}{2} \left[E_C(s+a_0) + E_C(s-a_0) - 2E_C(a_0) \right]$$
$$+ \left(\frac{\lambda}{2} \right) \left(\frac{s}{a_0} \right) \left[E_C(s+a_0) - E_C(s-a_0) \right]. \tag{4}$$

It is observed that the parameter λ appearing in the equation (4), which is related to the thermodynamic Grüneisen parameter and thereby determines the *anharmonicity*, may be treated as an adjustable parameter [12]. In principle, vibrational frequency depends on volume (so called QH approximation) and temperature both. This implies that constant value of λ may not be always sufficient to evaluate intrinsic anharmonism. We propose the following form for the λ: $\lambda = \lambda_0 + c \left(\frac{T}{\theta_D} \right)$. The form reduces to the one given by Wang and Li [11] with $\lambda = \lambda_0$ at T = 0 K, while parameter *c* (positive or negative real number) can be determined, for example, by requiring observed thermal expansion coefficient at Debye temperature. (For GaN, θ_D = 826 K.) In the present calculation, we take *c* = -1.0.

II.2. Quasiharmonic Debye Model (Model-2)

In this model (Model-2: M-2), the basic assumption is the quadratic dependence of the phonon frequency. Indeed, at low excitation energy (i.e., at low-T) phonon density of states (p-dos) is quadratic in ω, and the use of QH-Debye model is well justified. Using Debye (GIBBS-code) model [9], lattice-ion free energy is calculated as,

$$F_{ion}(\theta_D(V),T) = k_B T \left[\frac{9}{8} \frac{\theta_D(V)}{T} + 3\ln \left(1 - e^{-\frac{\theta_D(V)}{T}} \right) - D \left(\frac{\theta_D(V)}{T} \right) \right]. \tag{5}$$

Here, $D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx$ with $y = \frac{\theta_D(V)}{T}$ is the Debye integral. $\theta_D(V)$ is the volume dependent Debye temperature, which was calculated by adjusting the Poisson ratio (σ = 0.349) at T = 0 K.

Once the total free energy is calculated as an explicit function of volume and temperature various thermal properties [11] at different temperatures are determined.

III. Results and Discussion

We have first confirmed the validity of the TB-SMA by checking the reproducibility of equilibrium cohesive properties of ZB GaN: lattice constant a_0= 9.5153 (9.5151) a.u., isothermal bulk modulus B_T=127.147 (127.60) GPa, its pressure derivative $B_T^{'}$=4.7321 (4.6757), and cohesive energy per atom E_C = -6.7442 (-6.7574) eV. Here, values in parenthesis represent corresponding FP-LAPW results [8]. For the present case TB-SMA parameters are: A = 0.2887, ξ = 2.9511, p = 9.9932 and q = 3.3875. $E_C(V)$ so calculated is then used to estimate total Helmholtz free energy by both models, M-1 and M-2. Presently computed volume expansion coefficients are compared in the figure-1, along with recent QHA results [13] and classical MD results [5]. Overall good agreement is observed for MFP motivated M-1 findings for $T > \theta_D$, while only at low-T the QH-Debye model gives reasonable agreement. Discrepancy.
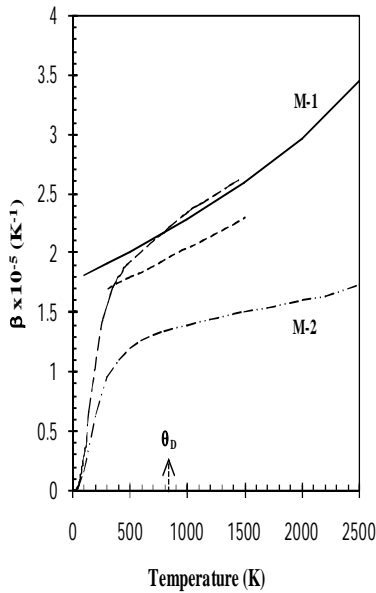

Fig.1. Thermal expansion coefficient for ZB-GaN using M-1 and M-2 models (see text for more information). QHA results (long-dashed line) due to Xu *et al.* [13], and MD results (dashed line) in [5] are also compared.
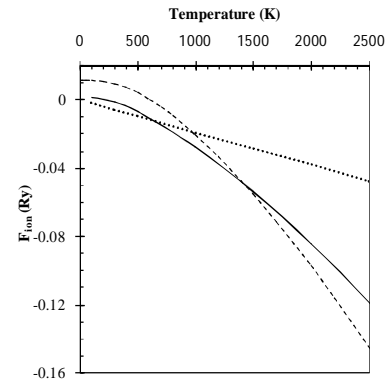

Fig.2. Lattice-ion vibrational free energy for M-1 and M-2 models. Dotted line represents free gas limit -3k_BT.

in M-1 as well as in MD [5] results at low-T is due to the use of classical partition function to evaluate F_{ion}, where quantum correlation effect is important. Considering the temperature domain of our interest, these results are consistent to our current understanding. At still higher temperatures, where anharmonic effects are dominant, one expects steep rise in expansion coefficient, and this sometimes leads to plastic deformation also. Fig.1 clearly reveals limitation of treating anharmonicity at high-T by M-2. In any case M-2 model underestimate the expansion effect. It is however to be noted that the results in [13] are derived for wurtzite phase of GaN, while present and those due to MD [5] findings are for ZB phase.

We then calculate vibrational free energy due to lattice ions (Fig.2). Qualitatively, both M-1 and M-2 models give similar results; starting with positive value to more rapidly negative values crossing zero at some characteristic temperature. For M-2, it is equal to Debye temperature, while for M-1 model it is at much lower temperature. In our earlier work [10], we have noticed that essence of MFP is to assume that the crystal vibrates with some *mean* characteristic single frequency, (or with
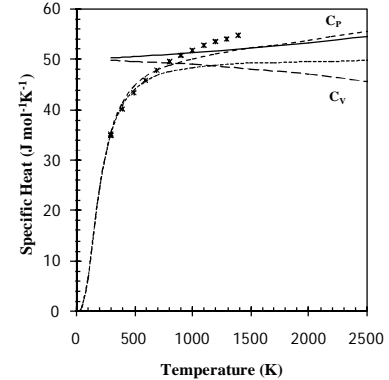

Fig.3. Constant pressure and volume specific heats, C_P and C_V, for M-1 and M-2 models. Symbols represent recent compilation for C_P due to Jacob *et al.* [4].
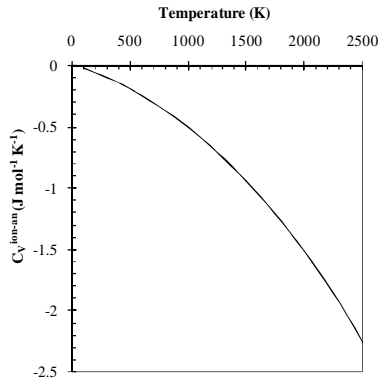
Fig.4. Anharmonic contribution to ionic C_V: $C_V^{ion-an} = C_V^{ion} - 3k_B$ due to MFP based model M-1.
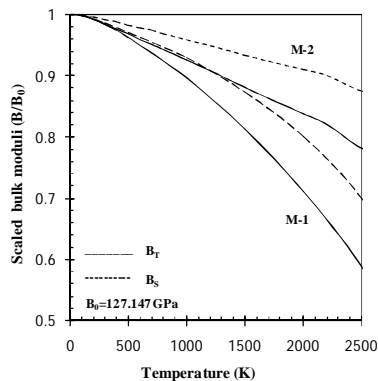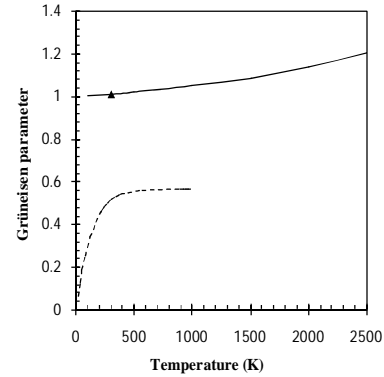

Fig.5. Bulk moduli (B_T and B_S) for M-1 and M-2 models.

Fig.6. Thermodynamic Grüneisen parameter: M-1 (continuous line) and QHA results (dashed line) in [13]. Symbol represents MD [5] datum.

characteristic temperature) lower than the Debye frequency (or temperature). Also shown in Fig.2 is the classical gas limit $-3k_BT$, which appears to be the oversimplified view to account for the true vibrational response of ions. Here, k_B is Boltzmann constant.

In figure 3, we have presented results for specific heats as a function of temperature. Though, both M-1 and M-2 models similarly underestimates C_P data as compared to most refined results of Jacob *et al*. [4], results for C_V show large deviation. C_V due to M-2 model attains the classical Dulong-Petit value ($3k_B$ per atom) at high-T, while those due to M-1 model decreases. Departure from it is the measure of anharmonicity, which is properly taken care by the M-1 approximation. As for the quantitative assessment of the anharmonic contribution to constant volume lattice heat due to ions C_V^{ion-an} is shown in Fig.4. It is clearly advocating the non-linear increase in anharmonicity with temperature.

As a further test of the M-1 model, we depict isothermal and adiabatic bulk moduli (B_T and B_S) in figure 5 along with the results due to QH M-2 model. For comparison, we scaled moduli as $\frac{B}{B_0}$; B_0 is the modulus at

ambient condition, (T, P) = (0, 0). Again one can infer from the figure that model M-1 accounts for anharmonicity in a better way as compared to QH approach. It is known that with temperature bulk moduli always decreases due to thermal expansion. Larger thermal expansion in M-1 calculations results in to larger decrease in bulk moduli.

Finally, we have compared thermodynamic Grüneisen parameter, which is the measure of anharmonism, in Fig. 5. Ours (M-1 result) as well as that in Ref. [5] coincides at ambient condition, while those due to QHA findings of Xu *et al*. [13] remain lower throughout the temperature range that is studied. According to Mie-Grüneisen hypothesis, Grüneisen parameter does not depend on temperature and in QHA theory it depends implicitly on temperature via volume. However, we found that it depends on temperature and increases from approximately 1.0 to 1.2 to T = 2500 K.

IV. Conclusion

In the present study, we have demonstrated the simple analytic, yet reliable, scheme (the M-1 model) to estimate anharmonicity in ZB-GaN. We have also shown the limitation of QH approach, particularly at $T > \theta_D$ in such materials. Accurate account of thermal expansion by M-1 model can be exploited for the selection of the appropriate substrate material for efficient performance of the device at higher thermal environment. Thus, we conclude that the improved MFP model M-1, which is unbiased to specific class of materials, can be generalised to any of the wide-bandgap semiconductor to achieve better thermal stability [14] in device applications.

Acknowledgement

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