Pseudopotential study of wide band-gap GaN at high pressures

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Abstract.   A pseudopotential approach is used to study the lattice and elastic properties of the wide band-gap GaN at zero and high pressures up to 120 kbar. When the pressure is 0 kbar, our findings are generally in agreement with the data reported in the literature. The pressure dependence of lattice constant, polarity, transverse effective charge, elastic constants and their related mechanical parameters, and microhardness has been examined and discussed. Our results show that all these features exhibit a monotonic behaviour against pressure. Upon compression up to 120 kbar, our results suggest that the material in question remains mechanically stable with higher stiffness, becomes more resistant to the deformations or deflections and its chemical bond and rigidity become stronger.

Keywords.   Gallium nitride; lattice properties; elastic properties; wide band gap; high pressure.

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1. Introduction

Nitride semiconducting materials belonging to group III are attracting a lot of interest owing to their utility in technological applications in high temperature and in violet, blue and green regions of the electromagnetic spectrum [1–12]. Among the nitrides, gallium nitride (GaN) is a semiconducting material with a large direct band gap. The material is very hard and commonly used in light-emitting diodes. It is characterised by large electron mobility, high thermal conductivity and low compressibility. These characteristics make GaN a useful candidate for applications in optoelectronics at extreme conditions [13–18]. In its bulk form, GaN is thermodynamically stable in the wurtzite structure [19]. Nevertheless, investigators have reported that the material of interest can also be grown in cubic form [2,13,20–22]. This depends on the growth conditions and the symmetry of the substrate. As a matter of fact, the metastable cubic phase has been of great interest for device applications such as easy cleavage (for laser facets), easy doping and high carrier mobility [22].

The behaviour of semiconducting materials under high pressure has increasingly become the field of current research [23–28]. High pressure influences the fundamental properties of materials leading thus to novel phases and new properties of crystals. Application of pressure gives opportunity for investigating the pressure dependence of the properties of semiconducting materials as distances between atoms are varied in a systematic way. Advancements in the diamond anvil techniques have provided the possibility to realise a wide range of experiments under high compression [25,26,29]. In addition, new developments in algorithms and quick increases in computer power have made it possible to study physics of high pressure [30–33]. These theoretical computations give useful complementary data to experiments.

The current contribution is concerned with the study of lattice and elastic properties of GaN. The structure is considered to be zinc-blende. The investigation is taken at various hydrostatic compressions. The computations are carried out within a pseudopotential approach. The objective of this contribution is to see how the studied

Table 1. Band-gap energies for zinc-blende GaN fixed in the fits at zero pressure.

$E_{\Gamma-\Gamma}$ (eV)	$E_{\Gamma-X}$ (eV)	$E_{\Gamma-L}$ (eV)
3.3[a]	4.57[b]	6.04[b]

[a]Exp. ref. [41]; [b]theor. ref. [42]

properties of GaN behave upon compression, by getting microscopic information from the examination of the band structure and related lattice and elastic parameters in the material in question at various elevated pressures. The results are tested and compared with previous results published in the literature. Generally, a good agreement is obtained between our findings and experiment.

2. Computational approach

The empirical pseudopotential method (EPM) [34–36] is mainly used in this work. The EPM is coupled with the Harrison model [37] to study the lattice and elastic properties of the semiconductor of interest. In the EPM, one has to adjust a small number of parameters, called pseudopotential form factors (PPFFs) to reproduce experimental energy band gaps at some selected high-symmetry points in the Brillouin zone. The nonlinear least-squares method as described in more detail in refs [38–40] has been used so as to optimise these parameters. Table 1 depicts the experimental and known band gaps for zinc-blende GaN used in the fitting procedure. These band gaps are taken at zero pressure. We consider 136 plane waves to achieve convergence.

Upon hydrostatic compression, PPFFs are determined for each considered pressure. We fit the first-order pressure coefficients of band-gap energies at Γ, X and L points in the Brillouin zone to those reported in refs [18,43] assuming a linear change of the band-gap energies vs. pressure. The lattice parameter for various pressures being considered here is obtained from the

Murnaghan equation of state, where the equilibrium bulk modulus (B_0) is taken to be 19.6×10^{11} dyn/cm^2 [43], whereas the first pressure derivative of $B_0(B_0')$ is taken to be 3.9 [43]. The final adjusted PPFFs of GaN at different pressures ranging from 0 to 120 kbar are listed in table 2.

3. Results and discussion

Figure 1 shows the crystal structure of the zinc-blende GaN semiconductor compound. The plot of lattice constant vs. pressure for zinc-blende GaN is illustrated in figure 2. We observe that when pressure is enhanced from 0 to 120 kbar, the lattice constant of the semiconductor under study decreases from 8.54 to 7.70 atomic units. The behaviour of the lattice constant vs. pressure in GaN appears to be monotonic and non-linear. The reduction of the lattice constant under hydrostatic compression is a consequence of the reduction of the bond length. In fact, when pressure is applied, more cloud
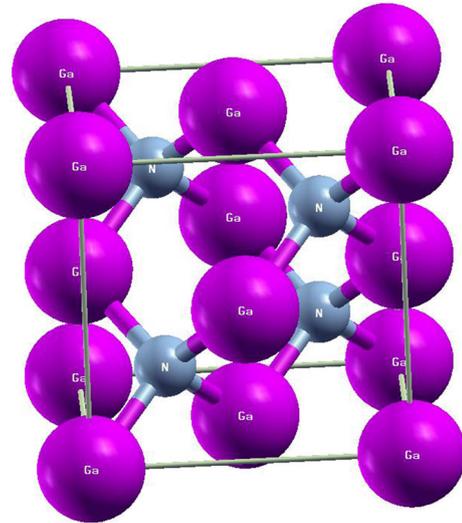
Figure 1. Crystal structure of the zinc-blende GaN semiconductor compound.

Table 2. Final adjusted pseudopotential form factors for zinc-blende GaN at various pressures up to 120 kbar.

Pressure (kbar)	$V_S(3)$	$V_S(8)$	$V_S(11)$	$V_A(3)$	$V_A(4)$	$V_A(11)$
0	−0.344053	−0.016	0.211642	0.159371	0.200	0.135
20	−0.371960	−0.016	0.216544	0.152122	0.200	0.135
40	−0.398173	−0.016	0.220940	0.140637	0.200	0.135
60	−0.425292	−0.016	0.225289	0.123768	0.200	0.135
80	−0.458416	−0.016	0.230167	0.095811	0.200	0.135
100	−0.489492	−0.021979	0.240655	0.063773	0.200	0.135
120	−0.497333	−0.033285	0.254084	0.058316	0.200	0.135
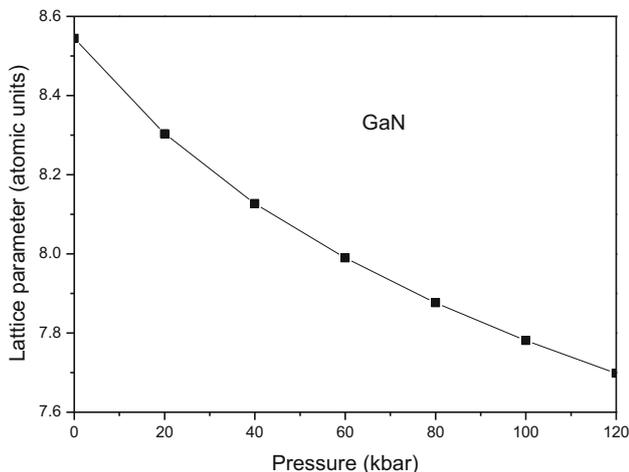
Figure 2. Lattice parameter vs. pressure in zinc-blende GaN.
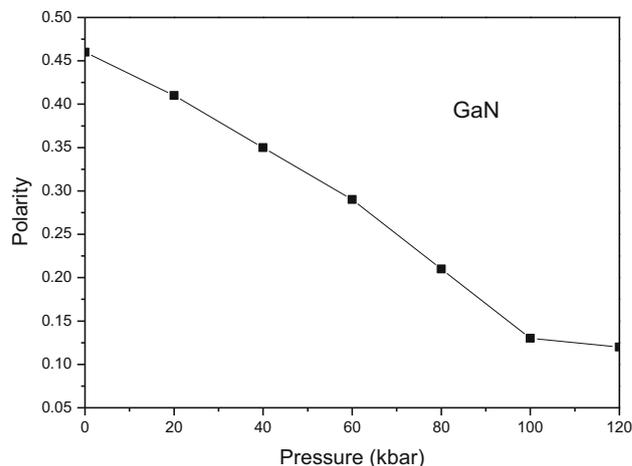
Figure 3. Polarity vs. pressure in zinc-blende GaN.

Figure 4. Transverse effective charge vs. pressure in zinc-blende GaN.

overlap of electrons appears, leading to an augmentation of the charges migrating from Ga to N.

The polarity α_p is an interesting concept that is related to the crystal ionicity. It is given by Vogl [44] as
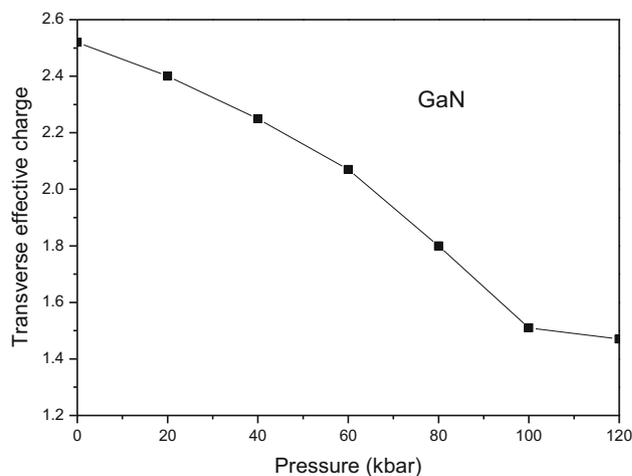
$$\alpha_p = -\frac{V_A(3)}{V_S(3)}. \tag{1}$$

Following the Vogl definition, α_p is determined for GaN at different pressures ranging from 0 to 120 kbar. Our obtained result when pressure is zero is found to be 0.46. Figure 3 shows the plot of α_p vs. applied pressure. We observe that when pressure is enhanced from 0 to 120 kbar, α_p decreases monotonically and non-linearly. Thus, one expects a reduction of the ionicity of the crystal by increasing pressure. This effect comes partially from the hybridisation that accompanies the change in bonding from ionic to covalent. The trend is consistent with the result generally reported for the ionicity in compound semiconductors subjected to pressure [45].

The Born transverse effective charge (e_T^*) is an important physical quantity which characterises the dielectric properties of materials. This quantity measures the variation in the electronic polarisation. In this work, e_T^* is calculated using the relation [46]

$$e_T^* = \frac{\Delta z}{2} + \frac{4\alpha_p}{1 + \alpha_p^2}, \tag{2}$$

where α_p is the polarity as defined by eq. (1) and $\Delta z = -z_{Ga} + z_N$, z are the valences. When pressure is 0 kbar, our findings yielded a value of 2.52 for zinc-blende GaN. Owing to the absence of both experimental and previous theoretical results for α_p and e_T^* of GaN, to the authors knowledge, our findings are for reference. The plot of e_T^* vs. pressure for zinc-blende GaN

is illustrated in figure 4. We observe that by enhancing pressure from 0 to 120 kbar, e_T^* decreases. The behaviour of e_T^* with respect to pressure is monotonic and non-linear. Qualitatively, the trend seems to be similar to that of α_p vs. pressure (figure 3). This is not surprising as e_T^* in eq. (2) depends on α_p. The decrease of e_T^* with increasing pressure can be attributed to the reduction of the inter-atomic distances upon compression which causes stiffening in the short-range forces leading to the decrease of the charge transfer for GaN under pressure.

The elastic constants (C_{ij}s) represent basic parameters in the investigation of mechanical properties of semiconducting materials [47–50]. In crystals with cubic structure, we deal only with three independent C_{ij}s which are C_{11}, C_{12} and C_{44}. In the present work, C_{11} and C_{12} have been calculated for GaN using the same methodology as reported by Bouarissa [51], whereas C_{44} is determined from the valence force field

Table 3. Elastic constants (C_{ij}), bulk modulus (B_S), shear modulus (C'), Young's modulus (Y_0) and microhardness (H) (in 10^{11} dyn/cm^2) for zinc-blende GaN at zero pressure.

C_{11}	C_{12}	C_{44}	B_S	C'	Y_0	H
31.16[a]	13.67[a]	12.51[a]	19.50[a]	8.75[a]	22.83[a]	1.53[g]
29.1[b]	14.8[b]	15.8[b]	19.60[b]	7.15[b]		2.55[h]
29.3[c]	15.9[c]	15.5[c]	18.8[f]			
29.6[d,e]	15.4[d,e]	20.6[d,e]	20.1[d,e]			

[a]This work; [b]calculated or estimated, quoted in ref. [43]; [c]theor. ref. [52]; [d]theor. ref. [47]; [e]theor. ref. [53]; [f]exp. ref. [53]; [g]this work using model 1; [h]this work using model 2.
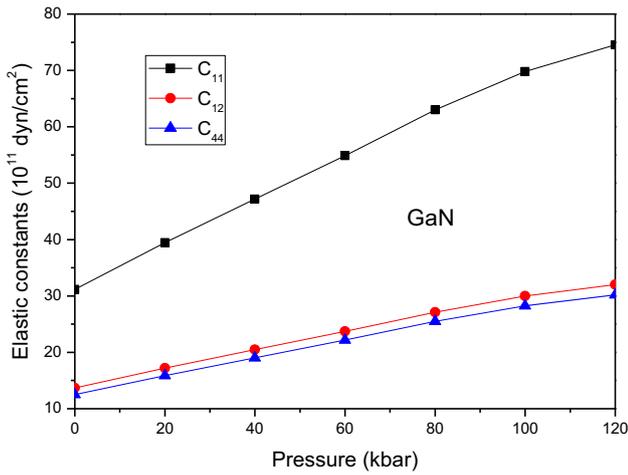
Figure 5. Elastic constants vs. pressure in zinc-blende GaN.

model [37]. The C_{ij}s obtained in the present work for GaN at 0 kbar are presented in table 3. For comparison, data available in the literature are also listed. Whereas C_{11} and C_{12} for zinc-blende GaN are within 7% and 14% off the values quoted in refs [43,47,52,53] respectively, the discrepancies for C_{44} appear to be larger, especially with those of refs [47,53]. The pressure dependence of C_{ij}s for GaN is shown in figure 5. We observe that C_{ij}s of interest exhibit a similar monotonous pressure dependence. Nevertheless, the magnitudes of C_{ij}s are different from each other. By enhancing pressure from 0 to 120 kbar, all C_{ij}s considered here increase. However, the rate of change of C_{11} vs. pressure seems to be larger than those of C_{12} and C_{44}.

For cubic crystals which are subjected to pressure effect, the generalised criteria regarding the elastic stability are expressed as [54–56],

$$M_1 = \frac{C_{11} + 2C_{12} + P}{3} > 0 \qquad (3)$$

$$M_2 = C_{44} - P > 0 \qquad (4)$$

$$M_3 = \frac{C_{11} - C_{12}}{2} - P > 0. \qquad (5)$$

M_1, M_2 and M_3 in eqs (3)–(5) are spinodal, shear and Born criteria, respectively. Using the values of C_{ij} calculated in the present work along with their corresponding pressure, the stability of GaN is verified via eqs (3)–(5). Our results show that all the criteria concerning the mechanical stability in the studied pressure range are fulfilled. This suggests that the zinc-blende GaN is mechanically stable for pressures ranging from 0 to 120 kbar. According to the plot of our C_{ij}s vs. pressure, one expects that the mechanical stability will be maintained beyond 120 kbar (i.e. all the mechanical stability criteria will be verified).

One of the interesting mechanical properties is the bulk modulus (B_S) that is related to the elastic constants C_{11} and C_{12} for cubic crystals by the expression [57],

$$B_S = \frac{C_{11} + 2C_{12}}{3}. \qquad (6)$$

Using eq. (6) along with our calculated C_{11} and C_{12} at different pressures in the range of 0–120 kbar, B_S has been obtained at different pressures. Our obtained value at zero pressure is presented in table 3. For comparison, quoted data in the literature are also presented. The deviation of our B_S calculated value from that of the experiment [53] is less than 4%. On the other hand, the agreement between our calculated B_S and the ones reported in refs [43] and [47,53] is within 1% and 3%, respectively. B_S vs. pressure for zinc-blende GaN is plotted in figure 6. From figure 6, we see that B_S augments monotonously showing a non-linear behaviour when the pressure is increased from 0 to 120 kbar. The behaviour of B_S vs. pressure suggests that the stiffness of zinc-blende GaN becomes higher under applied pressure.
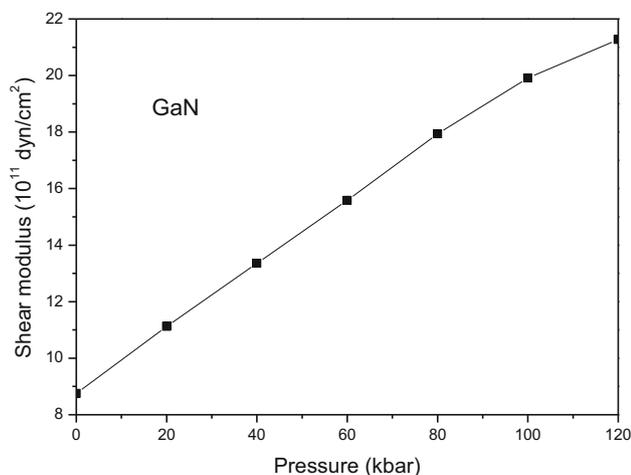
Another interesting mechanical parameter that can be obtained from the elastic constants is the shear modulus (C'). C' describes the response of the material to the shear stress and can be written as [57]

$$C' = \frac{C_{11} - C_{12}}{2}. \qquad (7)$$

Based on our computed C_{11} and C_{12} and using eq. (7), C' has been determined at different pressures in the
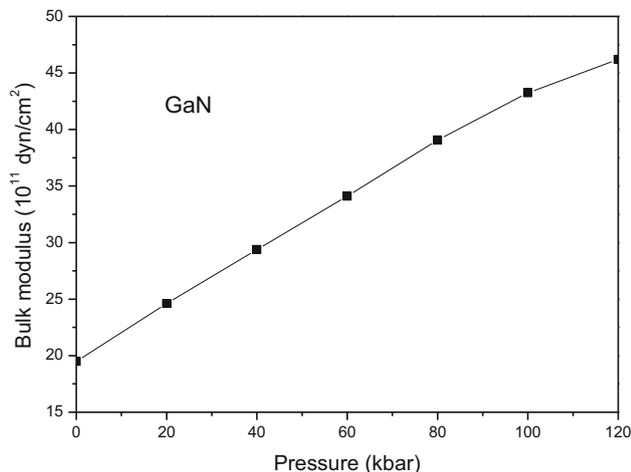
Figure 6. Bulk modulus vs. pressure in zinc-blende GaN.

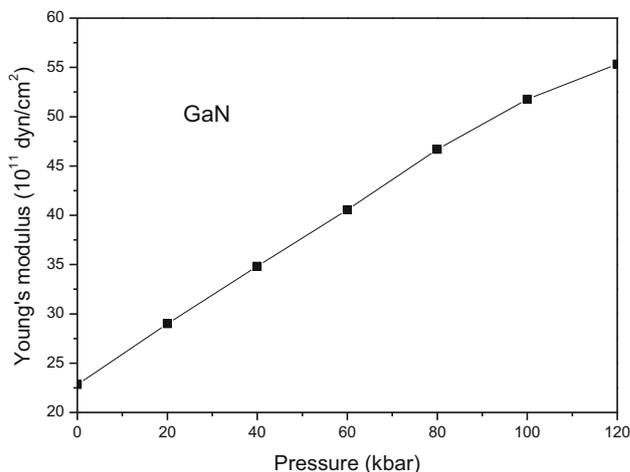**Figure 8.** [100] Young's modulus vs. pressure in zinc-blende GaN.

Figure 7. Shear modulus vs. pressure in zinc-blende GaN.

0–120 kbar interval. At 0 kbar, our determined value of C' for zinc-blende GaN is given in table 3 and compared to the value quoted by Adachi [43]. The agreement between our calculated C' and that of ref. [43] is within 22%. C' as a function of pressure is depicted in figure 7. We remark that C' increases monotonously when the pressure is increased from 0 to 120 kbar. The behaviour of C' vs. pressure for zinc-blende GaN seems to be quasilinear. The increase of C' with increasing pressure suggests that when pressure is applied, zinc-blende GaN exhibits more resistance to the transverse deformations.

Another interesting mechanical parameter to be studied is the Young's modulus (Y_0). This parameter describes the material strain response to the uniaxial stress along the direction of the stress. The [100] Y_0 is defined as [57]

$$Y_0 = \frac{(C_{11} + 2C_{12})(C_{11} - C_{12})}{(C_{11} + C_{12})}. \tag{8}$$

Using C_{11} and C_{12} obtained in this work at various pressures of interest along with eq. (8), [100] Y_0 has been determined for GaN. When the pressure is 0 kbar, the obtained value is shown in table 3. Owing to the absence of data concerning Y_0 in the literature for GaN, our value is only for reference. The variation in Y_0 vs. pressure for GaN is shown in figure 8. We remark that by enhancing pressure from 0 to 120 kbar, Y_0 increases from 22.83×10^{11} to 55.33×10^{11} dyn/cm^2. Y_0 varies monotonously and almost linearly with respect to pressure. This behaviour suggests that when pressure is applied, the situation for the semiconductor under investigation becomes different from that at zero pressure in that it resists much more to deflections or deformations.

The microhardness (H) is an important parameter which characterises semiconducting materials. The interest in this useful parameter is mainly due to their use in numerous device applications [43,58,59]. The parameter H can be determined using various models. In this work, two models have been used to obtain H:

(1) The Knoop microhardness model [43], where H is expressed as
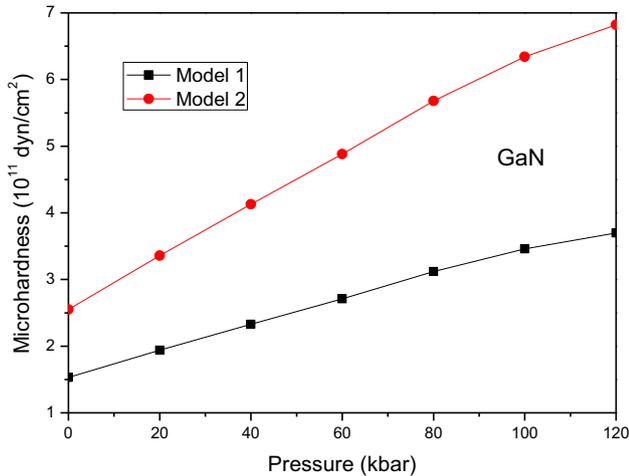
$$H = 0.139G_V, \tag{9}$$

where G_V is the Voigt-averaged shear modulus that depends on C_{11}, C_{12} and C_{44} and is given by [43]

$$G_V = \frac{3C_{44} + C_{11} - C_{12}}{5}. \tag{10}$$

(2) The model where H depends on the bulk modulus of the solid material as reported by Adachi [43] which is valid for III–V semiconductors,

$$H = 0.16B_S - 5.74. \tag{11}$$

H in eq. (11) is expressed in GPa. At zero pressure, our results concerning H for GaN using the two

Figure 9. Microhardness vs. pressure in zinc-blende GaN.

above-mentioned models are tabulated in table 3. Owing to the absence of data concerning H in the literature, our computed values are only for reference. Although the two models give different values for H, both of them give a high value compared, for example, to that of zinc-blende CdTe ($H = 0.31 \times 10^{11}$dyn/cm^2) [60]. However, it has been reported by Léger *et al* [61] that model 1 is a better indicator of H than model 2. The change of H vs. pressure for GaN is illustrated in figure 9. We remark that our findings show an augmentation of H with increasing pressure from 0 to 120 kbar. The augmentation varies monotonously and almost linearly. The increase of H with pressure suggests that the chemical bond strength and the bonding network rigidity of the material in question become stronger under applied pressure. The tendency to the metallic nature of the material under load at high pressures is reflected in the augmentation of shear modulus, Young's modulus and microhardness with raising pressure.

4. Conclusions

Based on a pseudopotential approach coupled with the Harrison model, the lattice and elastic properties of GaN were investigated. When the pressure is 0 kbar, our findings showed generally a reasonable agreement with those reported in the literature. The effect of the hydrostatic pressure on the studied properties was analysed and reported. All properties investigated here showed a monotonous behaviour under pressure. The generalised mechanical stability criteria were fulfilled over all the pressure ranges from 0 to 120 kbar indicating that the semiconductor under study remains mechanically stable under pressure of interest. The plot of the bulk modulus vs. pressure showed that the stiffness of GaN becomes high upon compression. The variation of the shear and Young's moduli with pressure indicated that the semiconductor in question becomes more resistant to the deformations or deflections. The microhardness of GaN was calculated using two different models. Both models showed that the microhardness augments with raising pressure up to 120 kbar suggesting thus that the chemical bond and rigidity of zinc-blende GaN become stronger under hydrostatic pressure.

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