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Band Structure and Bulk Modulus of GaN

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Due to its wide and direct band gap, gallium nitride, GaN, is a promising candidate in semiconductor technology. Now the zincblend modification of GaN is also receiving much attention in electronic and optoelectronic applications. We have done band structure calculations of the zincblend and wurzite modifications of this wide band gap semiconducting material by using the density functional and total-energy technique in the local density approximation which is the most powerful ab-initio quantum-mechanical method. The important energy gaps have been determined and compared with the previous theoretical and experimental results. The bulk modulus, density of state, charge density and other important parameters have also been calculated.

1. Introduction

Gallium nitride, GaN, is a member of the diamond-like group of III-V semiconductor compounds which have been investigated intensively in leading research laboratories throughout the world and have found extensive applications. Due to its wide and direct band gap, gallium nitride is a promising candidate in semiconductor technology.

There has been wide interest in hexagonal gallium nitride with potential applications in blue and ultraviolet (UV) light emitting diodes and detectors[1-2]. Due to its notable thermal and chemical stability, it is also ideally suitable for the applications in harsh environments, such as at high temperature. Large piezoelectric constants of GaN [3-4] point out possible applications of GaN-based materials in piezoelectric sensors. Due to wide band gap, these sensors are expected to operate in a broad temperature range and/or in a harsh environment. A. D. Bykhovski et. al.[5] have reported on the measurements of the piezoresistive effect in n-type wurzite GaN films which confirm these expectations.

Now the zincblend phase of GaN is also receiving much attention in electronic and optoelectronic applications. Recently, several reports have presented the applications of the cubic phase of GaN. X. Du et.al.[6] have reported the presence of cubic phase in the wurzite structured GaN thin films which improves the quality of GaN films. J. Kolnik et.al.[7] have presented the first calculations of the electron and hole initiated interband impact ionization rate in zincblend phase of GaN as a function of the applied electric field strength.

In spite of impressive technological achievements of the several years, there are still some problems concerning basic physical properties of this compound which have to be solved. Often, the properties quoted in the literature are based on early measurements on materials of poor quality. Moreover, compared to the situation at the time of pioneering studies, theoretical capabilities including computational programming has improved greatly. Therefore, it is important to restudy the fundamental properties of both polytypes of this important semiconductor.

We have done the band structure calculations of the zincblend and wurzite polytypes of this wide band gap semiconducting material by using the CASTEP code which is a First-Principle technique along with several approximations. According to our knowledge, it is the first report in which these approximations have been used to calculate the electronic structure, the bulk modulus, density of state, charge density and other important parameters of zincblend and wurzite polytypes of GaN.

2. Computational Method

For our calculations, we have used CASTEP code which is a part of CERIUS package. It implements the density functional and total-energy pseudopotential technique which is a quantum-mechanical ab-initio method. It has ability to simulate the electronic relaxation of the 'equilibrium' state for metals, insulators or semiconductors. Forces acting on the atoms and the stress on the unit cell can also be calculated.

The atomic forces can be used to find equilibrium structure or doing dynamic molecular simulations (with canonical or microcanonical assembly). The base of the castep theory is the density functional theory (DFT) in the local density approximation (LDA) or the corrected gradient version of LDA which has developed by Pedrew and Wang (GGA). The calculations were done at GGA level.

First of all, the crystalline structures of the cubic and hexagonal polytypes were simulated, after optimization the cell dimensions were a=b=3.26Å, c=5.18Å for 2H-GaN while a=b=c=3.20Å for 3C-GaN.

3. Results and Discussion

Fig. 1a shows the band structure of wurzite-GaN and important energy gaps have been calculated which are compared with the work of S. Bloom[8], D. Jones et.al.[12], and the previous experimental results[8]. Table 1 summarises the results for several important transitions of wurzite polytype of GaN.

From our band structure calculations it is found that Γ_{6v} is slightly higher than Γ_{1v} which is in agreement with the work of S. Bloom et.al. while the experimental field

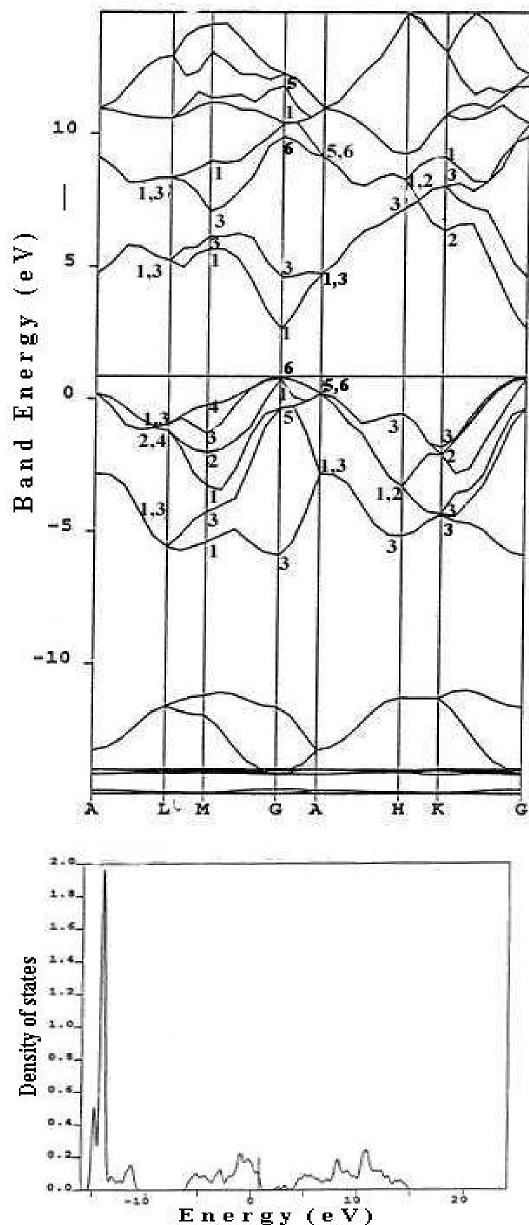


Fig. 1. Shows (a) The band structure and (b) The density of states for 2H-GaN.

splitting (+0.022) is also in agreement with the work of R. Dingle[10].

The smallest band gap is direct and occurs at the centre of the Brillouin zone i.e. the valence band maximum and the conduction band minimum are at Γ. The value of the fundamental band gap is $E_0 = \Gamma_{6v}$-Γ_{1c} (⊥) = 1.95 eV and = Γ_{1v}-Γ_{1c} (||) = 1.97 eV. This means that the fundamental gap calculated by our calculations is smaller (~40%) than the experimental and theoretical gap reported previously. The value of the fundamental gap is also smaller than the reflectance values of 3.47 eV (⊥), 3.49 eV (||) at room temperature[18] and 3.48 eV (⊥), 3.50 eV (||) at 2°K[10]. Where ⊥ and || indicate that significant absorption can occur for light polarized perpendicular and parallel to the c-axis respectively. Absorption measurements have given a range of values: 3.4 eV[19], 3.5 eV[20] and 3.8 eV[21], for the optical band gap. The higher transitions like $E_{1A}=\Gamma_5$-Γ_3=4.24 eV, K_{3C}-K_{2C}=7.9 eV etc. are in good agreement with the work of S. Bloom et.al. as shown in Table 1. According to the calculated density of state, DOS, for 2H-GaN, the valence band width is 7.6 eV with maxima at –1.0 and -3.0 eV as shown in the figure 1b. The conduction band maxima appeares at 5.5, 8.0 and 10.8 eV. Another strong peak appeares at –14.0 eV in our calculations. It is due to the reason that CASTEP assumes that in the case of the valence Ga atom, some shallow core states were treated as valence states during pseudopotential generation.

Figure 2a shows the band structure of the zincblend polytype of GaN according to which it is also a direct band gap semiconductor. The fundamental gap again appears at centre of the Brillouin zone i.e. at Γ which is purely p-like in zincblend structure. The fundamental gap Γ_{15}-Γ_1 = 1.8 eV is again smaller than the reported value of S. Bloom et. al.[8,9]. While the higher transitions like Γ_{15}-Γ_{15} = 10.24 eV, X_{5C}-X_{3C}=9.3 eV etc. are higher than the reported values but X_{5V}-X_{1C} = 6.1 eV is in agreement with S.Bloom et. al. as shown table 2. Figure 2b shows the DOS calculations for 3C-GaN according to which the valence band width is 7.8 eV with maxima at 0.0 and –4.7 eV.

Figure 3 shows the theoretical total charge density in the (100) plane for the wurzite and (111) plane for the zincblend polytype of GaN containing all the Ga and N atoms in the primitive cell. The bonding has a significant ionic nature because of the large difference between the Ga and N valence levels. compact orbitals. The 2s and 2p have about equal spatial extent as opposed to latter rows where the p-like valence orbitals tend to be more diffuse than the s-like orbitals.

Since N do not have p-like core-states below the 2p valence level, it has rather deep valence levels [23]. This is the reason that these elements have small lattice constants, high cohesive energies, and large elastic constants.

Table 1

Important energy gaps for Wurzite-GaN

Transition (eV)	Present calculations	S. Bloom et. al. [8]	D. Jones et. al. [12]	Experiment
Γ_{6V}- Γ_{1c}(⊥)	1.95	3.6	3.5	3.6
Γ_{1V}- Γ_{1c}(||)	1.97	3.62	3.68	
Γ_5-Γ_6	9.11	9.4		9.3-9.4
Γ_5-Γ_3	4.24	5.2	7.48	5.3
Γ_6-Γ_1	9.37	8.2-8.6		8.3-8.7
M_{2C} -M_{1C}	7.72	7.2	7.49	7.0-7.1
M_4-M_3	6.49	7.1	8.6	7.0-7.1
K_{3C} -K_{2C}	7.88	8.5		7.6-7.7

Table 2

Important energy gaps for Zincblend-GaN

Transition (ev)	Present calculations	S. Bloom et al. [8]
Γ_{15V}-Γ_{1C}	1.80	3.5
Γ_{15V}-Γ_{15C}	10.29	8.7
X_{5V}-X_{1C}	6.07	7.8
X_{5C}-X_{3C}	9.27	7.8

From the comparison of the data of the polarities of some of the compounds of interest as is given in the reference[24], it is observed that ionicity is higher for GaN which favours the wurzite structure while lower ionicity of SiC and BN favours the zincblend structure. Moreover, it has observed that the total energy calculated in the wurzite case is much lower than that of the zincblend-GaN case which is also a reason that the wurzite polytype of GaN is more stable that the zincblend structure.

4. Calculation of Bulk Moduli of GaN

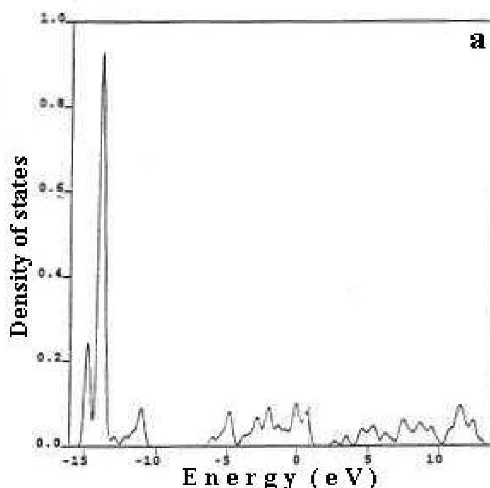
For the calculation of bulk moduli of zincblend and wurzite polytypes of GaN, total-energy calculations have done under hydrostatic pressure to obtain energy against volume curves for both polytypes of GaN separately. The lattice parameters, cell volume v_0, total energy and enthalpy have been calculated at pressures: 5.0, 2.0, 0 and –5.0 GPa. A linear fit was performed to the generated values of $\left[1-\frac{\Delta V}{V}\right]^{-2}$ Vs pressure, by using the Murnaghan's equation of state[25].

From this fit, the values of the lattice parameters of the equilibrium structure, the minimum energy, and the bulk modulus are obtained. These results are presented in table 3. The bulk modulus of 3C-GaN is 182.48 GPa while that of 2H-GaN is 175.6 GPa which is lower than the reported value of GaN which is 210 GPa.

The bulk modulus can also be calculated by evaluating the average distance value between nearest neighbours which is a semiempirical method used by Cohen et.al[26]:

$$B=\frac{19.71-220\lambda}{d^{3.5}}$$

where d(Å) is the bond length and λ is the ionicity parameter which is 1 for group-III nitrides. According to this equation, B=176.5 GPa for 3C-GaN and 172.5 GPa for 2H-GaN.



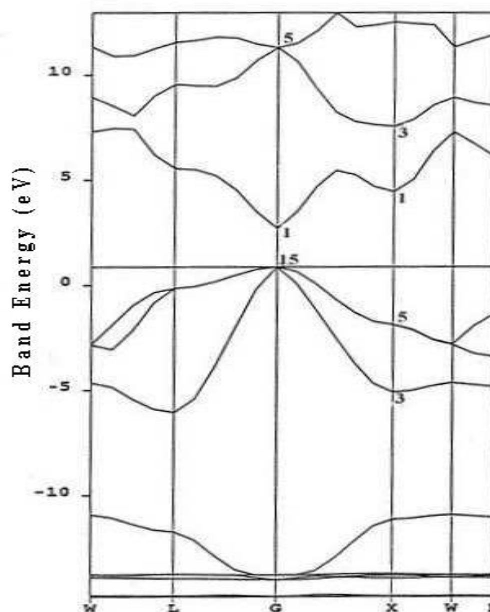


Fig. 2. Shows (a) The density of states and (b) The band structure for 3C-GaN.

Table 3.

	2H-GaN	3C-GaN
Lattice Parameters (Å) (After optimization)	a = 3.208 c = 5.216	a = 3.
Cell Volume (Å^3)	46.48	23.06
Minimum Energy (eV)	-2334.98	-2334.9
Bulk Moduli, B, by fitting Murnaghan´s equation of state	175.59	182.49
Interatomic distance d (Å)	1.973	1.96
Bulk Moduli, B, calculated by $B=\frac{19.71-220\lambda}{d^{3.5}}$	172.50	176.50

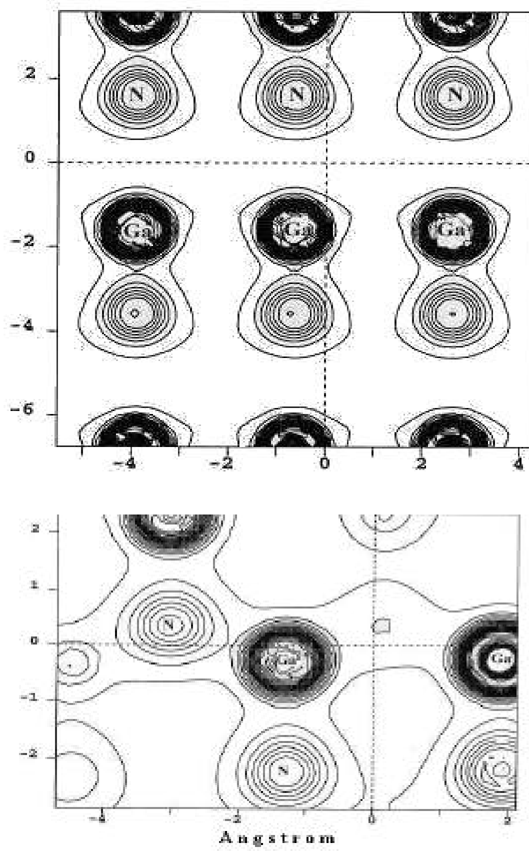


Fig. 3. Total charge density (a) in (100) Plane for the wurzite and (b) in (111) plane for zincblend polytypes of GaN.

5. Conclusion

We have done the band structure calculations of wurzite and zincblend polytypes of GaN by using the density functional and total-energy in the local density approximation. Density of state and charge density have also been calculated by the same method.

The results have compared with the previous theoretical calculations of S. Bloom et.al. who used the pseudopotential method, D. Jones et.al. who used a non-local model potential developed for nitrogen and the experimental values measured by the experiments of absorption and reflectance.

Another important parameter bulk moduli, B, which measures hardness, has been calculated for both polytypes of GaN by fitting the Murnaghan's equation of state and also by using the nearest neighbour distance 'd'. Both results have been compared with the reported experimental value of the bulk moduli.

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