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Band structures and pressure dependence of the band gaps of GaN

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Abstract. The linear muffin-tin orbital method is used with the atomic-sphere approximation to study the ground-state properties, band structures and pressure dependence of the band gaps of zincblende GaN. The equilibrium lattice constant calculated is smaller than the experimental value by about 2%. It is found that the fundamental band gap is direct from Γ_{15v} to Γ_{1c} and that the value (3.90 eV) is in good agreement with the experimental value. The linear pressure coefficient for this band gap is much smaller than those for GaAs and GaP. The total density of states and local density of states are discussed. Moreover, the band structure of wurtzite GaN is also studied. It is found that the band gap of wurtzite GaN is smaller than that of zincblende GaN, which agrees well with the experimental results.

1. Introduction

Gallium nitride (GaN) has attracted much attention because of the following two important properties. First, it possesses a wide energy gap in the ultraviolet region of the spectrum which makes it useful for fabricating near-ultraviolet optoelectronic devices, such as blue-light-emitting diodes [1]. Second, it is predicted to have a large saturated electron drift velocity [2], which results in a short transit time and thus allows the fabrication of high-frequency devices.

Usually, most of the GaN films grown have a wurtzite structure (α -GaN) [3-5] and n-type conductivity with a high carrier concentration; p-type doping has met with little success. Recently, zincblende GaN (β -GaN) has been reported to be grown on various substrates. Paisley *et al* [6] have reported the growth of zincblende GaN films on a closely lattice-matched β -SiC(100) surface, using a modified molecular beam epitaxy (MBE) technique. The lattice constants of the films are about 4.54 Å. Lei *et al* [7] have reported the epitaxial growth of zincblende and wurtzite GaN thin films on a large-lattice-mismatched silicon(100) surface by electron cyclotron resonance microwave plasma-assisted MBE and found that the lattice constant for β -GaN to be 4.49 Å. Okumura *et al* [8] have grown GaN films on GaAs substrates and found that the films have the zincblende structure on the GaAs(100) surface and have the wurtzite structure on the GaAs(111) surface. They have also found that the band-gap energy of β -GaN is around 0.37 eV larger than that of α -GaN whereas, for other compound semiconductors such as SiC, ZnS and ZnSe [8], the band gaps of the cubic phase (zincblende) are smaller than those of the hexagonal phase (wurtzite).

Although there have been some theoretical studies on the electronic properties of α -GaN [9-15], there have been very few theoretical studies on the electronic properties of β -GaN. In the present paper, we report the electronic band structures, pressure dependence of the band gaps and other ground-state properties of β -GaN. In addition, we also calculate the band structure of α -GaN and the results obtained agree with the earlier theoretical results.

2. Results and discussion

In the present calculation, the linear muffin-tin orbital (LMTO) method [16,17] is used within the framework of the atomic-sphere approximation (ASA), which has proved to be reasonable for the open structure [18,19] if empty spheres are introduced at interstitial sites. The exchange-correlation potential is approximated by the von Barth-Hedin [20] parametrization. The 3d orbitals of the Ga atom are considered as the valence orbitals, since their energy levels are very close to that of the 2s valence orbital of the N atom.

The calculated equilibrium lattice constant a_0 of β -GaN in the present work is 4.40 Å, which is smaller than the experimental lattice constant of 4.49 Å [6] by about 2%. The bulk modulus B_0 is 3.09 Mbar. To our knowledge, no experimental value nor other theoretical calculation of the bulk modulus has been reported. Using the same method, we have obtained the bulk modulus B_0 of β -SiC which is in very good agreement with experiments and other theoretical calculations [21]; therefore, the present value of the bulk modulus for β -GaN is reliable.

The calculated variation in V/V_0 for zincblende GaN is plotted in figure 1 for pressures up to 600 kbar. This pressure corresponds to a volume compression down to about $0.874V_0$ and the lattice constant is isotropically reduced by about 4% from its equilibrium value. The equation for V/V_0 is linear under 120 kbar pressure, and non-linearity occurs above this pressure.

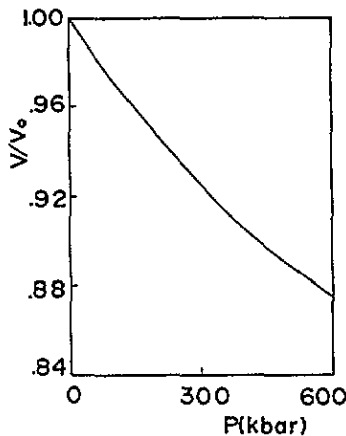


Figure 1. Plot demonstrating the equation of state for zincblende GaN.

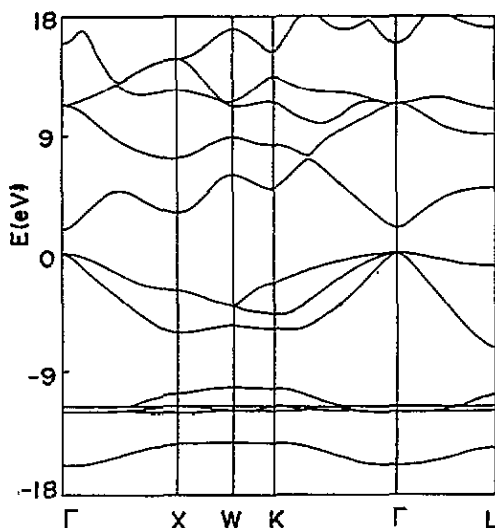


Figure 2. Electronic band structures of bulk β -GaN. The energy zero point is chosen to be at the valence band maximum.

The energy bands for β -GaN calculated with the LMTO method are given in figure 2. The zero-point energy is chosen to be at the valence band maximum. Some difference between the results shown here and the energy bands of other III-V semiconductors exists. Fully filled 3d states of the Ga atom are located between s-like and p-like bands for β -GaN, while for other III-V semiconductors these d states are located below the sp band. This is due to the interaction between Ga 3d and N 2s; the energy level of the 3d orbital of the Ga atom is very close to that of the 2s valence orbital of the N atom. This indicates that the Ga 3d orbitals must be included in the basis set as mentioned before. By comparing the band structure of β -GaN with that of an elemental semiconductor, it is found that the valence band splits into three parts. The first part (between 0 and -6.0 eV) and the third part (between -15.0 and -16.0 eV) are mainly contributed by Ga 3s and 3p and N 2s and 2p states. The second part near -12.0 eV consists of Ga 3d states mainly. The splitting value of the valence band at the special point X between the first and the second parts is about 5.0 eV and is larger than those for GaP and GaAs (about 3.0 eV). This splitting is a measure of the ionicity, which indicates that β -GaN has a higher ionicity than GaP and GaAs do. This might be a consequence of the difference between the core sizes of N and Ga.

The calculated energy bands for α -GaN are shown in figure 3. Similar to the energy bands of β -GaN, the N 2s and Ga 3d bands are localized and are not plotted in figure 3. The valence band given in the figure is contributed mainly by the N 2p and Ga 3s and 3p states. The present band structures for α -GaN agree qualitatively with other theoretical results [13-15].

It is found that the fundamental band gap of β -GaN is direct from Γ_{15v} to Γ_{1c} and that of α -GaN is also direct from Γ_{6v} to Γ_{1c} . Experiments show that β -GaN has a band gap larger than that of hexagonal GaN by about 0.37 eV [8]. The band gap of hexagonal GaN is about 3.50 eV [22], whereas the band gap of β -GaN is about 3.87 eV [8]. The values calculated for the band gaps are 2.29 eV and 2.04 eV for

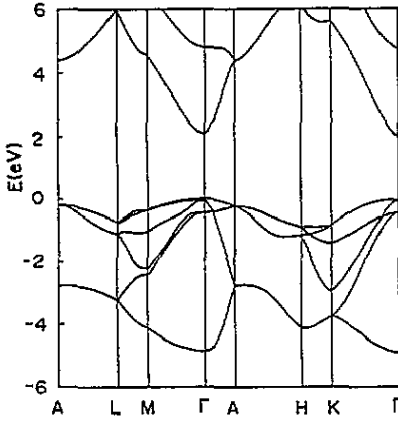


Figure 3. Electronic band structures of bulk α -GaN. The energy zero point is chosen to be at the valence band maximum.

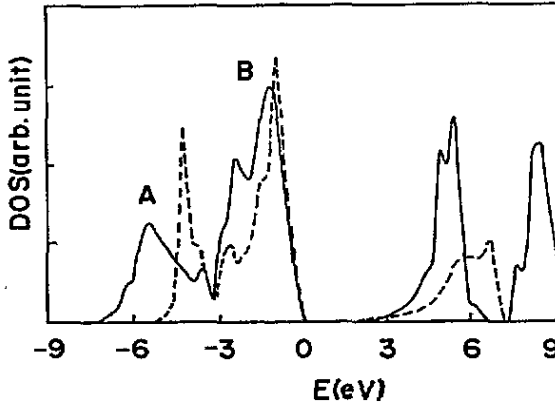


Figure 4. Total DOS for bulk β -GaN (—) and α -GaN (---).

β -GaN and α -GaN, respectively, which are narrower than the experimental values by about 41%. As is generally known, this underestimation is a result induced by the local-density approximation (LDA). In order to improve the calculated results, the following approximate self-energy correction to the band gaps will be introduced.

In general, a better calculation for taking into account the excitation energies is the GW approximation of Hedin [23] and Hedin and Lundquist [24]. However, it is not easy to calculate the self-energy. In order to overcome the difficulties, Bechstedt and Del Sole [25] have made a simplified tight-binding analysis of the GW approximation and obtained a simple analytic expression for the correction Δ to the LDA band gap:

$$\Delta = e^2 q_{\text{TF}} / \epsilon_0 (1 + 7.62x) \quad (1)$$

where ϵ_0 is the high-frequency dielectric constant taken from [22]. q_{TF} is the Thomas-Fermi wavenumber and

$$x = q_{\text{TF}} [(1 - \alpha_p)r_A + (1 + \alpha_p)r_B] / 2 \quad (2)$$

where α_p is the polarizability as defined by Harrison [26] and only affects the band-gap correction slightly. A variation of 0.1 in α_p gives a change of only 0.02 eV in the correction. A value of 0.6 can be appropriately chosen for α_p [26]. r_A and r_B are the cation and anion ionic radii, respectively [25]:

$$r_A = a/4\pi\beta_A \quad (3a)$$

$$r_B = a/4\pi\beta_B \quad (3b)$$

where a is a lattice constant, $\beta_A = 1.6$ and $\beta_B = 1.8$ for III-V group semiconductors.

When equation (1) is used to calculate the band-gap correction, the approximation $7.62x \gg 1$ is adopted, which is reasonable for most materials [25]. The result of band-gap correction is 1.61 eV. It follows that the values of the corrected fundamental band gaps are 3.90 eV and 3.65 eV for β -GaN and α -GaN, respectively. The band gap of β -GaN is larger than that of α -GaN. Although the above correction is empirical, the results obtained are in good agreement with experiments.

However, for other compound semiconductors the situation is different. Usually, the band gap of the cubic phase (zincblende) is smaller than that of the hexagonal phase (wurtzite). We have calculated the energy bands of silicon carbide. Within the LDA, the fundamental band gaps of β -SiC and α -SiC calculated are about 1.50 eV [21] and 2.20 eV, respectively. By using the above correction, the high-frequency dielectric constant ϵ_0 is also taken from [22] and the polarizability α_p from [26]; it is found that the band-gap correction calculated from equation (1) is about 0.97 eV. Then the corrected band gaps of β -SiC and α -SiC are 2.47 eV and 3.17 eV, respectively. The above results are in good agreement with the experimental values [22].

It has also been found that the fundamental band gaps of both β -SiC and α -SiC are indirect from Γ_{15v} to X_{1c} for the zincblende structure and from Γ_{6v} to M_{1c} for the wurtzite structure. The value of the band gap for β -SiC is less than that for α -SiC. The calculated direct gaps at the Γ point for β -SiC and α -SiC are 6.1 eV and 3.5 eV, respectively. The direct band gap at the Γ point of β -SiC is larger than that of α -SiC, which is similar to the fundamental band gaps of GaN. Moreover, it is found that the indirect band gap $\Gamma_{15v}-X_{1c}$ of β -GaN (4.79 eV) is smaller than the indirect band gap $\Gamma_{6v}-M_{1c}$ of α -GaN (6.22 eV) (see table 1). It can be seen that the direct band gaps at the Γ point of zincblende GaN and SiC are larger than the direct band gaps of their respective wurtzite phases, whereas the indirect band gaps $\Gamma_{15v}-X_{1c}$ of their zincblende phases are smaller than the indirect band gaps $\Gamma_{6v}-M_{1c}$ of their wurtzite phases. Since the fundamental band gaps of both β -GaN and α -GaN are direct at the Γ point, the fundamental band gap of β -GaN is larger than that of α -GaN.

Table 1. Direct and indirect band gaps of gallium nitride and silicon carbide.

	Band gap (eV)			
	$\Gamma_{15v}-\Gamma_{1c}$	$\Gamma_{6v}-\Gamma_{1c}$	$\Gamma_{15v}-X_{1c}$	$\Gamma_{6v}-M_{1c}$
α -GaN	—	3.65	—	6.22
β -GaN	3.90	—	4.79	—
α -SiC	—	3.50	—	3.17
β -SiC	6.10	—	2.47	—

The density of states (DOS) is calculated by means of the tetrahedron technique [27]. The total DOS of β -GaN and α -GaN in the energy region from -9 to 9 eV

is plotted in figure 4. There are two main peaks A and B at about 5.0 eV and 1.0 eV for β -GaN and at 4.0 eV and 1.0 eV for α -GaN below the valence band maximum. These two peaks are mainly contributed by N 2p and Ga 3s and 3p states. By comparing the total DOS of β -GaN with that of α -GaN, it is found that they are very similar. This is because the difference between the zincblende and wurtzite structures lies only in the stacking order, whereas the bond lengths and bond angles of these two structures remain almost the same. N 2s and Ga 3d states localized at 15 eV and 12 eV below the valence band maximum are not shown in figure 4. The total DOS of α -GaN is in good agreement with the empirical pseudopotential calculation [12].

The local DOS of Ga and N atoms and empty spheres E_1 and E_2 for β -GaN is given in figure 5. It can be seen that the DOS of empty spheres in the valence band is negligible. The DOS of the N atom in the valence band is much larger than that of the Ga atom.

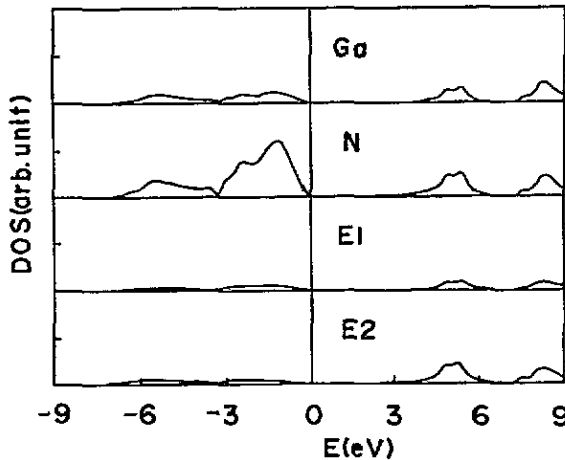


Figure 5. Local DOS for Ga and N atoms and the two empty spheres of β -GaN. The vertical line indicates the valence band maximum.

The pressure dependences of the fundamental band gap $\Gamma_{1c}-\Gamma_{15v}$ and the other band gaps $X_{1c}-\Gamma_{15v}$ and $L_{1c}-\Gamma_{15v}$ for β -GaN are plotted in figure 6. The gap $X_{1c}-\Gamma_{15v}$ is almost constant at 3.18 eV, i.e. this gap is not affected by the isotropic compression or expansion of the lattice constant. The gaps $\Gamma_{1c}-\Gamma_{15v}$ and $L_{1c}-\Gamma_{15v}$ increase monotonically with pressure varying from negative to positive. When the pressures are between -100 and 100 kbar, the variation is linear; otherwise it is non-linear. By using the least-squares fitting, as done in [21], the band gaps up to the second order in pressure can be expressed as

$$\Gamma_{1c}-\Gamma_{15v} = 2.29 + 1.46 \times 10^{-3}p - 2.90 \times 10^{-7}p^2 \quad (4)$$

$$L_{1c}-\Gamma_{15v} = 5.39 + 1.55 \times 10^{-3}p - 4.53 \times 10^{-7}p^2. \quad (5)$$

In the above expressions, the energy is in electronvolts and the pressure in kilobars. The linear pressure coefficient for the direct fundamental gap is 1.46 meV kbar⁻¹; which is smaller than those of GaAs and GaP (about 10 meV kbar⁻¹) [22]. This

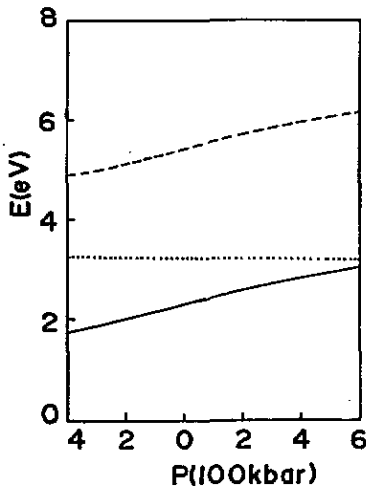


Figure 6. Pressure dependences of the band gaps of β -GaN: —, the $\Gamma_{15v}-\Gamma_{1c}$ gap; ---, the $\Gamma_{15v}-L_{1c}$ gap; ·····, the $\Gamma_{15v}-X_{1c}$ gap.

small pressure coefficient for β -GaN might arise because the d-state energy for the N atom is much higher than those for the P and As atoms. The sublinear coefficient is also very small. The linear and sublinear coefficients for the $L_{1c}-\Gamma_{15v}$ gap have the same orders of magnitude as those for the fundamental gap.

The experimental value in [28] for the linear coefficient of the direct band gap of α -GaN is $4.2 \text{ meV kbar}^{-1}$. The theoretical value obtained by Peilin *et al* [15] is $4.1 \text{ meV kbar}^{-1}$. The present value for β -GaN ($1.5 \text{ meV kbar}^{-1}$) is small; however, it is meaningless to compare the linear coefficient of β -GaN with that of α -GaN because of the different structures of these two phases.

3. Summary

In summary, in the present paper the ground-state properties, electronic band structures and pressure dependences of the band gaps of β -GaN are calculated. The equilibrium lattice constant calculated is smaller than the experimental value by about 2%. The bulk modulus B_0 calculated is 3.07 Mbar. It is interesting that the fundamental gap of β -GaN (α -GaN) is direct from Γ_{15v} (Γ_{6v}) to Γ_{1c} . Their values in the LDA calculation are underestimated by about 41%, whereas the corrected values using the model of Bechstedt and Del Sole [25] are in good agreement with the experimental values [8, 22]. The fundamental band gap of β -GaN is larger than that of α -GaN whereas that of β -SiC is smaller than that of α -SiC. This might be because the fundamental band gaps are direct at the Γ point for GaN and indirect for SiC. Moreover, it is found that the linear pressure coefficient for the band gap of β -GaN is smaller than those of GaAs and GaP.

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