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2009 J. Phys.: Condens. Matter 21 025501

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Electronic and structural properties of group III nitrides and phosphides using density functional theory

Uma Shankar Sharma², P S Bisht¹ and U P Verma¹

¹ School of Studies in Physics, Jiwaji University, Gwalior 474011, India

² Department of Physics, RJIT, BSF Academy, Tekanpur, Gwalior 475005, India

E-mail: umashankar_rjit@yahoo.co.in and upv.udai@gmail.com

Received 17 June 2008, in final form 5 October 2008

Published 9 December 2008

Online at stacks.iop.org/JPhysCM/21/025501

Abstract

In recent years group III nitrides have gained recognition as being the most important materials for optoelectronics and electronics applications. The zinc-blende modification of GaN and AlN is receiving much attention over their wurtzite structure. Our present work deals with the detailed *ab initio* calculations of group III nitrides and phosphides in the zinc-blende phase. The plane wave pseudopotential approach is used to study the different properties of the material based on the concept of density functional theory (DFT). The converged plane wave cut-off energy (E_{cut}) is used to set the number of plane waves, which varies from material to material. The calculated energy bandgaps are based on our theoretical equilibrium lattice constants. Our reported energy bandgap for InN (0.86 eV) is in good agreement with the recently reported experimental result (>0.7 eV and <1.0 eV).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent developments, semiconductor materials constitute basic building blocks of emitters and receivers in cellular, satellite and fiber glass communication. With respect to 'classical' III–V semiconductors, the group-III nitride semiconductors have attracted much attention to their great potential for technological applications [1–7].

The excitement generated by recent developments, which is well illustrated by the number of review articles [1, 3, 4, 8], stems from the fact that the nitride and phosphide semiconductors belong to a family of common anion and common cation group III–V semiconductors. The energy bandgaps of BN, AlN, BP, AlP and GaP are indirect in nature, while GaN, InN and InP possess direct bandgaps. What is more, they form a complete series of ternary alloys which spans the whole of the visible spectrum and extends well into the ultraviolet (UV) region; i.e., in terms of wavelength their bandgaps are continuously variable from 650 to 200 nm.

The series of group III nitrides has a high melting point, a high thermal conductivity and a large bulk modulus. These properties and the wide bandgaps are closely related to strong

ionic and covalent bonding. Such materials can, therefore, be used for short-wavelength light-emitting diodes (LEDs), laser diodes and optical detectors as well as for high-temperature, high-power and high-frequency electronic devices. This makes them ideal candidates for carefully tailored optoelectronic devices operating anywhere within the visible wavelength range, specifically for visible light emitters in the previously difficult blue and green parts of the spectrum.

The series of boron compounds BN and BP is of great technological interest for high-temperature, electronic and optical applications. These materials present a strong covalent character, since the electronegativity of the anions is slightly less than that of the cation.

The discovery of the narrow bandgap of InN (~ 0.86 eV) [17] in contrast to the previously reported bandgap (1.89 eV) [17] greatly expands the range of applications of energy gaps of group III nitrides. The direct gap of the nitride alloys continuously extends from the near infrared to the deep UV region, offering potential for new applications of this material. The narrow bandgap of InN extends the possible emission range of optoelectronic devices.

InP is also an established technology platform for making active optical components such as laser and photo detectors. Its energy bandgap can be tuned between 920 and 1650 nm, which makes it ideal for optical communication applications. InP is also used to produce mostly standalone active components, while devices such as couplers and waveguides tend to be formed from different material platforms optimized for each application. This multi-functionality makes InP an excellent platform for monolithic integration.

The lattice constant plays an important role in semiconducting technology. Owing to their technological significance, it is important to know different electronic and structural properties of these semiconductor compounds. Theoretical investigations as well as experimental research are, therefore, of vital interest to all those working in the area of research.

Most optoelectronic devices are fabricated by depositing one type of layer on top of another. It turns out that the only way to make high quality devices is by making sure that the lattice constants of various layers are as equal as possible. The crystalline quality of the layer degrades very quickly with any lattice constant mismatch.

In this paper, we planned to use a single theoretical approach to retain consistency for a uniform explanation of the electronic structure of group III nitrides and phosphides. The density functional theory was the basis of the studies of structural and electronic properties of the bulk materials. All the *ab initio* calculations were carried out using a plane wave basis with a Hamann type norm conserving pseudopotential [18], which was generated using the generalized gradient approximation (GGA), and the exchange–correlation effect was added by using the BLYP scheme.

2. Computational details

The computation of the band structure of group III nitrides and phosphides was performed using the FHI98md code, which is based on the framework of DFT and developed by the group of Scheffler [19, 20]. This package has been used on the Windows-XP platform.

The norm conserving pseudopotential used in the present calculation is based on a Hamann type scheme, which depends on the atomic configuration of the atoms. It was obtained using the FHI98pp code proposed by Fuch and Scheffler [25].

In the present work the exchange–correlation energy of the electrons is computed using the BLYP functional [21–24]. In the generalized gradient approximation (GGA), DFT allows a description of the many body electronic ground states in terms of the single particle equation and an effective potential. The effective potential consists of the ionic potential due to the atomic core, the Hartree potential describing the electrostatic electron–electron interactions and the exchange–correlation potential, that takes into account the many body effects. In the computation, the core shell electrons of B($1s^2$), Al($1s^2 2s^2 2p^6$), Ga($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$), In($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$), N($1s^2$) and P($1s^2 2s^2 2p^6$) and the valence electrons of B($2s^2 2p^1$), Al($3s^2 3p^1$), Ga($4s^2 4p^1$),

In($5s^2 5p^1$), N($2s^2 2p^3$) and P($3s^2 3p^3$) were distinguished from each other in calculations.

For the calculation of electronic and structural properties, we set the symmetry parameter, atomic coordinates (0.0, 0.0, 0.0) for group III atoms and (0.25, 0.25, 0.25) for group V atoms and the type of lattice as ZB. In the plane wave pseudopotential approach the number of plane waves is achieved on the basis of convergence of the total energy w.r.t. plane wave cut-off energy (E_{cut}). Different materials have different basis functions so the number of plane waves varies from material to material.

To obtain the theoretical equilibrium lattice constants we put the total energy corresponding to a wide range of theoretical lattice constants in the Murnaghan equation of states. Corresponding to the minima of the total energy curve we obtain the theoretical equilibrium lattice constant, the bulk modulus and the pressure derivative of the bulk modulus.

3. Results and discussion

In order to study the structural properties, the optimum values of total energy of the primitive unit cell for the materials considered in this paper have been calculated, along with their bulk modulus and pressure derivatives.

From table 1 it is observed that our calculated values of lattice constants are higher than experimental values of lattice constants, while the values reported by other authors are less than the experimental values of lattice constants. This significant difference in theoretical values is due to BLYP in GGA and LDA schemes. The differences between our present values of lattice constants and experimental values are almost the same as the difference between experimental lattice constants and earlier reported theoretical results. These differences may be correlated to the under-binding and over-binding of the lattice constants.

The experimental lattice parameters for the group III nitrides (3.61 Å for BN, 4.36 Å for AlN and 4.50 Å for GaN and 4.98 Å for InN) [17] are smaller as compared to those for the corresponding group III phosphides (4.54 Å for BP, 5.45 Å for AlP, 5.45 Å for GaP, 5.86 Å for InP) [17]. These differences can be correlated to two basic properties of the group V atoms, i.e. the small covalent radius of N (0.7 Å) as compared to the covalent radius of P (1.10 Å) and the nature of chemical bond, which depends on the electronegativity and ionicity of the elements forming the bond. Both the length of the chemical bond and its nature are critical to the growth of bulk crystals as well as to epitaxy.

Figure 1 exhibit two types of plots: (1) the graph between total energy and lattice parameter and (2) energy bandgaps along Γ – Γ and Γ –X directions within the mesh of 40 special k -points in first Brillouin zone versus lattice parameter. From the plots in figure 1 it is clear that with an increase in the size of the cation, having the same anion, the energy bandgap decreases and the nature of the bandgap changes from indirect to direct. The change in energy bandgap with respect to the change in lattice parameter is linear in all nitrides and phosphides (except in the case of BP). In nitrides the energy bandgap Γ – Γ and Γ –X increases with a decrease in lattice parameter while in

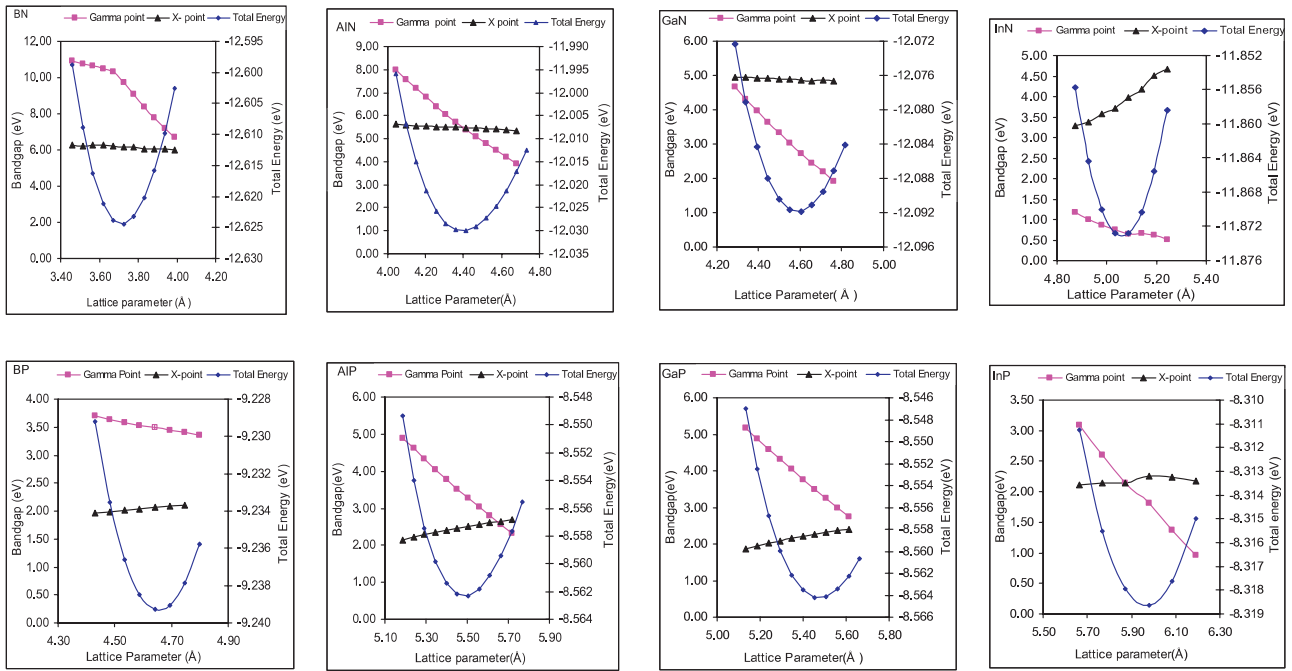


Figure 1. Total energy and lattice parameter graph along with the plot of energy bandgaps at Γ - and X-positions of the high symmetry k -points.

Table 1. Calculated lattice constants, a , along with their experimental and earlier reported values, and energy gaps Γ - Γ and Γ -X along with their experimental and earlier reported values. (Note: PW = present work, I = indirect bandgap, D = direct bandgap.)

Compound	Lattice constant a (Å)			Energy gap (eV) at				Band gap type
	PW	Expt	Others	Γ - Γ (PW)	Γ -X (PW)	Expt	Others	
BN	3.71	3.615 [9]	3.600 [13]	11.22	6.260	6.1–7.50 [10]	4.20 [15]	I
AlN	4.41	4.360 [10]	4.323 [12]	5.918	5.858	6.00–6.11 [10, 26]	6.10 [17]	I
GaN	4.58	4.500 [10]	4.335 [12]	3.333	4.901	3.33–3.36 [10]	3.35 [17]	D
InN	5.06	4.980 [10]	4.921 [12]	0.860	3.501	\sim 0.9 [17]	0.70 [17]	D
BP	4.64	4.538 [11]	4.475 [14]	3.587	1.902	2.00 [10, 27]	1.51 [14]	I
AlP	5.49	5.467 [10]	5.417 [12]	3.528	2.466	2.45–3.62 [10]	3.06 [16]	I
GaP	5.49	5.451 [10]	5.322 [12]	3.500	2.262	2.26–2.78 [10, 27]	1.50 [16]	I
InP	5.96	5.869 [10]	5.700 [12]	2.144	2.148	1.35–1.46 [10, 27]	0.37 [16]	D

phosphides the Γ - Γ bandgap increases but the Γ -X energy bandgap decreases with a decrease in lattice constant.

The calculated values of the energy bandgaps in the present work are included in table 1 along with experimental and earlier reported values. In almost all cases there is a range of the experimental energy gap. The factors that affects the properties of these compounds are the energies of the ‘s’ and ‘p’ orbitals of nitrogen and phosphorus. In the case of nitrogen, the energy of the ‘s’ orbital is -18 eV and that of the ‘p’ orbital is -7 eV; on the other hand, the ‘s’ and ‘p’ orbital energies for phosphorus are -14 and -5 eV, respectively.

Table 2 includes slopes of direct as well as indirect energy gaps versus lattice constants (shown in figure 1), plane wave cut-off energy, bulk modulus and derivatives of bulk modulus. The slopes of Γ - Γ versus lattice constants are negative in all cases, while slopes of Γ -X are either approximately zero or positive with respect to lattice constants. From table 1 it is also clear that all nitrides have higher values of bulk modulus in comparison to phosphides. The values of plane wave cut-

Table 2. Calculated slope of the lines in the plots of energy gaps at Γ - and X-points versus lattice parameters, optimum values of plane wave energy cut-off limits, bulk modulus and pressure derivative.

Material	Slope of plots E_g versus a		E_{cut}^a (in Ryd)	B (Mbar)	B' (Mbar $^{-1}$)
	Γ - Γ	Γ -X			
BN	-0.5300	~ 0	75	1.754	3.105
AlN	-0.3889	~ 0	75	0.866	3.815
GaN	-5.7289	~ 0	85	0.730	4.003
InN	-1.6314	3.8627	75	1.784	2.852
BP	-0.9073	0.4427	80	0.727	3.238
AlP	-4.8527	1.0379	70	0.375	5.868
GaP	-5.1003	1.1238	75	0.393	5.050
InP	-3.9625	0.1825	55	0.245	1.686

^a Plane wave cut-off energy.

off energy are ~ 80 Ryd except in the case of InP, where it is 55 Ryd. The bulk modulus derivative is ~ 3 in nitrides and boron phosphide. It is ~ 2 in the case of InP and ~ 6 and ~ 5 , respectively, for AlP and GaP.

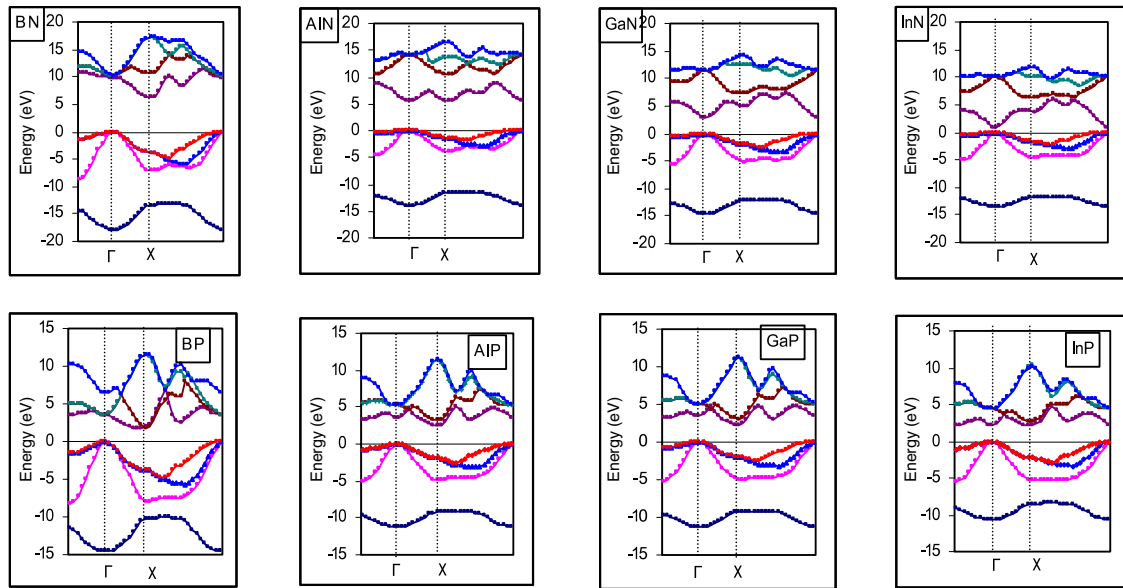


Figure 2. Energy band structure of group III nitrides and phosphides versus wavevectors (k). The top of the valence bands corresponds to the Fermi energy levels.

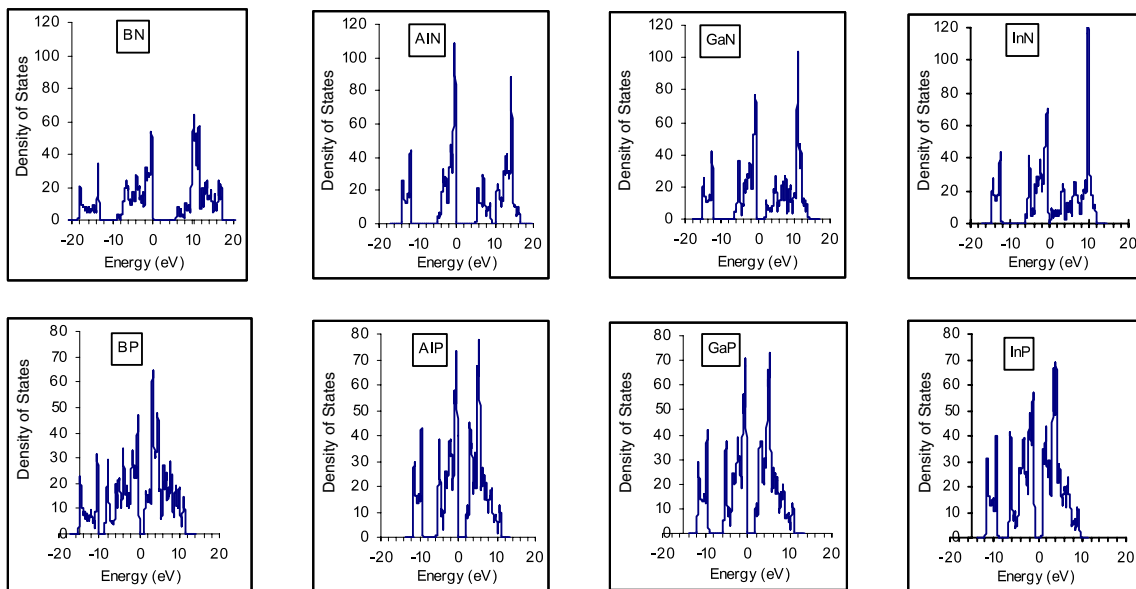


Figure 3. Density of states (DOS) of group III nitrides and phosphides versus energy.

The eigenvalues of Kohn–Sham equations were calculated along some high symmetry directions in the first Brillouin zone using the BLYP scheme under GGA and the obtained band structures of group III nitrides and phosphides are shown in figure 2. An overall similarity is clearly visible in all the band structures related to valence bands except differences in the case of their semicore energy levels, which are below -15 eV for nitrides and -12 eV for phosphides. However, the nature of conduction bands in the case of nitrides and phosphides are four different ones; in nitrides the top three conduction bands show less dispersion than the lowest conduction band, while in the case of phosphides the upper side conduction bands show more dispersion than the lower conduction band(s).

Hybridization near the Fermi level is very clear in the DOS plots shown in figure 3. In the plots the behavior of boron compounds is different from that of other compounds. The upper part of the valence band shows that for the same anion the DOS decreases with an increase in size of the cations. In the conduction band the position of higher DOS is shifted towards the lower energy side

4. Conclusions

We have investigated the electronic and structural properties of group III nitrides and phosphides using DFT, employing a consistent computational approach for all the materials. We

have observed that the nature of energy bandgaps changes from indirect to direct with an increase in the size of the cation for the same anion. The group III nitrides have negative volume deformation potential at both Γ - and X-points and also follow the common anion rule. The group III phosphides have negative volume deformation potential only at the Γ -point and show an anomaly at the X-point because with the decrease in volume of the group III phosphides the corresponding bandgap decreases. The computed bandgap energies are in good agreement with the experimentally reported bandgap energies in all cases except InP, in which it is slightly on higher side. The reported theoretical lattice parameters are very close to the experimentally reported values (within 3% of error limits). Thus, we summarize that the BLYP scheme is a good alternative to find values of the exchange–correlation functional.

The change in energy bandgap with respect to the change in lattice parameter is linear in all the nitrides and phosphides except BP. In nitrides the energy bandgap increases with the decrease in lattice parameter, while in phosphides the energy bandgap decreases with the decrease in the lattice parameter. Hybridization is very well supported by the plots of density of states (DOS).

Acknowledgments

We would like to thank Professor Peter Kratzer of Fritz Haber Max Planck Institute and Professor P B Patil of Aurangabad for his cooperation in bringing our work to its present form. The cooperation and facilities provided by Professor Neeraj Jain, Head, SOS in Physics, Jiwaji University, are also acknowledged. One of us, U S Sharma, acknowledges Er D R Yadav, Principal RJIT, BSF Academy, Tekanpur, for his encouragement.

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