DOI 10.31489/2022PH1/107-116

UDC 539.893

T.M. Inerbaev[1,2*], T. Matsuoka[3], Y. Kawazoe[3,4,5]

[1]*V.S. Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russian Federation;*
[2]*L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan;*
[3]*New Industry Creation Hatchery Center, Tohoku University, Japan;*
[4]*Physics and Nanotechnology, SRM Institute of Science and Technology, Tamil Nadu, India;*
[5]*School of Physics, Institute of Science, Suranaree University of Technology, Thailand;*
[*]*E-mail: inerbaevtm@igm.nsc.ru; inerbaev@yahoo.com*

Optical band gap energy values in wurtzite $In_xGa_{1-x}N$

The narrow bandgap in InN has been known as a notorious example of local density approximation or generalized gradient approximation (*LDA* or *GGA*) calculations to give a metallic state. Various density functional methods are applied to optimize the atomic structures of the systems. These numerical results are used as the input values for the subsequent GW calculations, which can be applied to estimate the band gap value without phenomenological parameters. It is found that *LDA* with GW_0 or the hybrid functional with self-consistent GW_0 approximation provides sufficient theoretical results for both of the investigated compounds of GaN and InN. Although they are still time-consuming, due to less computational cost the former method is selected as a trial to compute the electronic structure in the entire range in ternary $In_xGa_{1-x}N$ alloys without any arbitrary parameters. The present theoretical studies in ternary $In_xGa_{1-x}N$ alloy were carried out by *LDA* with GW_0. As a result, a good agreement between theoretical and experimental results is obtained, and it is also shown that zone bending could be well-approximated using a quadratic function with a constant, independent of x, parameter equal to 1.85 eV, which is close to the recent experimental results.

Keywords: $In_xGa_{1-x}N$ alloys, density functional theory, GW_0 modeling, band structure, bowing parameter, band gap tuning, ternary alloy.

Introduction

The application of optical and electronic properties in nitride semiconductors with wurtzite structure has been focused on optical devices such as blue and white light-emitting-diodes [1–3], and electronic devices such as high electron mobility transistors used in the base station of cellular phones. Transistors with high power and high breakdown-voltage are expected in automobile industries for highly efficient inverters in vehicles. In these industrial applications to be realized in short time, the precise theoretical study is required for nitride semiconductors. The fundamental band gap value in InN has been uncertain up to 1980s. In early experiments in 1972 and 1986, the band gap values of about 1.9 eV and 2.1 eV were reported by measuring polycrystalline InN which was epitaxially grown with the sputtering technique and non-leak tight molecular beam epitaxy system (MBE) [4, 5]. Matsuoka predicted that this value is too large from his experiments on InGaN and single crystalline InN showed much smaller band gap energy value [6]. These values are much larger than the value of 0.7 eV reported later, which was measured from single crystalline InN [7–10]. These single crystalline InN samples were prepared by using the Molecular Beam Epitaxy (MBE) and the metalorganic vapor phase epitaxy (MOVPE) methods. A possible explanation of the results is that polycrystal is oxidized and mixed crystals of InN and In_2O_3 which band gap is 2.7 eV. The purity in single crystalline InN mentioned above is also poor. Its residual carrier concentration of 10^{17} to 10^{18} cm^{-3} is too high to accurately determine the band gap energy value because there is the Burstein-Moss effect due to the presence of residual charge carriers. It is difficult to epitaxially grow InN with high quality because the equilibrium vapor pressure of nitrogen between solid and gas phases is exceptionally high, compared with AlN and GaN [6]. Therefore, it is essential to theoretically determine the absolute band gap energy value in InN. In the present paper, the values of the band gap energy for the entire range of $In_xGa_{1-x}N$ ternary alloys are calculated using *ab initio* calculations without any empirical fitting parameters.

Experimental

The density-functional theory (*DFT*) within the local density approximation (*LDA*) or the generalized gradient approximation (*GGA*) has been extensively employed to investigate various electronic properties in post-transition metal (TM) compounds including both oxides and nitrides. *DFT* is a complete many-body the-

ory, but it is basically applicable only to the non-degenerated ground state. When *DFT* is used to estimate the band gap, the main drawback of *DFT* is that the band gap value is seriously underestimated in the ranges over 50 %-70 % for most of the post-TM compounds and reaches the value of 80 % reduction in the case of ZnO [11].In the case of InN, *DFT* gives even the negative band gap, *i.e.*, predicts InN to be metallic [12,13, 14]. For gallium nitride, the *DFT* calculation yields a strongly underestimated band gap value [13, 15]. Basically this extensional usage of *DFT* for the band gap estimation is theoretically incorrect since it is a ground state theory, and higher level of theoretical methods such as *GW* approximation is requested.

The band gap underestimation in post-TM compounds could be addressed in part by considering the on-site electron correlation energy *U*. Such an empirical treatment tries to include the effect of correlations of *d*-electrons which increases in the band gap value. However,we note that the *DFT+U* method violates the necessary condition of the virial theorem (*2T+V=0*), and tends to give the effect on other physical parameters to be non-physical. For example, the lattice-constants are reduced and also contribute widening the band gap. Alternatively, the hybrid functional scheme incorporating the exact exchange term from Hartree-Fock approximation is used to improve the band gap. However, the fraction of the exact exchange energy again should be varied among post-TM compounds to fit the band gap and it is only a phenomenological treatment [11, 12].

Modern methods of the theoretical modeling allow predicting the fundamental band gap value with high accuracy without any parameter by combining *DFT* and the quasiparticle (*QP*) theory with the exchange-correlation self-energy in *GW* approximation [16]. Taking into account *QP* corrections, this band gap problem can be solved with an accuracy of about 0.1 eV [17]. The first attempt to calculate the electronic properties of $In_xGa_{1-x}N$ ternary alloys with parameter-free theoretical technique was made in Ref. [18] using the *LDA-1/2* method [19]. This method approximately includes the self-energy of excitations in semiconductors and gives results close to calculations by the *GW* method.

The many-body perturbation theory in the *GW* approach presents a *QP* theory that overcomes the deficiencies of *LDA* and *GGA* and provides a suitable description of the band structure for weakly correlated solids such as GaN and InN. The *GW* approximation is formallythe first term in an expansion of the nonlocal and energy-dependent self-energy in the screened Coulomb interaction [20]. The self-energy operator is described as follows:

$$\sum(r,r' \in) = \frac{i}{4\pi}\int_{-\infty}^{\infty} e^{i\omega'\delta} G(r,r' \in +\omega')W(r,r')d\omega' \quad (1)$$

where *G* is Green's function, *W* is screened Coulomb interaction, and δ is infinitesimal. The evaluation of self-energy requires the wave functions and corresponding eigenvalues. If these quantities are fixed to *DFT* results, it is usually called as single-shot G_0W_0 calculations. GW_0 and *GW* approximations correspond to the case of iterative updates of the eigenvalues in the computation of *G* and *W*, respectively. A full update of the orbitals can be performed by specifying self-consistent *GW* calculations. If the orbitals and eigenvalues are updated in *G* and *W*, it is *scGW* approximation whereas $scGW_0$ corresponds to orbitals and eigenvalues update only in *G* calculations. In addition to the level of self-consistency of calculations, the results also depend on the initial conditions, i.e., from which method the eigenvalues and orbitals are derived in *GW* calculations.

Numerous studies using *GW* method have shown that the numerical results strongly dependon the initial geometry of the structure as well as on the choice of the starting wave functions [12, 13, 21-30]. Thus, the use of source structures optimized with the help of various functionals leads to a variation of the resulting numerical values of the band gap, for example from 3.366 eV (*GGA-PBE*) to 3.847 eV (*LDA*) optimized GaN wurtzite structure [30].

The choice of starting wave function for *GW* calculations is also crucial. Kang et al. [11] tested various levels of self-consistency and starting conditions to establish the most proper *GW* calculation scheme for the best exact description of the band gap value for post-TM oxides. It was found that the GW_0 scheme with *GGA+U* as the *DFT* functional turned out to give the best results in every aspect of the band structures. In one specific case of ZnO, it was proposed a modified scheme where on-site term *U* on Zn-*d* orbital was used within GW_0 scheme. Higher level of self-consistent *scGW* and employment of hybrid Heyd-Scuseria-Ernzerhof (*HSE06*) functional [31] to calculate wave functions and eigenvalues as starting conditions for G_0W_0 calculations were found to overestimate the band gap value. Pure *DFT* calculations with *LDA* or *GGA* functionals predict metallic state for InN [12, 21]. Kumar et al. [27] used the *DFT+U* to calculate the starting wave function, which made it possible to open the optical gap in the electron structure of indium nitride.

In the present paper, we tested various *GW* approaches on GaN and InN to compare their validity and accuracy. One important point is to minimize the computational time required forelectronic structure calculations, since we should use an extra-ordinally high demand computing resources for the ternary systems of InxGa1-xNas. With all of these careful theoreticalconsiderations, the optimal computational method was employed to calculate the accurate valueof the band gap energy for the $In_xGa_{1-x}N$ ternary alloy. To investigate the electronic structure in InGaN alloys, we used 2×2×2 supercells containing 32 atoms. Supercells with 25 %, 50 %, and 75 % concentration of In atoms were considered and should provide a good approximation for the random alloy [12].

To obtain the initial calculations, all numerical calculations were performed using HSE06, Perdew-Burke-Ernzerhof (*PBE*) [32] and local density approximation (*LDA*) functionals by employing the projector augmented wave (*PAW*) method [33] as implemented in the Vienna *Abinitio* Simulation Package, *VASP* [34, 35]. The atomic structures of both InN and GaN were modeled by a fully relaxed wurtzite structure of 4 atoms (C^4_6v-*P63mc*: space group number 186) [36, 37]. The In-4*d* and Ga-3*d* electrons were treated as valence electrons. The electronic wavefunctions are described using a plane wave basis set with an energy cut-off of 600 eV. Γ-point centered k-point meshes of 6×6×6 are used throughout the calculations to obtain well-converged results for GaN and InN. Since the *DFT* calculations predict a metallic state for InN,to open the optical gap, the additional on-site correlation *DFT+U* in the Dudarev parameterization [37] was taken into account with the value of $U = 3.5$ eV.

In Ref. [21], the dependencies of theoretical band gap values were calculated depending on the choice of cutoff energies and k-space partitions. It was shown that the convergence of the calculated band gap occurs at the cut-off energy of 600 eV. By selecting a 4×4×4 k-point mesh, the calculated fundamental band gap values differ from thoseobtained on a 6×6×6 by 1.5 %. For this reason, the present numerical calculations are performed using the 2×2×2 k-point mesh.

From the theoretical point of view, state-of-the-art calculations within many-body perturbation theory allow to rigorously obtain band gap energy values. The *GW* approximation method used to compute self-energy corrections is a quite well-established and standard technique, giving energy levels generally in good agreement with experiments, even for complicated systems like reconstructed surfaces and clusters [39]. Due to high complexity and large computational require ments of *ab initio* calculations of the self-energy, this approach has rare been used to study systems with a large number of atoms in a unit cell. In the present study, were performed the investigation of the $In_xGa_{1-x}N$ alloy to estimate the band gap value in the entire composition range with GW approximation, predicting its properties without any experimental/fitting parameters.

Previous studies of $In_xGa_{1-x}N$ compounds showed poor agreement of the *DFT* band gap values with experimental data [12, 22, 40–44]. To improve consistency between theory and experiment, hybrid functionals in *DFT* have been used as an empirical simulation method. In the case of zinc blende $In_xGa_{1-x}N$ alloys, the overestimation of the band gap in the In-rich regionwas found [45]. For AlN, GaN, and InN with wurtzite structure, the resulting band gap values depend on the mixing ratio of the exact exchange energy functional, Mixing ratio is required to match the experimental band gaps increases with experimental band gaps [12].

Result and Discussion

To solve the problem of describing the band gap in the ternary alloy system, it is necessary to choose a suitable theoretical method that would equally accurately describe both compounds of GaN and InN. The available results in published literatures on InN and GaN *GW* band gap calculations are summarized in Table 1. It is astonishing to recognize that to date, only one study has been published in the literature which shows that the optimized effective potential (*OEP*) calculations predict well both the lattice geometry and the band gap for both nitrides.

[13] Unfortunately, this method requires enormous computational effort and cannot be applied to the study of large model cells as required by the present research on ternary alloys. Base onthis reason, we tested different approaches as initial stages to *GW* calculations in the framework of *GGA*, *LDA*, and hybrid functionals.

Besides choosing the initial wave function for calculating *GW*, which means selecting the appropriate density functional, the geometric structure of the model cells also largely determines the theoretical values of the band gap. The lattice constants of $In_xGa_{1-x}N$ ternary alloys can be obtained both as a result of theoretical calculations for lattice optimization and using interpolation formulae if we assume that the lattice parameters

of the alloys are governedby Vegard's laws. Another potential source of calculation errors is the inability to perform structural optimization in a real calculation process using the *GW* method.

In the present study, in contrast to Ref. [13], where experimental values of lattice constants were used, we explore various functionals concerning their accuracy in predicting the geometry of the unit cells. The lattice geometry found in this way is then used for GW calculations with the initial wave functions obtained with various functionals. The functional that provides the best agreement between the calculated bandgap values and the experimental ones were used for calculations using a model supercell of $In_xGa_{1-x}N$ (x=0.5) compound with lattice constants calculated according to Vegard's law for comparison.

The results of the present numerical results on the lattice parameters in GaN and InN in comparison with the experimental data are given in Table 2. The data obtained are typical for calculations carried out by DFT. In the case of InN, the hybrid functional predicts almost exactlattice-constant values, whereas the *PBE* functional overestimates, while the *LDA* functional overestimates the value of the parameter a and underestimates c. In the case of GaN, the best values of the lattice-constants are given by the calculation using the *PBE* functional, while the*HSE06* and *LDA* functionals underestimate these parameters. Thus, none of the selected methods for the optimization of the crystal lattice is preferable in comparison with experimentaldata for both considered compounds.

Table 1

Summary of the literature available high-accuracy calculations of fundamental band gap value for InN and GaN of wurzite structure

Compound	Band gap, eV	Method (based on the WF obtained with thismethod)	Reference
InN	0.71	*GW0+RPA (HSE3)*	[24]
	0.99 0.74	*scGW (LDA)* Hybrid approach[a)]	[25]
	0.66	*HSE06*	[12]
	0.58 0.74 1.50	*LDA* with *SIC*[b)] Simplified *Gc*[c)] *GW SIC* (*LDA*)	[22, 23]
	0.82	*GW SIC* (*LDA*)	[26]
	0.8	*scGW0*	[27]
	0.7 (0.8 correction factor was applied)	*GW+RPA (LDA)*	[28]
	0.638, 0.765; 0.494[d)]	*G0W0+SOC*[e)] (*HSE*)	[30]
	0.711 0.694 0.805	*HSE06* *G0W0 (HSE06)* *scGW0*	[21]
	0.7	*OEPx*[6]*+G0W0(LDA)*	[13]
	0.0	*PBE*	[14]
	0.5	*HSE06*	[14]
	0.95	*LDA-1/2*	[19]
GaN	3.5	*GW*	[29]
	3.23	*HSE06*	[12]
	3.81 3.42	*scGW (LDA)* Hybrid approach[a)]	[25]
	3.6 (0.8 correction factor was applied)	*GW+RPA (LDA)*	[28]
	3.659; 3.847; 3.366[d)]	*G0W0+SOC*[e)] (*HSE*)	[30]
	3.24	*OEPx*[f)]*+G0W0(LDA)*	[13]
	3.52	*LDA-1/2*	[19]

a) Combines 80 % of the *GW* self-energy with 20 % of the *LDA* self-energy as it is described in Ref. [53]; [b)] Self-interaction corrections; [c)]Quasi-particle corrections to *DFT* within a simplified *GW* approximation; [d)] Data obtained for geometries optimized using different methods (*AM05, LDA, PBE*); [e)] Spin-orbit coupling; [f)]exact-exchange optimized effectivepotential

Further, all obtained equilibrium lattice geometries were used to calculate the band gap values. For each structure, three possible wave functions were used as the starting values for the numerical calculations within

GW approximation. The results are shown in Table 3. From the presented data it can be seen that only two approaches provide sufficiently good values was an error less than 0.1 eV for both indium and gallium nitrides; namely, (case 1) $scGW_0$ approach with optimized geometry by *HSE06* and starting wave functions by *LDA*, and (case 2) GW_0 calculations with *LDA* for both geometry optimization and starting wave functions.

Table 2

The equilibrium values of the lattice-constants for InN and GaN at atmospheric pressure calculated by various methods in comparison with experimental data. Parentheses indicate the relative error of calculations

Compound	*a*, Å (error, %)	*c*, Å (error, %)	Unit cell volume, Å^3	*c/a*	*u*	Method
InN	3.533	5.693	61.50	1.611	0.375	Exp. [36]
	3.530 (-0.08)	5.700 (0.1)	61.52	1.614	0.379	*HSE06*
	3.578 (1.3)	5.777 (1.5)	64.06	1.614	0.379	*PBE*
	3.503 (0.8)	5.655 (-0.7)	60.09	1.614	0.379	*LDA*
	3.62	5.83		1.61		*PBE/HSE06* [14]
GaN	3.19	5.28	46.53	1.655	0.375	Exp. [54]
	3.176 (-0.4)	5.173 (-2.0)	45.20	1.628	0.377	*HSE06*
	3.214 (0.8)	5.235 (0.9)	46.84	1.628	0.377	*PBE*
	3.156 (-1.1)	5.140 (-2.7)	44.34	1.628	0.377	*LDA*

Thus, two theoretical approaches provide approximately the same values of the perception of both the lattice geometry and the band gap in both nitrides under study. Moreover, for the calculated values of the cell parameters, the use of the hybrid functional is somewhat closer to experimental values. On the other hand, the inclusion of the Hartree-Fock exchange in the hybrid functional raises the computation cost very significantly, especially when one uses the plane-wave basis sets [46, 47]. Besides, for the exact prediction of the width of the band gap, in this case, the $scGW_0$ method is used, which includes an additional self-consistency procedure in comparison with GW_0, which also significantly increases computational costs. Thus, based on consideration of the balance of the ability of prediction and the required computational costs, in the present study, we employed the *LDA* for structure optimization and wave functions calculation for GW_0. In the latter case, the *LDA+U* method was used on indium atoms, as indicated in "Computational method" section.

Table 3

The values of the band gap for nitrides, calculated using various methods. The valuesthat most closely coincide with the experimental values for both considered compounds are highlighted in bold

Compound	Input geometry	Input wavefunction	Bang gap calculation method			
			DFT	*G0W0*	*GW0*	*scGW0*
			Band gap, eV			
1	2	3	4			
InN	*HSE06*	*HSE06*	0.76	0.71	0.71	0.89
		PBE+U	0.09	0.21	0.27	0.50
		LDA+U	0.11	0.43	0.51	**0.73**
	PBE	*HSE06*	0.60	0.49	0.48	0.66
		PBE+U	0.04	0.07	0.30	0.30
		LDA+U	0.03	0.14	0.14	0.40
	LDA	*HSE06*	0.85	2.65	2.59	2.63
		PBE+U	0.16	0.29	0.36	0.25
		LDA+U	0.26	0.67	**0.76**	0.94
GaN	*HSE06*	*HSE06*	3.30	3.77	3.85	3.97
		PBE	1.97	3.13	3.33	3.50

1	2	3	4			
		LDA	1.99	3.16	3.38	**3.44**
	PBE	*HSE06*	3.02	3.47	3.67	3.67
		PBE	1.73	4.66	5.00	5.26
		LDA	3.03	3.47	3.57	3.63
	LDA	*HSE06*	3.46	3.93	4.01	4.14
		PBE	2.10	3.29	3.51	3.74
		LDA	2.12	3.33	**3.55**	3.69

The estimated lattice-constant values for the $In_xGa_{1-x}N$ ternary alloy as a function of x are shown in Figure 1. The present numerical calculations were carried out for a 2×2×2 supercell and the data presented was reduced to a single cell. When creating model structures, the atoms in the cases x = 0.25 and = x = 0.5, the substitution of gallium atoms was carried out in such a way as to distribute the indium atoms uniformly throughout the cell, while avoiding both the clustering of indium atoms and their ordering. The latter could lead to the appearance of periodic superstructures. Earlier results show that the clustering of indium InGaN alloy leads to a greater curvature of the curve of the band gap dependence on *x* value [51]. The case x = 0.75 is identical to x = 0.25 up to the mutual permutation of indium and gallium atoms. Test calculations on three different supercells with x = 0.5 showed a weak (< 2 %) dependence of the band gap on the choice of the atomic configuration. The geometries of all supercells have been optimized. The optimization concerned both the positions of the ions inside the supercells and the volume of the supercells. In this case, the lattice constants changed so that the volume of the optimized cell corresponded to the system at zero external pressure. The lattice symmetry was maintained constant.

It can be seen that the cell parameters are linearly dependent on the In content according to Vegard's law. The resulting atomic structures were used to calculate the band gap using the start wave functions obtained using the *LDA* functional. The obtained data are presented in Figure 2 in comparison with the available experimental data and earlier calculations using hybrid *HSE06* functional [12]. The present theoretical results, without any parameters are in excellent agreement with the experimental results.

Figure 1. Calculated lattice parameters of $In_xGa_{1-x}N$ within *LDA* in comparison with experimental values [35, 53]

We also investigated the dependence of the theoretical band gap on the starting geometry of the model cell, implying that the lattice constants depend on the concentration of In and Ga according to Vegard's law. The obtained band gap for the ternary alloy of the composition $In_{0.5}Ga_{0.5}N$, obtained using *GW* calculations based on the *LDA* functional, is 1.36eV. This value is 0.29 eV less than the corresponding value calculated for a structure whose lattice constants are theoretically obtained.

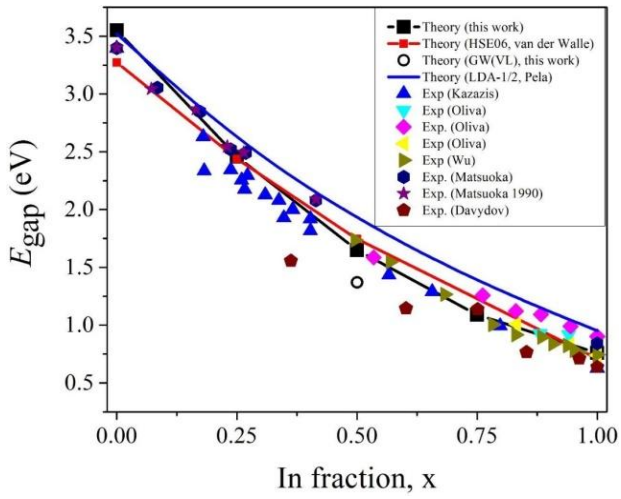

Figure 2. Theoretical and experimental values of the fundamental band gap values in Ga1-xInxNternary alloy as a function of the indium molar fraction. Theoretical results are obtained using *GW0* method (this work), *HSE06* hybrid functional [12] and *LDA*-1/2 method [18]. The band gap *GW*(VL) value was obtained for a model cell with lattice constants calculated using the Vegard's law. Experimental values are adopted from Refs. [6, 8–10, 55, 56]

The band gap in $In_xGa_{1-x}N$ as a function of the In content is of key importance for the analysis and design of efficient electronic devices. Qualitatively, there is an agreement that the band gap in $In_xGa_{1-x}N$ is a nonlinear function of the alloy composition. Conventionally, alloy band gap values are expressed as

$$E_g\,(In_x\,Ga_{1\,-\,x}N)\;=\;(1-x)\,E_g(GaN)\;+\;x\,E_{g(}InN)\,-\,bx(1-x), \qquad (2)$$

where *b* is the so-called bowing parameter. Since the most important parameter in the semiconductor alloy system is the band gap and its deviation from linear dependence characterized by the band gap bowing parameter *b*, which generally is a function of concentration. The various studies [22, 40, 43, 48–51] have disagreed on the magnitude and In concentration dependence of the bowing parameter. Some investigations show that the bowing cannot accurately be described by a composition-independent bowing parameter [12, 22, 40, 48, 52]. Wu *et al.* by optical absorption and photoluminescence measurements showed that band gap versus composition is well-described by a constant bowing parameter of 1.4 eV [10]. However, McCluskey *et al.*, obtained the bowing parameter value of 2.6 eV by carrying out optical absorption spectroscopy measurements [51]. Kazazis *et al.* measured that the intrinsic band gap value dependency on the In content is adequately expressed, for the entire range, by a bowing parameter value of 1.66±0.08 eV [8]. Fitting of our numerical results gives *b*=1.85 eV with a maximal absolute error less than 0.04 eV that is a good agreement with the most recent experiment of Kazazis *et al.*.

The above analysis corresponds to the use of a single parameter bowing calculating would be fitting (2). Moses et al. demonstrated that the bowing parameter varies with indium concentration. Namely, with an increase in the indium content, its value decreases [12]. Our results confirm this trend, although to a much lesser extent, and give *b* equal to 1.92, 1.85, and 1.79 eV for 25, 50, and 75 % of the indium content.

Conclusions

To solve the problem of band gap values in ternary InxGa1-xN alloys theoretically without phenomenological parameters, various functionals have been preliminarily tested both concerning using them to optimize the geometry of model cells and to calculate the initial wave functions for *GW* calculations applied to binary nitrides. For both InN and GaN, the acceptable accuracy is achieved either by *GW0* approximation with *LDA* or by *scGW0* method with hybrid HSE06 functional, especially the narrow band gap of InN was successfully reproduced without using the phenomenological parameters. With *LDA* the optical band gap in InN is estimated to be negative (metallic). To open it, it is necessary to use the *LDA+U* method. Since the former approach requires less computational costs, the present theoretical studies in ternary InxGa1-xN alloy were carried out by *LDA* with *GW0*. As a result, a good agreement between theoretical and experimental results was obtained, and it is also shown that zone bending could be well-approximated using a quadratic

function with a constant, independent of *x*, parameter equal to 1.85 eV, which is close to the recent experimental results.

Acknowledgements

The authors are grateful to JHPCN project as "jh190019-NAJ" on the supercomputer at Research Institute for Information Technology Kyushu University and the Center for Computational Materials Science, Institute for Materials Research, Tohoku University for their continuous support of the supercomputing system to be used for our simulation works.

References

1 Okamoto, K., Kashiwagi, J., Tanaka, T., & Kubota, M. (2009). Nonpolar *m*-plane InGaN multiple quantum well laser diodes with a lasing wavelength of 499.8 nm. *Appl. Phys. Lett.*, 94, 071105. https://doi.org/10.1063/1.3078818

2 Enya, Y., Yoshizumi, Y., Kyono, T., Akita, K., Ueno, M., Adachi, M., T. Sumitomo, T., Tokuyama, S., Ikegami, T., Katayama, K., & Nakamura, T. (2009). 531 nm Green Lasing of InGaN Based Laser Diodes on Semi-Polar {20$\bar{2}$1} Free-Standing GaN Substrates. *Appl. Phys. Express,* 2, 082101. https://doi.org/10.1143/APEX.2.082101

3 Wang, T. (2016). Development of overgrown semi-polar GaN for high efficiency green/yellow emission. *Semicond. Sci. Tech.*, No. *31*. -P. 093003. https://doi.org/10.1088/0268-1242/31/9/093003

4 Tansley T.L., & Foley, C.P. (1986). Optical band gap of indium nitride. *J. Appl. Phys.,* 59, 3241. https://doi.org/10.1063/1.336906

5 Guo, Q., & Yoshida, A. (1994) Temperature Dependence of Band Gap Change in InN and AlN. *Japanese J. Appl. Phys.*, 33, 2453. https://doi.org/10.1143/JJAP.33.2453

6 Matsuoka, T., Tanaka, H., Sasaki, T., & Katsui, A. (1990). Wide-Gap Semiconductor (In,Ga)N. *Inst. Phys. Conf. Ser.*, 199(106), 141–146.

7 Wu, J., Walukiewicz, W., Shan, W., Yu, K. M., Ager, J. W., Li, S. X., Haller, E. E., Lu, H., & Schaff, W. J. (2003). Temperature dependence of the fundamental band gap of InN. *J. Appl. Phys.*, 94, 4457. https://doi.org/10.1063/1.1605815

8 Kazazis, S. A., Papadomanolaki, E., Androulidaki, M., Kayambaki, M., & Iliopoulos E. (2018). Optical properties of InGaN thin films in the entire composition range. *J. Appl. Phys.,* 123, 125101. https://doi.org/10.1063/1.5020988

9 Oliva, R., Zelewski, S.J., Serafinczuk, L., Rudzunski, M., Ozbay, E., & Kudrawiec, R., (2018). Determination of the band gap of indium-rich InGaN by means of photoacoustic spectroscopy. *Semicond. Sci. Tech.,* 33, 035007. https://doi.org/10.1088/1361-6641/aaa908

10 Wu, J., Walukiewicz, W., Yu, K.M., Ager, J.W., Haller, E.E., & Lu, H. et al. (2002). Unusual properties of the fundamental band gap of InN. *Appl. Phys. Lett.,* 80, 3967. https://doi.org/10.1063/1.1482786

11 Kang, Y., Kang, G., Nahm, H.-H., Cho, S.-H., Park, Y.-S., & Han, S.-W. (2014). GW calculations on post-transition-metal oxides. *Phys. Rev. B,* 89, 165130. https://doi.org/10.1103/PhysRevB.89.165130

12 Moses, P.G., Miao, M.-S., Yan, Q.-M., & Van de Walle, C.G. (2011). Hybrid functional investigations of band gaps and band alignments for AlN, GaN, InN, and InGaN. *J. Chem. Phys,* 134, 84703. https://doi.org/10.1063/1.3548872

13 Rinke, P., Winkelnkemper, M., Qteish, A., Bimberg, D., Neugebauer, J., & Scheffler, M. (2008). Consistent set of band parameters for the group-III nitrides AlN, GaN, and InN. *Phys. Rev. B,* 77, 075202. https://doi.org/10.1103/PhysRevB.77.075202

14 Liang, D., Quhe, R., Chen, Y., Wu, L., Wang, Q., Guan, P., & Wangef, S. et al. (2017). Electronic and excitonic properties of two-dimensional and bulk InN crystals. *RSC Adv.,* 7, 42455. DOI 10.1039/c7ra07640a

15 Rani, A., & Kumar, R. (2017). LDA+U Study of Induced Half Metallicity in Cr-Doped GaN. *J. Supercond. Nov. Magn.,* 30, 1483. https://doi.org/10.1007/s10948-016-3938-8

16 Hybertsen, M. S., & Louie, S. G. (1986). Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies. *Phys. Rev. B,* 34, 5390. https://doi.org/10.1103/PhysRevB.34.5390

17 Bechstedt, F. (1992). *In Festkörperprobleme 32: Plenary Lectures of the Divisions of the German Physical Society (DPG)*. Berlin: Springer, 177. https://link.springer.com/book/10.1007/BFb0108617

18 Pelá, R.R., C. Caetano, C., Marques, M., Ferreira, L. G., Furthmüller, J., & Teles, L. K. (2011). Accurate band gaps of AlGaN, InGaN, and AlInN alloys calculations based on LDA-1/2 approach. *Appl. Phys. Lett., 98*, 151907. https://doi.org/10.1063/1.3576570

19 Ferreira, L. G., Marques, M., & Teles, L. K. (2008). Approximation to density functional theory for the calculation of band gaps of semiconductors. *Phys. Rev. B,* 78, 125116. https://doi.org/10.1103/PhysRevB.78.125116

20 Hedin, L., & Lundqvist, S. (1969). In Solid State Physics. *Academic Press,* 23, 1-181.

21 Duan, Y.-F., Qin, L.-X., Shi, L.-W., & Tang, G. (2015). More accurate predictions of band gap tuned by pressure in InN using HSE06 and GW approximations. *Comput. Mater. Sci.,* 101. 56. https://doi.org/10.1016/j.commatsci.2015.01.019

22 Bechstedt, F., Furthmuller, J., Ferhat, M., Teles, L.K., Scolfaro, L. M. R., & Leite, J. R. et al. (2003). Energy gap and optical properties of $In_xGa_{1-x}N$. *Phys. Status Solidi A,* 195, 628. https://doi.org/10.1002/pssa.200306164

23 Bechstedt, F., & J. Furthmuller (2002). "Do we know the fundamental energy gap of InN? *J. Cryst. Growth*, Vol. 246, 315. https://doi.org/10.1016/S0022-0248(02)01756-6

24 Piper, L.F.J., Colakerol, L., Learmonth, T., Glans, P.-A., Smith, K. E., & Fuchs, F. et al. (2007). Electronic structure of InN studied using soft x-ray emission, soft x-ray absorption, and quasiparticle band structure calculations. *Phys. Rev. B, 76*, 245204. https://doi.org/10.1103/PhysRevB.76.245204

25 Svane, A., Christensen, N.E., Gorczyca, I., van Schilfgaarde, M., Chantis, A.N., & Kotani, T. (2010). Quasiparticle self-consistent GW theory of III-V nitride semiconductors: Bands, gap bowing, and effective masses. *Phys. Rev. B,* 82, 115102. https://doi.org/10.1103/PhysRevB.82.115102

26 Furthmuller, J., Hahn, P. H., Fuchs, F., & Bechstedt, F. (2005). Band structures and optical spectra of InN polymorphs: Influence of quasiparticle and excitonic effects. *Phys. Rev. B, 72*, 205106. https://doi.org/10.1103/PhysRevB.72.205106

27 Kumar, M., Baldissera, G., Persson, C., David, D. G. F., da Silva, M. V. S., & Freitas, J. A., Tischler, Jr., J. G., Chubaci, J. F. D., Matsuoka, M., Ferreira da Silva, A. (2014). Bulk properties of InN films determined by experiments and theory. *J. Cryst. Growth*, 403, 124. https://doi.org/10.1016/j.jcrysgro.2014.06.001

28 Punya, A., & Lambrecht, W.R.L. (2012). Valence band effective-mass Hamiltonians for the group-III nitrides from quasiparticle self-consistent GW band structures. *Phys. Rev. B,* 85, 195147. https://doi.org/10.1103/PhysRevB.85.195147

29 Rubio, A., Corkill, J. L., Cohen, M. L., Shirley, E. L., & Louie, S. L. (1993). Quasiparticle band structure of AlN and GaN. *Phys. Rev. B,* 48, 11810. https://doi.org/10.1103/PhysRevB.48.11810

30 de Carvalho, L.C., Schleife, A., & Bechstedt, F. (2011). Influence of exchange and correlation on structural and electronic properties of AlN, GaN, and InN polytypes. *Phys. Rev. B, 84*, 195105. DOI:10.1103/PHYSREVB.84.195105

31 Heyd, J., Scuseria, G. E., & Ernzerhof, M. (2003). Erratum: Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* 118, 8207. DOI: 10.1063/1.2204597

32 32 Paier, J., Hirschl, R., Marsman, M., & Kresse, G. (2005). The Perdew-Burke-Ernzerhof exchange-correlation functional applied to the G2-1 test set using a plane-wave basis set. *J. Chem. Phys.*, 122, 234102. DOI:10.1063/1.1926272

33 Blöchl, P. E. (1994). A Projector augmented-wave method. *Phys. Rev. B,* 50, 17953. DOI:10.1103/PHYSREVB.50.17953

34 Kresse, G., & Furthmüller J., (1996). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54, 11169. DOI: 10.1103/physrevb.54.11169

35 Kresse G., & Joubert, D. (1999). From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B. 59, 1758. doi:10.1103/PhysRevB.59.1758

36 Juza, R., H. Hahn, H., & Anorg, Z. (1938). Über die Kristallstrukturen von Cu3N, GaN und InN Metallamide und Metallnitride. *Allg. Chem.*, 239, 282. https://doi.org/10.1002/zaac.19382390307

37 Hellwege, K. H., & Madelung, O. (1982). *Numerical data and functional relationships in science and technology*. New York: Springer. .P. 342.

38 Dudarev, S. L., Botton, G. A., Savrasov, S. Y., Humphreys, C. J., & Sutton, A. P. (1998). Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B,* 57, 1505. DOI:10.1103/PHYSREVB.57.1505

39 Aryasetiawan, F., & Gunnarsson, O. (1998). The GW Method. *Rep. Prog. Phys.*, 67, 237. https://doi.org/10.1088/0034-4885/61/3/002

40 Ferhat, M., & Bechstedt, F. (2002). First-principles calculations of gap bowing in In x Ga 1 − x N and In x Al 1 − x N alloys: Relation to structural and thermodynamic properties. *Phys. Rev. B,* 65, 075213. DOI:10.1103/PHYSREVB.65.075213

41 Bellaiche, L., Mattila, T., Wang, L. W., S. H. Wei, S. H., & Zunger, A. (1999). *Appl. Phys. Lett.,* 74, 1842. DOI:https://doi.org/10.1103/PhysRevB.57.1505

42 Wright, A. F., Leung, K., & Van Schilfgaarde, M. (2001) Effects of biaxial strain and chemical ordering on the band gap of InGaN. *Appl. Phys. Lett.*, 78, 189. https://doi.org/10.1063/1.1338490

43 Teles, L. K., Furthmuller, J., Scolfaro, M. R., Leite, J. R., & Bechstedt, F. (2001). Phase separation and ordering in group-III nitride alloys. *Phys. Rev. B,* 63, 085204. DOI: 10.1590/S0103-97332004000400014

44 Kim, K., Limpijumnong, S., Rambrecht, W. R. L., & Segall, B. (1997). Elastic constants and related properties of tetrahedrally bonded BN, AlN, GaN, and InN. *Phys. Rev. B,* 449, 929. DOI:https://doi.org/10.1103/PhysRevB.53.16310

45 Wu, X., Walter, E. J., Rappe, A. M., Car, R., & Selloni, A. (2009). Hybrid density functional calculations of the band gap of GaxIn1−xN. *Phys. Rev. B,* 80, 115201. DOI:https://doi.org/10.1103/PhysRevB.80.115201

46 Hafner, J. (2008). Ab-initio simulations of materials using VASP: Density-functional theory and beyond. *J. Comput. Chem.*, 29, 2044. DOI:10.1002/jcc.21057

47 Marsman, M., Paier, J., Stroppa, A., & Kresse, G. (2008). Hybrid functionals applied to extended systems. *J. Phys. Condens. Matter*. 20, 064201. DOI: 10.1088/0953-8984/20/6/064201

48 McCluskey, M. D., Van de Walle, C. G., Romano, L. T., Krusor, B. S., & Johnson, N. M. (2003). Effect of composition on the band gap of strained InxGa1ÀxN alloys. *J. Appl. Phys.,* 93, 4340. DOI: 10.1063/1.1560563

49 Caetano, C., Teles, L. K., Marques, M., & Dal Pino, A., Ferreira, Jr., L. G. (2006). Phase stability, chemical bonds, and gap bowing of InxGa1−xN alloys: Comparison between cubic and wurtzite structures. *Phys. Rev. B,* 74, 045215. https://doi.org/10.1103/PhysRevB.74.045215

50 Gorczyca, I., Suski, T., Christensen, N. E., & Svane, A. (2010). Limitations to band gap tuning in nitride semiconductor alloys. *Appl. Phys. Lett.,* 96, 101907. https://doi.org/10.1063/1.3357419

51 Gorczyca, I., Lepkowski, S. P., Suski, T., Christensen, N. E., & Svane, A. (2009). Band gap bowing in quaternary nitride semiconducting alloys. *Phys. Rev. B,* 80, 075202. https://doi.org/10.1063/1.3597795

52 Van de Walle, C. G., McCluskey, M. D., Master, C. P., Romano, L. T., & Johnson, N. M. (1999). Large and composition-dependent band gap bowing in $In_xGa_{1-x}N$ alloys. *Mat. Sci. Eng. B-Adv.,* 59, 274. https://doi.org/10.1016/S0921-5107(98)00340-7

53 Chantis, A. N., Van Schilfgaarde, M., & Kotani, T. (2006). Ab Initio Prediction of Conduction Band Spin Splitting in Zinc Blende Semiconductors. *Phys. Rev. Letters,* 96, 086405. doi:10.1103/PhysRevLett.96.086405

54 Petkov, V., Gateshki, M., Choi, J., Gillan, E. G., & Ren, Y. (2005). Structure of nanocrystalline GaN from X-ray diffraction, Rietveld and atomic pair distribution function analyses. *J. Mater. Chem.*, 15, 4654. DOI https://doi.org/10.1039/B509577H

55 Matsuoka, T., Okamoto, H., Nakao, M., Harima, H., & Kurimoto E. (2002). Optical bandgap energy of wurtzite InN. *Appl. Phys. Lett.* 81, 1246. https://doi.org/10.1063/1.1499753

56 Davydov, V. Y., Klochikhin, A. A., Emtsev, V.V., Kurdyukov, D. A., Ivanov, S. V., & Vekshin, V. A. et al. (2002). Band Gap of Hexagonal InN and InGaN Alloys. *J. Phys. Status Solidi B Basic Res.*, 234, 787. https://doi.org/10.1002/1521-3951(200212)234:3<787::AID-PSSB787>3.0.CO;2-H Изменила название учитывая смысл: Selection inoculated additives for modifying nickel alloys ---> Selection of inoculant additives for modifying nickel alloys

Т. Инербаев, Т. Матсиока, И. Кавазое

$In_xGa_{1-x}N$ вуртциттегі оптикалық жолақ саңылауының энергия мәндері

InN тар тыйым салынған аймақ жергілікті тығыздыққа жақындағанда немесе жалпыланған градиент жақындағанда (*LDA* немесе *GGA*) есептеулер жартылай өткізгіштің орнына заттың металдық күйін болжайтын белгілі мысал болып табылады. Бұл жұмыста зерттелетін жүйелердің геометриясын оңтайландыру үшін тығыздық функционалының әртүрлі әдістері қолданылды және бұл сандық нәтижелер феноменологиялық параметрлерсіз тыйым салынған аймақ енінің мәнін бағалау кезінде болуы мүмкін *GW* әдісімен кейінгі есептеулер үшін кіріс мәндері ретінде пайдаланылды. *LDA* комбинациясын GW_0 есептеулерімен немесе гибридті функционалды GW_0 өзіне сәйкес келетін жуықтауымен пайдалану зерттелген *GaN* және *InN* қосылыстары үшін жеткілікті дәл теориялық нәтижелер беретіні анықталды. Мұндай есептеулер әлі де компьютердің көп уақытын қажет ететініне қарамастан, есептеу құнының төмен болуына байланысты, бірінші әдіс $In_xGa_{1-x}N$ үштік қорытпаларындағы барлық диапазондағы электрондық құрылымды кез келген реттеу параметрлерінсіз есептеудің сынақ әдісі ретінде таңдалды. $In_xGa_{1-x}N$ үштік қорытпасының нақты теориялық зерттеулері *LDA* GW_0 жуықтау комбинациясында орындалды. Нәтижесінде теориялық және эксперименттік нәтижелер арасында өте жақсы келісім алынды, сонымен қатар тыйым салынған аймақтың енін *x* функциясы ретінде иілу квадраттық функцияны қолдана отырып, *x*-ге тәуелді емес, 1,85 эВ параметрімен жақсы жақындастыруға болатындығы көрсетілген, бұл соңғы эксперименттік нәтижелерге жақын.

Кілт сөздер: $In_xGa_{1-x}N$ қорытпалары, тығыздықтың функционалдық теориясы, GW_0 модельдеу, жолақ құрылымы, иілу параметрі, жолақ саңылауын орнату, үштік қорытпа.

Т. Инербаев, Т. Матсиока, И. Кавазое

Значения энергии оптической запрещенной зоны в вюрците $In_xGa_{1-x}N$

Узкая запрещенная зона *InN* представляет собой известный пример, когда расчеты в приближении локальной плотности или приближении обобщенного градиента (*LDA* или *GGA*) предсказывают металлическое состояние вещества вместо полупроводникового. В настоящей работе для оптимизации геометрии исследуемых систем применены различные методы функционала плотности, и эти численные результаты использованы в качестве входных значений для последующих вычислений методом *GW*, которые могут быть при оценке значения ширины запрещенной зоны без феноменологических параметров. Установлено, что применения комбинации *LDA* с GW_0 расчетами или гибридного функционала с самосогласованным GW_0 приближением дают достаточные точные теоретические результаты для обоих исследованных соединений *GaN* и *InN*. Хотя такие расчеты по-прежнему занимают очень много компьютерного времени, из-за меньшей вычислительной стоимости первый метод выбран в качестве пробного для расчета электронной структуры во всем диапазоне в тройных сплавах $In_xGa_{1-x}N$ без каких-либо подгоночных параметров. Настоящие теоретические исследования тройного сплава $In_xGa_{1-x}N$ были выполнены в комбинации *LDA* с GW_0 приближением. В результате получено очень хорошее согласие между теоретическими и экспериментальными результатами, а также показано, что изгиб ширины запрещенной зоны как функции *x* можно хорошо аппроксимировать с помощью квадратичной функции с постоянным, не зависящим от *x*, параметром, равным 1,85 эВ, что близко к последним экспериментальным результатам.

Ключевые слова: сплавы $In_xGa_{1-x}N$, теория функционала плотности, моделирование GW_0, зонная структура, параметр изгиба, настройка запрещенной зоны, тройной сплав.