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First Principles DFT + *U* Calculations of the Electronic Properties of ZnO/GaN Heterostructure

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ZnO/GaN heterostructures are promising systems for solar cells, light-emitting diodes and photocatalytic applications due to their appropriate band gaps that correspond to the wavelength range of visible light and thus have attracted wide attention over the past ten years. In this study, investigations of structural and electronic properties of bulk ZnO, GaN and ZnO/GaN superlattice have been performed based on first-principles calculations within the density functional theory. For a more accurate description of the electronic properties of bulk semiconductor crystals, Hubbard correction to generalized gradient approximation (GGA + *U*) was applied. The obtained results show that this calculation method allows to obtain reliable band edge positions, which are the defining parameters in determining the average electrostatic potential of each bulk material. Also, the use of the GGA + *U* method allows obtaining the lattice mismatch of bulk ZnO and GaN within no more than 0.5 % compared with experimental results, which confirms once again the reliability of this method. It should be noted not only good accuracy of the obtained results but also low computational and time costs when using the GGA + *U* method. For calculations of structural and electronic properties of ZnO/GaN heterostructure, the same method as for bulk crystals was used. Based on the obtained band diagram of heterojunction, the band offsets of ZnO/GaN heterostructure were determined. We have verified that these band offsets are in very good agreement with previous experimental and theoretical results. Thus, we obtained a highly efficient method for calculating the band offsets of ZnO/GaN heterostructure that produces fine accuracy at a rational computational expense.

Keywords: Band gap, Heterostructure, Electronic properties, Density functional theory, Band offset.

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1. INTRODUCTION

Semiconductor heterostructures are the object of intensive research attempts due to their important applications in technology, in particular solar cells, photocatalysis, and light-emitting diodes [1]. From this point of view, ZnO and GaN are perspective materials for such applications. They both have the same structure of wurtzite and slightly different band gaps of 3.43 eV (ZnO) and 3.50 eV (GaN) [2]. Also, pristine ZnO and GaN demonstrate piezoelectric properties and spontaneous polarization [2]. The difference between the band gaps of the two materials leads to a discontinuity of the energy levels at the interface of the heterostructure. This discontinuity, in other words, band offset, adjusts the carrier transport properties and is the crucial component for the implementation of a heterostructure. Hence, for ZnO/GaN heterostructures appliances, knowledge of band offsets is of special importance. Appreciable attempts have been made to establish this parameter both experimentally [3, 4] and theoretically [5], but these experimental studies show completely different values. For instance, Hong et al. determined the valence band offset at ZnO/GaN (0001) heterostructure using ultraviolet and X-ray photoemission spectroscopy (UPS/XPS), and the measured valence band offset was 0.8-1.0 eV [3]. Veal et al. measured the valence band offset of ZnO/GaN heterostructures using the transitivity rule of the natural band offsets between III-V and II-IV compounds. Their XPS data show a valence band offset value of 1.37 eV [4]. McDermott et al. [6] estimated ZnO/GaN solid solution systems and suggested a 1.6 eV band offset between ZnO and GaN compounds in such systems.

Besides the experimental attempts, density functional theory (DFT) calculations have an important role in understanding the process of the band offset of GaN/ZnO heterostructures. Usually, the electronic structure of ZnO/GaN heterostructures was calculated using the local density approximation (LDA) and the generalized gradient approximation (GGA). However, as known both LDA and GGA have the underestimation of the band gap of strongly correlated semiconductors. Earlier works [7] have shown that in both ZnO and GaN the band gap mainly results from interactions between the anion 2*p*-states and the cation 4*s* states. Particularly for ZnO, the Zn 3*d*-states are mixed strongly with the O 2*p*-states shifting up the valence band maximum and resulting in an underestimation of the calculated value of the band gap. These strong 2*p*-3*d* couplings represent especially difficult disagreement for standard LDA and GGA calculations and thus complicate the calculations of the electronic properties of ZnO/GaN heterostructures from first principles.

A popular strategy to fix this underestimation of the band gap is to use the hybrid functionals that combine the exact exchange from Hartree-Fock theory with the exchange calculated from some standard density-based

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approximation, exploiting reliable methods like PBE0, B3LYP or HSE. Di Valentin [8] has presented that using the hybrid B3LYP functional is a good DFT method for describing ZnO/GaN compound. However, obtained parameters are not optimal for the study of bulk ZnO and GaN materials. Yu [9] also modified the exchange functional of B3LYP to receive better accordance with band gaps of ZnO and GaN. Weston at al. [10] carried out a systematic study of the features that regulate the accuracy of heterostructure band alignments. Band alignments for a number of typical test structures using the GGA method or the most accurate hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) are calculated. They found that GGA demonstrates large errors in the location of the eigenvalues at the band extreme point corresponding to the average electrostatic potential and, as a result, all GGA band alignments are questionable. Using the HSE method leads to much more accurate band produce than GGA. However, the problem of using hybrid methods such as HSE or B3LYP is considerable time cost of computations.

Another alternative could be the DFT + U approximation, which empirically fixes the problem of delocalization of electrons. Previous studies for ZnO demonstrate the influence of correcting localization of not only Zn 3d-states but also O 2p-states described by parameters U_d for Zn and U_p for O [11]. Relevant scheme of U_d and U_p values has been shown to correct the calculated electronic structure to experimental data for both the energy band gap of 3.4 eV and the energy position of Zn 3d states, the location of them was overestimated in the GGA method.

Also, as known the valence band maximum (VBM) and the conduction band minimum (CBM) of GaN are mostly provided by N 2p-states, and Ga 3d-states are placed near the bottom of the valence band, about 10 eV below the VBM. So, the band gap is more reactive to the U_p N parameter. Lei at al. [12] used corrections of the on-site Coulomb interaction on the anion 2p and the cation 3d electrons and found that the GGA + U approximation can quite correct the underestimation of band gap of both ZnO and GaN.

In this paper, we presented the study of the electronic structure of ZnO/GaN heterostructure by applying DFT + U methods. We also compared the results of our calculations with the appropriate results obtained using hybrid functional, especially B3LYP and HSE, to determine optimal parameters for ZnO/GaN heterostructure, in particular, valence band offset.

2. COMPUTATIONAL DETAILS

For DFT calculation, we use the GGA approach based on the exchange-correlation potential of Perdew-Burke-Ernzerhof implemented in the QUANTUM-ESPRESSO package [13] with the Hubbard U correction [14]. We perform a plane-wave basis set with a cutoff energy of 400 eV and ultrasoft pseudopotentials. The Monkhorst and Pack scheme of k-point sampling for integration on the Brillouin zone was used. This calculation methodology has been successfully used for the investigation of the structural and electronic properties of ZnO nanostructures with different dimensions [15-18].

Both structures ZnO and GaN belong to the hexagonal space group P63mc. Band structures of bulk materials were calculated along the special high-symmetry points: G (0, 0, 0), A (0, 0, 0.5), H (0.333, 0.333, 0.5), K (0.333, 0.333, 0), M (0.5, 0, 0) and L (0.5, 0, 0.5) in the k-space.

To model nonpolar ($1\bar{1}00$) ZnO/GaN heterostructures, a slab model was applied, in which a restricted number of crystal layers in a three-dimensional periodic cell were modeled. After complete geometry optimization of slabs, band structure (BS) and density of states (DOS) were calculated.

For determining the band offsets, the scheme proposed by Van de Walle and Martin and Baldereschi et al. was performed. In addition to this scheme, the valence band offset (ΔE_{VBO}) of ZnO/GaN heterostructure can be represented as

$$\Delta E_{VBO} = \Delta V + (E_{VBM} - \overline{\overline{V}})_{ZnO} - (E_{VBM} - \overline{\overline{V}})_{GaN}\,, \quad (1)$$

where ΔV is the difference of average macroscopic electrostatic potential between two components of ZnO/GaN heterostructure, $(E_{VBM} - \overline{\overline{V}})$ corresponds to the electronic position of the VBM relative to the average electrostatic potential in bulk ZnO and GaN, respectively.

The average macroscopic electrostatic potential $\overline{\overline{V}}(z)$ was derived from the planar-averaged electrostatic potential $\overline{V}(z)$ across the interface ZnO/GaN, which is obtained using the following expression:

$$\overline{V}(z) = \frac{1}{S}\int_S V(\mathbf{r})dxdy\,, \quad (2)$$

where S is the area of the xy-surface of the unit cell.

The planar-averaged potential distribution demonstrates periodic oscillations along the z-axis due to the spatial distribution of electrons and ion cores. We remove these oscillations by calculating the macroscopic averaged potential $\overline{\overline{V}}(z)$ by averaging $\overline{V}(z)$ at each point in the interval corresponding to one oscillation period L

$$\overline{\overline{V}}(z) = \frac{1}{L}\int_{-L/2}^{L/2} \overline{V}(z')dz'\,. \quad (3)$$

Except for ΔE_{VBO}, we also can obtain the conduction band offset (ΔE_{CBO}) based on the band gap values calculated for bulk ZnO and GaN. The described above algorithm for calculating ΔE_{VBO} and ΔE_{CBO} was successfully applied in the case of a nonpolar interface of heterostructures such as GaN/ZnO [19], BN/C [20], AlN/GaN, AlP/GaP, AlAs/GaAs, Ge/Si, HfO_2/ZrO_2 [10].

3. RESULTS AND DISCUSSION

First of all, we performed relaxation of bulk ZnO and GaN crystal structures for search equilibrium lattice parameters for both structures.

It is known that the first-principles calculations predict a small error (~ 1 %) for the lattice parameter compared with experimental data [2]. If the experimental lattice parameters are applied to realization of the first-

principles calculations without any correction, for example, ZnO unit cell exposed to an undesired strain, this leads to errors in the calculation of the piezoelectric properties. As mentioned above, there is a dependence of the band gap on the Hubbard U parameter. In this study, we applied two parameters for Hubbard U parameter: U_d for Zn 3d or Ga 3d states and U_p for O 2p or N 2p states. Hence, by combining the two quantities, the lattice parameter and band gap, the exceptional values of U_d and U_p could be clearly determined.

Firstly, we investigated the bulk ZnO structure. Based on previous theoretical research [11, 12], we used several tens of combinations of U_d and U_p parameters in the ranges from 5 to 11 eV for U_d and from 4 to 8 eV for U_p. Complete optimization of the crystal structure of ZnO for the whole set of values was performed. For bulk ZnO, optimal parameters of U_d and U_p are 10 eVand 7 eV, respectively.

Calculated values of the band gap and lattice parameters for bulk ZnO are presented in Table 1. Using these parameters, BS (Fig. 1) and DOS (Fig. 2) were also calculated. The calculated total and partial DOS were subjected to Gaussian smearing, which takes into account the experimental separation and effects associated with the lifetime of excited electrons.

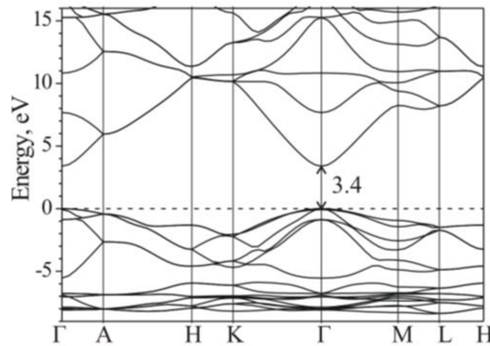

Fig. 1 – The band structure of bulk ZnO. The horizontal dash line is displayed at the Fermi level

Table 1 – Comparison of calculated lattice parameters and energy band gaps of bulk ZnO and GaN after structure optimization with other calculations and experiments

Compound	method	a, Å	c, Å	E_g, eV	Ref.
ZnO	GGA	3.259	5.218	0.78	[11]
	GGA + U	3.245	5.210	3.4	this work
	HSE	3.250	5.267	2.828	[10]
	Exp.	3.249	5.204	3.43	[2]
GaN	GGA	3.245	5.296	1.45	[9]
	GGA + U	3.201	5.211	3.51	this work
	B3LYP	3.256	5.268	3.40	[9]
	Exp.	3.190	5.190	3.50	[2]

As can we see from Fig. 1 and Table 1, the value of the band gap of ZnO is 3.4 eV that completely agrees with previous both experimental and theoretical results [2, 11].

Analysis of the total and partial DOS (Fig. 2) shows that the top of the valence band is formed mainly of Zn 4s-states and O 2p-states contributions, while the bottom of the conduction band is composed by mixture of Zn s- and p-states (Fig. 2b, c).

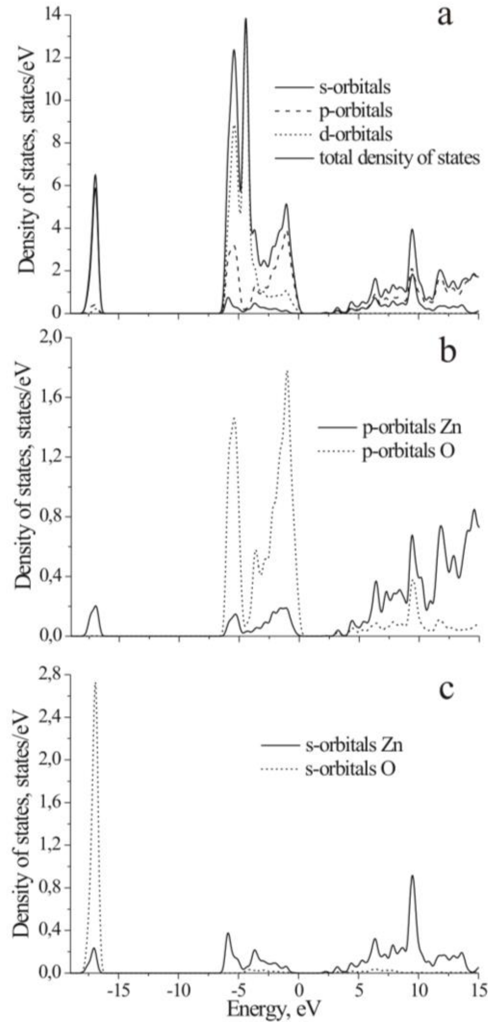

Fig. 2 – The total (a) and partial (b, c) DOS of bulk ZnO

Lattice parameters of ZnO calculated using the GGA + U method are no more 0.2 % different than the experimental parameters (see Table 1). A comparison of these parameters with lattice parameters received by other theoretical approximations that are presented in Table 1 shows more accurate values obtained for bulk ZnO. Good agreement between theoretical and experimental results once again confirms the effectiveness of the GGA + U method.

Next, we searched for optimal Hubbard U parameters for the bulk structure of GaN. Using the same approach considered above we established the values of $U_d = 10$ eV and $U_p = 5.5$ eV for bulk GaN. Applying obtained parameters, BS and DOS were also calculated which are displayed in Fig. 3. The obtained band gap and equilibrium lattice parameters of bulk GaN are presented in Table 1.

We can see from Fig. 3 and Table 1 that E_g is 3.51 eV and, as in the case ZnO, we obtained results that agree with the previous experimental and theoretical data [2, 9]. The calculated lattice parameters of GaN indicate an error by approximately 0.4 % compared with experimental parameters of the unit cell [9].

To establish the genesis of the top of the valence band and bottom of the conduction band, we proceed to consider the distribution of the total and partial DOS

(Fig. 4) of GaN. The top of the valence band composed generally by N p-states and Ga p-states. The states near the bottom of the conduction band are mainly formed by Ga sp-orbitals and N s-orbitals (Fig. 4b, c).

The intensive peak in the region − 17.2 eV (Fig. 4a) corresponds to the 3d-states of Ga atom with the contribution of N 2s-states. The bands in the range of – 15-10 eV correspond to the mixture of Ga and N s-states (Fig 4c).

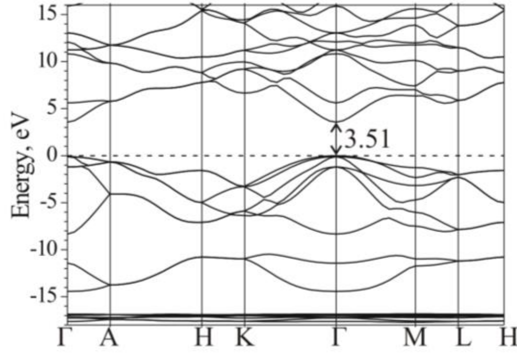

Fig. 3 – The band structure of bulk GaN. The horizontal dash line is displayed at the Fermi level

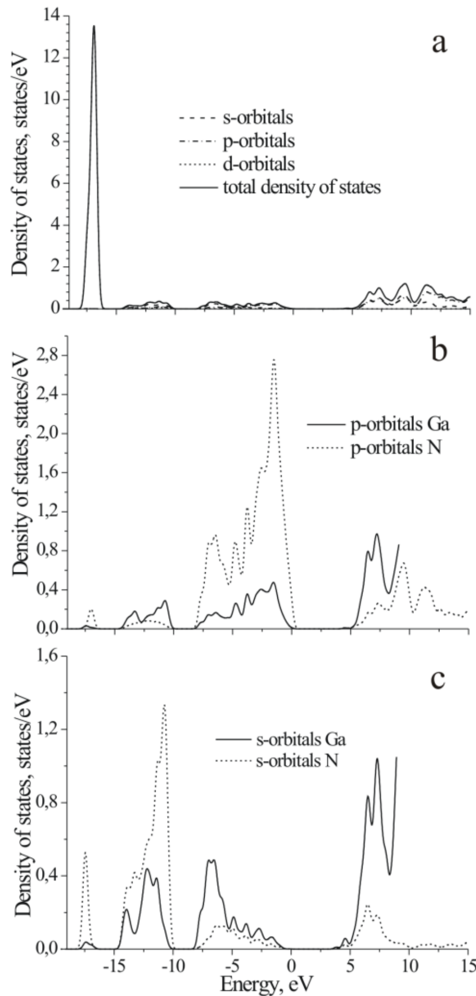

Fig. 4 – The total (a) and partial (b, c) DOS of bulk GaN

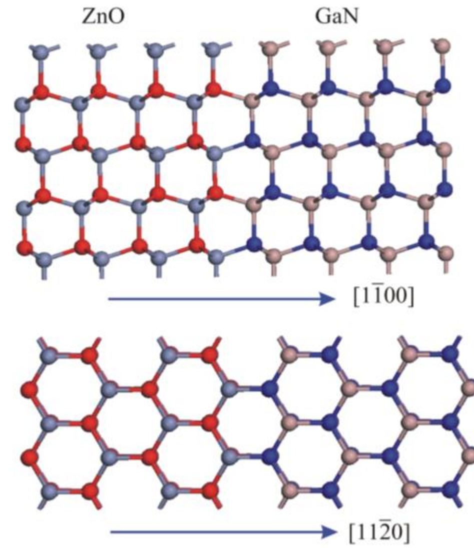

Fig. 5 – The structure of ZnO/GaN superlattice after geometry optimization. Grey, red, pink and blue balls represent Zn, O, Ga and N atoms, respectively

After the study of bulk ZnO and GaN, we investigated the heterostructure based on them. To describe ZnO/GaN heterostructure, we consider that ZnO is deposited on GaN. That is, GaN is the substrate and the band structure of GaN is calculated for equilibrium geometry.

Fig. 5 represents the structural supercell model of ZnO/GaN heterostructure which was composed of four bilayers of both compounds ZnO and GaN, respectively. To model a pseudomorphic heterojunction, the lattice parameters of ZnO in the plane of contact with GaN are chosen the same as those of the substrate material, while the other lattice parameters are optimized by the procedure of finding the equilibrium state of the heterosystem.

Fig. 6 shows the distribution of the planar-averaged potential across the ZnO/GaN interface obtained using equation (2). The electrostatic potential shift $\Delta V = 1.84$ eV is obtained from the figure. The corresponding values of the energy location of the top of the valence band are $(E_{VBM} - \overline{\overline{V}})_{ZnO} = 0.82$ eV and $(E_{VBM} - \overline{\overline{V}})_{GaN} = 4.02$ eV, respectively. Then, the valence band offset received using the GGA + U method is 1.36 eV. The corresponding conduction band offset is 1.49 eV.

Fig. 7 displays a schematic band diagram of ZnO/GaN heterojunction.

Table 2 – The valence band offsets (ΔE_{VBO}), and each component of the valence band offsets in Eq. (1) is obtained by using different functionals. The energies are in eV

Parameters / Method	E_{VBM}(ZnO)	E_{VBM}(GaN)	ΔE_{VBO}	ΔV
GGA [10]	0.924	− 0.632	0.27	1.329
GGA + U [this work]	0.818	4.02	1.36	1.84
mod-HSE [19]	– 0.33	3.258	1.588	2.03
PBE + U [19]	1.063	3.808	0.745	2.00
HSE [10]	2.525	1.946	1.28	1.329
Experiment [4]			1.37	

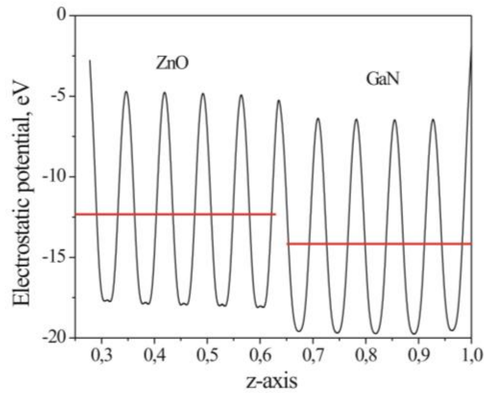

Fig. 6 – Profile of planar-averaged (oscillating curve) and macroscopic-averaged (horizontal lines) electrostatic potential at the ZnO/GaN interface

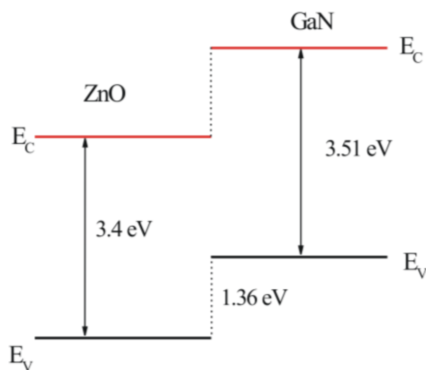

Fig. 7 – Schematic band diagram of ZnO/GaN heterostructure

The results of our calculations compared to the results of other theoretical calculations and experimental data are summarized in Table 2. As can be seen from this table, there is a very good correlation of our results with both theoretical and experimental data. It should also be noted that the use of the GGA + *U* method not only leads to a good agreement with the experiment but also is a much less time-consuming method compared with hybrid methods such as HSE and B3LYP.

4. CONCLUSIONS

Thus, using DFT calculation, we performed the investigation of structural and electronic properties of bulk ZnO, GaN and ZnO/GaN heterostructure constructed based on their basis. Also, we analyzed a methodology for calculating band offsets at the ZnO/GaN interfaces which lead to good accuracy for acceptable computational and time costs. The band structures of bulk ZnO and GaN were calculated applying the GGA method with Hubbard correction, so-called GGA + *U* method that is significant to obtain credible positions of band edge for appropriate determination of their average electrostatic potential. The band offsets of ZnO/GaN heterostructure were calculated using the same method as for bulk semiconductors. Analysis of calculation results shows very good agreement with experimental data and previous theoretical results indicating the reliability of the investigation method. Thus, the use of the GGA + *U* method allows achieving high accuracy of band structure and band offsets calculations at reasonable computational expense compared with very popular hybrid methods, in particular, HSE or B3LYP.

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Розрахунки з перших принципів електронних властивостей гетероструктур на основі ZnO/GaN

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Гетероструктури на основі ZnO/GaN є перспективними матеріалами для сонячних елементів, світлодіодів та фотокаталітичних пристроїв завдяки ширині забороненої зони базових сполук, з яких сформована гетероструктура, що відповідає довжині видимого світла, і привертають значну увагу дослідників протягом останніх десяти років. В цьому дослідженні ми представляємо результати розрахунків з перших принципів, в межах теорії функціонала густини, структурних та електронних властивостей об'ємних кристалів ZnO, GaN, а також гетероструктури на їхній основі. З метою точнішого опису електронних властивостей досліджуваних об'єктів використано наближення узагальненого градієнта з поправками Габбарда (GGA + *U*). Отримані результати розрахунків для об'ємних кристалів ZnO та GaN показують відмінне узгодження експериментальних даних з результатами наших теоретичних розрахунків щодо енергетичного положення основних смуг в кристалах, розміщення яких є визначальним для точного визначення усередненого електростатичного потенціалу. Розрахунки параметрів ґратки з використанням методу GGA + *U* показують відхилення від експериментальних даних в межах 0,5 %, що підтверджує надійність цього методу. Також слід відмітити не лише точність отриманих результатів, а й низьку ресурсозатратність цього методу в порівнянні з, наприклад, гібридними методами. Оптимізацію структури та електронні властивості гетероструктури ZnO/GaN розраховано тим самим методом, що й для об'ємних кристалів. На основі отриманої зонної діаграми гетеропереходу визначено відносні розриви електронних зон гетероструктури ZnO/GaN. Проведений аналіз отриманих результатів показує відмінне узгодження з даними експериментів і попередніх теоретичних розрахунків. Таким чином, ми отримали високоефективний метод розрахунку відносних розривів електронних зон гетероструктури ZnO/GaN, який дає високу точність при раціональній ресурсозатратності.

Ключові слова: Заборонена зона, Гетероструктура, Електронні властивості, Теорія функціонала густини, Розрив зони.