Wiley Online Library
Early View publication on www.wileyonlinelibrary.com
(issue and page numbers not yet assigned;
citable using Digital Object Identifier – DOI)

Phys. Status Solidi C, 1–5 (2014) / DOI 10.1002/pssc.201300756

physica status solidi c
www.pss-c.com
current topics in solid state physics

Ab initio study of macroscopic polarization of AlN, GaN and AlGaN

Irina Supryadkina[*,1,2], Karine Abgaryan[1], Dmitry Bazhanov[1,2], and Ilya Mutigullin[1]

[1] Dorodnicyn Computer Center of RAS, Vavilov st. 40, 119333 Moscow, Russia
[2] M.V. Lomonosov Moscow State University, Faculty of Physics, GSP-2, Leninskie Gory, 119991 Moscow, Russia

Received 21 November 2013, accepted 26 November 2013
Published online 20 January 2014

Keywords ab initio study, III-V nitrides, spontaneous and piezoelectric polarizations

[*] Corresponding author: e-mail supryadkina@gmail.com

In this work we report the results of theoretical study based on first-principles calculations of the polarization properties of semiconductors AlN, GaN and AlGaN with wurtzite structure. The values of the spontaneous and the piezoelectric polarizations and the piezoelectric constants were calculated for these nitride compounds. We study the nonlinear dependence of the spontaneous polarization on AlGaN composition.

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction III-V nitrides and their alloys are promising system for semiconductor applications, such as high-frequency light emitting devices and high-power transistors [1]. The macroscopic polarization, which is determined by the sum of the spontaneous and piezoelectric polarizations in the absence of external fields, exerts a substantial influence on the characteristics of semiconductor heterostructures. The macroscopic polarization leads to emergence of built-in electrostatic fields and charge accumulation at heterointerfaces [2]. This causes the motion limit of electrons in one direction and the formation of two-dimensional electron gas (2DEG).

III-V nitrides with wurtzite structure possess the large spontaneous polarization and piezoelectric constants [3] and the large macroscopic polarization respectively. Thus the charge density reaches high values at the interfaces of considered nitride semiconductor. Besides it was shown in works [4, 5] that the polarization of AlGaN doesn't follow Vegard's law and depends nonlinear on alloy composition strongly.

In this work we report the theoretical study of the spontaneous and piezoelectric polarizations of AlN, GaN, AlGaN, and the charge density at interfaces based on these structures.

2 Method All the calculations presented in this article were performed in the framework of DFT using the Berry phase approach [6, 7]. DFT calculations were carried out using both the local density approximation (LDA) and generalized gradient approximation (GGA) of exchange-correlation functional. Our calculations were performed using Vienna *Ab-initio* Simulation Package (VASP) [8, 9] based on pseudopotentials and a plane-wave basis set to solve the Kohn–Sham equations with periodic boundary conditions. The cutoff energy of plane waves was chosen to be 450 eV. The relaxation process was stopped when the residual force acting on each atom in the structure was less than 0.001 eV/Å.

Periodic cells with 4 atoms were taken to describe the AlN and GaN, and supercells containing 48 and 32 atoms were considered to describe $Al_{0.33}Ga_{0.67}N$ and $Al_{0.5}Ga_{0.5}N$ respectively. The Monkhrost-Pack scheme was used for k-point sampling over the irreducible part of the Brillouin zone [10]. We used the k-point mesh grid 8×8×8 for AlN and GaN, 4×4×3 for $Al_{0.5}Ga_{0.5}N$ and 4×4×2 for $Al_{0.33}Ga_{0.67}N$.

According to the modern theory proposed by R. D. King-Smith, D. Vanderbilt and R. Resta the spontaneous polarization is not determined by the absolute value of the dipole moment averaged over the volume and only the difference in polarization ΔP that occurs during some physical process has physical meaning [11]. Thus, the calculated values of the spontaneous polarization are reported relative to some reference structure with the value of polarization which is assumed to be zero. To find a reference value of polarization we used an ideal wurtzite ionic model [3, 12], where Al(Ga) and N atoms are replaced by point charges with the values $+3e$ and $-3e$, respectively with internal pa-

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

rameter u = 3/8 defined as anion-cation bond length along the [0001] axis in units of c. The polarization in this model is calculated using the formula:

$$P_{model} = -ec4V \quad (1)$$

where e is the elementary charge of an electron, c the cell parameters along the [0001] axis, V the volume of the unit cell.

Piezoelectric polarization occurs due to the mismatch of the lattice constants at the heterointerfaces and is determined by the formula [3, 13, 14]:

$$P_{pz} = e_{33}\varepsilon_3 + e_{31}(\varepsilon_1 + \varepsilon_2) \quad (2)$$

where e_{33} and e_{31} are piezoelectric constants, $\varepsilon_3 = (c - c_0)/c_0$ is the strain along the c axis, and the in-plane strain $\varepsilon_1 = \varepsilon_2 = (a - a_0)/a_0$.

We assume that AlN and AlGaN are growing pseudomorphically on GaN and thus lattice parameters of the strained AlN and AlGaN in basal plane are equal to the lattice parameter of structure GaN (a(AlN) = a(AlGaN) =a(GaN)) [13].

3 Results and discussions

3.1 Spontaneous polarization At the first we have considered the binary nitrides GaN and AlN with wurtzite structures. In order to determine more appropriate approximations, we calculated the structural parameters and spontaneous polarization using GGA and LDA. The interaction between ions and electrons was described using ultrasoft pseudopotentials (US-PP) and the projector augmented wave method (PAW-method). The obtained results for AlN are presented in Table 1 and for GaN in Table 2. The comparison of these values with another theoretical results [15] and with available experimental data [16, 17] is also shown. The received results for the lattice constant (a), ration of lattice constant along the [0001] axis to the constant in the basal plane (c/a-ration) and internal parameter Δu ($\Delta u = u - u_{ideal}$) are close to experimental results [16, 17]. Moreover the calculated values of the structural parameters and the spontaneous polarization are in good agreement with the results of other theoretical work [15]. Thus used a computational scheme allows to describe the nitride structural properties with sufficiently accuracy. It can be noticed from the tables that structural parameters obtained in GGA approximation has a smaller deviation from the experimental data than the parameters obtained with LDA approximation. Thus GGA approximation reproduced better the nitrides structure. This approximation has been used to describe the ground state properties of AlGaN.

It is well known from the works [4, 5] that the spontaneous polarization P_{sp} and the internal parameter u depend nonlinear on the microscopic structure of the alloy. The nonlinearities (i.e., non-Vegard behavior) of the spontaneous polarization and internal parameter can be described in first approximation by parabolic model with bowing parameter as [4, 5]:

$$Y(A_xB_{1-x}N) = x\,Y(AN) + (1-x)\,Y(BN) - b_{AB}x(1-x) \quad (3)$$

where x is molar fraction of element A and the bowing parameter b_{AB} is defined by the equation:

$$b_{AB} = 2Y(AN) + 2Y(BN) - 4Y(A_{0.5}B_{0.5}N) \quad (4)$$

Table 1 Results of calculation of the lattice constant in the basal plane (a), c/a-ratio, internal parameter ($\Delta u = u - u_{ideal}$) and spontaneous polarization of AlN.

AlN	a, Å	c/a	$\Delta u \cdot 10^{-3}$	P_{sp}, C/m^2
Present (LDA-US)	3.083	1.6015	7.0	-0.097
Present (LDA-PAW)	3.088	1.6002	7.0	-0.097
Theory (LDA-US) [15]	3.07	1.5997	7.1	-0.099
Present (GGA-US)	3.122	1.6041	6.6	-0.090
Present (GGA-PAW)	3.123	1.6031	6.5	-0.090
Theory (GGA-US) [15]	3.108	1.6033	6.4	-0.090
Experiment [16,17]	3.1106	1.6008	7.1	-

Table 2 Results of calculation of the lattice constant in the basal plane (a), c/a-ratio, internal parameter ($\Delta u = u - u_{ideal}$) and spontaneous polarization of GaN.

GaN	a, Å	c/a	$\Delta u \cdot 10^{-3}$	P_{sp}, C/m^2
Present (LDA-US)	3.144	1.6302	1.5	-0.031
Present (LDA-PAW)	3.150	1.6303	1.4	-0.030
Theory (LDA-US)[15]	3.131	1.6301	1.6	-0.032
Present (GGA-US)	3.207	1.6297	1.8	-0.033
Present (GGA-PAW)	3.209	1.6296	1.6	-0.032
Theory (GGA-US) [15]	3.197	1.6297	1.9	-0.034
Experiment [16,17]	3.189	1.6263	2	-

Using the theoretical approach described above we have calculated the spontaneous polarization and the internal parameter of $Al_{0.5}Ga_{0.5}N$ alloys (presented in Table 3) in order to determine the bowing parameter of the spontaneous polarization $P_{sp}(Al_xGa_{1-x}N)$ and internal parameter $u(Al_xGa_{1-x}N)$ as a function of x. The spontaneous polarization of AlGaN is given by

$$P_{sp}(Al_xGa_{1-x}N) = -0.090x - 0.032(1-x) + 0.039x(1-x) \quad (5)$$

and the internal parameters is defined by

$$u(Al_xGa_{1-x}N) = 0.3815x + 0.3766(1-x) - 0.0026x(1-x) \quad (6)$$

The dependencies of the spontaneous polarization P_{sp} and internal parameter of $Al_xGa_{1-x}N$ on molar fraction x are shown in Fig. 1(a, b).

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Contributed
Article

Table 3 Results of calculation with GGA-PAW approximation and theoretical estimate of the lattice constant in the basal plane (a), c/a-ratio, internal parameter ($\Delta u = u - u_{ideal}$) and spontaneous polarization of AlGaN.

AlGaN	a, Å	c/a	$\Delta u \cdot 10^{-3}$	P_{sp}, C/m^2
$Al_{0.33}Ga_{0.67}N$	3.178	1.6247	2	-0.0435
$Al_{0.5}Ga_{0.5}N$	3.163	1.6213	3	-0.0512
Estimate $Al_{0.33}Ga_{0.67}N$	3.181	1.6210	2.6	-0.0425

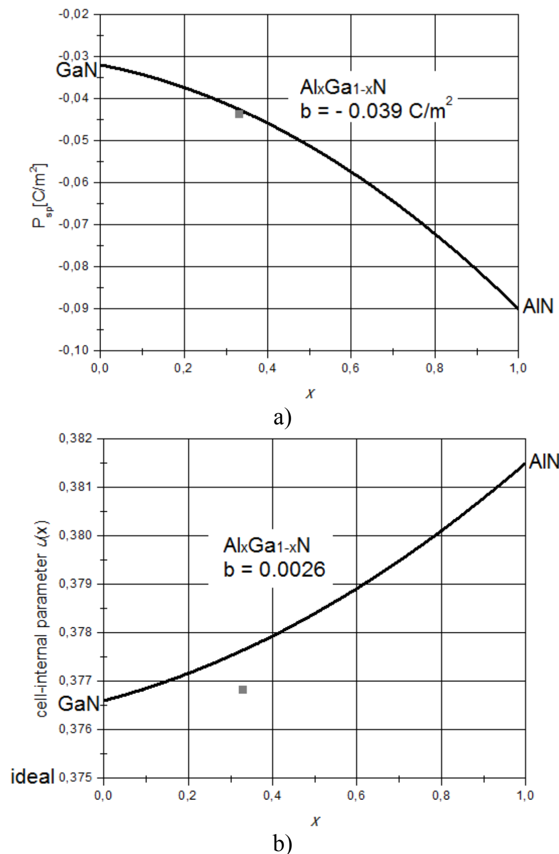

Figure 1 (a) The dependence of spontaneous polarization P_{sp} of $Al_xGa_{1-x}N$ on molar fraction x. The calculated value for $Al_{0.33}Ga_{0.67}N$ is shown by the grey point. (b) The dependence of internal parameter u of $Al_xGa_{1-x}N$ on molar fraction x. The calculated value for $Al_{0.33}Ga_{0.67}N$ is shown by the grey point.

It is known that molar fraction $x = 0.15 - 0.35$ of ternary alloy $Al_xGa_{1-x}N$ is used in the technology of the heterostructure AlGaN/GaN [18]. Therefore in our study we have used molar fraction $x = 0.33$ which belongs to this range.

Using the Vegard′s law for lattice constants a and c:

$$a(A_xB_{1-x}N) = xa(AN) + (1-x)a(BN), \quad (7)$$
$$c(A_xB_{1-x}N) = xc(AN) + (1-x)c(BN),$$

and Eqs. (5) and (6), we estimated of the lattice constant in the basal plane a, c/a-ratio, the internal parameter Δu ($\Delta u = u - u_{ideal}$) and the spontaneous polarization of $Al_{0.33}Ga_{0.67}N$. We compared the results of first-principles calculations with estimation of the structural parameters and the spontaneous polarization. These results are summarized in Table 3. One can see from the Table 3 and Fig. 1 that the structural parameters and the spontaneous polarization obtained by means of quadratic equations are in good agreement with DFT data.

3.2 Piezoelectric polarization As we noted before, in the absence of external fields the macroscopic polarization is determined by the sum of the spontaneous polarization and the piezoelectric polarization, which is caused by lattice strain at the interface. Therefore in order to determine the macroscopic polarization of AlN and AlGaN grown pseudomorphically on the GaN, the piezoelectric constants and piezoelectric polarization were calculated by means of Eq. (2). The obtained results are presented in Tables 4 and 5. One can see from Table 4 that the values of the piezoelectric constants of AlN are very close to an other theoretical calculation [19] and experimental data [20].

Table 4 Results of calculation the piezoelectric constants and the piezoelectric polarization of AlN.

AlN	e_{33}, C/m^2	e_{31}, C/m^2	e_{15}, C/m^2	P_{pz}, C/m^2
Present (GGA-PAW)	1.50	-0.60	-0.31	-0.0508
Theory (GGA-US) [19]	1.50	-0.53	-	-
Theory (LDA-US) [19]	1.80	-0.64	-	-
Experiment [20]	1.55	-0.58	-0.48	-

Table 5 Results of calculation the piezoelectric constants and the piezoelectric polarization of $Al_{0.33}Ga_{0.67}N$.

$Al_{0.33}Ga_{0.67}N$	e_{33}, C/m^2	e_{31}, C/m^2	e_{15}, C/m^2	P_{pz}, C/m^2
Present (GGA-PAW)	0.79	-0.44	-0.22	-0.0098

The comparison of the absolute values of the spontaneous and piezoelectric polarizations of these structures allows to conclude that the greater contribution to the macroscopic polarization comes from the spontaneous polarization. Besides, the piezoelectric polarization has the same sign as the spontaneous polarization. It means that these polarizations have the same directions (Fig. 2.). Thus, the piezoelectric polarization increases the macroscopic polarization.

3.3 Polarization-induced bound surface and interface charges The obtained values of the spontaneous and piezoelectric polarizations allowed to calculate the polarization-induced surface charge densities on AlN(0001), GaN(0001) and AlGaN(0001) surfaces as [5]:

$$\sigma = P_{macro} = P_{sp} + P_{pz} \quad (8)$$

 © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

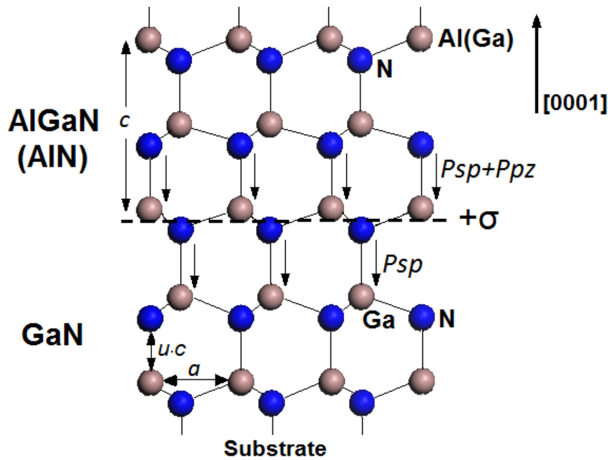

Figure 2 The crystal structure, the spontaneous and the piezoelectric polarizations, the polarization-induced charge density of AlGaN/GaN (AlN/GaN) heterostructure.

where P_{macro}, P_{sp} and P_{pz} are the macroscopic polarization, the spontaneous polarization and the piezoelectric polarization of nitride compounds respectively. The values of the bound charge densities of the nitride (Al, Ga, AlGa)N surfaces are presented in Table 6.

Table 6 Results of calculation the polarization-induced bound charges of AlN(0001), GaN(0001) and AlGaN(0001) surfaces.

Values	AlN(0001)	GaN(0001)	AlGaN(0001)
σ, C/m^2	-0.141	-0.032	-0.053
$\sigma e \cdot 10^{13}$, cm^{-2}	-8.77	-1.98	-3.33

Using the data from Table 6, the bound interface charge densities were calculated for AlN/GaN, AlGaN/AlN, AlGaN/GaN by using the formula [21]:

$$\sigma(AN/BN) = P_{macro}(BN) - P_{macro}(AN) = \sigma(BN) - \sigma(AN) \quad (9)$$

The obtained values of the bound charge densities at the different interfaces are as follows: σe (AlN/GaN) = 6.79x10^{13} cm^{-2}; σe (AlGaN/AlN) = -5.44x10^{13} cm^{-2}; σe (AlGaN/GaN) = 1.35x10^{13} cm^{-2}. Additional, the polarization-induced interface charges at AlN/GaN and AlGaN/GaN interfaces are found to be positive (see Fig. 2.). This result coincides with the result of theoretical work [5]. It should be noted that epitaxial growth of the AlN (as well as AlGaN with high molar fraction of Al) on the GaN is accompanied by various technological challenges related with large lattice mismatch (about 2%) at AlN/GaN heterostructure [22]. Therefore AlGaN/GaN heterostructure is more attractive from practical point of view.

Obtained results for the polarization-induced bound interface charges demonstrate that free electrons will accumulate in the quantum well at the interface with positive bound sheet charges, compensating positive charge density ($+\sigma$). As a consequence a 2DEG with a sheet carrier concentration close to the bound interface density $+\sigma / e$ can be formed. It should be noted that it is not necessary to dope the structure for the formation of the electron gas.

4 Summary In conclusion, we have calculated the piezoelectric constants, spontaneous and piezoelectric polarization of AlN, GaN and AlGaN within the framework of the DFT. We have obtained nonlinear interpolations of the spontaneous polarization and the internal parameter of $Al_xGa_{1-x}N$. The values calculated within the DFT are in good agreement with the values obtained using the quadratic equation. Besides we have calculated polarization-induced charge densities at the interfaces AlN/GaN, AlGaN/AlN, AlGaN/GaN. All obtained data are in good accordance with the results of other theoretical works and experimental data. Described models can be applied to other semiconductor structures.

Acknowledgements We acknowledge invaluable assistance of David Vanderbilt (Rutgers University, Department of Physics and Astronomy), and Andrew Malashevichi (University of California at Berkeley, Department of Physics) in the scientific discussion of the research.

References

[1] O. Ambacher, J. Phys. D **31**, 2653 (1988).
[2] F. Bernardini and V. Fiorentini, Phys. Rev. B **57**, R9427 (1998).
[3] F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. B **56**, R10024 (1997).
[4] F. Bernardini and V. Fiorentini, Phys. Rev. B **64**, 085207 (2001).
[5] O. Ambacher, J. Majewski, C. Miskys, A. Link, M. Hermann, M. Eickhoff, M. Stutzmann, F. Bernardini, V. Fiorentini, V. Tilak, B. Schaff, and L. F. Eastman, J. Phys.: Condens. Matter **14** 3399–3434 (2002).
[6] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).
[7] R. Resta, Rev. Mod. Phys. **66**, 899 (1994).
[8] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[9] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[10] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[11] R. Resta, Ferroelectrics **136**, 51 (1992).
[12] A. Malashevich, Abstract of dissertation, New Brunswick, New Jersey, The Graduate School-New Brunswick Rutgers, The State University of New Jersey, 2009.
[13] O. Ambacher, J. Phys. D: Appl. Phys. **31**, 2653 (1998).
[14] O. Ambacher, J. Smart, J. R. Shealy, N. G. Weimann, K. Chu, M. Murphy, W. J. Schaff, and L. F. Eastman, J. Appl. Phys. **85**, 3222 (1999).
[15] F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. B **63**, 193201 (2001).
[16] M. Tanaka, S. Nakahata, K. Sogabe, and H. Nakata, Jpn. J. Appl. Phys., Part 2 **36**, L1062 (1997).

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

[17] M. Leszczynski, H. Teisseyre, T. Suski, I. Grzegory, M. Bockowski, J. Jun, S. Porowski, K. Pakula, J.M. Baranowski, C.T. Foxon, and T.S. Chen, Appl. Phys. Lett. **69**, 73 (1996).
[18] A. Alekseev, D. Krasovitzkii, S. Petrov, and V. Tschaly, Kompon. i. Tekhnologiya No. 2 (2008).
[19] A. Zoroddu, F. Bernardini, P. Ruggerone, and V. Fiorentini, Phys. Rev. B **64**, 045208 (2001).
[20] K. Tsubouchi, K. Sugai, and N. Mikoshiba, IEEE Ultrason. Symp. **90,** 375 (1981).
[21] O. Ambacher, B. Foutz, J. Smart, J. R. Shealy, and N. G. Weimann, J. Appl. Phys. **87**, 334 (2000).
[22] X. Wang and A. Yoshikawa, Prog. Cryst. Growth Charact. Mater. **48-49**, 42 (2004).

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim