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SURFACES, INTERFACES, AND THIN FILMS

Study of the Polarizations of (Al,Ga,AlGa)N Nitride Compounds and the Charge Density of Various Interfaces Based on Them

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Abstract—The results of a theoretical study based on ab initio calculations of the polarization properties of AlN, GaN, and AlGaN semiconductors with the wurtzite structure are presented. The values of the spontaneous and piezoelectric polarizations, as well as the piezoelectric constants, are calculated for these nitride compounds. With the aim of further considering prospective heterostructures based on (Al,Ga,AlGa)N compounds, the charge densities at the AlN/GaN, AlGaN/AlN, and AlGaN/GaN interfaces and carrier concentration at the AlGaN/GaN heterointerface is estimated and compared with the experimental data.

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1. INTRODUCTION

III–V nitrides and their alloys are promising materials for the development of semiconductor devices such as photodiodes emitting in the optical and ultraviolet ranges and high-power high-frequency transistors [1]. It was shown in numerous theoretical studies [2–5] that the value of the macroscopic polarization at various interfaces substantially affects the characteristics of semiconductor heterostructures. The presence of macroscopic polarization leads to the appearance of a built-in electric charge and charge accumulation at the heterointerfaces of the nitride compounds, which in turn causes restriction of the electron motion in one direction and the formation of a two-dimensional electron gas [3].

In the wurtzite structure, III–V nitrides possess larger values of the spontaneous polarization and piezoelectric constants [2, 4], which leads to considerable macroscopic polarization. The macroscopic polarization in the absence of external fields is determined by the sum of the spontaneous and piezoelectric polarizations. For example, for the AlGaN/GaN heterostructure, the piezoelectric polarization of deformed AlGaN layers is largerer by a factor of >5 than for the AlGaAs/GaAs heterostructure, which provides a significantly higher carrier concentration at the AlGaN/GaN interface [6–10]. In addition, the spontaneous polarization, for example, of the wurtzite AlN structure, is weaker than the spontaneous polarization of ferroelectrics with the perovskite structure by a factor of only 3–5 [11].

The charge density at the interfaces of the semiconductor nitride heterostructures attains large values, which is caused by strong macroscopic polarization. This fact determines the advantage of using III–V nitrides in microwave devices compared with other semiconductor structures. In connection with this, it is topical to investigate the spontaneous and piezoelectric polarization of (Al,Ga,AlGa)N compounds, as well as to determine the charge densities at various interfaces AlN/GaN, AlGaN/AlN and AlGaN/GaN.

2. THEORY

Each covalent bond between the metal and nitrogen atoms in the structure of the (Al,Ga,AlGa)N nitride compounds is dipole. All bonds in the crystals with the sphalerite structure are of the same length and bond angle, which leads to the zero total dipole moment per unit cell. Dipoles in the wurtzite structure along the [0001] direction have different lengths and bond angles, due to which the total dipole moment per unit cell is uncompensated. The presence of the nonzero dipole moment leads to the appearance of spontaneous polarization.

In this study, the spontaneous polarization of the structure was calculated using Berry phases within the context of modern polarization theory suggested by King-Smith, Vanderbilt, and Resta [12, 13]. According to modern theory, the spontaneous polarization is determined by the difference between the polarizations of two different states of the system rather than by the absolute value of the dipole moment [14]. Thus, the spontaneous polarization of the structure is given relative to a certain reference structure, the polarization of which is assumed to be zero. When selecting such a structure, we used the model of point charges [2, 15]. In this model, metal and nitrogen atoms in the ideal wurtzite structure with the internal parameter $u = 3/8$, which determines the relative shift of atomic

Table 1. Results of calculation of the lattice parameter in the basal plane (a), the ratio of the lattice parameter along the [0001] direction to the parameter in the basal plane (c/a), the deviation of parameter u in relative units from the ideal value (Δu), and the spontaneous polarization for the AlN structure

System AlN	Our calculation		Theory (LDA-US) [21]	Our calculation		Theory (GGA-US) [21]	Experiment [22, 23]
	LDA-US	LDA-PAW		GGA-US	GGA-PAW		
a, Å	3.083	3.088	3.07	3.122	3.123	3.108	3.1106
c/a	1.6015	1.6002	1.5997	1.6041	1.6031	1.6033	1.6008
$\Delta u \times 10^{-3}$	7.0	7.0	7.1	6.6	6.5	6.4	7.1
P_{sp}, C/m^2	−0.097	−0.097	−0.099	−0.090	−0.090	−0.090	–

sublattices of different kinds along hexagonal axis c, were replaced with point charges with magnitudes of $+3e$ and $-3e$. Polarization in this model is calculated by the formula

$$P_{\text{model}} = -\frac{ec}{4V}, \quad (1)$$

where e is the elementary charge, c is the unit-cell parameter along the [0001] direction, and V is the unit-cell volume.

The polarization of the structure is determined by the ion and electron contributions to the total dipole moment. When calculating the structure ab initio with the ideality factor $u = 3/8$, the electron contribution to polarization is relatively large due to the noncentric-symmetry of the wurtzite structure. As for the model of point charges, it does not take into account the electron-density distribution; thereby, the electron contribution to the spontaneous polarization is disregarded. Therefore, polarization of this structure can be accepted to be zero.

It was already mentioned above that the macroscopic polarization is also determined by piezoelectric polarization, which emerges due to the lattice mismatch at the heterointerfaces. In this study, the piezoelectric polarization was determined by the formula [2, 16, 17]

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

where e_3 and e_{31} are piezoelectric constants, and ε_3 $(c - c_0)/c_0$ and $\varepsilon_1 = \varepsilon_2 = (a - a_0)/a_0$ are the relative strains along the z axis and in the basal plane (x, y), respectively. Since pseudomorphism occurs during the growth of nitrides, i.e., the lattice period of the substrate with the same symmetry is retained, it is assumed that the parameters of the strained AlN and AlGaN lattices in the basal plane are equal to the parameter of the relaxed GaN structure (a(AlN) = a(AlGaN) = a(GaN)) [16], which forms the buffer layer.

In this study, we performed ab initio calculations within the context of electron-density functional theory using the Vienna ab initio Simulation Package (VASP) software complex [18, 19]. Calculations are performed in the generalized gradient approximation (GGA) and in the local density approximation (LDA) for the exchange-correlation potential. To describe the interatomic interaction, we used the methods of the projector augmented wave (PAW) and ultrasoft pseudopotentials (US-PPs). The cutoff energy by the plane wave was selected to be equal to 450 eV. The atomic structure was relaxed until the forces affecting the atom reached a value smaller than 0.0001 eV/Å.

When simulating the AlN, GaN, and AlGaN structures, we used periodic supercells. To calculate AlN and GaN, we took cells with two metal atoms and two nitrogen atoms ($1 \times 1 \times 1$) in size, and to describe the AlGaN concentration with the specified concentration, we took a supercell containing 16 gallium atoms, 8 aluminum atoms, and 24 nitrogen atoms ($2 \times 2 \times 3$) in size. Calculations in the Brillouin zone were performed using a k mesh with the dimensionality $8 \times 8 \times 8$ for the AlN and GaN cells and $4 \times 4 \times 2$ for the AlGaN cells constructed by the Monkhorst–Pack method [20]. These parameters of the computational scheme allow us to describe the properties of the (Al,Ga,AlGa)N structures rather exactly.

3. RESULTS AND DISCUSSION

Most often, III–V nitrides and their alloys are met in nature in the wurtzite structure, which is of the hexagonal close packing type. At first, we considered binary GaN and AlN nitrides with the wurtzite structure. For these systems, we calculated the spontaneous polarization and main structural parameters within the context of the two approximations and methods (LDA-US, LDA-PAW, GGA-US, and GGA-PAW). The results for AlN are presented in Table 1, and these for GaN are presented in Table 2. In Tables 1 and 2, the found values are compared with theoretical values [21] and experimental data [22, 23].

It is seen from Tables 1 and 2 that the obtained values for the structural parameters and spontaneous crystallization agree well with the results of other theoretical calculations [21]. In addition, the parameters that describe the structure are close to the experimental results [22, 23]. Consequently, the used parameters of the computational scheme allow the properties of

Table 2. Results of calculation of the lattice parameter in the basal plane (a), the ratio of the lattice parameter along the [0001] direction to the parameter in the basal plane (c/a), the deviation of parameter u in relative units from the ideal value (Δu), and the spontaneous polarization for the GaN structure

System GaN	Our calculation		Theory (LDA-US) [21]	Our calculation		Theory (GGA-US) [21]	Experiment [23]
	LDA-US	LDA-PAW		GGA-US	GGA-PAW		
a, Å	3.144	3.150	3.131	3.207	3.209	3.197	3.189
c/a	1.6302	1.6303	1.6301	1.6297	1.6296	1.6297	1.6263
$\Delta u \times 10^{-3}$	1.5	1.4	1.6	1.8	1.6	1.9	2
P_{sp}, C/m^2	−0.031	−0.030	−0.032	−0.033	−0.032	−0.034	–

the atomic structure of these nitrides to be described rather exactly. It should also be noted that the lattice constants in the GGA approximation deviate less from the experimental value than in the LDA approximation. Thus, we can conclude that the GGA approximation better reproduced the structure of nitrides than the LDA approximation. Therefore, when describing the AlGaN structure, we used the GGA approximation.

In the industrial production of AlGaN/GaN structures, the $Al_xGa_{1-x}N$ alloy with a concentration of $x = 0.15$–0.35 is used [24]. When simulating the structure, we selected the concentration $x = 0.33$, which lies within this concentration range. Using the GGA approximation, we calculated the parameters of the structure and spontaneous polarization for the $Al_{0.33}Ga_{0.67}N$ system. The results are presented in Table 3. In addition, using Vegard's law

$$\begin{aligned} a(A_xB_{1-x}N) &= xa(AN) + (1-x)a(BN), \\ c(A_xB_{1-x}N) &= xc(AN) + (1-x)c(BN), \end{aligned} \quad (3)$$

we estimated the values of the lattice parameter in the basal plane and the ratio of the lattice parameter along the [0001] direction to the parameter in the basal plane (c/a). Using the data from [25] and the square approximation of the dependence of internal parameter u and the spontaneous polarization on the molar content of aluminum in the system suggested in [26], we estimated internal parameter u and the spontaneous polarization. All the data on the estimation are also presented in Table 3.

The data presented in Table 3 show that the result of the ab initio calculation is close to the expected estimated values. Therefore, these data can be used for further calculations of the charge density at AlGaN/AlN and AlGaN/GaN heterointerfaces.

In the absence of external fields, the total macroscopic polarization of the solid is determined by the sum of the spontaneous polarization of the equilibrium structure and the piezoelectric polarization caused by strain at the heterointerface. Therefore, in order to determine the total macroscopic polarization, we considered AlN and AlGaN structures. We calculated the piezoelectric constants and the piezoelectric polarization for these nitride compounds using formula (2). The results are presented in Tables 4 and 5. It is seen from Table 4 that the piezoelectric constants for AlN are very close to the results of other theoretical studies [27] and experimental values [28].

In addition, we estimated the piezoelectric polarization for $Al_{0.33}Ga_{0.67}N$ using the quadratic approximation [25, 26]. The estimated value was $P_{pz} = -0.011$ C/m^2. The calculated value of the piezoelectric polarization for $Al_{0.33}Ga_{0.67}N$ is close to that estimated. Comparing the absolute values of the spontaneous and piezoelectric polarization for these systems, we see that the spontaneous polarization largely contributes to the macroscopic polarization. Since the piezoelectric polarization has the same sign as the spontaneous polarization, the vectors of these polarizations are codirectional (see the figure); therefore, the presence of piezoelectric polarization leads to the enhancement of macroscopic polarization.

The obtained values of the spontaneous and piezoelectric polarization allowed us to calculate the charge density, which is determined by the macroscopic polarization at the AlN (0001), GaN (0001), and AlGaN (0001)surfaces using formula (25)

$$\sigma = P_{\text{macro}} = P_{sp} + P_{pz}, \quad (4)$$

where P_{macro} is the macroscopic polarization, P_{sp} is the spontaneous polarization, and P_{pz} is the piezoelectric polarization of the nitride. The charge density σ and its specific value σ/e ($e = 1.602 \times 10^{-19}$ C is the ele-

Table 3. Results of calculation and theoretical estimation of the lattice parameter in the basal plane (a), the ratio of the lattice parameter along the [0001] direction to the parameter in the basal plane (c/a), and the deviation of parameter u in relative units from the ideal value (Δu) of spontaneous polarization for the AlGaN structure

System AlGaN	Theory (GGA-PAW)	Theoretical evaluation
a, Å	3.178	3.181
c/a	1.6247	1.6210
$\Delta u \times 10^{-3}$	2	3
P_{sp}, C/m^2	−0.0435	−0.0478

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

System AlN	Theory (GGA-PAW)	Theory (GGA-US) [27]	Theory (LDA-US) [27]	Experiment [28]
$e33$, C/m^2	1.50	1.50	1.80	1.55
$e31$, C/m^2	–0.60	–0.53	–0.64	–0.58
$e15$, C/m^2	–0.31	–	–	–0.48
p_{pz}, C/m^2	–0.0508	–	–	–

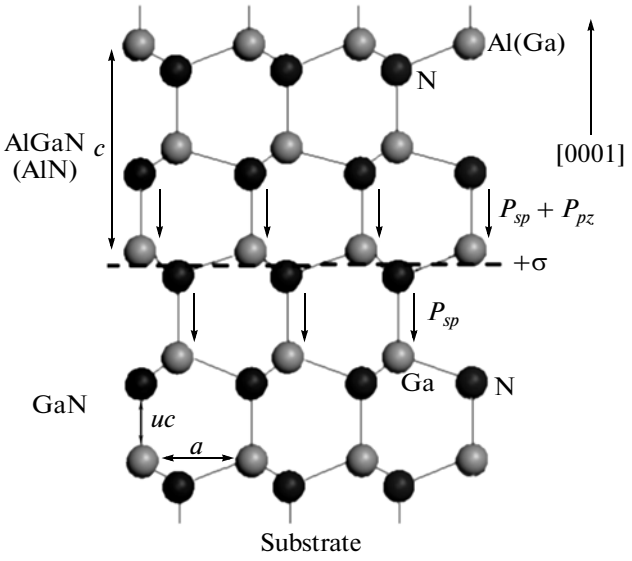
mentary charge) on the surface of the nitride compounds (Al,Ga,AlGa)N with metal polarity are presented in Table 6.

It is seen from Table 6 that the value of the charge density on the AlGaN (0001) surface lies in the range between the values of the charge densities for the AlN (0001) and GaN (0001) surfaces. In addition, the absolute value of the charge density on the AlN (0001) surface takes the maximal value, while on the GaN (0001) surface, it takes the minimal value. Therefore, we can assume that the absolute value of the charge density on the $Al_xGa_{1-x}N$ (0001) surface increases as the Al concentrations in the $Al_xGa_{1-x}N$ structure.

Using the data from Table 6, we calculated the density of the bound charge at the AlN/GaN, AlGaN/AlN, and AlGaN/GaN interfaces according to the formula [29]

$$\sigma(AN/BN) = P_{\text{macro}}(BN) - P_{\text{macro}}(AN) = \sigma(BN) - \sigma(AN). \quad (5)$$

The specific charge densities at the different interfaces were as follows: σ/e (AlN/GaN) = 6.79 × 10^{13} cm^{-2}, σ/e (AlGaN/AlN) = –5.44 × 10^{13} cm^{-2}, and σ/e (AlGaN/GaN) = 1.35 × 10^{13} cm^{-2}. The charge densities at the AlN/GaN and AlGaN/GaN interfaces turned out to be positive (figure), which agrees with the results of the theoretical study [25]. The epitaxial growth of AlN (similarly to AlGaN with a high molar content of Al) on GaN is accompanied by various technological difficulties, which are associated with the fact that the AlN/GaN heterostructure has a larger lattice mismatch of about 2% [30]. Therefore, the AlGaN/GaN heterostructure is of interest from the practical viewpoint.



Crystal structure, spontaneous and piezoelectric polarization, and density of the bound charge at the interface of the AlGaN/GaN (AlN/GaN) heterostructure.

To compensate the positive charge density, negative charge carriers (electrons) are collected in the quantum well at the AlGaN/GaN heterointerface. Their accumulation leads to the formation of an electron gas with a concentration close to that of bound charges, which is determined by the charge density at the interface, at this heterointerface. It should be noted that there is no need to dope this structure in order to form the electron gas. Therefore, the process of producing the AlGaN/GaN heterostructure is simplified, which determines technological interest in these systems.

It was already mentioned above that the formation of positive charges at the $Al_xGa_{1-x}N$/GaN heterointerface leads to the accumulation of electrons at this heterointerface and, consequently, to the formation of a two-dimensional electron gas. The concentration of charge carriers (electrons) of the two-dimensional electron gas is an important characteristic of these semiconductor heterostructures and determines the topicality of their practical application. According to the model suggested in [25], the carrier concentration for the pseudomorphic growth of AlGaN on GaN with an AlGaN barrier layer thicker than 15 nm has a quadratic dependence on the molar content of Al in AlGaN:

$$n_s = [-0.169 + 2.61x + 4.50x^2] \times 10^{13}\ \text{cm}^{-2}, \quad x > 0.06, \quad (6)$$

where x is the molar content of Al in AlGaN.

For the $Al_{0.33}Ga_{0.67}N$/GaN heterostructure under consideration, the carrier concentration at the interface calculated by formula (6) was 1.18 × 10^{13} cm^{-2}.

This value agrees well with the experimental values found by means of plotting the C–V curves [25, 31, 32].

Table 5. Results of calculation of the piezoelectric constants and the piezoelectric polarization for the AlGaN structure

System $Al_{0.33}Ga_{0.67}N$	Theory (GGA-PAW)
$e33$, C/m^2	0.79
$e31$, C/m^2	−0.44
$e15$, C/m^2	−0.22
p_{pz}, C/m^2	−0.0098

Table 6. Results of calculation of the charge density on the AlN (0001), GaN (0001), and AlGaN (0001) surfaces as well as its specific value

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

4. CONCLUSIONS

In this study, we performed the ab initio theoretical study of the pyroelectric properties of AlN, GaN, and $Al_{0.33}Ga_{0.67}N$ compounds and different interfaces based on them. We presented the values of the spontaneous and piezoelectric polarizations; calculated the densities of bound charges at the AlN/GaN, AlGaN/AlN, and AlGaN/GaN heterointerfaces; and estimated the electron concentration at the $Al_{0.33}Ga_{0.67}N$/GaN interface. All obtained values well agree with the experimental data. In addition, we considered the physical nature of the spontaneous and piezoelectric polarizations and the methods of their calculation. The described models can be applied to other semiconductor structures.

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