STRUCTURAL AND ELECTRONIC PROPERTIES OF AlN IN ROCKSALT, ZINC BLENDE AND WURTZITE PHASE: A DFT STUDY

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Aluminium Nitride (AlN) is a wide bandgap group III-V compound, and AlN exhibits in three different lattice structures. In this work, we investigate the different structural and electronic properties of AlN in rocksalt (RS), zincblende (ZB) and wurtzite (WZ) phase in the light of Density Functional Theory (DFT) with modified Becke-Johnson generalized-gradient approximation (mBJ-GGA) as exchange-correlation potential. The structural lattice parameters and energy bandgap obtained in this calculation are in agreement with the available experimental values. The structural calculation shows that the most stable phase is the wurtzite phase, and the metastable phase is the zincblende phase. The bandgap for the AlN in rocksalt, zincblende and wurtzite phase are found to be 6.33 eV, 4.7 eV, and 5.6 eV respectively. The bandgaps are indirect corresponding to the rocksalt and zincblende phase and direct in case of the wurtzite phase.

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*Keywords:*Crystal structure, Structure optimization, Density functional theory, Energy band gap, Density of states

1. Introduction

In recent days, the group III-V semiconductors are showing very much interest in the field of research. Among them, the highest thermal conductivity ceramic material Aluminium Nitride (AlN) has been studied on a large scale due to its potential application in solid-state cells, optoelectronic devices, *etc*. Theses solid-state cells that are photosensitive to ultraviolet radiation and other fields of electronics [1-5]. Due to this high thermal conductivity, AlN is used for the production of LED technology, ceramic substrates, and thermal interfaces for electronic lasers [6-8]. Recently, a large number of investigation is going on examining the properties of AlN for the production of sensors [9,10].In addition to the electric field, AlN is studied widely for the development of composite materials with high electrical resistance, mechanical strength, and thermal conductivity [11-14]. The non-metallic Aluminium nitride has been synthesized from the abundant elements of aluminum and nitrogen since it does not occur naturally. The crystal structure of AlN is reported first by Heinrich Otto in the year 1924. He found that AlN has a wurtzite structure ($a = b \neq c$) having a lattice constant 'a' ranging from 3.110 Å to 3.113 Å and that of 'c' ranges from 4.978 Å to 4.982 Å maintaining the c/a ratio between 1.000 to 1.60 [15]. While the cubic AlN have been synthesized by a numerous method [16-19]. In general, AlN exists in three different phases, namely rocksalt, zincblende, and wurtzite phase. Among the three phases, the wurtzite phase is the most stable. The metastable zincblende phase and the stable wurtzite phase of AlN can be found as bulk material at ambient pressure, whereas the rocksalt phase is stable only at 13-23 GPa pressure [20]. The experimental electronic bandgap corresponding to the wurtzite phase is found to be 6.28 eV [21]. The thermal conductivity of Aluminium nitride is similar to that of silicon.

The favorable Aluminium nitride has excellent dielectric properties along with excellent corrosion resistance. Based on the thermodynamic stability of zincblende phase of AlN due to various epitaxial strains, S.K. Yadav *et al.*, found that the energy of AlN in the zinblende phase is higher than that of the wurtzite phase [22]. The stable wurtzite phase of Aluminium nitride can be transformed into a rocksalt phase at a pressure of 22.0 GPa where the rocksalt phase persisted down to atmospheric pressure [23]. Hultman, S. Benhenda found that the zincblende structure of

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Aluminium nitride is stable only when it is skinny of the order of 1.5nm to 2.0 nm and the zincblende structure is transformed into wurtzite structure at a large thickness [24]. A. Siegel *et al.* found that the zincblende state is a metastable phase with enthalpy close to the wurtzite phase [25]. As a further matter, the wurtzite phase and the zincblende phases are transformed into rocksalt phases at a pressure of 17GPa and 15 GPa respectively [24], and this pressure is regarded as a transition pressure. S. Saib *et al.* found that the transition pressure for the transformation from wurtzite to rocksalt is 20.91 GPa, and the transition pressure for the transformation from zincblende to rocksalt is 19.69 GPa [26].

2. Computational details

In this present work, the calculations are accomplished using the full potential linearized augmented plane wave (FP-LAPW) method under the framework of the Density Functional Theory (DFT). Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA)[27] and modified Becke-Jhonson Potential generalized gradient potential (mBJ-GGA) [28] is used for the exchange-correlation potential as implemented in the WIEN2k code. In the FP-LAPW method, the lattice divides into non-overlapping spheres named Muffin tin (MT), which surrounds each nuclear site and an interstitial region and inside this muffin tin, the potential contains both the radial function and spherical harmonics.

The electronic configuration of Al and N are [Ne] $3s^2$ $3p^1$ and [He] $2s^2 2p^3$ respectively. AlN generally exists in three different phases; the zincblende structureAl at (0 0 0) and N at (1/4 1/4 1/4), the rocksalt structure Al at (0 0 0) and N at (1/2 1/2 1/2), and the wurtzite structure Al at (2/3 1/3 0) in position 1, (1/3 2/3 1/2) in position 2 and N at (2/3 1/3 *u*) in position 1, (1/3 2/3 ½+*u*) in position 2, where *u* is the internal parameter which gives the separation of atom Al and N along c-axis. The space group corresponding to zincblende, rocksalt, and wurtzite phase are 216-F-43m, 225-Fm-3m, and 186-p63mc,respectively.We use 5000 *k* points for all the three structures, which then generated 164 *k* points for the zincblende and the rocksalt structure, and 264 *k* points for the wurtzite structure. The convergence occurs at RMTKmax = 8.0, where RMT is the atomic sphere radii, and Kmax gives the plane wave cut-off. The convergence criterion of energy for the self-consistency is taken of the order of 10^{-4} eV. Modified Becke -Johnson potential generalized gradient potential (mBJ-GGA) is used for the calculation of the bandgap. The result obtained using this calculation is very much in agreement with the expensive GW calculation[29].The respective density of states (DOS), and partial DOS are calculated between the energy ranges from -8eV to 6 eV. All the calculations done in this work are at the zero pressure level.

3. Results and discussion

3.1. Structural properties

Birch-Murnaghan equation of state [30] is used for obtaining the different structural properties. For the rocksalt and zincblende phase, structural optimizations are done using energy as a function of volume, while optimization for the wurtzite phase is done in terms of energy as a function of three variables *c*/*a*, *u* and volume. Fig.1 shows the energy *vs.* volume curve of Aluminium Nitride for the three different phases, namely rocksalt, zincblende, and wurtzite phase. In every case, the results obtained for the different optimized parameters are in good agreement with the experimental value. The optimized cubic lattice parameter for the rocksalt structure obtained in this work is 4.0850 Å, while the experimental value is 4.06 Å [31]. And in the case of zincblende structure, the optimized lattice parameter is 4.4060 Å, nearly matches with the experimental value 4.37 Å [32]. For the wurtzite structure, from the fourth-order polynomial fit, the obtained optimized value of *a* and *c* respectively are 3.110 Å and 4.978 Å which are in good agreement with the experimental value 3.110 Å and 4.98 Å [33], while maintaining the constant *c*/*a* ration within the range [34]. The energy difference between rocksalt and zincblende phase is found to be 0.026 Ry, while in case of difference between rocksalt and wurtzite is 0.0294Ry and the energy difference between wurtzite and zincblende is found to be 0.0034 Ry. This energy gives

the stability of the compound. On comparing the volume *vs.* energy curve for three different phases of AlN, it is observed that the minimum energy occurs corresponding to the wurtzite phase.

This minimum energy indicated that the wurtzite phase is the most stable phase, which matches an experimentally observed stable phase of the AlN crystal found by Henrich Otto *et al.* [20]. The energy corresponding to the zincblende phase is found to be in between rocksalt and the wurtzite phase and is said to be a metastable phase. The metastable phase of AlN is the zincblende phase, confirmed by Neumann *et al.*,[21]. The transformation from one phase to another phase is possible under definite pressure. The different optimized parameters obtained from the energy *vs.* volume curve, along with experimental and other calculated values are listed in Table 1.

3.2. Electronic properties

The electronic structure calculations are done by taking the obtained equilibrium lattice parameters of the three AlN-phases, namely rocksalt, zincblende, and wurtzite. The electronic structure of AlN for the three different phases are examined with modified Becke-Johnson generalized-gradient approximation (mBJ-GGA) as exchange-correlation potential. The eigenvalues of the Kohn-Sham equation are evaluated using the FP-LAPW (Full Potential linearly augmented plane wave) method along some high symmetry direction in the Brillion zone.

3.2.1. Rocksalt phase

Fig. 2 shows the energy band diagram of the AlN rocksalt phase. It is observed that a bandgap of 5.8 eV separates the valance band and conduction band at **Γ** and **X** symmetry points that correspond to the indirect bandgap. The band separation at other high symmetry points **Γ, L** and **X** are found to be 6.33 eV, 8.12 eV, and 8.32 eV, respectively. Fig. 3(a, b, c) shows the density of states (DOS) calculation for the rocksalt phase of AlN. In Fig. 3(a),the total DOS calculation shows the valance band is contributed much more by the N atom compared to the Al atom. Above the Fermi level, as shown as a dotted line, there are no contribution of energy levels upto 6.3 eV, which indicates the bandgap of the compound, and the same is obtained in the band diagram. Partial density of states (PDOS) calculation further shows that *s*orbital of Al and *p* orbitalof N contributes more to the valance band, as shown in Fig.3(b) and 3(c).

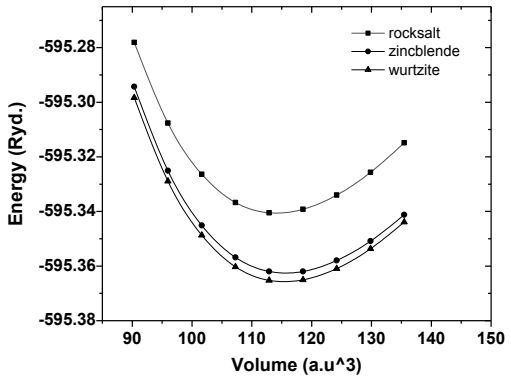

Fig.1. Energy vs. Volume curve of AlN in the three phases (rocksalt, zincblende, and wurtzite).

Table 1.Different optimized parameters along with experimental and other calculated values of AlN in rocksalt, zincblende and wurtzite phase.

AlN		**V_0 (bohr^3)**	**E_0 (Ry.)**	**a (Å)**	**c (Å)**	**B(GPa)**
Rocksalt	This work	115	-595.336	4.0850		247.323
	Expt. Values and Theoretical values			4.060[31] 3.978[35] 3.9820[23] 4.066[25]		221[36] 251[37] 252[38]
Zincblende	This work	114.302	-595.362	4.4060		193.401
	Expt. Values and Theoretical values			4.370[32] 4.400[39] 4.394[40] 4.421[41]		203[33] 195-228[20,41-43]
Wurtzite	This work	143.949	-595.365	3.110	4.978	194.805
	Expt. Values and Theoretical values			3.11[33] 3.06[40] 3.084[44] 3.099[45]	4.98[33] 4.91[40] 4.948[44] 4.997[45]	185-212 [36,46] 202[33] 205 [43]

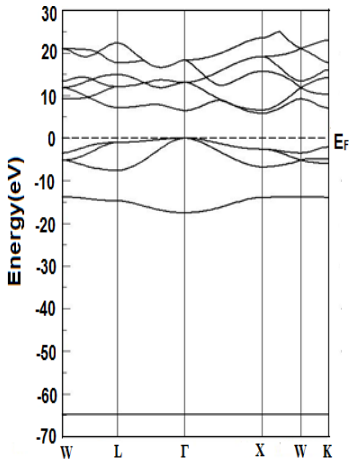

Fig. 2.Energy band diagram of AlN-rocksalt structure.

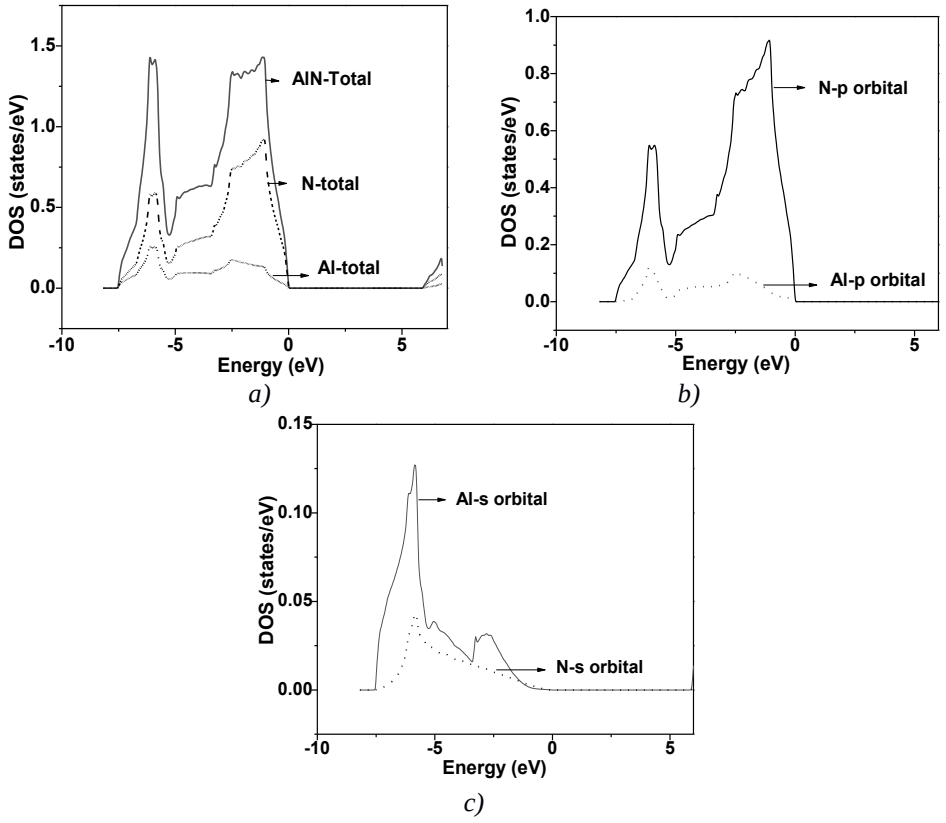

Fig. 3. (a)Total DOS showing contribution of Al and N in AlN-rocksalt phase; (b) Partial DOS showing the p orbital contribution for AlN-rocksalt phase; (c) Partial DOS showing the s orbital contribution for AlN-rocksalt phase.

3.2.2. Zincblende phase

The Electronic band structure calculation of the metastable zincblende phase of AlN is shown in Fig. 4. The top of the valance band at **Γ** point and the minimum of the conduction band at **X** point are separated by an energy gap of 4.7 eV and are not lying at the same high symmetry point, indicating the gap is indirect bandgap. The result is in good agreement with the result obtained by *Cheng et al.*, [23]. The band separation corresponding to the high symmetry **Γ** point is found to be 5.28 eV, which is smaller in comparison with the rocksalt phase. The gap corresponding to other high symmetry points **X** and **L** are 6.32eV and 8.907 eV, respectively. Further, DOS and PDOS calculations for the metastable zincblende phase are shown in Fig. 5(a,b,c). The total DOS calculation shows that the contribution in the valence band is mainly by N atom and is in the energy range 0 to -5 eV, while the contribution in the conduction band occurs beyond 5.2 eV energy. There is no contribution of orbitals in between 0 to 5.2 eV, showing the bandgap of the compound. From the PDOS calculation, it is observed that N atom is giving more contribution in valence band than the Al atom, and it is from the *p* orbital of N atom whiles orbital of N atom has a lesser contribution.

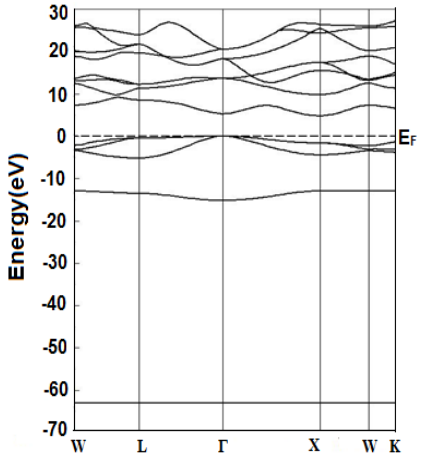

Fig. 4. Energy band diagram of AlN-zincblende structure.

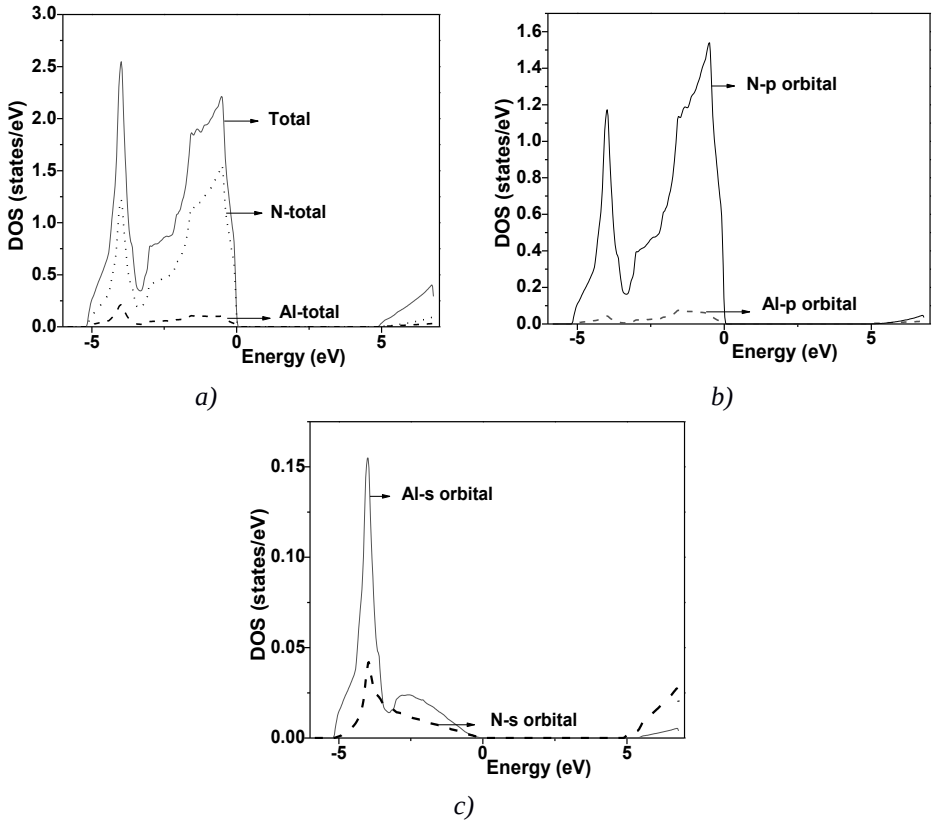

Fig. 5. (a)Total DOS showing contribution of Al and N in AlN-zincblende phase; (b) Partial DOS showing the p orbital contribution for AlN-zincblende phase; (c) Partial DOS showing the s orbital contribution for AlN-zincblende phase.

3.2.3. Wurtzite phase

It is the most stable phase of AlN. The calculated energy band structure of AlN in the wurtzite phase is shown in Fig. 6. At the high symmetry **Γ** point, the top of the valance band and bottom of the conduction bands are separated by a direct bandgap of 5.6 eV, which is smaller than the experimentally observed value 6.28 eV[21]. However, the result obtained in our calculation matches the result obtained by *Y. C. Cheng et al.*, [23].The total DOS and PDOS calculation for the wurtzite phase is shown in Fig.7(a,b,c). The total DOS calculation shows that the N atom is

giving more contribution to the valance band than the Al atom. Above the Fermi level, from 0 to 5.6 eV, there is no orbitals, which indicates the bandgap of the compound. The PDOS calculation shows the contribution due to partials *s*, *p* orbital of Al and N atom, that N-*p* orbital contributes more than Al-*p* orbital in the valence band, although there are small contributions from *s* orbital.

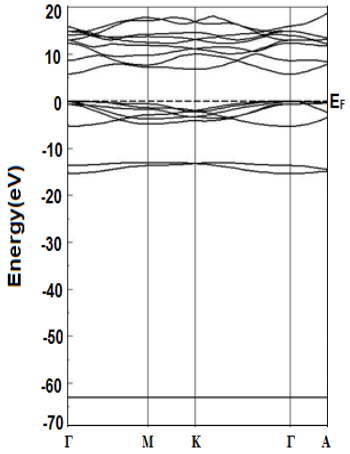

Fig. 6. Energy band diagram of AlN-wurtzite structure.

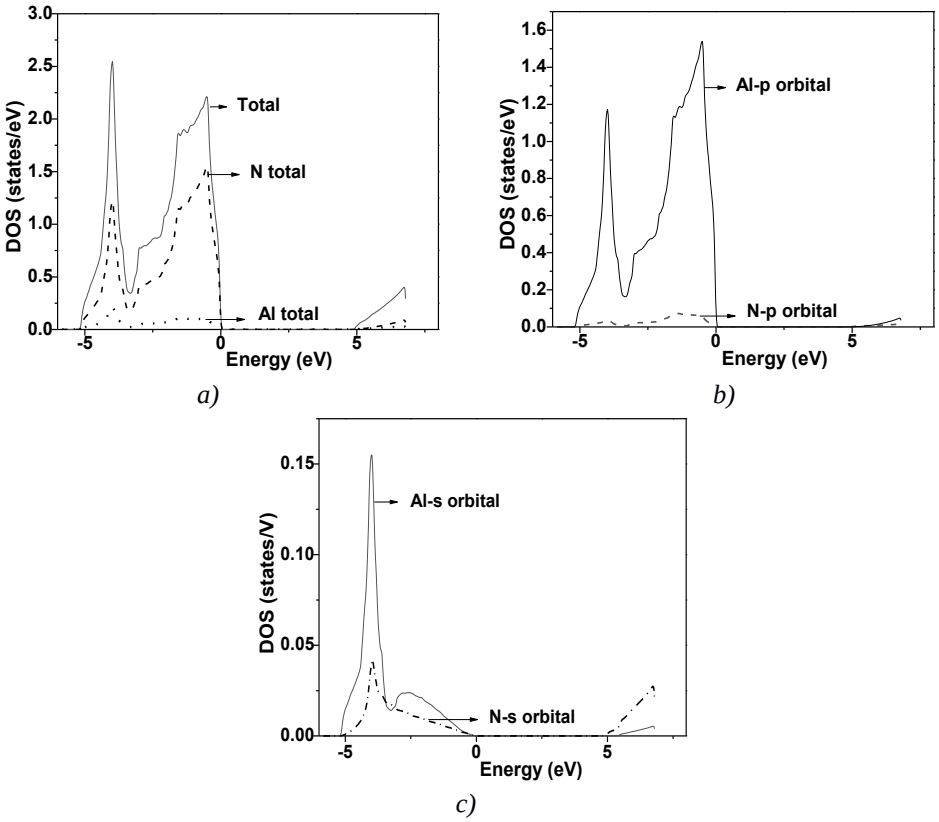

Fig. 7. (a)Total DOS showing contribution of Al and N in AlN-wurtzite phase; (b) Partial DOS showing the p orbital contribution for AlN-wurtzite phase; (c)Partial DOS showing the s orbital contribution for AlN-wurtzite phase.

4. Conclusions

The optimized structural lattice parameters and energy bandgaps of AlN in the three structures namely rocksalt, zincblende and wurtziteare in agreement with the available experimental values. Among the three phases, the most stable phase is the wurtzite phase, and the metastable phase is the zincblende phase. The bandgaps of AlN in rocksalt, zincblende, and wurtzite phase are found to be 6.33 eV, 4.7 eV, and 5.6 eV, respectively. The band gaps are indirect corresponding to the rocksalt and zincblende phase, and direct in the case of the wurtzite phase of AlN.

References

[1] S. Wang, H. Tian, Y. Luo, J. Yu, C. Ren, C. Sun, M. Sun,Applied Surface Science**481**, 1549(2019).
[2] L. Natta, V. Mastronardi, F. Guido, L. Algieri, S. Puce, F. Pisano, M. De Vittorio, 22nd European Microelectronics and Packaging Conference & Exhibition (EMPC), IEEE 1-6 (2019).
[3] E. Viswanathan, M. Sundareswari, S. Krishnaveni, M. Manjula, S. Jayalakshmi, Journal of Superhard Materials**41**(5), 321 (2019).
[4] F. Belyanin, L. Bouilov, V. Zhirnov, A. I. Kamenev, K. A. Kovalskij, B. V. Spitsyn, Diamond and Related Materials**8**(2-5), 369 (1999).
[5] B. Gil, III-Nitride Semiconductors and their modern devices, (OUP, Oxford), 18 (2013).
[6] Z. Lin, L. Rui, S. Chunhua, G. Longjiang, Preparation method of AlNpowder, Patent CN103771360 (2014).
[7] P. E. Zalba, M. E. Morosi, M. S. Conconi,Gondwana industrial clays: Tandilia System, Argentina-geology and applications, (Springer), (2016).
[8] J. Zhu, R. An, C. Wang, W. Zhang, G. Wen, Journal of Electronic Materials**44**(11), 4154(2015).
[9] A. Habib, A. Shelke, M. Vogel, S. Brand, X. Jiang, U. Pietsch, T. Kundu, ActaAcustica united with Acustica**101**(4),675 (2015).
[10] J. Liang, H. Zhang, D. Zhang, X. Duan, H. Zhang, W. Pang, Journal of Micromechanics and Microengineering**25**(3) 035016 (2015).
[11] C. Yingwen, Transformer Oil Containing Nano-Ferrocene-Aluminium Ni-trifide Particles and Preparation Method of Transformer Oil, Patent CN104194871, (2014).
[12] L. Dahai,P. Jianxun,L. Qinghua,C. Zhong,C. Yizhong,L. Yu,Method forcontinuously preparingaluminum nitride powder and equipment, Patent CN104016316, (2014).
[13] L. Yu, Y. Yushan,H. Jianjun,J. Qiangzheng, Y. Xu,Y. Ke, D. Yong,Aluminiumnitride porous ceramic filter element and preparation method, Patent CN103949117, (2014).
[14] X. Zhou, J. Cao, Preparation method for copper-aluminium nitride composite material, Patent CN104131184, (2014).
[15] W. Werdecker,F. Aldinger, IEEE transactions on components, hybrids, and manufacturing technology**7**(4), 399(1984).
[16] A. Y. Cho, Journal of Vacuum Science and Technology **8**(5), S31 (1971).
[17] J. R. Arthur, J. J. LePore, Journal of Vacuum Science and Technology**6**(4), 545 (1969).
[18] B. Abdallah, S. Al-Khawaja, A. Alkhawwam, I. M. Ismail, Thin solid films**562**, 152(2014).
[19] C. Balasubramanian, V. P. Godbole, V. K. Rohatgi, A. K. Das, S. V. Bhoraskar, Nanotechnology**15**(3),370 (2004).
[20] N. E. Christensen, I. Gorczyca, Physical Review B**50**(7),4397 (1994).
[21] H. Neumann, J. H. Edgar, EMIS Data reviews Series**11**, (1995).
[22] S. K. Yadav, J. Wang, A. Misra, X. Y. Liu, R. Ramprasad, First Principles Modeling of Metal/Ceramic Multilayer Nano-heterostructures,(Los Alamos National Lab, United States) (2012).
[23] Y. C. Cheng, X. L. Wu, J. Zhu, L. L. Xu, S. H. Li, P.K. Chu, Journal of Applied Physics **103**(7),073707(2008).

[24] L. Hultman, S. Benhenda, G. Radnoczi, J. E. Sundgren, J. E. Greene, I. Petrov, Thin Solid Films**215**(2), 152 (1992).
[25] A. Siegel, K. Parlinski, U. D. Wdowik, Physical Review B**74**(10),104116 (2006).
[26] S. Saib, N. Bouariss, P. Rodríguez-Hernández, A. Muñoz, Journal of Applied Physics**103**(1), 013506 (2008).
[27] P. Ziesche, S. Kurth, J. P. Perdew, Computational materials science**11**(2), 122 (1998).
[28] F. Tran, P. Blaha, Physical review letters **102**(22),226401 (2009).
[29] S. Biermann, F. Aryasetiawan, A. Georges, Physical review letters**90**(8),086402 (2003).
[30] F. Birch, Journal of Applied Physics **9**(4), 279 (1938).
[31] R. F. Zhang, S. H. Sheng, S. Veprek, Physical Review B**76**(7),075208 (2007).
[32] J. H. Edgar, Properties of group III nitrides, (Institution of Electrical Engineers), (1994).
[33] K. Kim, W. R. Lambrecht,B. Segall, Physical Review B**53**(24),(1996).
[34] B. Paulus, F. J. Shi, H. Stoll, Journal of Physics: Condensed Matter**9**(13),2745 (1997).
[35] J. Serrano, A. Rubio, E. Hernández, A. Muñoz, A. Mujica, Physical Review B**62**(24), 16612 (2000).
[36] Q. Xia, H. Xia, A. L. Ruoff, Journal of applied physics**73**(12), 8198 (1993).
[37] A. J. Wang, S. L. Shang, Y. Du, Y. Kong, L. J. Zhang, L. Chen, Z. K. Liu, Computational materials science**48**(3), 705 (2010).
[38] M. Fodil, A. Mounir, M. Ameri, H. Baltache, B. Bouhafs, Y. Al-Douri, Ameri, Materials Science-Poland**32**(2), 220 (2014).
[39] M. Van Schilfgaarde, A. Sher, A.B. Chen, Journal of crystal growth **178**(1-2), 8 (1997).
[40] C. Stampfl, C. G. Van de Walle, Physical Review B**59**(8),5521 (1999).
[41] K. Miwa, A. Fukumoto, Physical Review B**48**(11),7897 (1993).
[42] W. R. Lambrecht, B. Segall, Physical Review B**43**(9), 7070 (1991).
[43] A. Lachebi, H. Abid, Turkish Journal of Physics**32**(3), 157 (2008).
[44] A. F. Wright, J. S. Nelson, Physical Review B**51**(12),7866 (1995).
[45] C. Y. Yeh, Z. W. Lu, S. Froyen,A. Zunger, Physical Review B**46**(16),10086 (1992).
[46] M. Ueno, M. Yoshida, A. Onodera, O. Shimomura,K. Takemur,Physical Review B**49**(1), 14 (1994).