Journal of Ovonic Research Vol. 18, No. 6, November - December 2022, p. 797 - 804

A first-principles investigation into the electronic characteristics of phase changes in ZnO at high pressures

Y. Benkrima [a*], M.E. Soudani [b], D. Belfennache [c], H. Bouguettaia [d], A. Souigat [a]
[a]*Department of Exact Sciences, ENS Ouargla, Algeria.*
[b]*Laboratory of New and Renewable Energy in Arid and Saharan Zones (LENREZA),Faculty of Mathematics and Matter Sciences, Kasdi Merbah University 30000 Ouargla, Algeria.*
[c]*Research Center in Industrial Technologies CRTI, P.O. Box 64, Cheraga, 16014 Algiers, Algeria.*
[d]*Department of Physics, Faculty of Mathematics and Matter Sciences, Kasdi Merbah University, P.O. Box 511, 30000 Ouargla, Algeria.*

The current study focuses on the effect of pressure on zinc oxide, ZnO, which is considered an essential element in several fields. In this research, the method of calculation has been used from the commencement to find the ZnO compound's structural and electrical characteristics at various pressure levels. It is found that the obtained results related to the crystal structure of the compound with phase (B4) Wurtzite agree well with previous theoretical and experimental findings. In addition, the electronic properties showed that ZnO has a direct gap of 0.68 eV, and the density of states showed that the3d position of the zinc atom significantly contributed to building the density of the electronic states of the compound, followed by the P-terminal of the oxygen atom. As it became clear to us that changing the pressure applied to the oxide ZnO increases the value of its energy gap, while the pressure value of 13.38 GPa is the crystal transition point from phase (B4) to (B1).

(Received October 4, 2022; Accepted December 6, 2022)

Keywords: Density function theory (DFT), ZnO, Phases, Pressure, Electronic properties.

1. Introduction

Zinc oxide, ZnO is one of the most important semiconductor, with a broad direct and estimated energy gap of 3.4 eV, with very large exciton energy estimated at60 mega volts [1-4]. Recently, scientists have concentrated on a large number of semiconductors, due to their multiple advantages at the industrial and technological level [5-7]. Indeed, ZnO has remarkable and diverse applications, including gas sensors, photo catalysts and thin layers related to electronic and electro-optical devices [8-12].Under normal conditions, the dynamically stable phase of ZnO is the four surface wurtzite (B4) phase with covalently bonded Sp3[13]. Moreover, ZnO high-pressure behavior is of tremendous and unique interest, whereby many theoretical studies have been conducted in this field as presented in the works [14,15]. In this respect, experimental studies also showed that the stable phase wurtzite could change its phase to rock salt (B1) phase at about 10 GPa16.Likewise, the results of the experimental study carried out by John C. Jamieson [17] showed the transformation that occurs in semi-conductor compounds when pressurized within the temperature range of 300K.It has been emphasized by many researchers theta type II-VI semiconductor subjected to a high pressure, so to speak, (8±3) GPa, at room temperature, transforms its (B4) phase to (B1) phase. It has been proven that the Pseudo-Potential (PP) method is one of the most widely used for calculating electronic structures. In this respect, the present work tackles the effect of pressure on the compound ZnO (wurtzite) and on the energy gap. This was achieved by utilizing the Density Function Theory (DFT) and the Siesta program.

---

[*] Corresponding author: benkrimayamina1@gmail.com
https://doi.org/10.15251/JOR.2022.186.797

2. Theoretical calculation method

First principal calculations are performed on structural and electronic properties of wurtzite ZnO. In fact, a very accurate pseudo-Potential Linearized Augmented Plane Wave (PP-LAPW) approach was used, which is implemented in the Siesta code based on Density Functional Theory (DFT), to get trustworthy findings[18].Local Density Approximation (LDA) [19] and Perdew-Burke-Ernzerh of Generalized Gradient Approximation were used to tackle the exchange-correlation effect (PBE-GGA) [20].Thus, in the current work, we have chosen two fundamental parameters: the 350 eV kinetic cutoff energy for plane waves and the 3×3×3 k-point Monkhorst-Pack mesh. This resulted in a convergence of the overall energy to less than 5×10^5eV/atom and the maximum ionic Hellmanne Feynman force to less than 0.05 eV/Å. Additionally, we have worked to expand the k-points to 3×3×6 in order to obtain more precise answers for each of the electrical and optical aspects.

3. Results and discussion

3.1. Structural characteristics

In order to calculate the initial cell constants, we have adopted the density function theory DFT and the Siesta program, where the following values were found: 3.284Å for constant (a) and 5.339 Å for constant (c). Since it is a hexagonal structure in all cases, we have found that a=b, constants Angles $\alpha = \beta = 90.042°$, and $\gamma = 120.242°$; within the same context, we too, dealt with the calculation of μ, which is the internal variable that determines the length of the bond between zinc and oxygen, through which we got the value estimated at 0.7918. Itcould be noticed that the obtained results were very much in line with the theoretical and applied results presented in Table I, which is similar to the works [21-25].Furthermore, the proportion of error of the obtained values was calculated, and compared with those of the empirical values taken as a reference. Consequently, we have found the error value for the constant (a) 1.07% and the constant (c) 1.9 %. Thus, the calculated error values are very small, indicating that the calculation method is very accurate.

Table 1.Primary cell constants of ZnO oxide and their comparison with theoretical and applied results.

Method Used	a (Å)	c (Å)	c/a	h
Our Results	3.284	5.3391	1.6257	0.7918
GGA (PBE) [21]	3.288	5.305	1.6134	0. 7878
GGA (PBE) [22]	3.286	5.299	1.6125	0.7875
GGA (PBE) [23]	3.282	5.294	1.6130	0.7876
LDA [24]	3.186	5.150	1.6164	0.7888
Experimental work [25]	3.250	5.207	1.6021	0.7804

3.2. Zinc oxide formation energy

The formation energy of zinc oxide ZnO was calculated for each (Zn-O) pair according to the following relation:

$$E_C = E_T(ZnO) - E_T(Zn) - E_T(O) \tag{1}$$

Where:

E_C: Formation energy.E_T (ZnO): Total energy of free zinc oxide.E_T (Zn): Total energy of the free zinc atom. The results are displayed in Table 2:

Table 2.The pair formation energy (Zn-O) and its comparison with previous theoretical and applied results.

Pair Formation Energy (Zn-O) (eV)	
	PP-PBE-DZP (8.08) [26]
Our work	PBE-PW91 (8.93) [27]
GGA-PBE (10.50)	PBE-PW91 (8.93) [27]
	LDA (CA) (7.24) [28]
	(7.52) GGA [29]
	GGA (7.07) [29]
	PP-LDA-PW(10.57) [30]
	PP-PBE-PW (8.98) [30]

The value of the formation of zinc oxide obtained for the bonding of each pair (zinc atom, Zn, with an oxygen atom, O) is 10.50 eV. Here, it could be observed that this result is close to the theoretical results of *"M. Topsakal et al" "L. A. Mancera et al"*[26-30].

3.3. Electronic properties

3.3.1. Structure of energy bands

The energy needed to excite (transfer) electrons from the top of the valence band to the bottom of the conduction band is known as the forbidden energy (energy gap). It is called the forbidden because it is a free place of electronic states where electrons do not settle in pure semiconductors, through which the value of the energy gap allows distinguishing between insulators, semiconductor sand conductors. Effectively, the energy gap is considered as one of the most important optical constants in semiconductor physics that deter-mines the validity of semiconductors for the manufacture of many electronic devices such as solar cells, detectors, photodiodes and others. Equivalently, the Brillion region is considered the most appropriate area for studying the primary cell. Indeed, it is the first building block when it comes to the study of the electronic properties of the material body. For the sake of determining the energy gap of ZnO;we utilized the density function theory (DFT) and the generalized gradient approximation (GGA),as they are considered among the best appropriate and dedicated methods in studying the electronic structures of materials. Therefore, the energy band structure of ZnO was calculated for the lattice constant sobtained earlier: ($a = 3.284$ Å; $c = 5.339$ Å; $\alpha = \beta = 90.0428$; $\gamma = 120.224$).Fig.1 shows that the highest peak of the valence band and the lowest peak of the conduction band are located on the same line that passes through the point. That is to say, ZnO has a direct energy gap estimated at 0.68 eV. Hence, the findings of the energy bands structure calculated by the GGA method give lower results than the experimental ones. The latter indicates that this method does not provide results that are close to right- ness, unlike the (GGA + Ud) and (GGA + Ud+ Up) [31] methods. Accordingly, our value of the energy gap that was calculated by the generalized gradient approximation (GGA) is less than the experimental values, which is similar to the local density approximation (LDA), as shown by the work [32].

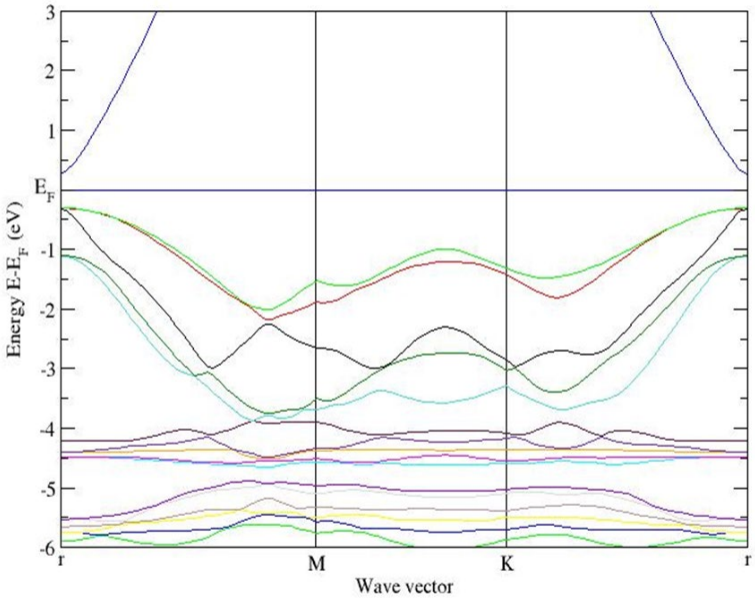

Fig.1. The energy band structure for zinc oxide, ZnO, phase Wurtzite.

To this end, Table 3gives the value of the obtained energy gap and its comparison with other experimental and theoretical values. From which, it could be readily seen that the computed value is close to the theoretical results. It is also noticed the value of Eg calculated using the DFT theory was about 79% less than that of the experimental one.

Table 3. The value of the energy gap, Eg, and its comparison with theoretical and applied values.

Experimental work [37]	GGA [36]	Experimental work [35]	Experimental work [34]	LDA [33]	GGA [22]	GGA [21]	Our works GGA	Method used
3.3	0.77	3.44	3.44	0.88	0.74	0.71	0.68	Eg (eV)

3.3.2. The total and partial density of states

To study the density of states, and in order to understand the movement of electrons close to the Fermi level, we need to know the density of the partial states of the elements zinc and oxygen, which contributed to the formation of the density of the total states of the oxide ZnO while it is in the solid state. Hence, we will explain the density of the total and partial states of the oxide ZnO as illustrated in Fig. 2.The total density of states belongs to the whole compound, that is to say, the contribution of all the atoms collectively in the compound(zinc and oxygen)This figure represents the variation of the density of state against energy. It is noticed in the domain extending from 0 to -20 eV representing the valence band, a peak of 1.9 states/eV. This corresponds roughly to -2 eV, through which the electron transfer potential is rather low, followed by the highest peak of states/eV near the Fermi plane and close to -5.2 states/eV what corresponds approximately to an energy value of -4.8 eV. Additionally, the values for the density of states were recorded in the range from0.68 to 15.5eV, which represents the conduction band. Furthermore, it was observed that there are small peaks of the densities of states in the region of the conduction band, while high peaks were recorded in the range (-6.5 to -4.5) eV that corresponds to the valence band, which is rich in the presence of electrons.

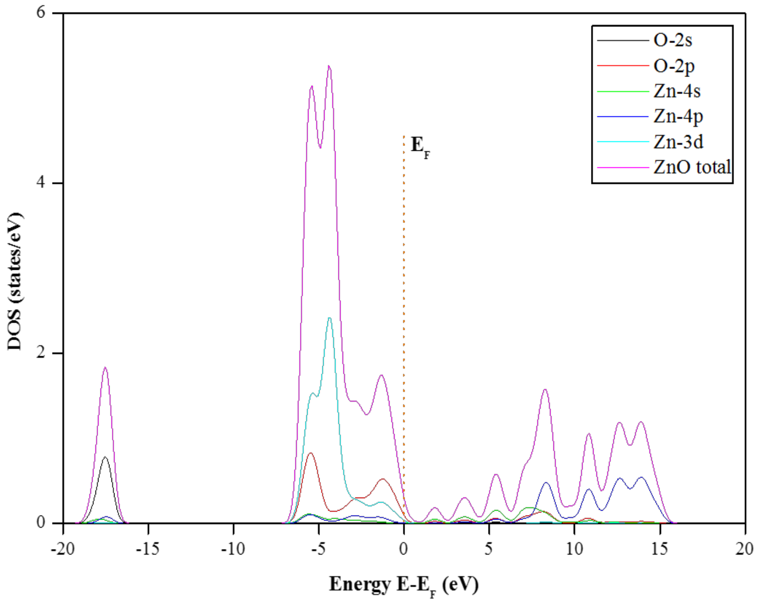

Fig. 2.Density of Total and Partial States of ZnO.

Fig. 2 illustrates the presence of peaks for the density of states in the valence band region. This is mainly due to the 3d position of the element (Zn) and the P-terminal of the element oxygen (O).The small peaks in the conduction band are attributed to the P-terminal of zinc (Zn) with the participation of the S and P-terminals of zinc. Hence, we can say that the responsible for the density of the state in the valence region is the d orbital of zinc and the p orbital of oxygen whereby the contribution of the d orbital is dominant. In this regard, there is a link station near the Fermi level at energy of -1.8 eV; and similarly next to the energy value of 2 eV where the probability of electrons transferring from the valence band to the conduction band is very high if the oxide is exposed to external stimulation such as pressure, light...etc.

3.4. The effect of pressure on the energy gap value

In this study, different pressure values were applied on ZnO in order to figure out the influence of the pressure on its electronic properties. The pressure values on the oxide ranged from 0 to 100 GPa. We have also used in our calculations the approximations of (GGA) and (LDA) and the comparison between them through which the effect of the value of the energy gap and the enthalpy of the compound were studied. To this effect, Fig. 3 shows how the energy gap is affected by the pressure change. This figure displays the variation of the energy gap for zinc oxide against the pressure using the approximations of GGA and LDA. Here, it is vividly seen that there is a gradual increase in the value of the energy gap with increasing pressure at both approximations. For example, the value of the energy gap at 20 GPa is recorded as 0.84 eV in the GGA approximation, while the 0.65 eV value was recorded at the LDA approximation, whereas the energy gap took the value 1.38 eV at the 80 GPA pressure for the GGA approximation. On the other hand, at the same pressure, the value of 1.05 eV was recorded for the LDA approximation. Thus, it turns out that the properties of the compound ZnO at different pressures are not the same, owing to the significant effect of the pressure.

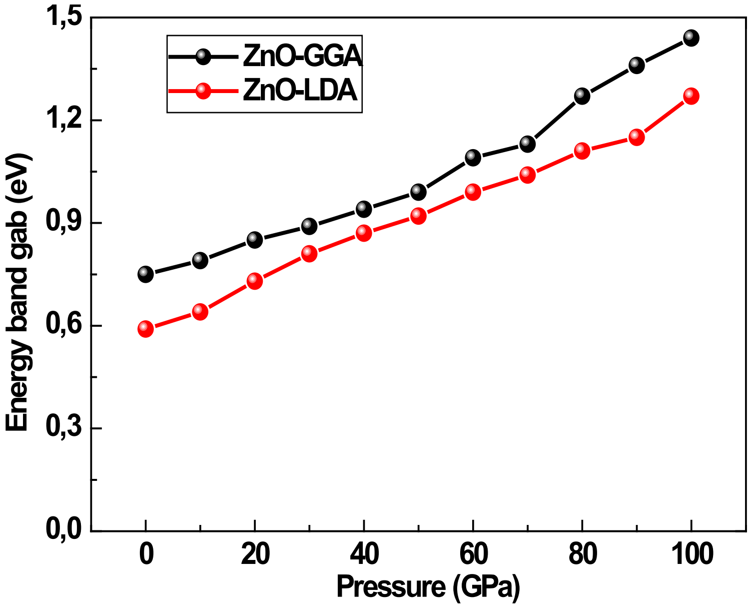

Fig. 3.Energy gap change in terms of pressure.

3.5. The effect of pressure on the phase

In the present study, the extent to which the structure of zinc oxide ZnO of type Wurtzite was affected by the pressure was investigated. Fig. 4 demonstrates the results of this effect on the enthalpy values of the compound.

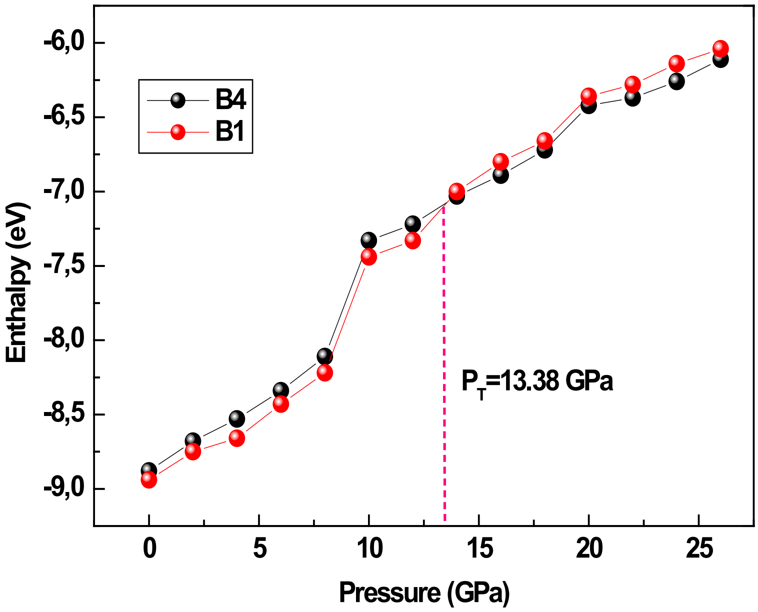

Fig. 4. Variation of enthalpy values in terms of pressure.

From the figure, it is clear that the enthalpy value plays an essential role in confirming phase stability whereby the pressure Pt=13.38 GPa, phases B4 and B1 have the same enthalpy value, while for lesser pressure values, the compound (B4) is the most stable structure of zinc oxide ZnO. From here, it becomes clear that the B4 phase turns into the B1 phase at a pressure of 13.38 GPa. This is evidence that changing the pressure changes the crystalline state of the oxide. The latter is close to the results reached in previous theoretical works [38-40].

4. Conclusion

In the current research, the calculations conducted by adopting the DFT method and the approximation GGA revealed that the crystal lattice constants of ZnO oxide obtained by using the Siesta code are very close to the results obtained theoretically and experimentally. Equivalently, our findings also showed that the compound has a direct energy gap whose value is close to the previously calculated theoretical works. The density of states near the Fermi level shows that the3d position of the Zn atom has effectively contributed. The variation of the energy gap with pressure has also been computed. The results revealed that with increasing the pressure, the maximum of the valence band moves towards lower energy, while the lower bound of the conduction band tends to higher energy, which leads to a widening of the energy gap. Moreover, our findings showed that the (B4) Wurtzite phase could transform into the rock salt (B1) phase at a pressure value of 13.38 GPa. Finally, and more importantly, these findings could offer a theoretical guide for ZnO applications in the UV field based on the possibility of changing its energy gap.

References

[1] J. Serrano, A. H. Romero, F.J. Manjon, R. Lauck, M. Cardona, A. Rubio, Phys. Rev B.**69**, 094306 (2004); https://doi.org/10.1103/PhysRevB.69.094306
[2] R. S. Ajimsha, A. K. Das, V. K. Sahu, P. Misra, ECS J. Solid State Sci. Technol.**8,** Q61 (2019); https://doi.org/10.1149/2.0171903jss
[3] L. P. Xiao, X. B. Li, L. Zeng, ECS J. Solid State Sci. Technol.**8,** Q85 (2019); https://doi.org/10.1149/2.0131904jss
[4] I. J. Gonzalez-Chan, P. Moguel, A. I. Oliva, ECS J. Solid State Sci. Technol.**8**, P536 (2019);https://doi.org/10.1149/2.0251909jss
[5] Y. B. Li, J. Zhang, J. X. Sun, T. P. Chen, ECS J. Solid State Sci. Technol.**10**, 115004 (2021); https://doi.org/10.1149/2162-8777/ac3ad1
[6] E. Suharyadi, A. Muzakki, N. I. Istiqomah, D. L. Puspitarum, B. Purnama, D. Djuhana, ECS J. Solid State Sci. Technol.**11**, 023004 (2022);https://doi.org/10.1149/2162-8777/ac4c7c
[7] T. T. Hien, V. T. Bich, P. T. Binh, M. T. T. Thuy, T. D. Nguyen, M. M. Tan, N. M. Hung, T. T. Trang, C. T. T. Hien, C. V. Tuan, ECS J. Solid State Sci. Technol.**11**. 073001 (2022); https://doi.org/10.1149/2162-8777/ac7d0b
[8] N. Shahi, A. Rahmati, ECS J. Solid State Sci. Technol. **8**. Q200 (2019); https://doi.org/10.1149/2.0101910jss
[9] X. Wang, J. Li, ECS J. Solid State Sci. Technol., **10**. 124003 (2021); https://doi.org/10.1149/2162-8777/ac4216
[10] Y. L. Chu, S. J. Young, T. T. Chu, A. Khosla, K. Y. Chiang, L. W. Ji, ECS J. Solid State Sci. Technol.**10**. 127001 (2021); https://doi.org/10.1149/2162-8777/ac3e43
[11] N.Takahashi, S. Sato, Y. Omura T. Saitoh, ECS J. Solid State Sci. Technol.**8**. P57 (2019); https://doi.org/10.1149/2.0201901jss
[12] J. Cheng K. M. Poduska, ECS J. Solid State Sci. Technol.**8** N1 (2019);https://doi.org/10.1149/2.0041901jss
[13] G. C. Zhou, L. Z. Sun, J. B. Wang,X. L. Zhong, Y. C. Zhou,Physica B.**403**. 2832-2837 (2008); https://doi.org/10.1016/j.physb.2008.02.018
[14] L. Bayarjargala, B. Winkler, Appl. Phys. Lett.**100**, 021909 (2012); https://doi.org/10.1063/1.3676057
[15] C. Kürkçü, Z. Merdan, C. Yamçıçıer, Indian. J. Phys.**93,** 979–989 (2019); https://doi.org/10.1007/s12648-018-01365-8
[16] C. H. Bates, W. B. White, R. Roy, New High-Pressure Polymorph of Zinc Oxide. Science. **137**, 993 (1962); https://doi.org10.1126/science.137.3534.993
[17] J. C. JamiesonPhys. Earth. Planet. Inter.**3**, 201 (1970); https://doi.org/10.1016/0031-9201(70)90056-7

[18] D. Chen, Y. Liu Y. J. Yuan,Russ.J. Phys. Chem. A.**94**, 423–428 (2020); https://doi.org/10.1134/S0036024420020089
[19] A. D. Becke, E. R. Johnson, J. Chem. Phys.**124**, 221101 (2006);https://doi.org/10.1063/1.2213970
[20] J. P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Lett.**77**, 3865 (1996); https://doi.org/10.1103/PhysRevLett.77.3865
[21] S. E. Huber, M. Hellstrom, M. Probsts, K. Hermansson, P. Broqvist, Surf. Sci. **628**, 50-61 (2014); https://doi.org/10.1016/j.susc.2014.05.001
[22] F. Oba, A. Togo, I. Tanaka, Phys. Rev B.**77**, 245202 (2008); https://doi.org/10.1103/PhysRevB.77.245202
[23] R. Farooq, T. Mahmood, A. W. Anwar, G. N. Abbasi,Superlattices Microstruct.**90**, 165 -169 (2016); https://doi.org/10.1016/j.spmi.2015.12.017
[24] M. Yaakob, N. Hussin, M. Taib, T. Kudin, O. Hassan, A. Ali, “Integr. Ferroelectr.**155**, 15 (2014); https://doi.org/10.1080/10584587.2014.905086
[25] E. H. Kisi, M. M. Elcombe,Acta crystallographica. SectionC.**45,** 1867-1870 (1989); https://doi.org/10.1107/S0108270189004269
[26] F. Decremps, F. Datchi, A. M. Saitta, A. Polian, Phys. Rev B.**68**, 104101 (2003); https://doi.org/10.1103/PhysRevB.68.104101
[27] M. Topsakal, S. Cahangirov, E. Bekaroglu, S. Ciraci,Phys, Rev B., **80,** 235119 (2009); https://doi.org/10.1103/PhysRevB.80.235119
[28] W. Q. Han, L. Wu, Y. Zhu, K. Watanabe, T. Taniguchi, Appl. Phys. Lett. **93**, 223103 (2008); https://doi.org/10.1063/1.3041639
[29] J. E. Jaffe, J. A. Snyder, Z. Lin, A. C. Hess,Phys. Rev B.**62**, 1660 (2000); https://doi.org/10.1103/PhysRevB.62.1660
[30] C. Li, W. Guo, Y. Kong, H. Gao, Phys. Rev B.**76**, 035322 (2007); https://doi.org/10.1103/PhysRevB.76.035322
[31] P. L. Hansen, J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. S. Clausen, H. Topsoe, Science.**295** , 2053-2055 (2002); https://doi/10.1126/science.abm3371
[32] S. H. Joo, S. J. Choi, I. Oh. J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, Nature.**412**, 169-172 (2001); https://doi.org/10.1038/35084046
[33] Y. N. XU, W. Y. ching,Phy. Rev B.**48**, 4335 (1993); https://doi.org/10.1103/PhysRevB.48.4335
[34] D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, G. Cantwell, W. C. Harsch,Phys. Rev B.**60**, 2340 (1999); https://doi.org/10.1103/PhysRevB.60.2340
[35] H. Landolt, R. Bornstein, K. H. Hellwege, Dieter Bimberg, M. Schulz, Harald Weiss, O. Madelung, Landolt-börnstein numerical data and functional relationships in science and technology., group 3 crystal and solid state physics. vol. **17** semiconductors. (Springer, Berlin)(1982).
[36] J. Wrobel, K. J. Kurzydlowski, K. Hummer, G. kresse, J. Piechota,Phys. Rev B.**80**, 155124 (2009); https://doi.org/10.1103/PhysRevB.80.155124
[37] L. Franklin, C. Ekuma, G. L. Zhao, D. Bagayoko,J. Phys. Chem. Solids. **74**,729-736 (2013); https://doi.org/10.1016/j.jpcs.2013.01.013
[38] F. G. Kuang, X. Y. Kuang, S. Y. Kang, M. M. Zhong, A. J. Mao,Mater. Sci. Semi-cond. Process.**23**, 63-71 (2014); https://doi.org/10.1016/j.mssp.2014.02.029
[39] M. P. Molepo, D. P. Joubert, Phys. Rev B.**84**, 094110 (2011); https://doi.org/10.1103/PhysRevB.84.094110
[40] B. Meyer, D. Mark, Phys. Rev B.**67**, 035403 (2003); https://doi.org/10.1103/PhysRevB.67.035403