PHYSICAL REVIEW B **78**, 193308 (2008)

Relaxation models of the (110) zinc-blende III-V semiconductor surfaces: Density functional study

Honggang Ye,[1] Guangde Chen,[1] Yelong Wu,[1] Youzhang Zhu,[1] and Su-Huai Wei[2]
[1]*Department of Applied Physics, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*
[2]*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*

(Received 25 September 2008; published 17 November 2008)

Clean III-V zinc-blende (110) surfaces are the most extensively studied semiconductor surface. For conventional III-V compounds such as GaAs and InP, the surface relaxation follows a bond rotation relaxation model. However, for III-nitrides recent study indicates that they follow a bond-constricting relaxation model. First-principles atom relaxation calculations are performed to explore the origin of the difference between the two groups of materials. By analyzing the individual shift trends and ionic properties of the top layer anions and cations, we attribute the difference between the conventional and nitride III-V compounds to the strong electronegativity of N, which leads to the s^2p^3 pyramid bond angle to be larger than the ideal one in bulk (109.5°). The general trends of the atomic relaxation at the III-nitrides (110) surfaces are explained.

DOI: 10.1103/PhysRevB.78.193308 PACS number(s): 68.35.bg, 68.47.Fg, 31.15.ae

I. INTRODUCTION

III-V semiconductor compounds such as GaAs and GaN are important materials for microelectronic and optoelectronic applications.[1] Their physical properties have been extensively studied for several decades. Among them, surface reconstruction and relaxation have attracted much attention because they are closely related to the crystal growth and doping in these materials.[2–4] As zinc-blende structure is favored by the majority of the III-V semiconductors, much of the attention has been focused on the low-energy close-packed nonpolar (110) surface. The zinc-blende (110) surface is characterized by a zigzag chain along the $[1\bar{1}0]$ direction with the (1×1) translational symmetry. Earlier works had established a well accepted bond rotation (BR) relaxation model for the (110) surface of conventional III-V compounds.[5–12] In this BR model, charge on the cation dangling bond is transferred to the anion dangling bond. To reduce the surface energy, the top layer anions move outward in favor of an s^2p^3 bonding with three neighboring cations and the cations move inward in favor of an sp^2 bonding with three neighboring anions, inducing a top layer buckling angle of about 30° and an almost conservation of the bulk bond length in the top layer. However, later studies for the III-nitrides found that they do not follow this established relaxation pattern.[13–21] For the III-nitrides, the top layer bonds are constricted, the buckling angle is much smaller ($\sim10°$), and the top layer N maintains nearly in the bulklike position after relaxation.

To explain the different relaxation patterns between conventional III-V semiconductors and III-nitrides (110) surface, it has been suggested that the strong ionic character in the III-nitrides causes less rehybridization at the surface to form a local anion-centered pyramidal geometry and the large charge transfer from cation to anion leads to a stronger Coulomb attraction between the surface anions and cations.[14–16] However, this explanation based on ionicity is not very strict and convincing. According to the ionicity scales given by Pauling,[22] Phillips[23] and others,[24,25] although the ionicity of III-nitrides is wholly strong, there is not an obvious jump between the ionicity of III-nitrides and conventional III-V semiconductors. Especially, BN is shown to be less ionic than GaAs and InP,[23,25] but BN behaves undoubtedly like other nitrides instead of conventional III-V semiconductors. So, interpretation beyond the bond ionicity picture is needed to explain the qualitatively different relaxation behavior between conventional III-V semiconductors and III-nitrides (110) surfaces.

In the present work, we calculated the (110) surface relaxation of all III-nitrides and GaAs, a prototype of conventional III-V compound, and obtained consistent results with previous reports. Different from previous reports, our analysis indicates that the intrinsic atomic Pauling electronegativity difference between the anions in the conventional III-V compounds and III-nitrides is the main reason that leads to different relaxation behavior at the (110) surface of these materials. This model can successfully explain the individual displacements of the anions and cations as well as the small buckling angle variation at the III-nitrides (110) surfaces.

II. CALCULATION METHOD

Density functional theory based calculations are performed within the generalized gradient approximation (GGA) (Ref. 26) framework as implemented by the Vienna *Ab initio* Simulation Package (VASP) code.[27,28] The Ga 3*d* and In 4*d* electrons are treated as valance electrons. The interaction between core and valence electrons are treated with the projector augmented wave method.[29] The energy cutoff for the basis function is 500 eV for III-nitrides and 350 eV for GaAs. We employ Monkhorst-Pack sampling scheme with *k*-point mesh of $7\times10\times1$ for BN, $6\times8\times1$ for AlN and GaN, $5\times7\times1$ for InN, and $4\times6\times1$ for GaAs.[30] The slab models are built containing eleven atomic layers with 12 Å vacuum spaces separating the slabs. The top three layers at both sides of the slab are allowed to relax by minimizing the quantum-mechanical force on each ion site to be less than 0.01 eV/Å. The other layers are fixed in the optimized bulk configuration. Test calculations show that the cell size is converged. Side and top views of the ideal and relaxed slab

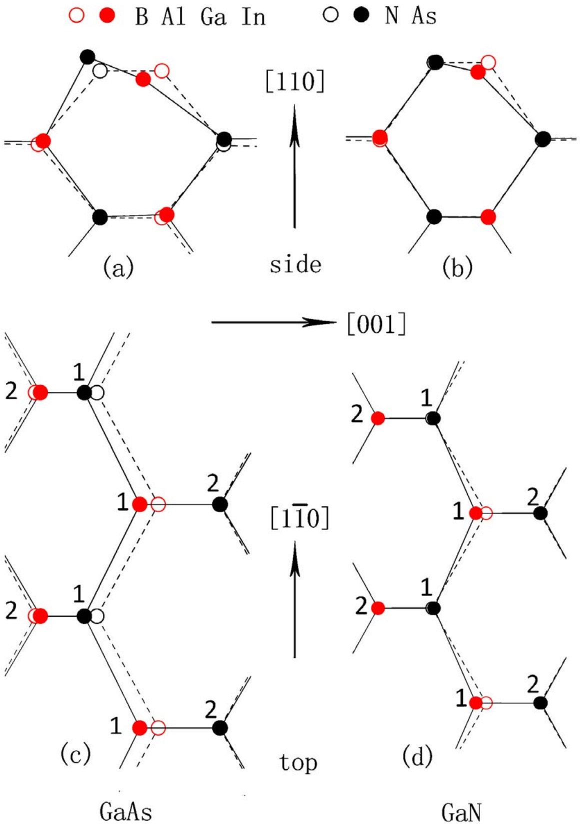

FIG. 1. (Color online) Schematic representation of the relaxed (filled circles) and unrelaxed (empty circles) atomic positions for GaAs and GaN. (a) side view of GaAs; (b) side view of GaN; (c) top view of GaAs; (d) top view of GaN. The numbers 1 and 2 in (c) and (d) denote the atom layers.

models for III-nitrides and conventional III-V compounds are shown in Fig. 1. The lattice parameters used in building the slab models are 3.625 Å for BN, 4.399 Å for AlN, 4.543 Å for GaN, 5.048 Å for InN, and 5.742 Å for GaAs, which are obtained by optimizing the corresponding bulk primitive cell and agree well with the experimental values.[31]

III. RESULTS AND DISCUSSION

When the (110) surface is cleaved from a zinc-blende crystal, the top layer anion and cation become threefold coordinated with one dangling-bond point away from the surface. To achieve lower energy, charges are transferred from the high-energy cation dangling bond to the low-energy anion dangling bond, thus satisfying the electron counting rule. Accompanied with the charge transfer, the anion tends to have the local pyramidal s^2p^3 configuration, whereas the cation tends to have the sp^2 local planar configuration, resulting in a buckled top layer. Following the custom, the main features of the (110) surface relaxation are described by two parameters:[11] the top layer rotation angle ω and the top layer bond constriction Δb. Additionally, the horizontal and vertical shifts of each anion and cation are represented by ΔA_i, $\Delta A_{i,\perp}$, ΔC_i, and $\Delta C_{i,\perp}$, respectively, where the index i denotes the atom layer. By symmetry, the horizontal shift here is along the [001] direction, and the vertical shift is along the [110] direction. The calculated data for each material are shown in Table I and compared with previous reports.[13–15] The relative displacement between anion and cation can be simply derived from the position shift of each atom.

It can be seen from Table I that the results of the present-work are consistent with previous reports. The top layer

TABLE I. Calculated structure parameters for the relaxed zinc-blende group-III nitrides and GaAs (110) surfaces in comparison with previous reports.

		ω (deg)	Δb (%)	ΔA_1 (Å)	$\Delta A_{1,\perp}$ (Å)	ΔC_1 (Å)	$\Delta C_{1,\perp}$ (Å)	ΔA_2 (Å)	$\Delta A_{2,\perp}$ (Å)	ΔC_2 (Å)	$\Delta C_{2,\perp}$ (Å)
BN	Present	17.7	7.06	0.06	−0.01	−0.18	−0.22	0.02	0.03	−0.01	0.06
	Ref. 15	15.74	7.8								
	Ref. 13	16.6	6.6								
AlN	Present	12.0	5.92	0.05	−0.02	−0.18	−0.20	0.02	0.01	0.00	0.05
	Ref. 15	11.61	3.6								
	Ref. 13	11.9	2.9								
	Ref. 14	11.7	5.9								
GaN	Present	14.3	5.59	0.02	0.02	−0.22	−0.21	0.02	0.01	−0.01	0.05
	Ref. 15	14.29	5.3								
	Ref. 13	17.5	2.8								
	Ref. 14	14.3	4.9	0.04	0.05	−0.17	−0.18	0.05	0.02	0.03	0.07
InN	Present	13.4	4.75	0.00	0.05	−0.23	−0.20	0.01	0.01	−0.01	0.04
	Ref. 15	13.13	4.9								
	Ref. 13	10.6	3.3								
	Ref. 14	14.4	4.3								
GaAs	Present	30.0	1.14	−0.15	0.24	−0.38	−0.45	0.04	0.02	0.05	0.09
	Ref. 14	30.1	0.9	−0.15	0.42	−0.37	−0.27	−0.06	0.13	−0.08	0.23

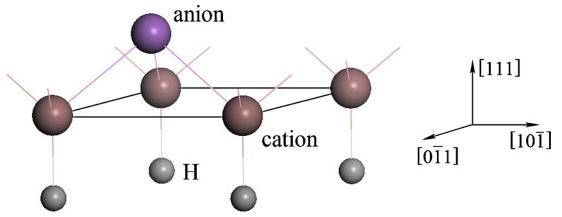

FIG. 2. (Color online) The model used to predict the bond angles of AC_3 pyramid with group-V anion A at the center and coordinated with three group-III cations. The dangling bonds of cations are saturated by 5/4 electrons charged hydrogen atoms.

buckling angles for III-nitrides vary from 13.4° for AlN to 17.7° for BN, much smaller than the values of 30.0° for GaAs. The top layer bond-length constriction for III-nitrides are between $4.75\sim7.06\%$, qualitatively different from the 1.14% for GaAs. The vertical displacement of top layer N is between $-0.02\sim0.05$ Å, i.e., it is close to the bulk position, however, the 0.24 Å displacement for top layer As indicates a large outward movement of top layer As in GaAs. The calculated results, thus, show the main features of (110) surface relaxation, i.e., the III-nitrides follow a bond-constricting rotation model with the top layer N atoms maintaining in the bulklike position; whereas for conventional III-V compounds, such as GaAs, they follow a bond-conserving rotation model with the top layer anions moving outward.

To understand the relaxation of the anions at the (110) surface, we first analyze the bond angles of the AC_3 in the pyramidal configuration. This is because when the anion A at the (110) surface forms the pyramid, the pyramid bond angle is directly correlated with the top layer rotation angle ω and the top layer atomic displacement. When anion moves outward, the rotation angle ω increases but the bond angle decreases, whereas when anion moves inward, the rotation angle ω decreases but the bond angle increases. For C=H and A=N, P, As, and Sb, the computed bond angles of NH_3, PH_3, AsH_3, and SbH_3 molecules are 106.6°, 92.4°, 90.8°, and 90.6°, respectively. For C=Ga, the computed bond angles, using the geometry described in Fig. 2, are 115.9°, 106.6°, 104.9°, and 104.7°, respectively, when the cation layer is fixed in bulk size (the bond angle and bond length are dependent) and 116.3°, 95.0°, 93.2°, and 92.9°, respectively, when the cation layer is allowed to relax freely (the bond angle and bond length are independent). The real bond angles at surfaces should be between them. The above data indicate that large difference exists between NC_3 and AC_3 (A=P,As,Sb) and that with the same cation C atom, the bond angles of AC_3 pyramid increases with the decreasing atomic number of anion A. This can be understood by valence shell electronic pair repulsion (VSEPR) model.[32] When the atomic number of A decreases, the Pauling electronegativity of A increases (the Pauling electronegativity of N, P, As, and Sb are 3.04, 2.19, 2.18, and 2.05, respectively),[33] thus the charges on anion-cation bonds become closer to each other. Therefore, to avoid the electronic repulsion between bond charges, the bond angle increases.

Although the bond angles of AC_3 pyramid configuration are mainly determined by the center atom A, the C atoms also have effect on them. The VSEPR model tells us that the bond angle should increase when the Pauling electronegativity of C decreases. This is exactly what we observed when H is replaced by Ga. It is interesting to notice that the bond angle of about 116° for NGa_3 is larger than ideal tetrahedral angle of 109.5°, but the bond angle for PGa_3, $AsGa_3$, and $SbGa_3$ is smaller than 109.5°. It indicates that, as the (110) surface is cleaved, the top layer N atom in the nitrides tend to move inward to increase the bond angle. On the other hand, the top layer P, As, and Sb atoms in conventional III-V semiconductors tend to move outward in order to reduce the bond angle from the ideal tetrahedral values.

For the top layer cations, they prefer to form a sp^2 configuration so they must move inward to form a plane and push the surface anion outwards (Fig. 1). For III-nitrides, the top layer N atoms try to move inward but the surface cations try to drive them outward so the top layer N atoms remain nearly in the bulklike positions, and the top layer cations only can partly realize sp^2 configuration by bond constriction, which result in a small top layer buckling angle. For other III-V compounds, the top layer anions tend to move outward and the cations also try to drive them outward, the two effects add to each other, making the anions to move outward in a large scale and the cations almost fully realize sp^2 configuration, which result in a large top layer buckling angle of about 30°.

Based on the above relaxation mechanism, the other parameters in Table I can also be explained. The top layer anion parallel shift ΔA_1 is small and positive for III-nitrides (0.00–0.06 Å) but relative large and negative for GaAs (−0.15 Å). This is also because the positive shift is helpful to increase the pyramid bond angle whereas the negative shift is helpful to decrease the bond angle. The two parameters ΔA_2, $\Delta A_{2,\perp}$ in Table I indicate that the second layer anions shift to top-right direction [relative to Figs. 1(a) and 1(b)] for both III-nitrides and GaAs. This is because this movement is driven by the top layer cations tending to form planar sp^2 configuration. The parallel shifts ΔC_2 of second layer cations for III-nitrides are negligible. Their vertical shifts $\Delta C_{2,\perp}$ are also helpful to the bond angle increase of top layer N. For GaAs, the second layer Ga moves upward along the bond with the top layer As because it tends to conserve the Ga-As bond length.

After understanding the relaxation pattern difference between III-nitrides and conventional III-V compounds, the variation in the top layer buckling angle between III-nitrides can also be understood conveniently based on the relaxation mechanism discussed above. As shown in Table I, the top layer buckling angles of III-nitrides decrease in the sequence of BN(17.7°) > GaN(14.3°) > In N(13.4°) > AlN(12.0°), which indicate that the bond angles of the NC_3 pyramid increases in the same order. According to the VSEPR model,[32] this trend can be easily understood by noticing that the electronegativity of cation decreases in the sequence of B(2.04) > Ga(1.81) > In(1.78) > Al(1.61) (Ref. 33) to avoid overlapping of valence electrons, the bond angle of the pyramid will increase.

IV. CONCLUSION

By analyzing the bond angle of (110) surface pyramidal configuration, the shift trends of top layer anions and cations are predicted individually. The top layer N tends to move inward to increase the pyramid bond angles, but top layer P, As, and Sb tend to move outward to decrease the pyramid bond angles. The opposite trends induce the final surface-atom configurations which are obviously different between III-N and conventional III-V semiconductors. Besides the main features, each displacement of the first and second layer atoms also is explained convincingly. Furthermore, based on this relaxation mechanism, the top layer buckling angle variation between III-nitrides is explained expediently by the Pauling electronegativity trend of group-III elements. It is thought that this relaxation mechanism can be further used to wurtzite and II-VI compounds.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the China National Natural Science Fund (Grant No. 10474078) and the computing support of the "Intelligent Information Processing and Computing Laboratory" of Xi'an Jiaotong University. The work at NREL is supported by the U.S. DOE under Contract No. DE-AC36-99GO10337.

---

[1] H. Morkoç, *Nitride Semiconductors and Devices* (Springer, Berlin, 1999).
[2] B. A. Haskell, S. Nakamura, S. P. DenBaars, and J. S. Speck, Phys. Status Solidi B **244**, 2847 (2007).
[3] K. Xu, J. Xu, P. Z. Deng, R. S. Qiu, and Z. J. Fang, Phys. Status Solidi A **176**, 589 (1999).
[4] T. Akasaka, Y. Kobayashi, and T. Makimoto, Appl. Phys. Lett. **90**, 121919 (2007).
[5] A. Kahn, E. So, P. Mark, C. B. Duke, and R. J. Meyer, J. Vac. Sci. Technol. **15**, 1223 (1978).
[6] Jose Luiz A. Alves, J. Hebenstreit, and M. Scheffler, Phys. Rev. B **44**, 6188 (1991).
[7] D. J. Chadi, Phys. Rev. B **19**, 2074 (1979).
[8] J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B **14**, 4724 (1976).
[9] G.-X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **37**, 1303 (1988).
[10] S. Y. Tong, A. R. Lubinsky, B. J. Mrstik, and M. A. Van Hove, Phys. Rev. B **17**, 3303 (1978).
[11] M. H. Tsai, J. D. Dow, R. P. Wang, and R. V. Kasowski, Phys. Rev. B **40**, 9818 (1989).
[12] A. R. Lubinsky, C. B. Duke, B. W. Lee, and P. Mark, Phys. Rev. Lett. **36**, 1058 (1976).
[13] R. Miotto, A. C. Ferraz, and G. P. Srivastava, Solid State Commun. **115**, 67 (2000).
[14] A. Filippetti, V. Fiorentini, G. Cappellini, and A. Bosin, Phys. Rev. B **59**, 8026 (1999).
[15] U. Grossner, J. Furthmuller, and F. Bechstedt, Phys. Rev. B **58**, R1722 (1998).
[16] Z. Q. Li, H. Chen, F. Q. Kong, Q. Sun, and Y. Kawazoe, J. Appl. Phys. **84**, 1977 (1998).
[17] B. K. Agrawal, P. Srivastava, and S. Agrawal, Surf. Sci. **405**, 54 (1998).
[18] R. Pandey, P. Zapol, and M. Causà, Phys. Rev. B **55**, R16009 (1997).
[19] J. E. Northrup and J. Neugebauer, Phys. Rev. B **53**, R10477 (1996).
[20] J. E. Jaffe, R. Pandey, and P. Zapol, Phys. Rev. B **53**, R4209 (1996).
[21] R. Miotto, G. P. Srivastava, and A. C. Ferraz, Surf. Sci. **426**, 75 (1999).
[22] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960).
[23] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).
[24] C. A. Coulson, L. B. Redei, and D. Stocker, Proc. R. Soc. London **B270**, 352 (1962).
[25] A. García and M. L. Cohen, Phys. Rev. B **47**, 4215 (1993).
[26] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[27] G. Kresse and J. Furthmuller, Comput. Mater. Sci. **6**, 15 (1996).
[28] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).
[29] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[30] J. D. Pack and H. J. Monkhorst, Phys. Rev. B **16**, 1748 (1977).
[31] I. Vurgaftman and J. R. Meyer, J. Appl. Phys. **94**, 3675 (2003).
[32] R. J. Gillespie, Coord. Chem. Rev. **252**, 1315 (2008).
[33] H. B. Gray, *Chemical Bonds* (Menlo Park, California, 1973).