The explanation of metallic nature of BBi(110) surface

Sadık BAĞCI[*1]

Abstract

In this study, the structural, elastic and electronic properties for zinc-blende BBi have been investigated by using plane wave ab initio calculations within the density functional theory. The local density approximation was employed to take account of electronic exchange and correlation energies. The lattice constant and bulk modulus are in good agreement with previous theoretical results. The elastic constants are also calculated using the volume-conserving tetragonal and monoclinic strains. The electronic band structure and density of states of BBi are also presented and discussed in detail. Using our results for bulk properties of BBi, we have obtained the atomic relaxed geometry and electronic band structure of the (110) surface of BBi for the first time in the literature. We have also discussed total and partial electronic density of states for BBi(110) surface to explain metallic nature of this surface. At the end of our study, we have compared our surface electronic structure with other metallic (110) surfaces of AlBi, GaBi and InBi.

Keywords: Ab initio calculations, BBi(110) surface, Surface electronic structure, Surface electronic DOS

1. INTRODUCTION

In recent years, III-Bi compounds and their alloys have attracted the attention of the researchers because of their remarkable physical properties [1-13]. The first member of this series Boron Bismuth (BBi) has been reported in several theoretical studies [1-13] due to its interesting properties such as a small band gap, low ionicity, high mechanical strength and high melting point [14-18]. Although there are several theoretical works about physical properties of BBi, it has not been synthesized yet. In some of these theoretical works, the ground state phase of BBi is confirmed as zinc-blend (ZB) [4-6]. The ground state properties and also electronic and optical properties of BBi have been investigated by several theoretical research group in recent years [1-12]. Ferhat and Zaoui have reported negative band gap for BBi using full potential linearized augmented plane-wave (FLAPW) method [4]. On the other hand, Shouxin et al. have obtained indirect band gap for BBi by using generalized gradient approximation (GGA) [2]. In addition, Wang and Ye [7] have also attained similar result for energy band gap

of BBi using local density approximation (LDA). Otherwise, Madouri and Ferhat [6], Deligoz et al. [3] and B. G. Yalcin et al. [8,9] have calculated direct band gap for BBi compound using DFT. The dynamical properties of BBi are also presented by Deligoz et al. [3] and Belabbes et al. [13] in different studies.

In this study, the structural properties such as lattice parameter and bulk modulus of BBi have been calculated by using an ab initio pseudopotential method based on the density functional theory within the local density approximation. Using calculated lattice parameters, the cubic elastic constants, C_{11}, C_{12} and C_{44}, have been obtained under favour of volume-conserving tetragonal and monoclinic strains. The electronic band structure and density of states (DOS) of bulk BBi have been investigated and discussed in detail. All obtained bulk properties for BBi have been also compared with previous theoretical works. Although there are wide range of theoretical works related to bulk properties of BBi, its surface properties are totally paid no attention in the literature. However, the surface properties of a material play an important role to obtain the application areas in electronic and optical devices. Therefore, using

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[*] Sadık Bağcı(sbagci@sakarya.edu.tr)
[1] Sakarya Üniversitesi Fen Edebiyat Fakültesi Fizik Bölümü Esentepe Kampüsü Serdivan / SAKARYA

bulk properties of BBi, we have obtained theoretical results of the relaxed atomic geometry of (110) surface of BBi, first time in the literature. The relaxed geometry of BBi(110) is similar with other III-V(110) surfaces: the cation-anion chain become tilted with the anions being raised. In addition to relaxed geometry of BBi(110), the surface electronic band structure and DOS have been also obtained and discussed. We have compared surface electronic states with projected bulk electronic spectrum to obtain surface electronic band structure of BBi(110) surface.

2. THEORY

The first principles calculations based on the density functional theory with the local density approximation have been performed by using the QUANTUM ESPRESSO package [19] in this study.

For the exchange and correlation effects were solved using local density approximation (LDA) [20,21]. The pseudopotentials for B and Bi are generated using a Troullier-Martin norm conserving scheme [22]. The 40 Ry cut off energy has been implemented to expand the electronic wave functions. We use ten special k points in the irreducible part of the Brillouin zone. We have used 15 atomic layers atomic slab and five atomic layers vacuum region to model a supercell geometry for the (110) surface of BBi. The Kohn-Sham equations have been used to achieve relaxation of atomic and electronic degrees of freedom [23]. For the relaxation of atomic geometry, all atoms were allowed to relax except the central plane of the atomic slab. The equilibrium positions of the atoms in the supercell geometry are ascertained by using the forces smaller than 0.1 mRy/au on the atoms. We have used nine special k points for surface calculations

The elastic constants for the ZB phase were extracted using the procedure discussed by Wang and Ye [7]. It is clearly known that three independent elastic constants namely C_{11}, C_{12} and C_{44} are used to describe elastic properties of a cubic crystal, basically. In this study we have used the volume-conserving tetragonal and monoclinic strains to calculate C_{11}–C_{12} and C_{44}, respectively. After these calculations, the elastic constants of C_{11} and C_{12} have been obtained by using the relation $B=1/3(C_{11}+2C_{12})$. B is determined as bulk modulus in this relation.

3. RESULTS AND DISCUSSIONS

3.1. Structural and Electronic Properties of BBi

First of all, we have calculated total energy of the unit cell using different lattice parameters (a) to attain the

equilibrium lattice constant (a_0) of the zinc blende phase BBi. By means of this lattice parameter, the equilibrium bulk modulus (B) and its pressure derivative (B') have been also determined by Murnaghan equations [24]. Table 1 presents our calculated results for BBi, in comparison with available theoretical studies [1-4,9]. In this table, we have compared our obtained structural parameters with other previous theoretical studies. It can be seen from Table 1 that our results and previous studies are in good agreement to each other. We have also presented our calculated cubic elastic constants (C_{11}, C_{12} and C_{44}) and available previous theoretical values for BBi in this table. According to the our knowledge, BBi has never been synthesized, yet. Therefore, it is important to investigate the mechanical stability for zinc blende phase of BBi. It is clearly known that there are four requirements to determine mechanical stability in cubic crystal: $C_{11}>0$, $C_{44}>0$, $C_{11}-C_{12}>0$ and $C_{11}+2C_{12}>0$. It can be seen from Table 1 that, our obtained elastic constants obey these stability conditions similar with other previous theoretical results.

Table 1. Structural and elastic properties of BBi and their comparison with previous theoretical results.

Source (Method)	a (Å)	B (GPa)	B'	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
This work (LDA)	5.365	87.70	4.09	122.16	70.47	85.97
Theory [1] (TBIP)	5.415	99.30	-	197.78	85.87	105.9
Theory [2] (GGA)	5.464	81.89	4.32	147.35	46.16	83.81
Theory [3] (LDA)	5.415	99.30	4.51	164.06	66.92	90.75
Theory [4] (LDA)	5.416	86.27	4.60	163.80	28.30	86.30
Theory [9] (GGA)	5.528	66.48	5.76	-	-	-

We have presented the calculated electronic band structure of BBi in Figure 1. The calculated overall band structures of BBi are similar with the obtained electronic band spectrum for the B-V compounds [25]. It can be seen from Fig. 1 that BBi has an indirect band gap with the valence band maximum locates at the Γ point and the conduction band minimum is along the Γ-

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X direction close to the X point. The calculated band gap value of BBi is 0.56 eV.
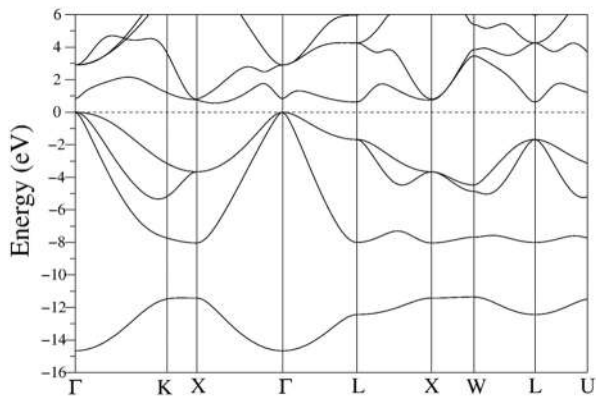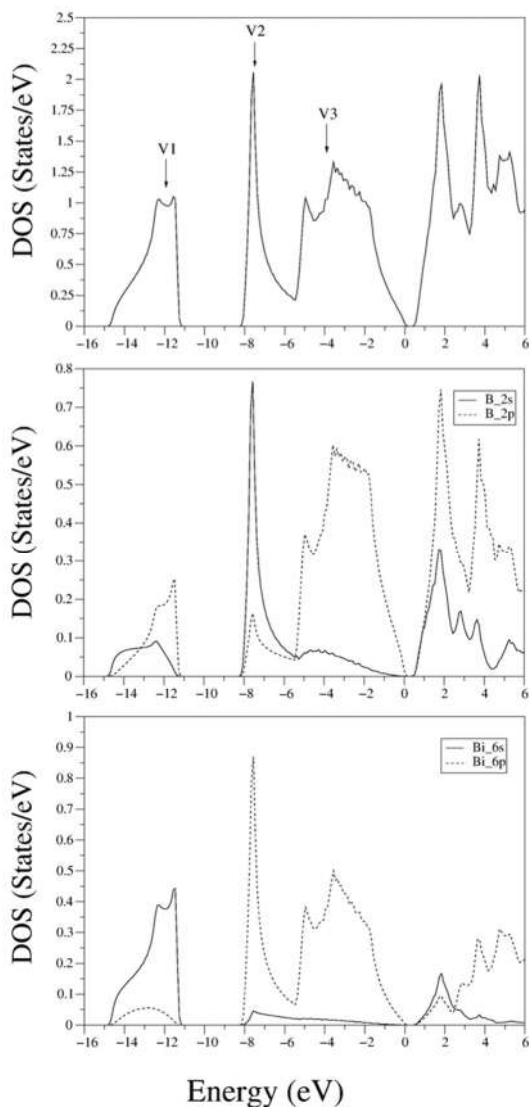

Figure 1. The electronic band structure for BBi.

Figure 2. Total and partial density of states (DOS) for BBi.

The total and partial density of states (DOS) for BBi are presented in Figure 2, in order to explain all band characters, clearly. There are three distinct regions named V1, V2 and V3 in the total valence DOS. V1 is localized between -16 eV and -11 eV and consist of B-2s, B-2p and Bi-6s orbitals. V2 is the sharpest peak localized nearly -7 eV and the main contributions to this peak comes from the 6p bands of Bi atom and 2s bands of B atom. V3 is occured by B and Bi p orbitals with the nearly same contributions. It can be seen from Fig. 2 that there is a strong p-p mixing in the V3 band which is mainly composed of Bi 6p hybridized with B 2p. For the conduction bands, main contribution to DOS comes from B 2p orbital hybridized with B 2s. As can be seen from Fig.2, there is also small contribution from Bi 6p orbital to DOS of conduction bands.

3.2. Structural and Electronic Properties of BBi(110) Surface

The clean cleaved (110) surface of zinc-blende materials retains the primitive (1×1) periodicity and the outermost layer of an ideal (110) surface contain equivalent cation and anion atoms. In our calculations, positions of the fourth layer atoms have been found to be very near the their classic bulk positions. Therefore, the relaxation of the (110) surface structure of BBi may be explained in terms of the tilt angles of the atomic chains in the three outermost layers. In Fig. 3, the schematic diagram of the relaxed top three layers of the BBi(110) surface and the key structural parameters have been presented. The relaxation of these surfaces is explained by the well known cation-anion chains become tilted with anions being raised, as displayed in Fig. 3.

Our computed surface structural parameters, defined in Fig. 3, are listed in Table 2 together with the previous theoretical results of other B-V(110) surfaces [25,26]. Our calculated surface bond length of top-layer atoms (2.285Å) is 2 % less than the calculated bulk bond length value of 2.323 Å. This shortening on the atomic bond length clearly indicates that interatomic bonding on BBi(110) surface is stronger than the corresponding bulk BBi bonding.
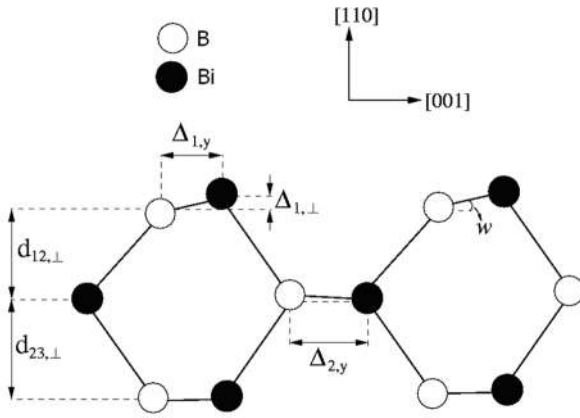
Figure 3. Schematic representation of the relaxed atomic positions indicating the key structural parameters for the cubic (110) surface of BBi.
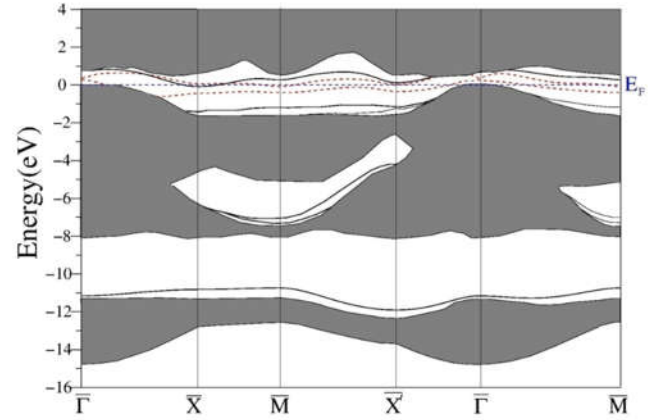

Figure 4. The electronic band structure of the BBi(110) surface. The projected bulk spectrum is shown by hatched regions. The localized surface states of the relaxed (solid curves) and unrelaxed (dotted red curves) BBi(110) surface. The Fermi level corresponds to 0 eV.

The surface tilt angle of BBi(110) is found to be 27.4^0. This means that the tilt angles of B-V(110) surfaces increases from BN(110) to BBi(110) as can be seen from Table 2. The another important surface structural parameter, the surface buckling $\Delta_{1,\perp}$ for BBi(110) is found to be 0.587 Å which is convenient to raise from BN(110) towards BBi(110). Thus, these results are confirmed by Duke law says that $\Delta_{1,\perp}$ increase almost monotonically with the d_{sb}.

Table 2. Calculated structural parameters (in Å) defined in Fig. 3 for BBi(110) surface and their comparison with other (110) surfaces of boron compounds.

BV(110) surface	$\Delta_{1,\perp}$	$\Delta_{1,y}$	$\Delta_{2,y}$	$d_{12,\perp}$	$d_{23,\perp}$	d_{sb}	ω
BBi(110)	0.587	1.131	1.337	1.306	1.722	2.285	27.4^o
BSb(110) [25]	0.549	1.102	1.421	1.284	1.674	2.224	26.5^o
BAs(110) [25]	0.485	0.992	1.161	1.177	1.524	2.007	26.1^o
BP(110) [25]	0.423	0.937	1.091	1.119	1.441	1.895	24.4^o
BN(110) [26]	0.213	0.660	0.870	1.124	1.300	1.440	17.9^o

The surface electronic band structure of BBi(110) is presented along the several symmetry directions of the surface Brillouin zone in Figure 4. In this figure, the solid curves are localized surface states for relaxed BBi(110) while the surface states in the fundamental gap shown as dotted curves are obtained from unrelaxed BBi(110) surface. It can be seen from Fig. 4 that the general pattern of surface electronic structure of BBi(110) is similar with other III-V(110) surfaces [25-28].

It is very important to note that BBi(110) surface is clearly metallic for both relaxed and unrelaxed structures with at least one surface state crossing the Fermi level, in contrast with bulk BBi is a narrow gap semiconductor. For the relaxed BBi(110) surface, there are five surface states in the gap regions between the projected bulk spectrum where the bulk states are not located in. Characters of these surface states are explained using electronic total and partial DOS shown in Figure 5. This figure presents total DOS for first three layer of BBi(110) and contribution of first, second and third layer atoms to total DOS, separately. The lowest surface state is derived from first and third layer Bi-6s orbitals, dominantly. Second layer Bi-6s and all three layer B-2p orbitals provide a small contribution to this surface state. There are two surface states in the stomach gap region. These surface states show strong dispersion along the $\overline{M} - \overline{X'}$ direction. These bands come from both Bi-6s and B-2s orbitals of all three layers. Other surface state with energy of -1 eV is nearly flat along the $\overline{X} - \overline{M} - \overline{X'}$ directions, and occured by Bi-6p and B-2p orbitals with together. The highest surface state, in the fundamental gap between the valence band and the conduction band, are mainly due to all three layer B atoms.
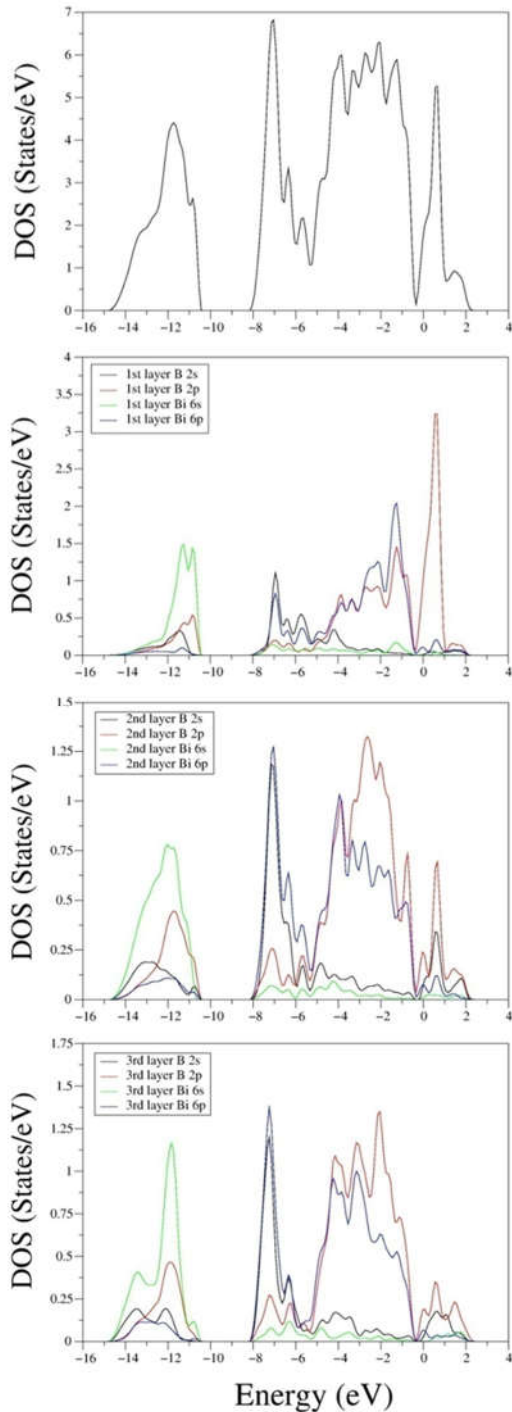
Figure 5. The total and partial density of states for first three layer of BBi(110) surface.

BBi(110) is that the E_g value for surface become narrow according to corresponding bulk result of energy gap and this difference leads a transition when bulk valueof energy gap is small enough. The second reason of this transition is binding characters of surface atoms are different from corresponding bulk ones.

4. CONCLUSION

In this study, the structural, elastic and and electronic properties of zinc-blende BBi have been presented by applying local density approximation within the density functional theory. The structural parameters are in good agreement with previous theoretical results. The calculated elastic constants of BBi indicates that the zinc-blende phase of BBi is mechanically stable. The electronic band gap of BBi is also calculated as 0.56 eV. The structural and electronic properties of BBi(110) surface are obtained using our calculated bulk properties of BBi, The relaxed geometry of BBi(110) is similar with other III-V(110) surfaces: the cation-anion chain become tilted with the anions being raised. The tilt angle of BBi(110) is 27.4^0 very close to the corresponding tilt angles 26.1^0 for BAs(110) and 26.5^0 for BSb(110) surfaces. It is very important to note that BBi(110) surface is found to be metallic in contrast with bulk BBi is a narrow gap semiconductor. We have also presented total and partial electronic density of states for BBi(110) surface to explain metallic nature of this surface. At the end of our study, we have compared our surface electronic structure with other metallic (110) surfaces like AlBi, GaBi and InBi.

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In addition, (110) surfaces of AlBi, GaBi and InBi are also metallic but only AlBi(110) has an insulator-metal transition with very narrow, nearly zero, energy band gap of bulk AlBi [29,30]. It is very interesting to note that BBi(110) surface shows more accurate transition from insulator to metal according to AlBi(110), because energy gap of bulk BBi clearly differ from zero. The first reason for insulator-metal transition for

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