Ab initio calculations of the structure, electronic states and phonon dispersion of the BSb(110) surface

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Abstract.
We have studied the structural and electronic properties of BSb(110) by employing plane-wave pseudopotential method within density functional theory. The relaxed geometry shows a tilt of 26.5° of the top-layer B-Sb atomic chain, a result typical of non-nitride III-V(110) surfaces. Four surface electronic states have been identified. Several surface phonon branches have been determined from the application of a density-functional linear response theory. The eigensolutions of some of the surface modes are explained in terms of the large cation-anion mass difference and the small B core without any p electrons.

1. Introduction
Boron compounds (BP, BAs and BSb) are of central importance in a variety of areas of current technological and scientific interest. This is due to their extreme properties, such low ionicity, short bond lengths, hardness, high melting point and wide band gap. The characteristic properties of these compounds, compared to traditional III-V semiconductors, is largely due to the small core size and the absence of p electrons in the B core. While the lattice, electronic and transport properties of BP and BAs have been reported experimentally [1], no measurements are available for BSb. On the theoretical side, considerable progress has been made in the description of the structural, elastic, electronic and vibrational properties of these boron compounds [2, 3, 4, 5]. Structural and elastic properties of all boron compounds have been studied using the full potential linearised augmented plane wave method [2, 3]. An ab-initio pseudopotential method has been also used to obtain structural, electronic, elastic and vibrational properties of these three boron compounds [4, 5].

To the best of our knowledge no experimental or theoretical work on surface properties of boron compounds has appeared in the literature. In this paper we present results of first-principle calculations to describe the structural, electronic and vibrational properties of the BSb(110) surface. The results are analysed and their similarity and dissimilarity with other III-V(110) surfaces discussed.

2. Theory
The calculations have been performed by employing the ab initio planewave self-consistent method, based on the density functional theory within the local density approximation (LDA). We adopted the Ceperley-Alder [6] exchange and correlation functional with the parametrisation
of Perdew and Zunger [7], and modelled the electron-ion interaction using norm-conserving pseudopotentials [8]. The surface was modelled within a repeated slab geometry, with a slab containing fifteen layers of BSb and a vacuum layer equivalent to at least five atomic layers. The initial atomic positions are chosen according to the calculated equilibrium bulk lattice constant. All atoms were allowed to relax according to calculated Hellmann-Feynmann forces, except for the atoms in the middle of the slab which are kept frozen. The electronic wave functions were expanded in a basis set of plane waves, up to a kinetic-energy cutoff of 40 Ry. A set of six special \( k \)-points were used for sampling the irreducible segment of the surface Brillouin zone. The phonon dispersion curves have been obtained by applying the density functional scheme within the pseudopotential theory, using the the PWSCF code [9]. We calculated twenty five dynamical matrices corresponding to a \( 8 \times 8 \times 1 \) \( q \) points mesh within the irreducible segment of the surface Brillouin zone. Then, a two-dimensional Fourier interpolation was used to calculate the phonon eigensolutions for a desired number of \( q \) points.

3. Results

The calculated structural parameters of the relaxed BSb(110) surface are displayed in Fig.1. The relaxation pattern of this surface is similar to other III-V(110) surfaces [10]. The surface layer anions relax out of the surface and acquire a \( p \) bonding configuration, and cations relax inwards acquiring a planar \( sp^2 \)-like bonding configuration. The tilt angle of the surface layer is 26.5°. The surface inter-atomic bond length is 2.22 Å, approximately 2 % shorter than our theoretically calculated bulk bond length value of 2.27 Å. The calculated electronic band structure is displayed in Fig. 2. We have identified three occupied states labelled \( S_1 \), \( S_2 \), \( S_3 \) and the lowest unoccupied electronic state labelled \( S_4 \). The general pattern of the electronic structure of this surface is the same as for other III-V(110) surfaces [10]. The lowest unoccupied state is localised at surface cations and the highest occupied state is localised at surface anions. The LDA value of the splitting between these states is found to be around 2.3, 2.6 and 3.3 eV at the symmetry points \( \Gamma \), \( X \), \( M \) and \( \overline{M} \), respectively.

The phonon dispersion curves and density of states are shown in Fig 3. Several states have been identified, which lie below the bulk continuum, within the acoustic-optical gap, and above the bulk continuum. The results bear similarity to the (110) surface of other III-V compounds which have large cation-anion mass ratio. We find it particularly interesting to compare the surface phonon spectrum of BSb(110) with the corresponding spectra for the GaSb(110) and

![Figure 1](image1.png) **Figure 1.** A side view of the BSb(110) surface. The relaxed bond lengths are given in Å.

![Figure 2](image2.png) **Figure 2.** The electronic band structure of BSb(110). The hatched regions show bulk projection. Surface states are labelled as \( S_i \).
AlSb(110) surfaces [10, 11], due to a large cation and anion mass difference in each case. Firstly, for the BSb(110) surface, the highest surface optical phonon branch lies well above the bulk continuum while this branch lies very close to the bulk edge for GaSb(110) and AlSb(110) surfaces [10, 11]. Secondly, it has been observed that localised gap surface phonon modes lie just above the edge of the bulk acoustic bands and below the optic bulk phonon edge for the AlSb(110) surface [10] for which $m_{\text{anion}} > m_{\text{cation}}$. Although the anionic (Sb) mass is much larger than the cationic (B) mass, we have observed that localised gap phonon branches are well separated from the bulk edges for the BSb(110) surface. Moreover, different from GaSb(110) and AlSb(110) [10, 11], our calculations clearly indicate that surface acoustic modes on BSb(110) are localised for a much larger part of the surface Brillouin zone. We relate these differences to the small core size and the absence of p electrons in the B core, which result in shorter bond length and lower ionicity of B-V compounds. Atomic vibrations on the BSb(110) surface lead to at least four distinct peaks in the phonon density of states, labelled $P_1$ - $P_4$ in Fig. 3. The flatness of the lowest acoustic branch (Rayleigh wave) close to the zone edges $X$ and $M$ leads to the $P_1$ at around 8 meV. The peak $P_2$ is due to a nearly dispersion-less gap phonon branch at around 40 meV. The peak $P_3$ at around 61 meV also comes from localised gap phonon modes. Finally, the peak labelled $P_4$ is dominated by the surface state lying above the bulk continuum.

![Figure 3](image_url)

**Figure 3.** Phonon dispersion and density of states on the BSb(110) surface. The calculated results are shown by thick curves, while the bulk results are shown by the hatched regions for the dispersion curve and dashed lines for the density of states.

The atomic displacement patterns for some interesting zone-centre phonon modes are displayed in Fig. 4. A surface rotational mode is identified at 16.08 meV which is due to the opposing motion of top two layer atoms in the surface normal direction. Two localised gap phonon modes are observed at 39.73 and 62.21 meV. These phonon modes result from vibrations of the first and second layer B atoms, respectively. Only first layer B atoms vibrate in both the [110] and [001] direction for the highest surface optical phonon mode at 85.71 meV. This picture is different from the corresponding picture for other III-V(110) surfaces [10, 11] for which the highest phonon mode includes large atomic vibrations from second and third layer atoms.

### 4. Summary

We have presented a complete theoretical analysis of the structural, electronic, and vibrational properties of BSb(110) by employing the local density approximation and *ab initio*
pseudopotentials. The calculated relaxed geometry for this surface has a pattern similar to other III-V(110) surfaces with a relaxation angle of 26.5°. Several surface phonon branches have been determined, including two localised gap phonon states in the acoustic-optical gap region. The lower of these is nearly flat along the all considered symmetry directions while the higher one shows a dispersive behaviour along principal symmetry directions. These phonon modes result from vibrations of the first and second layer B atoms, respectively. Only first layer B atoms vibrate in both the [110] and [001] direction for the highest surface optical phonon mode at 75.71 meV. This picture is different from the corresponding picture for other III-V(110) surfaces for which the highest phonon mode includes large atomic vibrations from second and third layer atoms. Differences in the vibrational behaviour on the BSb(110) surface and other III-V(110) surfaces have been explained in terms of the large mass difference between B and Sb atoms and the small B core without any p electrons.

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