Structural, electronic and lattice dynamical properties of the BeS(110) surface

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Abstract.
We present results for the relaxed atomic geometry, electronic states, and lattice dynamics of the BeS(110) surface. Our investigations are based on first principles pseudopotential calculations within the local density approximation of the density functional theory. The relaxed geometry of this surface follows the general trend observed for traditional III-V(110) and II-VI(110) surfaces, with a surface tilt of 26.3°. Surface localised phonon modes below and above the bulk continuum, and within the acoustic-optical gap region have been determined.

1. Introduction
Beryllium chalcogenides (BeS, BeSe and BeTe) have attracted a great deal of attention, due to their appealing optoelectronic properties. These materials exhibit a much higher degree of covalent bonding as compared to other wide-gap II-VI semiconductors. Using the molecular beam epitaxy technique, these materials can be grown in the zinc blende structure on various substrates. Although the ground-state properties of these materials are well understood now (see, e.g. [1] and references therein), their surfaces have not been fully studied yet. In order to gain an optimized growth it is necessary to fully understand the fully relaxed geometry, electronic structure, and phonon modes on their surfaces. Recently, the structural and electronic properties of the clean cleaved (110) surface of these materials have been investigated theoretically [2]. Although microscopic investigations of surface phonon modes on these surfaces are important in view of their increasing role in optoelectronic devices, no systematic efforts have been made to investigate dynamical properties of these surfaces.

In this work, the structural and electronic properties of the BeS(110) surface are presented by using an ab initio pseudopotential study within the local density approximation. Using our structural parameters, an ab initio linear response approach has been applied to determine surface phonon dispersion curves and density of states on this surface. Characteristic surface modes and their dispersion are discussed and a brief comparison is made with the corresponding modes on III-V(110) and other II-VI(110) surfaces [3, 4].

2. Theory
The present calculations are performed by first-principles calculations based on the density functional theory in the local density approximation (LDA). The parametrised Perdew and
Zunger [5] form of the Ceperley-Alder [6] electron correlation scheme was used and the electron-ion interaction was described by using norm-conserving pseudopotentials [7]. The electronic wave functions were expanded in a plane-wave basis, with a kinetic energy cutoff of 40 Ry. The (110) surface of BeS was modelled in a supercell geometry, with an atomic slab of fifteen atomic layers and a vacuum region equivalent to five atomic layers. During the relaxations, all atoms were allowed to relax into their minimum-energy configuration, except for the atoms in the middle of slab which were kept frozen. The equilibrium bulk lattice constant of 4.81 Å was used in these calculations. Six special \( \mathbf{k} \)-points were used for sampling the irreducible segment of the surface Brillouin zone. Phonon calculations are carried out by employing the linear response approach, based on the density functional perturbation scheme [8]. We calculated twenty five dynamical matrices corresponding to a \( 8 \times 8 \times 1 \) \( \mathbf{q} \) points mesh within the irreducible segment of the surface Brillouin zone. Then, a two-dimensional Fourier interpolation was used to calculate phonons for the desired number of \( \mathbf{q} \) points needed for phonon dispersion curves and vibrational density of states.

3. Results

Figure 1 shows an schematic relaxed side view of the first three layers of the BeS(110) surface together with the key structural parameters and bond lengths. The relaxed geometry of this surface is characterised with tilted cation-anion chains on the surface layer, with an angle of 26.3° and the anions being raised. This tilt angle is close to the corresponding tilt angles 27.1° for ZnS(110) and 28.3° for BeSe(110) [2, 4]. The surface layer Be-S bond length is found to be 2.00 Å which is slightly smaller than the bulk bond length value of 2.083 Å. The shortening of atomic bond length on the (110) surface of zinc-blende semiconductors has been well documented [9] and clearly indicates that inter-atomic bonding on semiconductor surfaces is stronger than the corresponding bulk bonding. The surface electronic structure for BeS(110) is shown in Fig. 2, together with the BeS projected bulk band structure (shaded in grey). The general pattern of the electronic structure of this surface is similar to that on other II-VI(110) surfaces [4]. We have identified three occupied (\( S^1 \), \( S^2 \) and \( S^3 \)) surface states in the gap regions between the projected bulk band structures. \( S^3 \) is the highest occupied state, and lies rather flat along \( \overline{X-M} \overline{X'} \) at approximately 0.8 eV below the top of the bulk valence band. This state is made of the \( s^2p^3 \) like orbital of the dangling bond at the surface S atoms, while the lowest unoccupied surface state \( S^4 \) is related to the empty cation-derived dangling bond. \( S^4 \) is found to lie below the bulk conduction band around the \( \overline{X} \) and \( \overline{M} \) points on the surface Brillouin zone. The splitting between the highest occupied and lowest unoccupied states is found to be around 3.5 eV and 4.9 eV at the zone edges \( \overline{X} \) and \( \overline{M} \), respectively.

Our calculated phonon dispersion curves with the projection of the BeS bulk results and corresponding density of states for the BeS(110) surface are presented in Fig. 3. There is a large gap between the acoustic and optical bulk phonon regions, in accordance with the cation-anion mass difference. Although there are several surface phonon branches, at least three are easily identified as being separated from the bulk projected regions. The lowest lying surface phonon branch, the so-called Rayleigh branch, falls below the bulk acoustic continuum and become truly localised along the \( \overline{X-M} \overline{X'} \) directions. There is one localised gap phonon branch which lies inside the acoustic-optical gap region throughout the surface Brillouin zone. The highest surface optical phonon branch is found to lie above the projected bulk phonon spectrum along the all symmetry directions.

Our calculated zone-centre phonon modes and their polarisation characteristics for the BeS(110) surface are listed in Table 1. These phonon modes can be divided into two groups according to their polarisation characteristic: \( A'' \) if vibrations are along the atomic zig-zag chain direction and \( A' \) if vibrations take place perpendicular to this direction. The energies of \( A' \) modes are found to be 28.38, 41.06, 44.38, 60.90, 71.62 and 86.40 meV respectively. The
first one includes large atomic vibrations from the top two layer S atoms and thus can be called an anionic mode. The mode at 41.06 has a rotational character with opposing motion of surface layer atoms in the surface normal direction. Another interesting vibration in the surface dynamics is a bond-stretching character which is due to opposing motion of surface layer atoms in the [110] direction. The phonon mode at 60.90 lies in the acoustic-optical gap region. Only localised surface phonon modes can be found in this gap region. For higher phonon energies, atomic vibrations are mainly localised on Be atoms with small mass. Thus, we have observed a cationic phonon mode with an energy of 71.62 meV. Different from III-V(110) and II-VI(110) surfaces, the highest $A'$ phonon mode at 86.50 meV includes large atomic vibrations from first layer Be atoms with components along [110] as well as along the surface normal direction. For III-V(110) and II-VI(110) surfaces, this phonon mode does not include large atomic vibrations from first layer atoms. Moreover, there are large atomic vibrations from third layer atoms for the corresponding phonon mode on III-V(110) and II-VI(110) surfaces [3, 4]. This difference between BeS(110) and III-V(110) surfaces (or traditional II-VI(110)) can be related to very small mass of the Be atom. A similar observation was also made for BN(110) [10], with large atomic vibrations from first layer light cation atoms.

4. Summary
In this paper, the structural and electronic properties of the BeS(110) surface have been investigated and discussed by employing the local density approximation of the density functional theory and *ab initio* pseudopotentials. The calculated relaxed geometry for this surface has a
pattern similar to other III-V(110) and II-VI(110) surfaces. The resulting tilt angle of Be-S chains is found to be 26.3°. The general pattern of the electronic structure of this surface is also similar to that on other II-VI(110) surfaces. The splitting between the highest occupied and lowest unoccupied states is found to be around 3.5 eV and 4.9 eV at the zone edges \( \Gamma \) and \( M \) respectively. The phonon spectrum and corresponding surface vibrational density of states are also calculated using a linear response approach. Energy locations and polarisation characteristics of rotational, bond stretch, surface layer chain mode and sub-surface layer chain modes have been determined and discussed. For higher phonon energies, atomic vibrations are localised on Be atoms while very small contributions come from S atoms. In particular, first layer Be atoms vibrate with very large amplitudes for the highest surface optical phonon mode. A similar observation has been made for the BN(110) surface which also has very small cation mass.

Acknowledgments

This work was supported by the Scientific and Technical Research Council of Turkey (TUBITAK).

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