III–V (110) /Sb (1 ML): structural and dynamical properties

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Abstract

We present results of first-principles pseudopotential calculations for an ordered monolayer of antimony adsorbed on the (110) surface of GaAs, InAs, GaP and InP. For all systems the epitaxially continued layer structure has been found to be the ground state of the surface. We find that the buckling of the overlayer atoms can be related both to the geometric and electronic inequivalence of the substrate atoms. Hellmann–Feynman forces are used to calculate the dynamical matrix at the Γ-point. The resulting phonon frequencies and eigenmodes are compared with experimental data and discussed in terms of a chemical trend.

Keywords: Antimony; Density functional calculations; Gallium arsenide; Gallium phosphide; Indium arsenide; Indium phosphide; Low-index single-crystal surfaces; Metal–semiconductor interfaces; Phonons; Single-crystal epitaxy; Surface relaxation and reconstruction

1. Introduction

The investigation of physical and chemical processes at interfaces between metals and semiconductor substrates on a microscopic level is of considerable interest both for technological reasons and for fundamental aspects. One prototypical example in this direction is the deposition of Sb onto III–V(110) surfaces. Antimony has been found to form epitaxial one-monolayer (1 ML, i.e. two Sb atoms per surface unit cell) films [1,2] on GaAs(110), InP(110), InAs(110) and GaP(110), which are stable and show an ordered (1 × 1) adsorbate structure. A review of the structural and electronic properties of these systems has been given by LaFemina [3]. More recent first-principles total-energy calculations [4–6] have determined the geometry of the antimony-covered (110) surface of GaAs, InP and GaP, in excellent agreement with low-energy electron diffraction (LEED) and X-ray standing wave (XSW) studies. Relatively fewer studies concerning the dynamical properties of these interfaces have been reported. By analysing the results of Raman scattering measurements carried out for 1 ML Sb-covered III–V(110) surfaces, interface phonons have been observed [7–10]. These phonon modes correspond to vibrations involving the epitaxial layer of Sb and the upper substrate layer. For Sb/InP(110) eight pronounced peaks have been reported, whereas the scattering intensities for Sb/GaAs were found to be less impressive. By means of a restricted dynamical model the observed phonon frequencies could be assigned to characteristic eigenmodes of the interface atoms for Sb/GaAs and Sb/InP [11,12].
The aim of the present study is to determine by means of accurate first-principles calculations the geometry of 1 ML Sb on InAs(110) and to calculate the phonon modes and frequencies at the $\Gamma$-point for the monolayer Sb-covered (110) surfaces of GaAs, InAs, GaP and InP. The results for the structural and dynamical properties of these overlayer systems are then analysed in order to examine the chemical trend.

2. Method

Our calculations are based on the application of the density-functional theory within local-density approximation (DFT-LDA). We considered an artificially constructed periodic geometry along the surface normal. The unit cell included an atomic slab with eight layers of III–V(110), 1 ML of the overlayer Sb on each side of the slab, and a vacuum region equivalent in thickness to six substrate atomic layers. The electron–ion interaction was accounted for by using fully separable norm-conserving pseudopotentials [13]. The many-body electron–electron interaction was simulated, using the exchange and correlation potential as given by Ceperley and Alder [14]. Single-particle orbitals were expanded into plane waves up to an energy cut-off of 15 Ry. $k$-space integrations were replaced by a sum over four special points in the surface Brillouin zone (SBZ). The minimum of the total-energy functional [15] with respect to both the electronic and atomic degrees of freedom was found by employing a molecular dynamical approach which has been described in more detail in Refs. [6,16].

3. Results

3.1. Structural properties

Although the formation of an ordered and stable monolayer of Sb on GaAs(110) with $1 \times 1$ symmetry was observed more than a decade ago, recently various models concerning the actual surface geometry have been proposed [5]. The epitaxial continued-layer structure (ECLS), the epitaxial on-top structure (EOTS), and the $p^3$ structure were most discussed. In recent first-principles studies the ECLS has been found to be most favourable for 1 ML of Sb on the (110) surface of GaAs, InP and GaP not only on grounds of the total energy but also with respect to a more indirect comparison between calculated and measured geometrical parameters [4–6]. The ECLS describes a geometry where the Sb atoms occupy the “next lattice layer” on a nearly unrelaxed III–V(110) surface. A side and top view of this structure is given in Fig. 1.

From the calculated total energy for InAs(110)/Sb(1 ML) we find that the adsorption energy per Sb atom is 4.30 eV, 4.05 eV and 3.96 eV for the ECLS, EOTS, and $p^3$ structure, respectively. So, from energy point of view we decisively favour the ECLS over the other structures. It is interesting to note that these adsorption energy values and their differences between the different structural models for InAs(110)/Sb(1 ML) are quite close to the val-
ues for antimony overlayers on other III–V(110) surfaces. In particular, we have calculated [17] adsorption energies of 4.33, 4.39 and 4.36 eV per antimony atom in the ECLS on the (110) surface of GaAs, InP and GaP, respectively.

The geometrical parameters which minimise the total energy for InAs(110)/Sb(1 ML) in the ECLS are given in Table 1 and refer to Fig. 1. We are not aware of any experimental studies concerning these structural parameters. However, since the calculated geometries for 1 ML Sb on GaAs, InP and GaP (110) surfaces compare well with LEED, XSW and SEXAFS studies as shown in Refs. [4–6], we may conclude that the calculated surface structure for InAs(110)/Sb(1 ML) is a reasonable description of the actual geometry. For the sake of comparison we also give in Table 1 the structural parameters for 1 ML antimony on GaAs, GaP and InP (110) surfaces. Some values differ by a few hundreds of an Å from previously published results [4–6]. These differences are due to a different energy cut-off for the plane-wave basis set and different starting configurations and characterise the accuracy of the method employed. Now the question arises if a characteristic parameter of this structure, such as the vertical shear between the two inequivalent Sb atoms, can be correlated to simple empirical concepts as covalent radii or the ionicity of the substrate. In Fig. 2a we have plotted the magnitude of the overlayer buckling versus the relative difference of the tetrahedral radii of the substrate atoms as given in Ref. [18]. We find that the vertical shear between the overlayer atoms increases nearly linearly with the geometrical inequivalence of the substrate atoms. However, also the electronic inequivalence between the substrate atoms can be used to define the chemical trend. In Fig. 2b the vertical shear between the overlayer atoms is plotted versus the charge asymmetry [19] of the III–V compounds. Obviously also this diagram shows a nearly linear relation. No such relation has been found for the Sb–Sb bond length. It varies between 2.78 Å for GaP/Sb and 2.84 Å for InAs/Sb and resembles the sum of the covalent radii of the antimony atoms of 2.82 Å [18]. This indicates, together with the similar adsorption energies for Sb on the different III–V compounds, that the chemical bonding within the Sb zig-zag chain and between adatoms and substrate is essentially the same for all the systems considered.

### Table 1

<table>
<thead>
<tr>
<th>Surface</th>
<th>(\Delta_{1,\perp})</th>
<th>(\Delta_{1,y})</th>
<th>(d_{12,\perp})</th>
<th>(d_{12,y})</th>
<th>(\Delta_{2,\perp})</th>
<th>(\Delta_{2,y})</th>
<th>(d_{23,\perp})</th>
<th>(d_{23,y})</th>
</tr>
</thead>
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<tr>
<td>GaAs/Sb</td>
<td>0.05</td>
<td>2.00</td>
<td>2.37</td>
<td>4.52</td>
<td>0.09</td>
<td>1.41</td>
<td>2.01</td>
<td>2.73</td>
</tr>
<tr>
<td>GaP/Sb</td>
<td>0.10</td>
<td>2.03</td>
<td>2.38</td>
<td>4.34</td>
<td>0.07</td>
<td>1.35</td>
<td>1.91</td>
<td>2.61</td>
</tr>
<tr>
<td>InAs/Sb</td>
<td>0.12</td>
<td>1.94</td>
<td>2.31</td>
<td>4.63</td>
<td>0.08</td>
<td>1.51</td>
<td>2.14</td>
<td>2.88</td>
</tr>
<tr>
<td>InP/Sb</td>
<td>0.16</td>
<td>1.98</td>
<td>2.44</td>
<td>4.44</td>
<td>0.07</td>
<td>1.46</td>
<td>2.04</td>
<td>2.77</td>
</tr>
</tbody>
</table>

Fig. 2. The vertical shear between Sb atoms, \(\Delta_{1,\perp}\), plotted as a function of (a) the relative difference of the tetrahedral radii of the substrate atoms, and (b) as a function of the charge asymmetry defined in Ref. [19]. The solid line is to guide the eye.

3.2. Dynamical properties

The 1 ML Sb-covered III–V(110) surfaces give rise to interface phonons which have been detected...
by means of Raman spectroscopy [7–10]. The interface phonons at the centre of the surface Brillouin zone, \( \Gamma \), can be classified according to the irreducible representations of \( C_\text{m} \) (or \( m \)), the point-group symmetry of the surface unit cell. Thereby \( A' \) modes describe lattice distortions along the [110] direction, i.e. along the Sb zig-zag chain, and \( A' \) modes correspond to atomic movements perpendicular to the chain direction. If one considers a four-atom basis in the surface unit cell, i.e. the two-overlayer antimony atoms and the uppermost substrate anion and cation, one would expect to find 12 branches, 3 acoustic and 9 optical (thereby 6 \( A' \) and 3 \( A' \) modes). Raman scattering experiments have revealed 8 optical phonons (6 \( A' \) and 2 \( A' \) modes) at the \( \Gamma \)-point for InP(110)/Sb(1 ML). For GaAs/Sb, GaP/Sb and InAs/Sb fewer modes have been detected.

In an earlier publication [12] it was shown that the experimental results can be relatively well described using a simple restricted dynamical model. We follow that approach, but consider a larger dynamical problem. Proceeding from the relaxed geometries as given in Table 1, six atoms (two Sb atoms of the overlayer and the substrate atoms of the two outermost substrate layers) were treated as coupled three-dimensional harmonic oscillators. The interatomic force constants were used to build up the dynamical matrix. Due to the symmetry of this matrix we end up with more force constants than really needed. This redundancy can be conveniently used to fight any round-off errors in the numerical calculation. Once the dynamical matrix \( K \) is specified, solution of the eigenvalue matrix equation

\[
M \ddot{r} = K \ddot{r},
\]

where \( M \) contains the masses, yields the surface-atom vibrational normal modes and frequencies at the \( \Gamma \)-point. In order to get a feeling for the accuracy of the method employed we have calculated the bulk \( \Gamma(\text{TO}) \) frequency for the III–V compounds. For GaAs and GaP the calculated values of \( \hbar \omega = 33.9 \) and 46.1 meV are respectively 1.5% and 2.2% larger than the experimental findings [20]. For the more ionic compounds InAs and InP the deviation between the calculated and measured frequencies is more distinct: our values are larger than experimental results by 2.5 and 3.9 meV, respectively. This could be due to the overestimation of the chemical bonding as an artifact of our LDA calculations. However, the accuracy of this bulk result does not imply the same for the interface phonons, since their calculation is more complex.

In Table 2 we present the zone-centre frequencies corresponding to the eigenmodes localised at the overlayer Sb atoms and/or in the first substrate layer. The eigenmodes are classified according to their representations and numbered with increasing frequency. This notation is different from the one introduced by Godin et al. [11], but more consistent. Obviously most of the calculated frequencies compare quite well with the experimental results. This is especially valid for the \( 2A' \) modes, which are highly

<table>
<thead>
<tr>
<th>Mode</th>
<th>GaP/Sb</th>
<th>InP/Sb</th>
<th>GaAs/Sb</th>
<th>InAs/Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present results</td>
<td>Exp. results</td>
<td>Present results</td>
<td>Exp. results</td>
</tr>
<tr>
<td>( 1A' )</td>
<td>11.1</td>
<td>11.0</td>
<td>11.9</td>
<td>9.8</td>
</tr>
<tr>
<td>( 2A' )</td>
<td>13.1</td>
<td>17.7</td>
<td>19.5</td>
<td>11.1</td>
</tr>
<tr>
<td>( 3A' )</td>
<td>21.9</td>
<td>20.9</td>
<td>22.9</td>
<td>23.2</td>
</tr>
<tr>
<td>( 4A' )</td>
<td>26.6</td>
<td>24.0</td>
<td>35.8</td>
<td>24.1</td>
</tr>
<tr>
<td>( 5A' )</td>
<td>39.7</td>
<td>37.5</td>
<td>39.8</td>
<td>34.6</td>
</tr>
<tr>
<td>( 6A' )</td>
<td>51.3</td>
<td>47.6</td>
<td>43.9</td>
<td>7.8</td>
</tr>
<tr>
<td>( 1A' )</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>19.9</td>
</tr>
<tr>
<td>( 2A' )</td>
<td>20.8</td>
<td>20.7</td>
<td>19.6</td>
<td>30.5</td>
</tr>
</tbody>
</table>
localised shear modes and therefore appropriate for our restricted approach. However, we expect the presently calculated $\text{A}'$ modes also to be more accurate compared to Ref. [12], due to the consideration of a larger atomic basis in the unit cell. This is especially true in the case of GaAs/Sb. The largest deviation between experimental and theoretical data concerns the 4$\text{A}'$ mode for InP/Sb. The difference of more than 30% is certainly too large to be due only to calculational or experimental uncertainties. Perhaps the origin of the feature experimentally observed is a mode which deeply penetrates into the bulk and which cannot be described by our restricted model.

Obviously not all optical modes possible from a group theoretical point of view were detected experimentally. This is however little surprising. It could be due to experimental difficulty in preparing the ordered Sb monolayer and/or due to the low scattering efficiency for some modes. In particular a strong multiphonon signal, masking the interface peaks, has been reported for GaP/Sb [7]. In this case only one sharp peak has been found.

In Fig. 3 we have plotted the 6$\text{A}'$ and 3$\text{A}''$ modes versus the square root of the inverse reduced mass of the substrate atoms. We find a nearly linear relation, which shows that the bonding at the surface for the different III–V compounds is of similar strength. However, the slope of the curve slightly increases if one goes from InAs to GaP. This shows that the strength of bonding, although comparable, slightly increases in accordance with the increase in the heat of formation as one goes from InAs to GaP [20]. The 6$\text{A}'$ mode gives rise to a distortion pattern similar to the bulk $\Gamma$(TO) phonon and is mainly localised between the first and second substrate layers. For all the considered systems the frequency of 6$\text{A}'$ is appreciably higher than the bulk $\Gamma$(TO) frequency. In case of InP/Sb this is in accordance with the experimental results, although our value is still about 8% higher than the one observed experimentally [7]. Possible reasons for this overestimation could be the application of the LDA as discussed for the calculation of the bulk $\Gamma$(TO) phonon and the finite size of the slab as discussed in Ref. [21]. The frequency of the 3$\text{A}''$ mode, which corresponds to a shear mode of the atoms of the uppermost substrate layer in [110] direction, is much closer in energy to the bulk $\Gamma$(TO) mode. No such trend is to be expected for the 2$\text{A}''$ mode, which is a shear mode involving only the Sb overlayer atoms. Due to the strong Sb–Sb bonds, irrespective of the substrate, these modes lie in the same energy range for all systems.

In order to assess the influence of the antimony overlayer on the dynamical properties of the surface we used the same approach as described above to calculate the surface phonons of the free GaAs(110) surface. In contrast to a recent theoretical study by Fritsch et al. [21], we find two modes in the energy range of about 10 meV which can possibly explain results of inelastic helium atom scattering [22]. The 1$\text{A}'$ mode at 11.1 meV corresponds to a rotational movement of the GaAs chains, whereas the 1$\text{A}''$ mode at 8.6 meV arises from an opposing motion of the GaAs chains in [110] direction. The frequencies of the corresponding eigenmodes for GaAs/Sb amount to $\hbar \omega = 9.8$ and 7.8 meV, respectively. A rather simple distortion pattern which only involves the two outermost surface atoms is given by 2$\text{A}''$. This shear mode of the surface zig-zag chain has a much higher frequency ($\hbar \omega = 31.7$ meV) in the case of the free GaAs surface compared with the GaAs/Sb system ($\hbar \omega = 19.9$ meV) due to the mass difference and the strongly sp$^2$ bonded Ga atom at the free surface. The other modes are however difficult to compare since in these cases the eigenmodes differ appreciably. However, we find that apart from the

![Fig. 3. Frequencies of the 6$\text{A}'$ and 3$\text{A}''$ modes (filled and empty diamonds) versus the square root of the inverse reduced mass of the substrate atoms. Circles indicate the bulk $\Gamma$(TO) frequency of the III–V compounds (Ref. [20]).](image-url)
example discussed above, the frequencies of clean and covered surface are nearly comparable. This can be interpreted in such a way that the strong covalent Sb–Sb and Sb–substrate bondings stabilise the surface.

4. Summary

We have made first-principles calculations for the epitaxial deposition of one monolayer of Sb on the (110) surface of GaAs, InAs, GaP and InP. We find that the surface geometry of these systems is very similar and follows clearly a chemical trend both with respect to the geometric and electronic inequivalence of the substrate atoms. The ground state of these III–V(110)/Sb(1 ML) systems is the ECLS.

Using a relatively simple approach we calculated the zone-centre vibrational eigenmodes and frequencies of the interface in an overall good agreement with recent Raman experiments. The analysis of the obtained data with respect to bulk Γ(TO) phonon frequencies and calculations for the free GaAs(110) surface indicates that the III–V(110) surfaces are somewhat stabilised by the deposition of the antimony overlayer.

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References


[17] In contrast to the present results in Refs. [4,6] no spin polarisation effects were taken into account when the energy of the free Sb atom was calculated. The results of Ref. [5] were obtained with a different energy cut-off. Thus the values given there differ slightly compared to the values given above. Despite the inclusion of spin polarisation effects the adsorption energies seem to be slightly overestimated. This is a well known failure of the DFT-LDA. Nevertheless the values provide a consistent comparison between the different structures and substrates.


