Structure and dynamics of hydrogenated GaAs(110) and InP(110) surfaces

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Abstract. We have investigated the structural and vibrational properties of hydrogen-covered GaAs(110) and InP(110) surfaces in the framework of the density-functional theory. The plane-wave pseudopotential method combined with the slab supercell description for the surfaces has been employed to determine the relaxation geometries of H:GaAs(110) and H:InP(110) for the half- and one-monolayer coverages. Our results are in good agreement with all available experimental data. For both surfaces and for all coverages we have determined the surface vibrations by means of an *ab initio* linear-response formalism. The calculated bond-stretching frequencies compare very well with the results from high-resolution electron-energy-loss spectroscopy. The half-monolayer coverages on InP(110) exhibit vibrational states which are related to the mechanism which leads to the structural decomposition of the surface experimentally observed at high hydrogen exposures.

1. Introduction

Hydrogen-covered GaAs(110) and InP(110) surfaces are prototype systems for the research of chemisorption processes at semiconductor surfaces. Numerous experiments have been focused on the detection of the chemically active adsorption sites. In the case of GaAs(110), the experimental data from high-resolution electron-energy-loss spectroscopy (HREELS) [1, 2, 3, 4] and core level photoemission spectroscopy [5] show that hydrogen atoms bind simultaneously to Ga and As in each stage of the adsorption. The hydrogenation is saturated at one monolayer (ML) with two hydrogen atoms per surface unit cell [5]. The 1 ML coverage has the (1×1) periodicity of the substrate. By means of HREELS [2, 6, 7] and ultraviolet spectroscopy [8], it has also been demonstrated for InP(110) that hydrogen chemisorbs on the surface cations as well as on the surface anions. The data from Auger electron spectroscopy and low-energy electron diffraction (LEED) [9] indicate that the adsorption on InP(110) saturates even at the stage of 0.5 ML with one hydrogen atom per surface unit cell.

An important effect of the hydrogenation of GaAs(110) and InP(110) is the removal of the relaxation in the first layer of the substrate. This is evident from the decrease of the ionization energy [9, 10] and the experimental data from photoemission spectroscopy [9, 11]. For the hydrogen-covered GaAs(110) surface direct information about the structural details has been obtained from surface-shift photoelectron diffraction [12] and grazing-incidence x-ray diffraction (GIXD) [13].

While the phonon dispersion curves of both clean surfaces have recently been obtained from first principles [14, 15, 16], only some *ab initio* calculations have been performed in order to explore the adsorption of hydrogen on the GaAs(110) surface [14, 17, 18, 19, 20].

The theoretical investigations confirm the experimentally observed elimination of the surface relaxation [20] and predict a slight counter-rotation in the first plane of the substrate with a coverage of 0.5 or 1 ML [14, 18, 19]. Moreover, the calculated frequencies of the stretching modes of the H–Ga and H–As bonds agree with the experimental results from HREELS [1, 2, 3, 4]. However, the bond-stretching frequencies of the hydrogenated InP(110) surface have not yet been determined within the density-functional theory.

In the present paper, we report the results of an *ab initio* calculation of the structural and dynamical properties of the hydrogenated GaAs(110) and InP(110) surfaces. By means of the density-functional linear-response approach suggested by Baroni and co-workers [21, 22], we have been able to investigate both the atomic equilibrium positions and the surface vibrations within a consistent formalism. We have determined the optimized structure of the GaAs(110) and InP(110) surface with hydrogen coverages of 0.5 and 1 ML for each of the two compounds. For both surfaces and for both coverages we have determined the surface-localized phonon modes at the zone centre of the surface Brillouin zone (SBZ). Assuming the 1 ML coverage, we have calculated the complete phonon dispersion along the $\overline{\Gamma X}$ and the $\overline{\Gamma X'}$ direction for H:GaAs(110) and H:InP(110). We compare our results for the bond-stretching frequencies with the experimental data from HREELS [1, 2, 3, 4, 6, 7]. For both surfaces we analyse the effects of the hydrogen-induced removal of the relaxation on the vibrational spectrum and compare our results for the different coverages.

The paper is organized as follows. Section 2 briefly describes the details of the density-functional formalism used in our calculations. The results for the optimized structures are reported in section 3. Section 4 is focused on the surface-localized phonon modes determined in our calculations. Our results are summarized in section 5.

2. Theoretical method

Our calculations are based on the density-functional theory in the local-density approximation (LDA). For the exchange–correlation potential we use the form of Ceperley and Alder [23] in the parametrization of Perdew and Zunger [24]. The electronic wave functions are expanded in plane waves up to a kinetic energy of 10 Ryd. For the electron–ion interaction we use nonlocal norm-conserving pseudopotentials. The potentials for H, Ga, and As are taken from [25]. For In and P we use the pseudopotentials already applied in [16] and [26].

The hydrogen-covered surfaces are described via periodically repeated thin crystal films. A single slab comprises seven substrate layers forming a thin film which is covered on both of its surfaces with hydrogen. Two neighbouring films are separated by a distance corresponding to six interlayer distances prior to hydrogenation. The lattice constant of the slabs is fixed to match with the theoretical value a_0 determined for the bulk at a cut-off energy of 10 Ryd. For GaAs we obtain $a_0 = 5.613$ Å; for InP we find $a_0 = 5.822$ Å. The optimized surface geometries are determined by minimizing the total energy by means of the Hellmann–Feynman forces. We start the relaxation procedure from a configuration in which the substrate atoms are located in the ideal positions. The hydrogen atoms are placed in the dangling bond direction of the substrate. For a coverage of 0.5 ML, hydrogen atoms are introduced into the system either only above the surface anions or only above the surface cations. In the 1 ML case, hydrogen atoms are placed in the two dangling bond directions. For the k-point sampling we use six special points in the irreducible wedge of the SBZ.

By means of the *ab initio* linear-response approach of Baroni and co-workers, we

determine the dynamical matrices of the fully relaxed hydrogenated thin crystal films. We use the results of the self-consistent calculation performed for systems with seven substrate layers to construct the dynamical matrices of slabs containing 23 substrate layers. This is accomplished by describing the interactions in the central layers by the bulk force constants. The force constants in the surface regions of the large crystal films are assumed to be the same as those in the surface regions of the thin crystal films [15].

For a coverage of 1 ML hydrogen on GaAs(110) and InP(110), we have determined the phonon dispersion curves along and perpendicular to the anion–cation chains of the first substrate plane ($\overline{\Gamma X}$ and $\overline{\Gamma X'}$ direction, respectively) by calculating the interplanar force constants from four dynamical matrices in the $\overline{\Gamma X}$ and three dynamical matrices in the $\overline{\Gamma X'}$ direction. For the surfaces covered with 0.5 ML of hydrogen, we have restricted our calculations to the $\overline{\Gamma}$ point of the SBZ.

3. Structure of the hydrogenated surfaces

The optimized geometries of the hydrogen-covered crystal films are determined by minimizing the Hellmann–Feynman forces using a modified Broyden scheme [27]. All atoms in the slabs are allowed to move. To prevent the slabs from a translation we fix the centre of mass of the two central-layer atoms in the slab supercell at the corresponding bulk position. We regard the atomic positions as fully relaxed when all forces are smaller than 0.1 mRyd au^{-1}. At this stage the calculated atomic positions are defined with an uncertainty of less than 0.01 Å.
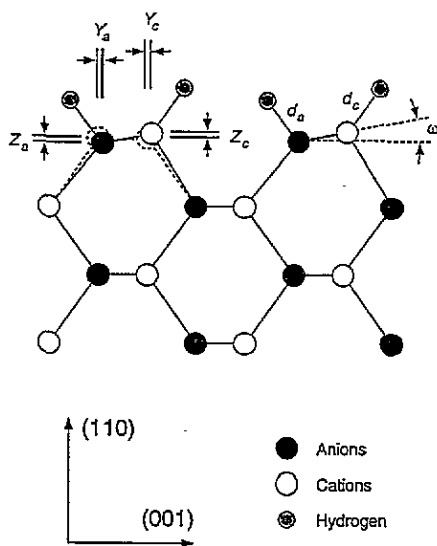

Figure 1. A side view of the first four layers of the (110) surface of GaAs (or InP) covered with 1 ML of hydrogen. The black circles indicate the anions and the open circles the cations of the substrate. Grey circles symbolize the hydrogen atoms. The relaxation parameters Y_a, Y_c, Z_a, and Z_c indicate the atomic shifts in the first layer with respect to the ideal (bulk-derived) positions. The bond lengths between hydrogen and the substrate are are labelled as d_a and d_c.

Our results for the optimized structure of the two surfaces are similar. For all coverages considered in this paper we obtain the experimentally observed removal of the substrate relaxation [9, 10]. Figure 1 illustrates the (110) surface of GaAs (or InP) covered by 1 ML

of hydrogen in a side view of the first four substrate layers. In the zero-force configuration of all coverages, the substrate atoms are close to the ideal (bulk-derived) positions. The atoms of the second and all deeper substrate layers essentially reside the bulk positions. In tables 1 and 2 our results for the final shifts of the first-layer atoms with respect to the ideal positions as well as the bond lengths between the hydrogen atoms and the substrate are summarized together with the structural parameters determined by GIXD [13] for H:GaAs(110). The calculated structural details of the hydrogenated GaAs(110) surface are in good agreement with the *ab initio* calculations of [14, 17, 18, 19, 20] and support the GIXD data [13, 28].

Table 1. Optimized structure of the GaAs(110) surface with 1 ML of hydrogen (first row) and 0.5 ML of hydrogen chemisorbed on As (second row) or Ga (third row). The atomic shifts and bond lengths are given in Å. The quantities are defined in figure 1. The data from grazing incidence x-ray diffraction (GIXD) are taken from [13].

	Y_a	Y_c	Z_a	Z_c	d_a	d_c	ω
1 ML	0.078	0.084	−0.089	0.086	1.535	1.571	−7.1°
0.5 ML on As	0.072	0.083	−0.079	0.115	1.537		−7.8°
0.5 ML on Ga	0.129	0.046	−0.117	0.127		1.566	−10.5°
GIXD	0.110	0.055	−0.075	0.040			−5.0°

Table 2. Optimized structure of the InP(110) surface with 1 ML of hydrogen (first row) and 0.5 ML of hydrogen chemisorbed on P (second row) or In (third row). The parameters are defined in figure 1.

	Y_a	Y_c	Z_a	Z_c	d_a	d_c	ω
1 ML	0.088	0.102	−0.101	0.092	1.441	1.734	−7.8°
0.5 ML on P	0.093	0.139	−0.091	0.138	1.441		−8.7°
0.5 ML on In	0.213	0.127	−0.172	0.140		1.726	−12.9°

With the total energies of the fully relaxed clean and hydrogenated GaAs(110) and InP(110) surfaces, we are able to calculate the energy gain obtained from the chemisorption. The adsorption energy per hydrogen atom is defined by

$$E_{ad} = \frac{1}{n_H} [E_A - (n_H E_H + E_{clean})]$$

where n_H is the number of hydrogen atoms in the unit cell of the periodic slab configuration, E_A is the total energy of the hydrogen-covered surface, E_{clean} is the total energy of the relaxed clean surface, and E_H is the total energy of an isolated hydrogen atom placed in a large supercell. The total energies of the clean surfaces are evaluated by subtracting the bulk energy of two anion–cation pairs from the results obtained for fully relaxed nine-layer slabs [15, 16]. All energies have been determined by using a basis set of plane waves up to 10 Ryd. For this small basis set, the degree of convergence for the different energies is decreasing from the systems without hydrogen to the case of the isolated hydrogen atom. Therefore, the adsorption energies are overestimated in their magnitude. The differences between the particular adsorption energies are expected to be more accurate, as the deviations from the exact energies essentially cancel out in the subtraction.

In the case of GaAs(110), our calculation yields an energy gain E_{ad} of −2.61 and −2.60 eV for hydrogen adsorbed solely on Ga or As, respectively. The energy gain is

increased to $E_{ad} = -3.47$ eV per hydrogen atom for a coverage of 1 ML. These values agree with the previous LDA calculations of [17, 18, 19]. The small difference between the adsorption energies of the 0.5 ML coverages corresponds to the similarity of the bond lengths of $d_a = 1.537$ Å and $d_c = 1.566$ Å in H:GaAs(110).

In the H:InP(110) surface the bond lengths amount to $d_a = 1.441$ Å and $d_c = 1.726$ Å for the 0.5 ML coverages. These values compare with the interatomic distances of the monohydrides ($d_{PH} = 1.432$ Å and $d_{InH} = 1.838$ Å [29]). We obtain $E_{ad} = -2.94$ eV for hydrogen adsorbed on P, while the energy gain is significantly lower for the chemisorption on In ($E_{ad} = -2.28$ eV). In the 1 ML case the adsorption energy amounts to $E_{ad} = -3.51$ eV per hydrogen atom.

While As and Ga appear to be very similar with respect to the adsorption energies and the bond lengths d_a and d_c, large differences occur between In and P. Analogously, HREELS indicates the simultaneous chemisorption of hydrogen on As and Ga from the lowest coverages up to the saturation of about 1 ML [1]. In the early stages of hydrogen adsorption on a cleaved InP(110) surface, however, only the In atoms have been identified as being the active sites of the chemisorption [6, 7]. In the regime between low coverages and the saturation (at about 0.5 ML) the hydrogen adsorbs on In and also on P with an increase in the intensity of the H–P line compared to the H–In line.

The dominance of the cationic adsorption sites for very low coverages may be explained in terms of the electronic structure of the clean InP(110) surface [30, 31]. While the dangling bonds of the anions are occupied, the cation-derived dangling bonds are empty. This supports the interaction between the indium and the hydrogen atom which donates its charge to the formation of the bond. Our calculated electronic band structure of the InP(110) surface covered by 0.5 ML of hydrogen chemisorbed on the cation sites exhibits a surface state at the Fermi level located at 0.15 eV above the bulk valence band maximum. The observed surface state is occupied by only one electron and corresponds to the dangling bonds of the phosphorus atoms. This illustrates that the adsorption of hydrogen on the In atoms leads to a charge transfer from the anion-derived dangling bonds to the H–In bond. The dangling bonds of the phosphorus atoms become partially unoccupied and consequently start to be active adsorption sites. This agrees with the observation of the HREELS experiment of [6]. The large differences in the calculated adsorption energies and the bond lengths (d_a and d_c) suggest that at higher exposures the bonding of hydrogen to phosphorus may dominate above the chemisorption of hydrogen on indium. This agrees with the experimentally seen signatures of the formation of PH_x molecules partially desorbing into vacuum and the appearance of metallic In clusters on the surface [6, 7, 9, 32].

4. Phonons of the hydrogenated surfaces

Our results presented in the previous section for the 1 ML and 0.5 ML coverages indicate that the interaction between the two hydrogen atoms adsorbed per surface unit cell in the 1 ML case is sufficiently small. The effect of the removal of the surface relaxation is similar for all three coverages analysed in this paper. We use thin substrate films covered by a complete overlayer of hydrogen to study the surface vibrations of H:GaAs(110) and H:InP(110). Additional calculations show that the bond-bending and bond-stretching frequencies are only weakly dependent on the coverage. The surface relaxation is eliminated upon hydrogenation and replaced by a slight counter-rotation. We compare the localized phonon modes of the substrate characterized by the counter-relaxation with our results obtained for the clean surfaces [15, 16].

In the case of H:InP(110) it is important to determine the surface phonon modes also

for the 0.5 ML coverages, which have to be regarded as the more realistic description of the hydrogenated InP(110) surface. We therefore repeat the calculation of the phonons at the $\bar{\Gamma}$ point of the SBZ for both surfaces covered by only 0.5 ML of hydrogen. The dangling bonds, which are not directly involved in the adsorption of the hydrogen overlayer on the substrate, appear in our calculations in the form of a pair of nearly dispersionless branches in the electronic band structure located at the Fermi level in the gap region of the bulk band structure. The results presented in section 2 for the 0.5 ML coverages have been obtained by dealing carefully with the Fermi surface using the Gaussian broadening scheme [33]. We have repeated the determination of the optimized structures by assuming that the lower state of the pair is occupied while the upper one is completely empty. This assumption leads to only very small variations in the equilibrium positions. Along the same line, we have used the formalism of [21] and [22] without any modifications for all coverages. The validity of this assumption for the half-monolayer coverages has been confirmed by comparing the dynamical matrices at the $\bar{\Gamma}$ point with additionally performed frozen-phonon calculations for atomic displacements in the first substrate layer. In the frozen-phonon calculations the metallic behaviour of the dangling bond states at the Fermi level has been taken into account.

4.1. Bond-stretching and bond-bending vibrations

Besides the Fuchs-Kliewer phonon mode of the substrate, the most prominent features seen in the HREEL spectra are the stretching modes of the hydrogen atoms vibrating in the bond direction [1, 2, 3, 6, 7]. In table 3 our results for the stretching frequencies at the $\bar{\Gamma}$ point of the SBZ are summarized together with the HREELS data and the results of the LDA calculations of [14] and [19] performed for H:GaAs(110). For all coverages, our formalism is able to reproduce the measured frequencies with an underestimation of at most 1–3%. The slight underestimation is partially due to the small cut-off energy of 10 Ryd used in the calculations. The dispersion of the stretching modes is negligible ($\leqslant 1$ meV) along and perpendicular to the first-layer anion–cation chains. The molecular data are in good agreement with the HREELS measurements for the anionic adsorption sites, while the stretching frequencies of the hydrogen atoms adsorbed on In or Ga are larger than the vibrational frequencies in the molecules. This discrepancy has partially been attributed to the presence of second-nearest neighbours with higher electronegativity [7] which increases the strength of the bond between the hydrogen atoms and the cations. Our results for the equilibrium distance (1.893 Å) and the bond stretching frequency (153 meV) obtained for an isolated indium monohydride molecule placed in a large supercell support this assumption [34]. A more converged calculation of the molecular properties, which is not necessary for the purpose of our discussion, would require a larger cut-off energy than 10 Ryd.

For each atom adsorbed on the surface we observe two bending vibrations. One mode is polarized along the $(\bar{1}10)$ direction (parallel to the anion–cation chains of the first layer), while the other is characterized by displacements in the plane perpendicular to the $(\bar{1}10)$ direction. The phonon branches associated with the bending modes are nearly flat showing a dispersion of at most of 3 meV. For H:GaAs(110) we obtain four narrow bands between 62 and 68 meV. This agrees with the results of the LDA calculation of [19], while the molecular dynamics simulations of Di Felice and co-workers [14] predict bending vibrations with energies between 56 and 63 meV. In H:InP(110) we observe a gap of about 7 meV between the H–In and the H–P vibrations. Table 4 summarizes the bending frequencies at the $\bar{\Gamma}$ point of the SBZ for both surfaces and for both coverages.

The small differences between the 1 ML and the 0.5 ML coverages for the stretching and bending vibrations indicate that the interaction between neighbouring hydrogen atoms

Table 3. Bond-stretching frequencies ν_c^s and ν_a^s (in meV) at the Γ point in comparison with the experimental data from HREELS [1–7] and the LDA results of former calculations [14, 17]. The molecular data for Ga and As (In and P) hydrides are taken from [3] ([2]).

Source of data	ν_c^s H–Ga	ν_a^s H–As	ν_c^s H–In	ν_a^s H–P
Present, 1 ML	222	259	204	278
Present, 0.5 ML	225	258	210	274
[1, 6]	229	262	208	281
[7]	233	264	211	282
[2]	233	262	211	292
[3]	235	267		
[14]	219	246		
[19]	218	242		
Molecular data	226	263	180	282

Table 4. Bond-bending frequencies (in meV) of H:GaAs(110) and H:InP(110) at the $\overline{\Gamma}$ point of the SBZ. The vibrations polarized in the $(\overline{1}10)$ direction are labelled as (1), while the modes polarized perpendicular to the chain direction are labelled as (2).

	1 ML	0.5 ML
In(1)	54.5	54.0
In(2)	56.8	53.5
Ga(1)	62.0	60.6
Ga(2)	62.7	58.9
As(1)	64.8	62.0
As(2)	68.7	65.3
P(1)	67.1	62.2
P(2)	72.0	68.4

is weak and that the strength of the bonds between the hydrogen and the substrate atoms is only slightly dependent on the coverage.

4.2. Surface vibrations of the substrate

One important effect of the hydrogenation of GaAs(110) and InP(110) is the elimination of the surface relaxation, which is achieved even at a coverage of less than 1 ML. While the bulk band gap is free from any surface state in the 1 ML case, partially occupied dangling bond states appear in the gap region for the 0.5 ML coverages. In the case of H:InP(110) especially, this has to be taken into account, as the hydrogenation of this surface saturates at 0.5 ML.

4.2.1. H:GaAs(110).

In figure 2 the dispersion of the GaAs(110) surface covered by 1 ML of hydrogen is shown together with the surface-projected bulk band structure of the substrate. As can be seen in the comparison with our results for the clean surface (figure 3 and [15]), most of the localized phonon modes are also present after hydrogenation with similar dispersion and similar eigenvectors. However, two important differences have to be pointed out. The third acoustic phonon mode in the $\overline{\Gamma X'}$ direction also resolved by He atom scattering at the clean surface [15, 35] is not prominent in the hydrogenated surface. For the clean surface, we have reported a surface-localized phonon mode above the bulk

phonon bands characterized by an opposing motion of the surface cations and the second-layer anions [15]. Using HREELS, Nienhaus and Mönch have resolved this phonon mode in good agreement with our theoretical predictions [36]. In the hydrogenated surface, the branch of this surface optic phonon is shifted downwards into the optic bulk bands. It mixes strongly with bulk states and cannot be identified as a surface state.
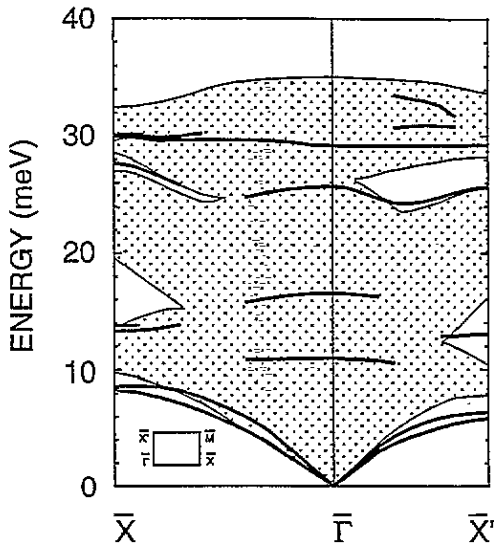

Figure 2. Phonon dispersion of the GaAs(110) surface covered by 1 ML of hydrogen. The surface-projected bulk bands are represented by the shaded area. Surface-localized phonon modes of the substrate are indicated by the solid lines. The bond-stretching and bond-bending modes of the hydrogen coverage are not represented. The irreducible wedge of the SBZ is shown in the inset.

The surface-localized phonon modes of GaAs(110) covered by 0.5 ML resemble the results obtained in the 1 ML case. The only exception consists in a high-frequency vibration with an energy of 34.1 meV at the $\overline{\Gamma}$ point appearing for hydrogen chemisorbed only on the cations. It is characterized by an opposing motion of the surface anions and their second-layer nearest neighbours in the $(\overline{1}10)$ plane.

4.2.2. H:InP(110).   Similarly to the case of GaAs(110), we obtain for the clean InP(110) surface three acoustic phonon branches in the $\overline{\Gamma X'}$ direction and a high-frequency optic mode above the bulk phonon bands [16]. The surface optic vibration and the third acoustic phonon branch are suppressed upon hydrogenation also in the case of 1 ML on InP(110), as can be seen from figure 4. Most of the other acoustic surface phonons remain nearly unaffected irrespective of the hydrogen coverage.

The large gap between the acoustic and optic bulk bands is of particular interest. For the clean InP(110) surface, the flat branch of a surface phonon mode has recently been resolved by HREELS with a dispersion between 30.5 and 33.5 meV [37]. In good agreement with the HREELS data we obtain for the clean surface two localized phonon modes in the same energy range. Their dispersion is indicated by the broken lines in figure 4. In the hydrogen-covered surface, we observe similar vibrational states with a zone-centre energy of 26.2 and 39.7 meV. The eigenvectors of these states are illustrated in figure 5. The two states are separated by a gap of about 10 meV. This large splitting places the two branches far apart
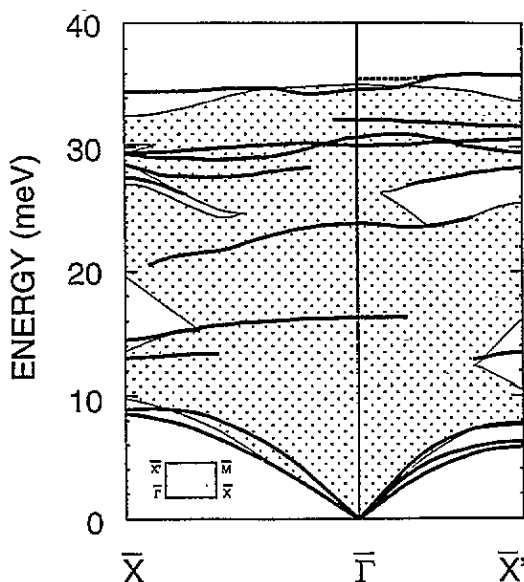
Figure 3. Phonon dispersion of the clean GaAs(110) surface.
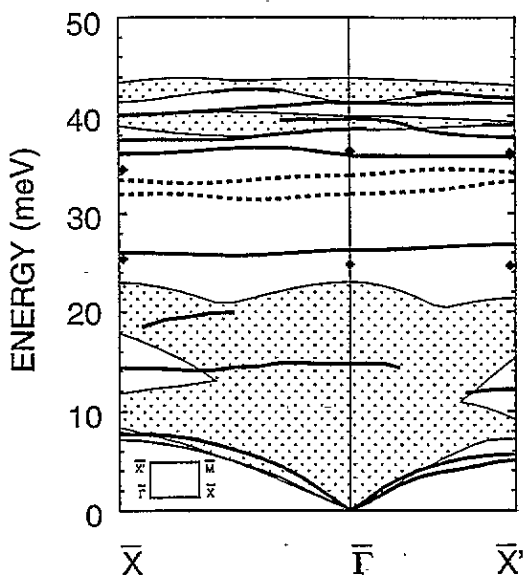

Figure 4. Phonon dispersion of the InP(110) surface covered by 1 ML of hydrogen. The dotted lines indicate two surface-localized gap modes of the clean InP(110) surface obtained at a cut-off energy of 10 Ryd [16]. The diamonds indicate the corresponding phonon modes obtained for the ideal, unrelaxed InP(110) surface.

from the feature resolved by HREELS for the clean surface.

The removal of the relaxation induced by the hydrogenation can be simulated by fixing artificially the atoms in their ideal, bulk-derived positions. We have performed an additional calculation of the surface phonons at the $\overline{\Gamma}$, $\overline{X}$, and $\overline{X'}$ points for a completely unrelaxed nine-layer slab without hydrogen coverage. In the gap region we obtain two localized
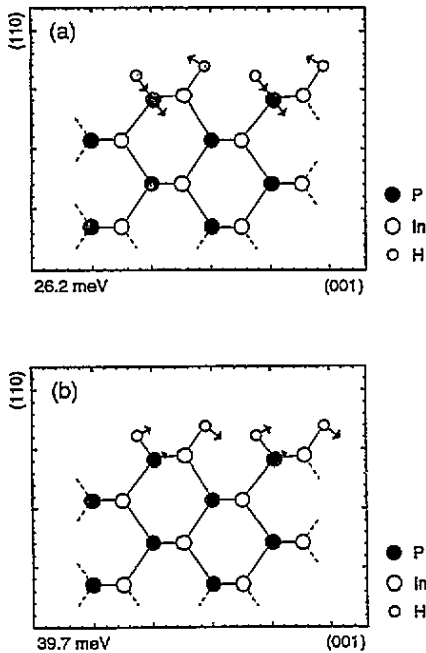
Figure 5. The side view of the first four substrate layers for the displacement pattern of two vibrational states occurring in the InP(110) surface covered by 1 ML of hydrogen. The mode (a) originates in the lower gap state and mode (b) in the upper gap state of the clean surface (indicated by the broken lines in figure 4). The phosphorus atoms are illustrated by the filled circles, the indium by the open circles. Grey circles indicate the hydrogen atoms. The directions (110) and (001) correspond to figure 1.
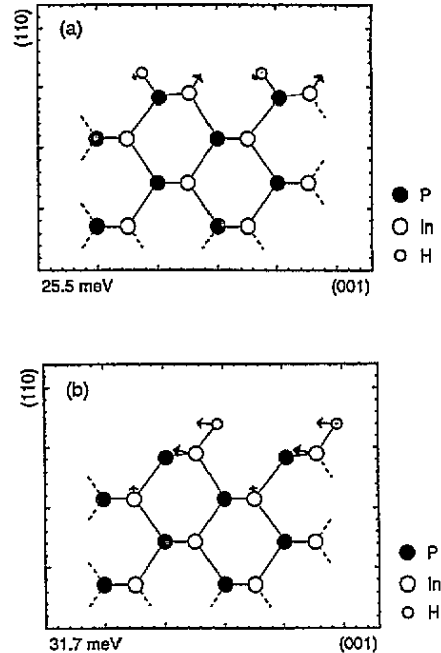
Figure 6. The displacement pattern of two typical gap modes of InP(110) covered by 0.5 ML of hydrogen. (a) One of the vibrational states for hydrogen adsorbed on P. (b) One of the vibrational states for hydrogen adsorbed on In.

features with atomic displacements similar to the eigenvectors shown in figure 5 (with the hydrogen removed). Also the dispersion of these states, which is indicated by the diamonds in figure 4, compares with the results obtained for the hydrogen-covered surface.

Already at a hydrogen coverage of 0.5 ML the surface optic phonon mode above the bulk bands is removed. In addition, another very interesting effect appears in the 0.5 ML case. For hydrogen chemisorbed only on In or only on P, we observe a series of surface-localized states in the gap between the acoustic and optical bulk phonons. These states are characterized by large vibrational amplitudes of the first-layer In atoms. In the case of hydrogen bond to the anions, three states with energies of 25.5, 34.3, and 35.3 meV are present. For hydrogen chemisorbed on the cation sites, we observe four features at 28.8, 31.7, 35.5, and 36.9 meV. Representatively for all of these phonon modes, figure 6 illustrates the displacement pattern of two of these states appearing in the two different adsorption geometries.

The gap states originate in the surface-localized phonon modes of the clean InP(110) surface which are indicated by the broken lines in figure 4. In the clean surface, the phonon modes are characterized by large displacements of the phosphorus atoms and only small displacements of the In atoms, due to the large mass mismatch between In and P. The same behaviour is found for InP(110) covered by 1 ML of hydrogen (figure 5). At a coverage of

0.5 ML, however, the situation is completely different. While the phosphorus atoms exhibit only small vibrational amplitudes, the first-layer indium atoms are characterized by large displacements (figure 6). This changes arise from a reduction of the force constants between the anions and the cations caused by the incomplete hydrogenation. The influence of the 0.5 ML coverage on the strength of the bonds indicates the ability of the hydrogen atoms to break In–P bonds on the surface. Together with the larger energy gain for the formation of H–P bonds with respect to H–In bonds, this result agrees with the experimentally observed decomposition of the surface above a coverage of 0.5 ML. Signatures of the formation of PH_x molecules ($x = 2$ or 3) partially desorbing into vacuum and the presence of metallic In clusters at very high exposures have been reported [6, 9, 32].

5. Summary

By means of the plane-wave pseudopotential method, we have investigated the structural and vibrational properties of the hydrogen-covered GaAs(110) and InP(110) surfaces. Adsorption geometries with one (0.5 ML) and two hydrogen atoms (1 ML) chemisorbed per surface unit cell have been considered. For both surfaces and for both coverages our results confirm the experimentally observed removal of the relaxation [9, 10, 11], which is replaced by a slight counter-rotation of the first-layer anion–cation chains by -8°. The adsorption energies of the H–Ga and the H–As bonding configurations are very similar. For H:InP(110), however, our calculation yields a significantly larger energy gain for the chemisorption of the hydrogen on the phosphorus atoms with respect to the adsorption on the cations. The calculated bond-stretching frequencies for H:GaAs(110) and H:InP(110) are in good agreement with the experimental data from HREELS [1, 2, 3, 4, 6, 7] for both coverages. Our results for the bending modes are compared to the findings of the LDA calculation of [14] and [19] performed for H:GaAs(110).

The analysis of the phonon dispersion of GaAs(110) and InP(110) covered by 1 ML of hydrogen exhibits two important changes with respect to the clean surface. The third acoustic phonon mode appearing for the clean surface in the dispersion perpendicular to the anion–cation chains of the first substrate layer, and the surface optical phonon mode above the bulk bands are suppressed upon hydrogenation. The surface vibrational features of InP(110) lying in the gap between the projected acoustic and optical bulk bands are strongly dependent on the hydrogen coverage. In the 1 ML case, the vibrational states resemble the phonon modes of the clean surface. For a coverage of 0.5 ML, a series of phonon modes characterized by large displacements of the first-layer indium atoms appears. These vibrations indicate the ability of the hydrogen atoms to break In–P bonds. The large difference in the adsorption energies and the appearance of large vibrational amplitudes of the first-layer In atoms agree with the experimentally observed structural decomposition of the surface at higher exposures of InP(110) to hydrogen [6, 9, 32].

Acknowledgments

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