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Chemisorption of arsenic on InP(110)

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Abstract

We present a comprehensive picture of As adsorption on InP(110) based on ab-initio density functional calculations. The total energy surface for single As adatoms on InP(110) is characterized by diffusion channels along [1$\bar{1}$0], with energy minima for As bonded to the P dangling bond. There is an attractive interaction between the adatoms for submonolayer coverages. The epitaxial continued-layer structure represents the ground state of the surface for one ordered As monolayer adsorbed on InP(110). However, an exchange-reacted surface, where the top P atoms are replaced by As, is energetically stable over a wide range of the In and As chemical potentials. This explains the recent experimental finding of two interface phases. We discuss geometrical, electronic and vibrational features of the interface.

Keywords: Arsenic; Chemisorption; Density functional calculations; Indium phosphide; Low index single crystal surfaces; Molecular dynamics

1. Introduction

The adsorption of group-V elements on surfaces of group III–V semiconductors is of considerable interest, both for fundamental reasons and for technological applications. Whereas the adsorption of Sb or Bi on group III–V (110) surfaces has been studied extensively both experimentally and theoretically (see, e.g., Ref. [1]), the As/III–V(110) interface is less well understood. Tulke and Lüth [2] and Chassé et al. [3] conclude from their low-energy electron diffraction (LEED) and photo-emission studies that the annealed As/InP(110) interface is characterized by a partial incorporation of As into the surface. Very recently this system has also been subjected to optical spectroscopy measurements [4]. In that work, the existence of two interface phases has been stated: a poorly ordered phase obtained after As deposition at room temperature, and a highly-ordered phase with coverage in the monolayer range, formed after annealing at about 300°C. In contrast to the previous studies [2,3], Santos and co-workers conclude in their work [4] that an As→P exchange reaction starts at room temperature immediately after As deposition.

The aim of the present study is to provide a comprehensive picture of As chemisorbed on InP(110), based on accurate total-energy calculations.

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2. Method

Our calculations are based on the density-functional theory within the local density approximation (DFT-LDA). We consider an artificially constructed periodic geometry along the surface normal. Its unit cell includes an atomic slab with eight layers of InP, covered by 1/4, 1/2 and 1 monolayer (ML) of As atoms on each side of the slab, and a vacuum region equivalent in thickness to six substrate atomic layers. For the exchange-reacted geometry, the slab is increased to ten III–V(110) atomic layers, where the P atoms of the uppermost layer are replaced by As. Depending on the coverage, calculations for (2×1) and (1×1) translational symmetries are performed. An energy cutoff of 15 Ry is applied to the plane-wave basis set of the electronic orbitals. We sample the k-space with four special points in the irreducible part of the surface Brillouin zone. The total-energy functional is minimized with respect to both the electronic and atomic degrees of freedom until the ions were fully relaxed towards the nearest local minimum on the total-energy surface and the wave functions were fully self-consistent. This approach has proved to be successful in determining precisely the structural and dynamical properties of other III–V(110) surfaces [5]. A detailed description of the method can be found in Refs. [1,6].

3. Results

In order to explain especially the less ordered As/InP interface phase observed after deposition at room temperature [4], we consider a variety of submonolayer geometries. A total-energy Born–Oppenheimer surface is calculated for this system considering one As atom adsorbed at 32 different lateral positions in the irreducible part of the relaxed InP(110)-(2×1) surface. The preferred adsorption site for such a single adatom is in front of the P dangling bond. We observe diffusion channels along the $[1\bar{1}0]$ direction and energy barriers perpendicular to the InP surface chains. A similar shape of the total-energy surface has already been reported for Sb adsorption on GaAs(110)[1]. The adsorption energy per adatom in the minimum-energy position amounts to 4.35, 4.75 and 5.52 eV for coverages of 1/4, 1/2 and 1 ML, respectively. The increase in adsorption energy with increasing coverage indicates the existence of an attractive interaction between the adatoms. Obviously, the intermediate position of the As electronegativity between the respective values of In and P prevents Coulomb repulsion between the adatoms. A similar behaviour has been noted for a series of group-V/III–V(110) interfaces [1].

The epitaxial continued-layer structure (ECLS) (Fig. 1) represents the ground state of the surface for an ordered, adsorbed monolayer. The corresponding geometrical details are given in Table 1. We observe an overlayer buckling of 0.11 Å, quite close to the corresponding value of ordered Sb overlayers on III–V(110) [1], but somewhat larger than that calculated for As adsorption on GaAs(110) [7]. The other calculated parameters are, however, very similar to those of Ref. [7]. We have also calculated the surface band structure for

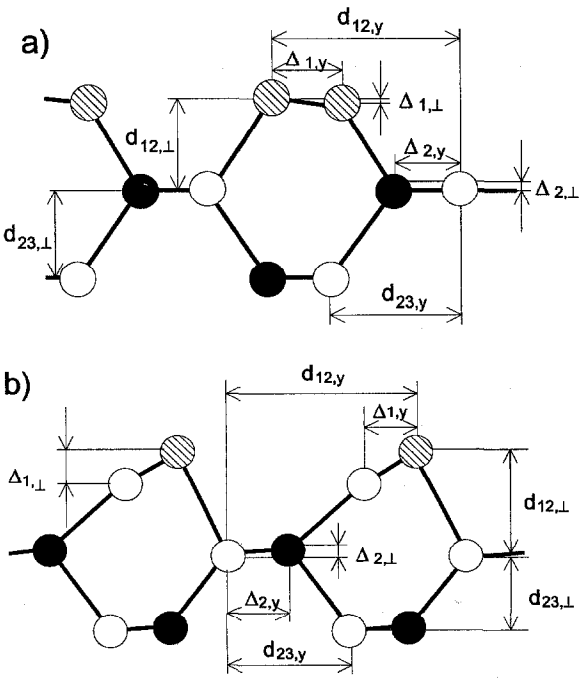

Fig. 1. Side view of the relaxed As/InP(110) interface for the ECLS (a) and exchange-reacted surface (b). Substrate anions (substrate cations, arsenic atoms) are denoted by full (empty, shaded) symbols.

Table 1
Geometrical parameters (in Å) of the ECLS and the exchange-reacted As/InP(110) surface according to Fig. 1

	ECLS	Exchange
$\Delta_{1,\perp}$	0.11	0.80
$\Delta_{2,\perp}$	0.06	0.15
$\Delta_{1,y}$	1.59	1.24
$\Delta_{2,y}$	1.50	1.42
$d_{12,\perp}$	2.10	2.25
$d_{23,\perp}$	2.07	2.14
$d_{12,y}$	4.15	4.48
$d_{23,y}$	2.75	2.87

As adsorption on InP(110) in the ECLS (Fig. 2). Its main features closely resemble the surface band structures obtained for other V/III–V(110) interfaces [1]. We find, however, that the highest occupied state does extend slightly into the bulk band-gap region.

In a series of experimental papers [2–4], it has been suggested that the highly ordered As/InP phase probably undergoes an anion exchange. In order to test this suggestion, we studied a surface geometry where the uppermost phosphorus atoms are replaced by arsenic. Indeed, this gives rise to a minimum in the total energy. Details of the resulting exchange geometry are given in Table 1. The observed buckling of the uppermost layer is related to a more planar, sp^2-like bonding situation of the surface cation and a p-bonding of the surface anion, as discussed for clean III–V(110) surfaces in Ref. [8]. Thereby we determine a buckling of 0.8 Å, which lies in-between the values determined by LEED for the clean InAs(110) and InP(110) surfaces (0.88 and 0.73 Å, respectively [9]). Starting from the relaxed structure, we also determined the surface phonons at the Γ point of the exchange-reacted surface using the method described in Ref. [5]. Apart from several phonons which have a mixed bulk-surface character, we find a clear-cut surface phonon with A″ symmetry at 29.3 meV. The clean InAs(110) surface has a surface phonon with a similar eigenmode at 28.8 meV [5]. The slight shift towards a higher frequency for the system considered here indicates that the uppermost InAs layer is exposed to a compressive stress, induced by the lattice misfit of about 2.8%. Experimental findings of peaks in the Raman scattering intensity at 5.6 and 7.4 meV [10] are related to the high density of bulk phonon states in this energy region, according to our calculation. The surface band structure of the exchange-reacted surface (Fig. 2) closely resembles the features known from free III–V(110) surfaces [8]. The surface relaxation shifts the bands related to the anion (cation) dangling bonds to the bulk valence (conduction) band edge. Bound surface states appear only around the X point in the fundamental gap. Therefore, in photoemission experiments, both electronic structures in Fig. 2 should be clearly distinguishable.

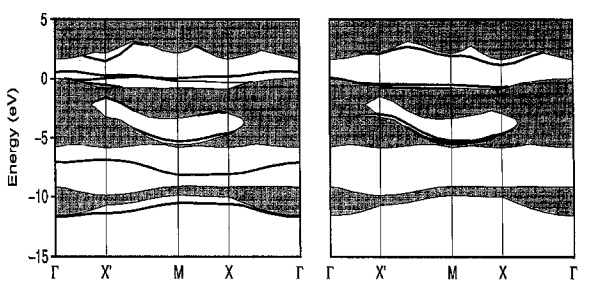

Fig. 2. Surface band structure of the ECLS (left) and exchange-reacted (right) As/InP(110) surface. Bound surface states are indicated by solid lines, and shaded regions mark the projected bulk band structure.

Due to the varying number of As and In atoms per surface unit cell, the comparison of the total energy for the different adsorption configurations considered here has to take into account the chemical potentials of the respective species. Upper limits on the chemical potentials μ are set by the bulk elements. To estimate the stability of the ECLS versus the exchange-reacted surface we show the phase diagram obtained as a function of the In and As chemical potentials in Fig. 3. Only for very low values of the In chemical potential is the ECLS more favourable than an exchange-reacted surface. We find a clear preference for an exchange reaction in most of the appropriate region of the chemical potentials of the surface constituents. This is in agreement with the conclusions drawn from a measurement of the surface optical properties [4], i.e. that As incorporation starts immediately after deposition. We have also studied a geometry where the exchange takes place only partially, and half of the (2×1) surface unit cell consists of the bare

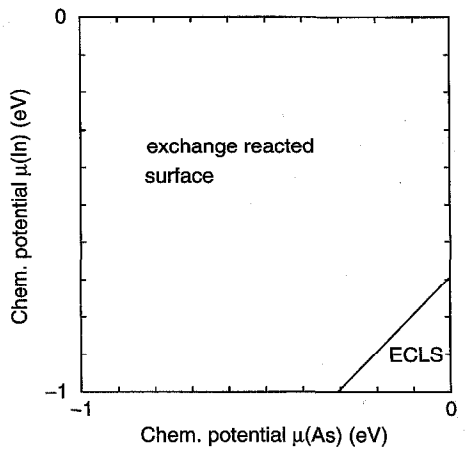

Fig. 3. Phase diagram of the As/InP(110) interface versus the In and As chemical potentials in the respective range $-1\ \text{eV} \leq \mu - \mu_{\text{bulk}} \leq 0$.

InP(110) surface. We find such a configuration, however, to be less favourable than complete exchange. This is also in agreement with the experimental finding of a highly ordered (1×1) symmetry for the annealed interface phase.

4. Conclusions

Based on ab initio calculations of the As/InP(110) interface, we give a comprehensive picture of the chemisorption involved. For submonolayer coverage there is an attractive interaction between the adatoms. Adatom diffusion takes place in the $[1\bar{1}0]$ direction. The minimum-energy configuration for an ordered adsorbate overlayer is the ECLS. However, a substitution of the surface P atoms by As is energetically preferred over a wide range of the chemical potentials of the surface constituents. We suppose that such an As incorporation into the surface starts immediately after As deposition at room temperature. The geometrical, electronic and vibrational properties of the exchange-reacted surface closely resemble those of the clean III–V(110) surface.

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