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Boron and indium incorporation in GaP(0 0 1) surfaces by vapour deposition: Density-functional supercell calculations of the surface stability

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ABSTRACT

Using surface supercells and the density-functional method, surface formation energies are calculated for probable GaP(0 0 1) reconstructions without and with indium or/and boron substitutions. Obtained surface stability diagrams provide surface compositions and surface structures in dependence on the growth conditions: indium atoms are built into the c(4 × 4) patterns under strongly P-rich conditions and into the β2(2 × 4) reconstruction under less P-rich conditions. Under In-rich and non-P-rich conditions, initial structures of metallic InGa phases are formed in the (2 × 4) mixed-dimer reconstruction. In the c(4 × 4) and (2 × 4) mixed-dimer patterns the full range of In:Ga content is accessible by variation of the In:Ga ratio in the gas phase. Boron can be built into the c(4 × 4) patterns of the GaP(0 0 1) surface in form of isolated atoms or nearest-neighbours under strongly P-rich and moderately to strongly B-rich conditions. The boron incorporation is strongly enhanced at the surface in respect to theoretical predictions for the bulk, what explains the larger content found experimentally. Assuming P-rich conditions, which are suitable for the growth of the ternary alloys, the obtained surface stability diagram for the quaternary (BInGa)P shows that nearly the full range of In:Ga content is accessible. However, the boron content in the alloy is restricted as found analogously for (BGa)P and is independent of the indium content. The expected increase of the boron content in presence of indium cannot be confirmed. Contrary to the analogous GaAs systems, boron atoms do not substitute phosphor atoms (antisite position) in GaP, (InGa)P, (BGa)P, and (BInGa)P.

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1. Introduction

Contrary to (InGa)P, the (BGa)P is less investigated and the (BInGa)P is not investigated both experimentally and theoretically. However, they might become important in future for optoelectronic devices by reason of wide band gaps.

(InGa)P can grow over the whole composition range by MOVPD at a substrate temperature of 650 °C [1]. Isoelectronic substitution of boron isotopes in GaP is found at first by Robbie et al. [2]. $B_xGa_{1-x}P$ with x up to 0.04 is obtained by Gottschalch et al. [3]. (BInGa)P alloys are not investigated up to now by our knowledge. They could be more stable than ternary ones by compensation of different atomic sizes.

In this study we investigate the thermodynamic stability of GaP(0 0 1) reconstruction patterns with indium and boron substitutions in dependence on the chemical potentials of the constituents (growth conditions). For that, the most stable In- and B-substituted GaP(0 0 1) reconstructions have to be found out by density-functional supercell calculations. At first, we present the surface models and the calculation method. Then, the obtained surface stability diagrams are discussed: firstly, for the ternary alloys (InGa)P, (BGa)P, and Ga(PB) (antisite substitution) and, afterwards, for the quaternary alloy (BInGa)P. We obtain access to the surface composition and surface structure in dependence on the growth conditions.

2. Surface models and calculation method

The GaP(0 0 1) surface shows a number of surface reconstructions in dependence on the preparation conditions [4–6]: Froyen and Zunger [4] find under Ga-rich conditions the β2(4 × 2), under P-rich conditions the c(4 × 4), and in the intermediate region the β2(2 × 4) reconstruction. Later Pulci et al. [5] consider also some other patterns and find under P-rich conditions a two-P-dimer structure (p(2 × 2)td2 or (2 × 2)-2D) with two phosphorus monolayers, under Ga-rich conditions the (2 × 4) mixed-dimer pattern ((2 × 4)md), under extremely Ga-rich conditions the top-Ga-dimer structure ((2 × 4)tGd), and in the intermediate region the β2(2 × 4) reconstruction. In a review paper Schmidt [6] presents the

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following structures: (2×4)tGd, (2×4)md, $\alpha2(2\times4)$, $\beta2(2\times4)$, $c(4\times4)$ (from Ga-rich to P-rich conditions).

In this study all these patterns plus the $c(4\times4)(n)$ reconstructions (n = 1–6), which are important for the GaAs(0 0 1) surface [7–12], are investigated. In the $c(4\times4)(n)$ reconstructions n top-layer P atoms are exchanged by gallium atoms. At first, we test the suitability of the used method by calculation of the surface stability diagram of the pure GaP(0 0 1) surface and compare the results with the well established data from the literature. Afterwards, we select the most stable reconstructions and incorporate indium or boron atoms as described in [12].

Within the periodic supercell approach a surface is modelled by a slab and a vacuum region. The slab contains eight or nine gallium and phosphorus layers depending of the reconstruction. The vacuum region has a thickness of nine or eight atomic layers, so that the cell size is constant for all the reconstructions. For consistency the calculations for the (2×2) patterns are done with a (2×4) cell. The cell volume is fixed using the optimised bulk lattice constant (a = 5.4675 Å): $2a\times2a\times4a$ for $c(4\times4)$ and $\sqrt{2}a\times2\sqrt{2}a\times4a$ for the other reconstructions. The atoms in the lowest double layer are kept frozen in the calculated ideal bulk structure. All the other atoms are allowed to relax. The artificial dangling bonds at the bottom gallium layer are saturated by true hydrogen atoms as demonstrated in [12,13]. For the characterization of the substituent structures the position of an atom in the supercell is given by (xyz) in units of a/2 and is measured in respect to a reference position (0 0 0).

The equilibrium structures and the total energies E of the surfaces are obtained by the density-functional theory (DFT) in the generalized-gradient approximation (GGA) using the CASTEP program [14,15]. Furthermore, the gradient-corrected exchange-correlation functional of Perdew and Wang [16] (PW91) and ultrasoft Vanderbilt-type pseudopotentials (usp) [17], as implemented in CASTEP, are used. The d electrons are explicitly considered for gallium and indium atoms. The energy convergence requires a cutoff energy of 350 eV. The Brillouin-zone sampling is done using a $3\times3\times1$ (for the $c(4\times4)$ cell) and $4\times2\times1$ (for the other cells) Monkhorst–Pack special k-point grid [18], which corresponds to five or four k-points, respectively.

In order to compare the stability of surfaces with different stoichiometry the surface formation energy with respect to a reference structure is calculated in dependence on the chemical potentials of the constituent atoms. A thermodynamic equilibrium is assumed between the gas phase reservoir and the GaP bulk [19]: $\mu(\mathrm{GaP^{bulk}}) = \mu(\mathrm{Ga}) + \mu(\mathrm{P})$.

In analogy to [12], $\Delta_F E$ is obtained for the isovalent indium (l) and boron (k) substitutions and the antisite boron substitutions (o) by:

$$\begin{aligned}\Delta_F E = {} & E(\mathrm{B_k In_l Ga_m P_n B_o}) - E_{\mathrm{ref}}(\mathrm{Ga_{m'}P_{n'}}) \\ & - (m-m')\mu(\mathrm{GaP^{bulk}}) - (m'-m+n-n')[\Delta\mu(\mathrm{P}) + \mu(\mathrm{P^{bulk}})] \\ & - (k+o)[\Delta\mu(\mathrm{B}) + \mu(\mathrm{B^{bulk}})] - l[\Delta\mu(\mathrm{In}) + \mu(\mathrm{In^{bulk}})]\end{aligned}$$

with $\Delta\mu(X) = \mu(X) - \mu(X^{\mathrm{bulk}})$, X = B, In, Ga, P.

$\Delta\mu(X) = 0$ means X-rich conditions. Decrease of $\Delta\mu(X)$ leads to X-poor conditions. $\Delta_F E$ is referred to a (1×1) surface cell ($\Delta_F E/8$). The $\alpha2(2\times4)$ reconstruction is used as reference structure (m' = 30, n' = 26). For the chemical potentials of the elements we have calculated: $\mu(\mathrm{P^{bulk}}) = -180.9813$ eV (black phosphorus (A17)), $\mu(\mathrm{B^{bulk}}) = -77.7615$ eV (T-50 boron (A_g)), $\mu(\mathrm{Ga^{bulk}}) = -2061.4384$ eV (αGa), $\mu(\mathrm{In^{bulk}}) = -1565.8905$ eV (A6 face-centered tetragonal lattice). With these values and the bulk energies of the binary compounds we obtain the following heats of formation: $\Delta_F H(\mathrm{BP}) = -0.969$ eV, $\Delta_F H(\mathrm{GaP}) = -0.850$ eV, $\Delta_F H(\mathrm{InP}) = -0.392$ eV. These values well agree with the experimental data related to black phosphorus [20]: BP: −0.99 eV [21] and −0.79 eV [22], GaP: −0.81 eV [23,24], −0.83 eV [25], and −0.85 eV [26], InP: −0.36 eV [26] and −0.41 eV [24].

3. Results and discussion

3.1. GaP(0 0 1) surface

Fig. 1 shows the considered reconstructions for the pure GaP(0 0 1) surface. From the calculated surface formation energies we construct the surface stability diagram (Fig. 2). The obtained most stable reconstructions in the different potential regions are in good agreement with the results of Schmidt [6]. From the obtained stability diagram we select the eight most stable reconstructions for the following investigations of indium and boron substitution: (2×4)tGd, (2×4)md, $\alpha2(2\times4)$, $\beta2(2\times4)$, $c(4\times4)$(3), $c(4\times4)$(2), $c(4\times4)$(1), $c(4\times4)$(0).

3.2. Indium incorporation

The surface stability diagram for the (InGa)P(0 0 1) surface (Fig. 3) shows the most stable reconstructions (Fig. 4) in dependence on the phosphorus and indium chemical potential. The indium incorporation in GaP is energetically very favourable. In consequence, structures with very high indium content (which means pure or nearly pure InP surface structures) occur in the In-rich region of the diagram.

Indium atoms are deposit in three patterns: (2×4)md, $\beta2(2\times4)$, and $c(4\times4)$. Under non-P-rich (Ga-rich) conditions no indium atoms are built into the (2×4) mixed-dimer pattern, so that a Ga-rich surface layer is probable, which can be an initial structure for a metallic phase. Under a balanced Ga:P ratio and In-rich conditions InGa structures are formed in the surface dimers of the (2×4) mixed-dimer reconstruction. These structures can lead to the formation of an InGa alloy. Under more P-rich and strongly In-rich conditions the gallium-dimer atoms are completely substituted by indium atoms, which can be an initial structure for a metallic indium phase. Our results agree with experimental findings of Shimomura et al. (LEED, STM) [27], where a (4×2) pattern with row and hump structures is obtained under In-rich conditions. Indium incorporation into the (2×4)tGd and $\alpha2(2\times4)$ structures provides no stable structures.

A balanced Ga:P ratio and moderately In-rich conditions lead to In-substituted $\beta2(2\times4)$ structures. Up to five indium atoms are built into the first Ga layer below the upper and lower phosphorus dimers. The substituents form nearest-neighbour arrangements, which are alike to fragments of twisted $(\text{–In–P–})_n$ chains into the [1 1 1] direction. These chains are not the most stable structures found for the (InGa)P bulk [28]. However, the calculated gaps for such substituent structures in the bulk environment well agree with experimental data, so that they could be real.

Higher phosphorus exposure allows the deposition of indium and gallium in the first group-III-atom layer of the $c(4\times4)(0)$ reconstruction. Thereby, the full range of the In:Ga content is accessible. The most stable structure with six indium atoms ($\mathrm{In_6}$) is not shown in Fig. 3. Its stability is only a little smaller than that of the $\mathrm{In_5}$ and $\mathrm{In_7}$ structure. Indium atoms are built into the first Ga layer outside the phosphorus dimer block what leads to the formation of $(\text{–In–P–})_n$ chains into [1 1 0] direction or fragments of these chains. Such chains are not the most stable structures found for the (InGa)P bulk and the calculated gap widths [28] do not agree with the experimental results. This means that a rearrangement (annealing) takes place in the surface-near bulk during the growth. This effect is e.g. also found for (InGa)As [12,29] and (InGa)(AsN) [30].

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