

Local aspects of the As-stabilized 2×3 reconstructed (001) surface of strained $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys: A first-principles study

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Using the first-principles total-energy pseudopotential method, we study local aspects of an anion-terminated model of the (2×3) reconstructed (001) surface of strained $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys. The structural model is based on recent in-plane x-ray-diffraction data [M. Sauvage-Simkin *et al.*, Phys. Rev. Lett. **75**, 3485 (1995)] and the in-plane coordinates of atoms are found in excellent agreement with the experiment. We demonstrate that values of some atomic coordinates are mainly due to strongly local features, such as arsenic dimerization and indium adaptation to the GaAs substrate. We finally discuss a way leading to some unknown quantities in this experiment, i.e., the atomic coordinates along the z axis.

I. INTRODUCTION

Recently,¹ a structural model, based on x-ray diffraction data, has been proposed for the 2×3 reconstruction occurring on the arsenic rich (001) surface of $\text{In}_x\text{Ga}_{1-x}\text{As}$ ternary alloy. The $\times 2$ periodicity occurs in the $[1 \bar{1} 0]$ direction of the (001) plane, whereas the $\times 3$ reconstruction is observed in the $[1 1 0]$ direction. In this model (Fig. 1), chemisorbed arsenic dimers along $[1 \bar{1} 0]$ sit on a full As layer having two types of atoms: the first ones (labeled 1) are bound to the chemisorbed As atoms and the second ones (labeled 2) dimerize along $[1 \bar{1} 0]$. The subsurface cation layer contains both indium and gallium atoms with the indium occupying the more open site labeled 3 in Fig. 1. This In-Ga distribution sets the subsurface In composition at the value $x=0.67$. The deeper layers are assumed to be bulk GaAs.

Although the measured diffraction data involve only in-plane momentum transfer and do not contain information on the surface perpendicular z atomic displacements, a tentative displacement pattern in the normal direction was suggested in Ref. 1 by considering "reasonable" bulklike interatomic distances for the Ga-As and In-As bonds; compared to the bulk structure, the pattern involves quite large z displacements.

The aim of the present paper is to examine, by total-energy calculations, a few local aspects of the surface shown in Fig. 1, in order to verify to which extent the proposed reconstruction pattern corresponds to energy minima at $T=0$ K and to obtain more definite information on z coordinates of the surface atoms.

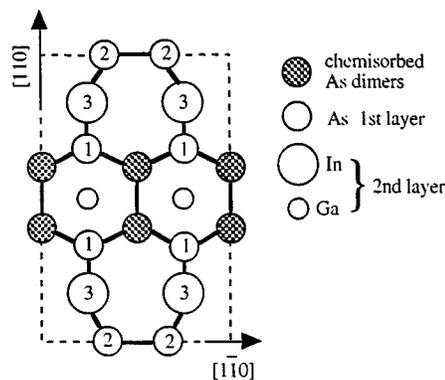


FIG. 1. Schematic representation of the model proposed in Ref. 1 for the As-stabilized 2×3 reconstructed (001) surface on strained $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys.

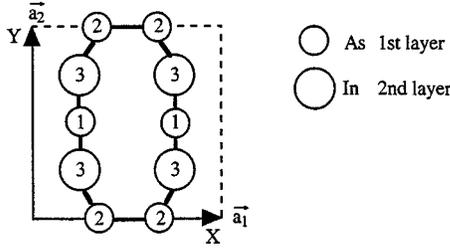


FIG. 2. Schematic representation of the presently studied (2×2) reconstruction. The x axis is parallel to the \mathbf{a}_1 vector defined in the text and chosen along the $[1 \ 1 \ 0]$ direction; the y axis is parallel to the \mathbf{a}_2 vector along the $[1 \ 1 \ 0]$ direction.

The local aspects we are interested in concern essentially the length of the arsenic dimer bond and the position of the indium atom with respect to the dimerized arsenics of the upper layer and to the bulklike arsenics in the lower layer.

Having this in mind, we can restrict our calculations to the 2×2 surface cell described in Fig. 2, which keeps each indium atom still linked to the two kinds of arsenic in the upper layer (the dimerized and the nondimerized), and which does not take into account the gallium atoms belonging to the subsurface cation layer shown in Fig. 1.

Furthermore, such a limitation will also make the chemisorbed arsenic dimers disappear from the calculations; however, it should be noticed that part of the effect of the missing atoms will be retained: the arsenics that are bound to them in Fig. 1 [those labeled As(1)] will be forbidden to move along the z axis. Moreover, several calculations, corresponding to selected fixed values of the z coordinate of these As(1), will be performed, in order to probe their influence on the other atoms' coordinates.

Throughout this paper, we will use the following 2×2 surface basis: $\mathbf{a}_1 = [1 \ \bar{1} \ 0] a_0$, $\mathbf{a}_2 = [1 \ 1 \ 0] a_0$, $\mathbf{a}_3 = [0 \ 0 \ 1] a_0$, where a_0 is the lattice constant of the bulk GaAs.

The Cartesian coordinate axes are oriented along the \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 , with the origin placed on a bulk Ga atom, and the notation $A(n)-i$ represents the i coordinate of the atom A labeled by n ; for example, As(1)- x is the x coordinate (in the above basis) of the arsenic labeled 1.

II. METHOD OF CALCULATION

The surface energies are calculated from first principles, within the local-density approximation² and using the plane-wave pseudopotential method in momentum space.³

We employ the norm-conserving pseudopotentials of Ref. 4, the Ceperley-Alder exchange and correlation⁵ as parametrized by Perdew and Zunger,⁶ and perform the self-consistent calculations with the plane-wave cutoff of 9 Ry.

The $3d$ and $4d$ electrons of Ga, As, and In atoms are considered as core electrons, assuming that the surface reconstructions are mainly affected by the s and p valence electrons.⁷

In order to test the accuracy of our approximations, we first calculate the total energy and the ground-state properties of bulk GaAs. The calculated equilibrium lattice constant is $a_0^{\text{th}} = 5.52 \text{ \AA}$, which is 2.3% smaller than the experimental value of 5.65 \AA ;⁸ this is, incidentally, exactly the same value as the lattice constant obtained in Ref. 9 using soft pseudopotentials and the higher kinetic-energy cutoff of 12 Ry. The calculated bulk modulus is equal to 75.9 GPa, in excellent agreement with the experimental value of 75.6 GPa.¹⁰

Concerning the (2×2) reconstructed surface, we use a periodic slab geometry, with seven atomic planes and the equivalent of five “planes” of vacuum repeated along the $[001]$ direction. The lattice constant, in the x - y plane parallel to the surface, is $\sqrt{2}a_0^{\text{th}}$, where a_0^{th} is the calculated bulk equilibrium value mentioned above. For such a slab, calculations with the kinetic-energy cutoff of 9 Ry correspond approximately to 3100 plane waves. The Brillouin-zone summation is accomplished using three “special points” which,

TABLE I. Surface atomic positions for the calculated 2×2 reconstruction shown in Fig. 2 and within the 2×3 reconstruction model proposed in Ref. 1. Labeling of atoms refers to Fig. 2, x , y , and z axes are parallel to the \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 vectors defined in the text; the origin of the coordinates is placed on the bulk Ga atom. All atomic positions are given in the $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ basis — i.e., in $\sqrt{2}a_0$ units for x and y coordinates and in a_0 units for the z coordinates; the bulk GaAs lattice constant a_0 is equal to $a_0^{\text{th}} = 5.52 \text{ \AA}$ in the calculations and 5.65 \AA in the experiment. Calculations 1, 2, and 3 correspond to different values of the z coordinate of As(1).

	Calculation 1	Calculation 2	Experiment ^c	Calculation 3
As(1)- x	0.25 ^a	0.25 ^a	0.25	0.25 ^a
As(1)- y	0.5 ^a	0.5 ^a	$0.5 + 0.025 \pm 0.006$	0.5 ^a
As(1)- z	0.75 ^a	$0.75 + 0.030^a$	$0.75 + 0.03^b$	$0.75 + 0.017^a$
As(2)- x	$0.25 + 0.098$	$0.25 + 0.098$	$0.25 + 0.095 \pm 0.015$	$0.25 + 0.098$
As(2)- y	0	0	0	0
As(2)- z	$0.75 + 0.108$	$0.75 + 0.110$	$0.75 + 0.10^b$	$0.75 + 0.109$
In(3)- x	$0.25 + 0.003$	$0.25 + 0.003$	0.25	$0.25 + 0.003$
In(3)- y	$0.25 - 0.029$	$0.25 - 0.022$	$0.25 - 0.025 \pm 0.005$	$0.25 - 0.025$
In(3)- z	$0.50 + 0.031$	$0.50 + 0.037$	$0.50 + 0.04^b$	$0.50 + 0.034$

^aFrozen atomic coordinates.

^bAtomic coordinates that cannot be obtained from the experimental data.

^cExperiment and model proposed in Ref. 1.

in the Monkhorst-Pack notation,¹² corresponds to $(q_1, q_2, q_3) = (4, 4, 2)$.

The atomic positions in the three central planes are frozen throughout the calculations, so as to represent the bulk GaAs. The coordinates of two of the four As atoms in the top layer [those that are bound to the chemisorbed As in Fig. 1 and labeled As(1)] are frozen, as well, at the *quasiideal* surfaces sites, since a certain freedom exists for the choice of their z coordinates: we first perform two calculations, one, labeled 1, with an ideal z position for As(1) and a second one, labeled 2, in which the z coordinate of As(1) is the one proposed in Ref. 2. A third calculation, labeled 3, taking into account the results of calculations 1 and 2, will then be performed and produce a third value of As(1)- z , which we will discuss later.

The positions of the other two arsenic atoms [labeled As(2)] in the top layer, and those of the indium atom [labeled In(3)] in the second layer are relaxed, until the calculated Hellmann-Feynman forces are smaller than 0.02 mdyn.

III. RESULTS AND DISCUSSION

The (2×2) reconstruction, which energetically involves mainly the arsenic dimerization, lowers the total energy by about 0.7 eV per 1×1 surface area, in both calculations; this is larger than the energy gain of 0.48 eV per 1×1 surface area for the (2×2) As-terminated missing row model, with As vacancies and dimers, of the GaAs (001) surface.¹⁰

The atomic positions obtained by the two local-density approximation (LDA) calculations are compared to the corresponding experimental ones in Table I. All these positions are given in the basis \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 specified in Sec. I.

Since the x and y coordinates of the As(1) are determined by the symmetry constraint of the (2×2) surface cell, the calculations can only deal, in the plane, with x and y coordinates of As(2) and In(3); on the other hand, nothing prevents the calculations from dealing with z coordinates.

It is immediately apparent from Table I that, both calculations reproduce accurately the experimental x and y coordinates of As(2) and In(3), which are directly related to the data collected in Ref. 1. Furthermore, concerning the z coordinates, which cannot be obtained by the experiment, a quite good agreement occurs between our calculations and experimental estimates. It thus appears that the 2×2 model could give an accurate description of local aspects of the experimentally investigated 2×3 reconstruction.

Let us now examine more closely the atomic positions of As(2) and In(3).

The predicted length of the arsenic As(2)-As(2) dimer, which is formed along the x axis, is equal to 0.304 in both calculations, in excellent agreement with the experimental value of 0.310 ± 0.03 . It thus turns out that this arsenic bond length is fully imposed by strongly local considerations, e.g., is independent both of the As(1)- z value and of the actual reconstruction involving this dimer (2×2 or 2×3). As a matter of fact, calculations 1 and 2 show that As(2)- z is also insensitive to the variation in the z coordinate of the arsenic As(1). It is interesting to note that both calculations support the picture proposed in Ref. 2, in which the z value of the dimerized arsenic is higher than As(1)- z .

Furthermore, the difference between the x coordinates of

As(2) and In(3) is exactly the same in both calculations and experiment. The value of In(3)- x is thus entirely fixed by the arsenic dimerization and, as shown in Table I, does not seem to depend on As(1)- z . However, since In(3) is bound to As(1), the y and/or the z coordinates of the indium atom must respond to a shift of As(1)- z . Inspecting Table I, we notice that In(3)- y is more sensitive to As(1)- z than In(3)- z is: in a_0 units, a shift of As(1)- z equal to 0.03 leads to a shift of 0.01 for In(3)- y but of only 0.006 for In(3)- z . In order to understand the different behavior between the y and z coordinates of the indium, we first remember that In(3) is strained on a x - y GaAs bulk, which induces a rearrangement of its z coordinate with respect to a bulk arsenic atom. Such a rearrangement can be quantified by the value of the perpendicular strain

$$\varepsilon_{\perp} = \frac{c - a_0}{a_i}. \quad (1)$$

Here a_i is the InAs bulk lattice constant and c is the distorted lattice parameter of InAs perpendicular to the x - y plane of bulk GaAs. Calculations done with the assumptions specified in Sec. II give $a_i = 5.91 \text{ \AA}$, which is 2.5% smaller than the experimental value of 6.06 \AA ,⁸ furthermore, for the studied reconstruction, c is given by multiplying by $4a_0$ the difference of the coordinates of In(3) and a bulklike arsenic atom along the z axis.

Calculations 1 and 2 lead, respectively, to the perpendicular strain of 5% and 7.2%, which is of the same order as the value of 7.3% predicted by the continuum elasticity theory, for a (001)-oriented layer of InAs embedded in a GaAs host, and confirmed by first-principles total-energy methods.¹³ We can conclude that the value of In(3)- z is mainly given by the adaptation of In(3) to a x - y GaAs substrate, which explains why only the y component of the indium is quite sensitive to a shift of As(1)- z .

Having this in mind, we could try to derive accurately what must be the actual value of As(1)- z , assuming that each reconstruction (the virtual 2×2 or the real 2×3) leads to the same value for this coordinate. This is the aim of calculation 3.

The simplest idea for that is to look for the frozen value of As(1)- z , which leads, through the energy minimization, to the theoretical value of In(3)- y equal to the experimental one, i.e., 0.225. In principle, such a procedure usually requires several choices of As(1)- z before reaching the right value. However, we have found out that simple linear interpolation between the results of calculations 1 and 2 for In(3)- y is enough: calculation 3 thus leads to the As(1)- z value of $0.75 + 0.017$. This calculation is performed in the same conditions as the previous ones; for example, the forces on As(2) and In(3) must then become smaller than 0.02 mdyn.

The results of this calculation are reported in the last column of Table I. We again find the same behavior for the different atomic coordinates with respect to a shift of As(1)- z : (1) total insensitivity of As(2)- x and In(3)- x ; (2) fairly weak sensitivity of As(2)- z ; (3) rather small sensitivity of In(3)- z ; and (4) quite large sensitivity of In(3)- y .

Since the results of calculation 3 are essentially dependent on the mean experimental value of In(3)- y and considering that calculations 1 and 2 give values more or less at either

end of the error bar for In(3)-y, we may say that calculation 3 leads to a realistic expectation value for As(1)-z with an accuracy of ± 0.015 . In addition, owing to the strong cross dependence between In(3)-y (accessible to the experiment) and As(1)-z and to the good matching between the measured and calculated atomic coordinates in the common parts of our model 2×2 cell and the real 2×3 structure, we can be quite confident in the x, y, z description obtained by this combined approach. However, a complementary diffraction experiment allowing perpendicular momentum transfer and thus directly sensitive to the z coordinates would bring a definite confirmation, particularly in the case of As(1), since the release of As(1)-y might modify the picture.

IV. SUMMARY

We have performed *ab initio* calculations for the (001) $\text{In}_x\text{Ga}_{1-x}\text{As}$ surface in an anion-terminated (2×2) reconstruction at $T=0$ K. This 2×2 reconstruction can be considered as part of a (2×3) reconstruction model, based on in-plane x-ray-diffraction data,¹ and involves three different kinds of atoms: an arsenic As(1) for which only the z coordinate is allowed to shift from its ideal position, a second arsenic As(2) that participates in a dimer, and an indium In(3). We found out that the calculations reproduce very accurately the experimental in-plane coordinates of As(2) and

In(3). In addition, the behavior of each coordinate of As(2) and In(3), with respect to a variation of the z coordinate of As(1), has been examined and understood: a strong or a total insensitivity to such shift is either related to the strength of the arsenic dimerization or to the adaptation to a GaAs substrate. In fact, we find that the most sensitive coordinate is the y coordinate of In(3). By adjusting the theoretical value of this sensitive coordinate exactly at the mean experimental value, we could obtain precisely the coordinates missing in the experiment, i.e., the z coordinates of As(1), As(2), and In(3), assuming that these z coordinates are not sensitive to the considered reconstruction (2×2 or 2×3). The resulting z values are not much different from the ones constructed in Ref. 1. We are now preparing an x-ray-diffraction experiment allowing normal momentum transfer, in order to check our predictions.

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¹M. Sauvage-Simkin, Y. Garreau, R. Pinchaux, M. B. Véron, J. P. Landesman, and J. Nagle, *Phys. Rev. Lett.* **75**, 3485 (1995).

²P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

³J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).

⁴G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 2314 (1982).

⁵D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).

⁶J. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

⁷C. H. Park and D. J. Chadi, *Phys. Rev. B* **49**, 16 467 (1994).

⁸*Physics of Group IV Elements and III-V Compounds*, edited by O. Madelung, Landolt-Bornstein, New Series Group III, Vol. 17, Pt. a (Springer, Berlin, 1982).

⁹Gui-Xin Qian, R. M. Martin, and D. J. Chadi, *Phys. Rev. B* **38**, 7649 (1988).

¹⁰J. S. Blakemore, *J. Appl. Phys.* **53**, R123 (1982).

¹¹H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).

¹²J. E. Bernard and A. Zunger, *Appl. Phys. Lett.* **65**, 165 (1994).