PHYSICAL REVIEW B VOLUME 56, NUMBER 24 15 DECEMBER 1997-II

Theoretical investigations of As overlayers on InP(110) surfaces

S. Mankefors, P. O. Nilsson, and J. Kanski
Department of Physics, Chalmers University of Technology, S-41296 Göteborg, Sweden

K. Karlsson
Department of Natural Science, Högskolan i Skövde, S-54128 Skövde, Sweden

(Received 17 July 1997)

As adsorption and interaction with InP(110) is investigated by means of total-energy minimization calculations. We find that the As-P exchanged configuration has higher energy than the As/InP(110) epitaxially continued layer structure (ECLS), for all types of As reservoirs considered. In the presence of an additional As layer in ECLS (i.e., 1.5 ML adsorbed As), however, the exchanged configuration is only slightly higher in energy than the nonexchanged one. We conclude that the As-P exchange process is energetically unfavorable, and should in any case not be complete at room temperature, as suggested in a recent report. Our conclusion is supported by results of a photoemission study, including As adsorption, desorption, and redeposition, according to which the process is nonreversible. [S0163-1829(97)05947-X]

I. INTRODUCTION

Adsorption of group-V elements on (110) surfaces of III-V semiconductors has been a subject of extensive research for many years.[1] Much of the early work was focused on Sb adsorption, mainly because Sb was found to form exceptionally abrupt and well-defined overlayers, providing ideal conditions for, e.g., Schottky barrier investigations. Further investigations in this field have dealt with adsorption of Bi (Ref. 2) and more recently also with As,[3] aiming primarily at establishing the adlayer structure. The interest in adsorbed As has been additionally motivated by the need of a deeper understanding of As-substrate interaction in the context of molecular beam epitaxy growth and surface passivation. The exchange reaction between As and P was established on InP(100),[4] and later also on InP(110).[5] So far, most of the detailed information concerning the adsorption interaction has been based on electron spectroscopic and electron-diffraction investigations. Recently, however, the As/InP(110) system was also investigated by means of optical methods.[6] The results concerning the As-P exchange derived from these studies were found to be in conflict with previous ones based on core-level photoemission.[7] More specifically, the optical data, supported by calculational results, implied that the exchange reaction takes place at room temperature. According to earlier photoemission data, however, the adsorbed nonreacted As layer is stable to temperatures around 250 °C. In an attempt to resolve this controversy, we have performed detailed high-resolution core-level studies, including redeposition of As. Our results indicate that an exchange reaction at room temperature is not possible. This experimental result, to be reported in a separate paper,[8] urges a reexamination of the theoretical predictions. In the present paper we report a computational investigation of the interaction between As and InP(110).

II. THEORETICAL FRAMEWORK

The calculations reported here are based on the density-functional theory within the gradient corrected local-density approximation (LDA),[9–11] and performed with a modified and extended version of fhi94md.[12] For each atom, fully separable, nonlocal pseudopotentials are used after the formulation of Kleinman and Bylander.[13,14] These potentials are based on free-atom calculations, solving the relativistic Dirac-equation self-consistently.[15–17] To solve the Kohn-Sham equations[9,10] each single-particle wave function is expanded in momentum space using plane waves. The charge density is set up using atomic pseudo-wave-functions. Furthermore, 18 special Monkhorst-Pack k points[18] were used in the IBZ to sample the wave functions, corresponding to 144 k points in the full zone. The single-particle wave functions are generated by a diagonalization of the starting Hamiltonian in a reduced plane-wave basis. In the following iterations, the electronic part of the solution is achieved by a Williams-Soler algorithm until the wave functions are stabilized. The idea is to introduce a fictive time evolution of the problem with time steps δt. The Hamiltonian is applied to the wave function to obtain the time-induced change,

$$\Psi_j^{t+1} = \Psi_j^t + \delta t H \Psi_j^t + \text{orthonormality terms.}$$

In this way we avoid the diagonalization of H, which is very time consuming for large systems. Apart from the electronic solution, atomic relaxation is allowed in order to find the nearest (local) energy minimum of the atomic positions. Since each atomic movement is relatively large, the system is relaxed purely by electronic iterations before the next atomic movement is allowed.

The pseudopotentials were thoroughly tested on separate problems. Indium metal in the fcc structure was investigated for a lattice constant of 4.74 Å and the results were in good agreement with Ref. 19. The bulk InP band structure was calculated and very good agreement was obtained with the experimental (quasiparticle) bands. Furthermore, the lattice constant was found to coincide with the experimental value. This last point is worth stressing, since lattice constants are usually underestimated in LDA.

0163-1829/97/56(24)/15847(6)/$10.00

In order to describe the surfaces we used a large supercell. We have investigated seven different structures and in each case the slab contained five central InP layers. For the clean InP surface (case I), we added one layer on each side, resulting in a seven-layer InP(110) slab and eight layers of vacuum. When studying As adlayers we kept the five InP(110) layers and added As layers in a symmetric way on both sides. Case II consists of a pure InAs layer in an epitaxially continued layer structure (ECLS) geometry [see Fig. 1(b)], while case III contains a single As atom in P position on top of the clean InP(110) surface, resulting in a 0.5 ML As overlayer [Fig. 1(c)]. Case IV is similar to case III, but with 1.0 ML InAs [Fig. 1(d)], and in case V a second As atom was added, resulting in a full As layer on top of the InAs layer with positions chosen to match the ECLS [Fig. 1(e)]. In contrast, case VI [Fig. 1(f)], consists of 1 ML As grown in ECLS on top of InP(110) without any exchange reaction. Finally, we also investigated the possibility of keeping the exchanged P atom on the surface. This results in the case VII geometry [see Fig. 1(g)] with 0.5 ML As and 0.5 ML P together in an ECLS on top of the InAs layer. No other geometries with fully As/P-terminated surfaces were considered since previous investigations[6,20,21] have shown that the ECLS geometry appears to be the most favorable one for III-V semiconductors.

All atomic positions except those in the midlayer of the slab were relaxed. Significantly changed atomic positions were noted only in the outermost layers, showing that the number of bulk layers is sufficient. The equilibrium geometry was considered as established when all forces were smaller then 0.005 eV/Å, corresponding to an estimated numerical uncertainty of maximum 0.05 Å.

A cutoff energy of 8 Ry for the plane waves was used, which by experience has been found to give reliable values for energy differences. To explicitly verify the validity of this assumption, we calculated the energies gained (see below) from forming case II and VII surfaces from gaseous As and clean InP, using a cutoff energy of 16 Ry, comparing them with the results given by the calculations using a 8 Ry cutoff. The resulting energy differences coincided completely within numerical accuracy, thus sustaining the current approach. In addition the atomic positions were only very slightly changed.

To check that the thicknesses of the slabs were sufficient in a more quantitative way, we investigated the averaged electrostatic and total potentials perpendicular to the surface. We found that the potentials are bulklike inside the slab and vanish in the vacuum region. This is the correct behavior if the supercell is large enough, allowing the electron density to decay completely. In Fig. 2 the potentials are displayed in the case of a smooth epitaxial 1 ML As overlayer.

With respect to the energy calculations one must keep in mind the nature of the physical problem. There have recently been several calculations employing an unspecified chemical potential for the atom sources.[22–24] In the present calculations we have chosen rather to consider different specific molecular sources. In the actual experiment[6,8] the InP(110) surface is exposed (at room temperature) to a flux of As_4 molecules. However, surface reactions are not likely to involve these molecules directly, but rather physisorbed or chemisorbed species As_n ($n=1$, 2, or 4). Since the reaction paths are unknown, and our calculations only treat the static equilibrium conditions, we shall assume that any As-P exchange process with adsorbed As involves the same type of reacting species (this assumption is based on the similarity between As and P). Note also that the choice of specific species dictates the energies of As and P, which means that the different cases (I–VII) must be calculated explicitly.

The relevant physical system thus contains the InP(110) surface, a reservoir of As in some form (to be drained), and a reservoir of already exchanged P (to possibly be filled further). In the calculations we evaluate the ‘‘surface cell energy’’ $E_{\mathrm{InP}}^{\mathrm{surf}}$, which is the total energy divided by the number of surface cells. We also introduce the total electronic energy of the individual As and P atoms, E_{As} and E_{P}, taking all environmental effects into account. The total energy for the physical system consisting of one surface cell (and all the bulk layers beneath) and the As and P reservoirs then becomes

$$E_{\mathrm{tot}}^{\mathrm{surf}}=E_{\mathrm{InP}}^{\mathrm{surf}}+N_{\mathrm{As}}E_{\mathrm{As}}+N_{\mathrm{P}}E_{\mathrm{P}}, \tag{1}$$

where N_{As} and N_{P} are the (unknown) numbers of each species in the reservoirs. In the case of As adsorption and As-P exchange we get an energy for the surface cell and bulk layers beneath ($E_{\mathrm{AsInP}}^{\mathrm{surf}}$), and a reduced $(-n)$/increased $(+m)$ number of atoms in the reservoirs respectively,

$$E_{\mathrm{new}}^{\mathrm{surf}}=E_{\mathrm{AsInP}}^{\mathrm{surf}}+(N_{\mathrm{As}}-n)E_{\mathrm{As}}+(N_{\mathrm{P}}+m)E_{\mathrm{P}}. \tag{2}$$

In the different cases mentioned above we have $n=m=1$ (case II), $n=1$, $m=0$ (case III), $n=2$, $m=1$ (case IV), $n=3$, $m=1$ (case V), $n=2$, $m=0$ (case VI), and $n=2$, $m=0$ (case VII), which directly gives the energy difference per surface cell (three first rows in Table I)

$$\Delta E^{\mathrm{surf}}=E_{\mathrm{InP}}^{\mathrm{surf}}-E_{\mathrm{AsInP}}^{\mathrm{surf}}+nE_{\mathrm{As}}-mE_{\mathrm{P}}. \tag{3}$$

This energy gain (or loss) is physically relevant since the energies of the bulk layers now are subtracted, and the system will tend towards the largest possible gain. There are, however, a few additional points to consider. Due to numerical limitations we calculated the energies of the free As_n and P_n with zero kinetic energy inside a large supercell by increasing the cell size until convergence. For example, if we consider As_4 molecules, E_{As} is the total As_4 energy divided by four. The missing physisorption energy introduces an error for each atom. It is, however, mainly a scaling parameter, which will cancel when comparing different adsorption models involving the same number of atoms. For models involving different amounts of adsorbed species before and after reaction, the cancellation is, of course incomplete. These errors are estimated, however, to be within the numerical accuracy of the calculations (~0.2 eV).

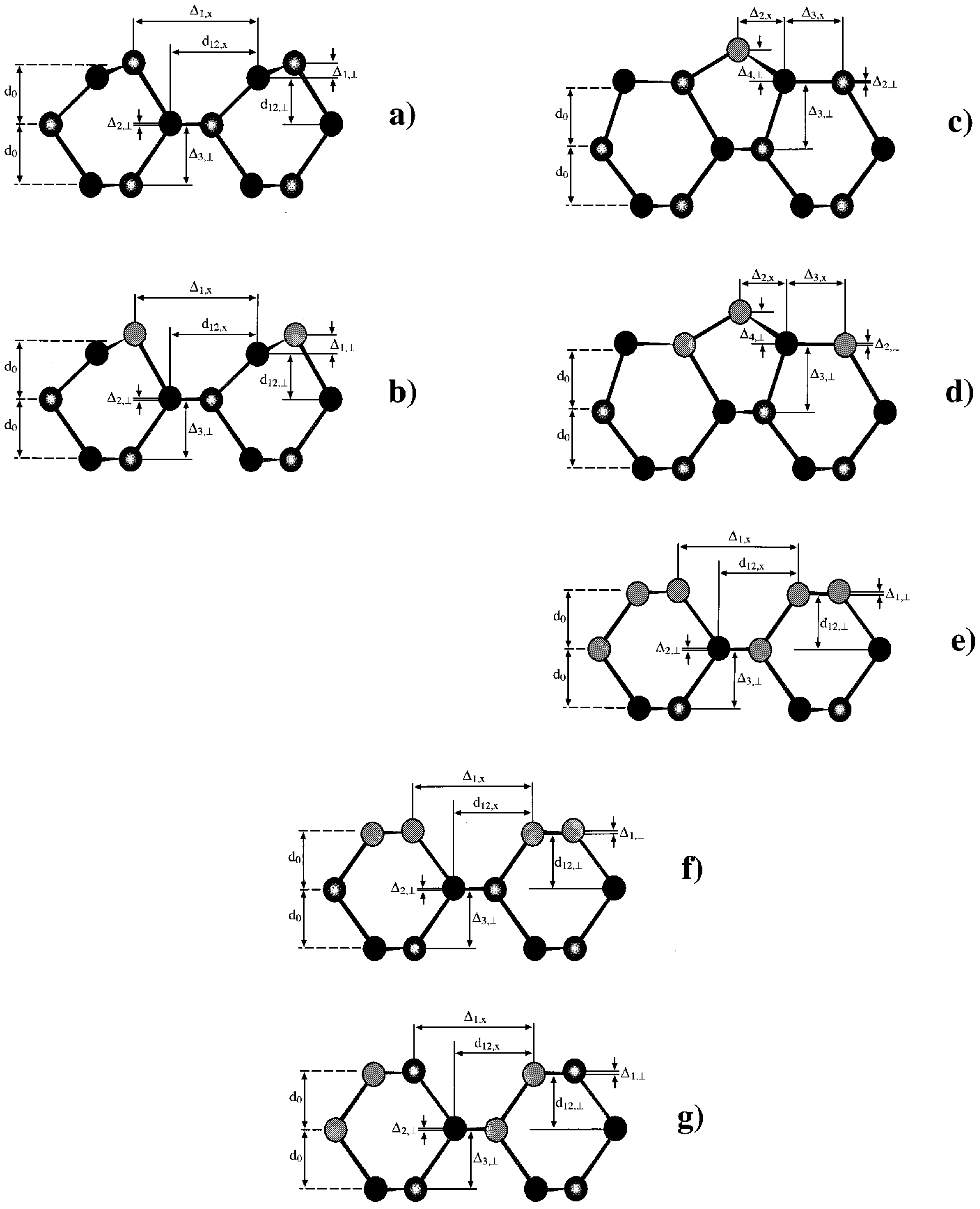

FIG. 1. The different surface geometries considered in the calculations: (a) clean InP(110) surface (case I), (b) 0.5 ML As in ECLS on InP(110) with P-As exchange (case II), (c) 0.5 ML As on InP(110) without exchange (case III), (d) 1.0 ML As on InP(110) surface with P-As exchange (case IV), (e) 1.5 ML As in ECLS on InP(110) with P-As exchange (case V), (f) 1.0 ML As on InP(110) in the ECLS without exchange (case VI), and (g) 1.0 ML As in an ECLS structure on InP(110) with P-As exchange (case VII). In the last case the released P is kept on the surface. The P, In, and As atoms are represented by shiny, black, and gray balls, respectively.

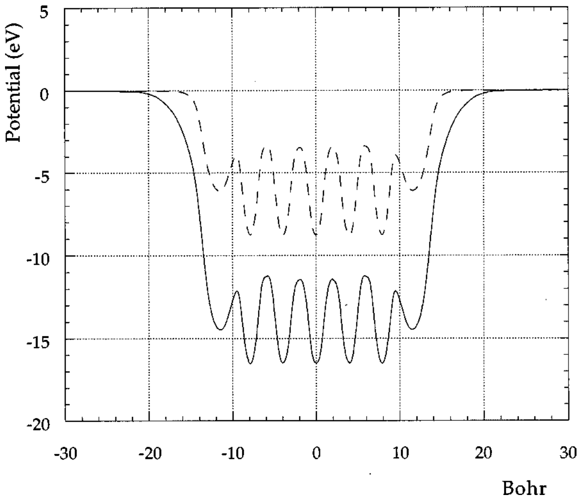

FIG. 2. The electrostatic (dashed line) and full effective potential (solid line) of the slab representative of 1 ML As in ECLS on InP(110) (case V). The potentials are averaged parallel to the surface and plotted vs the distance from the central atomic layer.

Although the reaction paths are unknown, as already pointed out, it appears likely that the reacting species is in a chemisorbed state prior to the reaction. If we assume that the chemisorbed state is the fully relaxed one (which is, of course, not necessarily the case), then we can refer the different reacted cases to the nonreacted ones, namely, cases III and VI. (For chemisorbed P we only considered the case VII geometry since this seems to be the most energetically favorable one, see below and Table I. Several other possible geometries with exchanged phosphorus kept on the surface were also investigated, but all turned out less favorable. Phosphorus on the surface is, however, not a true ''P reservoir,'' since all the available P atoms are derived from the initial InP(110) surface. Thus, case VII is treated as any other geometry in Table I.) The energy gains relative to these chemisorbed configurations can be extracted directly from the first three rows in Table I, and are listed in rows 4 and 5 of Table I. The dependence on the P reservoirs still remains in the cases with P desorption though.

In a similar way it is easy to show that the energy gained when the system transforms from one geometry to another is given simply by comparing the values for each column, within the same row (the physical conditions have to be the same). We have taken case I as our reference geometry. However, energy differences between phases are of course independent of this choice. Further applications of Table I are simple generalizations of this line of thought.

III. RESULTS AND DISCUSSION

Our results for the surface relaxation are summarized in Table II. The relaxation of the clean InP(110) surface, case I, results in a buckling of 0.64 Å, in good agreement with earlier investigations.[25] Using the correct lattice constant, some parameters are in better agreement with the experimental values then in previous works.[7,22,25] In case II the main difference is the larger buckling, 0.75 Å, which results directly from the larger lattice constant of InAs. This result is slightly smaller then in previous investigations[6,22] (0.80 Å), mainly due to a lower-energy cutoff and also a different lattice constant. [Using a 16 Ry cutoff in a test run (see Sec. II), the agreement is improved considerably.] The surface bands resulting in cases I and II are displayed in Figs. 3(a) and 3(b). The low-lying surface band in the heteropolar gap together with some of the upper-surface bands merge into the projected bulk bands. Inside the band gap only the lower occupied surface band moves slightly upwards; otherwise there are no effects of the As-P exchange.

Cases III and IV offer the most altered atomic configuration with the second layer significantly relaxed outwards and the terminating As atom positioned nearly in between the P/As and In atoms beneath. The atoms in the second layer of InP/InAs also move away from each other parallel to the surface and consequently the buckling from case II vanishes.

The three fully As/P-terminated surfaces, cases V–VII, are very similar to each other. The buckling is reduced to about 0.1 Å and the second layer is almost bulklike concerning the atomic positions, regardless of it being InP or InAs. Case VI is in good agreement with previous results,[22] while,

TABLE I. The energy gain of the complete physical system [As reservoir +P reservoir+InP(110) surface] divided by the number of surface cells. Calculational details and discussion, in Secs. II and III, respectively. The numerical accuracy is estimated to ±0.2 eV.

Type of Reservoir	Case II InAs InP	Case III As InP	Case IV As InAs InP	Case V As As InAs InP	Case VI As As InP	Case VII As P InAs InP
As(gas phase)/P	−0.44	4.80	4.30	10.25	10.95	10.58
As$_2$(gas phase)/P$_2$	0.15	0.67	0.76	2.58	2.70	2.32
As$_4$(gas phase)/P$_4$	0.08	−0.12	−0.10	0.93	1.11	0.74
As(Case III[a])/P	−5.24	0.00	−5.30	−4.15	1.36	0.98
As(Case III[a])/P$_2$	−0.52	0.00	−0.58	0.57	1.36	0.98
As(Case III[a])/P$_4$	0.20	0.00	0.14	1.29	1.36	0.98
As(Case VI[a])/P	−5.92	−0.68	−6.65	−6.18	0.00	−0.37
As(Case VI[a])/P$_2$	−1.20	−0.68	−1.94	−1.47	0.00	−0.37
As(Case VI[a])/P$_4$	−0.48	−0.68	−1.21	−0.74	0.00	−0.37

[a] Normalized to the number of As atoms.

TABLE II. Structural parameters (in Å) for the surface relaxations as defined in Figs. 1(a)–1(b).

Case	$\Delta_{1,x}$	$\Delta_{2,x}$	$\Delta_{3,x}$	$\Delta_{1,\perp}$	$\Delta_{2,\perp}$	$\Delta_{3,\perp}$	$\Delta_{4,\perp}$	$d_{12,\perp}$	$d_{12,x}$
I	4.63			0.64	0.10	2.06		1.59	3.34
II	4.57			0.75	0.12	2.04		1.59	3.32
III		1.94	2.09		0.07	2.31	1.20		
IV		1.74	2.17		0.07	2.35	1.21		
V	4.35			0.12	0.09	2.12		2.00	3.04
VI	4.35			0.15	0.06	2.09		1.94	3.09
VII	4.36			0.02	0.08	2.14		1.97	2.97

to our knowledge, cases V and VII have not been investigated earlier. Comparing with cases I and II, two new surface bands above and below the lower projected bulk bands appear with the introduction of a layer with five valence electrons/atom [see Fig. 3(c)–3(e)]. These bands originate from the localized states of the adsorbed As/P atoms and the anion in the second layer. The three band structures are in remarkable agreement with each other, and differ only significantly in the heteropolar gap along $\bar{X}\,\bar{M}$, and in the stomach gap, where a new band appears for the case VII geometry. This suggests future experimental studies in these regions. The lowest bulk bands appear to be slightly shifted upwards due to the relatively low cutoff used.

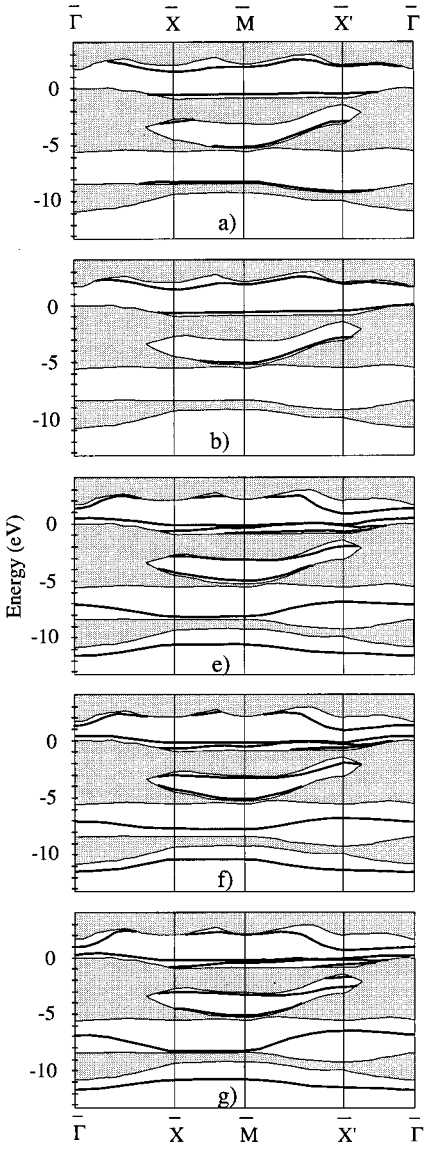

FIG. 3. The surface projected bulk electronic states (shadowed regions) and surface states (bold lines) for the different surface geometries considered in the calculations. The notations (a)–(g) are explained in Fig. 1.

The energy gains/losses have been calculated according to the method described above for different types of As and P sources, see Table I. Assuming that the exchange process starts from the fully relaxed chemisorbed structure with a full As overlayer, we thus see that all energy gain values in Table I are negative. Note, however, that the large negative values for cases II, IV, and V when using reservoirs of chemisorbed As (rows 4–9) are mainly due to the desorption of P in atomic or molecular form. When keeping the P on the surface, case VII, the energy gains no longer are affected by this and the value becomes independent of the choice of P reservoir.

When taking the possible errors into account, cases V–VII are degenerated within numerical uncertainty for the As-P and case III-P_4 combinations and nearly degenerated in the remaining combinations as well. In absolute numbers however, case VI is the most stable geometry for all combinations of reservoirs. These results are supported by recent experiments, according to which no exchange interaction occurs without thermal activation at around 600 K.[8] Furthermore, according to these experimental data the exchange is far from complete (i.e., significantly less than one monolayer P is replaced by As). The partial exchange would then probably be due to a Boltzmann-like population process, and thus the 1 ML As in an ECLS on InP(110) is the true ECS in contrast to the result reported in Ref. 6.

IV. SUMMARY AND CONCLUSIONS

We have performed *ab initio* calculations in order to study the interaction between As and InP(110), with emphasis on possible As-P exchange. Our investigations resulted in three configurations with nearly the same total energy. In the simplest case, the As is deposited as a single monolayer on top of the InP(110) surface. In terms of the average energy per As atom this situation is preferable. Considering the cases with the surface layer P exchanged with As, forming one monolayer InAs on top of InP(110), and an additional layer of As, or As and P, we find that all such configurations have higher energy than the 1 ML As on InP(110). However, the energy differences are sufficiently low that some As-P exchange cannot be excluded, in particular at elevated temperatures. These results contradict an earlier conclusion that the exchange process is fully established at room temperature.

ACKNOWLEDGMENTS

We wish to thank U. Groβner and W. G. Schmidt for making some of their unpublished work available to us and for useful discussions. The work has been supported by the Swedish Natural Science Research Council.

---

[1] P. Skeath, C. V. Su, W. A. Harrison, I. Lindau, and W. E. Spicer, Phys. Rev. B **27**, 6246 (1983).

[2] J. J. Joyce, J. Anderson, M. M. Nelson, and G. J. Lapeyre, Phys. Rev. B **40**, 10 412 (1989).

[3] Z. Q. He, Y. O. Khazmi, J. Kanski, L. Ilver, P. O. Nilsson, and U. O. Karlsson, Phys. Rev. B **52**, 16 602 (1995).

[4] J. M. Moison, M. Bensouassan, and F. Houzay, Phys. Rev. B **34**, 2018 (1986).

[5] A. Tulke and H. Lüth, Surf. Sci. **211/212**, 1001 (1989).

[6] P. V. Santos, B. Koopmans, N. Esser, W. G. Schmidt, and F. Bechstedt, Phys. Rev. Lett. **77**, 759 (1996).

[7] T. Chassé, G. Neuhold, and K. Horn, Surf. Sci. **331/333**, 511 (1995).

[8] Z. Q. He, Y. O. Khazmi, S. Mankefors, J. Kanski, L. Ilver, and P. O. Nilsson (unpublished).

[9] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[10] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[11] R. O. Jones and O. Gunnarson, Rev. Mod. Phys. **61**, 689 (1989).

[12] R. Stumpf and M. Scheffler, Comput. Phys. Commun. **79**, 447 (1994).

[13] B. Hamann, Phys. Rev. B **40**, 2980 (1989).

[14] X. Gonze, P. Käckell, and M. Scheffler, Phys. Rev. B **41**, 12 264 (1990).

[15] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[16] G. B. Bachlet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[17] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

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

[19] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[20] W. G. Schmidt, F. Bechstedt, and G. P. Shrivastava, Surf. Sci. Rep. **25**, 141 (1996).

[21] P. Mårtensson and R. M. Feenstra, Phys. Rev. B **39**, 7744 (1989).

[22] U. Grossner, Ph.D. thesis, Department of Physics, Astronomy and Technology (Friedrich-Schiller University, Jena, 1996).

[23] N. Moll, A. Kley, E. Pehlke, and M. Scheffler, Phys. Rev. B **54**, 8844 (1996).

[24] W. G. Schmidt and F. Bechstedt, Phys. Rev. B **54**, 16 742 (1996).

[25] J. L. A. Alves, J. Heibenstreit, and M. Scheffler, Phys. Rev. B **44**, 6188 (1991).