$[P_{In}]^{(n)}$ antisite clustering in InP

T. M. Schmidt* and R. H. Miwa
Departamento de Ciências Físicas, Universidade Federal de Uberlândia, Caixa Postal 593, 38400-902, Uberlândia, MG, Brazil

A. Fazzio
Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, 05315-970, São Paulo, SP, Brazil

R. Mota
Departamento de Física, Universidade Federal de Santa Maria, 97.105-900, Santa Maria, RS, Brazil
(Received 29 June 1999)

A systematic first-principles total energy calculation is performed to investigate the structural and electronic properties of $[P_{In}]^{(n)}$ antisite clusters in InP, with n up to four. Isolated P_{In} antisites generate a defect level in the gap region with a relatively large energy dispersion in our 128 atoms supercell. For clusters formation with 2, 3, and 4 antisites, the corresponding energy dispersion of the defect levels decrease and a confinement tendency of the carrier density is observed, mainly for clusters in the two-dimensional topology. The resulting character of the defect levels in the gap and their corresponding energy dispersions are associated with the origin of the n-type conductivity in intrinsic InP growth at low temperature. Our calculation indicates that the clustering of P_{In} antisites is an energetically favorable process. A hypothetical planar doping system, formed by high concentration of antisites, is proposed as a possible structure. [S0163-1829(99)05547-2]

I. INTRODUCTION

Recent experimental results indicate the possibility of epitaxial growth of n-type modulation doping in InP-based heterostructures, where intrinsic defects can provide high concentration of carrier density.[1] The mechanism responsible for the n-type conductivity has been attributed to an abundant presence of P_{In} antisites, introduced during off-stoichiometric InP growth at low temperature.[2] The presence of carrier density has been explained by the autoionization of the P_{In}, via the excited $(0/+)$ level.[3] The antisite defects in III-V materials have been intensively studied, and particularly in GaAs, Arsenic antisite (EL2 defect) is responsible for the semi-insulating behavior.[4,5] In InP, the presence of these defects seems to have different character compared to other III-V compounds, and the origin of the conductivity is still not clear, and the chemical nature of the donors is unknown. High-carrier concentrations are observed, implying high concentrations of defects, with the possibility of the presence of antisite complex defects and the formation of low-dimensional systems.[1] The confinement of high-carrier concentrations has been an intensive area of study, particularly in doped III-V compounds. It has been recognized to be one of the most promising electronic material system, besides to provide an excellent area for the understanding of the quantum effects.

In this paper the electronic and structural properties of the $[P_{In}]^{(n)}$ antisite clusters in InP are investigated with n up to 4. Isolated P_{In} antisite defects in InP are shown not to be a shallow hydrogeniclike donor, but the defect level is *inside the band gap* with a large energy dispersion in our 128 atoms supercell calculation. The formation of complex defects, involving more than one antisite, is energetically favorable with the confinement of the carrier density. Also, a low-dimensional system, forming a hypothetical planar doping $[\delta(P_{In})]$-system, is proposed as a possible structure. In the next section we present the methodology used in the calculation. Section III we discuss the results and in the last section we summarize our conclusions.

II. METHOD OF CALCULATION

The Kohn-Sham equations are solved in a basis of plane waves within local-density approximation (LDA).[6] The total energy and band-structure are self-consistently calculated, using normconserving fully separable pseudopotentials.[7,8] The $\vec{k}$-summation in the reduced Brillouin zone has been checked to ensure a good description of the charge density and, consequently, the total energy. The $\vec{k}$ sampling to describe correctly a system is dependent on the supercell size. A Chadi-Cohen[9] special points analysis is performed for different supercell sizes. Our results show that for 128 atoms supercell, the Γ point describes appropriately the defect character and the ionization energies.[10] This is checked by the observation of similar results obtained using the first Chadi-Cohen special points for the same supercell in InP systems. The total energy convergency is reached to 20 Ry kinetic energy cutoff with the equilibrium lattice constant for bulk InP of 5.82 Å, which is close to the experimental value, 5.87 Å. The absolute convergency in the total energy is necessary to describe correctly the electronic structure as the position of the defect level in the gap and the character of the state. The calculated band gap is 1.05 eV, which is smaller than the measured value 1.42 eV, as is expected in LDA calculations. All studied systems have been relaxed until forces are lower than 0.025 eV/Å.

III. RESULTS AND DISCUSSIONS

Similarly to obtained by previous works,[4,11] our total energy calculations show that for isolated P_{In} neutral antisites

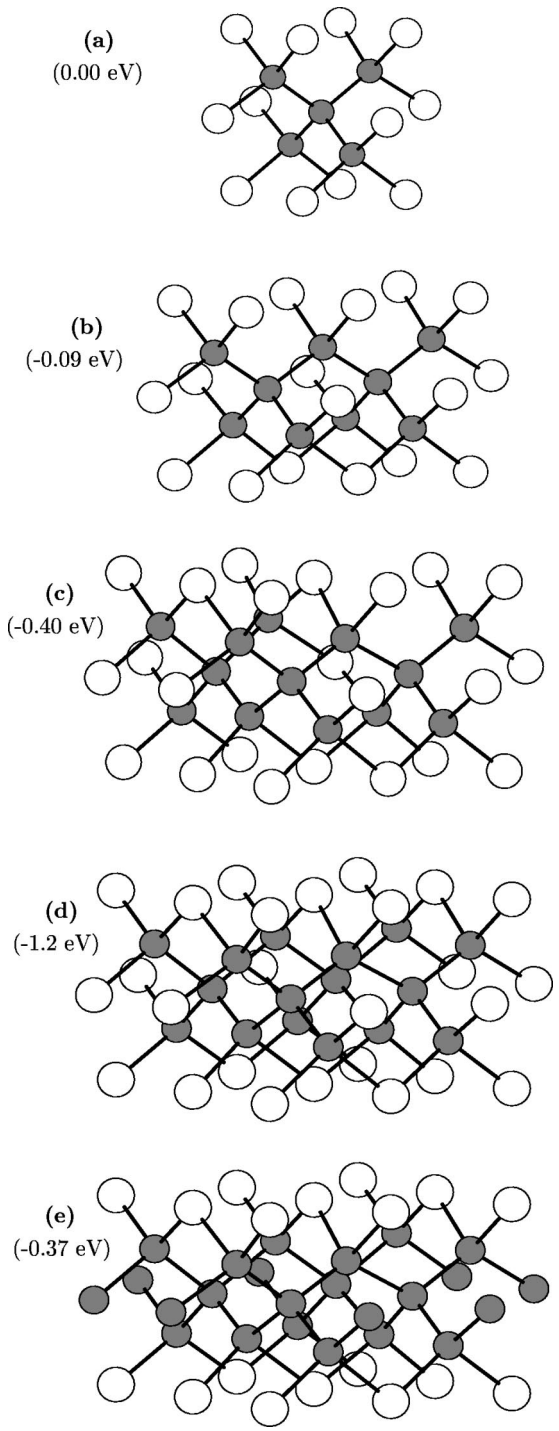

FIG. 1. Schematic representation of the 2D antisite clusters formation for: (a) one antisite; (b) two antisites; (c) three antisites ($3nnn$); (d) four antisites ($4nnn$), and (e) $\delta(P_{In})$-system. White balls represent In atoms and black balls P atoms.

[Fig. 1(a)] a defect level result *inside the band gap*. We compute the ionization levels by the total energy differences,[12] taken as the reference the top of the valence band.[13] In the $(++)$ charge state, the defect-induced a_1 state in the gap is empty. In the $(+)$ and (0) charge states, the a_1 gap state is occupied by one and two electrons, respectively. Consequently, considering that in these charge states all bound states in the gap are unoccupied, or only the a_1 orbital states are occupied, no Jahn-Teller relaxations are observed and the tetrahedral symmetry is preserved for the three charge states (0, + and ++). The calculated ionization levels are 0.60 and 0.54 eV for the $(0/+)$ and $(+/++)$ transitions, respectively. We verified a symmetric inward displacement of the antisite nearest neighbors for all charge states. This breathing mode relaxation is 0.16, 0.23, and 0.30 Å for the (0), $(+)$, and $(++)$ charge states, respectively. Different from the results obtained by Seitsonen *et al.*,[11] we do not find a negative U for the neutral state, but a small and positive U. There are some differences between the two calculation procedures. The lattice constant obtained in this work is 5.82 Å and they used 5.61 Å (1% and 4% smaller than the experimental value, respectively). Besides that, they used a supercell with 64 atoms, and a plane wave cutoff of 15.3 Ry (instead of supercell of 128 atoms and 20 Ry cutoff, as used here).

The one-particle energy level, in our calculation, is inside the band gap, located around 0.7 eV from the valence-band maximum (VBM) (at the Γ point), and presents a relative large energy dispersion (0.31 eV) along the Γ-X direction. This dispersion can be attributed to the interaction between the defects in the adjacent supercells. Usually, for localized point defects, moderate size supercells as 64 atoms and a set of special points are enough to describe appropriately the electronic and configurational structures. Here, we use 128 atoms, where the distance between two defects is $2\sqrt{2}a_0$, a_0 is the lattice parameter. This supercell corresponds to a defect concentration of $\sim 10^{20}$ cm^{-3}, distributed perfect homogeneously in the bulk InP. Dreszer *et al.*[3] observed a free carrier concentration of 4×10^{18} cm^{-3} at low-temperature growth InP. In the same experiment[3] has been verified a drop of this carrier concentration with the increasing of the growth temperature, which can be attributed to the reduction of the P_{In} antisite. If we denote one carrier for each defect, to calculate a system with the concentration of 4×10^{18} cm^{-3}, we should have at least 1000 atoms supercell (which still unpracticable for an *ab initio* calculation). As the high carrier concentrations are obtained out of the thermodynamic equilibrium growth, a homogeneosly distribution for the P_{In} defects is not expected, with the possibility of the formation of trapping complex defects. So, regions with high P_{In} concentrations should be present.

In our 128 atoms supercell calculation we are simulating a region without trapping defects and high-P_{In} concentration. The deep donor position found for the P_{In} antisite indicates that the origin of the *n*-type conductivity in InP growth at low temperature is not a shallow hydrogeniclike donor. This is in agreement with the reduction of the mobility observed in samples with high-free carrier concentrations,[3] which can be explained by the scattering in the presence of localized states. In this way, we conclude that the conductivity comes from the auto-ionization, due to the interaction between the defects, which occurs in high concentration regime of P_{In} antisites.

Next, we consider two nearest-neighbors P_{In} [see Fig. 1(b)], forming the complex defect $[P_{In}]^{(2)}$. Two energy levels result in the gap with the eigenvalues positioned at 0.77 and 0.20 eV above the VBM. The energy dispersions of these levels in the ΓX direction are 0.17 eV for the upper level and 0.33 eV for the lower level. Figure 2 shows these two a_1 occupied impurity levels, presenting tipically anti-

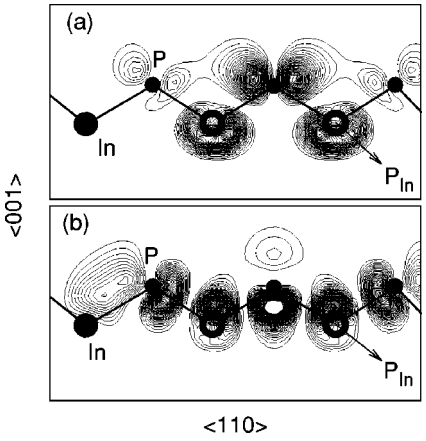

FIG. 2. Electronic charge densities for the (a) last occupied defect level, and (b) last but one occupied defect level for the $[P_{In}]^{(2)}$ cluster.

bonding characters, where the lower level is seen to be more delocalized than the upper level. Both P impurities suffer a displacement towards each other by just 0.04 Å, while their nearest neighbors are displaced around 0.16 Å towards the impurities, maintaining almost the same relaxations observed for the nearest neighbors for the single P_{In} defect. As each defect contributes with two electrons to the system, occupying antibonding orbitals, the small displacements between the two antisites are due to the characters of the bonds (see Fig. 2).

For $n=3$, we consider two possible configurations, one with the 3 antisites in the nearest neighbor positions ($3nn$) [Fig. 1(c)], another with 2 antisites in the nearest neighbor positions and the third one in the next nearest neighbor position ($2nn+1nnn$). In the second configuration, the distances between the P impurities are kept almost the same of the In bulk atomic positions. In this configuration, the P nearest neighbors to the impurities have two kinds of bonds: bonding and antibonding characters. As can be seen in Fig. 3, some bond lengths are reduced up to 0.34 Å, while others are increased up to 0.25 Å. We observe that each antisite always presents one bond with strong antibonding character. In the ($2nn+1nnn$) configuration an energy dispersion of 0.21 eV is verified for the two lower levels and 0.15 eV for the upper level. This dispersion is smaller than the corresponding dispersion for the single defect P_{In} antisite, and observing that the level positions related to the VBM are 0.14, 0.32, and 0.73 eV, we can draw a confinement tendency of the system when n increases.

For $n=4$, two configurations are considered, one with the

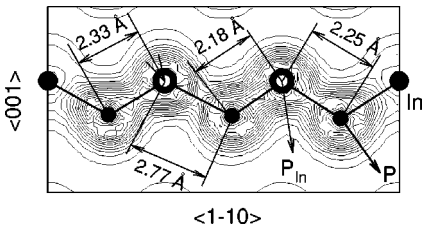

FIG. 3. Total valence charge density for the $[P_{In}]^{(3)}$ cluster in $3nn$ configuration. The two P_{In} antisites belonging to the (110) plane are shown in the figure.

4 antisites in the nearest neighbor positions ($4nn$) forming a small three-dimensional (3D) cluster of P_{In}, and another with the 4 antisites in the closest positions in the same plane (001), forming a two dimensional (2D) cluster [Fig. 1(d)]. The last one is more stable by 0.12 eV/antisite related to the first one. For the 4 antisites in the same plane, the calculated dispersions of the last occupied defect level are 0.01 eV along the ΓZ direction, perpendicular to the (001) plane, and 0.23 eV along the ΓX direction, parallel to the (001) plane. This again makes it clear the tendency of the system to confine the electronic levels as the number n increases, in this case a carrier confinement with 2D character. The presence of high concentration of antisites, either forming a plane defect or a cluster defect, leads to the formation of two distinct energy bands in the gap region, one below the midgap and another above the midgap, becoming closer to the conduction-band minimum. In this clusterization process with the 4 antisites, the antibonding character of the defect levels again is important, producing assymmetric relaxations, with one bond length greather than the P-In bond length for each P_{In} antisite.

In order to verify the possibility of the formation of $[P_{In}]^{(n)}$ antisite clusters, we have calculated the total energy differences between n antisites, close to each other, and n isolated P_{In} antisites. These total energy differences can be written as

$$\delta[\Delta E^{(n)}]=\frac{\Delta E[P_{In}]^{(n)}}{n}-\Delta E[P_{In}]^{(n=1)},$$

where $\Delta E[P_{In}]^{(n)}$ represents the total energy difference between a supercell of InP, with a cluster of n ($n=1$, 2, 3, and 4) P_{In} antisites and a supercell of InP free of defects ($n=0$). For an isolated P antisite, the lowest energy formation, in P-rich growth condition materials, is around 2.0 eV.[11] We obtain a reduction of the total energy by 0.1 eV per antisite for two near-neighbor antisites ($\delta[\Delta E^{(n=2)}]=-0.1$ eV). For $n=3$, forming a 3D cluster ($3nn$), the total energy decreases by 0.1 eV compared to one antisite ($n=1$), and it is similar to two nearest neighbors ($n=2$). For the ($2nn+1nnn$) case, forming a 2D cluster, the total energy decreases 0.4 eV compared to the isolated antisite, $\delta[\Delta E^{(n=3(2nn+1nnn))}]=-0.4$ eV. For $n=4$ (4nn) case, forming a 3D cluster, the total energy also decreases by 0.7 eV, $\delta[\Delta E^{n=4(4nn)}]=-0.7$ eV, and for $n=4$ forming a 2D cluster, a planar topology, the total energy decreases by 1.2 eV. The relative formation energy per antisite as a function of the number of antisites can be seen in Fig. 4.

The reduction of the total energy ($\delta[\Delta E^{(n)}]$), as a function of the number n of antisites, up to $n=4$, mainly in a planar topology for P_{In}, suggests the possibility of the formation of a planar $\delta(P_{In})$ system.[14,15] Similar structures have been proposed, like InAs/AlSb interface,[16] where the source of the donors was suggested to be antisite defects in a δ configuration.

Finally, we consider a total energy calculation of $\delta(P_{In})$ system [Fig. 1(e)]. The calculations are performed using a tetragonal unit cell,[17,18] with 2×2 interface periodicity, and half a monolayer of P_{In} antisites in a plane perpendicular to the growth direction (001) are introduced. The distance between two δ layers, along the (001) direction, is equal to four

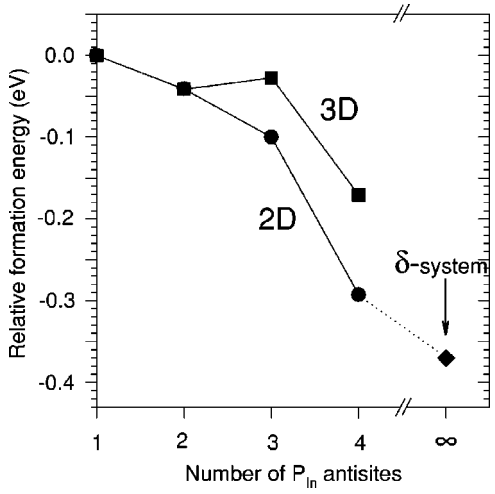

FIG. 4. Relative formation energy per antisite as a function of the number n of P_{In} antisites. Full squares are the energies corresponding to 3D defect clusters and full balls are the 2D defect clusters. The zero reference is the total energy difference between a cell of pure crystal and the same cell with one P_{In}.

lattice parameters of InP, ≈ 23 Å. The full relaxation of InP atomic layers results a P_{In}–P (first neighbors) bond length of 2.41 Å, which corresponds to the tetrahedric displacement of 0.11 Å towards the P_{In} antisite position, showing a very localized relaxation around the $\delta-P_{In}$ plane. The In–P bond length (near to the δ-plane) is 2.51 Å, which is very similar to the bond length of the bulk InP (2.52 Å), conserving the covalent character of these bonds. The reduction of the total energy, for this configuration, is equal to 0.37 eV, $\delta[\Delta E] = -0.37$ eV per antisite, which indicates that the formation of P_{In} antisite, in a $\delta-P_{In}$ configuration, is a system energetically stable. Therefore, off-stoichiometric InP growth at low temperature can induce the formation of low dimensional systems without an external doping.

IV. CONCLUSIONS

In summary, our electronic and structural calculations show that, for isolated P_{In} neutral antisites, a defect level results inside the band gap with a relatively large energy dispersion in our 128 atoms supercell. The corresponding energy dispersions of the defect levels decrease as the number n in the $[P_{In}]^{(n)}$ cluster increases, indicating a confinement tendency of the carrier density. Our total energy calculations also show that the clustering formation of P_{In} antisites is an energetically favorable process. The relative formation energies per antisite decrease as the number of antisites (close to each others) increases. The planar topology, 2D clusters, has been shown to be more stable than the 3D clusters. The reduction of the antisite relative formation energy in a 2D configuration indicates that the formation of a low-dimensional system, $\delta-P_{In}$, is energetically favorable. The last occupied defect level of the antisites get close to the bottom of the conduction band (eigenvalue position + energy dispersion), mainly for the isolated defect and the 2D clusters. These defects can be related to the origin of the n-type conductivity in InP growth at low temperature, where the carriers come from the auto-ionization, due to the interaction among the defects, which occurs in systems with high concentrations of P_{In} antisites.

ACKNOWLEDGMENTS

This work was supported by the Brazilian agencies FAPEMIG, FAPERGS, and CNPq.

*Electronic address: tschmidt@inga.ufu.br

[1] W.M. Chen, I.A. Buyanova, A.V. Buyanov, and T. Lundstrom, Phys. Rev. Lett. **77**, 2734 (1996).
[2] W.M. Chen, P. Dreszer, A. Prasad, A. Kurpiewski, W. Walukiewicz, E.R. Weber, E. Sorman, B. Monemar, B.W. Liang, and C.W. Tu, J. Appl. Phys. **76**, 1 (1994).
[3] P. Dreszer, W.M. Chen, K. Seendripu, J.A. Wolk, W. Walukiewicz, B.W. Liang, C.W. Tu, and E.R. Weber, Phys. Rev. B **47**, 4111 (1993).
[4] M.J. Caldas, J. Dabrowski, A. Fazzio, and M. Scheffler, Phys. Rev. Lett. **65**, 2046 (1990).
[5] M. Kamiska and E.R. Weber, Mater. Sci. Forum **83-87**, 1033 (1991).
[6] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).
[7] G.B. Bachelet, D.R. Hamann, and M. Schluter, Phys. Rev. B **26**, 4199 (1982).
[8] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[9] D.J. Chadi and M.L. Cohen, Phys. Rev. B **8**, 5747 (1973).
[10] A. Janotti, A. Fazzio, P. Piquini, and R. Mota, Phys. Rev. B **56**, 13 073 (1997); Solid State Commun. **110**, 457 (1999).
[11] A.P. Seitsonen, R. Virkkunen, M.J. Puska, and R.M. Nieminen, Phys. Rev. B **49**, 5253 (1994).
[12] J. Ihm, A. Zunger, and M.L. Cohen, J. Phys. C **12**, 4409 (1979).
[13] T. Mattila and A. Zunger, Phys. Rev. B **58**, 1367 (1998).
[14] C.E.C. Wood, G. Metze, J. Berry, and L.F. Eastman, J. Appl. Phys. **51**, 383 (1980).
[15] E.F. Schubert, J. Vac. Sci. Technol. A **8**, 2980 (1990).
[16] G. Tuttle, H. Kroemer, and J.H. English, J. Appl. Phys. **67**, 3032 (1990).
[17] T.M. Schmidt and A. Fazzio, Phys. Rev. B **51**, 7898 (1995).
[18] R.H. Miwa and T.M. Schmidt, Appl. Phys. Lett. **74**, 1999 (1999).