VOLUME 66, NUMBER 16 PHYSICAL REVIEW LETTERS 22 APRIL 1991

Surface-Induced Ordering in GaInP

Sverre Froyen and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401

(Received 26 November 1990)

$Ga_{0.5}In_{0.5}P$ alloys order spontaneously during growth into a (111) monolayer superlattice despite the fact that this is not the lowest-energy structure of the three-dimensional bulk compound. Using first-principles total-energy calculations, we show that a novel electronically driven surface reconstruction provides a driving force for such ordering.

PACS numbers: 71.45.Nt, 61.55.Hg

Most III-V ternary semiconductor alloys exhibit spontaneous long-range order when grown homogeneously by gas-phase epitaxy in certain temperature ranges.[1-4] Two such examples are $Al_{0.5}Ga_{0.5}As$ which orders in a CuAu-I-like (CA) structure when grown on [110] substrates[1] and $Ga_{0.5}In_{0.5}P$ which orders in a CuPt-like (CP) structure when grown on [001] GaAs substrates.[4] A description of these structures as superlattices is given in the first two columns of Table I. These observed structures cannot represent stable bulk equilibrium since the disordered alloys are known to have positive mixing enthalpies[5] and tend to phase separate into their binary constituents[6] at low tempertures. Even if phase separation were disallowed (e.g., by kinetic limitations), calculations on bulk formation enthalpies[7,8] have shown that the next lowest state of the lattice-mismatched $Ga_{0.5}In_{0.5}P$ alloy is the chalcopyrite (CH) structure (observed[2] in $GaAs_{0.5}Sb_{0.5}$ alloys), not the observed CP structure, whereas for the lattice-matched $Al_{0.5}Ga_{0.5}As$ alloy the next states are the [111] superlattices and the random alloy,[9] not the CA structure. Therefore, if ordering were governed by *bulk* energetics, it would not result in the structures that are actually observed for $Ga_{0.5}In_{0.5}P$ and $Al_{0.5}Ga_{0.5}As$. In the case of $Ga_{0.5}In_{0.5}P$, epitaxial growth on a substrate that is lattice matched to the alloy will tend to suppress phase separation;[10] however, the relative energies of different structures with the same composition are not affected.[8] For the lattice-matched alloys such as AlAs/GaAs the alloy lattice constant is independent of the composition, and epitaxial constraints have little effect. Indeed, the following experimental observations suggest that the CP-type ordering is induced at the free surface during growth. If the [111] ordering were of bulk origin, one would expect all four {111} variants to be present (these are equivalent in the bulk by symmetry); only two, however (the $[1\bar{1}1]$ and $[\bar{1}11]$ denoted as CP_B; the other two are CP_A), are seen.[4,11] Furthermore, a given type of ordering is frequently observed only for growth on a given substrate orientation.[12]

TABLE I. 3D structures characterized by stacking of the (001) bilayers shown in Fig. 1. The structure is identified both by a superlattice notation (the direction **G** and the repeat period $2n$) and by the notation used in the text. Each layer is shifted laterally as indicated in parentheses (in units of the zinc-blende lattice constant). Several other structures are degenerate with those tabulated: [110] $n=1$ is identical to [001] $n=1$ CA; [201] $n=2$ CH is degenerate with [021] $n=2$ CH; and [010] CA is degenerate with [100] CA. The [102] $n=2$ and [012] $n=2$ CH structures have (001) layers that cannot be represented by the 2×2 patterns in Fig. 1. Notice that the d layer occurs only in the observed CP_B phase and in the $[1\bar{1}0]$ $n=2$ superlattice. The two are distinguished only by the third-layer stacking.

Structure		Layer number			
G,n	Name	1	2	3	4
(Binary)	A	$a(0,0)$	$a(\frac{1}{2},0)$	$a(0,0)$	$a(\frac{1}{2},0)$
(Binary)	B	$b(0,0)$	$b(\frac{1}{2},0)$	$b(0,0)$	$b(\frac{1}{2},0)$
[021],2	CH	$e(0,0)$	$e(\frac{1}{2},0)$	$e(\frac{1}{2},\frac{1}{2})$	$e(0,\frac{1}{2})$
[100],1	CA	$e(0,0)$	$e(\frac{1}{2},0)$	$e(0,0)$	$e(\frac{1}{2},0)$
[001],1	CA	$a(0,0)$	$b(\frac{1}{2},0)$	$a(0,0)$	$b(\frac{1}{2},0)$
[111],1	CP_A	$c(0,0)$	$c(\frac{1}{2},0)$	$c(\frac{1}{2},\frac{1}{2})$	$c(0,-\frac{1}{2})$
[110],2	···	$c(0,0)$	$c(\frac{1}{2},0)$	$c(0,0)$	$c(\frac{1}{2},0)$
$[\bar{1}11]$,1	CP_B	$d(0,0)$	$d(\frac{1}{2},0)$	$d(\frac{1}{2},-\frac{1}{2})$	$d(0,\frac{1}{2})$
$[\bar{1}10]$,2	···	$d(0,0)$	$d(\frac{1}{2},0)$	$d(0,0)$	$d(\frac{1}{2},0)$

We ask here whether the (001) surface energetics of an alloy can explain (i) the preference for CP over other structures (CA, CH, etc.), (ii) the preference of CP_B over CP_A, and (iii) the absence of order in the lattice-matched $Al_{0.5}Ga_{0.5}As$ alloy [where order is seen only on (110) substrates[1]]. These questions can be phrased in terms of the relative stability of the five prototype (001) alloy layers shown in Fig. 1. By stacking these layers in different ways, many of the commonly observed 3D structures can be obtained (Table I). Previous theories[12-14] suggested that surface ordering is driven by the need to minimize the strain associated with packing cations of different sizes at the surface. Contrary to the previous expectations,[12-14] we find that size mismatch is readily accommodated by relaxations perpendicular to the surface and that surface relaxations produce energy differences between the various competing cation arrangements that are far too small to account for ordering at a (typical) growth temperature (T_g) of 900 K. We next allowed surface reconstructions. We find that sur-

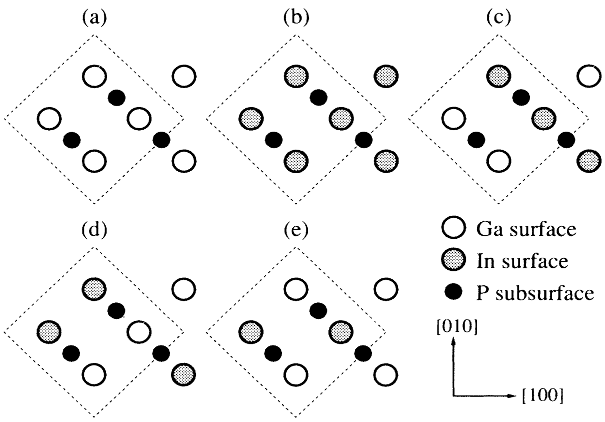

FIG. 1. Surface atomic arrangements for the 2×2 surface cell. See Table I for description of corresponding bulk structures.

face dimerization coupled with buckling and tilting of the dimers (see below) stabilizes the *d* surface (which is the 2D analog of the observed CP_B structure) of $GaInP_2$ (but not of $AlGaAs_2$) by 84 meV per surface atom —comparable to kT_g. Since the CP_B structure is unstable in the bulk,[7,8] its experimental observation in thick films could then imply that coverage of the surface by subsequent growth freezes in the surface-stable topology (i.e., the atomic connectivity). To see how quickly such coverage, which immediately undoes the surface reconstructions, removes the preference for the *d* topology, Bernard, Froyen, and Zunger[15] compared the energies of the five 2D cation structures in Fig. 1 each covered by *h* monolayers of either Ga/In or P. For the cation-terminated surfaces none of these 2D structures is strongly preferred; however, for the anion-terminated surfaces a strong (as much as 90 meV) preference for the *d* topology exists in the third sublayer ($h=3$). We conclude that if atomic mobility is limited either to the top surface layer only or to the top four layers, then surface-induced CP_B ordering can propagate into macroscopic film thicknesses.

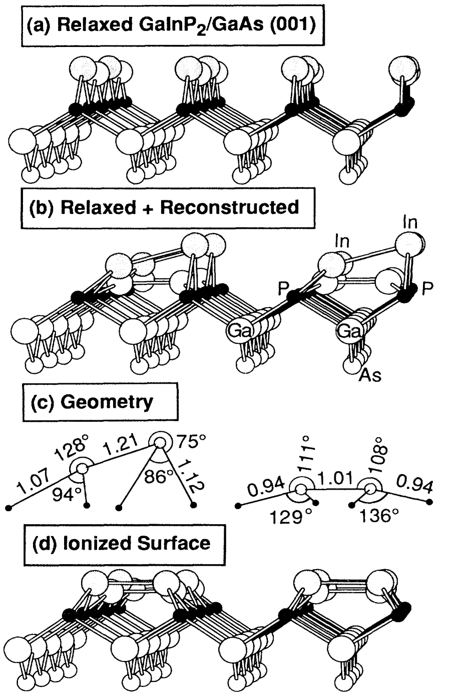

FIG. 2. Side view of relaxed atomic geometries for the *d* surface of $GaInP_2$ on (001) GaAs. The surface atoms are Ga (white), In (grey), and P (black) on top of a substrate GaAs layer (white). (a) Relaxed but undimerized, (b),(c) fully reconstructed with buckled and tilted dimers, and (d) ionized. The bond lengths in (c) are given in units of the average of the bond lengths of bulk GaP and InP. In these units, the bulk bond lengths of GaP and InP are 0.96 and 1.04, respectively.

The energy of each surface was calculated using a supercell. For the cation-terminated surfaces, we used a repeated slab consisting of three atomic GaAs (substrate) layers covered on each side by single, cation-terminated bilayers of $GaInP_2$ (or $AlGaAs_2$) in the topologies *a*–*e*. Figures 2(a) and 2(b) depict the upper half of two such slabs. For the P-terminated surfaces, where elastic relaxations propagate deeper, we used an eight-layer slab with a single $GaInP_2$ bilayer on top of the GaAs substrate which was terminated on the bottom by a semiconducting half monolayer of Ga.[16] The first-principles local-density pseudopotential method was used to calculate the total energies and quantum-mechanical forces were used to find equilibrium geometries for each of the five surfaces. In order to check that interactions between the two surfaces of our seven-layer slab did not bias our results, we compared the two types of slabs, varied the thickness of and the separation between the slabs, and translated the top surface with respect to the bottom. Based on these tests, we estimate that energy differences between the various surfaces are accurate to better than 10 meV per surface atom.

Calculated energies for relaxed but unreconstructed surfaces [Fig. 2(a)] are given in Table II, line 1. In agreement with the results (but not the conclusions) of Boguslawski,[13] all *unreconstructed* surfaces (alloyed or phase separated) have energies that are equal within $\ll kT_g$. Electronically, we find that all the unreconstructed surfaces are metallic.

Surface dimerization results in heteropolar (Ga-In) dimers on surfaces *c* and *e* and homopolar (Ga-Ga or In-In) dimers on surfaces *a*, *b*, and *d*. Relative to the undimerized surfaces, dimerization lowers the energy by an average of 600 meV per surface atom (Table II, line 2).[17] In all cases we find two additional, energy-lowering reconstructions within the 2×2 surface unit cell. First, neighboring dimers along the $[\bar{1}10]$ dimer rows buckle, i.e., relax perpendicularly to the surface creating

TABLE II. Surface energies for the following reconstruction modes: unreconstructed (UR), dimerized (D), dimerized and buckled (DB), and dimerized, buckled, and tilted with Ga up (DBT-Ga) and with In up (DBT-In). The energies are in meV per surface atom relative to the unreconstructed $a+b$ phase-separated surface (surfaces a and b have their own separate zero of energy).

Surface	Surface type					
geometry	a	b	$a+b$	c	d	e
UR	0	0	0	14	−9	2
D	−785	−366	−575	⋯	⋯	−620
DB	−732	−448	−590	⋯	−692	−602
DBT-Ga	−836	−564	−701	−698	−623	−715
DBT-In	−836	−564	−701	−684	−799	−705

chains of alternating high and low dimers. This lowers the energy for the b surface but the energies of the a and e surfaces increase slightly upon buckling (Table II, line 3).[18] Second, the high dimer tilts in the [110] direction becoming nonhorizontal, whereas the low dimer remains virtually horizontal. This leads to a uniform energy lowering of 100 meV but does not affect the relative stability of the surfaces (Table II, line 4). Since the four surface sites are inequivalent in the final geometry, there are two distinct ways to distribute the two Ga and two In atoms in each of the topologies c, d, and e. We characterize these by the type of atom occupying the site on the high dimer that tilts upwards. We find that the d surface strongly prefers the larger In atoms on the high dimer, whereas the c and e surfaces show a slight preference for the more electronegative Ga atom tilted up. The final minimum-energy surface geometry is illustrated in Fig. 2(b). As shown in Table II, the reconstructions (dimerization, buckling, and tilting) considerably lower the energy of all the surfaces and, most significantly, make the surface corresponding to the observed CP_B order (d) the lowest in energy by 84 meV per surface atom. Thus, surface reconstruction not only favors atomic arrangements that are unstable in the bulk, it may also result in energy differences large enough to produce ordering at T_g. All the fully reconstructed surfaces are semiconducting.

Since $Al_{0.5}Ga_{0.5}As$ does not order (or orders only weakly) when grown on (001) substrates,[1] it is interesting to compare the energies of the $GaInP_2$ surfaces to those of $AlGaAs_2$. Like the $GaInP_2$ surfaces, we separately considered Ga and Al occupying the "up" site. In the absence of size effects, the former, which places extra electrons on the more electronegative Ga atom (see below), results in the lowest energy. The energy of surface d is now only 9 meV per atom below that of the e surface—negligible compared to kT_g—so the resulting surface topology is likely to be disordered. This is consistent with experiment[1] where strong ordering is seen only for growth on the [110] surface (which is not addressed here).

The reconstructions are electronically driven. The unreconstructed cation surfaces have two broken bonds per surface atom, each containing $\frac{3}{4}$ electron. When the surface dimerizes, two electrons per dimer occupy σ-type bonding orbitals [see Figs. 3(c) and 3(d)]. This leaves one unpaired electron per dimer, making the unbuckled, dimerized surface metallic. The surface breaks the "symmetry" by buckling and tilting. Of the four atoms on a dimer pair, three relax towards planar sp^2 configurations and the fourth atom moves up into a pyramidal s^2p^3 configuration with bond angles approximating 90° [see Fig. 2(c)]. This allows the fourth atom to bind the two unpaired electrons in a dangling-bond orbital [Fig. 3(b)]. The lowest unoccupied state is a bonding p_π state

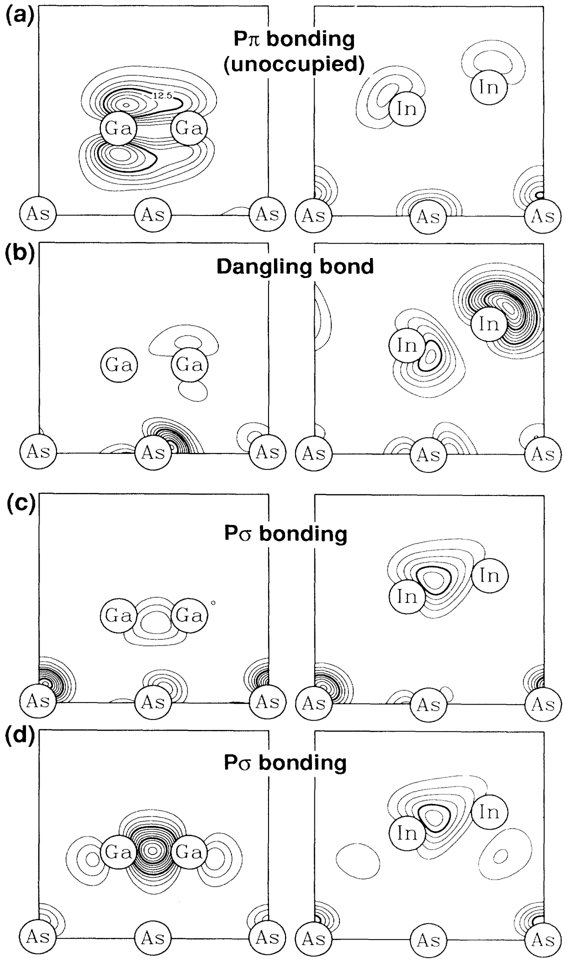

FIG. 3. Contour plots of selected surface states for the d surface at Γ in two cuts (through the low Ga-Ga dimer, left, and the high In-In dimer, right). (a) A Ga-Ga p_π bonding state (lowest unoccupied state), (b) an In dangling-bond state (highest occupied state), and (c),(d) the deeper Ga-Ga and In-In p_σ bonding states.

on the low dimer [Fig. 3(a)]. Thus, a pair of dimers forms a "negative-U" system where two neutral (horizontal) dimers are unstable with respect to disproportionation into a positively charged low dimer and a negatively charged high dimer. This analysis suggests that if the two electrons in the dangling-bond state [Fig. 3(b)] on the high dimer could be removed, e.g., by heavy p-type doping or by excitation, both dimers would prefer planar sp^2 arrangements and the energy advantage of the d surface should vanish. Our calculations show that the energy difference between the d and e surfaces is indeed reduced to 1 meV per surface atom upon the removal of two electrons per surface unit cell. The resulting geometry for the d surface is shown in Fig. 2(d). This is a possible reason for the reduced ordering observed in p-doped samples.[19] The surface electronic structure also depends on the cation coverage θ. If θ is less than $\frac{3}{4}$ monolayer, all the high-dimer dangling-bond electrons can transfer to P dangling bonds, and for $\frac{3}{4} < \theta < 1$, the transfer is partial. We would therefore expect the ordering to be reduced for surfaces with $\frac{3}{4} < \theta < 1$ and to vanish for $\theta \leq \frac{3}{4}$.

To examine the extent of topological selectivity of buried layers, we calculated the energies of the cation arrangements a, b, d, and e placed in the first subsurface ($h=1$) layer under a P-terminated dimerized surface. The e topology now has the lowest energy but the d and the phase-separated ($a+b$) surfaces are only 3 and 33 meV per surface atom higher. These energy differences are clearly too small to produce ordering in this layer. Structurally, we find that the P dimers buckle slightly. Calculations of deeper ($h>1$) layers require thicker slabs and were done[15] using a valence-force-field approach with force constants fitted by first-principles calculations. The energy was minimized with respect to relaxation of all but the top two layers (which were kept fixed in their pseudopotential geometry). For $h=2$ (under cation-terminated surfaces), it is found that all cation arrangements lead to similar energies. For $h=3$ (anion terminated), the d arrangement is again preferred over the next contender (c or e) by 40 meV per surface atom (90 meV if surface buckling is disallowed). This third-layer preference is caused by dimer-induced sublayer relaxation similar to that proposed by LeGoues *et al.*[20] to explain the observed order in SiGe alloys. It is absent in the second sublayer because cation dimers induce less sublayer deformation than the tightly bound P dimers. Finally, for $h=4$, the energy difference between the two types of d-layer stacking, given in the last two lines of Table I, can be estimated. It is found that CP$_B$ stacking is favored over the [$\bar{1}$10] superlattice by 55 meV per surface atom. Surface steps therefore appear not to be needed for correct CP$_B$ layer stacking and may serve only to distinguish between the two equivalent CP$_B$ ordering directions.[12]

Our calculations have shown that equilibrium thermodynamics (*not* kinetics[21]) of a reconstructed cation-terminated surface can selectively drive CP$_B$-type ordering in GaInP$_2$. This surface ordering can evolve into macroscopic dimensions either if a P layer immobilizes the cation layer under it or if diffusion exists up to the third subsurface layer.

---

[1] T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie, Phys. Rev. Lett. **54**, 201 (1985).

[2] H. R. Jen, M. J. Cherng, and G. B. Stringfellow, Appl. Phys. Lett. **48**, 1603 (1986).

[3] M. A. Shahid, S. Mahajan, D. E. Laughlin, and H. M. Cox, Phys. Rev. Lett. **58**, 2567 (1987).

[4] A. Gomyo, T. Suzuki, and S. Iijima, Phys. Rev. Lett. **60**, 2645 (1988).

[5] G. B. Stringfellow, J. Phys. Chem. Solids **34**, 1749 (1973).

[6] M. B. Panish and M. Ilegems, Prog. Solid State Chem. **7**, 39 (1972).

[7] R. G. Dandrea, J. E. Bernard, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **64**, 36 (1990).

[8] J. E. Bernard *et al.*, Phys. Rev. B **38**, 6338 (1988); J. E. Bernard *et al.*, Appl. Phys. Lett. **56**, 731 (1990).

[9] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **61**, 1505 (1988).

[10] D. M. Wood and A. Zunger, Phys. Rev. Lett. **61**, 1501 (1988).

[11] I. J. Murgatroyd, A. G. Norman, and G. R. Booker, J. Appl. Phys. **67**, 2310 (1990).

[12] T. Suzuki, A. Gomyo, and S. Iijima, J. Cryst. Growth **93**, 396 (1988).

[13] P. Boguslawski, Phys. Rev. B **42**, 3737 (1990).

[14] N. Hamada and T. Kurimoto, in *Proceeding of the Twentieth International Conference on the Physics of Semiconductors,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 300.

[15] J. E. Bernard, S. Froyen, and A. Zunger (unpublished).

[16] D. J. Chadi, J. Vac. Sci. Technol. A **5**, 834 (1987). We used Ga in a checkerboard 2×2 vacancy pattern.

[17] The heteropolar dimers on the c and e surfaces were allowed to tilt naturally.

[18] For the e surface, we allowed asymmetric dimers and found a local, possibly metastable energy minimum with slightly tilted dimers. For the c surface, we were unable to find such a local minimum.

[19] S. Kurtz *et al.*, J. Electron. Mater. **19**, 825 (1990).

[20] F. K. LeGoues *et al.*, Phys. Rev. Lett. **64**, 2038 (1990).

[21] M. Kondow, H. Kakibayashi, T. Toshiaki, and S. Minagawa, Phys. Rev. Lett. **63**, 884 (1989).