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Surface-Induced Ordering in GaInP

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GaoqinoqP 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.

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Most III-V ternary semiconductor alloys exhibit spon-taneous long-range order when grown homogeneously by gas-phase epitaxy in certain

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(a) (b)

. 0. 0 ~

'
.

. .

. 0

0,::.0 0
0 '. 0

(c)

0 0

0 0; '. 0.' 0

(a) Relaxed GalnP2/GaAs (001)

(e)

0

0 Ga surface
O In surface

~ P subsurface
[010]

(b) Relaxed + Reconstructed

ln

(c) Geometry

FIG. 1. Surface atomic

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Surface
geometry

Surface type
a+b c

UR
D
DB
DBT-Ga
DBT-In

0 —785 —732 —836 —836

0 —366 —448 —564 —564

0 —575 —590 —701 —701

14

—698 —684

—692 —623 —799

2 —620 —602 —715 —705

TABLE II. Surface energies for the following reconstruc-tion 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).

dressed here).
The reconstructions are electronically driven. The un-reconstructed cation surfaces have two broken bonds per surface atom, each containing 4 electron. When the surface dimerizes, two electrons per dimer occupy o.-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 config-urations and the fourth atom moves up into a pyramidal s p 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 state

chains of alternating high and low dimers. This lowers the energy for

leaves