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Structure of ordered and disordered $In_xGa_{1-x}P(001)$ surfaces prepared by metalorganic vapor phase epitaxy

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Abstract

Ordered and disordered InGaP(001) films were grown by metalorganic vapor-phase epitaxy and studied by low energy electron diffraction, reflectance difference spectroscopy, and X-ray photoemission spectroscopy. Both alloy surfaces were covered with a monolayer of buckled phosphorus dimers, where half of the phosphorus atoms were terminated with hydrogen. Ordered InGaP(001) appeared indium rich, and exhibited a reflectance difference spectrum like that of InP(001). These results support a model whereby the strain energy on the ordered InGaP surface is reduced by aligning the group III atoms in alternating [110] rows, with the indium and gallium bonding to the buckled-down and buckled-up phosphorus atoms, respectively.
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Indium gallium phosphide lattice-matched to gallium arsenide is widely used in heterojunction bipolar transistors and quantum well lasers [1,2]. The InGaP/GaAs interface has a large valence band discontinuity, less deep-donor-level trapping, and a lower interface recombination velocity than the AlGaAs/GaAs interface [3,4]. However, due to the $CuPt_B$-type ordering of the group-III sublattice a shift in the band alignment can occur [5–8]. The degree of $CuPt_B$-type ordering is defined by an order parameter, η, having values between 0 (completely disordered) and 1 (completely ordered). The quantitative relationship between the bandgap energy and η can be found elsewhere [8].

It has been proposed by several authors that the surface structure of the InGaP film influences the ordering of the group III sublattice [9–14]. For example, detailed thermodynamic studies show that the disordered $In_{0.48}Ga_{0.52}P$ alloy represents the equilibrium state, with the bulk ordered phase is a metastable configuration corresponding to a local energy minimum [10,11]. Calculations on a dimer reconstructed surface found that the lattice was alternately dilated and compressed in the subsurface region [11–13]. Zorn et al. [9] reported that ordered alloys were formed when the surface exhibited a P-rich (2×1) lattice, whereas disordered alloys were formed when the less P-rich (2×4)-like phase was present. Nevertheless, no clear picture has emerged of the relationship between the surface structure and the bulk-ordering phenomenon.

Herein, we report on the surface properties of disordered and ordered InGaP films grown by metalorganic vapor-phase epitaxy (MOVPE). Lattice matched alloys, 200 nm thick, were deposited on GaAs(001) substrates in an Aixtron 200 MOVPE reactor at Hahn–Meitner-Institut, Germany. Growth was carried out at a V/III ratio of 60 using trimethylindium, trimethylgallium, and tertiarybutylphosphine (TBP) in 100 mbar of hydrogen at 600 °C at a rate of 1.7 μm/h. Disordered InGaP films were achieved by heavily doping the material with ditertiarybutylsilane at a IV/III ratio of 0.1. Then, the samples were placed in a nitrogen glove box and brought to a second MOVPE

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system at the University of California, Los Angeles where they were deoxidized in TBP and H_2 at 550 °C for 15 min, and transferred directly to an ultrahigh vacuum system without air exposure.

The ternary surfaces were analyzed in the UHV system by a Princeton Instruments low energy electron diffractometer (LEED), a J-Y NISEL reflectance difference spectrometer (RDS), and a Physical Electronics X-ray photoelectron spectrometer (XPS). Core level photoemission spectra of the Ga $2p_{3/2}$, In $3d_{5/2}$, and P $2p_{3/2}$ peaks were collected using Al K_α X-rays at a pass energy of 23.5 eV. The bandgap energy was determined by photoluminescence, and for the ordered alloy, η was calculated to be 0.36 [8].

Following TBP treatment, the LEED pattern for ordered InGaP exhibited a sharp and streaky (2×1), identical to that seen for InP and GaP (001) surfaces [14,15]. After annealing this sample in UHV at 500 °C for 15 min, a group III-rich (2×4) reconstruction was obtained, in agreement with the results of Vogt et al. [16]. In contrast, disordered InGaP exhibited a weak (2×1) after TBP exposure at 550 °C in the reactor. Annealing this sample in UHV at temperatures up to 550 °C did not produce any LEED patterns other than a weak (1×1).

Reflectance difference spectra of the InGaP surfaces and those of InP and GaP(001) are presented in Fig. 1. The RD spectrum of an oxidized film was subtracted from the spectral data of the clean, reconstructed films in order to reveal the line shape due solely to the surface. The positive and negative peaks observed for the ordered InGaP are more intense and narrower compared to those recorded for the disordered InGaP. In the (2×1) spectra, the strongest positive peak shifts from 3.1 to 3.2 to 3.3 to 3.4 eV on InP, ordered InGaP, disordered InGaP, and GaP, respectively. Note that this peak has been assigned to electronic transitions involving phosphorus dimers [17,18]. In the same set of spectra, the negative band at low energy shifts from 1.9 to 2.1 to 2.3 eV and decreases in intensity on going from InP to the ordered and disordered InGaP surfaces, respectively. This feature is not present in our room temperature spectrum for GaP (2×1), but appears at 2.6 eV in the low temperature RD spectrum taken by Toben, et al. [19]. This peak stems exclusively from the surface reconstruction and deteriorates rapidly with decreasing atomic order on the surface. An overall comparison of these data for the (2×1) surfaces reveals that the RD spectrum of ordered InGaP is like that of InP, whereas the RD spectrum of disordered InGaP is like that of GaP.

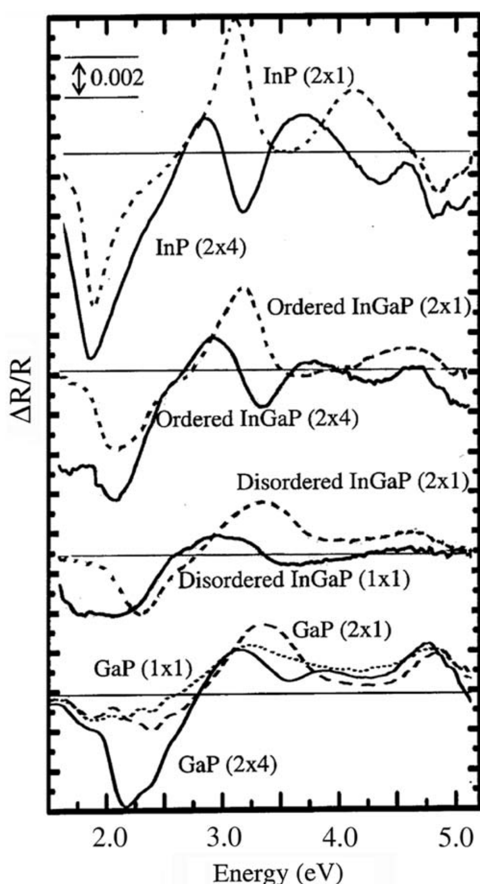

Fig. 1. Reflectance difference spectra of InP, ordered and disordered InGaP, and GaP(001) surfaces at 30 °C.

Upon annealing, the ordered alloy reconstructs to form a (2×4) structure. The RD line shape for this surface contains the same negative band and three positive bands that are found in the spectrum of InP (2×4) [17,20–24], except these features are lower in intensity and slightly blue shifted. On the ordered InGaP (2×4), the negative band appears at 2.0 eV, and the three positive bands are centered at 2.9, 3.8, and 4.6 eV. On InP (2×4), the negative peak is centered at 1.8 eV, while the positive peaks are at 2.8, 3.8, and 4.6 eV. Finally, the disordered InGaP (1×1) reconstruction exhibits an RD spectrum that is similar to that of the GaP (1×1) surface. Two broad bands are evident in each line shape, with positive peaks at 2.9 and 4.6 eV on disordered InGaP, and 3.2 and 4.8 eV on GaP.

The difference between the ordered and disordered phosphorus-rich alloy surfaces are further evident in the XPS measurements, which are summarized in Table 1. The atomic percentages were determined from the integrated intensities of the In $3d_{5/2}$, Ga $2p_{3/2}$, and P $2p_{3/2}$ peaks, excluding C 1s and O 1s contributions, which were minimal. The atomic sensitivity factors used in the calculations were 4.36, 3.72, and 0.49 for In $3d_{5/2}$, Ga $2p_{3/2}$, and P $2p_{3/2}$, respectively. The In/Ga ratio is 1.0 ± 0.1 for the disordered film, as expected for a random distribution of indium and gallium in the group III sites. On the other hand, this ratio is 1.4 ± 0.2 for the ordered InGaP (2×1). This indicates that the In atoms at or near the surface on the ordered film are located in different sites from the Ga atoms, such that

Table 1
Atomic composition of P-rich ordered and disordered InGaP(001)

Sample	LEED	In%	Ga%	P%	In/Ga
Disordered InGaP	Weak (2×1)	26.7	26.4	46.9	1.0
Ordered InGaP	Streaky (2×1)	30.0	22.2	47.8	1.4

their photoelectrons are less screened by the phosphorus dimers.

Our results show that the InGaP(001) surfaces produced in the MOVPE environment exhibit (2 × 1) periodicity as is observed for InP and GaP(001) [14,15,19,24,25]. This structure is composed of a complete layer of phosphorus dimers, in which half the dangling bonds on the dimers are attached to hydrogen, and the other half are filled with lone pairs of electrons [24,25]. A ball-and-stick model of the InP (001)-(2 × 1) is shown in Fig. 2(a). The asymmetric bonding on the phosphorus dimers causes them to buckle: the P atoms attached to H are pulled into the surface plane, while the P atoms containing the lone pairs are pushed out.

On InP(001), the strain induced by dimer buckling is relieved by forming zigzagging rows, where the H atoms hop back and forth between opposite ends of the dimer [14,24]. Depending on whether adjacent rows are in phase or out of phase, the structure exhibits a local p(2 × 2) or c(4 × 2) lattice. In the figure, the out of phase orientation is shown with the (2 × 1) and c(4 × 2) unit cells highlighted with solid and dashed lines, respectively. In STM images of the InP(2 × 1), the p(2 × 2) and c(4 × 2) domains are randomly distributed over the surface [14]. These structures contribute to the streaks observed in ×2 direction in the LEED pattern. Note that the ×2 streaks can also be produced by the dimer rows shifting one lattice space in the $[\bar{1}10]$ direction across a domain boundary.

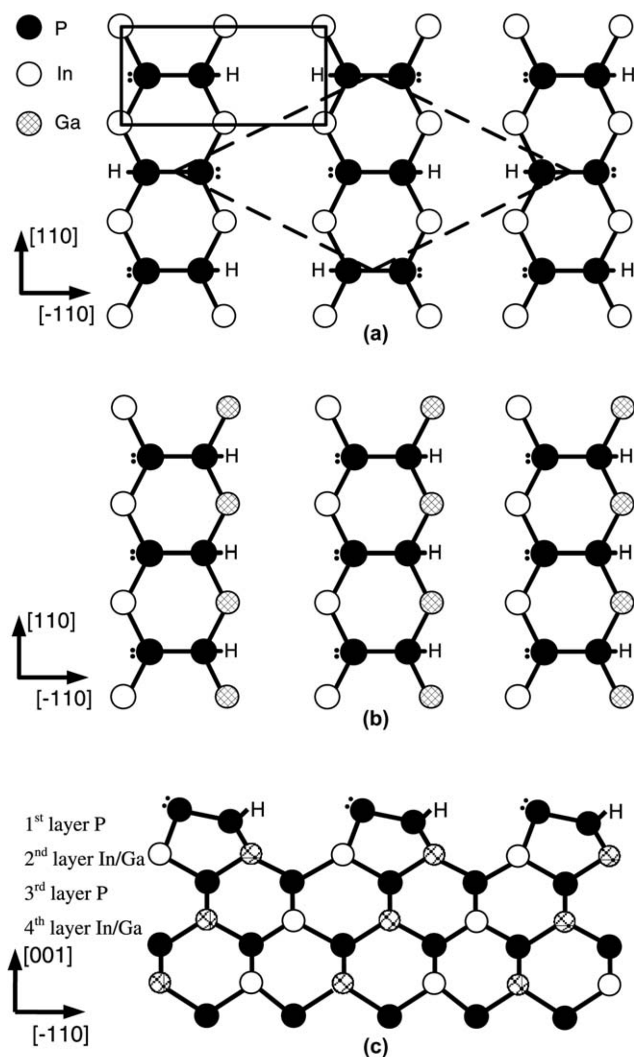

Fig. 2. Ball-and-stick models of the (2 × 1) reconstruction of: (a) InP [22,24]; (b) ordered InGaP, top view and (c) ordered InGaP, sideview [9].

The P-rich (2 × 1) surface of ordered InGaP may relieve the strain induced by dimer bucking in an alternative way from InP. Here, the surface energy may be minimized by anchoring the buckled-up P atom to two In atoms and the buckled-down P atom to two Ga atoms. A ball-and-stick model for this structure is shown in Fig. 2(b). The bond angle between the P dimer and the group III elements in the underlying layer is larger for the atom attached to H than for the atom containing the lone pair. Molecular cluster calculations for the buckled dimer on InP(001) indicate that these two bond angles are 109° and 96°, respectively [25]. We postulate that the strain would be minimized by matching up the smaller gallium atoms with the tetrahedral bonds and the larger indium atoms with the pyramidal bonds.

A side view of the proposed ball-and-stick model for the ordered InGaP (2 × 1) structure is shown in Fig. 2(c). This structure is taken from the model of Zorn et al. [9], except that it is modified by adding the hydrogen atoms to the phosphorus dimers. The phosphorus dimers are attached to the group-III sublattice of the second layer such that the bucked-down (hydrogen bonded) P atom is bonded to Ga, while the buckled-up (lone pair) P atom is attached to indium. The In and Ga atoms take up different 4th layer sites, with indium positioned between the dimer rows and gallium directly underneath them. Richters' group has calculated that these positions reduce the surface strain by 0.26 eV [9]. The different 4th layer sites could account for the In/Ga ratio of 1.4 ± 0.2 observed by us for the ordered alloy. Photoelectrons emitted from the fourth layer In atoms are screened by the third layer of phosphorus only, whereas photoelectrons from fourth layer Ga atoms must travel past the third and first layers of P atoms to escape.

Our reflectance difference spectra support the model shown in Fig. 2(c) for the ordered alloy. The positive peak at 3.1 eV for the InP (2 × 1) is thought to be due to electronic transitions involving indium and the lone-pair-bonded P atom of the dimer [17,18]. Previous experiments showed that the 3.1 eV peak disappears upon adsorbing hydrogen on to the phosphorus dimers [17]. In the same manner, it seems likely that the 3.4 eV peak for the GaP (2 × 1) involves gallium and the lone-pair-bonded P atom of the dimer [15,21]. For the ordered InGaP (2 × 1), this peak occurs at 3.2 eV and is a relatively sharp feature like that observed on InP (2 × 1). By contrast, the peak on disordered InGaP (2 × 1) shifts to 3.3 eV and is reduced in intensity like that on GaP (2 × 1). These trends would support the model presented in Fig. 2(c) in which the In and Ga atoms are placed in alternating [110] rows on opposite

ends of the phosphorus dimers. Unfortunately, we were unable to obtain STM images of sufficiently high resolution to directly observe this surface structure.

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