PHYSICAL REVIEW B **83**, 155316 (2011)

Direct observation of dimer flipping at the hydrogen-stabilized GaP(100) and InP(100) surfaces

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(Received 18 May 2010; revised manuscript received 25 January 2011; published 21 April 2011)

Using scanning tunneling microscopy, we have observed changes of the dimer configurations at the well-defined, atomically ordered P-rich GaP(100) and InP(100) surfaces, prepared by metal organic vapor phase epitaxy. Our measurements reflect the $p(2\times2)/c(4\times2)$ surface reconstructions, where the surfaces are terminated by alternating buckled phosphorus dimers stabilized by one hydrogen atom per dimer. Comparison of successive images reveals flipping of the P dimers in several locations, which requires shifting of the H termination between the P atoms in the respective dimers.

DOI: 10.1103/PhysRevB.83.155316 PACS number(s): 68.35.bg, 68.37.Ef, 81.05.Ea, 68.43.Fg

I. INTRODUCTION

Both GaP and InP have been important materials in electronic or optoelectronic applications for several decades.[1–3] Recently, the GaP(100) surface has gained renewed attention as part of an almost-lattice-matched III-V compound on a silicon substrate,[4–6] while InP(100) has been employed as a substrate material for a low-band-gap tandem solar cell.[7] We have investigated both homoepitaxial and heteroepitaxial GaP(100) and InP(100) films, prepared by metal organic vapor phase epitaxy (MOVPE), using a variety of surface science techniques.[4,8] In the MOVPE environment, the well-known GaP(100) surface reconstructions[9] include a mixed (Ga-P) dimer surface for Ga-rich conditions and a P-rich surface that has often been referred to as the $(2\times1)/(2\times2)$ surface. The InP(100) surface reconstructs in the same manner as evidenced by several theoretical[10] and experimental[11] studies. Here we present results of a scanning tunneling microscopy (STM) study of the P-rich surfaces, prepared by MOVPE under *in situ* reflectance anisotropy spectroscopy (RAS) control.[8] These surfaces can only be obtained in the presence of hydrogen (available as a carrier gas in the MOVPE environment or as a precursor by-product).[9–13] In the low-energy electron diffraction (LEED) image these surfaces result in a (2×1) pattern with streaks at half order in the $\times1$ direction.

According to Schmidt *et al.*[10] and Hahn *et al.*,[14] this $(2\times1)/(2\times2)$ reconstruction is due to a hydrogen-adsorbate structure, where the surface is terminated by buckled phosphorus dimers, each stabilized by a hydrogen atom that saturates one of the dangling bonds in the dimer.[10,11,14] The resulting structure is shown in Fig. 1: In a (2×2) cell, there are two phosphorus dimers in the top layer, which are oppositely buckled, with one hydrogen atom bonded to the "down" atom of the P dimer. This leads to rows of buckled phosphorus dimers, where adjacent rows can be arranged in phase or out of phase. The in-phase arrangement results in a $p(2\times2)$ unit cell, while the out-of-phase arrangement corresponds to a $c(4\times2)$ unit cell, so a more accurate denotation of this surface reconstruction is $p(2\times2)/c(4\times2)$, which we will adhere to in the following. A mixture of these surface reconstructions results in the above-mentioned LEED pattern.[6]

Several groups have also reported on the preparation of GaP(100) in ultrahigh vacuum (UHV) using tertiary-butylphosphine (TBP). Although there have been some contradictory results, the most recent studies[15–18] agree that the mixed dimer (2×4) and the $p(2\times2)/c(4\times2)$ phase are obtained, where the $p(2\times2)/c(4\times2)$ phase corresponds to the atomically ordered P-rich conditions. This phase has been analyzed by several groups, and proposed models include a P-P dimer[18] and a Ga-P[16] termination. However, Kadotani *et al.*[12] and Töben *et al.*[9] using a similar surface preparation, provided direct experimental evidence by high-resolution electron-energy-loss spectroscopy and STM that this phase is terminated by hydrogen. In the case of InP(100), solid-source molecular beam epitaxy (MBE) results in a multitude of different surface reconstructions.[19,20] However, only the $c(4\times4)$ and the $c(2\times8)/(2\times4)$ reconstructions exhibit local ordering.[19,21] When prepared in the presence of TBP, the P-rich $p(2\times2)/c(4\times2)$ reconstruction of InP(100) can be obtained.[11]

The presence of hydrogen bonds at this P-rich InP(100) surface was established by Letzig *et al.*[22] for the MOVPE-prepared surface using Fourier transform infrared spectroscopy. They confirmed that there are two P-H bonds belonging to two different P-P dimers per surface unit cell, in agreement with the structural model in Ref. 10. Furthermore, it was shown that the InP(100) $p(2\times2)/c(4\times2)$ reconstruction can only be prepared in MBE if atomic hydrogen is supplied during growth.[10] Theoretical STM images of the H-terminated P-rich InP(100) surface were calculated by Schmidt *et al.*[10] in agreement with the experimental results by Vogt *et al.* on MOVPE-grown P-rich InP(100).[11] Hahn *et al.*[14] provided calculations of the expected filled-state STM images of the $p(2\times2)$ structure of GaP(100), based on density functional theory. They obtained a zigzag pattern where the bright spots are due mainly to the electron lone pair of the "up" atom of the buckled P dimer, while the hydrogen-terminated down atom is less pronounced. These calculations were in agreement with the experiments of Töben *et al.*[9] and Kadotani *et al.*,[12] showing a zigzag pattern where only the bright spots due to the up atom were observed.

II. EXPERIMENT

We prepared the InP and GaP(100) surfaces in a commercial horizontal MOVPE reactor (Aixtron AIX 200) and studied surfaces of samples that were prepared by either (i) annealing

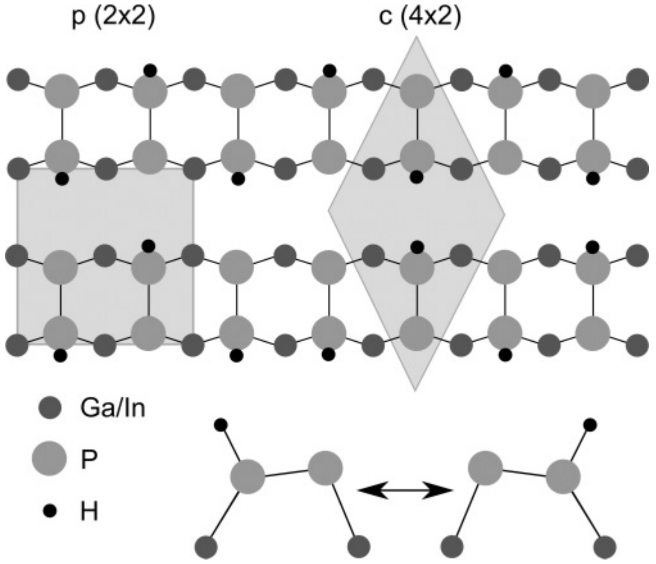

FIG. 1. Top view and side view of hydrogen-stabilized GaP(100) and InP(100) surface structure after Hahn *et al.*[14] and Schmidt *et al.*[10] The unit cells are indicated in the top view.

under TBP supply in the MOVPE reactor only, (ii) MOVPE growth of a homoepitaxial buffer layer, (iii) MOVPE growth and subsequent annealing in UHV,[11] or (iv) heteroepitaxial growth of GaP on Si(100). All of these processes lead to the well-established H-terminated, buckled P-dimer configuration. Deoxidation of the GaP substrates (S-doped, 2×10^{18} dopants/cm^3) was achieved by annealing under TBP at 630 °C for 5 min using H_2 as a carrier gas. The samples were subsequently cooled to 300 °C under TBP, resulting in a P-rich surface with excess phosphorus.[9] Removing the excess phosphorus was then achieved by annealing at about 390 °C for at least 7 min in the absence of TBP. The formation of the P-rich surface was controlled by RAS[8,13] using a commercial RAS system (Laytec EpiRAS 200). After the completion of the MOVPE process, the samples were transferred to UHV using a special system for contamination-free transfer to UHV, and a mobile UHV chamber was used for further transfer of the samples to the STM chambers.[23] Measurements were carried out either with a commercial SPECS 150 Aarhus STM or with an Omicron STM in UHV ($<5 \times 10^{-10}$ mbar). Images were recorded in constant-current mode at sample bias around −3.5 V and tunneling currents between 100 and 300 pA, using etched tungsten tips cleaned *in situ* by argon ion sputtering. The bias values refer to the sample voltage with respect to the STM tip. In agreement with previous studies,[9,12,14] we observed that, only at these large negative sample-bias voltages, a contrast is obtained when performing STM measurements of this surface. Experimental details of the measurements of the P-rich InP(100) surfaces were as previously published.[11]

III. RESULTS AND DISCUSSION

Figure 2 shows an image of one of the GaP(100) surfaces at room temperature after transfer to UHV. The image quality compares favorably with the images presented in Refs. 9 and 12. A direct comparison with the calculated images[14] is possible, and in region A of Fig. 2 the zigzag pattern of the calculated filled-state image is clearly visible with only the up atoms contributing to the image. As mentioned above, this corresponds to the $p(2 \times 2)$ reconstruction. In region B the honeycomb structure is observed, which corresponds to the $c(4 \times 2)$ reconstruction. The regions of these reconstructions only extend over a few unit cells, leading to numerous locations, where transitions between the two symmetries exist. This indicates that the additional energy required for neighboring dimers to buckle in the same direction and therefore to violate the symmetry of the two reconstructions is relatively low. In a few places, irregular bright structures are visible. These are likely due to residues from precursor fragments, which have not been removed completely by the annealing procedure, or due to missing H atoms or impurities. Such precursor fragments have also been observed on MOVPE-grown P-rich InP(100).[24]

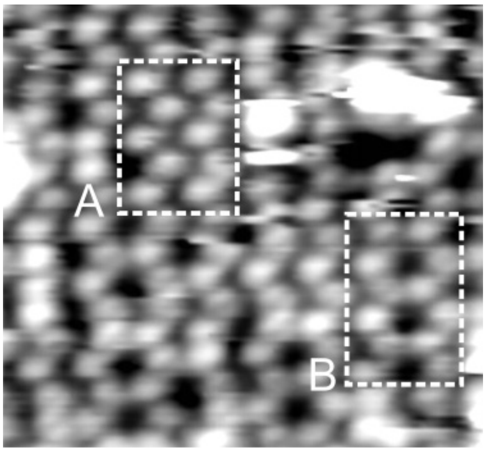

FIG. 2. Filled-state image of GaP(100) surface at room temperature. Regions A and B exhibit $p(2 \times 2)$ and $c(4 \times 2)$ reconstructions, respectively. Scale is 65 Å × 60 Å.

The image of the GaP(100) surface in Fig. 2, which results directly from MOVPE preparation, may be compared with images in Ref. 11 of the P-rich InP(100) surface, which were obtained after an annealing step in UHV. Although the defect density is higher in Fig. 2, the similarity of the underlying surface structure is striking. Figure 2 confirms that this surface should be referred to as $p(2 \times 2)/c(4 \times 2)$ reconstructed.

The clean Si(100) surface possesses some similarity to this surface; in the case of (2×1)-reconstructed Si(100), a complete layer of dimers terminates the surface without involving hydrogen, forming a (2×1) reconstruction and leaving one electron in each dangling bond. These electrons form π bonds, and the dimers tilt, with charge being transferred from the down atoms to the up atoms,[25] giving rise to buckled dimers that exhibit $p(2 \times 2)$ and $c(4 \times 2)$ unit cells.[26,27] However, STM images at room temperature show symmetric dimers,[28] which are attributed to a flip-flop motion, where the dimers fluctuate between the two equilibrium positions at a rate too high to be resolved at room temperature, and buckled dimers are observed in STM images only in the vicinity of defects or at sufficiently low temperature. Clearly, in the case of GaP(100) and InP(100) the dimers do not appear symmetrically at room temperature. However, we investigated the possibility that they undergo a flip-flop motion at a much lower rate by comparing successive images of the surface.

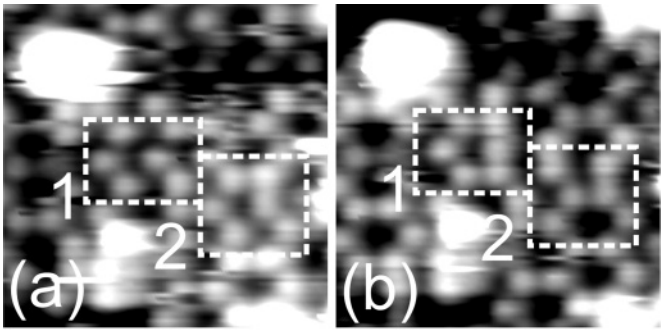

FIG. 3. Consecutive filled-state images of GaP(100) surface at room temperature. Frames 1 and 2 indicate regions where dimer flipping occurs between the images. The time elapsed between images is about 1 min, while the time required to completely image one atom is about 1.5 s. Scale is 45 Å × 45 Å.

Figure 3 shows a region of two successive images at room temperature for this comparison. The rectangular frames indicate positions, where the surface changes between the two images. In frame 1 there are six protrusions, of which the three on the left-hand side in the frame remain unchanged. The three protrusions on the right-hand side appear in a zigzag arrangement in Fig. 3(a), while in Fig. 3(b) they are aligned vertically. In frame 2 the three protrusions on the right-hand side remain unchanged, while the zigzag arrangement of the three protrusions on the left-hand side is flipped with respect to a vertical axis. The process, which is associated with the flipping of a protrusion with respect to a vertical axis, becomes clear when one considers the atomic model according to Hahn *et al.*[14] The protrusions in the images are due to the electron lone pair of the up atom of the P dimer. The flipping therefore implies that the up atom shifts downward and vice versa, so that the buckling of the dimer reverses (i.e., the dimer is mirrored). According to the atomic model, this means that the H atom, which stabilizes the P dimer, changes position from one P atom in the dimer to the other. This is distinctly different from the case of the Si(100) (2 × 1) surface, where the flip-flop motion only results from a charge transfer from one Si atom to the other and their related rehybridization. One may speculate that the motion and change of the bonding arrangement of the H atom required in the case of the GaP(100) surface are the reason for the comparatively low rate of the dimer flipping in this case. In order to investigate the possibility of a thermally activated process, we carried out experiments at the lower sample temperature of 120 K (while the scanner remained at room temperature in our setup).

Figure 4 shows sections of three successive images recorded at 120 K in which the rectangular frames highlight a region where dimer flipping can be observed. Between Figs. 4(a) and 4(b) two dimers belonging to adjacent rows flip, while from Figs. 4(b) to 4(c) they flip back again. Hence, even at 120 K the buckling of the dimers is not frozen. The sequence of the images shown, containing the dimers flipping back and forth, gives an indication of the rate at which the processes occur. We can estimate upper and lower limits of this rate based on the time to image one atom during which its appearance does not change and on the number of changes between images, respectively. For both temperatures, these rates lie between 10 and 0.03 s^{-1}. A difference of many orders of magnitude in frequency should result in the case of simple thermal activation of the same system at room temperature and at 120 K, but the images are inconsistent with a difference of significantly more than two orders of magnitude. The flip-flop motion seen in Fig. 4 should increase to a frequency at room temperature that would prevent resolution of the dimer in the STM image, in disagreement with the observation.

On the other hand, the energy required to flip a particular dimer may depend on the direction of the buckling of its neighbors and of the dimers in adjacent rows. The configuration of these dimers in the vicinity of the flipping event is different for the images at room temperature and at 120 K.

Considering an idealized surface consisting of a $p(2 \times 2)$ region and a $c(4 \times 2)$ region with only one boundary and an otherwise perfect surface lattice, a dimer at the boundary would be the most likely to change its tilt because this would represent the smallest possible modification of the lattice symmetry, converting only one unit cell from one symmetry to the other and changing the boundary between the two regions by one lattice constant without introducing additional defects. Any other dimer flipping event would necessarily introduce a further deviation from the two ideal surface reconstructions.

In the image at 120 K the dimers flip between configurations that correspond to the situation at the boundary between the two ideal reconstructions if one considers only the dimers surrounding the event in the same dimer row. Here the two configurations are closest to being energetically equivalent

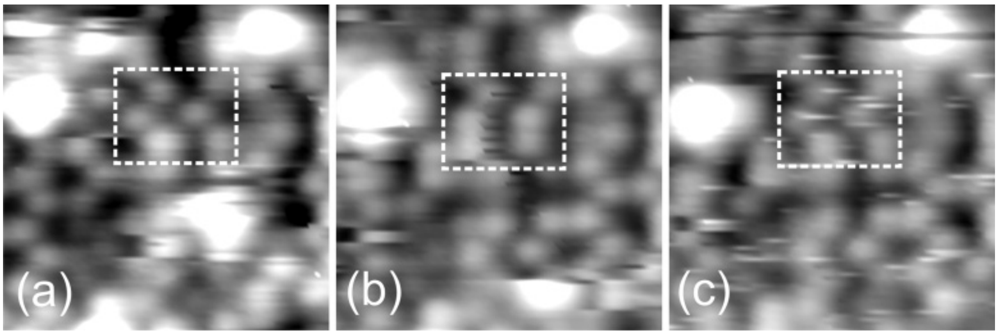

FIG. 4. Consecutive filled-state images of GaP(100) surface at 120 K. The frame indicates a location where two dimers flip back and forth in the images. The time elapsed between consecutive images here is about 16 s, while the time required to completely image one atom is about 0.4 s. Scale is 45 Å × 45 Å.

(in each configuration, one of the two neighboring dimers is oriented in the same direction as the one that flips, while the other neighbor is oriented in the opposite direction), which may facilitate the observed flipping. In the images at room temperature we observe events that also conform to these considerations, while others are in complete disagreement, e.g., the events shown in Fig. 3(a), frame 1. Also, in the images at room temperature, some dimers within one row flip individually, while in other locations several neighboring dimers are seen to flip together between images. We conclude that the events shown in Figs. 3 and 4 could be governed by different energy barriers, which might compensate the difference in thermal energy and lead to comparable transition rates. Here theoretical considerations might provide further clarification. Since the room-temperature data contain several events different from simple transitions at the boundary between the two ideal surface reconstructions, the dimer flipping is not limited to the location of such boundaries.

In order to gain further insight into the mechanism underlying the observed dimer flipping processes, we also studied the InP(100) $p(2\times2)/c(4\times2)$ surface, where the sample was subjected to an additional annealing step in UHV after MOVPE growth. This annealing step resulted in a surface identical to that of Vogt *et al.*,[11] with reduced defect density compared to the GaP(100) surface described above. However, some defects remain and seem unavoidable in the preparation of P-rich group III phosphides. Figure 5 shows two successively measured filled-state room-temperature STM images containing one dimer flipping event, as indicated by the arrows. It can be seen that the bright protrusion of the zigzag unit highlighted by the arrows is moved to the other side in Fig. 5(b) with respect to Fig. 5(a). Such flipping processes have been observed several times at different locations on this surface. There is a tendency on this postannealed surface for these events to occur in the vicinity of the remaining defects (such as voids or adsorbates). However, besides the flipping event, no other changes appear in the STM images, implying a stable STM tip and stability of the defect itself. The flipping event occurs not directly adjacent to the defect, but at a distance of a few surface lattice cells. A direct interaction between the defect and the affected dimer is therefore unlikely, as the dimers nearer the defect remain unchanged. A more probable influence is through the strain-induced change of the potential landscape around the affected dimer, leading to a reduced barrier for the observed transition. Nevertheless, the process itself could be thermally activated or tip induced.

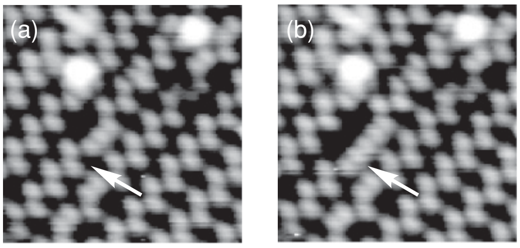

FIG. 5. STM observation of a dimer-flipping process at a InP(100) $p(2\times2)/c(4\times2)$ surface unit (indicated by arrows) in two successive filled-state STM images measured at room temperature. Such flipping processes have been observed several times at different locations on the surface. Scale is 58 Å × 58 Å sample bias voltage is −5.2 V.

The temperature-dependent measurements suggest that a tip-induced process takes place, comparable to other systems with tip-induced motion of surface atoms,[29–31] which may be aided by surface strain due to defects in the vicinity. In our case, the observed motion of the proton is likely to be governed by a potential that is determined not only by the configuration of the neighboring dimers but also by features at the surface a few unit cells away from the location of the process. Modeling of such a process therefore has to extend beyond the surface unit cell of the dimer in question and should consider an ensemble of interacting dimers. Possible mechanisms of tip-sample interaction include heating due to the high local current density or the influence of the high electric field caused by the STM tip. On the other hand, the activation energies of the dimer configurations observed at 120 K may be sufficiently different from those observed at room temperature to compensate for the difference in available thermal energies at the two different temperatures. Theoretical studies could elucidate the relation between the configurations and the energies involved.

The dimer flipping also provides additional support for the model of a H-stabilized phosphorus dimer. The calculations by Pulci *et al.*[32] and Schmidt *et al.*[10] have shown that unterminated P-P dimers at the InP(100) surface are inconsistent with a buckled dimer structure. Hence, the 2×1 cell at the surface must be due to a mixed dimer or an adsorbate at the P-P dimer. The dimer flipping contradicts the mixed dimer structure, as an exchange of different kinds of dimer atoms as the basis for the observed flipping is highly unlikely. As an adsorbate, hydrogen is the only possible candidate since soft x-ray photoemission spectroscopy measurements on these surfaces (not shown here) would have revealed the presence of other elements.[33] Hence, the only structure in agreement with our experimental observation is the hydrogen-stabilized P-P dimer.

IV. CONCLUSION

We have carried out a scanning tunneling microscopy study of the MOVPE-prepared P-rich GaP(100) and InP(100) surfaces showing the $p(2\times2)/c(4\times2)$ reconstruction.[14] This surface reconstruction consists of buckled H-stabilized P-P dimers, where, in many locations, the symmetry is broken and transitions between $p(2\times2)$ and $c(4\times2)$ occur. The high quality of our images enables a comparison between successive images, which show flipping of the P dimers in a few positions at the surface. Based on the model by Hahn *et al.*[14] and Schmidt *et al.*,[10] the dimer flipping involves shifting of the proton from one P atom to the other within the dimer. We have shown that this process is typical of the MOVPE-prepared P-rich group III phosphides. It can be compared with the flip-flop motion of dimers at the clean Si(100) surface, with the important difference of the transport of a proton as opposed to a change of the electronic configuration only in the case of Si(100). In contrast to Si(100), where defects prevent the flip-flop motion in the adjacent region, dimer flipping in the III phosphides seems to be aided by the vicinity of defects.

Our results indicate that interaction with the surrounding ensemble of dimers as well as surface defects must be taken into account in the analysis of the dimer-flipping processes. We observed such processes at room temperature and 120 K with comparable rates. Processes observable at 120 K should result in a flip-flop motion of much higher frequency at room temperature if they were thermally activated. Our observation does not support this frequency change, and therefore, an influence of the STM tip in the process, aided by surface strain due to neighboring defects, is considered. This opens the possibility to investigate manipulation of individual dimers by the tunneling tip (irrespective of whether vicinity to a defect is necessary). Further experiments are required to study the influence of the tunneling parameters on the dimer flipping and the feasibility of such manipulation. In particular, we will investigate the dependence of the dimer flipping on bias voltage and tunneling current and whether some control of the observed effect by targeted local variation of the tunneling parameters can be obtained. If, however, an intrinsic process underlies the observed behavior, this would be of technological importance for III-V epitaxy. Theoretical analysis could provide valuable additional insight by quantification of the energies involved in the processes.

ACKNOWLEDGMENTS

The authors would like to acknowledge helpful discussions with W. G. Schmidt, H. Eisele, Ph. Ebert, F. Große, and S. Gemming. This work was supported by the BMBF (Project No. 03SF0329C).

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