Scanning-tunneling-microscopy study of InP(001) surfaces prepared by UHV decapping of metal-organic vapor-phase-epitaxy-grown samples

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In this study we report on an investigation of the microscopic structure of InP(001) surfaces grown by metal-organic vapor-phase epitaxy (MOVPE). InP(001) homoepitaxial layers were grown in a MOVPE reactor and capped *in situ* with a P/As sandwich layer by photodecomposition of the phosphine and arsine precursors in the gas phase. The passivated samples were transferred through atmosphere into a separate UHV system. After thermal desorption of the capping layers, a clear (2×4) LEED pattern was achieved. STM images show large, flat surface areas. Images with atomic resolution reveal a (2×4) surface structure corresponding to an In-rich surface. The microscopic surface structure is discussed in the light of recently proposed structure models. [S0163-1829(96)52016-3]

Despite the technological importance of InP(001), the microscopic structure of this surface is still unclear. InP(001) has not yet been characterized in much detail by surface sensitive techniques because the growth of InP is performed by metal-organic vapor-phase epitaxy (MOVPE) to a very large extent. This requires growth equipment and conditions totally incompatible with ultrahigh-vacuum (UHV) standards, which, on the other hand, are of crucial importance for a thorough surface analysis under well-defined conditions. Studies of InP(001) surfaces thus rely so far on preparation by ion sputtering and annealing.[1–6] By this method In-rich surfaces of (4×1), (4×2), and c(8×2) reconstructions have been prepared.[1,3,5] However, it is well known that the sputter/anneal process leads to nonideal surfaces due to P depletion of the near surface region,[1,5] and consequently direct characterization of as-grown InP(001) surfaces would be much more favorable. *In situ* reflection high-energy electron diffraction (RHEED) experiments, for instance, performed on InP(001) in a standard molecular-beam epitaxy (MBE) setup (using InP material as an evaporation source for P supply) yielded (2×4) reconstructions, after P as well as after In supply.[7] As another attempt the cleaning of InP(001) surfaces by annealing in an As flux was reported,[8] which, however, leads to the formation of an InAs-surface layer by a P-As exchange reaction. For analyzing as-grown InP(001) surfaces, the incompatibility between growth equipment (especially in case of the standard MOVPE growth technique) and analysis equipment must be overcome. This could be achieved by an effective surface passivation technique, which would enable the sample transfer through atmospheric surrounding from growth to UHV-analysis apparatus. For GaAs(001) surfaces, for example, such a surface passivation by a thick As layer is known to work well.[9] For InP, however, neither P nor As passivation layers can be used for surface protection. P passivation layers are very reactive under atmospheric conditions, whereas a P-As exchange reaction at the surface occurs during thermal re-evaporation of the As cap.[10,11]

Previous experiments using plasma-stimulated MOVPE have indicated that a P/As sandwich cap layer, i.e., an As cap on top of a P interlayer in order to stabilize the InP(001) surface layer, might solve the InP passivation problem.[11] In the present study the group-V precursors were decomposed in the gas phase for deposition of the P and As capping layers by photodecomposition using an excimer laser source.[12] Here we focus on the surface structure and quality of decapped InP(001) MOVPE-grown samples. Nominally undoped InP layers were homoepitaxially grown by MOVPE and capped by a P layer followed by an As layer. After capping and intermediate storage under nitrogen atmosphere for several days, the samples were inserted into an UHV chamber equipped with STM, a cylindrical mirror analyzer (CMA) for Auger analysis, and a LEED system. Clean surfaces were prepared by thermal desorption of the As/P cap. LEED patterns of the decapped InP(001) surfaces were recorded using a four-grid reverse-view LEED optic equipped with a digital video camera. The STM images were taken in constant current mode. The bias values refer to the sample voltage with respect to the tip held at virtual ground. All measurements were performed at a base pressure below 1×10^{-10} mbar.

The preparation of the surface was performed by annealing the sample in several steps from 300 to 550 °C, while monitoring the pressure rise during annealing and the changes in the LEED patterns after cooling to room temperature for each annealing step. The desorption of the As/P cap layer is indicated by a large pressure increase followed by a decrease during annealing to approximately 400 °C. Thereafter, a diffuse (1×1) LEED pattern is observed. Subsequent annealing to around 480 °C produces a (2×4) pattern (Fig. 1). The (1×4) spots appear sharp and intense whereas in between the (1×4) rows stripes occur with intensity maxima at the (2×4)-spot locations. This LEED pattern indicates the presence of a nonideally ordered (2×4) symmetry, i.e., in competition with local c(2×8) regions. With regard to the orientation of the InP substrate wafer, the fourfold symmetry occurs along the [110] direction, the twofold symmetry along [$1\bar{1}0$]. After decapping, no significant traces of As, C, or O contaminations could be detected by Auger-electron spectroscopy (AES). Further annealing to even higher temperatures causes degradation of the surface, the spot intensities of the (2×4) pattern are diminished at the cost of an increasing

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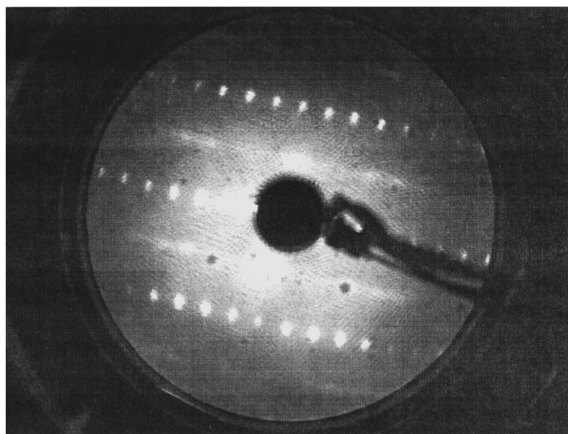

FIG. 1. (2×4) LEED pattern observed after decapping of the InP(001) sample by annealing to 480 °C. The fourfold symmetry is along the [110], and the twofold symmetry along [1$\bar{1}$0] direction, respectively. The pattern is obtained at an electron energy of 62 eV after cooling the sample to room temperature.

diffuse background. No other surface reconstructions could be prepared by the annealing process. Finally, visual inspection of the degraded sample reveals surface roughening, which can safely be attributed to the formation of In droplets being responsible for worsening the surface quality at prolonged annealing above 500 °C.

Figure 2 shows a large-scale STM image (1000×866 Å^2) of a sample having a LEED pattern of optimum quality. At a sample bias of −3 V filled surface states are imaged. The surface consists of several large, atomically flat terraces. The step height at the terrace edges corresponds to one double-layer step, i.e., the minimum height difference between two equivalent (001) planes. On the terraces, long, straight rows are observed separated by 16.6 Å, corresponding to the fourfold symmetry along the [110] direction. The straight rows extend over large parts of each terrace without noticeable

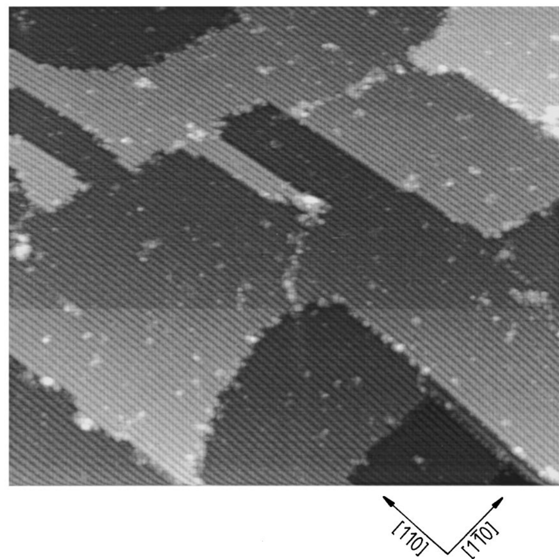

FIG. 2. STM image obtained after decapping of the InP(001) sample. The scan area is 1000×866 Å^2, sample bias is −2.9 V. The bright rows are separated by 16.6 Å corresponding to the fourfold lattice constant.

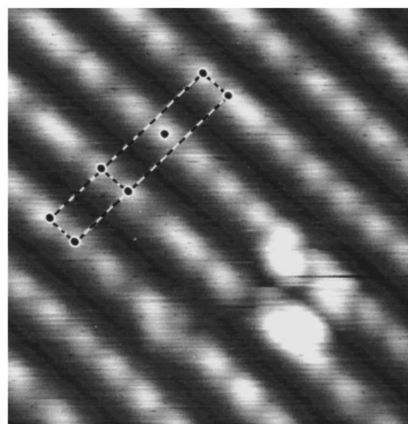

FIG. 3. High-resolution STM image, scan area is 80×80 Å^2, sample bias is −2.9 V. Corrugation maxima in the bright rows are clearly resolved separated by 8.3 Å corresponding to the twofold lattice constant. As indicated by the dashed surface unit cell, $c(2\times8)$ regions exist on the mainly (2×4)-ordered InP(001) surface.

irregularities. A high-resolution STM image is shown in Fig. 3. On a scale of 80×80 Å^2, additional corrugation in the bright, straight rows is clearly resolved exhibiting twofold periodicity along [110]. No regular structure, however, can be resolved in the dark lines separating the bright rows. On the high-resolution scale local irregularities are clearly resolved, which are due to the coexistence of (2×4) and $c(2\times8)$ regions as already indicated by the LEED pattern.

The STM images demonstrate unambiguously, that clean, atomically ordered (2×4) reconstructed InP(001) surfaces can be prepared in UHV using the P/As capping-decapping technique for MOVPE-grown samples. Although the detailed atomic structure of the surface is not yet clear, one should expect with almost certainty that the surface is an In-rich one. This conclusion is strongly suggested by the finding that during the annealing process at higher temperatures this surface structure coexists with In droplets on the surface. Furthermore, HREELS experiments after low H dosage on the (2×4)-InP(001) surfaces show only H-In but no inclination of H-P vibrations, as expected for In-rich surfaces.[13] For In-rich InP(001) surfaces, a (4×2) structure[1–6] as well as a (2×4) structure[6,7] have been reported and atomic structure models have been suggested. The (4×2) structure is explained in analogy to the Ga-rich GaAs(001) (4×2) surface structure[14,15] as consisting of a regular arrangement of In dimers and missing In dimers.[2] This type of surface structure, however, can be ruled out for the InP(001) (2×4) surface from the orientation of the LEED and STM patterns with respect to the [1$\bar{1}$0] and [110] direction of the substrate. Consequently, this structure model does not explain the results of our study. For the In-rich (2×4) surface recently a structure model was suggested based on In trimers terminating the surface and P dimers in the second layer.[6] This model could explain both the LEED and STM results obtained on the decapped InP(001) surface. The bright rows in the STM image would then be attributed to the charge accumulated in the filled dangling bonds of the second-layer P dimers. The twofold periodicity would arise from the dimerization of the second-layer P along the [1$\bar{1}$0] direction, the fourfold one to

the separation of the second-layer P dimers by In trimers along the [110] direction. The $c(2\times8)$ structure could be derived by a slight modification of the (2×4) one, just by shifting two adjacent P-dimer rows by one lattice constand along the $[1\bar{1}0]$ direction, similar as previously proposed for the $c(2\times8)$-reconstructed GaAs(001) surface.[15] However, it must be pointed out that the interpretation of our STM results in terms of microscopic surface structures is very tentative at present and needs further clarification.

In conclusion, we have investigated MOVPE-grown InP(001) surfaces by LEED and STM under UHV conditions. To our knowledge, for the first time we were able to obtain atomically resolved STM images of the clean, well-ordered InP(001) surface showing a rowlike surface structure of (2×4) symmetry. We have demonstrated that the As/P capping is a versatile technique to protect MOVPE-grown InP surfaces against contamination during transport through air. Thus, this technique allows one to study the InP(001) surface properties in detail by UHV-based surface analytical methods.

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