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# Atomic scale structure of InAs(001)-(2 × 4) steady-state surfaces determined by scanning tunneling microscopy and density functional theory

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## Abstract

The structure of InAs(001)-(2 × 4) surfaces equilibrated under typical MBE conditions is studied by scanning tunneling microscopy (STM). Depending on the magnitude of the As flux, typical surfaces are found to contain a mixture of  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$  reconstructions. The relative populations of the  $\alpha 2$  and  $\beta 2$  reconstructions are found to depend on substrate temperature and the magnitude of the As flux. The atomic-scale details of the reconstructed units on these mixed-phase surfaces are definitively determined by comparing atomic-resolution dual-bias STM images to first-principles calculations. The imaging mechanism for revealing atomic-scale details, particularly the trench dimer, is found to be qualitatively similar to that for GaAs, although the effect is less pronounced. Additionally, a significant population of ad-atom related structures are observed on quenched surfaces, apparently unrelated to any equilibrium ad-atom population. © 2001 Published by Elsevier Science B.V.

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Identifying the low energy surface reconstructions for the (001) surfaces of arsenide-based compound semiconductors (GaAs, InAs, and

AlAs) has been a matter of intense research for several decades, particularly in the (2 × 4) regime relevant for typical device growth [1–4]. While most effort has focussed on GaAs, InAs has become of particular interest recently as part of the nearly lattice-matched “6.1 Å” family of materials, including GaSb and AlSb. The question of how surface atoms rearrange within the unit cell observed by electron diffraction is not only a question of academic interest: for the 6.1 Å materials, the

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stoichiometry of the reconstructed surface can also have implications for interface roughness in device heterostructures [5].

A variety of possible structural units have been proposed for the anion-rich surfaces of InAs(001) and GaAs(001)-(2 × 4) [2]. The most definitive structural determinations for InAs have been made using X-ray diffraction techniques [6], although these studies typically relied on sputter/anneal-type preparation techniques for sample preparation, rather than a true MBE environment. Recently, the  $\beta 2(2 \times 4)$  structure has been definitively determined by STM and first-principles calculations to be the lowest energy reconstruction on GaAs(001) that is relevant for MBE growth of device material [7]. Significant work has been done by Yamaguchi and Horikoshi [4] on MBE grown InAs(001)-(2 × 4) surfaces using in vacuo STM, suggesting that the primary structural units in the (2 × 4) regime are the  $\beta 2(2 \times 4)$  and  $\alpha 2(2 \times 4)$  structures. However, these studies, while compelling, lack conclusive evidence for the atomic scale details of these structural units, and do not address the issue of thermodynamic stability. It has been predicted by ab initio theory [8] that the (2 × 4) growth regime in fact comprises two *thermodynamically stable* (2 × 4) structures:  $\beta 2(2 \times 4)$  and  $\alpha 2(2 \times 4)$ .

In this work we present experimental observations of these structures on InAs using atomic-resolution STM measured on whole substrates in a true MBE environment. Significantly, the atomic details, including trench structures, in both  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$  have been imaged for the first time in both filled and empty states (i.e. in dual-bias imaging mode). We confirm our identification of these structures as  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$  units by comparing to theoretical images generated from the electronic wave functions that were obtained from density-functional theory (DFT) calculations [8]. We also demonstrate that the novel low-bias mechanism for imaging the  $\beta 2(2 \times 4)$  reconstruction on GaAs [7] is also applicable to imaging the (2 × 4) reconstructions on InAs.

InAs surfaces were prepared using a VG 80H MBE chamber and transferred in vacuo to a connected UHV chamber containing a full-wafer

Omicron STM [9]. Prior to stabilizing the surfaces for reconstruction studies, 0.5–1  $\mu\text{m}$  thick, unintentionally doped InAs layers were grown on 0.05° miscut n-type (undoped) InAs(001) substrates at 450 °C. Group III fluxes were measured using RHEED oscillations during growth, and group V incorporation rates were measured using the method of uptake oscillations [10,11]. Temperature was measured using a thermocouple calibrated using an in situ pyrometer. To ensure that the surfaces were well equilibrated, all surfaces were cooled at  $\sim 3$  °C/min from the growth temperature to the stabilization temperature. As the substrate temperature was lowered, the incident As<sub>2</sub> flux was stepwise changed to the target flux for the anneal. After a period of time at the anneal temperature (typically 20 min, unless otherwise noted) the surfaces were quenched by simultaneously cutting the heater power, rotating the sample away from the effusion cells, valving off the As<sub>2</sub> source, and removing the samples quickly from the growth chamber. From 380 °C the quenching rate is estimated to be  $\sim 3$  °C/s using this method, as judged by in situ pyrometry measurements. Given the background As pressure of <0.005 ML/s (estimated by uptake measurements with the sample facing the effusion cells) we might expect changes in As coverage due to adsorption of no more than  $\sim 5\%$ . All filled- and empty-state STM images were acquired in constant current mode using bias voltages between 1.1 and 3.0 V and tunneling currents between 0.03 and 0.2 nA.

Simulated STM images were computed from the surface local density of states (LDOS) using the method of Tersoff–Hamann [12]. These surface LDOS were obtained from DFT calculations of fully relaxed surface structures, in the local-density approximation (LDA), using norm-conserving pseudopotentials [13,14], and the computer code FHI98MD [15]. The electronic wave functions were expanded in a plane wave basis that was truncated at a cutoff energy of  $E_{\text{cut}} = 12Ry$ . The equivalent of  $8 \times 8$   $k$ -points in a  $1 \times 1$  cell are used for  $k$ -point summation, generated according to the scheme proposed by Monkhorst and Pack [16].

The surface structure of InAs appears to be very dynamic in character within the temperature and pressure regime common to device growth. That

this is true during growth is not particularly surprising. However, we have found this to be the case even under “equilibrium” conditions, where a sample is annealed at constant temperature while exposed to a steady state As flux that stabilizes the surface in the  $(2 \times 4)$  phase region. This is illustrated in Fig. 1(a), where we show a sample that was annealed at 380 °C for 30 min while exposed to a constant As<sub>2</sub> flux of  $\sim 0.08$  ML/s. The surface is composed of a variety of reconstruction-related features as well as larger structures. The relative proportions of these various structures depends on anneal temperature and As flux, as illustrated by comparison of Fig. 1(a) and (b) (as a function of temperature) and Fig. 1(c) and (d) (as a function of As pressure). For instance, the relative proportion

of  $\alpha 2(2 \times 4)$  units on the surface increases as either the As<sub>2</sub> pressure is decreased or substrate temperature is increased. We discuss the larger, bright features that occur atop and between the rows later in the paper.

In Fig. 2(a) and (b), we present high-resolution experimental STM images of the  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$  structural units, respectively, occurring within the regime of flux and temperature we have studied. We find excellent agreement between the predicted, Fig. 2(c) and (d), and measured images, allowing for some tip-induced broadening of the features in the measured images. The trench dimers are well-resolved for both  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$ , and the corrugation due to the supporting In atoms on the  $\alpha 2(2 \times 4)$  structure are

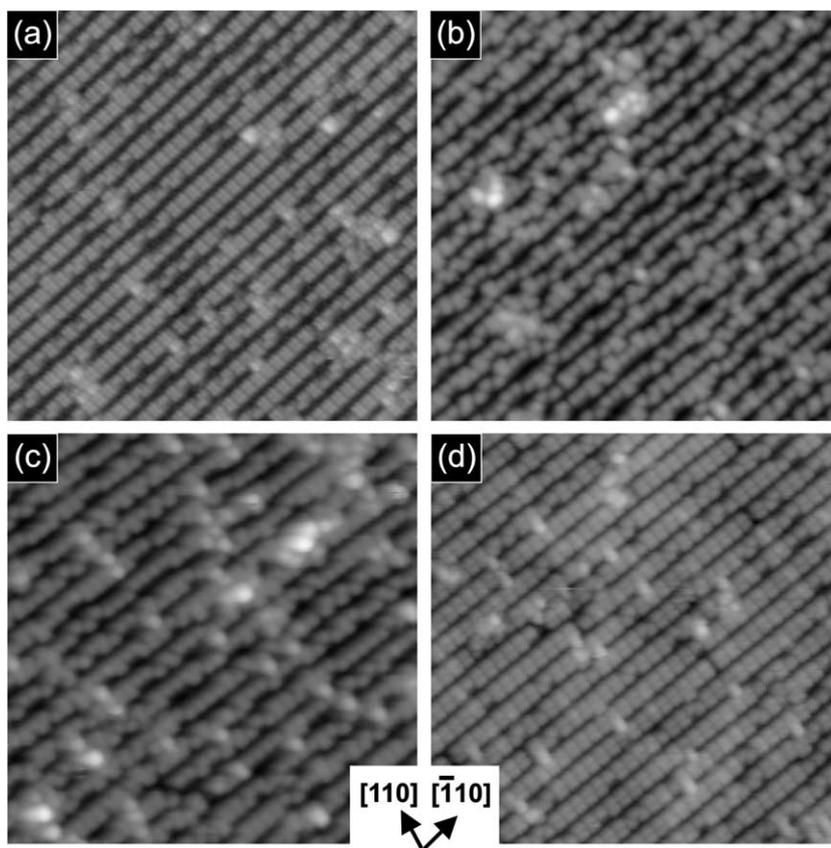


Fig. 1. STM images showing reconstruction-level detail for InAs(001) surfaces annealed for 20 min as a function of: (top) substrate temperature at a constant As flux of 0.08 ML/s: (a) 380 °C and (b) 440 °C and (bottom) as a function of varying As flux at constant substrate temperature of 420 °C: (c) 0.01 ML/s and (d) 0.8 ML/s. All images are taken in filled-states,  $30 \times 30$  nm<sup>2</sup>.

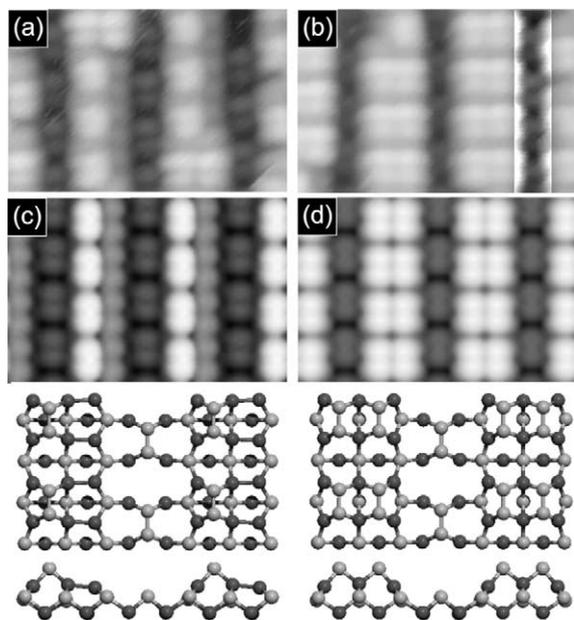


Fig. 2. STM of  $\beta 2(2 \times 4)$  and  $\alpha 2(2 \times 4)$  structural units on InAs(001) under filled states tunneling conditions (a and b), compared to simulated images from DFT (c and d). Below each experimental-simulated image pair is a model for the  $\beta 2(2 \times 4)$  and  $\alpha 2(2 \times 4)$  structures created using relaxed coordinates from the DFT calculation. Dark balls represent In atoms, light balls represent As atoms.

distinctly observed. The excellent agreement we find between experiment and simulation lead us to conclude that we have definitively determined the structure of the reconstructions present on the InAs(001)-(2 × 4) surface.

Fig. 3 illustrates the effect of bias on the resolution observed with STM, in both empty and filled states. For filled states, we find that the resolution effectively increases at lower biases, allowing clearer imaging of the trench structures. This is an illustration of the imaging mechanism discovered first on GaAs [7], that can allow imaging of certain surface features within one range of bias voltage that, due to combined steric and electronic effects, are unobservable outside of that bias range. For the case of InAs and GaAs, the dangling bond orbitals from the top dimers extend spatially over the trench, with the higher energy states extending more than lower lying states. At higher biases, the top-dimer dangling

bond orbitals effectively shield the tip from accessing the dangling bond states of the trench dimers. At lower biases, however, the tip interacts with a surface of constant density of states that is effectively closer to the atomic cores of the top dimers, and the steric interference that they presented at higher biases is relieved and hence the trench dimers can be imaged. The effect is less pronounced in InAs relative to GaAs, presumably due to the larger lattice parameter, but it is nevertheless visible.

The resolution appears to be somewhat diminished in empty states relative to filled states, for reasons that, at present, are unclear. However, we find a weaker effect of bias, with slightly improved resolution at lower biases. Interestingly, it is primarily As dimer features that appear to be affected. As indicated in Fig. 3(d), on  $\alpha 2(2 \times 4)$  at lower biases we clearly observe sharp features in empty states that are associated with the In dangling bonds on the row edge. However, at all positive bias voltages we investigated the top dimers are rather indistinct and the trench dimers completely absent.

Aside from the reconstructed units on the surface, we find that there are numerous larger, non-periodic defect structures such as trench-filling defects (TFDs) and bright “on-row” features that appear to sit either symmetrically or asymmetrically atop the dimer rows, as well as more extended, island-like structures. These structures have been observed previously on quenched growth surfaces [17], and their presence on these annealed surfaces as well as on surfaces quenched much more rapidly [18] indicates that they may be *intrinsic* features. In Fig. 3(b) and (e), we highlight a TFD, one of the simplest of these features. Interestingly, both the apparent height of the feature ( $\sim 1.5$  Å) and its symmetry relative to the top row As dimers indicates that it resides on the group III sublattice, and as such may represent an In dimer. Absent from the image, however, is any indication of what atomic substructure might be present underneath it. We are currently calculating the stability of several candidate structures using DFT. The structure of the “on-row” features is even less clear, as they appear quite diffuse in both filled and empty states, and hence even fewer structural de-

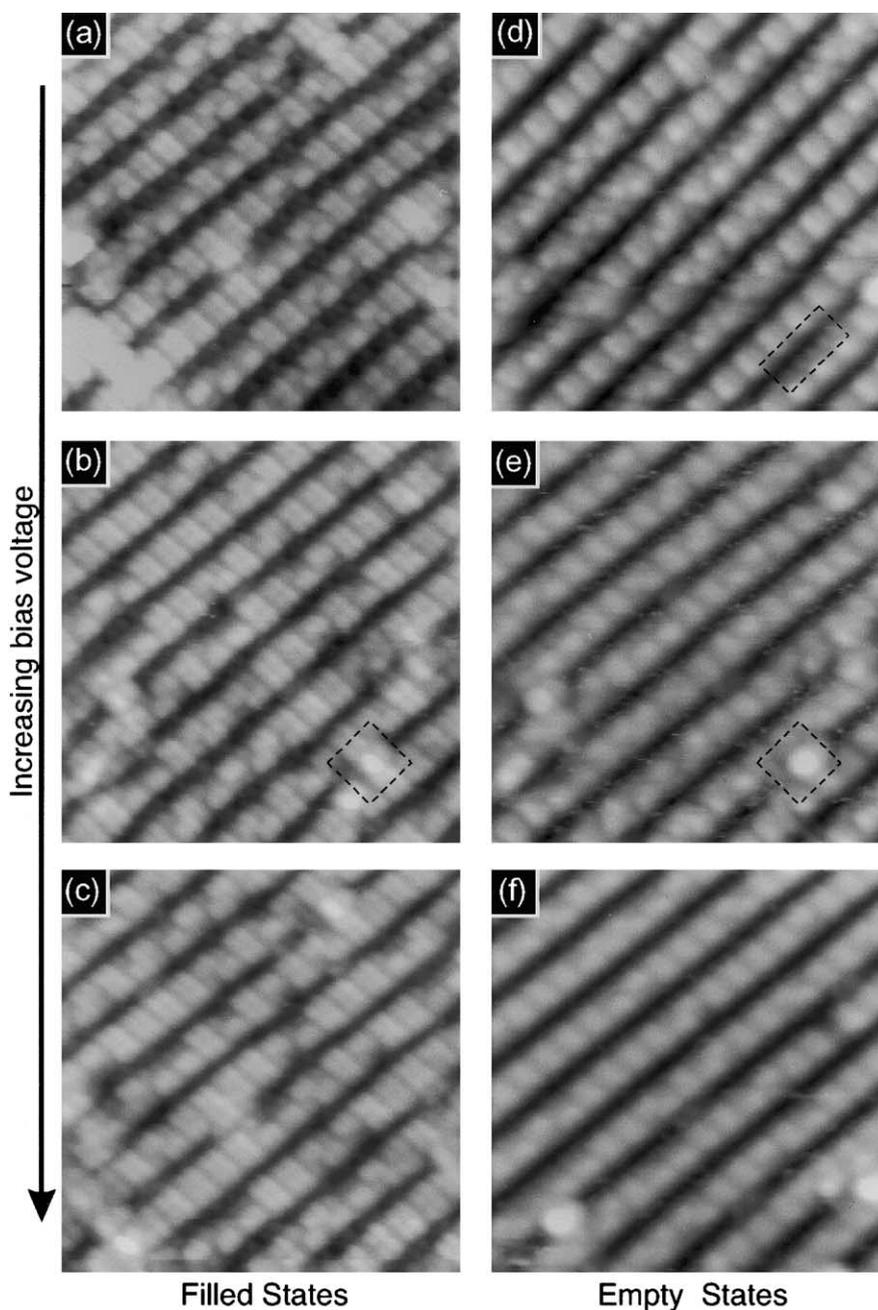


Fig. 3. Bias dependent imaging of the  $(2 \times 4)$  surface illustrated using high-resolution images in filled states: (a) 1.2 (b) 1.5 and (c) 2.0 V, and empty states: (d) 1.2, (e) 2.0 and (f) 2.5 V. Note that (b) and (e) are a matched dual-bias pair of the same area of the surface. Some tip-dependent distortion is also evident in the dimer units as the bias is decreased. Note in (d) sharp features arising from In dangling bonds in the trench. Also in (b) and (e) we indicate TFD structure. Anneal conditions for this sample are those listed for Fig. 1(a).

tails can be gleaned from the images. However, our STM images of these features are not consistent

with DFT-based simulated images of structures (not shown) such as simple single or dimerized In

atoms sitting in either bonding or non-bonding configurations atop the rows. In these cases, ad-atoms and ad-dimers appear as rather localized features that should be easily distinguished in STM. Another possibility is that these features may represent clusters of In atoms in a local bonding configuration that gives rise to a LDOS that is more metallic than covalent, and hence is less localized in nature.

Although these defect structures appear to be intrinsic to the surface, their source is at present unknown. It is possible that they may condense from an equilibrium ad-atom population during the quenching process. If this is the case, then the fact that we observe fewer of the extended structures at lower temperatures and higher As fluxes is in agreement with previous observations on GaAs by Johnson et al. [19] who found that the density of quenched ad-atoms followed the same trend. However, unlike the observations on GaAs, these extended structures, while sometimes spanning several dimer rows, fall short of appearing as *reconstructed* islands, even when quenching from the highest anneal temperatures we investigated (440 °C). Additionally, the quantity of smaller structures (particularly TFDs) does not appear to depend on the As flux during the anneal. It is also possible, therefore, that these structures may have formed at the growth temperature of 470 °C, and persisted during the subsequent slow ramp of the substrate temperature to the anneal temperature. Our preliminary calculations show that certain features, such as In ad-dimers, are remarkably stable on the surface, and at lower temperatures may prove quite difficult to equilibrate with sources and sinks on the surface such as step-edges. Once formed, these structures might persist even after a ramp as slow as 1 °C/min and/or longer anneals.

In conclusion, we have studied the structure of the MBE-grown InAs(001)-(2 × 4) surface using in vacuo UHV STM. By comparing to images simulated from ab initio DFT calculations, we find that typical surfaces contain a mixture of  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$  structures. The proportion of  $\alpha 2(2 \times 4)$  relative to  $\beta 2(2 \times 4)$  on the surface depends on the substrate temperature and the mag-

nitude of the incident As<sub>2</sub> flux. We find that the same imaging mechanism operates on this surface as it does on GaAs, enabling the details of the  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$  unit cells to be more easily imaged at lower biases. Finally, we observe significant numbers of defects, possibly related to ad-atoms or ad-dimers, that appear to be intrinsic to annealed InAs(001) surfaces.

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