Absence of long-range ordered reconstruction on the GaAs(311)*A* surface

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We have investigated the decapped GaAs(311)*A* surface using both scanning tunneling microscopy and synchrotron-radiation photoemission. While our data are in broad agreement with the structural model of GaAs(311)*A* proposed in a recent study [Wassermeier *et al.*, Phys. Rev. B **51**, 14 721 (1995)], we find considerable differences in the surface order. In particular, the As dimer rows are unbroken over much shorter length scales and are highly kinked. We observe a correspondingly lower degree of anisotropy in the surface roughness than that previously reported. An (8×1) reconstruction was not observed. An analysis of As $3d$ and Ga $3d$ core-level photoemission spectra suggests that surface As atoms are in only one bonding configuration while surface Ga adopts two different bonding states. We discuss possible origins for the core-level spectra surface components. [S0163-1829(97)01420-3]

A number of methods for the direct fabrication of low-dimensional semiconductor structures during epitaxial growth have been proposed.[1,2] The structures formed using these methods are said to be ''self-assembled'' as no *ex situ* lithographic patterning or processing is required in their production. An extremely low defect density and associated high optical efficiency is therefore expected for the *in situ* grown, self-assembled structures. Most recently, an intense experimental and theoretical research effort has been devoted to investigating the formation and properties of coherently strained InAs islands on GaAs(001) substrates.[3,4] These islands are sufficiently small to exhibit strong electron confinement effects and are therefore effective quantum dots.

The formation of ultra small InAs islands on GaAs(001) occurs via the Stranski-Krastanow mode of growth. Prior to exploiting this growth mode for quantum dot formation, an alternative method for self-assembled nanostructure formation was proposed by Nötzel *et al.*[1] The direct synthesis of quantum wire structures on non-(001)-oriented GaAs substrates was proposed based on reflection high-energy electron-diffraction (RHEED) observations of periodic faceting of the GaAs(311)*A* surface. However, a number of independent measurements, in particular, the recent scanning tunneling microscopy (STM) study of Wassermeier *et al.*[5] did not support the facet induced GaAs(311)*A* surface corrugation suggested by Nötzel *et al.*[1]

A study of the structure and bonding at GaAs(311)*A* surfaces is required to understand the phenomena described above and, more generally, epitaxial growth processes on high index planes. Information on the geometric and electronic structure of GaAs(311)*A* is limited and the effects of annealing on surface bonding and stoichiometry are not known. In this paper we report a scanning tunneling microscopy (STM) and synchrotron-radiation photoemission investigation of decapped GaAs(311)*A* surfaces annealed over a 350–500 °C temperature range.

The samples used in this study were grown by molecular-beam epitaxy (MBE) at a temperature of 580 °C on GaAs(311)*A* substrates oriented to within $\pm0.5°$. 500-nm-thick epilayers were grown with a Si-doping density of 5×10^{17} cm^{-3}. Following growth the sample was cooled to 300 °C in an As_4 overpressure. The As Knudsen cell was switched off, the sample cooled to -30 °C overnight, and a protective amorphous As (''capping'') layer was then deposited. The sample was then removed from the MBE growth chamber and transported through air to the STM or photoemission UHV system. Clean GaAs(311)*A* surfaces were prepared by thermally desorbing the As cap. We have previously used a very similar capping and decapping procedure to prepare GaAs(001) and GaAs(111)*B* surfaces for STM studies.[6,7] In both cases the surface quality was comparable to that of samples that were grown and transferred to a STM without As capping or breaking the ultrahigh vacuum. In our case, therefore, the decapping procedure does not induce the formation of defects.

The STM experiments were carried out using a commercially available instrument[8] with electrochemically etched *W* tips cleaned by electron bombardment. Photoelectron spectra of the surface were taken on beam line 6.2 of the synchrotron radiation source (SRS), Daresbury, U.K. The synchrotron radiation was monochromatized by a toroidal grating monochromator and the energy distribution of the photoelectrons measured using a VG ADES 400 spectrometer. A photon energy of 90 eV was chosen for core-level analysis with overall instrumental resolution at this energy being approximately 0.30 eV.

Figures 1(a) and 1(b) are filled state STM images of the decapped GaAs(311)*A* surface following annealing at 400 °C. The surface consists of short, meandering rows of

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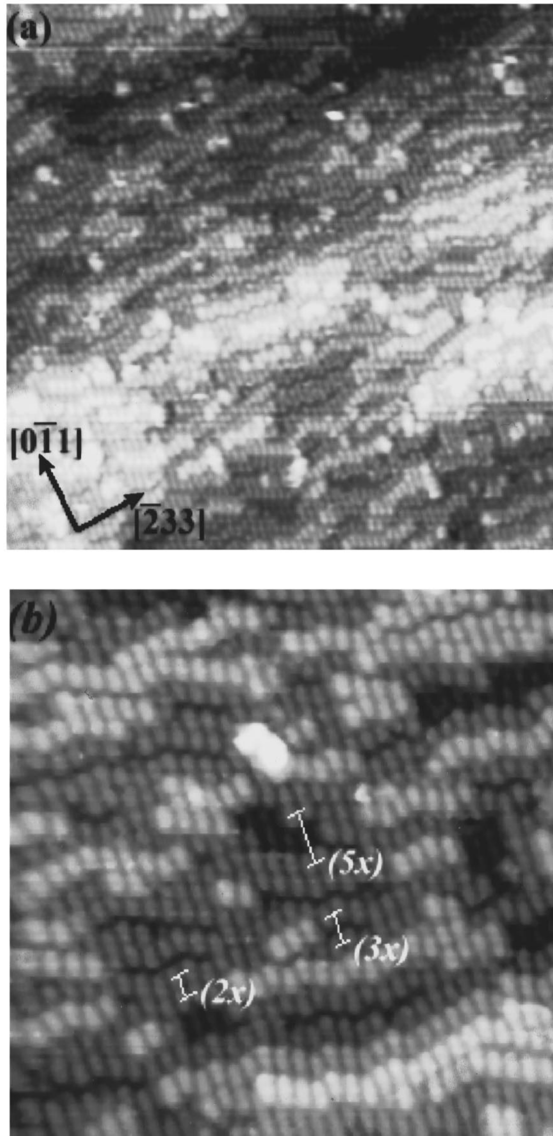

FIG. 1. (a) 450×450 Å^2, and (b) 200×200 Å^2 filled states (−3.5 V, 100 pA) images of the decapped GaAs(311)*A* surface. Arsenic dimer rows having separations of 2×, 3×, and 5× the unreconstructed (311)*A* surface lattice constant along [0$\bar{1}$1] are highlighted in (b).

features that predominantly run along the [$\bar{2}$33] direction. Features within the rows, clearly visible in the high-resolution image of Fig. 1(b), are separated by 6.6±0.2 Å. From both Figs. 1(a) and 1(b) it is clear that the surface is not particularly smooth on the atomic scale with up to a 5-ML height variation visible in the 450×450-Å^2 scan.

Wassermeier *et al.*[5] recently presented a detailed, high-resolution STM study of GaAs(311)*A* which showed that the surface formed an (8×1) reconstruction characterized by a dimerization of As atoms in the uppermost layers. Their study conclusively demonstrated that the anisotropy in the transport and optical properties reported for AlAs/GaAs(311)*A* interfaces arose not from periodic faceting, as previously suggested,[1] but from the highly anisotropic nature of this reconstruction. Note that the surfaces prepared by Wassermeier *et al.* exhibited a much higher degree of ordering than that visible in Fig. 1. Rows well aligned with the [$\bar{2}$33] direction were seen to extend, uninterrupted, over distances of, typically, 1000 Å. In this study, as evident from Fig. 1, the length of an individual row running along [$\bar{2}$33] rarely exceeds 150 Å. The surface roughness we observe is therefore considerably less anisotropic than that noted by Wassermeier *et al.*[5] Furthermore, a well-defined row separation of 32 Å (along [0$\bar{1}$1]) was reported in Ref. 5. Considering the ideal, unreconstructed GaAs(311)*A* surface unit cell, this 32-Å value corresponds to an 8× periodicity. It is clear from Fig. 1 that although there is a distinct periodic structure along [$\bar{2}$33], we observe no evidence for a 32-Å periodicity in the [0$\bar{1}$1] direction. We believe, as discussed below, that the differences between our STM data and that presented by Wassermeier *et al.* most likely arise from variations in growth conditions.

Wassermeier *et al.*[5] explained the 8× periodicity observed in their images in terms of a surface reconstruction that was derived from electron counting principles. Although we do not observe the 8× periodicity and therefore the model proposed by Wassermeier *et al.*[5] is not directly applicable to the images shown in Fig. 1, some structural features are common to both sets of STM data. Chadi[9] has shown that dimerization of As atoms on GaAs(311)*A* considerably decreases the surface energy. Individual features resolved within the rows in Fig. 1 may be identified with As dimers.

The lateral separation of neighboring As dimer rows in consecutive surface layers is approximately 10 Å, in good agreement with the value measured by Wassermeier *et al.*[5] However in our case, due to a much higher degree of disorder, the separation of neighboring As dimer rows in the *same* surface layer (i.e., those having the same contrast level) varies quite considerably. In Fig. 1(b) regions of third layer As dimer rows having a separation of approximately 12 (the value measured by Wassermeier *et al.*), 20, and 8 Å are highlighted. In terms of the unreconstructed (311)*A* surface, these values represent a 3×, 5×, and 2× periodicity, respectively. The latter value is that expected for a fully dimerized (311)*A* surface with no vacancies between the dimer rows. From electron counting principles we would not expect to observe large areas consisting solely of 8-Å-spaced As dimer rows. This is verified in our STM images.

It has been suggested that the presence of periodic faceting implied by the RHEED studies of GaAs(311)*A* by Nötzel *et al.*[1] arose from growth under As-deficient conditions.[10] We note that for annealing temperatures up to 600 °C there was little change in the general morphology of the decapped GaAs(311)*A* surface and no evidence for the formation of periodic faceting.

Core-level photoelectron spectra from the decapped GaAs(311)*A* surface, decomposed into bulk- and surface-derived components, are shown in Fig. 2. The fitting parameters (Table I) were within the range of previously reported values for decapped GaAs surfaces,[11,12] except for the Gaussian widths which were significantly broader than those reported for either the GaAs(001) (Ref. 11) or GaAs(111)*B* surfaces.[12] It is likely that the high degree of surface disorder observed in the STM images leads to large surface-potential variations and this contributes to the broader Gaussian widths.

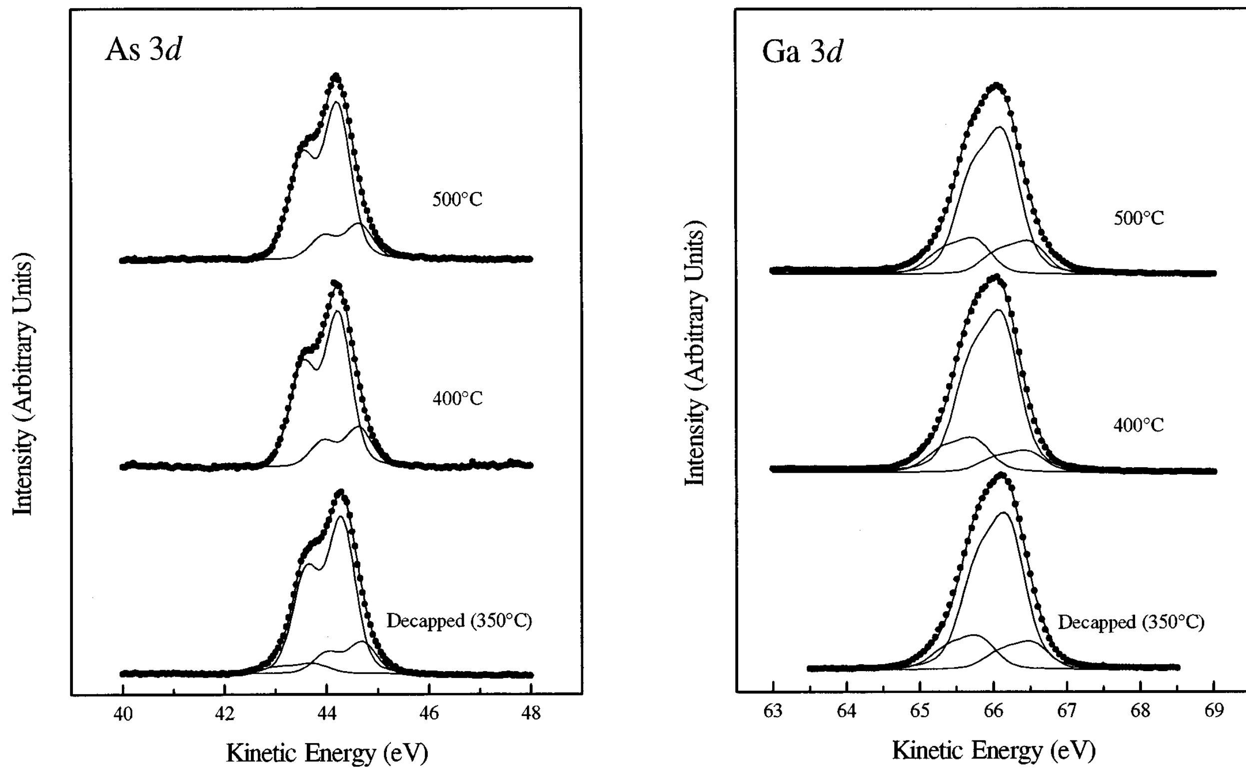

FIG. 2. (a) Arsenic $3d$ and (b) gallium $3d$ core-level spectra from the decap GaAs(311)A surface annealed at various temperatures. The photon energy was to 90 eV.

The As $3d$ spectra can be fitted, following the 400 °C anneal, with a single surface component with a binding energy (BE) of -0.40 eV relative to the bulk As-Ga peak. A component observed at higher relative BE (+0.56 eV) in the spectrum directly following decapping may be attributed to excess amorphous As remaining from the cap. The lack of a surface component at higher relative BE in the As $3d$ spectra following annealing above 400 °C suggests that reconstructions involving chemisorbed arsenic atoms [as are observed for GaAs(001)-$c(4\times4)$ (Ref. 13) or GaAs(111)B-(2×2) (Ref. 14)] do not form on GaAs(311)A. This observation strengthens the argument that the rows in the STM images are due to dimerization of As atoms in the uppermost surface layers.

Two surface components at relative binding energies of -0.39 and 0.35 eV are present in the Ga $3d$ spectra following annealing in the 350–500 °C range. This is indicative of two separate bonding configurations for surface Ga atoms. For the GaAs(311)A surface structure model proposed by Wassermeier *et al.*[5] there are in fact two slightly different bonding environments for Ga atoms in the second and third atomic layers. However, it should be stressed that if the GaAs(311)A surface observed in the STM images of Fig. 1 conformed to electron counting principles we would not expect to observe two Ga surface components in the Ga $3d$ photoemission spectra. The electron counting rule dictates a transfer of charge from Ga to As dangling bonds and (in an initial-state picture) we should therefore only observe a Ga surface peak at higher relative BE. The Ga $3d$ surface component at -0.39 eV may in fact be related to emission from the large number of defect sites that are present (due to surface disorder) on the decapped GaAs(311)A surfaces we have investigated.

TABLE I. Fitting parameters for the GaAs(311)A surface Ga $3d$ and As $3d$ core-level spectra.

	Ga $3d$	As $3d$
Branching ratio	0.66	0.65
Spin-orbit splitting	0.43 eV	0.69 eV
Lorentzian width	0.18 eV	0.14 eV
Gaussian width	0.45 eV	0.55 eV
Shift of high BE component	0.35 eV	0.56 eV
Shift of low BE component	-0.39 eV	-0.40 eV

From valence-band spectra of the decapped surface the Fermi level was found to be 0.8, 0.7, and 0.6 eV above the valence-band maximum (VBM) following annealing at 350 °C, 400 °C, and 500 °C, respectively. Considering the p-type doping level of the epilayer we would expect, under flat-band conditions, the Fermi level to be within 0.1 eV of the VBM. The Fermi-level position measured from the valence-band spectra directly implies the presence of surface states within the band gap. Therefore, as expected from the STM and core-level data described above, bonding configurations failing to conform to electron counting principles exist at the surface. However, as also noted by Olsson *et al.*[15] for the ion-bombarded and annealed GaAs(311)A surface, there was no photoelectron emission detected at or near the Fermi level. The states within the band gap therefore must arise from defect sites. Considering the STM images, it is clear that these defect sites are primarily disorder induced.

As noted above, we do not believe that the decapping process creates a significant number of surface defects. The difference between our results and those of Wassermeier *et al.*[5] regarding the degree of GaAs(311)*A* surface order must therefore be related to variations in growth conditions. A recent investigation into the mechanism of kink-related disorder on GaAs(001)-(2×4) surfaces[16] has indicated that the As flux during growth plays a critical role in the surface dimer row kink density. A similar As flux-dependent kinking of dimer rows on GaAs(311)*A* may occur, however, a systematic study of GaAs(311)*A* surfaces grown under various conditions is needed to develop a detailed understanding of the disordering process.

In conclusion, we have found a significant degree of disorder on MBE grown GaAs(311)*A* surfaces. Due to this disorder, a reconstruction having (8×) periodicity along the $[0\bar{1}1]$ direction was not observed. Periodic faceting of the surface did not occur under the annealing conditions used in this study. Core-level photoelectron spectra supported the previous assignment of features in STM topographs as As dimers, but suggested that a significant number of Ga atoms were bonded in arrangements failing to conform to electron counting principles. Surface states within the gap giving rise to a band bending of 0.5–0.7 eV were proposed to arise from disorder-induced atomic configurations.

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