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Comparison of the (2×2) reconstructions of GaAs{111} surfaces

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The {111} surfaces of GaAs have been examined using scanning tunneling microscopy and soft x-ray photoelectron spectroscopy and a comparison has been made between the three different (2×2) reconstructions observed. We find that both the $(111)A$ and $(111)B$ surfaces initially exhibit (2×2) ordered adstructures following the thermal desorption of an As cap, though spectroscopy shows them to be chemically inequivalent. With increasing temperature, the $(111)A$ surface is found to develop into a Ga-vacancy (2×2) structure, in many ways similar to a (110) surface. The GaAs$(111)B$ surface, however, loses its (2×2) periodicity with increasing annealing temperature, following a sequence of less As-rich structures.

I. INTRODUCTION

When compared with other orientations, the {111} surfaces of GaAs have to a large extent been overlooked with regard to their physical and electronic structure. The reasons for this are both practical and technological in that (110) surfaces are the most easily created through the exploitation of the natural cleavage plane, and in the ideal case yield nonpolar surfaces free from electronic states in the band gap. Such surfaces have, therefore, offered a useful platform from which to observe the development of gap states and Schottky barriers with the deposition of metal overlayers. The (001) surface has also been at the forefront, with much effort being expended in the study of the As-rich (2×4) reconstructed surface; that most commonly used during the molecular beam epitaxial (MBE) growth of GaAs. The understanding of the (001) surface is of obvious benefit to the crystal growth community, though using epitaxially prepared surfaces as a substrate for Schottky barrier studies has also been prevalent.[1] One area of contention has been the effect of excess As on the Schottky barrier height from decapped GaAs when compared with as-grown surfaces, though this is largely symptomatic of the influence of surface stoichiometry on the electronic and physical structure of GaAs surfaces.

A new interest in GaAs {111} has developed recently however, mainly due to the properties of epitaxial strained heterostructures grown on these surfaces. They have been demonstrated to show characteristics associated with large internal piezoelectric fields, such as a redshift in photoluminesence features, relative to identical structures grown on the (001) surface.[2] This is principally a result of a lack of inversion symmetry about the polar interface. In developing growth techniques for these structures, large differences in doping properties[3] between the GaAs $(111)A$ and $(111)B$ surfaces suggest the kinetic behavior of adatoms and dopant incorporation mechanisms are markedly different between the two.[4]

Although the bulk termination of both the {111} surfaces gives the same geometric structure, the differences in energy between having the Ga or As atoms outermost in the surface bilayer [$(111)A$ or B, respectively] become apparent when comparing the surface reconstructions. This is yet another manifestation of the relationship between surface stoichiometry and structure, though in this case it is subtly different in that Ga or As "rich" surfaces are created only by the bilayer spacing found in {111}-oriented zinc-blende crystals, and not by a distinct surface layer. Both the $(111)A$ and $(111)B$ exhibit (2×2) reconstructions, with the $(111)B$ transforming into a $(1 \times 1)_{\mathrm{LT}}$, $(\sqrt{19} \times \sqrt{19})$, and $(1 \times 1)_{\mathrm{HT}}$ phases at higher temperatures as the proportion of surface layer As diminishes.[5] A scanning tunneling microscopy (STM) study has shown two of these structures on an as-grown surface,[6] and core-level photoemission data has also been presented from the (2×2) reconstruction.[7,8] As yet, however, no conclusion regarding the physical and electronic structure has been reached, due to the differences in sample preparation and experimental detail. Interesting as the phase changes on the $(111)B$ surface are, we restrict our attention to the (2×2) reconstructions in this study.

By comparison, the $(111)A$ surface remains as a (2×2) reconstruction under a vast range of As fluxes and temperatures.[5] Some reflection high energy electron diffraction (RHEED) studies have shown temperature and flux variations in 1/2 order intensities during MBE growth,[9] while others have observed variations in the doping concentration of the epilayer,[10] and hence with the dopant incorporation rate. Furthermore, a change from layer-by-layer to a step-flow growth mode with increasing temperature has also been reported on this surface, which suggests that a change in the surface mobility of Ga adatoms occurs.[4] All of these results point to the (2×2) surface changing significantly as a function of

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temperature, yet keeping the same overall periodicity. It would appear, therefore, that the (111)A-(2 × 2) surface is considerably more complex than an initial inspection of the evidence might reveal.

Ab initio theoretical studies have predicted a number of possible (2×2) structures, which might be stable under various conditions on {111} surfaces.[11,12] Two of these have become widely accepted following scanning tunneling microscopy (STM), photoemission, low energy electron diffraction (LEED), and theoretical studies on the (111)A (Refs. 13–15) and (111)B (Refs. 6 and 7) surfaces, though as mentioned above, all of the previous experiments have used differing sample preparation and experimental technique. On the (111)A surface, a Ga-vacancy (2 × 2) structure has been predicted at typical surface As concentrations,[11] and was observed with STM following an ion bombardment and anneal preparation.[13] The (2 × 2) reconstruction on the (111)B surface has been predicted to be due to an As-trimer structure,[12] and has been observed as such using STM on MBE-grown material.[6] Photoemission studies are in agreement with this, as they confirm the existence of two surface As environments (trimer and rest atom), as well as the absence of a Ga surface environment.[7,8]

In this work, we bring together surface sensitive core-level photoemission and STM to examine the physical and electronic structure of (2 × 2) reconstructed surfaces of GaAs {111}. All samples were prepared in the same way, and so the results can bear direct comparison, without variations in surface stoichiometry causing unnecessary confusion. Furthermore, by examining each orientation under a range of conditions, we have attempted to gain further insight into the observed behavior of these surfaces during epitaxial growth.

II. EXPERIMENT

The STM experiments were performed using an Omicron instrument operating in ultra-high vacuum (UHV) at a base pressure of 5×10^{-11} mbar. The tungsten tip, which is held at ground potential while the sample is biased, was Ar^+ ion sputtered prior to use. Images were recorded using both negative and positive sample biases, i.e., tunneling from and into filled and empty states, respectively. Low energy electron diffraction was also used to determine the reconstruction of the sample surface following each anneal. Zn-doped ($P \simeq 10^{19}$ cm^{-3}) on-axis GaAs(111)A and Si-doped ($N \simeq 10^{18}$ cm^{-3}) GaAs(111)B substrates were employed for this study. Details of the substrate preparation and MBE growth parameters are reported elsewhere.[5] Following the thermal desorption of the oxide layer, a 0.1 μm thick GaAs buffer layer was grown on the {111} surfaces, which were doped p and n type with Si [(111)A and B, respectively] to a concentration of $\simeq 10^{18}$ cm^{-3}. At all stages of the growth process after oxide removal, a sharp, clear reconstruction was observed by RHEED. At the cessation of growth each sample was cooled within the reactor growth chamber to a temperature between −40 °C and −50 °C, whereupon the surface was capped with a protective layer (several micrometers thick) of amorphous As. This preparation allowed the samples to be transferred between laboratories in air, and then be loaded into the experimental UHV system through a fast-entry load lock. The samples were mounted onto previously outgassed Mo holders using Ta clips. Decapping was achieved by electron-beam heating the sample to ∼ 315 °C, at which the As desorbed as seen using a mass spectrometer. When the As_2 partial pressure dropped after about 10 min and normal UHV was regained, the As cap could be seen to have desorbed, as the mirror polish of the GaAs crystal surface was again visible. The sample temperature was then ramped up to 350 °C and finally allowed to cool before examination with LEED, which revealed a sharp (2 × 2) pattern. The patterns from the (111)A samples always had a lower background than those from the (111)B surface, though both would normally be described as "good quality LEED." The sample was then transferred to the STM and allowed to reach thermal equilibrium. Unless otherwise stated, the images shown here are either raw data, or have simply been filtered to remove "speckle" noise.

The photoemission experiments were performed at the synchrotron radiation source, Daresbury Laboratory, U.K. using the grazing incidence monochromator on beamline 6.1. This provided a photon flux in the energy range 50–170 eV, with the measurements made using 70 eV and 95 eV radiation. A double pass cylindrical mirror analyzer (CMA) was used to collect the data, resulting in a total instrumental resolution of ≃ 150 and 200 meV at photon energies of 70 and 95 eV, respectively. Identical samples to those used for the STM measurements were bonded to Mo holders using In, with both (111)A and B orientations mounted together so that a direct comparison could be made. The samples were loaded into the vacuum system using a load lock and then degassed at 200 °C, until the pressure returned to 7×10^{-11} mbar. The temperature was then ramped to 315 °C, at which point the As_2 was seen to desorb, and the decapping proceeded as detailed above. On cooling to room temperature, LEED revealed (2×2) patterns indistiguishable from those seen in the STM study. Further anneals to higher temperatures were subsequently performed incrementally, with LEED and spectroscopic measurements made at all stages.

III. STM RESULTS

A. GaAs(111)A

The STM images shown in Fig. 1 show raised areas of (2 × 2) structure (8 Å spacing) surrounded by flat dark regions. These images are from the same (250 × 250)Å^2 area, but they are wholly representative of the entire sample surface. Large terraces of this 1:1 (raised:lower) morphology were found at this anneal temperature, with up to only a few 4 Å (double) steps within a 2000 Å square. It is useful to remember here that this surface is the result of a decapping procedure, and so is inherently disordered by the presence of excess As. It is possible to imagine that if prepared by MBE with an As flux, the entire surface might occur with the structure of the islands seen here. The images were obtained with a negative sample bias, and, therefore, reflect tunneling from the filled states on the surface. The regular array of light features raised from the surrounding level in Fig. 1(a) indicates a localization of filled states at −1.0 V, which are attributed to As dangling bonds. The image at −2.2 V [Fig. 1(b)] shows light areas, due to less localized filled states punctuated by dark features with the (2×2) periodicity. These dark features originate from a position between the light features of Fig. 1(a), and so represent a localized reduction in the filled state density within the surface unit cell.

Topographic line profiles along the rows of raised features and steps as marked on Figs. 1 (a) and (b) reveal a number of interesting points. First, the step height is larger than the ~ 3.2 Å for a single step in GaAs{111}, being 3.8 Å in Fig. 1(a)(−1.0 V) and 3.5 Å in Fig. 1(b)(−2.2 V). The two step profiles are shown in Figs. 1(c) and (d). The difference in the step height with magnitude of sample bias highlights how STM images reflect both geometric, electronic and tip effects, not simply the surface geometry alone. This is also seen in the peak-to-peak corrugation changing from 2.8 Å to 0.5 Å [Figs. 1(c) and (d)], which reveals the high sensitivity of the measured corrugation to tunneling conditions. It is, however, impossible to deconvolve all the various components from these images, and so we rely on comparison and estimation in the same manner as for the $(111)B$-(2×2).[6] Despite the sensitivity of the images to the sample bias, we believe these data reflect the atomic geome-

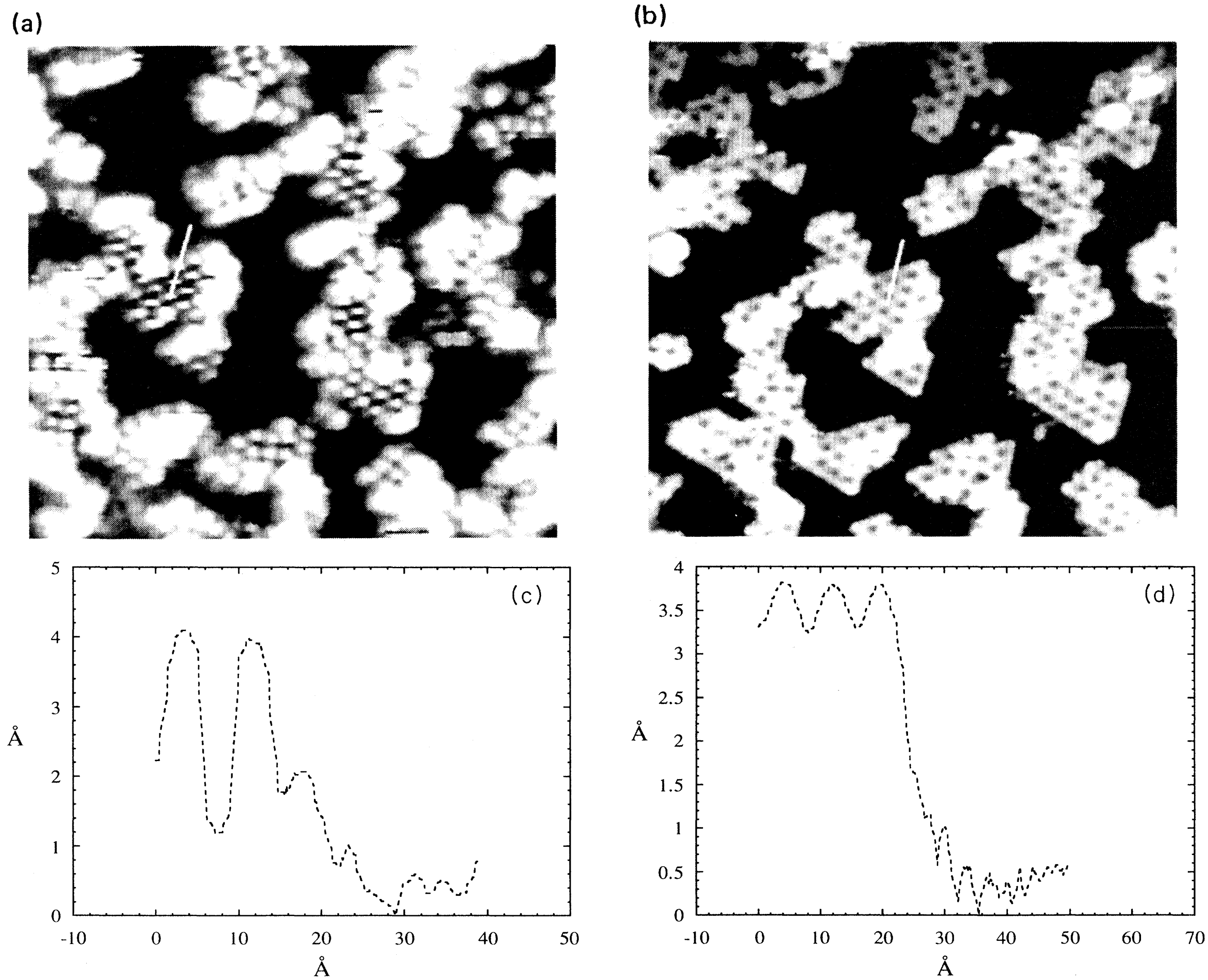

FIG. 1. Topographic STM images from the same region of the GaAs$(111)A$-(2×2) surface after decapping at 350 °C. Tunneling conditions were −1.0 V, 1.0 nA (a) and −2.2 V, 1 nA (b). The (2×2) periodicity (spacing 8 Å) is visible in the islands, which are raised ~ 3 Å relative to the flat dark regions. Topographic linescans of the step from raised to lower regions [as marked in (a) and (b)] are shown in (c) and (d). Note the difference in step height and corrugation with only a small change in sample bias.

try for a number of reasons. First, we can rule out spurious tip electronic effects since the images were stable, repeatable, and were seen using a number of different samples and tips. Second, As and other similar adsorbates have not been seen to cause such a large electronic corrugation on the surface of GaAs or any similar semiconductors. On As-rich surfaces such as GaAs(001) (2×4) reconstruction, steps of 2.8 Å are seen,[16] which correspond to the (001) interplanar spacing. On the GaAs(111)B-(2×2), a corrugation of 1.3 Å has been observed,[6] which was interpreted as an As-trimer structure. The only large height variations seen on GaAs have been for adsorbed oxygen,[17] and was ascribed to the electronegativity of the adsorbate, and is therefore inappropriate to describe a clean, As-rich surface of GaAs. These images, therefore, show a periodic adstructure not seen before on the GaAs(111)A surface.

We must therefore consider possible adstructure geometries which may give us large step heights, corrugation, and a (2×2) periodicity. The surfaces observed were all a result of thermally desorbing an As cap, and must therefore pass through an As-rich stage before the excess As is desorbed. An As-adstructure seems the most obvious, especially if we consider the total-energy calculations of Kaxiras *et al.*[11] All the possible (2×2) configurations were considered, with As adatom and As-trimer models being the two As adstructure possibilities. Under As-rich conditions, as found in our data, where the relative chemical potential is large and positive, the As trimer is favored, and has the lowest energy of any structure under any conditions [-5.0 eV per (2×2) unit cell relative to the ideal surface]. Interestingly, the next lowest is that of the Ga-vacancy structure, which has no adatoms, and was observed clearly under different conditions as described below. Using energetic arguments therefore, our As-rich (2×2) surface could possibly be due to As-trimers. Geometrically, we would expect an As-trimer layer to be $\sim$ 2.3 Å above the surface layer, whereas an As adatom would be only $\sim$ 1.1 Å above, and the Ga vacancy would display only depressions. It seems more likely that an As trimer is responsible for the $\sim$ 3.8 Å step and $\sim$ 2.8 Å corrugation, rather than a single adatom, though this is of course open to question.

In support of this, positive bias images were also obtained of inferior quality, though they do reveal the same (2×2) periodicity in the raised regions, with empty states localized on the protrusions. This is consistent with an isolated adatom structure, similar to findings from the (111)B surface.[6] In the case of GaAs(111)A, however, any As trimers are expected to bond to a Ga terminated surface, so the "rest" atom should also be Ga. This might explain the (2×2) array of dark features in Fig. 1(b), since filled dangling bonds would not be expected on such a structure. Following the theoretical predictions, and the hints from the variation in RHEED intensities with As flux in MBE,[9,10] it is not so surprising that another reconstruction should be found on an As-rich surface, though, to our knowledge, this work is the first direct evidence for its existence.

Turning now to the dark regions of Fig. 1, no detail could be seen under these conditions, though it was possible to determine that the areas were very flat, with a corrugation below $\sim$ 0.4 Å in these images. Although they could not be imaged in detail, it is clear that the dark regions are highly ordered, since they could not display such a high degree of flatness otherwise. Interestingly, the flat regions are $\sim$ 0.8 Å lower than the base of the adstructures, which might be expected to be coplanar. The difference corresponds closely to the GaAs(111) interlayer spacing of 0.82 Å, suggesting that the lower areas are images of the lower (As) atoms in the surface bilayer. This suggests the coexistence of a surface structure where filled and empty states are separated between As and Ga atoms, respectively, as found on the GaAs(110) surface.[18]

The samples were then heated to $\sim$ 400 °C in order to thermally desorb the excess As on the surface, which forms the (2×2) adstructures and again LEED displayed a sharp, low background (2×2) pattern. Once imaged by the STM, however, it became clear that the surface was no longer exactly as before. With increasing temperature, the As-rich islands were diminished through As desorption, eventually resulting in large flat terraces visible over the entire sample, and occasionaly disrupted by large pits several hundred angstroms across. These took the form of triangular pyramidal pits due to facetting, which is consistent with similar defects observed on MBE grown material at this temperature.[3] Another form of imperfection in the surface were pinholes of $\sim$ 20 Å in diameter, which could also be seen in an otherwise perfect terrace.

The formation of large, high quality domains now allowed the detailed atomic scale structure to be seen on these surfaces, as shown in Figs. 2(a) and (b). It is immediately clear from these images that the (2×2) reconstruction now takes the form of a Ga vacancy, confirming that the previous structure must be due to an As adstructure. The empty state image (+2.0 V, 1 nA) shows the Ga dangling bonds on individual Ga atoms, each separated by $\sim$ 4 Å [Fig. 2(a)]. The dark features are due

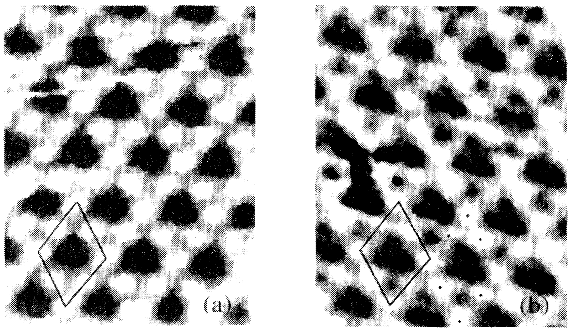

FIG. 2. Drift-corrected topographic images (30×41)Å^2 from neighboring areas on the GaAs(111)A-(2×2) surface following an anneal to 400 °C. Empty states are imaged in (a), with a sample bias of +2 V; filled states in (b) with -2 V. The unit cells marked are arbitarily bounded by Ga atoms in (a) and As in (b). Notice also the groups of As atoms marked with dots in (b) highlighting their lateral movement towards the vacancy.

to the absence of every fourth Ga atom (vacancy), which results in the (2×2) periodicity. The unit cell marked on the image is arbitarily the most obvious one, bounded by Ga atoms, and marked by a dashed line in Fig. 3. Furthermore, if the images shown here are Fourier transformed, a (2×2) pattern very similar to the observed LEED pattern is seen. The corrugation along the rows of empty Ga dangling bonds is 0.3 Å, and 1.1 Å along the vacancies, which is considerably less than the As-adstructure seen earlier. This large difference in corrugation not only emphasizes the difference in the two phases, but also highlights the difficulties in imaging neighboring regions of different structure, due to the limited dynamic range of the instrument. Although we cannot be definite, we believe the dark flat regions between As islands in Fig. 1 is due to coexistence of this vacancy structure. Once the adstructure islands are removed, it is then possible to attain the very high vertical resolution needed to image the vacancy structure. These empty state images represent the same surface as seen by Haberern and Pashley,[13] and are of considerably greater quality. This may well be due to factors such as sample preparation, which in their case included an Ar^+ ion bombardment. Such treatment not only causes physical disruption, but may also modify the doping of the near surface region, a possible cause for their inability to image filled states.

Despite the high quality of the empty state images, it is those from the filled states (−2.0 V, 1 nA) which are directive towards the detailed atomic structure of this reconstruction [Fig. 2(b)]. This image is from the same region of the sample as the empty state image, though not the identical area. Here, we see the filled dangling bonds on the As atoms prominent, with a corrugation of $\sim$ 0.1 Å. Furthermore, it is possible to see a lateral distortion in the position of the As atoms, perhaps most easily seen by comparing the groups of three As atoms at each end of the marked unit cell (arbitarily chosen as bounded by As atoms). This unit cell is marked by a chain line in Fig. 3, and is offset from the empty state image unit cell. The group of three atoms surrounding the vacancy (at the top of the cell) are closer together than the three at the bottom, whose movement is correlated with the Ga vacancy in neighboring unit cells, and so move apart. From the difference between the positions, it is possible to estimate the movement of the As atoms from their bulk-terminating positions to be (0.3 ± 0.1)Å towards the Ga vacancy.

Just such a movement has been predicted by both theory[15] and experiment[14] (LEED) in accompaniment with a downward relaxation of the Ga atoms (Fig. 3). These movements allow the Ga atoms to bond close to their (coplanar) sp^2 ideal, and for the As atoms around the vacancy to attain a near p^3 configuration. The dangling bonds are also able to minimize their energy in that six partially filled orbitals become three filled (As) and three empty (Ga). The surface is therefore rather similar to the (110) surface, on which the Ga and As states can be imaged separately. Further confirmation for the predicted structural model comes from the lack of lateral movement in the Ga dangling bonds, which is predicted to be $\sim$ 0.1 Å. Such a displacement is on the limit of detection, and so our results are entirely consistent with this. Another point of agreement is found in the position of the As atom not associated with any vacancy. We find it to be $\sim$ 0.15 Å lower than the other atoms, which is close to the 0.14 Å predicted.[15] Although we have measured atomic scale corrugation in both positive and negative biases, they do not necessarily accurately reflect the ver-

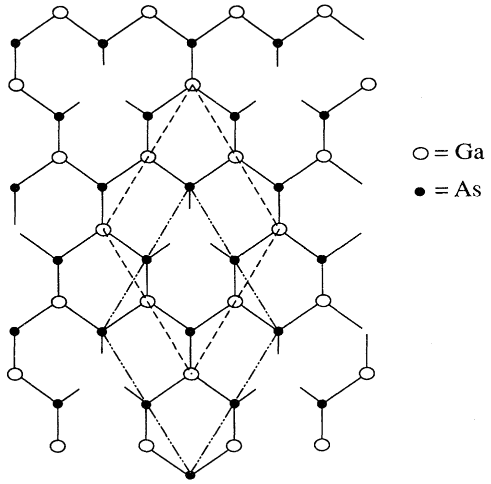

FIG. 3. Structural model for the GaAs(111)A-(2×2)-Ga vacancy reconstuction, showing the two offset unit cells marked on the data. The dashed line marks the cell on the empty state image [Fig. 2(a)], while the chain-line marks the cell on the filled state image [Fig. 2(b)]. Ga atoms relax downwards (into the page) while the As atoms move laterally into the vacancy.

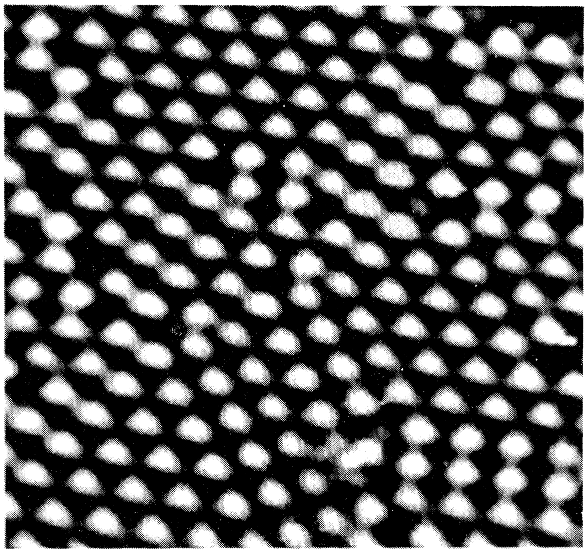

FIG. 4. Topographic STM images from the GaAs(111)B-(2×2) surface after decapping at 350 °C, where tunneling conditions were −1.8 V, 1.0 nA. The (2×2) periodicity (spacing 8 Å) is visible in the areas with threefold symmetry, while stacking faults are visible elsewhere.

tical positions of the atoms, and hence the interplanar spacing. Rather than use such direct data, an inferral from the observed lateral distortion of the As atoms is more appropriate. All of our observations are in excellent agreement with the predicted Ga-vacancy model,[15] in which a relaxation occurs in the surface bilayer, and therefore the spacing is believed to be ~ 0.15 Å. It would be interesting to compare spectroscopic STM data from this surface with that from the (110) to see if the initial similarity in nature bears a more rigourous inspection.

B. GaAs(111)*B*

Following decapping and an anneal to 350 °C, the GaAs(111)*B* sample surfaces yielded STM images like that in Fig. 4, which is a filled state image of area $(100 \times 100)\text{Å}^2$. The image was collected at −1.8 V, 1 nA (constant current) and so largely represents the surface topography. Large areas of well ordered (2 × 2) structure could be seen, though the highest quality images were those of the region shown, which also displays some stacking faults. This image is very similar to that observed on the MBE grown surface of Biegelsen *et al.*,[6] and so the disorder is not due the decapping preparation procedure. The photoemission results [Sec. IV C] for this surface show that there is not a surface Ga environment, and so the disorder would appear not to disrupt the two-dimensional nature of the surface, even in the areas which were not imaged.

An enlarged area of Fig. 4 is shown in Fig. 5(a) in which the triangular nature of the raised (white) features is clearly apparent. The spacing between features is ~ 8 Å, corresponding to the (2 × 2) unit cell dimension with the unit cell marked for clarity. The peak-to-peak (black to white) corrugation was found to be ~ 2 Å, which suggests an As adatom structure of some kind, though this is smaller than the 2.8 Å seen on the (111)*A* surface. Indeed, calculation has predicted the existence of an As-trimer structure on the GaAs(111)*B* surface,[12] and the STM images from MBE grown material are in accord with this.[6] Although the lateral resolution of our images constrains any possible conclusion, we believe that these images also represent the As-trimer structure, with each white triangle the result of tunneling from the filled dangling bonds expected from such a structure. The large corrugation is also indicative of directional electronic states enhancing the corrugation expected from the atomic geometry alone. In this case, the trimer to first-layer perpendicular separation should be 2.28 Å, which is close to the ~ 2 Å measured, though the STM tip would not be expected to posess sufficient height resolution to measure this under these conditions. This again demonstrates the highly convoluted nature of STM images in general, and that care must be taken not to overinterpret the data.

Unlike the images seen from MBE-grown surfaces, our raw data does not exhibit any sign of the "rest atom," which was observed at a position between the As trimers and marked by an "*X*" in Fig. 5(a). It would be difficult to explain a trimer structure without such an atom present, since the total energy is sensitive to the number of dangling bonds per unit cell, and the minimum energy was found to be calculated with a rest atom in the structure.[12] In addition, photoemission from these surfaces also exhibits a feature previously attributed to the "rest atom."[7] If the image in Fig. 5(a) is processed using an "unsharp-mask" filter, which subtracts a smoothed form of the image from the original, a raised feature is revealed at position *X* in Fig. 5(b). Clearly, such processing cannot yield definitive results, since tip effects or filtering artifacts can never be discounted, though in this case, the consistency with all other data does lend weight to the argument for the existence of a "rest atom"in the

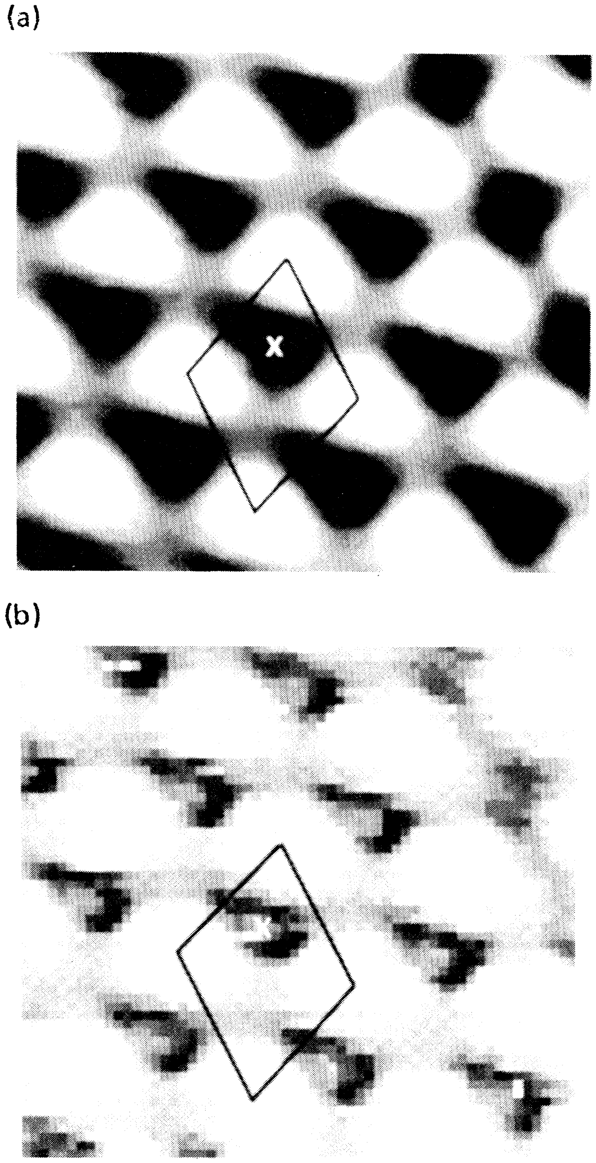

FIG. 5. An enlarged area of the (2 × 2) structure is shown in (a) where the unit cell is marked. The white triangles are due to filled dangling bonds on As-trimer structures, and *X* marks the position of the "rest atom" seen on MBE grown surfaces. In (b), the same image has been enhanced to reveal the "rest atom" feature on this surface.

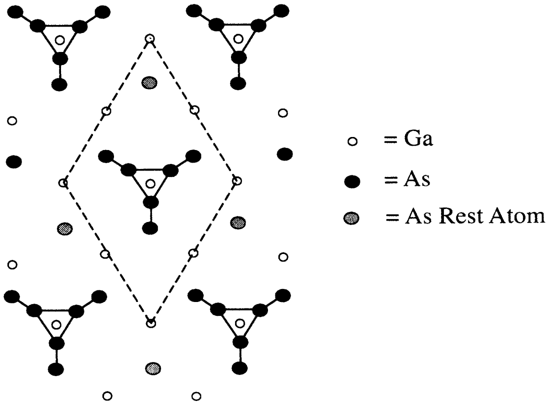

FIG. 6. Structural model for the GaAs(111)B-(2 × 2)-As-trimer reconstruction assuming the T_4 site.

structure observed. There seems little reason therefore, to conclude that the decapped GaAs(111)B-(2 × 2) surface is in any way different to that prepared by MBE directly. A possible model for this structure is shown in Fig. 6, where the T_4 site has been assumed for the trimer. Total-energy calculations have shown that little difference might be expected between the T_4 and H_3 sites,[6] though no evidence for coexistent domains of both structures was observed.

IV. PHOTOEMISSION RESULTS

A. Core-level fitting procedure

The deconvolution of core-level peaks obtained using surface-sensitive photoemission is a complicated affair, in which it is easy to go astray unless sensible constraints are imposed on the fitting parameters. This is especially the case when considering compound semiconductors such as GaAs, since at least one surface core-level shift (SCLS) can usually be expected, and complications such as phonon broadening, surface roughness, and inhomogeneous pinning of the Fermi level can also occur. These factors result in broadening of the peak lineshapes, making the peak width parameters of any fitting procedure dependent on them rather than the measured resolution of the combined monochromator/electron analyzer arrangement. The broadened peak width is usually modeled by increasing the Gaussian component of the line shape, which is also used to describe the effect of the electron analyzer on the data. This is only a first approximation, though generally it has proved adequate to the task, and has been used almost exclusively in this field thus far.[1,19,20] We have extended this assumption to the SCLS's, in that a difference in the peak width of these components from that of the bulk peak should not in principle be precluded. In practice, however, it is usually possible to obtain a "good" fit without resorting to such measures, and so in our analysis, a single Gaussian has been used for all components within each core level. The widths of the Lorentzian components to the fitted peaks, which represent the lifetime broadening of the core-level emission, were chosen to be 0.155 and 0.170 eV for the Ga and As 3d core levels, respectively (Table I). These follow the analysis of Le Lay *et al.*[19] of the (001) surface, which proved to be in good agreement with our data.

Throughout the fitting procedure, a consistent policy was adhered to that the simplest fit be achieved, using the minimum of components and keeping as many parameters constant as possible. To this end, fixed spin-orbit splittings and branching ratios were used (Table I), and an emphasis on relative energy differences between bulk and surface components, and that between the Ga and As bulk peaks. The most surface-sensitive spectra were collected using 95 eV radiation, and the consistency of the fits between the two sets of data obtained with different photon energies is another indicator of the quality of fit. The energy shifts of the SCLS's were found to remain constant between the two datasets, and their intensity ratio with respect to the bulk emission behaved as expected from escape-depth considerations, adding further weight to the peakshape analysis. The energy difference between the Ga and As 3d bulk components was kept fixed at 21.95 eV, which was determined from the (111)B spectra collected with the more bulk-sensitive photon energy of 70 eV. It is important to keep this as a fixed parameter if meaningful fits are to be made to the essentially featureless Ga 3d peaks. Cubic or quadratic backgrounds were subtracted from the data simultaneously in the fitting routine, which used both Levenberg-Marquardt and conjugate gradients minimization techniques.

From the figures in Table I, it is clear from the variation in Gaussian peak widths that the intstrumental resolution is not the single limiting factor. Some increase is needed to fit the data taken at the higher photon energy, as expected from the monochromator used.[21] The width of the Ga 3d peak is narrower for the (111)B sample, which is expected since this surface is As rich, and therefore Ga is only likely to exist in its bulklike environment. This is in agreement with the findings of Cai *et al.*,[7] which observed only a single Ga 3d component in a similar ex-

TABLE I. Parameters used to fit the Ga and As 3d core levels from GaAs(111)A and (111)B surfaces taken with 70 eV and 95 eV radiation. All energies are in eV, with binding energy (B.E.) shifts relative to the bulk-peak energy. All intensity ratios are for data taken with 95 eV radiation, and have an uncertainty of ±0.04. For the (111)A surface, they refer to the largest ratio (i.e., least mixed phases).

	Ga 3d		As 3d	
	(111)A	(111)B	(111)A	(111)B
Lorentzian	0.155	0.155	0.170	0.170
Gaussian (70 eV)	0.40	0.36	0.43	0.40
Gaussian (95 eV)	0.42	0.38	0.45	0.42
Spin-orbit splitting	0.45	0.45	0.69	0.69
Branching ratio	1.50	1.50	1.50	1.50
B.E. shift of S_1	-0.29		-0.31	-0.53
B.E. shift of S_2	0.31		0.51	0.50
Intensity ratio S_1/Bulk	0.58		0.62	0.28
Intensity ratio S_2/Bulk	0.39		0.63	1.14

periment. It is less clear why the Gaussian required to fit the As 3*d* should be less for the (111)*B* surface than the (111)*A* however. The STM data show no significant difference in the roughness of these two surfaces, and without further information to imply that less phonon broadening occurs on the As-rich surface, the most likely explanation is the effect of inhomogeneous Fermi-level pinning. Indeed, the difference in energy between the valence band maximum (VBM) and the Fermi-level position measured from the sample holder reveals that the (111)*B* surface is close to a flat-band condition (within 100 meV), whereas the (111)*A* sample has its Fermi level only 0.35 eV lower in the gap when completely decapped. From the sample doping, one would expect (E_F−VBM) from the two samples to differ by ∼ 1.1 eV, and so the Fermi level at the (111)*A* surface appears to be pinned just above midgap. Just after decapping, however, the (111)*A* surface also appears to be in a near flat-band condition, when an extra As layer is still present on the surface. The effect of surface photovoltage is expected to be negligible in this work, due to the relatively high doping levels and the data being collected at room temperature. This was confirmed by finding no relationship between the incident flux and the Fermi-level position.

B. GaAs(111)*A*

The Ga and As 3*d* core levels from the GaAs(111)*A* surface are shown as a function of annealing temperature in Fig. 7. They were obtained using the more surface-sensitive photon energy of 95 eV, and therefore exhibit larger SCLS intensities relative to the bulk peaks than those taken using 70 eV radiation, which are shown in Fig. 8. The more bulk sensitive data still exhibit significant SCLS's, and are also of higher resolution than those obtained with 95 eV radiation.

Consider first the As 3*d* core levels, which just after decapping can only be fitted with at least two SCLS peaks (S_1, S_2) in addition to the bulk. They bear close similarity to the (001) surface following a similar preparation,[1,19] in which a low binding energy (LBE) component was attributed to As dimers in the (2 × 4) structure, or threefold-coordinated As in the (4 × 2). Yet another LBE component on the As 3*d* peak is seen from the (110) surface, due to its three Ga neighbors, and so it appears that a variety of threefold coordinated sites for As on a GaAs surface result in a LBE shifted component on the As 3*d* peak. The high binding energy (HBE) component, (S_2), is attributed to excess, bulklike As, again in agreement with the previous (001) studies. As the annealing temperature increases, it is clear that the bulklike excess As desorbs after only a small increment, and the As 3*d* emission is then best fitted with just the bulk and LBE shifted components (S_1), which remains the situation right up to 400 °C. We know from the STM images that for low temperature anneals, we can expect to find the As-adstructure (2 × 2) reconstruction on this surface. It, therefore, appears perplexing to find only one shifted surface component throughout this temperature range, though careful analysis of the Ga 3*d* emission unravels the apparent mystery.

By keeping the energy difference between the bulk As and Ga components to 21.95 eV, it is evident that just after decapping at 315 °C, there is a shifted component to lower binding energy on the Ga 3*d* peak, S_1 (Figs. 7, 8). The intensity of the peak is larger in the spectra taken with 95 eV photons, confirming that it is due to a sur-

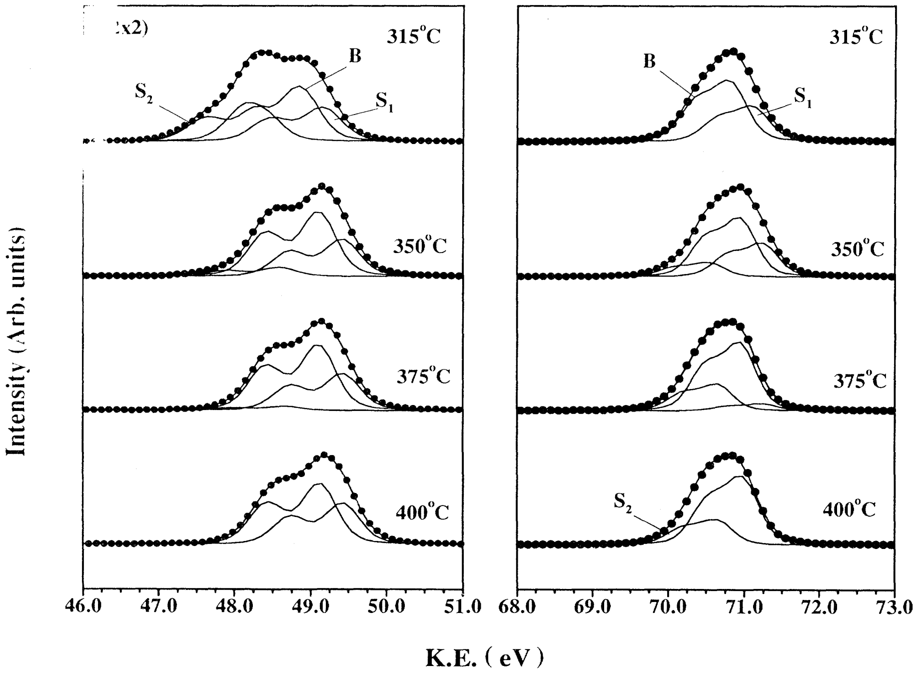

FIG. 7. Curve-fitted photemission spectra of the Ga and As 3*d* core levels from the GaAs(111)*A* surface as a function of annealing temperature. The photon energy was 95 eV. Peak B marks the bulk emission, while S_1 and S_2 are surface core level shifts.

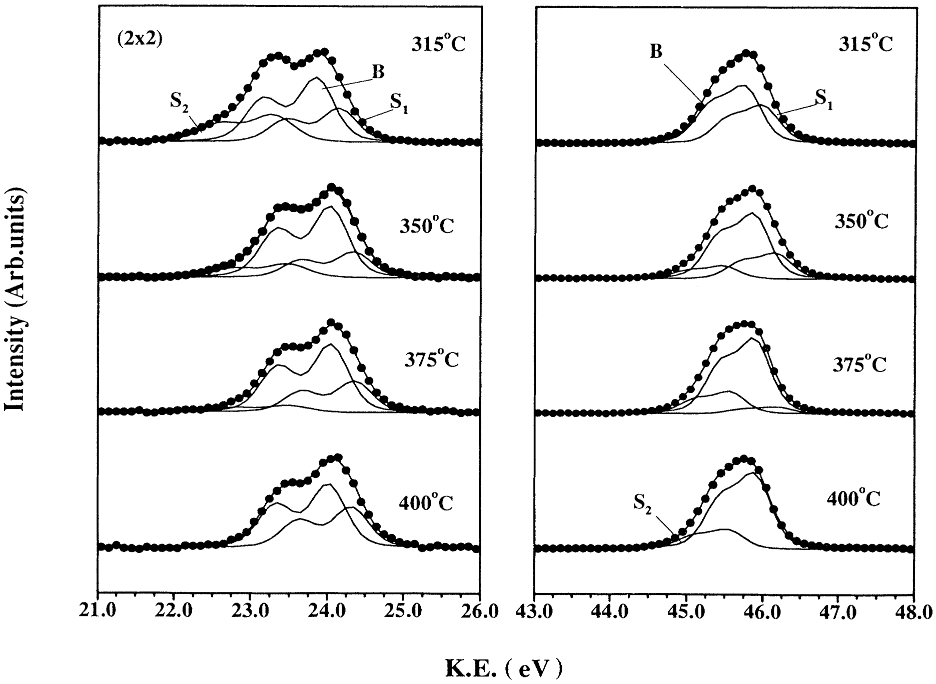

FIG. 8. Equivalent spectra to Fig. 7, but taken with 70 eV radiation.

face environment. With a small increase in temperature up to 350 °C, a HBE component, S_2, is needed to obtain a fit to the data. Higher temperatures result in the further diminution of S_1, and the increase in intensity of S_2. This transition in the components required to fit the Ga 3*d* peakshape is entirely consistent with the STM data, which show a transition from (2×2) adstructure to (2×2)-vacancy reconstructions. The higher anneal temperature peakshapes of both the Ga and As 3*d* levels closely resemble those of the (110) surface, which might be expected following the results of the STM. They showed that a surface relaxation occurs, in which the surface bilayer collapses, and rehybridization in a manner very close to the (110) surface takes place (Fig. 2). In particular, the As is in a threefold coordinated site, where the As atom is host to a localized filled dangling bond, similar to the (110) surface. We, therefore, attribute the SCLS's on the Ga and As 3*d* core levels to be associated with the surface Ga atoms, and As atoms surrounding the Ga vacancy, respectively. The similarity of core-level emission between the two orientations is not so surprising, since the local bonding and electronic structure are remarkably close.

Having identified the core-level components after a higher temperature anneal, we must now consider those obtained at lower temperatures. The fact that the Ga 3*d* is not completely bulklike, as found for the (111)*B* surface, reveals that there is a surface Ga environment. Furthermore, that only one extra component is required to lower binding energy in order to fit the data is indicative that the Ga-vacancy structure is not visible at this stage. The S_1 component diminishes with increasing anneal temperature, and so appears to be intimately linked with the (2 × 2) As adstructure, which is seen to desorb at these temperatures. We therefore assign the S_1 component to a single Ga surface environment in the (2 × 2) As adstructure, possibly a Ga "rest atom" if the structure is due to As trimers. The conclusion from the Ga 3*d* emission that the Ga-vacancy structure is not present at 315 °C determines that the component S_1 in the As 3*d* emission at 315 °C is not due to the Ga-vacancy structure either. One conclusion is that the S_1 SCLS is due to threefold coordinated As in a (2 × 2) As adstructure at low temperatures, which then transforms into threefold coordinated As around a Ga vacancy at higher temperatures. If the threefold coordinated As adstructure is in the form of an As trimer, we would expect the intensity to remain constant, since both structures have the same number of surface As atoms per (2 × 2) unit cell. It appears a remarkable coincidence that both environments should produce the same SCLS on the As 3*d* emission, though if we consider the similarity in As 3*d* peakshape from the (110), (001)-(2 × 4) and (001)-(4 × 2) surfaces, it is not so unusual.

C. GaAs(111)*B*

The ideal GaAs(111)*B* surface is terminated by a half bilayer of As, and so we expect to find an As-rich surface, especially after a thermal decapping of As. From our STM of these decapped surfaces, we can also expect to find spectra consistent with the existence of As trimers, as well as As rest atoms if similarity exists with MBE-grown surfaces also observed with STM.[6] Ga and As 3*d* core levels obtained using 70 eV radiation are shown in Fig. 9. Only the data taken using 70 eV photons are

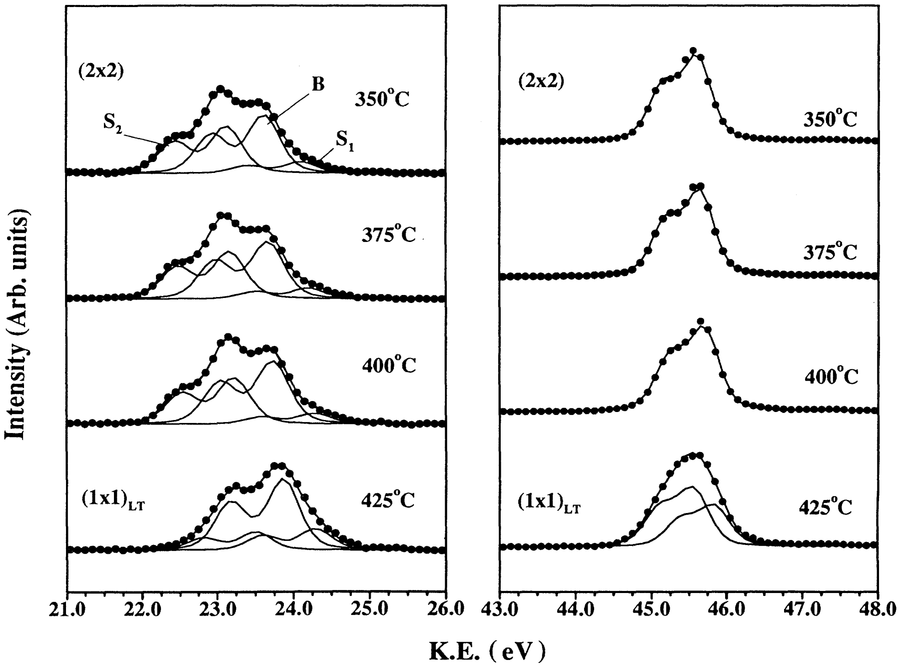

FIG. 9. Curve-fitted photoemission spectra of the Ga and As $3d$ core levels from the GaAs(111)B (2×2) surface as a function of annealing temperature. The photon energy was 70 eV. Spectra from the $(1\times1)_{LT}$ are also included.

shown, since the energy resolution is marginally better than in those taken using 95 eV, and no extra information is forthcoming from them.

The first thing to notice is the complete lack of surface components on the Ga $3d$ peaks up to 400 °C. This confirms that the top two layers of the (2×2) reconstructed surface are comprised entirely of As, and that the STM images showing large, high quality domains are entirely representative of the whole surface. Any significant disorder would result in Ga atoms becoming apparent, and this is clearly not the case here.

The As $3d$ core levels are much more complex, requiring two extra SCLS peaks to fit the data. These are similar to those observed by Cai *et al.*,[7] though our data is angle integrated, due to the CMA electron analyzer used, and of higher resolution. With our STM images of these surfaces showing the highly corrugated As-trimer reconstruction also seen on the MBE-grown surface, and with these core-level peakshapes in agreement with Cai *et al.*,[7] we assign the HBE component to bulklike As trimers, and the LBE component to the As rest atom [i.e., surface terminating As atom, not bonded to a trimer (Fig. 6)]. There is, therefore, no discernable difference between MBE-grown and decapped GaAs(111)B surfaces when investigated with the techniques used. It is worth noting here that the As trimers on this surface are bonded to As atoms, and so appear bulklike at higher binding energy, whereas the As adstructures on the (111)A surface are bonded to Ga atoms, and so are manifested by a shifted peak to low binding energy relative to the bulk GaAs.

Although not a major part of this work, the core level peaks from the $(1\times1)_{LT}$ reconstruction at 425 °C are also included. The increased temperature causes the desorption of the As trimers, and so the HBE shifted peak on the As $3d$ is immediately reduced. A dramatic change to the Ga $3d$ peak also occurs, where a large SCLS to low binding energy appears, in the same manner as the S_1 peak on the (111)A surface. There is also similarity with the Ga $3d$ emission from the (110) surface, and so it would appear as though the surface Ga site in the $(1\times1)_{LT}$ surface is involved with a rehybridization, and an empty dangling bond. Of course a full understanding requires a much more involved study of this surface. The (2×2)-$(1\times1)_{LT}$ phase transition temperature of 425 °C appears rather low if one compares it with published phase maps of this surface.[5] It should be realized, however, that the minimum As flux of such maps is 10^{14} s^{-1}, at which the transition occurs at $\sim$ 500 °C. After decapping, any residual As flux would be at least an order of magnitude down on this, and so a transition temperature of 425 °C is to be expected if the phase map boundaries are extrapolated.

V. CONCLUSIONS

We have thermally decapped protective As layers from both GaAs(111)A and (111)B surfaces, and examined the resulting (2×2) reconstructions using STM and surface-sensitive photoemission. On the GaAs(111)A surface, a new (2×2) As-adstructure phase has been observed using STM. Photoemission studies confirm the phase transition from the As adstructure (2×2) to the Ga vacancy (2×2) seen after a higher temperature anneal. This helps to explain why the GaAs(111)A surface has only been seen to exhibit (2×2) RHEED patterns over a vast range of MBE growth conditions. Furthermore, the transition temperature between the two is consistent with that seen for growth-mode and dopant incorpoation rates from this surface, which may be explained by the change in surface structure. The STM images of the Ga-vacancy (2×2) surface show the localization of filled and empty states onto the As and Ga surface atoms, respectively, in a manner similar to that for the (110) surface. Accordingly, the photoemission data also appear similar to that obtained from the (110) surface. This rehybridization of the surface electronic structure is also manifested in the physical structure in that it has been possible to measure a relaxation of the surface atoms, in good agreement with LEED and theoretical predictions. The GaAs(111)B (2×2) surface following decapping was found to yield virtually identical STM images to those observed from MBE grown sample, with an As-trimer and "rest atom" structure identified. Photoemission was able to distinguish the two surface-As sites, and that no surface-Ga site exists. The decapped GaAs(111)B (2×2) surface is therefore indistinguishable, using these techniques from the MBE-grown surface. In this work, we have observed large differences in the reconstruction phase boundaries, chemical states and electronic structure of (2×2) reconstructions of GaAs$\{111\}$, which further emphasizes the importance of surface stoichiometry on the nature of compound semiconductor surfaces.

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[1] C. J. Spindt, M. Yamada, P. L. Meissner, K. E. Miyano, T. Kendelewicz, A. Herrera-Gomez, W. E. Spicer, and A. J. Arko, Phys. Rev. B **45**, 11 108 (1992).

[2] B. K. Laurich, K. Elcess, C. G. Fonstad, J. G. Beery, C. Mailhot, and D. L. Smith, Phys. Rev. Lett. **62**, 649 (1989).

[3] D. A. Woolf, D. I. Westwood, and R. H. Williams, Semicond. Sci. Technol. **8**, 1075 (1993).

[4] A. M. Dabiran, P. I. Cohen, J. E. Angelo, and W. W. Gerberich, Thin Solid Films **231**, 1 (1993).

[5] D. A. Woolf, D. I. Westwood, and R. H. Williams, Appl. Phys. Lett. **62**, 1370 (1993).

[6] D. K. Biegelsen, R. D. Bringans, J. E. Northrup, and L.-E. Swartz, Phys. Rev. Lett. **65**, 452 (1990).

[7] Y. Q. Cai, R. C. G. Leckey, J. D. Riley, R. Denecke, J. Faul, and L. Ley, J. Electron Spectrosc. Relat. Phenom. **61**, 275 (1993).

[8] A. D. Katani, H. W. Sang, P. Chirardia, and R. S. Bauer, J. Vac. Sci. Technol. B **3**, 608 (1985).

[9] A. Y. Cho and J. R. Arthur, Prog. Solid State Chem. **10**, 157 (1975).

[10] D. A. Woolf, J. P. Williams, D. I. Westwood, Z. Sobiesierski, J. E. Aubrey, and R. H. Williams, J. Cryst. Growth **127**, 913 (1993).

[11] E. Kaxiras, Y. Bar-Yam, J. D. Joannopoulos, and K. C. Pandey, Phys. Rev. B **35**, 9625 (1987).

[12] E. Kaxiras, Y. Bar-Yam, J. D. Joannopoulos, and K. C. Pandey, Phys. Rev. B **35**, 9636 (1987).

[13] K. W. Haberern and M. D. Pashley, Phys. Rev. B **41**, 3226 (1990).

[14] S. Y. Tong, G. Xu, and W. N. Mei, Phys. Rev. Lett. **41**, 1693 (1984).

[15] D. J. Chadi, Phys. Rev. Lett. **52**, 1911 (1984).

[16] M. D. Pashley, K. W. Haberern, W. Friday, J. M. Woodall, and P. D. Kirchner, Phys. Rev. Lett. **60**, 2176 (1988).

[17] J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **58**, 1668 (1987).

[18] R. M. Feenstra, J. A. Stroscio, J. Tersoff, and A. P. Fein, Phys. Rev. Lett. **58**, 1192 (1987).

[19] G. Le Lay, D. Mao, A. Kahn, and G. Margaritondo, Phys. Rev. B **43**, 14 301 (1991).

[20] T. Miller and T. C. Chiang, Phys. Rev. B **29**, 7034 (1984).

[21] F. M. Quinn and P. Bailey (unpublished).

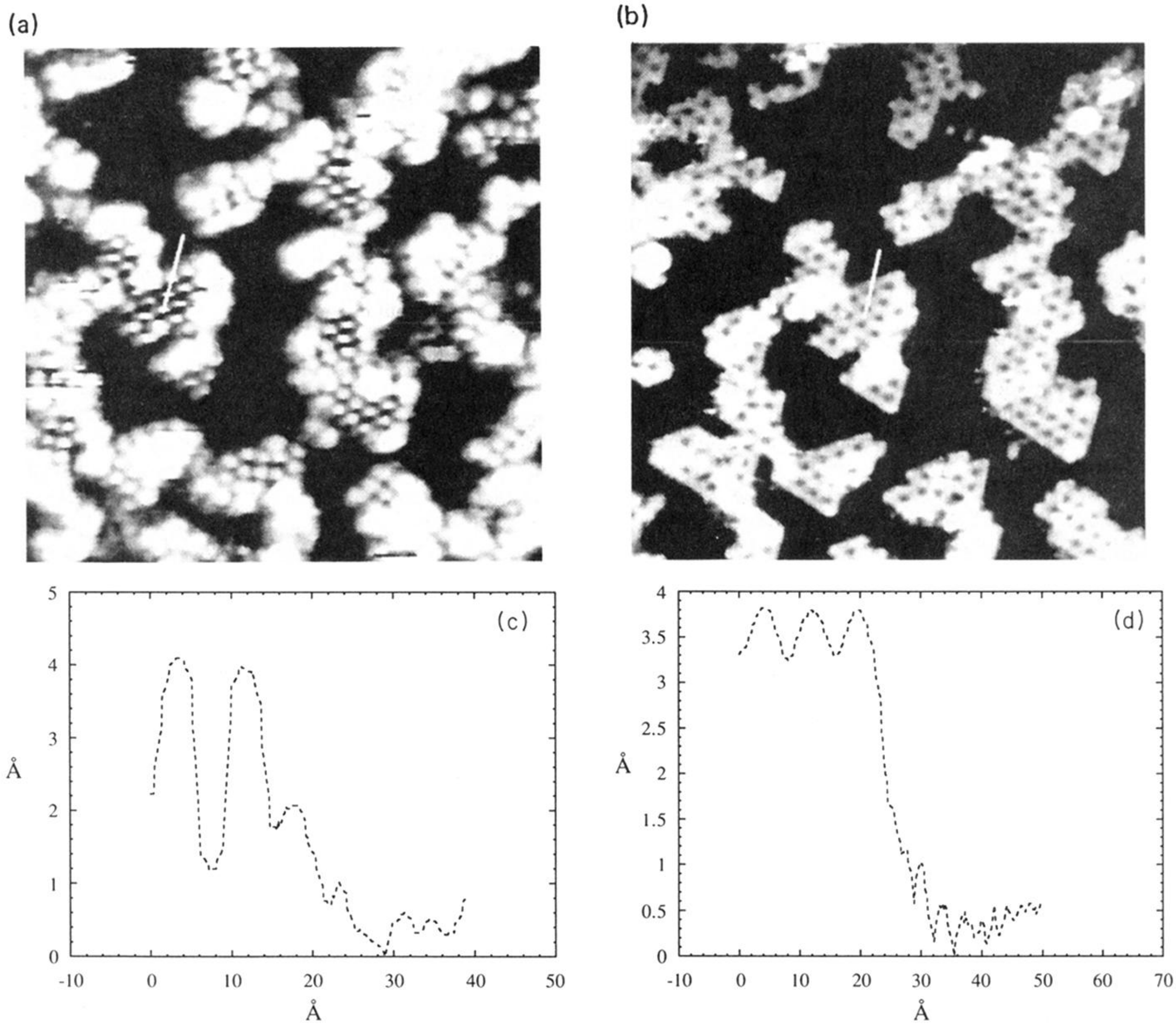

FIG. 1. Topographic STM images from the same region of the GaAs(111)A-(2×2) surface after decapping at 350 °C. Tunneling conditions were −1.0 V, 1.0 nA (a) and −2.2 V, 1 nA (b). The (2×2) periodicity (spacing 8 Å) is visible in the islands, which are raised ∼ 3 Å relative to the flat dark regions. Topographic linescans of the step from raised to lower regions [as marked in (a) and (b)] are shown in (c) and (d). Note the difference in step height and corrugation with only a small change in sample bias.

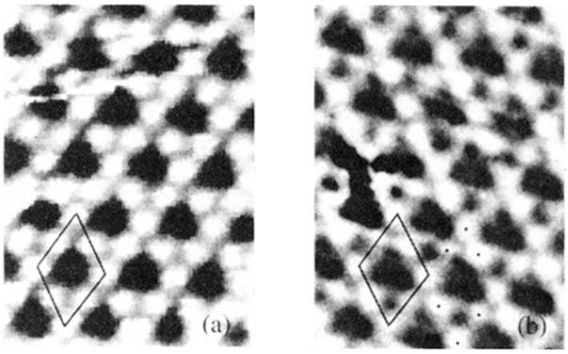

FIG. 2. Drift-corrected topographic images $(30 \times 41)\text{Å}^2$ from neighboring areas on the GaAs(111)A-(2×2) surface following an anneal to 400 °C. Empty states are imaged in (a), with a sample bias of +2 V; filled states in (b) with −2 V. The unit cells marked are arbitarily bounded by Ga atoms in (a) and As in (b). Notice also the groups of As atoms marked with dots in (b) highlighting their lateral movement towards the vacancy.

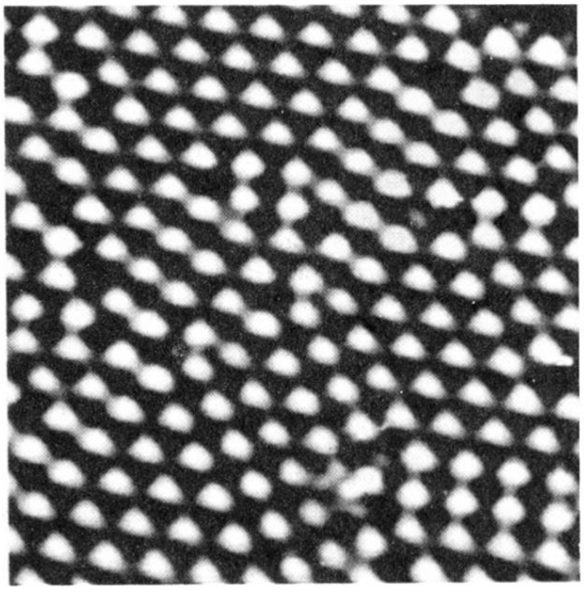

FIG. 4. Topographic STM images from the GaAs(111)B-(2×2) surface after decapping at 350 °C, where tunneling conditions were -1.8 V, 1.0 nA. The (2×2) periodicity (spacing 8 Å) is visible in the areas with threefold symmetry, while stacking faults are visible elsewhere.

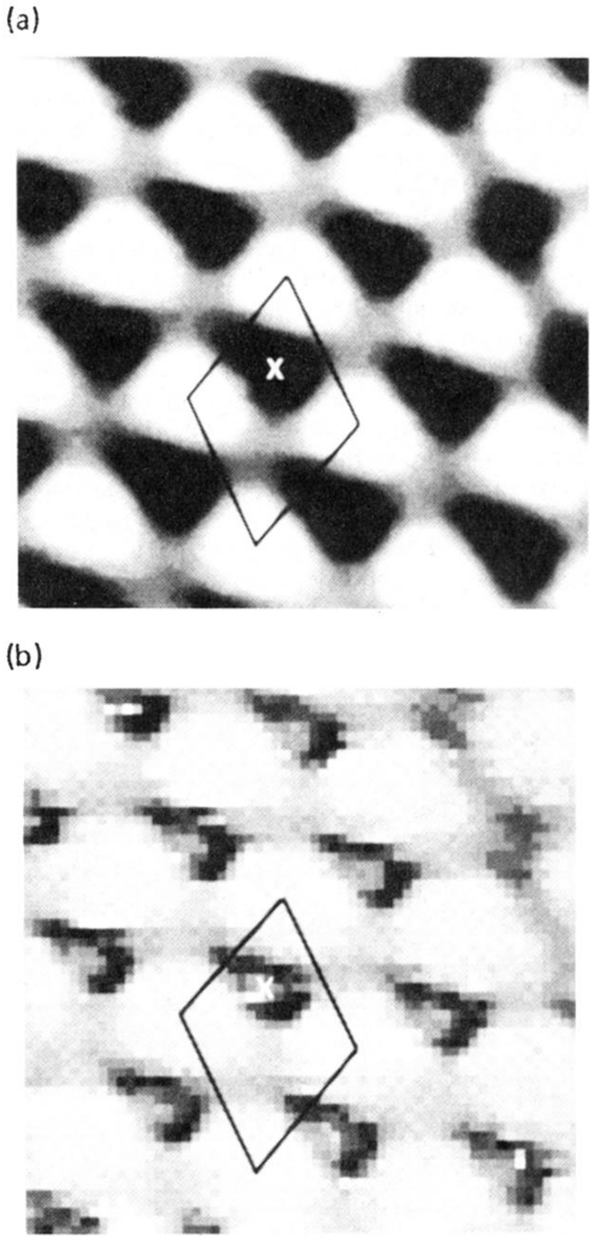

FIG. 5. An enlarged area of the (2×2) structure is shown in (a) where the unit cell is marked. The white triangles are due to filled dangling bonds on As-trimer structures, and X marks the position of the "rest atom" seen on MBE grown surfaces. In (b), the same image has been enhanced to reveal the "rest atom" feature on this surface.