Mechanism for Disorder on GaAs(001)-(2 × 4) Surfaces

A. R. Avery,[1] C. M. Goringe,[2] D. M. Holmes,[1] J. L. Sudijono,[1] and T. S. Jones[1,*]

[1]*Interdisciplinary Research Centre for Semiconductor Materials and Department of Chemistry, Imperial College, London, SW7 2AY, United Kingdom*

[2]*Department of Materials, University of Oxford, Oxford, OX1 3PH, United Kingdom*

(Received 5 September 1995)

An atomistic model is presented based on scanning tunneling microscopy results and tight binding calculations which explains the observation of disorder on the GaAs(001)-(2 × 4) surface grown by molecular beam epitaxy. Calculations show that occupation by As of vacant Ga sites in the missing dimer trenches of the (2 × 4) unit cell is responsible for the surface disorder in the form of kinks in the dimer rows. The disordered surface is energetically favorable for a range of additional As coverage up to 0.25 monolayer.

PACS numbers: 61.16.Ch, 68.35.Md, 71.10.–w, 81.15.Hi

A number of studies have been directed at the atomic details of the GaAs(001)-(2 × 4) surface, with initial studies confirming the presence of As dimers as the cause of the twofold symmetry, while a regular array of missing As dimers is responsible for the fourfold periodicity [1,2]. Despite a number of subsequent studies, the exact details of the (2 × 4) reconstruction have been difficult to determine.

The situation is complicated by the behavior of the (2 × 4) reconstruction as a function of the growth conditions. Early reflection high energy electron diffraction (RHEED) studies showed that the intensity of the $\frac{2}{4}$ fractional order feature for the $[\bar{1}10]$ azimuth varies with surface temperature for a given As flux. This was initially interpreted in terms of one dimensional disorder in the surface plane [3]. An alternative explanation suggested that variations in the unit cell structure occurred as a function of temperature and therefore As content [4]. Three regimes were subsequently defined within the (2 × 4) phase, denoted α, β, and γ.

The α phase occurs at the highest substrate temperatures, the γ phase is formed in the lowest substrate temperature range, and the β phase exists between these two. Theoretical studies have shown that three structures for the (2 × 4) surface are energetically favorable [5–8] and these correspond to the α and β phases [Figs. 1(a)–1(c)]. Two of the models have been attributed to the β phase. Using the recent notation of Northrup and Froyen [8], the $\beta(2 \times 4)$ structure contains three As dimers in the uppermost atomic layer. The $\beta 2(2 \times 4)$ structure contains two As dimers in this layer with a third As dimer situated in the third atomic layer, within the trench formed due to missing dimers. The α phase is described by the $\alpha(2 \times 4)$ structural model, which also has two As dimers in the top layer. However, in contrast to the $\beta 2(2 \times 4)$, this structure contains second layer Ga atoms in the missing dimer trench.

Recent detailed scanning tunneling microscopy (STM) studies of molecular beam epitaxy (MBE) grown material have shown that the three top layer As dimer structure $\{\beta(2 \times 4)\}$ is not observed for *in situ* MBE grown samples under any preparation conditions; the unit cell always contains two As dimers in the top layer [9,10].

Total energy calculations have shown that a fourth structure proposed for the low temperature γ phase and consisting of an extra As dimer on top of the $\beta(2 \times 4)$ structure [Fig. 1(d)] is not stable. For the (2 × 4) surface prepared under the most As-rich conditions, STM images confirm that the cause of the weak intensity of the $\frac{2}{4}$ fractional order feature in the RHEED pattern along $[\bar{1}10]$ (the γ phase) arises from disorder rather than a fundamentally different unit cell structure [9,10]. The disordered images obtained under these conditions are similar to those obtained for (2 × 4) surfaces grown with a high level of bulk Si doping ($\sim 10^{19}$ cm^{-3}) [11]. In this case, the disorder was explained in terms of a correlation between the number of Si donors and the density of surface defect sites, with the defects (kinks)

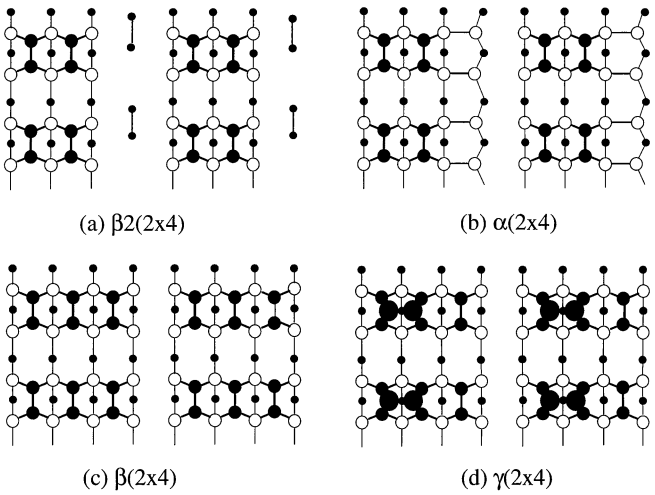

FIG. 1. Structural models for the GaAs(001)-(2 × 4) surface. Filled circles represent As atoms and open circles represent Ga atoms. The larger filled circles in (d) represent an additional As dimer on top of the $\beta(2 \times 4)$ structure.

 0031-9007/96/76(18)/3344(4)$10.00

acting as acceptor states and compensating for the charge introduced by the Si dopant atoms.

Here, we use tight binding calculations to show that there is an alternative mechanism for the formation of the disordered surface as seen by STM. The γ-phase surface involves kink formation due to the preferential occupation by additional As atoms of second layer Ga sites in the missing dimer trenches of the ordered $\beta 2(2 \times 4)$ surface. In this case, there is no influence of the bulk doping.

The experimental apparatus, substrate, and buffer layer preparation procedures have been described previously [10]. The final 100 layers were grown without Si doping in order to prevent the formation of kinks due to charge compensation [11]. The samples were then annealed at either 580 or 520 °C, for 5–10 min under a constant arsenic pressure, in order to produce the β- or γ-phase surface as determined by the RHEED pattern along $[\bar{1}10]$ [10]. The samples were quenched to 400 °C while monitoring the RHEED pattern before rapid transfer to the STM chamber.

STM images of surfaces corresponding to the β and γ phases are shown in Fig. 2. Corresponding RHEED patterns obtained along $[\bar{1}10]$ showed strong and weak intensities for the $\frac{2}{4}$ fractional order streaks, respectively [10]. The images show the characteristic bright and dark rows which alternate along [110]. The bright regions represent the As dimers and the dark regions correspond to the As-dimer vacancy region [9,10]. The image for the β-phase surface is characterized by very straight dimer rows, with the ordered regions extending over domains of several hundred Å [Fig. 2(a)]. In contrast, the γ-phase surface is much more disordered [Fig. 2(c)].

The atomic details of the β- and γ-phase surfaces are shown in more detail in Fig. 2. The β-phase surface clearly shows the presence of two top layer As dimers per unit cell with two missing dimers [Fig. 2(b)]. The unit cell structure of the more As-rich γ-phase surface also contains only two As dimers in the top layer, although this image shows the dimer row units to be displaced along the [110] direction due to the presence of kinks arising from the addition of more As to the structure [Fig. 2(d)]. Occasionally there are three successive dimers along the [110] direction at a kink site.

Preparation of the γ phase is achieved by cooling the well ordered β-phase surface under a constant As pressure, resulting in more As-rich conditions and the adsorption of As onto the β-phase surface. The only difference in the preparation of these two surfaces was therefore in the final annealing stage under identical As flux but at different substrate temperatures. The amount of additional As has previously been determined by temperature programmed desorption (TPD) experiments, which suggest a variable As content for the γ-phase surface of up to 0.24 ML (monolayer) in excess of the β-phase As content [12]. Our STM results clearly show that this additional As is not accommodated on top of, or within, the first As layer.

The only structural model for the ordered (2×4) surface which can accommodate this much extra As and remain consistent with these and recent STM observations is the $\beta 2(2 \times 4)$ structure [Fig. 1(a)]. The additional As can occupy the vacant Ga sites in the missing dimer trenches of the $\beta 2(2 \times 4)$ structure. While this can explain the structural similarities between the β and γ surfaces apparent in the STM data (each contains only two top layer As dimers per unit cell), it should be stressed that there is no *direct* STM evidence for such an assignment to Ga vacancy sites.

To establish the structural details of the disordered γ-phase surface, we have modeled the transition from the $\beta 2(2 \times 4)$ to the $\gamma(2 \times 4)$ structure using tight binding calculations. Previous *ab initio* calculations have shown that the $\alpha(2 \times 4)$, $\beta(2 \times 4)$, and $\beta 2(2 \times 4)$ structures of GaAs(001) are sufficiently similar in energy to make direct comparison difficult [6]. Significant relaxation in the third and fourth atomic layers of the structures requires a computational slab of around ten layers to ensure accurate energy differences. For this reason, we have taken an indirect approach to evaluate the kink energy E_{kink}, which we define as

$$E_{\text{kink}} = (E_{\text{bind}}^{\text{kinked}} - E_{\text{bind}}^{\text{perfect}})/N_{\text{kinks}}, \qquad (1)$$

with E_{bind} representing the binding energy for a given structure and N_{kinks} the number of kinks. Periodic boundary conditions were used, with eight (2×4) unit cells within the repeat distance to ensure that the kinks were sufficiently isolated. The slab was 11 layers thick, giving a total of up to 688 atoms in the system. In order to handle this number of atoms, a linear scaling code was used based on density matrix methods [13].

The parameters used for the calculations were obtained by fitting with a database of local density approximation (LDA) energy curves for bulk GaAs and isolated sheets of Ga and As atoms. Relaxed structures for all three reconstructions considered in this work compare favorably with previous LDA results [7]. Details of the parametrization have been published elsewhere [14].

Kink energies have been calculated for the $\alpha(2 \times 4)$, $\beta(2 \times 4)$, and $\beta 2(2 \times 4)$ structures. These are very small for $\alpha(2 \times 4)$ and $\beta(2 \times 4)$; 0.09 and 0.12 eV, respectively. Since they are of the order of kT at growth temperatures, neither of these structures can explain the long lengths of unkinked missing dimer rows which are observed for the ordered β-phase surface [Fig. 2(a)]. In contrast, the $\beta 2(2 \times 4)$ reconstruction has a kink energy of 1.02 eV. This high kink energy is a result of the As dimer (involving third layer As atoms) in the trench, which is offset in the $[\bar{1}10]$ direction from the surface dimers, and must be broken in order to introduce a kink [Fig. 3(a)]. The high kink energy for this

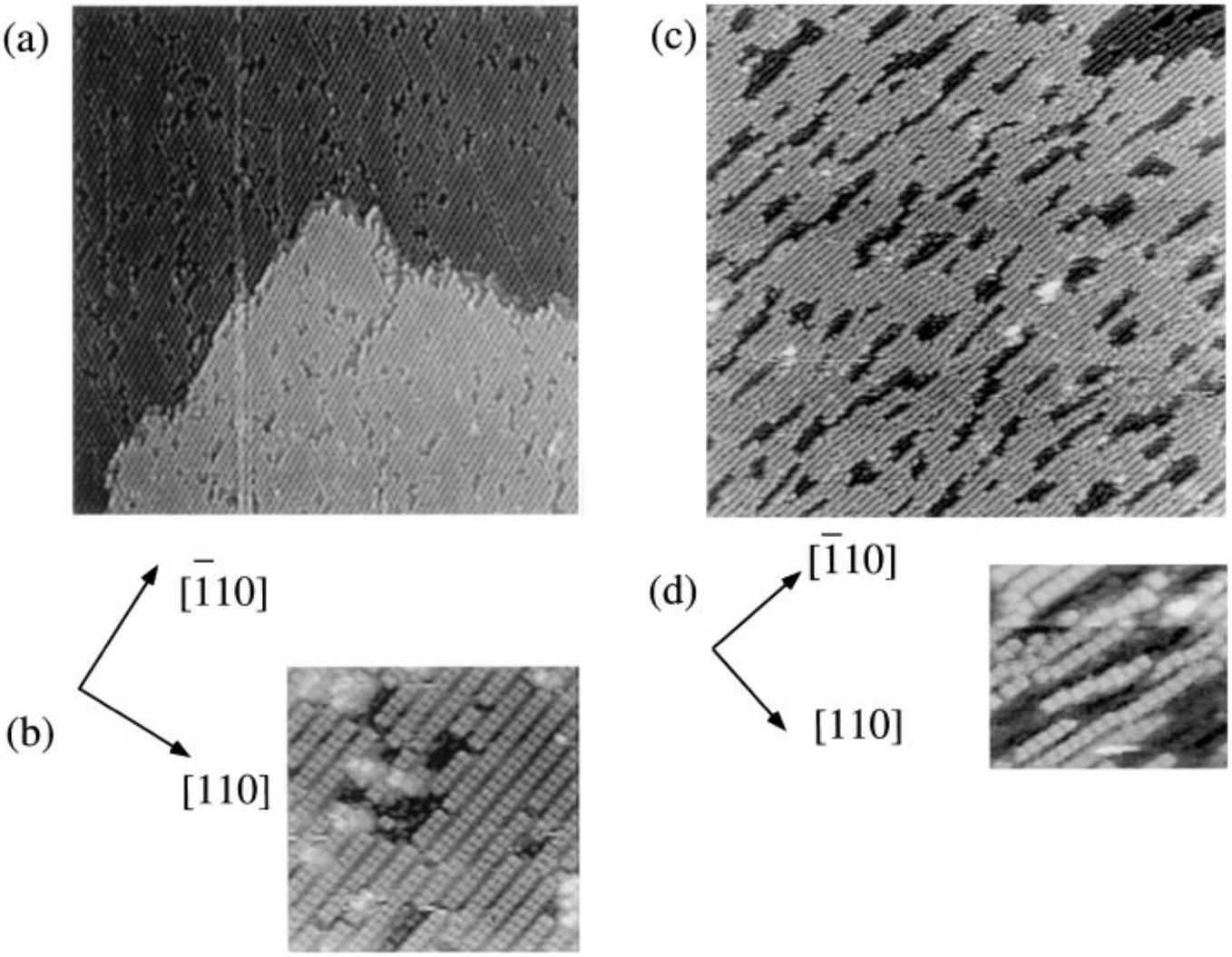

FIG. 2. Filled states STM images for (a),(b) the β-phase (2×4) surface and (c),(d) the γ-phase (2×4) surface. Image dimensions are (a) 1200 Å $\times$ 1200 Å, (b) 200 Å $\times$ 200 Å, (c) 1000 Å $\times$ 1000 Å, and (d) 190 Å $\times$ 160 Å. The depth of the missing dimer trenches is 1.4 Å. The depth of the holes in (c) is 2.8 Å, i.e., one bilayer.

reconstruction is consistent with the $\beta 2(2 \times 4)$ structure being appropriate for the ordered β-phase surface.

To describe the $\gamma(2 \times 4)$ phase, a small amount of extra arsenic was added to the $\beta 2(2 \times 4)$ computational cell. A number of adsorption sites for a single additional As atom were considered including insertion into surface and trench dimers, and bridging sites between two dimers both within and between (2×4) unit cells. The lowest energy adsorption site for a single additional As atoms is to insert into the trench dimer and form a bond across to one of the three coordinate gallium atoms in the second layer of the structure [Fig. 3(b)]. This is the only site in which As can be three coordinate without considerable distortion of the surface, and is lower in energy by more than 0.5 eV compared with any other site considered.

The kink energy for this structure is -0.20 eV indicating that in the presence of extra As kinks spontaneously form in the missing dimer row leading to the formation of the disordered $\gamma(2 \times 4)$ phase [Fig. 3(c)]. This result occurs for a range of extra As coverages from 0.016 (the minimum that can be added to the computational cell) to 0.25 ML (representing an arsenic atom inserting into every trench dimer); the range of coverages is consistent with previous TPD results [12]. For As coverages up to 0.125 ML, the kink energy is -0.20 eV, whereas between 0.125 and 0.25 ML it is -0.09 eV. It should be noted that although tight binding is not a self-consistent method, all charge transfers in the structures proposed for the kinked surface are towards the local charge neutrality limit. In this limit, tight binding is self-consistent [15]. Other structures, for which this is not the case, are already energetically unfavorable and imposing self-consistency is likely to make them worse.

An important result of the calculations is that the additional As prefers to be isolated, i.e., the structure with a single kink per As atom is more stable than one with two As atoms per kink [Fig. 3(d)]. The implication is that energetically As will form kinks for coverages up to

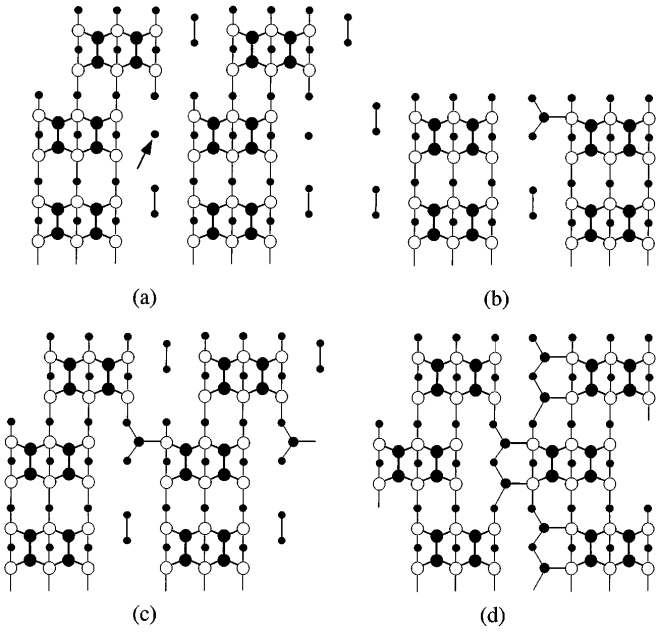

FIG. 3. A model based on tight binding calculations showing the transition with additional As from the β-phase to γ-phase GaAs(001)-(2 $\times$ 4) surface. The As occupies vacant Ga sites in the missing dimer trenches of the initial $\beta 2(2 \times 4)$ surface leading to disorder via kink formation. Filled circles represent As atoms and open circles represent Ga atoms.

0.125 ML, whereas from 0.125 to 0.25 ML it will simply fill the trenches without forming any additional kinks.

The possibility that two As atoms could form a more stable dimer at a site outside the trench was also considered. Tight binding calculations show that filling the missing dimer trench with 0.25 ML of additional As is preferred to the formation of As-As dimers above the two top layer As dimers of the (2 $\times$ 4) structure. The difference in energy is 5.8 eV per unit cell.

The calculations are therefore consistent with our model proposed on the basis of STM studies of the grown material. The $\beta 2(2 \times 4)$ structure is the appropriate structure for the β-phase surface. It is characterized by large domains of ordered dimer rows, with two As dimers per unit cell, two missing dimers, and Ga atoms absent from the missing dimer trenches [Fig. 1(a)]. Additional As (up to 0.25 ML) occupies the vacant Ga sites, inserting into the third layer As dimer and leading to kink formation (Fig. 3). It should be noted that while all the structural models in Fig. 1 for the well ordered β-phase surface satisfy electron counting models, the disordered nature of the γ-phase structure makes treatment by electron counting unsuitable.

The disorder observed in the γ-phase STM images presented here results from a different effect to that previously reported by Pashley and Haberern [11] due to n-type bulk doping. Both the β- and γ-phase surfaces shown in Fig. 2 were grown with the same low level of bulk Si doping; the kinks in the γ-phase surface *do not* arise from bulk doping effects. Instead, the disorder in this case is due to kink formation arising from the preferential occupation of second layer Ga sites by additional As atoms in the missing dimer trenches of the $\beta 2(2 \times 4)$ structure. The tight binding calculations show that the kinked trench dimer structure with no excess As is very unstable; in addition, it is neither a donor nor an acceptor since the two-coordinate As atoms have a full lone pair orbital. However, the kink structure which involves a single additional As atom is expected to be a good acceptor site since there is a deficiency of one electron per kink site. We suggest that the two kinking mechanisms may be related and that the $n+$ doped surfaces prepared by Pashley and Haberern [11] were more As rich than the unkinked surfaces.

In conclusion, we have proposed a mechanism for the introduction of disorder on the (2 $\times$ 4) reconstructed GaAs(001) surface prepared under As-rich conditions. The disorder manifests itself in the form of kinks in the missing dimer rows, whereby dimers adjacent along $[\bar{1}10]$ are offset by fractions of a unit cell dimension in the [110] direction. The ideal β-phase (2 $\times$ 4) surface has vacant second layer Ga sites which are potential sites for adsorption of any incident species. The preparation of the (2 $\times$ 4) surface under more As-rich conditions results in the adsorption of As on the surface by occupation of these sites. Tight binding calculations support the kinked structure as the most stable, with As atoms present in the missing dimer trench.

*Electronic address: t.jones@ic.ac.uk

[1] P. K. Larsen *et al.*, Phys. Rev. B **26**, 3222 (1982).
[2] M. D. Pashley *et al.*, Phys. Rev. Lett. **60**, 2176 (1988).
[3] J. H. Neave, B. A. Joyce, and P. J. Dobson, Appl. Phys. Lett. **34**, 179 (1984).
[4] H. H. Farrell and C. J. Palmstrom, J. Vac. Sci. Technol. B **8**, 903 (1990).
[5] D. J. Chadi, Vac. Sci. Technol. A **5**, 834 (1987).
[6] T. Ohno, Phys. Rev. Lett. **70**, 631 (1993).
[7] J. E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1993).
[8] J. E. Northrup and S. Froyen, Phys. Rev. B **50**, 2015 (1994).
[9] T. Hashizume, Q. K. Xue, J. Zhou, A. Ichimiya, and T. Sakurai, Phys. Rev. Lett. **73**, 2208 (1994).
[10] A. R. Avery, D. M. Holmes, J. Sudijono, T. S. Jones, and B. A. Joyce, Surf. Sci. **323**, 91 (1995).
[11] M. D. Pashley, and K. W. Haberern, Phys. Rev. Lett. **67**, 2697 (1991).
[12] C. Sasaoka, Y. Kato, and A. Usui, Surf. Sci. **265**, L239 (1992).
[13] X. P. Li, W. Nunes, and D. Vanderbilt, Phys. Rev. B **47**, 10 891 (1993).
[14] C. M. Goringe and A. P. Sutton, in Proceedings of EMRS, Strasbourg, 1995 (to be published).
[15] A. P. Sutton, M. W. Finnis, D. G. Pettifor, and Y. Ohta, J. Phys. C **21**, 35 (1988).