PHYSICAL REVIEW B **70**, 081313(R) (2004)

STM observation of Ga-dimers on a GaAs(001)-$c(8\times2)$-Ga surface

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(Received 6 July 2004; published 31 August 2004)

Using *in situ* scanning tunneling microscopy (STM) we have obtained high-resolution empty-state images exhibiting triple-protrusion rows on GaAs(001)-$c(8\times2)$-Ga surface. We assign the middle protrusion rows to the surface Ga dimers in the ξ model proposed by Lee *et al.* [Phys. Rev. Lett. **85**, 3890 (2000)]. The surface Ga dimers, which are responsible for the $c(8\times2)$ periodicity, are the key feature of the ξ structure and have never been imaged in previous STM studies. The current study provides direct evidence for the ξ model, while all other existing models can be readily excluded from our STM images.

DOI: 10.1103/PhysRevB.70.081313 PACS number(s): 68.35.Bs, 71.55.Eq, 07.79.Cz, 73.20.At

The GaAs(001) surface is of technological interest since it is an excellent substrate for both homoepitaxial and heteroepitaxial growth required in the fabrication of GaAs-based devices. GaAs(001) is also a prototype surface in semiconductor surface physics owing to the large variety of surface reconstructions observed under different preparation conditions.[1] Numerous experimental and theoretical studies have been performed since the type of reconstruction is expected to have significant impact on the quality of the epitaxial layers.[2] Existing knowledge on (001) surfaces of III-IV group semiconductors often leads to dimer-based reconstruction models. Strong evidence,[3–5] however, does suggest that some of these surfaces reconstruct in a more complicated way, one example being the GaAs(001)-$c(8\times2)$-Ga surface.

Since the observation of the GaAs(001)-$c(8\times2)$-Ga surface by Jona in 1965,[6] various structure models have been proposed for this surface. The first model, β [cf. Fig. 1(a)], was proposed by Frankel *et al.* based on their high-resolution electron energy loss spectroscopy analysis.[7] From their scanning tunneling microscopy (STM) observations, Biegelsen *et al.* and Skala *et al.* suggested the $\beta2$ model [cf. Fig. 1(b)] and As-rich model [cf. Fig. 1(c)], respectively.[8,9] A later STM study by Xue *et al.* supports the $\beta2$ model.[10] However, Cerdá *et al.* analyzed the three models by means of quantitative low-energy electron diffraction (LEED) and their analysis showed preference for the β model.[11] Recently, Lee *et al.* identified a ξ structure [cf. Fig. 1(e)] from their first-principles calculations and quantitative LEED analysis.[3]An independent study by Kumpf *et al.* using surface x-ray diffraction (XRD) with direct methods has led to a structure basically the same as the ξ structure.[4,12] The ξ structure is no longer based solely on dimers like the models proposed previously. Instead, it is characterized by a mixed structure of sp^2-bonded and dimerized Ga atoms, where the Ga dimers exist in both the *surface* and *subsurface* Ga layers. Recent studies by XRD,[13] reflection high-energy electron diffraction,[14] and noncontact atomic force microscopy[15] have offered support for the ξ model. However, we note that it is the Ga dimers that produce the $c(8\times2)$ periodicity[4] and these Ga dimers have never been imaged by STM, as pointed out by Mishima *et al.*[5] Imaging Ga atoms requires the STM to operate in empty-state mode, i.e., positively biasing the sample, since the Ga atoms provide unoccupied orbitals which accept electrons tunneling from the tip. To the best of our knowledge, only one empty-state STM study with atomic resolution on this surface has been conducted so far, where only double-protrusion rows, which correspond to the sp^2-bonded Ga atom rows in the ξ structure,[3] were observed by Xue *et al.*[16] In this paper, we present high-resolution

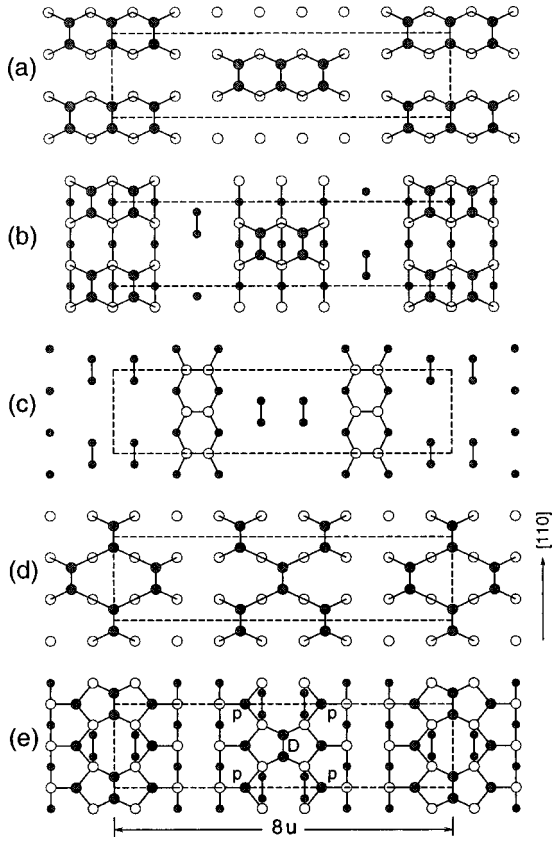

FIG. 1. Various reconstruction models proposed on a GaAs(001)-$c(8\times2)$-Ga surface. (a) β, (b) $\beta2$, (c) As-rich, (d) β', and (e) ξ models. Open circles denote As atoms. Bigger solid circles denote top layer Ga atoms and smaller ones second layer Ga atoms. The second layer Ga atoms in the β and β' models are in the bulk-truncated configuration and not shown. In the As-rich model, the surface is As-terminated.

empty-state STM images exhibiting triple-protrusion-rows on the GaAs(001)-$c(8\times2)$-Ga surface prepared by ion sputtering and annealing. The protrusions in the middle rows have a spacing of the length of two (1×1) basis vectors (denoted by $2u$ hereafter, cf. Fig. 1) and these are interpreted as the surface Ga dimers in the ξ structure. This observation provides direct evidence for the ξ model.

Experiments were carried out in a multichamber ultrahigh vacuum system equipped with an Omicron VT-STM as well as x-ray photoelectron spectroscopy (XPS). The base pressure of this system is better than 2.0×10^{10} mbar. The experimental details have been described previously.[17] In brief, the sample of dimension 2×10 mm used in this study was cut from an *n*-type GaAs(001) wafer. *In situ* cleaning was carried out by repeated cycles of Ar-ion sputtering at 1 kV and annealing at 500°C until no contamination can be detected by XPS. The STM experiment was conducted in a constant current mode with a dc-etched tungsten tip. All images were captured with a tunneling current of 0.1 nA at room temperature. In order to determine the reconstruction periodicity, the piezoelectric scanning tube was calibrated by scanning a standard Si(111)-(7×7) surface with the same tip after the experiment.

The $c(8\times2)$ phase is known to be the most prominent high-temperature phase and often coexists with one of several proposed As-rich $(n\times6)$ phases at the temperature range 500–650°C.[14,18] In our experiment, the $(n\times6)$ reconstruction was obtained by annealing the sample to 550°C. After increasing the annealing temperature to 580°C for 30 min, the $c(8\times2)$ phase developed. In Fig. 2 we show the large-scale filled-state and empty-state STM images obtained on the same area. The sample biases are −1.9 V and +1.9 V, respectively. On both images, it can be seen that the $c(8\times2)$ domains are surrounded by $(n\times6)$ domains which are one atomic layer higher. The protruding rows on the two domains are perpendicular to one another. As measured by XPS, the Ga to As atomic ratio increases from 0.96 to 1.18 before and after the $c(8\times2)$ phase develops. These results indicate that the topmost As layer on the $(n\times6)$ structure has partially evaporated revealing the $c(8\times2)$ phase with a Ga-rich structure.

Comparing the filled-state with the empty-state images in Fig. 2, it can be seen that distinct images of the $c(8\times2)$ domain can be obtained by using negative and positive sample biases. However, the bias dependence on the $(n\times6)$ domain is relatively weaker than on the $c(8\times2)$ domain. The filled-state image [Fig. 2(a)] looks as if the $c(8\times2)$ domain is composed of single-protrusion rows. This observation is consistent with previous large-scale filled-state STM images.[14] Using high-resolution STM, the single-protrusion rows have been resolved into double-protrusion rows,[8–10] which are attributed to the As atom rows in either the topmost or the second As layer, depending on the magnitude of the negative sample bias.[3] In both high-bias and low-bias conditions, the two rows in a double-protrusion-row have a spacing of just $1u$. Also, any two protrusions within a row have a spacing of $1u$. This explains why, in large-scale filled-state images, individual As atoms are somewhat hard to resolve and look like single-protrusion rows as in Fig. 2(a). In contrast, in the empty-state image [Fig. 2(b)], the $c(8\times2)$ domain can be seen with more detail since, as will be shown, each bright row on this image actually consists of three rows of protrusions and any two protrusions within the middle rows have a spacing of $2u$.

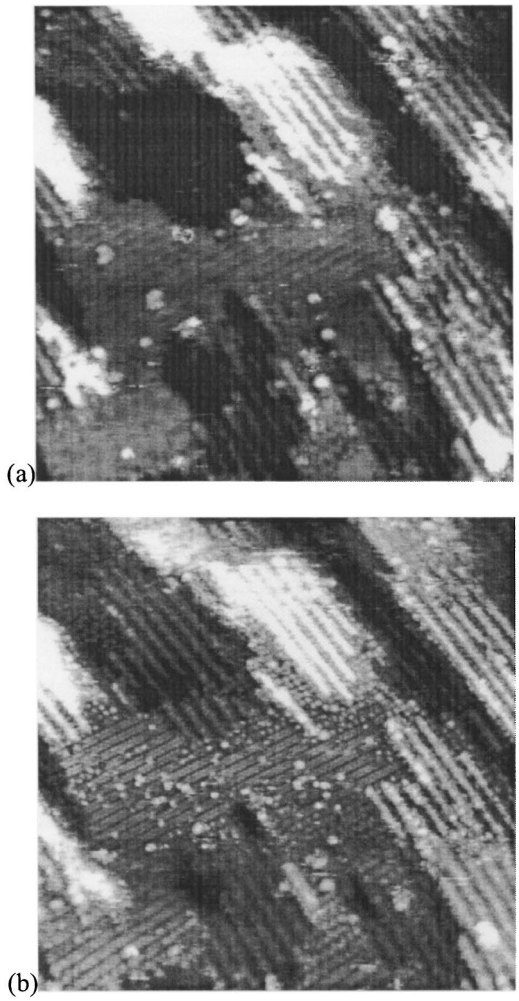

FIG. 2. STM images of GaAs(001) surface illustrating the Ga-rich $c(8\times2)$ domains surrounded by original As-rich $(n\times6)$ domains. The scan size is 720×720 Å. The images are captured simultaneously. (a) A filled-state image captured at $V_s=-1.9$ V. (b) An empty-state image captured at $V_s=+1.9$ V.

To reveal the detailed structure of the $c(8\times2)$ domain, we performed high-resolution empty-state scans. Figure 3(a) shows an image captured at +1.9 V sample bias and Fig. 3(b) at +1.6 V. Triple-protrusion rows can be clearly seen in both images, where the bright rows are separated by dark trenches and the distance between the centers of two adjacent trenches is $4u$. In both images, the protrusions in the middle rows have a spacing of $2u$. However, in the two outside rows the spacing is $1u$ at +1.9 V bias and $2u$ at +1.6 V. Hence, it is easier to identify individual protrusions in Fig. 3(b).

To interpret the triple-protrusion-row image in Figs. 3(a) and 3(b), we find the ξ model particularly appealing. We assign the middle protrusion rows to the surface Ga dimers in the ξ model, labeled "D" in Fig. 1(e), where each Ga dimer produces one protrusion. The two outside rows are

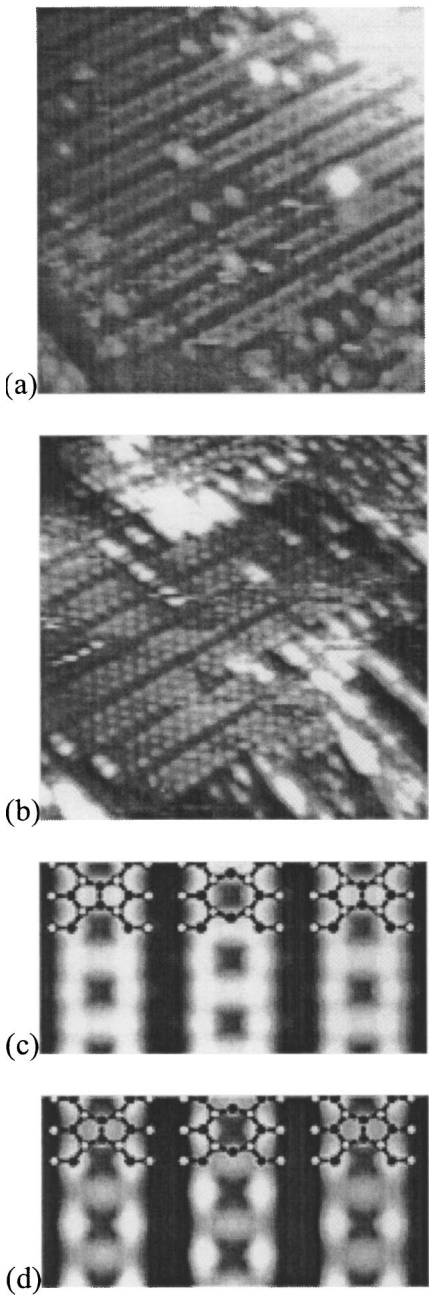

FIG. 3. Atomically resolved GaAs(001)-$c(8\times2)$ surface at $V_s = +1.9$ V (a) and $V_s = +1.6$ V (b). The scan size is 150×150 Å. Simulated STM images at +1.8 V (c) and +1.5 V (d) bias voltages, which are given with respect to the valence-band maximum (Ref. 3).

produced by the p_z states of the sp^2-bonded Ga atoms. The simulated STM images by Lee *et al.* at sample biases +1.8 V and +1.5 V are reproduced in Figs. 3(c) and 3(d), respectively.[3] It is noted that there are two inequivalent sp^2-bonded Ga atoms. In the +1.8 V image, both can be seen. However, in the +1.5 V image, only the one labeled by "p" in Fig. 1(e) is responsible for the protrusions. This results in the spacing of $2u$ between two adjacent protrusions in the +1.5 V image. Our STM observations are consistent with the simulation results.

We now show that no other existing models can give a reasonable explanation to the images in Fig. 3. Firstly, the $\beta2$ model and the As-rich model can be safely excluded. On both models, the first layer Ga atoms are grouped in dual chains, which would not produce the triple-protrusion-row image. Moreover, the distance between each pair of dual chains is $3u$, hence the expected trench width in empty-state STM images from the two models is wider than observed. Neither is the β model a suitable candidate since the three Ga dimers in this model are collinear, an arrangement that is not consistent with the staggered rows of protrusions observed in Fig. 3(b).

Notwithstanding the apparent success of the ξ model, there is still another feasible model that accounts for our STM images. This is based on a slight modification of the β model and has not been previously mentioned in the literature. We name this β' [cf. Fig. 1(d)], and its structure is such that the middle row of Ga dimers is shifted by $1u$ relative to the other two rows along the [110] direction. If each protrusion is attributed to one Ga dimer, the β' model is consistent with the triple-protrusion-row image. To test the validity of the β' model, we performed first-principles total-energy calculations.

Our first-principles total-energy calculations are based on density functional theory. We use the program package VASP employing plane waves as the basis functions.[19] The interactions between valence electrons and ion cores are described by Vanderbilt-type pseudopotentials.[20,21] The local density approximation[22] is used for the exchange-correlation functional. The cutoff energy for the plane-wave basis set is set to 20 Ry. The surface is modeled by periodically arranged slabs. Each slab consists of four Ga layers and four As layers. The bottom As layer is saturated by partially charged hydrogen atoms.[23] Adjacent slabs are separated by a vacuum layer of about 10 Å. Instead of using a (4×2) unit cell to simulate the $c(8\times2)$ periodicity,[3,24] we use the unit cell illustrated in Fig. 1, which can be reduced to a rhombic primi-

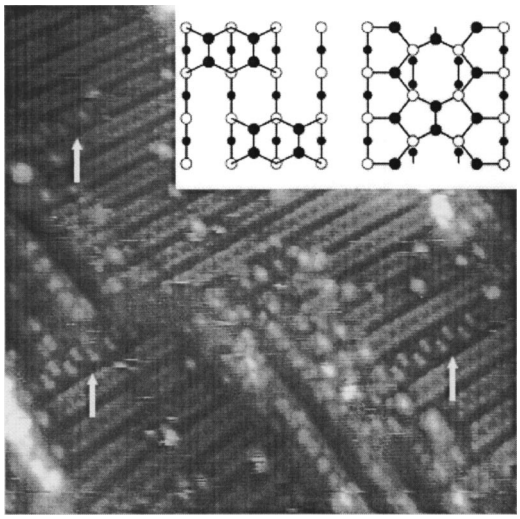

FIG. 4. STM images of GaAs(001)-$c(8\times2)$ surface with zigzag shape defects. The scan size is 280×280 Å. Sample bias $V_s = +1.9$ V. The inset shows a proposed model for the coexistence of the defective β structure and the ξ structure.

tive cell having the same area as the (4×2) unit cell. Two irreducible k points were used to sample the surface Brillouin zone. The structural optimizations were conducted according to the Hellmann-Feynman forces until the force on each ion becomes less than 1 mRy/Bohr (about 25.7 meV/Å).

Our calculations show that the β' model is energetically less favorable compared to the ξ model by 1.1 eV per $c(8\times2)$ primitive cell. Since the numerical error of our calculations is estimated to be less than 0.1 eV per $c(8\times2)$ primitive cell, this total-energy difference is considered significant. For comparison, we conducted the same calculation on the original β model, which has a total energy 0.8 eV per $c(8\times2)$ primitive cell higher than the ξ model. This is in good agreement with the previous calculation by Lee *et al.*[3] Despite the high total-energies of the β' and β structures, due to the same chemical potential (number of atoms) possessed by these two structures as the ξ structure, it is reasonable to postulate that the more complex ξ structure may be evolved from one of the two structures.

In Fig. 4 we show a 280×280 Å topography of the ξ surface. It can be noticed that several protrusion rows of the ξ structure are terminated by the zigzag shape protrusion rows marked by arrows. This structure can be easily matched to a defective β structure with one of the three dimers missing, as illustrated in the inset of Fig. 4. We postulate that these defects may be the residuals of the β structure which did not evolve to the ξ structure in the transition from β to ξ due to the large chemical potential difference. This implies that the change in the chemical potential by introducing (or removing) a Ga dimer into (from) the system is larger than the total-energy difference between the ξ and β structures, i.e., 0.8 eV.

In conclusion, high-resolution empty-state images with triple-protrusion rows on the GaAs(001)-$c(8\times2)$-Ga surface have been observed by *in situ* STM. A reasonable interpretation of this image has been provided by the ξ model, where the middle protrusion row is assigned to surface Ga dimers and the two outside rows are attributed to sp^2-bonded Ga atoms. This result may be considered as the best direct evidence for the ξ model at the present time.

The authors acknowledge M. Scheffler and W. Moritz for providing us with the simulated STM images. We wish to thank E. S. Tok for helpful discussions. This work was supported by the National University of Singapore Grant No. R-144-000-022-112.

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