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Structural features of Ga-rich GaAs(001) surfaces: Scanning tunneling microscopy study

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We present the study of GaAs(001) reconstructed surfaces using scanning tunneling microscopy. None of the previously published structural models of (6×6) and (4×6) reconstructions can sufficiently describe our observations. In order to explain observed images, As atoms at faulted positions and surface Ga-As mixed dimers are proposed to be the elements included in the structural models. The mechanism of transition between $c(8\times2)$ and (6×6) structures via line-aligned defects of $c(8\times2)$ is also discussed.

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Surfaces of the group III-V semiconductors are of great scientific interest for development of many—mostly electronic—devices with unique properties. Detailed knowledge of the surface reconstructions is crucial for both homo- and heteroepitaxy on the surfaces. To give an example, metal films grown on the reconstructed GaAs(001) surfaces show strong uniaxial magnetic anisotropy,[1,2] of interest in the frame of "spin electronic" progress.

The atomic structures of As-rich reconstructions $c(4\times4)$,[3–6] (2×4),[7–10] and Ga-rich $c(8\times2)$,[11,12] have been well established. However, despite considerable efforts,[13–15] no well-established model has been proposed for Ga-rich (6×6) and (4×6) reconstructions, also called $(n\times6)$, (2×6), or $(2\times6)/(3\times6)$ in case of (6×6). It has been reported that the Ga-rich $c(8\times2)$ structure is stable only at high temperatures and changes to (6×6) as the substrate temperature is decreased.[12,15,16] Thus, the structure identification of the (6×6) surface is a key to understanding surface reconstructions and the related surface phase transitions on the GaAs(001) surfaces under Ga-rich conditions.

Several structural models of the (6×6) surface,[13–15] based on the interpretation of scanning tunneling microscopy (STM) images, have been proposed during the last 15 years. All these models contain Ga-Ga and As-As dimers as basic surface structural elements. Recently,[16] several reasons to discard the proposed models have been reported: (1) all the structures are at least energetically metastable; (2) calculated reflectance anisotropy spectra calculated from the proposed structure models do not agree with the measured data.

The (6×6) reconstruction is usually obtained by cooling the more Ga-rich $c(8\times2)$ surface and the coexistence of both phases is easily achieved, as we will show later. Thus, the promising structural elements for (6×6) are Ga subsurface dimers (resulting in surface As atoms in faulted positions comparing to bulk) used successfully to explain the structure of the $c(8\times2)$ reconstruction (Fig. 1).[11,12] Furthermore, the presence of another structural element—surface mixed Ga-As dimer—has been suggested for the $(n\times6)$ reconstructions[16] as the configuration more stable than the surface As-As dimers.

The area of both (4×6) and (6×6) reconstructions can be divided into dark troughs and bright rows according to filled-state STM images (Fig. 2). The difference in the apparent height of the bright rows and the dark troughs is approximately 2 Å. This high corrugation of the surfaces makes the STM observation difficult because of the tip-screening effect.

In this paper, we present the STM images of GaAs(001)-(6×6) and (4×6) surfaces with a high resolution of the bright rows and dark troughs. The resolution allows us to identify the presence of the proposed structural features—As atoms at faulted positions within the dark troughs and mixed Ga-As dimers coexisting with As-As dimers in bright rows. We have distinguished As atoms in faulted and unfaulted positions comparing to the bulk similarly to the pattern of the $c(8\times2)$ reconstruction. The presented structure models are completely different from the models already published.

The experiments were performed in a system of interconnecting ultrahigh vacuum (UHV) chambers for the molecular-beam epitaxy (MBE) growth and for on-line surface characterization by means of STM.[9,17] The MBE chamber is equipped with RHEED and reflectance difference spectra (RDS) apparatuses. Samples of Si-doped and nominally on-axis GaAs(001) (epi-ready) were used. Cleaned GaAs(001)-(2×4) surfaces were first obtained by growing

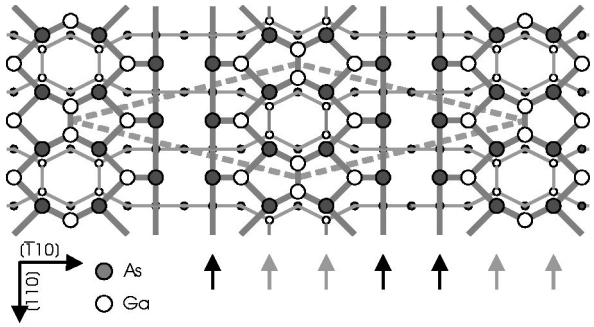

FIG. 1. A schematic structure of the $c(8\times2)$ reconstruction with the subsurface Ga dimers (Ref. 11). Black (gray) arrows mark the lines of As atoms in unfaulted (faulted) positions comparing to the bulk positions.

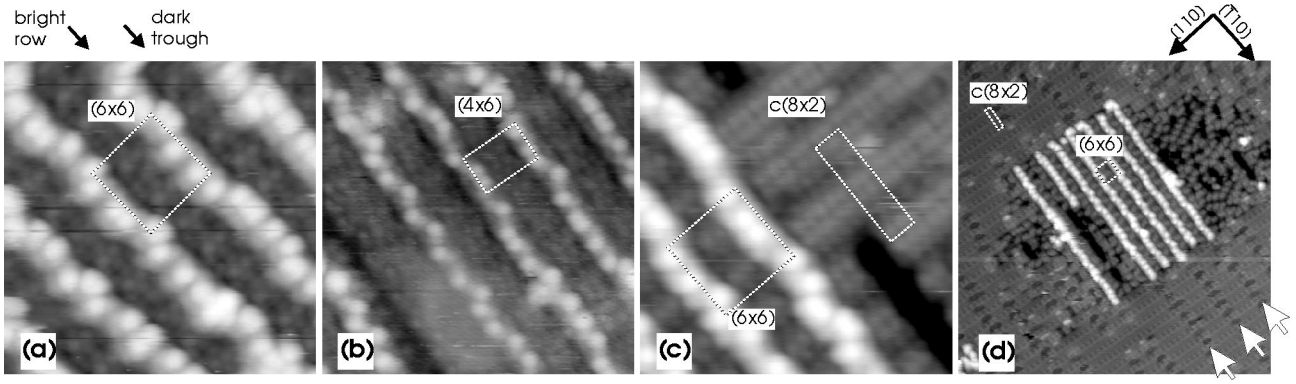

FIG. 2. STM filled-state images of (a) (6×6) reconstruction (tip voltage -3.5 V), (b) (4×6) reconstruction (-3 V), (c) detail of coexisting (6×6) and $c(8\times2)$ phases (-4.7 V), and (d) coexisting (6×6) and $c(8\times2)$ with lines of defects marked by white arrows (-2.8 V).

an undoped homoepitaxial layer on a thermally cleaned substrate. Then, the more Ga-rich reconstruction of $c(8\times2)$ was obtained by heating the (2×4) surface above 600 °C in a good UHV condition of $\approx5\times10^{-11}$ Torr. During the preparation processes, the RDS measurements and the RHEED observations were carried out, in order to identify the surface reconstruction. The sample prepared in the MBE chamber was transferred via the UHV modules to the STM chamber (Omicron micro-STM), where the observations were performed at room temperature (RT) in the constant-current mode.

The well-ordered (6×6) surfaces were obtained by slowly cooling the Ga-rich $c(8\times2)$ surface from 620 to 500 °C (0.05 °C/s). The (6×6) surface can be also prepared by annealing the As-rich (2×4) surface at 500 °C for a relatively long time (typically ≈1 h). After dosing of at least 0.2 monolayer (ML) of Ga at 500 °C the (6×6) reconstruction changes to (4×6). For a lower amount of dosed Ga the coexistence of $6\times$ and $4\times$ symmetry is observed (Fig. 3). During cooling the (4×6) and (6×6) from 500 °C to RT the shapes of the RHEED rocking curves and the RDS spectra stayed essentially unchanged; the structures are therefore almost preserved.

The STM images of (4×6) and (6×6) surfaces are distinguishable only within the dark troughs; the structure of the bright rows is therefore supposed to be very similar or identical. The similarity of both structures was also confirmed by the RHEED observations: we could not distinguish the RHEED patterns from both surfaces along the $[\bar{1}10]$ direction. Therefore, appropriate atomistic models of both reconstructions have to consist of very similar structural elements.

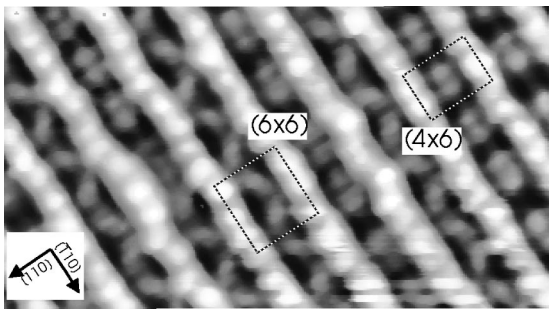

FIG. 3. STM image of coexisting (6×6) and (4×6) reconstructions. The sample was prepared by depositing 0.1 ML of Ga on the (6×6) surface at 500 °C. The local equalization filter has been used to show both dark troughs and bright rows. The tip voltage is -2.8 V.

In order to obtain details about the (6×6) structure, the observation of coexisting phases has been performed. When the sample with the $c(8\times2)$ symmetry is rapidly cooled from 600 °C (1.0 °C/s), the coexistence of (6×6) and $c(8\times2)$ reconstruction is achieved. The pattern of the dark troughs of (6×6) shows similar features as the pattern of $c(8\times2)$, as shown in the high-resolution image [Fig. 2(c)]. In the filled-state STM image of $c(8\times2)$ the positions of the topmost As atoms are highlighted; two rows of the faulted (brighter) and two rows of the unfaulted (darker) As atoms repeat along the $[\bar{1}10]$ direction.[18] A recently proposed structural model of $c(8\times2)$ (Fig. 1), supported by the x-ray diffraction[11] and by calculations,[18] contains half of the surface As atoms at positions faulted comparing to the bulk positions, due to the presence of the subsurface dimerized Ga atoms. From the similarity of the patterns of the (6×6) dark troughs and $c(8\times2)$ we derive that bright dots of dark troughs have the same explanation; only the symmetry is changed to two rows of 3 atoms unfaulted and one row of 2 atoms faulted [see the detail shown in Fig. 4(a)]. The six dots corresponding to unfaulted atoms are not symmetric with respect to the axis of the dark trough; one pair of dots is less intensive. A periodic repeating of the two possible orientations of the 2×3 dots together with two dots at faulted positions results in the $6\times$ periodicity along $[\bar{1}10]$ and in the zigzag pattern observed at some STM conditions (Fig. 3). The corresponding atomistic model with two Ga subsurface dimers per unit cell is shown in Fig. 4(c).

Using the same structural elements as in Fig. 4(c) the $4\times$ periodicity of the (4×6) structure can be also achieved, as shown in Fig. 4(d).

Figures 2(a) and 2(b) show typical images of the bright rows of $(n\times6)$ reconstructions, observed as random sequences of bright spots aligned in two 4-Å distanced lines. The separations between the spots along the $[\bar{1}10]$ direction can vary a lot. The $2\times$ periodicity is expected within the

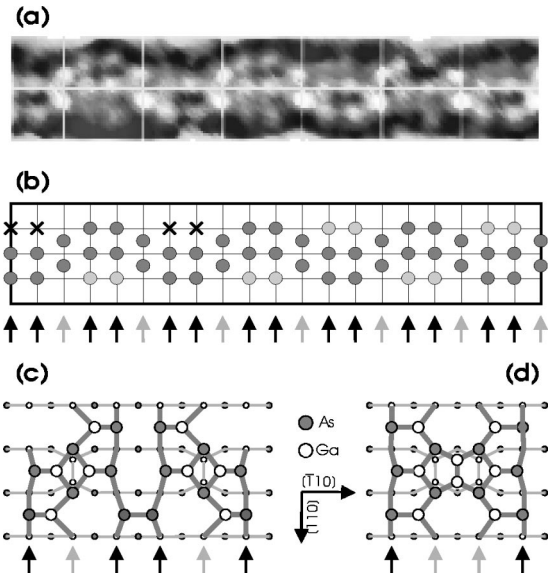

FIG. 4. (a) STM detail of the dark trough of the (6×6) surface. Corresponding positions of spots are schematically shown in (b) for better orientation. Crosses mark the defects—missing spots in the pattern. Black (gray) arrows mark As atoms in unfaulted (faulted) positions. (c) The schematic atomic model of the (6×6) dark trough. (d) Modification of structural elements used in (e) resulting in the $4\times$ periodicity along the $[\bar{1}10]$ direction.

bright rows from the RHEED patterns taken along the [110] direction.[16]

According to the detail shown in Fig. 5 we propose the following explanation of the $2\times$ periodicity in agreement with the observed images: the bright spots correspond to dangling bonds of As atoms of mixed Ga-As and As-As dimers.

Since only As atoms are imaged in the STM images, the coexistence of Ga-As, As-Ga, and As-As dimers results in the various separations between the bright spots along the $[\bar{1}10]$ direction (discussed, e.g., in Ref. 19). Such a coexistence in dimers, however, does not disturb the $2\times$ periodicity observed by the RHEED, because the atomic scattering factors of Ga and As are quite close.

In our images we are able to distinguish both types of dimers: the mixed dimer pattern consists of one bright spot and a much less intensive spot on the axis of the bright line. The separation along $[\bar{1}10]$ of two bright spots corresponding to As atoms of neighboring Ga-As and As-Ga dimers [e.g., "MD3" and "MD4" in Fig. 5(b)] is 4.5 Å, corresponding to relaxation of As atoms of the mixed dimer along $[\bar{1}10]$ close to the Ga position. The similar relaxation is observed at the As-rich $c(4\times4)$ structure containing the mixed dimers,[9] as well as in case of InP(001)-(2×4) reconstructions.[20] The position of the less intensive spot corresponds to the on-axis Ga bulklike second layer atom [position "×" in Fig. 5(d)]. Note that the interpretation of the less intensive spot as the multiple-tip image of the brighter spot can be excluded, as all four possible orientations of the pair less intensive spot-brighter spot are observed. The image of As-As dimer consists of two bright spots separated by 2.5 Å with no observed less intensive spots [see the profile plots in Fig. 5(c)]. When

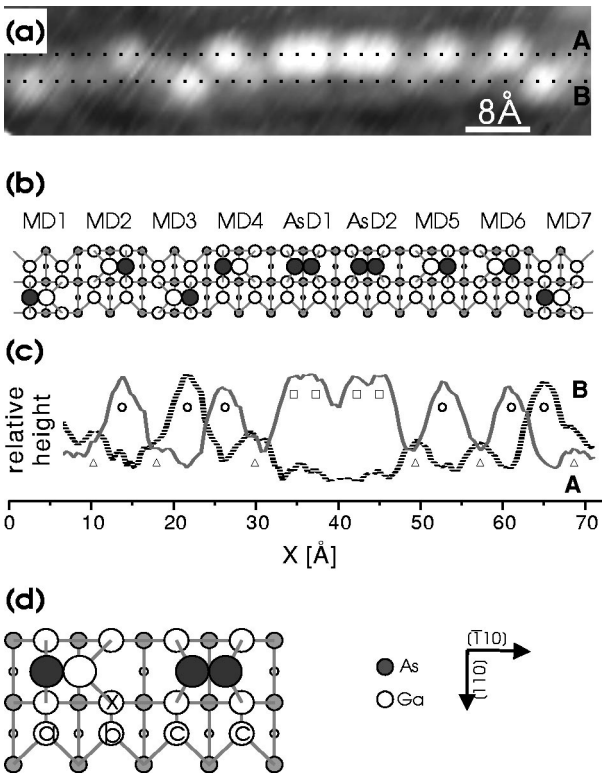

FIG. 5. (a) STM detail of the bright line of the (4×6) reconstruction; (b) corresponding proposed structural model (MD: mixed dimer, AsD: As dimer); (c) line profiles of two parallel lines distanced 4 Å [marked "A" and "B" in (a)]. Peaks corresponding to the As bond of the mixed dimer (circle), the As bond of the As dimer (square), and the less intensive spot of the mixed dimer (triangular) are marked. (d) Detail of the proposed model with positions marked according to text.

the STM resolution is not good enough the two spots are observed as one protrusion.

The ratio of mixed dimers has been evaluated by the analysis of the STM images as 75% and 92% for (6×6) and (4×6), respectively. Although the ratio can probably vary for different preparation conditions, we give the experimental evidence that the mixed dimers are more favorable than the As-As dimers.

An approximate structure of the bright row is shown in Fig. 5(d). Due to the tip-screening effect we are not able to specify for certain the structure of the second layer. The possible modifications of the presented model are: As atom in position marked "b" or "x," unoccupied positions "a," "b," or "c." *Ab initio* calculations and diffraction experiments will be necessary to clarify the detailed structure.

In the images of coexisting (6×6) and $c(8\times2)$ the bright lines are often continued over the boundary of the reconstructions by the lines of defects of $c(8\times2)$, appearing darker than the surrounding area at the tip voltage -3 V [Fig. 2(d)]. The similar lines have been observed, e.g., by Moosbühler *et al.*[1] We suggest that the defects of $c(8\times2)$ relate to rearranged subsurface Ga dimers, resulting in the bright lines with no subsurface dimers after transition to (6×6). However, the atomic structure and the reason for the aligning of defects are still missing.

In conclusion, we present elements of structural models of (6×6) and (4×6) reconstructions. We have clarified the $2\times$ periodicity of the bright rows with respect to the high-resolution STM images. The combination of the mixed Ga-As dimers and the As-As dimers agrees perfectly with our STM observations when considering a relaxation of As atom of the mixed dimer along $[\bar{1}10]$ close to the position of the second layer Ga atom. The mixed dimers are more favorable for both structures. Furthermore, we have shown the atomically resolved images of the dark troughs of (6×6) and (4×6) reconstructions, and from resemblance to the image of $c(8\times2)$ we proposed the presence of As atoms at faulted positions comparing to the bulk. The presence of the faulted atoms is explained by the subsurface Ga dimerization. The frequency of the subsurface dimers results in the $3\times$ and $4\times$ periodicities along the $[\bar{1}10]$ direction. The $6\times$ periodicity of (6×6) is observed due to the repetition of two possible orientations of the (3×3) blocks.

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