Structure of GaAs(001) (2×4)-$c(2\times8)$ Determined by Scanning Tunneling Microscopy

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The scanning tunneling microscope (STM) has been used to study the (2×4)-$c(2\times8)$ reconstruction on the arsenic-rich surface of GaAs(001). The STM images show that the $4\times$ periodicity is due to a regular array of missing arsenic dimers. The (2×4) units are arranged so as to give small domains of either (2×4) or $c(2\times8)$ reconstructions. These images are the first high-resolution STM images obtained from a surface grown by molecular-beam epitaxy. Features are seen which may be important in the mechanism of growth.

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The GaAs(001) surface is the most widely used gallium arsenide face in molecular-beam-epitaxy (MBE) growth of device structures. A series of reconstructions dependent on surface stoichiometry have been reported. They range from the arsenic-rich (2×4) [or $c(2\times8)$] reconstruction to the gallium-rich (4×2) [or $c(8\times2)$] reconstruction. The detailed structure of these surfaces has been under investigation for several years. The most important of these in MBE growth is the arsenic-rich (2×4)-$c(2\times8)$ surface, since growth usually begins and ends with this surface. In order to understand the detailed mechanisms of growth, it is essential to determine the initial surface structure. Two principal models for the arsenic-rich (2×4) surface have been proposed. In this paper, we present the first scanning-tunneling-microscope (STM) images of this surface which clearly differentiate between these models. These images also represent the first high-resolution STM images of an MBE-grown surface.

Most of the structural determination on the arsenic-rich surface has been done during growth by reflection high-energy electron diffraction (RHEED), showing a (2×4) or $c(2\times8)$ reconstruction.[1-3] LEED results from this surface show a disordered $c(2\times8)$ structure.[4,5] The difference between the (2×4) and $c(2\times8)$ reconstructions arises from the way in which the basic (2×4) units are arranged relative to one another. Both RHEED and LEED show disorder on the surface which could be explained by the presence of both (2×4) and $c(2\times8)$ domains.[6] An unreconstructed GaAs(001) arsenic-rich surface would consist of a square array of arsenic atoms (unit cell 4×4 Å^2), bonded to two gallium atoms in the layer below, with two partially filled dangling bonds upwards oriented parallel to the $[\bar{1}10]$ direction [Fig. 1(a)]. Since this surface reconstructs with a $2x$ periodicity along the $[\bar{1}10]$ direction, all models assume that the arsenic atoms pair up to form dimers in this direction. The problem has always been to determine the arrangement of these dimers which results in a $4\times$ periodicity along the [110] direction. The first model for this surface con-

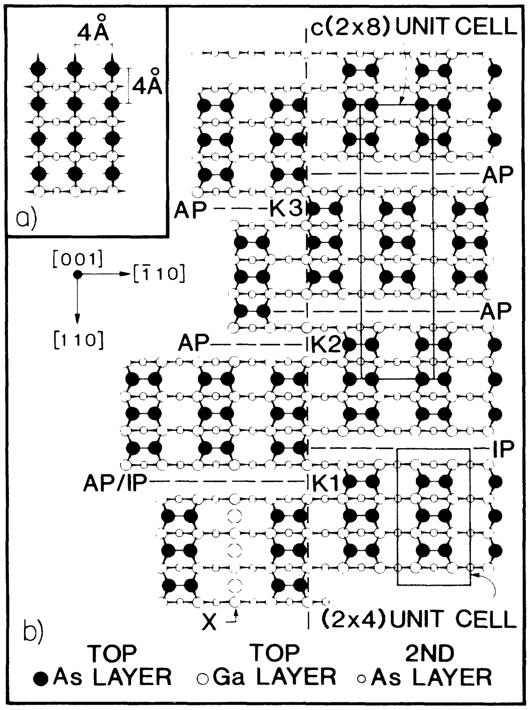

FIG. 1. (a) The structure of the unreconstructed GaAs(001) arsenic-rich surface. (b) The missing-dimer model for the GaAs(001) (2×4) surface. The two types of missing-dimer boundary, in-phase (IP) and antiphase (AP), are shown giving rise to (2×4) and $c(2\times8)$ structures. The intersection of a domain boundary along the [110] direction with the IP and AP boundaries is shown giving rise to three types of boundary kinks: K_1, K_2, and K_3. Disorder in the arsenic pairing (X) with three missing arsenic atoms (dashed circles) is also shown.

sists of a complete layer of arsenic dimers which are tilted so that one atom moves up and the other down.[7] These tilted dimers are then arranged to give a $4\times$ periodicity in the [110] direction. This model is not fully consistent with the details of the diffraction features seen in RHEED. It is therefore necessary to invoke a tilting and twisting of the dimers in order to be consistent.[8] Even then, this model cannot fully explain photoemission data and the effects of hydrogen adsorption.[3] More recently, vacancy models have been proposed.[9,10] Chadi[9] has carried out total-energy calculations showing that a unit cell with three arsenic dimers and one missing dimer is energetically the most favorable for the (2×4) surface [Fig. 1(b)]. This model appears to be consistent with experimental data. Since this surface involves some disorder, and the unit cell is relatively large, it has proved difficult to make an absolute structure determination from diffraction. We have obtained real-space images of this surface with the STM. Our results show that the $4\times$ periodicity does arise from a regular array of missing dimers.

The tunneling microscope used for these experiments (described in detail elsewhere[11]) is inside an ultrahigh-vacuum (UHV) system which includes facilities for Auger-electron spectroscopy, LEED, RHEED, and surface preparation. It is possible to transfer both sample and tip out of the UHV system without the breaking of vacuum. A key feature of this study was the ability to transfer the MBE-grown GaAs(001) sample to the STM chamber through air. We used the Kowalczyk *et al.*[12] technique of capping the sample with As prior to removal from the MBE system. A 1-μm GaAs film was deposited on a GaAs(001) substrate at 600 °C in 1 h, both doped with Si ($n=2\times10^{18}$ cm^{-3}). Once cooled to near room temperature, the sample was exposed to an As_2 flux for 6 min followed by an As_4 flux for 15 min. Once inside the STM's UHV system, the arsenic capping layer was removed by our heating it to about 370 °C for several minutes. The specimen was heated briefly to about 450 °C and allowed to cool to room temperature for both LEED and STM studies. The surface was found to be free of oxygen and carbon contamination by Auger-electron spectroscopy. LEED showed a $c(2\times8)$ pattern with streaking of the half-order features along the [110] direction as has been reported by others.[4,5] We have confirmed that we are looking at the arsenic-rich surface by heating the specimen to about 550 °C. We then observe a $c(8\times2)$ structure with LEED, corresponding to a gallium-rich surface.[4,5] The LEED data provide the orientation of the specimen with respect to the scan direction of the STM.

It was found that stable tunneling could only be achieved with the sample negative with respect to the tip, that is, tunneling from filled states in the sample. In the opposite polarity, tunneling was very unstable and it proved impossible to obtain images. This behavior was found with many different tips and so is likely to be characteristic of the arsenic-rich (2×4) surface. The images obtained from filled states were made with a voltage in the range -2 to -3 V and a tunneling current of typically 0.2 nA. As for the GaAs(110) surface,[13] we expect filled states to be concentrated on the arsenic and empty states to be concentrated on gallium. Thus on the arsenic-rich (001) surface which has only arsenic in the outer layer, the density of filled states should be high, whereas the density of empty states is expected to be low. Our observation that stable tunneling is restricted to filled states is therefore consistent with the surface being arsenic. On a surface that has been heated to produce a $c(8\times2)$ LEED pattern, we find equally stable tunneling in either polarity. In this case we might expect the density of empty states to be higher than on the arsenic-rich surface. This further indicates that the stability of the tunnel current is related to the GaAs surface and not the tip.

The STM image shown in Fig. 2 is typical of the images obtained from this surface. The image is displayed as a gray scale with black low and white high. The most obvious features are dark bands running along the $[\bar{1}10]$ direction with a spacing in the [110] direction of 16 Å [calibration being made from previous observations of the Si(111) (7×7) surface[11]] corresponding to the $4\times$ spacing. The width of these dark bands is 4 Å with the bright regions in between being 12 Å wide. The bright areas also have a periodicity along the $[\bar{1}10]$ direction of 8 Å corresponding to the $2\times$ spacing. The resolution of this image is not sufficient to see detail within the 8×12-

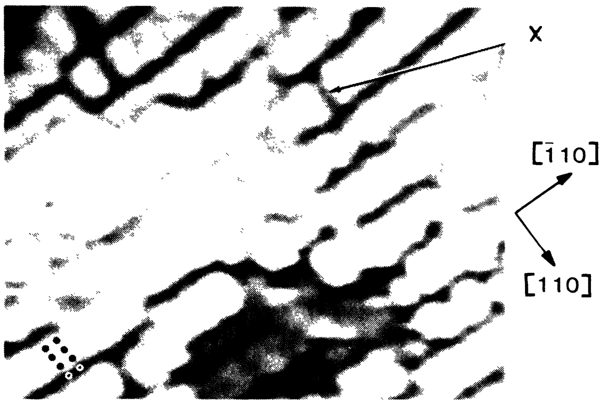

FIG. 2. A typical STM image of the GaAs(001) (2×4) surface showing a 165×130-Å^2 area including small islands one plane up (light) and one plane down (dark), each having the same structure as the main plane. Disorder in the pairing of arsenic atoms can be seen at *X*. The upper right-hand side of the image is a region of well-ordered (2×4). The atom positions are marked with filled circles and the missing-atom sites are marked with open circles. The image was taken with the sample at -2.3-V and 0.2-nA tunneling currents. The gray scale covers a vertical height of 7 Å.

Å^2 bright features. Since filled states are localized on the arsenic atoms,[13] the bright regions of the image should correspond to the positions of arsenic atoms. The STM images are consistent with each unit cell containing three dimers and a missing dimer as shown in Fig. 1(b). The dark bands correspond to the rows of missing dimers and the bright features correspond to the three dimers within a (2×4) unit cell. The six arsenic atoms forming the three dimers in a unit cell, together with the sites of the two atoms of the missing dimer, have been drawn in for one unit cell in Fig. 2. This image also shows several types of defects which are discussed below. Thus, although the unit cells are clearly resolved, we are generally not able to resolve the individual dimers. Figure 3 shows an image which does have slightly better resolution (probably because of a favorable tip condition). In this case there is some detail within the bright regions of the unit cell. This is most easily seen around the kink marked K_3 in Fig. 3. It is clear that the bright region corresponding to the dimers is divided into at least two. This division splits the bright feature into $\frac{1}{3}$ and $\frac{2}{3}$ (not halves). Careful examination of some of the unit cells (particularly around K_3) shows the $\frac{2}{3}$ section is itself divided in half, resulting in the bright feature being divided into thirds, corresponding to the three dimers. The unit cells on either side of the kink are displaced by 4 Å (i.e., one dimer) along the [110] direction. The width of the dark rows (corresponding to missing dimers) is the same as the width of one dimer (4 Å). Since the features described in Fig. 3 are not easily seen, we have included a drawing of the region around the kink, as an inset to the figure. The solid lines represent distinct features, while the dotted lines are features seen at the limit of the resolution of this image. The difference in appearance of the two boundaries between dimers within a unit cell probably relates to the tip condition rather than an asymmetry within the unit cell. The tip was scanning the surface from left to right in the image. The first boundary within the block of dimers that was encountered after the tip moved from the missing-dimer row to the dimers is clearly seen, whereas the second is either missing or only just visible. This could be explained by a slightly asymmetric tip. Effects resulting from asymmetric tips have been observed by others.[14] The unit cell structure would be expected to be symmetrical. However, we cannot completely rule out an electronic effect leading to such an asymmetry. There are a few unit cells in Fig. 3 which appear to have two dimers and two missing dimers per unit cell. Our many images of this surface show that this type of unit cell occurs only occasionally. The additional missing dimer can thus be thought of as a local defect in the equilibrium (2×4) structure. Calculations have shown that a unit cell with two missing dimers is 0.2 eV per (1×1) unit higher in energy than a (2×4) unit cell with only one missing dimer.[9] We conclude that our STM images show the 4× periodicity on this surface to arise from missing dimers, and that the data are best explained by Chadi's model of three dimers and one missing dimer per unit cell.[9] The 4× periodicity does not arise from tilting of the dimers as suggested in earlier models.[7,8] Although we see no evidence of tilting of the dimers, our images are not of sufficient resolution to determine if they are precisely planar.

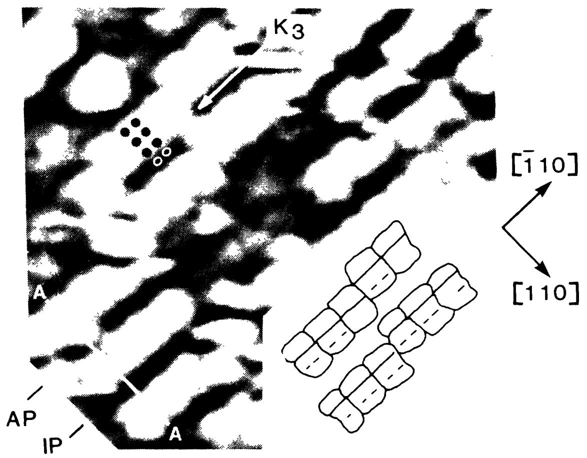

FIG. 3. STM image of the GaAs(001) (2×4) surface. Some of the individual arsenic dimers are just resolved. The unit cell is 8×16 Å^2. The atom positions are marked with filled circles and the missing-atom sites are marked with open circles. The two possible types (IP and AP) of missing-dimer boundary are seen leading to areas which are (2×4)-like and areas which are $c(2\times8)$-like. The line A-A shows the unit cells to be in phase across the IP boundary and out of phase across the AP boundary. A K_3 kink is marked on the image. Inset: Drawing of the unit cells around the kink. Solid lines represent well-resolved features and dashed lines represent features at the limit of resolution for this image. The image was taken with the sample at −2.4-V and 0.2-nA tunneling currents. The gray scale covers a vertical height of 3.5 Å.

If we consider the rows of missing dimers as boundaries between units of three dimers, then it can be seen from Fig. 3 that there are two different types of boundary present on the surface. An in-phase boundary (marked IP in Fig. 3) occurs when the units of three dimers line up on either side of the boundary. By comparison with Fig. 1(b), it can be seen that this corresponds to the (2×4) reconstruction. An antiphase boundary (AP) occurs when the center of a block of three dimers on one side of the boundary lines up with the interface between two dimer units on the other side of the boundary. This leads to a larger unit cell [Fig. 1(b)] which is $c(2\times8)$. Thus the $c(2\times8)$ structure is actually built up from subunits of (2×4), the two structures only differing by the type of boundary (in-phase or antiphase) formed by the missing-dimer rows. Calculations on the difference in energy between these two show it to be only 0.12 eV per $c(2\times8)$ unit cell, the $c(2\times8)$ structure having the lower energy of the two.[9] The upper right of Fig. 2 shows a region of well-ordered (2×4). Our STM images clearly show that both types of boundaries are present on the surface, with domains being as small as a few unit cells across.

In addition to the determination of the structure of the unit cell, the STM is able to directly image disorder and defects on the surface. We have already discussed the boundaries leading to the (2×4) and $c(2\times8)$ unit cells. There are other possible disorder structures which might also exist on the surface. An in-phase boundary can become an antiphase boundary by a local disorder in the pairing up of arsenic atoms to form dimers [Fig. 1(b)]. This leaves three unpaired As atoms between two unit cells. We have seen several examples of this type of disorder where the three unpaired As atoms are actually missing (Fig. 2). It is possible to have domain boundaries along the [110] direction [Fig. 1(b)]. These produce kinks in the missing-dimer rows. As shown in Fig. 1(b), the intersection between these boundaries and an in-phase boundary forms only one type of kink structure (K_1). However, there are two types of kink structure which can be formed with the antiphase boundary; an open kink (K_2) and a closed kink (K_3) [Fig. 1(b)]. None of our STM images show extended domain boundaries along the [110] direction. A few kinks in the missing-dimer rows are seen, but these do not involve extended [110] domain boundaries. They are associated either with steps or regions of disorder (Figs. 2 and 3). Examples of a K_3-type kink are clearly seen in both Figs. 2 and 3, both on small ordered regions of only a few unit cells in size. No examples of a K_2-type kink have yet been seen. Other local defects seen on the surface include unit cells with two or more missing dimers, as well as a few unit cells with no missing dimers (Fig. 2).

In terms of growth mechanisms, the types of defects that are more important are steps and island structures. The STM images show that the surface is generally flat. When steps are observed, they are 2.8 Å high, corresponding to the spacing between arsenic planes and not between arsenic and gallium planes (Fig. 2). Thus the arsenic-rich surface is preserved at steps. No larger height steps have been seen. One of the more interesting features seen from the point of view of growth mechanisms is the small "islands" of only a few unit cells in size, and they are either one 2.8-Å step up or step down from the main plane. These may be important nucleation sites for growth.

We have made the first STM study of an MBE-grown surface and provided further evidence for the structure of the arsenic-rich GaAs(001) (2×4) reconstruction. The 4× periodicity arises from an ordered array of missing dimers. Because of both in-phase and antiphase boundaries being formed along the missing-dimer rows, the surface reconstruction involves regions of (2×4) and $c(2\times8)$ structures. Further, we have shown that the technique is able to image localized surface features such as steps and small islands which are of great importance in the mechanisms of growth. The STM will certainly be very important in the further study of MBE surfaces and growth mechanisms.

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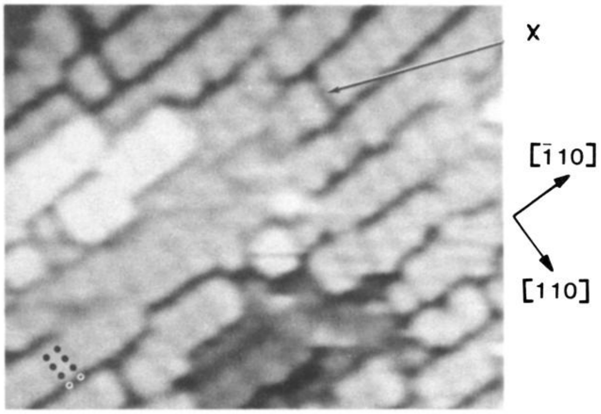

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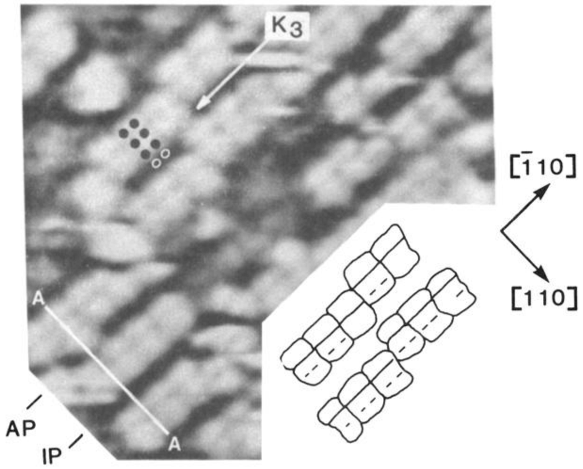

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