Brief Reports

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GaAs(111) A-(2×2) reconstruction studied by scanning tunneling microscopy

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Atomic-resolution scanning tunneling microscope (STM) images have been obtained from the GaAs(111) A (gallium-terminated) surface. The STM images conclusively show that the (2×2) periodicity arises from a regular array of gallium vacancies in agreement with a previously proposed model. It is shown that this reconstruction is explained by the reduction in energy that is achieved by the complete transfer of electrons from gallium dangling bonds into arsenic dangling bonds, which are then exactly filled.

In the past few years there has been considerable interest in the surface structure of polar semiconductors such as gallium arsenide.[1,2] The (110) cleavage surface is nonpolar but the (111) and (100) surfaces are polar and thus the bulk terminated surface will have a net surface charge.[1] These surfaces reconstruct to remove this surface charge. It is believed that many of the surface reconstructions on these surfaces mvolve vacancy structures, resulting in a surface having less than full monolayer coverage. Our scanning tunneling microscope (STM) studies on the GaAs(001)-(2×4) surface[3] have shown that the surface reconstruction arises from dimer vacancies. We now present the first STM images of the GaAs(111) A-(2×2) surface, which show that this surface reconstruction arises from single gallium vacancies. We will also show that the same simple electron counting model which explains the GaAs(001)-(2×4) reconstruction also explains the GaAs(111) A-(2×2) reconstruction.

The GaAs(111) A-(2×2) reconstruction has been previously studied by both low-energy electron diffraction (LEED) (Ref. 4) and angle-resolved photoemission.[5] As a result of LEED studies, Tong *et al.*[4] proposed a vacancy-buckling model with one in four surface gallium atoms missing. The remaining surface gallium atoms and the arsenic atoms in the layer below then buckle so that the gallium atoms move down relative to the unreconstructed surface. This leaves them in a configuration which is similar to the (110) surface. Lateral shifts of the surface gallium and arsenic atoms are small. Total-energy calculations support this model.[6] This model is shown in Fig. 1, where the top gallium and arsenic layers are shown viewed from above. Other models have been proposed for different surface preparation conditions based on *ab initio* theoretical calculations.[7] Under gallium-rich conditions, which include annealing in vacuum, the vacancy model described above is favored, but under arsenic-rich conditions encountered during molecular-beam epitaxy growth, an arsenic trimer model has been proposed.[7]

The STM experiments were performed in an

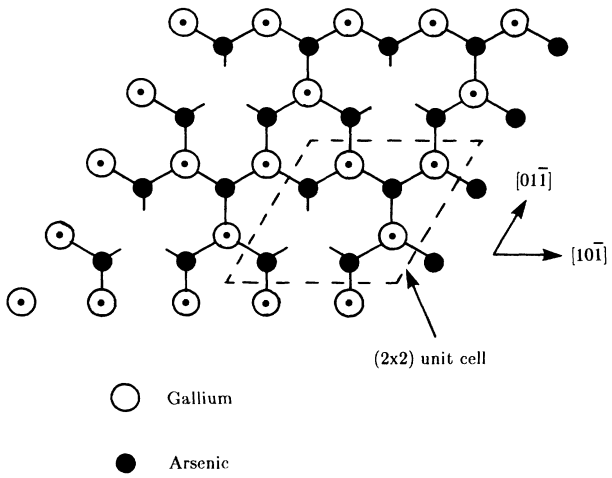

FIG. 1. Top view of the single-gallium-vacancy model of the GaAs(111) A-(2×2) reconstruction proposed by Tong *et al.* (Ref. 4) showing the surface gallium atoms and the arsenic atoms immediately below. The (2×2) unit cell is 8 Å on the side. Dangling bonds on the arsenic atoms resulting from the gallium vacancy are shown. The gallium dangling bonds out of the surface are shown as dots on each gallium atom.

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ultrahigh-vacuum (UHV) system that includes an argon-ion gun, LEED, and Auger-electron spectroscopy (AES). Specimens and STM tips are transferred to the UHV chamber through an air entry lock. The STM uses a mechanical lever arrangement for the approach of the specimen to the tip, and has been described in detail elsewhere.[8] The STM x, y, and z piezoelectric drives were calibrated by imaging the Si(111)-(7×7) reconstruction. This also provided crystallographic orientation and a measure of the xy cross talk of the instrument. Images were corrected for thermal drift by taking two successive images of the same area and measuring the xy drift that had occurred in the time required for the acquisition of the images. The samples used in these experiments were (111)-oriented GaAs substrates doped with Si ($n = 3\times10^{18}$ cm^{-3}). They were chemically and mechanically polished on the gallium face with an etchant solution of NaOCl and mounted on a previously degassed molybdenum sample holder with molybdenum clamps. Once in the UHV system, the samples were argon ion bombarded (500 eV) and annealed at about 550°C for several cycles until a sharp (2×2) LEED pattern was obtained and AES showed that the surface was free from carbon and oxygen contamination.

The STM image shown in Fig. 2 is of a (2×2) reconstructed region of surface approximately 128×100 Å. The image was taken with the sample positive (2.4 V) with respect to the tip, that is, imaging empty states on the surface, with a tunnel current of 0.1 nA. A regular array of dark features is seen which lies on a hexagonal lattice with principal axes in the ⟨110⟩ directions. The separation of these features is 8 Å corresponding to the 2× spacing. The surface structure is seen to be well ordered and two single height (i.e., 3 Å) steps are visible (top right and bottom left). Steps seen on this surface were generally fairly kinked, but locally ran along one of the three ⟨110⟩ directions. In this image it is not possible to resolve any detail in the bright regions between the dark features. Figure 3 shows a similar region of the surface at higher magnification. The image is shown in perspective view to help highlight the distinct features seen within the bright regions of the image. The same image is shown in plane view in Fig. 4. The image is approximately 32 Å across. The corrugation between features within the bright regions is rather small (approximately

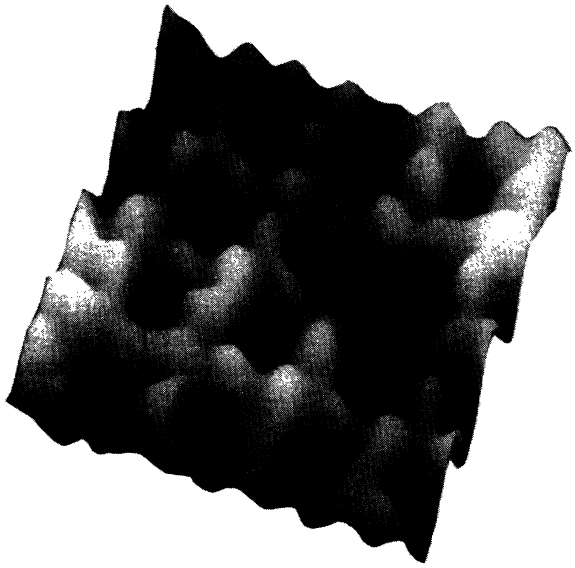

FIG. 3. A perspective view of the (2×2) reconstruction. The total height variation in the image is approximately 1 Å.

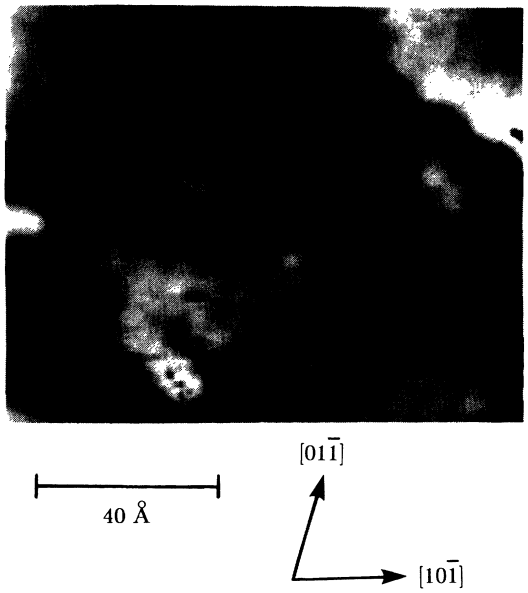

FIG. 2. A STM image of a GaAs(111)A-(2×2) surface. A regular (2×2) periodicity of dark features is evident. Single height steps are present at the top right and bottom left of the image.

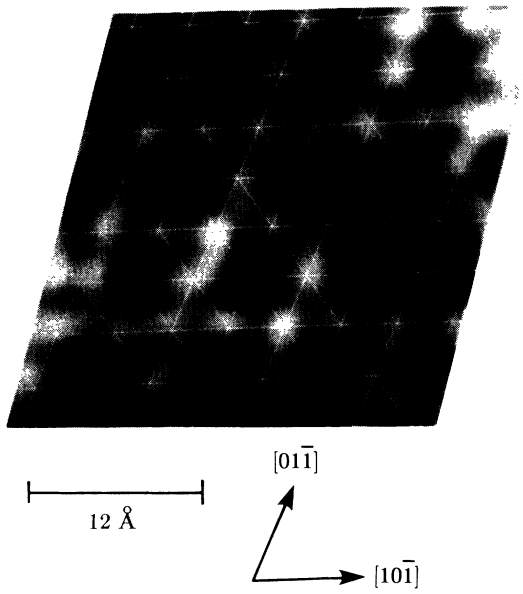

FIG. 4. A plane view of the same image as shown in Fig. 3. Each bright feature corresponds to one gallium atom. The grid intersections mark the bulk-terminated gallium sites.

0.1 Å) and it is therefore difficult to resolve features in the unprocessed image. In order to remove high-frequency noise from the image, it was Fourier transformed and then filtered with a "top hat" filter that removed all frequencies above that corresponding to the 1× spacing. The features within the bright region are then clearly resolved as seen in Figs. 3 and 4. It should be noted that although these features are difficult to see in the unprocessed image, they can be seen despite the relatively low signal to noise ratio of the image.

Due to the polar nature of GaAs, we expect that an increased density of empty states will be localized on the gallium atoms and an increased density of filled states localized on the arsenic atoms. This has been very nicely demonstrated for the GaAs(110) surface by Feenstra *et al.*,[9] where images of empty states revealed the gallium sites and images of filled states revealed the arsenic sites. Since the model of Tong *et al.*[4] for the GaAs(111)*A* surface suggests that the structure has strong similarities to the structure of the (110) surface, we expect the same distinction between filled and empty states. The STM image of empty states shown in Figs. 3 and 4 is therefore interpreted as an image of the gallium sites on the surface. We have attempted to obtain images of filled states from this surface, but have been unable to resolve any distinct features although a stable tunnel current was achieved. This may reflect a particularly low corrugation in the density of filled states across the surface.

A hexagonal grid has been superimposed over the image in Fig. 4. The grid was fitted to three dark features in the image, spaced 16 Å apart. The grid spacing is 4 Å (the 1× spacing) and oriented along the three ⟨110⟩-type directions. If the surface structure was ideally bulk terminated, there would be a gallium atom at each grid intersection. In Fig. 4, three out of four grid intersections coincide with a bright feature and one out of four intersections coincides with the center of one of the dark features. Comparison of Fig. 4 with the model of Tong *et al.*[4] (Fig. 1) shows that the STM image of empty states coincides with the predictions of the model, that is, one in four gallium atoms is missing. The image suggests that the remaining gallium atoms sit laterally on their bulk-terminated sites, however the vacancy model for the surface predicts a small lateral shift (0.1 Å). This is too small to be observed in the STM images, and so we are not able to verify these shifts. Without images in both polarities it is not possible to make a determination of the buckling out of the plane of the surface as was done by Feenstra *et al.*[9] for the GaAs(110) surface. However, the STM images presented here do provide very clear and convincing evidence for the gallium vacancy model on the GaAs(111)*A*-(2×2) surface.

The gallium vacancy structure is one of several surface reconstructions found on compound semiconductors that result from surface vacancies. These reconstructions can be explained by a simple electron counting model. The dangling-bond states of GaAs are sp^3 hybrid orbitals. The energy of the arsenic dangling bonds is in the valence band, and so they must be filled. The energy of the gallium dangling bonds is in the conduction band and so they must be empty.[10] Thus a surface will be stable if there are exactly the correct number of electrons required to satisfy these two conditions. This is the same condition that is required to have zero net charge at the surface.[11] This simple idea has been used successfully to explain the GaAs(001)-(2×4) reconstruction which involves surface dimer vacancies.[11] In the case of the GaAs(111)-*A* ideal bulk-terminated surface, the surface layer consists of gallium atoms, each bonded to three arsenic atoms in the layer below, and each having one dangling bond normal to the surface. The arsenic atoms in the layer below are all in bulklike configurations. The three valence electrons on each surface gallium atom are distributed equally between the bonds to arsenic (i.e., bulklike bonds) and the dangling bond. The dangling bond is thus partially filled, which is energetically unfavorable. The (2×2) reconstruction provides a way of satisfying the electron counting model. The removal of $\frac{1}{4}$ of the surface gallium atoms leaves three gallium atoms (and hence three gallium dangling bonds) per (2×2) unit cell. The gallium vacancy leaves three of the four arsenic atoms per unit cell with one dangling bond each. Thus there are three gallium dangling bonds and three arsenic dangling bonds per unit cell (see Fig. 1). The $\frac{3}{4}$ electron per gallium dangling bond can transfer to the arsenic dangling bonds each having $\frac{5}{4}$ electrons, to give a surface with empty gallium dangling bonds and filled arsenic dangling bonds, satisfying the electron counting model. It must be noted, however, that the electron counting model does not uniquely define the correct surface reconstruction for a particular surface. There may be several structural models which satisfy the electron counting model. It represents only one term in the total energy of the surface, although it is generally the most important term. More detailed total-energy calculations need to be performed in order to determine which of the possible models will be the most stable. These STM results, together with our previous work on GaAs(001),[3] demonstrate that the application of the electron counting model to the structure of polar semiconductor surfaces is valid.

We have performed the first STM study of the GaAs(111)*A*-(2×2) reconstruction. The real space imaging capability of the STM clearly resolves individual surface gallium atoms. As a result, we are able to conclusively support the single gallium vacancy model for this surface. This structure has also been explained on the basis of a simple electron counting model, which has been used successfully to explain other surface reconstructions on compound semiconductor surfaces.

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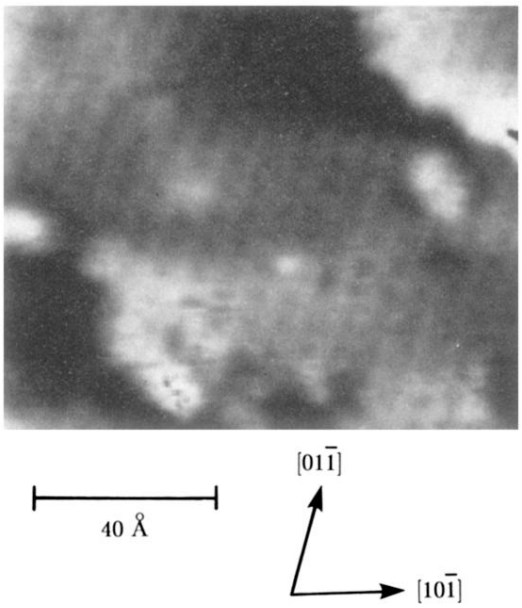

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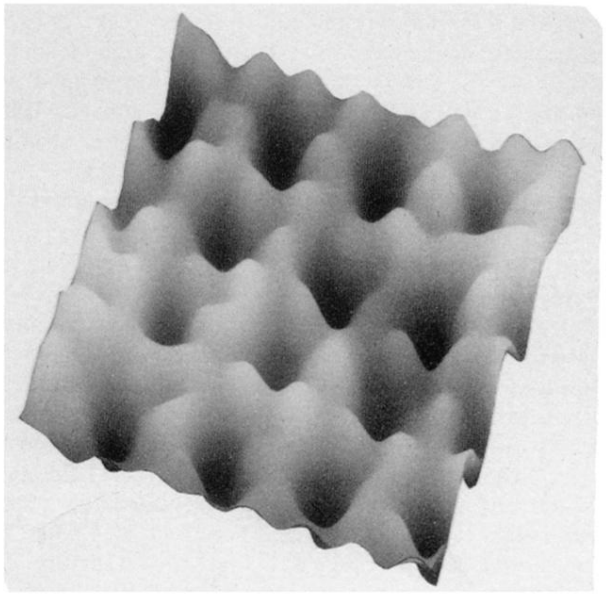

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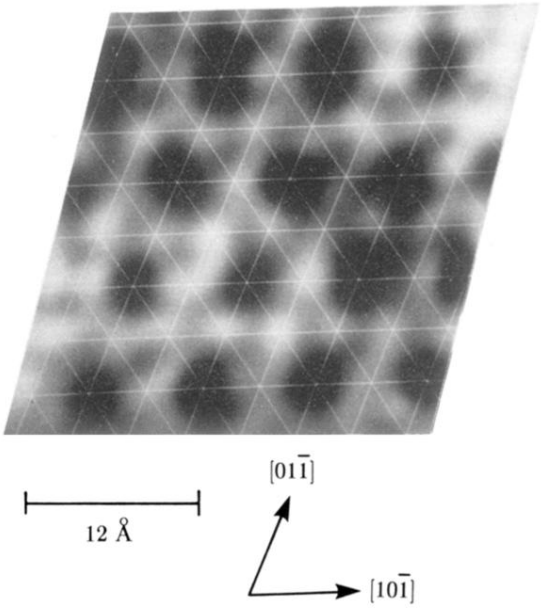

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