STM: Seeing is Believing

J.L. Sudijono[1], C.F. McConville[2] & T.S. Jones[1]

In the last ten years the scanning tunnelling microscope (STM) has completely changed the way in which we look at the surfaces of semiconductor materials. However, due to the conflicting experimental geometries of the two techniques, it is only recently that it has been possible to combine high resolution STM imaging with a full scale MBE system. In this article we demonstrate the application of this technique in obtaining both morphological and atomic resolution images of MBE grown GaAs(001) surfaces and the same surfaces after deposition of Si.

Epitaxial growth techniques have advanced to a stage where it is now possible to construct novel device structures with atomic precision. Techniques such as molecular beam epitaxy (MBE) and metalorganic vapour phase epitaxy (MOVPE) have made it possible to tailor a particular device by a judicious choice of substrate surface and appropriate growth conditions. It is therefore possible to grow structures such as quantum wells, quantum wires and quantum dots, all of which rely on the physical confinement of electrons in one, two or three dimensions. Examples of such structures have been grown using a variety of materials combinations, with the greatest attention being directed at near-lattice matched systems involving GaAs, AlAs and $Ga_{1-x}Al_xAs$.

In order to fully understand and exploit these advances in atomically controlled growth, a detailed understanding of the surface structure of these materials, and more specifically the growth surface, is required at the atomic level. In general, our understanding of the structure of semiconductor surfaces has come from diffraction techniques such as reflection high energy electron diffraction (RHEED). The development of the scanning tunnelling microscope (STM), pioneered initially in 1982 by Binnig & Rohrer at IBM Zurich, resulted in a technique which pro-
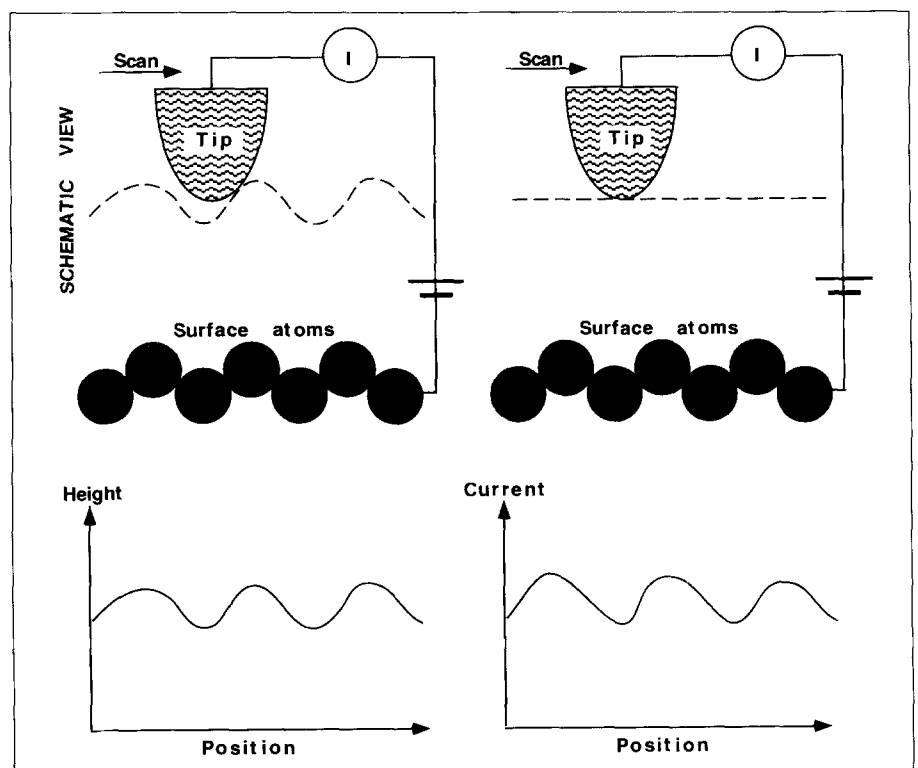

Figure 1. The underlying principles of STM illustrating the two most common modes of operation.

vides a unique atomic level perspective of the surface structure as it effectively allows individual atoms at the surface to be "seen" directly.

Scanning Tunnelling Microscopy (STM)

The underlying principles involved in the operation of the STM are relatively simple and are illustrated in Figure 1. A sharp metallic tip is brought to within a few angstroms of a conducting surface such that the wave functions associated with the atoms in the tip and the surface overlap. A small bias voltage is then applied between the two materials

which results in the flow of a quantum mechanical tunnelling current, with electrons flowing either from occupied (filled) or into unoccupied (empty) states of the surface depending on the sign of the applied bias. In the most commonly used mode of operation, the tip is scanned across an area of the surface maintaining a constant tunnelling current and monitoring the tip-surface separation. The resulting plot is a topographical map of the density of filled (or empty) electronic states at the surface. The area scanned can either be wide area ($\sim 5\ 000\ \text{Å}^2$), so that morphological features on the surface can be seen at relatively low resolution, or small area ($\sim 100\ \text{Å}^2$) so that structural information can be obtained at the atomic scale. The vertical resolution of STM ($< 0.1\text{Å}$) is determined by the tip-surface separation, since the tunnelling current varies exponentially with this distance. The lateral resolution is not so well defined and is typically 1-2 Å. The beauty of STM is not only its ability to provide atomic resolution images but, unlike the majority of other techniques for determining surface structure, the imaging takes place in real space rather than reciprocal space.

Imaging III-V surfaces grown by MBE

Application of STM to the study of MBE grown semiconductor surfaces ideally requires the MBE chamber and STM, both held under conditions of ultra-high vacuum, to be linked directly in such a way that samples can be
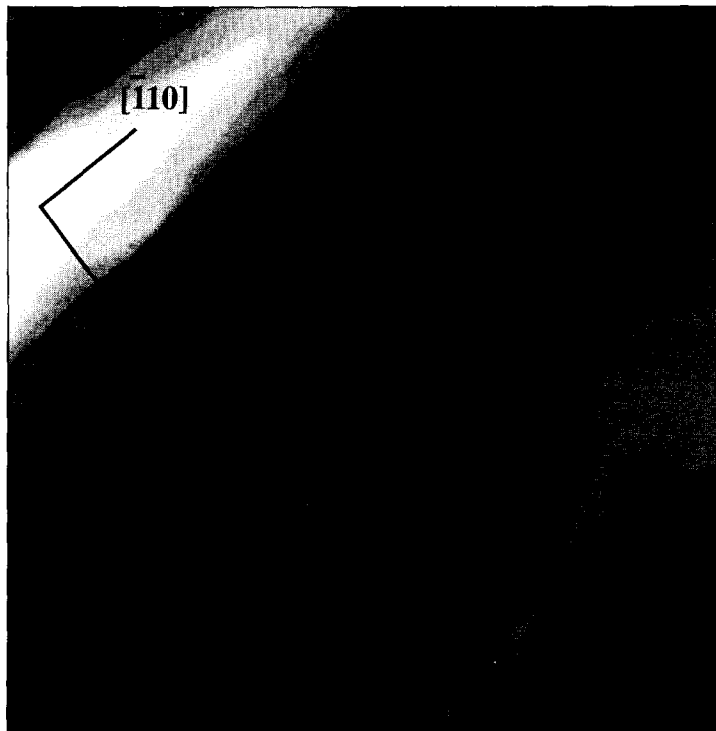

Figure 2. A typical wide area STM image of a GaAs(001) surface formed after deposition of a buffer layer of 0.3 μm. Each grey scale level corresponds to a GaAs step of 2.8 Å. Image dimensions are 6000 Å x 6000 Å. (J. Sudijono, M.D. Johnson, M.B. Elowitz, C.W. Snyder & B.G. Orr, Surface Science, 280 (1993) 247).
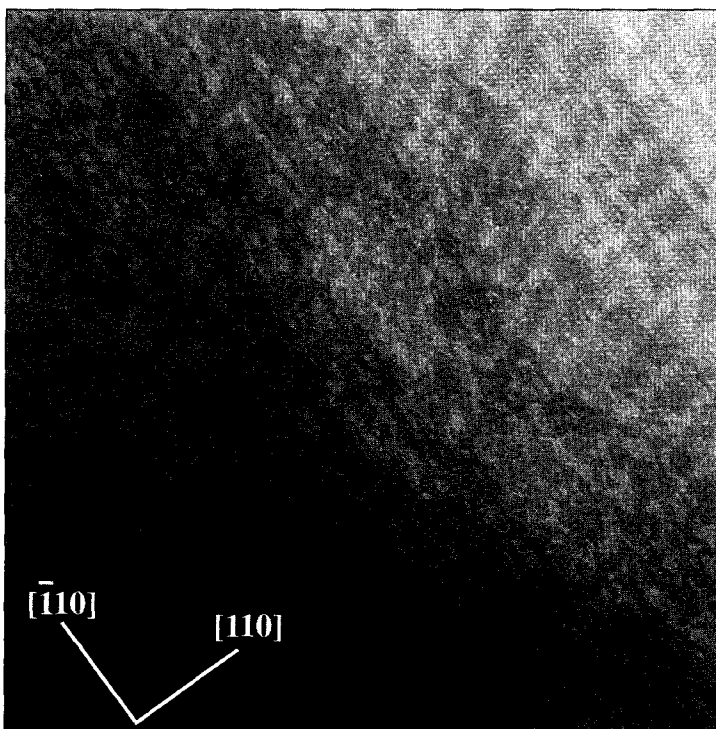

Figure 3. A wide area STM image of the GaAs(001) surface after growth was stopped at the minimum in the specular beam intensity of the RHEED oscillation; the amount of GaAs deposited was 3.5 monolayers. Notice the large number of two dimensional islands on the terraces. Image dimensions are 8000 Å x 8000 Å. (J. Sudijono, M.D. Johnson, M.B. Elowitz, C.W. Snyder & B.G. Orr, Surface Science, 280 (1993) 247).

transferred *in situ* without breaking the vacuum and contaminating the sample surface. Using this procedure, the surface structure and morphology can be monitored during growth, using conventional diffraction techniques such as RHEED, prior to transfer of the sample to the STM. The subsequent surfaces are then of suitable quality in that they are clean, ordered and of the correct stoichiometry. The dedicated STM-MBE (Omicron, GmbH and DCA Instruments, Finland) system at Imperial College is an example of such a system. The approach this type of system allows is particularly advantageous for the study of deposition processes and growth modes in order to tailor specific quantum structures.

Surface Morphology of GaAs

More than any other III-V semiconductor material, the growth of GaAs(001) by MBE has received detailed *in situ* study by surface sensitive techniques such as RHEED, which due to the geometry of conventional MBE growth chambers, is ideally suited to monitor the long range order at the growing surface. The polar (001) surface can be terminated with either As or Ga and a large number of different surface structures (surface reconstructions) have been observed depending on the actual growth conditions, *i.e.* the substrate temperature and Group III/V flux ratio. For most applications, GaAs growth is carried out under As-rich conditions so the surface

is terminated with As. Two different structures have been observed with RHEED having either (2 x 4) or c(4 x 4) symmetry. The most common structure for MBE growth at substrate temperatures in excess of 500°C is the (2 x 4) surface, although the c(4 x 4) surface is more relevant for growth processes carried out at relatively low substrate temperatures (typically 400°C).

Figure 2 shows a typical wide area STM image (6000 Å x 6000 Å) of a GaAs(001)-(2 x 4) surface after deposition of 0.3 micron thick buffer layer of GaAs onto an epi-ready substrate. This represent a typical starting surface for the atomically controlled growth of GaAs based structures. The central region of the image clearly shows that the surface is very smooth with the lower left hand corner showing a series of "staircase" like steps. Each step, corresponding to the difference in height between alternate As layers, is 2.8 Å high and is regularly spaced with a typical terrace width of ~1500Å. Step bunching can also be seen in the upper left and lower right hand corners of the image, with the groups of steps appearing as large, highly anisotropic islands.

The growth of GaAs onto this surface can be monitored in situ by following the intensity of the specular beam in the RHEED pattern; the so-called RHEED intensity oscillation technique, which provides detailed information regarding the growth dynamics. As growth proceeds, the specular beam intensity oscillates and Figure 3 shows a wide area STM image taken after the growth of 3.5 monolayers of GaAs, i.e. corresponding to a minimum in the RHEED intensity. The image clearly shows a large density of small two dimensional islands separated by about 300 Å.

Atomic Resolution Images

An example of an STM image obtained at atomic resolution for the As-terminated GaAs(001)-(2 x 4) surface is shown in Fig. 4. It is characterised by a series of alternate dark and bright rows, the origin of which can be understood by considering the nature of the surface reconstruction. Figure 5 shows a model of

an ideal bulk termination, with each As atom in the top layer having two dangling bonds directed away from the surface. The (2 x 4) reconstruction involves neighbouring As atoms pairing up to form As dimers with the dimer bond aligned along the [$\bar{1}$10] direction therefore giving rise to a twofold periodicity. The fourfold periodicity in the [110] direction arises from missing dimers and the resulting (2 x 4) unit cell, which has dimensions 8 A x 16 A, is characterised by two As dimers and two missing dimers (Figure 5). The bright rows in the filled states STM image shown in Figure 4 therefore correspond to tunnelling from occupied orbitals which are located on the four As atoms in the top layer of the unit cell, with the dark rows due to the missing dimer trenches.

Two STM images of the more As-rich c(4 x 4) reconstruction are shown in Figure 6. The image shown in Fig. 6a is visually very different to that obtained for the (2 x 4) surface and is characterised by a "brickwork-like" pattern of bright rectangular blocks. As shown in figure 7, the c(4 x 4) reconstruction differs fundamentally from the (2 x 4) surface in that it is terminated with two layers of As atoms, with the outermost layer of As atoms not bonded to any Ga atoms (i.e. only As-As bonding exists within the top most layer and between this and the second layer). Each complete rectangle in the STM image corresponds to six top layer As atoms.

The second image shown in Figure 6 demonstrate the power of STM in providing detailed structural information at the atomic level. This surface also gives rise to a clear c(4 x 4) diffraction pattern but the STM image reveals a considerable number of incomplete rectangular blocks with many examples of one, two or three atoms missing. The c(4 x 4) structure
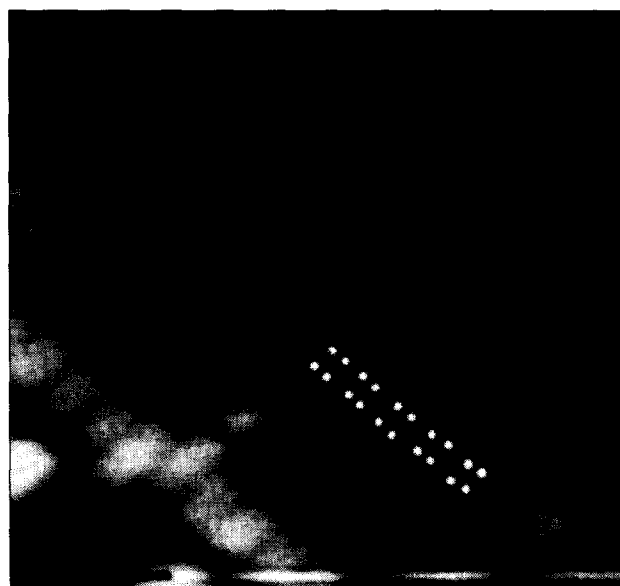

Figure 4. A filled states STM image of the (2 x 4) reconstruction formed by GaAs(001) surfaces grown by MBE. The image is characterised by a series of alternate dark and bright rows along the [$\bar{1}$10] direction, the bright rows corresponding to arsenic dimers and the dark rows to missing dimers. Image dimensions are 100 Å x 100 Å. (A.R. Avery, D.M. Holmes, J.L. Sudijono, T.S. Jones & B.A. Joyce, Surface Science, 1-323 (1995) 91).

is known to exist over a wide As coverage range (ideally from 1.25 - 1.75 monolayers) which, on the basis of these STM images, can easily be explained by the removal of individual As atoms from the groups of six that form the rectangular blocks.

Silicon adsorption on GaAs

Mechanisms for the introduction of a controlled quantity of an impurity to increase the electron concentration in a particular region of a material or device are extremely important. Silicon is the most commonly used n-type dopant in III-V semiconductor materials. Deposition of high concentrations of Si in single atomic planes, by interrupting the growth of GaAs(001) by closing off the Ga flux, leads to the formation of so-called delta (δ)-doped structures which show considerable promise for the confinement and localisation of high electron concentrations in semiconductor layer structures. Device applications include diodes, field effect transistors and lasers, all of which have shown real or potential improvements in performance as a result of using δ-layers. In an ideal situation, the dopants are confined to a single two-dimensional
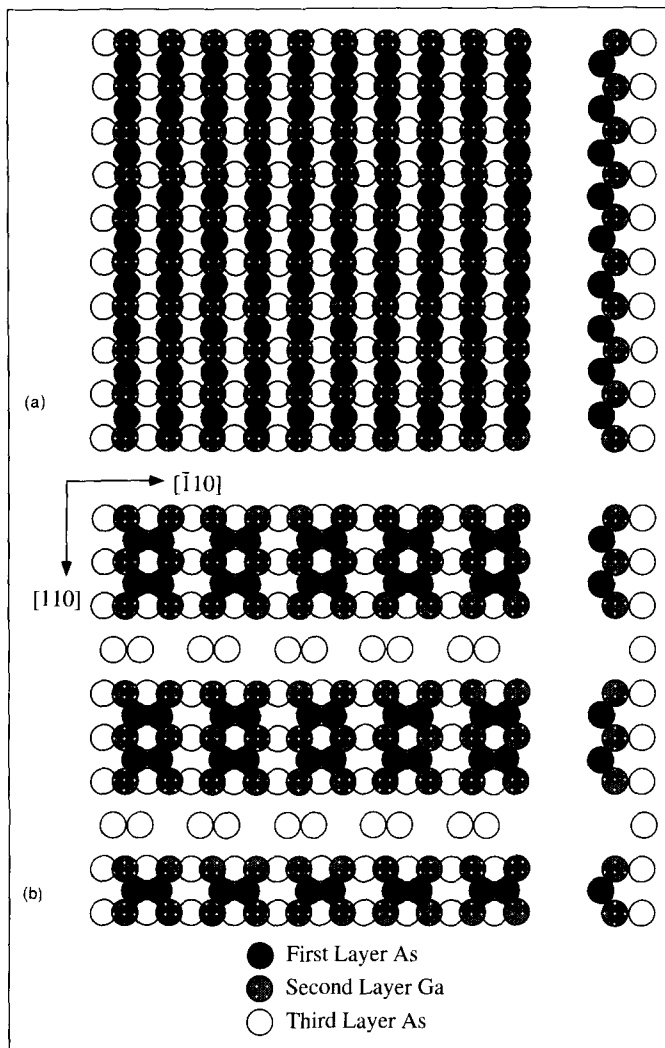
First Layer As
Second Layer Ga
Third Layer As

plane and the doping profile of the resulting layer should show a delta-function-like spike at the position of growth interruption. In practice, however, this cannot be achieved as there is always some spreading of the dopant atoms away from the plane, even for growth at relatively low substrate temperatures. X-ray diffraction measurements have shown that confinement of the dopant atoms is best achieved by growing the structure at low temperatures ($\sim 400°C$). With an arsenic flux present this corresponds to growth on the c(4 x 4) surface.

Figure 8 compares the deposition of the same amount of Si (about 0.2 monolayers) onto the two different As-terminated reconstructions at 400°C. It clearly illustrates the importance of the underlying surface reconstruction in determining the nature of adsorption, the island formation and the subsequent development of the Si/GaAs interface. On the c(4 x 4) surface a series of anisotropic "needle-like" islands are formed, each of which are two atoms wide, resulting in a more ordered outermost surface layer. In contrast, random clusters each made up of

several Si atoms can be seen when adsorption occurs on the (2 x 4) surface, finally resulting in a much more disordered surface. The key difference here between the two reconstructions is the additional top layer of As on the clean c(4 x 4) surface (Figure 7). It is known from vibrational spectroscopy measurements of the bulk structure that Si atoms only occupy gallium sites. Hence, for the (2 x 4) reconstruction, which has only one outer layer of As (Figure 5), this is straightforward and the Si atoms can simply adsorb on top of the (2 x 4) layer inserting into the
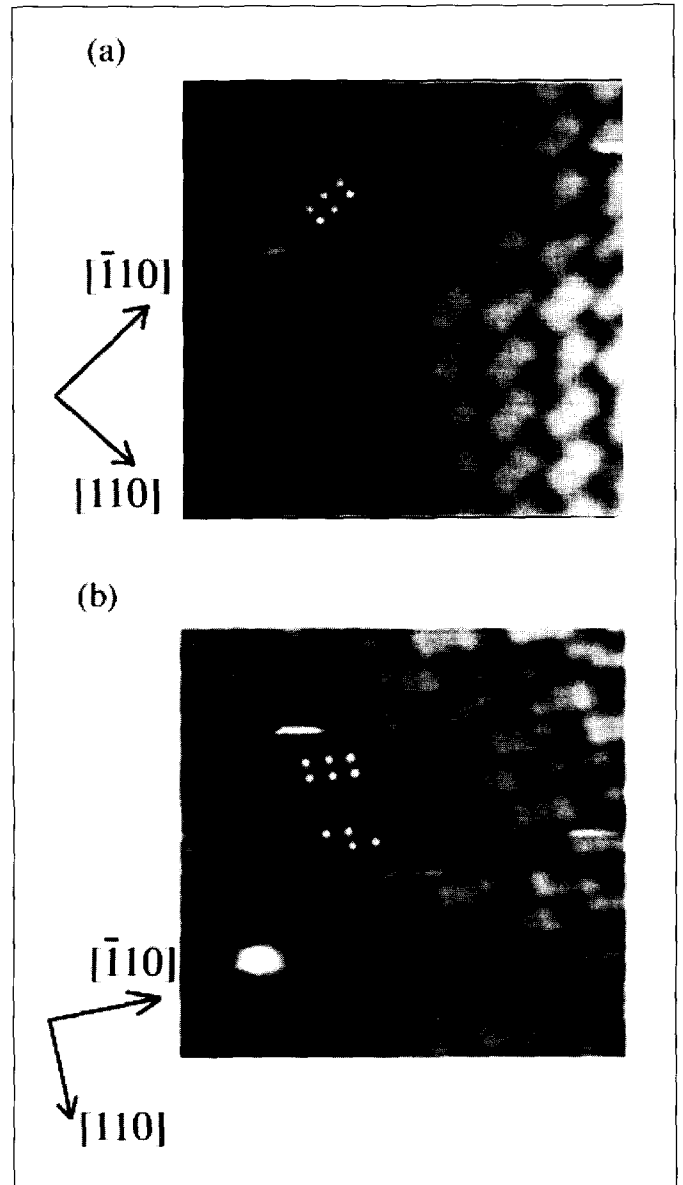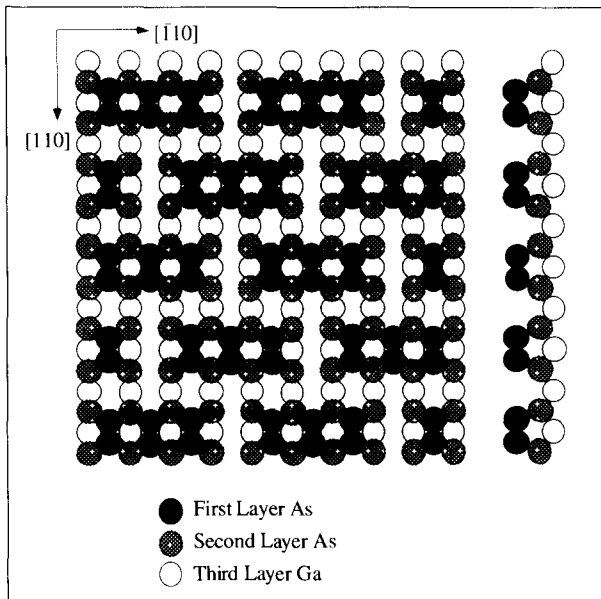
Figure 7. The general structural model for the c(4 x 4) reconstruction formed by the (001) surfaces of GaAs. The structure is characterised by rectangular blocks of six arsenic atoms and the structure is terminated with two layers of arsenic; the top layer of arsenic atoms are only bonded to arsenic atoms and not gallium atoms.

As dimers at the surface. This cannot occur on the c(4 x 4) surface because of the second arsenic layer, so the silicon atoms exchange place with the top layer arsenic atoms and the needle-like islands observed in the STM image are, in fact, made up of displaced arsenic atoms. The relatively ordered nature of the resulting Si/GaAs interface formed on the c(4 x 4) reconstruction at low temperatures, compared with the (2 x 4) surface, may well explain the formation of good quality δ-layers when Si is deposited in the presence of arsenic at low substrate temperatures

Summary

STM offers a unique perspective of the detailed surface structure of a growing semiconductor material in the form of a real-space image over, either a wide area of the sample to show macroscopic and morphological detail, or on the atomic scale, giving detailed information on atomic positions. Both modes of operation provide information which can be used to improve the growth and quality of epitaxially grown semiconductor materials, such as GaAs, and ultimately enhance the performance of any device structure subsequently constructed from this improved material.
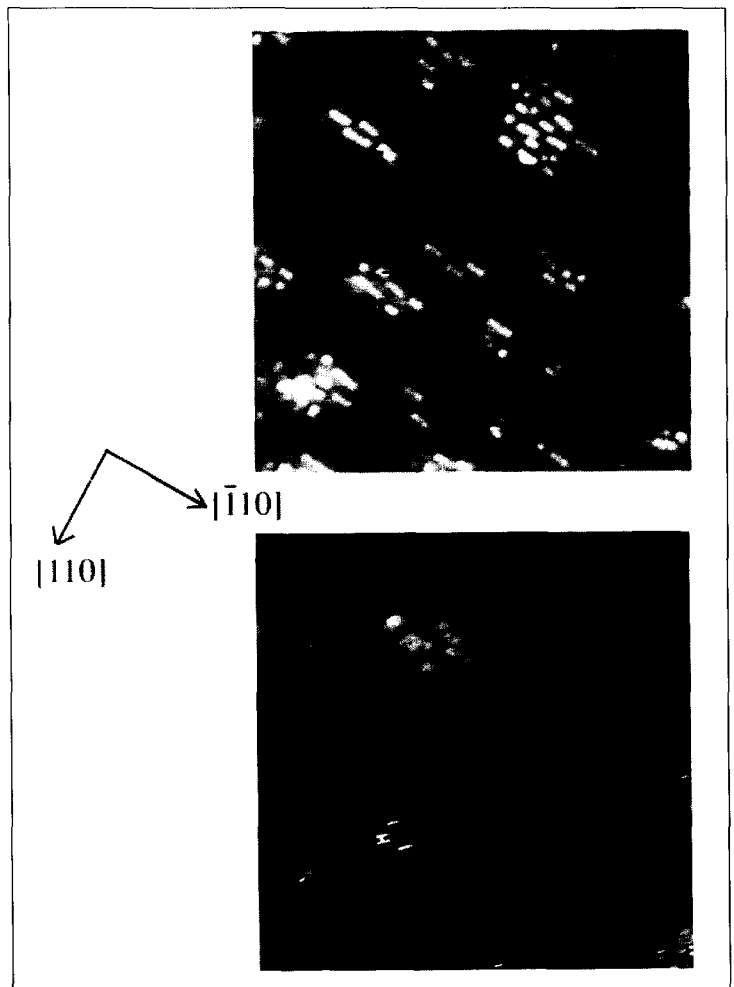
Figure 8. Filled states STM images of one quarter monolayer of silicon deposited on the two different As-terminated reconstructions formed by GaAs(001) at 400 °C; (a) in the absence of arsenic the (2 x 4) surface and (b) in the presence of arsenic the c(4 x 4) surface. Note the more disordered nature of the Si/GaAs interface formed in (b). The image dimensions are 200 Å x 200 Å. (A.R. Avery, J.L. Sudijono, T.S. Jones and J.A. Tye, Surface Science [in press]).

Footnotes

[1]Department of Chemistry and Interdisciplinary Research Centre for Semiconductor Materials, Imperial College, London, SW7 2AY, UK UK.
Tel: [44] (0)171-594-5794.
Fax: [44] (0)171-594-5801.
Email: tsj@icac.uk

[2]Department of Physics, University of Warwick, Coventry, CV4 7AL, UK.
Tel: [44] (0)1203 524-236.
Fax: [44] (0)1203 692-016.
E-mail: spcm@spec.warwick.ac.uk