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Atomic scale modifications of GaAs using a scanning tunneling microscope

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We have created atomic scale modifications on the GaAs(111)B surface by applying voltage pulses between the tip of a scanning tunneling microscope and a GaAs sample under ultrahigh vacuum conditions. A voltage pulse of 5 V (sample negative) for 25 ms results in the creation of a disordered region (approximately, 3 nm \times 3 nm in area) of As trimers. In addition, surface stacking faults are formed which extend over distances of order 10 nm and terminate on surface defects. A pulse with the same parameters, but opposite polarity, creates a nanometer scale crater. We argue that the smallest features are formed by electric field induced diffusion (for negative bias pulses) or field desorption (positive bias pulses). © 1995 American Institute of Physics.

The use of the scanning tunneling microscope (STM) to create nanometer scale features on semiconductor and metallic surfaces is currently a topic of great interest. This is due in part to the potential of this method for fabricating experimental nanostructures, but also for the information provided regarding the behavior of these materials on the nanometer scale. The most striking example of atomic scale modification is the manipulation of Xe atoms on a Ni surface by Eigler *et al.*¹ Patterning Si surfaces on an atomic scale in an ultrahigh vacuum (UHV) environment is also well established and may be achieved by applying voltage pulses between the tip and the sample to extract single atoms.^{2,3} Alternatively, features may be formed in H-passivated Si with dimensions of order 1 nm^{4,5} when performed in UHV (via H desorption), or 20 nm⁶ when performed in air (via the formation of a thin oxide layer). However, there has so far been less work on STM modification of GaAs surfaces although this material is commonly used for the fabrication of nanostructures. Dagata *et al.* have formed features on aqueous sulfide passivated GaAs in air⁷ and Whitman *et al.* have used voltage pulses to induce diffusion of Cs atoms on GaAs(110) in UHV.⁸ In each case the modified area is of order 100 nm.

In this letter we discuss the modification of GaAs(111)B-(2 \times 2) surfaces with a STM operated under UHV conditions. For this study we have used As-capped epitaxial n^+ Si-doped GaAs layers 100 nm thick grown on an n^+ GaAs (111)B substrates. See Ref. 9 for more details on the molecular beam epitaxial (MBE) growth. After loading into the UHV system (base pressure $\sim 5 \times 10^{-11}$ Torr) and outgassing for several hours the As cap was desorbed by heating the sample to 300 °C. The sample was then annealed at 375 °C for periods ranging from 10 to 60 min. After cooling to room temperature the sample holder was loaded onto the STM (provided commercially by W. A. Technology) which is housed in an adjacent vacuum chamber. Electrochemically etched (5M KOH) W tips were used throughout. The tips are

cleaned in vacuum by electron beam heating to approximately 1600 °C.

A typical STM image of the clean surface taken with a sample bias of -2 V and a tunneling current of 100 pA is shown in Fig. 1(a). Biegelsen *et al.*¹⁰ have shown that the topographic maxima may be identified as As trimers chemisorbed in T_4 sites on an underlying unreconstructed As layer. The separation of trimers in the predominant hexagonal arrangement in Fig. 1 is 0.8 nm corresponding to a 2 \times 2 reconstruction. Note that it is energetically favorable for the As trimers to sit above subsurface Ga atoms in T_4 sites than in the hollow H_3 site.¹⁰ This should result in a flatband condition with the surface Fermi level being located at the bulk position—approximately 0.05 eV above the conduction band minimum for the doping density of the samples used. However, in agreement with Kim *et al.*¹¹ we find from tunneling spectroscopy measurements that the Fermi level is pinned 0.5–0.6 eV from the valence band maximum. Kim *et al.*¹¹ have proposed that the high density of surface stacking faults present on the GaAs(111)B-(2 \times 2) surface cause this pinning. It is clear that there are several domains of the (2 \times 2) reconstruction visible in Fig. 1 and at the boundaries between domains there are surface defects.

In our experimental arrangement the bias voltage is applied to the sample. Voltage pulses of magnitude ΔV are then applied with the feedback loop turned off for the pulse duration τ . A comparison of Figs. 1(a) and 1(b) shows the effect of applying a pulse with $\Delta V = -5$ V and $\tau = 25$ ms while the tip is held at the center of the image. The main effects of the pulse are confined to a region of order 3 nm wide at the center of the image. This area was initially covered by a regular hexagonal ordering of (2 \times 2) unit cells [see Fig. 1(a)], but is disordered by the application of the voltage pulse. The bright features in Fig. 1(b) have approximately the same dimensions as those in Fig. 1(a) and of those in Fig. 1(b) in areas unaffected by the pulse. We, therefore, believe that they correspond to As trimers. The disordering of As

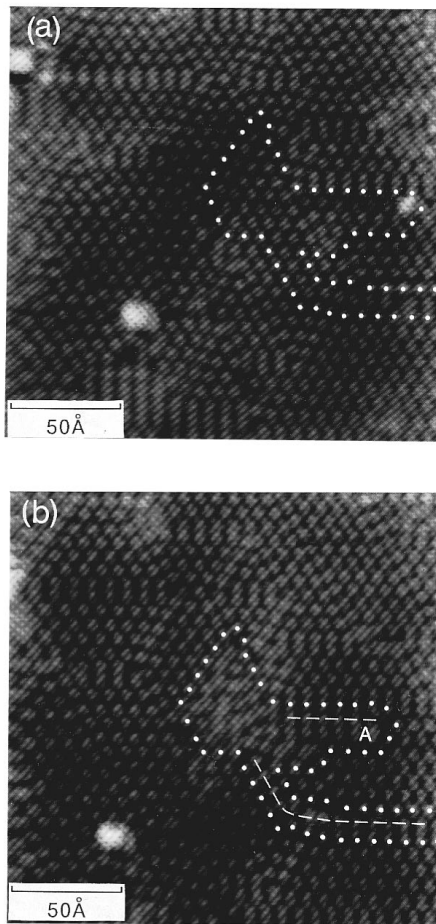


FIG. 1. (a) 20 nm×20 nm topographic image of the GaAs(111)B surface. The maxima (bright parts of the image) correspond to As trimers (Ref. 10); (b) the same area after applying a negative voltage pulse at the center of the image ($\Delta V = -5$ V, $\tau = 25$ ms). The white dots mark trimers which have not been changed by the pulse. The dotted lines represent the surface defects induced by the pulse. The tunnel current and voltage for both images was 100 pA and -3.0 V, respectively.

trimers is most apparent at the center of the image [see Fig. 1(b)], but the effect of the pulse is more widespread. To illustrate this we have marked the boundary of the modified region formed by As trimers which have remained unaffected by the pulse by dots in Figs. 1(a) and 1(b). It is clear that following the voltage pulse there are two additional line defects which extend out from the central disordered region and run parallel to the principal axes of the surface. These are marked by dotted lines in Fig. 1(b). The upper of these [marked A in Fig. 1(b)] terminates at a surface point defect and represents a shift of one row of As trimers by half a reconstructed unit cell. This may be seen from a comparison of Figs. 1(a) and 1(b). The lower additional line defect is also due to a shift of one row of As trimers. Part of this displaced row runs along the edge of a domain boundary which was present prior to the voltage pulse.

We have repeated this procedure with different values of voltage and pulse times. For ΔV in the range -4 to -6 V modification of a comparable area was observed after all pulses. For $\Delta V \leq -7$ V the modified area was much larger and it was difficult to identify regions within a 20 nm square area which were unaffected by the voltage pulse. The nature

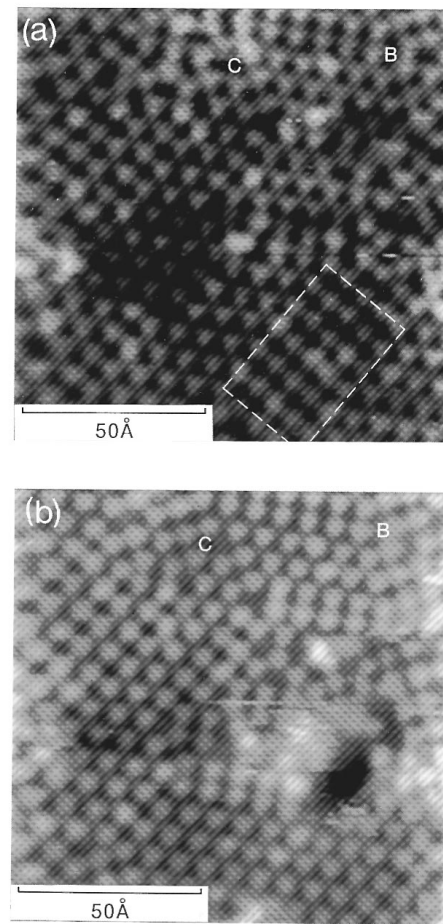


FIG. 2. Topographic image (12 nm×12 nm) of an area of GaAs(111)B before (a) and after (b) the application of a positive voltage pulse ($\Delta V = 5$ V, $\tau = 25$ ms). The pulse was applied while the tip was positioned over the area where a pit was formed. The area enclosed by the dotted line in (a) has a square symmetry which reverts to a hexagonal symmetry following the pulse. The letters B and C identify surface defects which are unaffected by the pulse. The tunnel current and voltage for both images was 100 pA and -2.5 V, respectively.

and extent of the damaged area was independent of τ over the experimental range 20–250 ms.

The effect of a positive voltage pulse on the sample is qualitatively different. Figures 2(a) and 2(b) show a region of GaAs before and after a pulse with $\Delta V = 5$ V and $\tau = 25$ ms. A small pit (width ~ 2 – 3 nm) is formed by the pulse where As trimers have been removed. Profiles through a number of nanofabricated pits reveal a value for the pit depth of 0.21 nm [we have calibrated the vertical motion of our piezoelectric transducers from bilayer steps present on the GaAs(111)B surface—nominally, 0.33 nm in height]. In addition, we find that a larger area around the pit is modified. However, this area is generally not disordered but reordered so that it has a similar or in some cases a greater degree of order after the pulse. Comparison of Figs. 2(a) and 2(b) reveals an example of this effect. An area with local square symmetry [which corresponds to a $c(4 \times 2)$ reconstruction] is identified in Fig. 2(a). Small areas with this arrangement are often seen on our samples. After a voltage pulse this area is reordered into the predominant hexagonal arrangement of (2×2) unit cells [see Fig. 2(b)]. Thus the effect of a voltage

pulse on this area is not to damage but to heal out surface defects.

These effects are independent of pulse duration for 20 ms < τ < 250 ms. For $\Delta V > 7$ V an area greater than 20 nm square is affected. For intermediate voltages $\Delta V \approx 6$ V we find that deeper pits are formed in which one, or in some cases two, subsurface atomic layers may be resolved.

Various mechanisms have been proposed for surface modification by voltage pulsing including field evaporation,¹² electric field induced surface diffusion⁸ and local heating¹³ (see also Ref. 14). Tsong¹⁵ provides a critical comparison of these mechanisms. We consider first our observations for negative voltage pulses. For this case electrons flow from the sample to the tip so the modification cannot be due to local heating of the GaAs. Since the number of As trimers is approximately the same before and after the pulse we argue that field desorption (of negatively charged As ions or trimers) cannot account for our observation. The most likely explanation for our observations is field induced diffusion of As trimers. This arises from the nonuniform electric field produced by the STM tip which acts to polarize surface atoms resulting in a lower potential energy close to the tip. Generally, this potential energy variation $U(r)$ is given as a function of r , the radial coordinate ($r=0$ corresponds to the apex of the tip) by^{8,14}

$$U(r) = -\mu \cdot \mathbf{E}(r) - \alpha E(r)^2/2, \quad (1)$$

where $\mathbf{E}(r)$ is the electric field at the surface, μ is the dipole moment of the surface species, and α is its polarizability which we consider as a scalar quantity for simplicity. Each As atom in the trimer is bonded to the three other As atoms and the trimer has a high degree of symmetry. We, therefore, expect that the dipole moment is small and neglect the first term in Eq. (1). The electric field is expected to be strongest directly beneath the apex of the tip and to fall away to zero over a length scale comparable with the tip radius of curvature ρ . During a voltage pulse we estimate $E(0) = \Delta V/d$, where d (~ 0.8 nm) is the tip-sample separation. Following Whitman *et al.*⁸ we, therefore, expect that a voltage pulse will give rise to a potential well beneath the tip which has a minimum value of $U_{\min} = \alpha E(0)^2/2$. The value of α for a free As atom is 4.7×10^{-40} C m² V⁻¹ and we would expect that the value for a trimer is of order three times higher. We, therefore, estimate $\alpha = 14 \times 10^{-40}$ C m² V⁻¹. This gives $U_{\min} = 0.18$ eV. Biegelsen *et al.*¹⁰ have calculated a difference in energy of 60 meV for an As trimer bonded at a H₃ site as compared with the T₄ site. This energy difference is small compared to the energy minimum induced by a voltage pulse. We, therefore, argue that the disordering induced by the voltage pulse is due to the diffusion of As trimers towards the tip via sites which are not energetically favorable in the absence of the voltage pulse. Following the voltage pulse the trimers are frozen in their new positions. The changes to the surrounding area are due to the surface relaxing in response to the central disordered region. This is achieved by a rearrangement of surface defects.

The changes induced by a positive voltage pulse shown in Fig. 2(b) may be explained in terms of field induced desorption of As trimers. This is the origin of the nanometer

size pit in Fig. 2(b). The 0.21 nm value determined for the pit depth is close to the 0.23 nm distance between the As trimer layer and underlying As layer.¹⁰ A similar field desorption mechanism has been proposed by Uchida *et al.*³ for the removal of single Si atoms using voltage pulses with similar parameters. The most likely explanation for the modification of the region around the pits is a relaxation of the surface following the field desorption of surface atoms. The reordering shown in Fig. 2(b) is highly suggestive of annealing due to local heating. Marella and Pease¹⁴ have shown that the overall temperature rise from the power dissipated by a voltage pulse of the magnitude we apply (the current rises to ~ 100 nA for both forward and reverse bias pulses) is very small—of order 1 K. Thus the reordering does not result from a local increase of temperature.

The effects described above are reproducible and have been observed with many different samples and tips. In particular, the difference in the effects of pulses with different polarity has been observed for all samples and tips. In addition, the application of several positive pulses at predetermined sites has been used to form small arrays of pits.

We have shown that it is possible to form nanometer scale features on a clean GaAs surface. There are significant differences which depend on the polarity of the pulses in contrast to the results for similar experiments on Si surfaces. We emphasize that the formation of local pits and disordered regions on the GaAs surface changes the surface profile and the local density of states. We believe that the application of positive voltage pulses to locally remove material offers a means of directly fabricating GaAs based nanostructures, for example on thin heavily doped epilayers, with characteristic dimensions and separations less than 10 nm.

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