InAs/GaAs(001) molecular beam epitaxial growth in a scanning tunnelling microscope

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Abstract. The growth on InAs on GaAs(001) has attracted great interest and investigation over the past few decades primarily due to the opto-electronic properties of the self-assembled quantum dot (QD) arrays formed. Scanning tunnelling microscopy (STM) has been extensively employed to investigate the complicated and spontaneous mechanism of QD growth via molecular beam epitaxy (MBE). Classically, combined MBE-STM requires quenching the sample after growth and transferring it to an arsenic-free high vacuum chamber which houses the STM system. However, without access to the phenomenon as a dynamic process a basic understanding remains elusive. In order to access surface dynamics, MBE and STM must be combined into a single element. The system herein discussed allows the operation of MBE sources in an STM system relating to InAs/GaAs(001) surfaces.

1. Introduction
GaAs(001) exhibits a myriad of reconstructions depending on As overpressure, Ga:As flux ratio and sample temperature [1], however the (2×4) and c(4×4) reconstructions have received the greatest attention [2,3] due to their existence within the temperature and flux range typically used for high quality GaAs and InGaAs growth. An improved fundamental understanding of these surfaces could play a significant role in future device fabrication, especially for self-assembled InGaAs quantum dots, since here a partial transition from (2×4) to c(4×4) can be observed in the early stages of growth just before an InAs wetting layer (WL) forms.

It is well established that the 2D WL growth is thinner than would be accounted for by the actual deposited In and that at the point when quantum dots (QDs) form the material constituting the dot accumulates faster than deposition rates supply [4-6]. The In segregation mechanism explains the mobile In population as due to segregation induced surface strain, which inhibits In incorporation on lattice sites [7-9]. This principle explains why the In is so mobile on the surface, however, consider the mobile In: it does not form large metallic clusters during epitaxy, as this liquid metal would be detrimental to growth. It can form small clusters, trimers, for instance, where In(As) occupation has occurred. Otherwise, In terminated As-rich, or As-terminated In-rich, reconstructions could accommodate excess In locally, thus providing temporary storage.

Scanning tunneling microscopy (STM) has been employed to study GaAs surfaces since the 1980s. More recently, in vacuo molecular beam epitaxy (MBE) combined with STM has allowed preservation of the growth surface affording a wealth of understanding of the fundamental properties of MBE [10-12]. In such systems the MBE and STM chambers are isolated, and growth must be terminated and the...
sample cooled prior to imaging. This so called quenching process offers snapshots of the growth surface, however the unknown effects of the quenching process may ultimately alter the “as grown” morphology [11]. Combining MBE and STM into a concurrent system allows access to growth dynamics and transient phenomena without the negative influence of sample quenching.

2. MBSTM System

In general, STM can be applied to investigate either atomic binding/reconstruction phenomenon at high resolution (~0.1nm) or islanding/step edge profiles at low resolution (100nm). The ultimate resolution capabilities are usually dominated by tip quality and various noise effects. MBE is a dynamic process, where single ML deposition times can range from 10 to 1000 s and individual adatom site hopping is significantly faster. Similarly, STM is governed by image capture cycles of ~200-400s.

In our molecular beam scanning tunnelling microscope (MBSTM) system, atomic resolution has been observed at up to 450°C on GaAs(001). Thermal drift is substantial during sample temperature ramping (~0.5nm/s), however this settles to a constant 0.01-0.05nm/s after several hours and hence can be easily compensated. Images are assembled from rastered line scans of the surface, and capture times are typically 400s for high resolution images.

Heating is supplied through a custom heating plate, where a piece of pyrolytic boron nitride (PBN) is held in close proximity to the sample (figure 1). Current contacts available in both MBE and MBSTM chambers provide heating current for the PBN element. The plate provides stable heating up to 750°C and allows near 360° reflection high energy electron diffraction (RHEED) access in the MBE chamber.

E-beam sources are utilized for group III and V deposition; after careful alignment the small capacity crucibles (0.7cc) can supply very low fluxes, suitable for slow MBE growth. Each cell is equipped with an integral flux monitor which is calibrated to known beam equivalent pressure (BEP) (figure 2). The sources are more suited to group III evaporation, where the radiant heating effects of the filament (~300°C) do not effect the evaporation rate, however stable group V fluxes from 100nA-10µA can be obtained. The main advantage of e-beam sources for STM is that the low cell temperatures do not induce additional sample drift during shutter operation.

**Figure 1.** Construction diagram of the PBN heating plate.

**Figure 2.** BEP vs. flux for As e-beam cell. Squares and black line are As data and linear fit respectively. Circles and red line are corresponding In cell data.
Tip-flux interaction creates a small but non-negligible shadowing effect on the sample surface. In order to minimize shadowing, the tip is rastered toward the sources (into the beam), hence the surface is imaged prior to shadowing effects. Ultimately this creates a deposition gradient across the scan area, which is partially compensated by adatom diffusion into the partially-shadowed region. The upper section of the image, therefore, receives a larger flux than the lower section.

A similar system has been outlined by Tsukamoto [13], where an STM module was integrated into an existing MBE chamber, so called STMBE. The challenges presented in such a system are biased toward STM operation and dampening. Here results are presented from a series of high temperature images captured in the presences of none, one and all of the In and As fluxes. The intention has been to observe GaAs(001) surface stability, dynamics and InAs/GaAs(001) wetting layer formation.

3. Experimental Procedure

The molecular beam scanning tunnelling microscope (MBSTM) is a commercially available Omicron system combining two e-beam MBE sources with an atomic resolution variable temperature scanning tunnelling microscope (VT-STM) head. For high quality InAs MBE an As:In flux ratio of 10:1 was utilised where applicable. The sources are tailored to low deposition rates and can supply stable fluxes at <0.001ML/s growth rates. Hence a typical ~1.5ML Stransi-Krastanow (S-K) transition for InAs/GaAs at 400°C can be imaged over several hours.

A Si-doped vicinal GaAs(001) epi-ready wafer was cleaved to 10 x 3.9mm² in order to accommodate the sample mounting. This plate has been shown to provide uniform heating with 2°C variation across the entire sample when observed by thermography camera. With no additional ex situ cleaning, standard oxide removal was performed in the MBE chamber under a 3.0E-6 mbar As₄ BEP at 580°C and then a 0.5µm buffer layer was grown at this temperature with As:Ga flux ratio of 30:1. This resulted in a strong (2x4) RHEED pattern and STM observations showed a smooth surface comprised of single bilayer steps.

The sample was then quenched to ~420°C in a similar manner to that outlined by Yang et al. [14]. The RHEED pattern was monitored throughout the quenching, with particular attention given to the intensity of the 2nd order diffraction rods. With the sample held at 420°C all additional As was pumped from the growth chamber before the sample heating was removed and the sample was swiftly transferred into the MBSTM chamber.

STM tips were prepared with a 2 step process. The first involved electro-chemically etching high purity <111> 0.4mm W wires in 3M NaOH solution. Tips that showed short shanks and sharp apices under light optical microscopy were then placed in a custom designed heating plate and inserted into the vacuum system. Six 10s heating cycles were then applied to the apex at 900°C, subliming the oxide.

Initial STM scanning at room temperature revealed a highly ordered β2(2x4) reconstruction across the entire surface. The sample was then ramped to 250-450°C within the STM stage and left for 5 hours to stabilise. Scanning commenced and continued until the z-drift was negligible and the xy-drift was in the order of 0.05 nm/s and could be compensated.

Whilst this range is lower than the temperatures normally used for GaAs/GaAs (570-590°C) or InAs/GaAs (480-510°C) it is necessary in this instance to choose a lower temperature. We believe that As-rich (2x4) reconstruction is only stable in the absence of an As flux from 400-430°C. Since the sample temperature must be allowed to stabilize for several hours prior to imaging in the absence of an As flux, this temperature was chosen to maintain a highly ordered (2x4) surface. Since this represents the lowest temperature at which (2x4) is stable in the absence of As, any external flux will instigate a transformation to c(4x4). This allows a very low flux to be applied, hence prolonging the transition to accommodate multiple STM images. In the case of pure As deposition the flux was 200nA, equivalent to 2.0E-8mBar, for InAs growth the fluxes were In: 100nA=1.0E-8mBar, As: 1µA=1.0E-7mBar.
4. Results and Discussion

4.1. Variable Temperature STM (VT-STM)

This section demonstrates the high temperature atomic resolution of the MBSTM. Atomic resolution is essential for identifying reconstruction domains during high temperature MBE growth. The minimum required resolution is 0.4nm, corresponding to a 1× pattern in the (1×3) and (3×1) reconstructions.

High temperature STM on GaAs(001)-(2×4) surfaces up to 320°C is arguably similar to RT-STM. In the absence of impinging flux, the surface remains static, with the low thermal energy insufficient to enhance adatom mobility. After compensating thermal drift, the (2×4) surface appears identical to RT surfaces. This range represents the temperature at which all surfaces are stable.

Upon heating to 320-350°C the dimerized As surface atoms become thermally mobile. The surface begins to transform into a c(4×4) reconstruction, which is energetically favourable at this temperature. The limited mobility prevents a surface-wide reconstruction change. STM of this surface can detect both 0.8nm (2×) and 1.6nm (4×) atomic spacings in the [110] direction, and hence distinguish between (2×4) and c(4×4) domains (figure 3a).

Figure 3. High temperature STM images of GaAs(001). a) 50x50nm² image at 350°C: (2×4) dimer rows can be seen running from top-left to bottom-right, however c(4×4) is clearly visible on the step edge in the upper-right, in the dark pits and on the white central island that start as an isometric (2×4) island. b) 50x50nm² image at 400°C: (2×4) dimer rows are dominant running from top-left to bottom right, some c(4×4) pits are visible after 24 hours of heating. c) 75x75nm² image at 415°C: surface roughening. Some (2×4) dimer rows are visible, but mainly the surface is littered with various 2× and 3× domains.

Heating directly from RT to 350-410°C has a different effect. Whilst the As surface atoms are thermally mobile, arguably more thermally mobile than between 320-350°C, the surface (2×4) reconstruction remains stable (figure 3b). The majority of the surface remains (2×4) even after 24 hours of heating, with small c(4×4) pitting.

Heating to 410°C results in large scale As desorption into the vacuum. The surface is now unstable, due to the volatility of As at this temperature, and hence becomes increasingly Ga rich. The original (2×4) can be identified with 1.6nm (4×) spacing in the [110] direction, as previously, however, 0.8nm and 1.2nm spacings are evident, implying the excess Ga has caused localized, transient reconstruction domains before the surface stabilizes at (3×1) (figure 3c).
4.2. Molecular Beam STM (MBSTM)
Operation of the STM during flux irradiation adds a further complication, especially for III-V MBE where the group V flux typically exceeds the group III flux by 30 times. This section discusses the effects of e-beam sources on STM imaging.

4.2.1. As flux.
Typically the STM is operated in UHV with a background pressure of 1.0E-11 mBar. The operation of the e-beam cell in the STM chamber, without liquid nitrogen cooling, results in a high background pressure, which is ~1/4 of the beam flux. Hence, during initial heating of the cell to achieve a stable flux, the effect of the background As on the surface reconstruction is noticeable. Ultimately, at a sample temperature of 400 °C, the As background pressure is sufficient to induce a partial transformation to c(4×4). This is shown in figure 4a, where As dimers have appeared on top of the (2x4) and similar sized pits decorate the surface. Nevertheless, the β2(2×4) (figure 4c) is still dominant and the induced roughness is similar to that of the γ(2×4) surface (figure 4d).

Figure 4. a) 100x50nm² image at 400°C, (2×4) dimer rows run from upper-left to lower-right: bright spots indicate adsorbed As from the background flux. b) 40x24nm² image at 400°C, c(4×4) is now dominant, only isolated (2×4) domains remain (upper right of image). c) β2(2×4); dark circles: Ga, light circles: As. d) γ(2×4); dark circles: Ga, light circles: As.

The first shutter operation results in a brief loss in imaging capabilities, due to the initial interaction of the flux with the tip, this typically lasts <1s. From this point on the resolution remains remarkably stable throughout the subsequent images, with a few scan lines and contrast changes due to adatom-tip interaction. The surface slowly undergoes a transformation from (2×4) to c(4×4), with c(4×4) islands forming 1 atomic layer above the (2×4) and pits forming 1 atomic layer below [15]. The resolution of the 150x150nm² images is high enough to identify the 2 domains and the 0.8nm spacing of the c(4×4) reconstruction is clearly visible. Reconstruction change preferentially takes place at step-edges, which are known to act as catalysts for growth phenomena [16]. The reconstruction change continues from
image to image, with step edges spreading and small islands coalescing until the c(4×4) reconstruction is dominant and only isolated dimer rows remain of the original (2×4) (figure 4b).

4.2.2. In and As flux.
Imaging of InAs/GaAs wetting layer formation has been performed at low magnification (500x500nm²) in order to image step edge profiles, 2D roughening and 3D island formation. Growth of InAs on GaAs(001) comprises of a number of phases. Initially the InAs adopts the lattice spacing of GaAs(001)-c(4×4) and 2D growth ensues under an alloyed (1×3) reconstruction (figure 5a). Both c(4×4) (figure 5c) and (1×3) (figure 5d) occupy the same atomic layer, hence the surface undergoes planarization. This continues up to around 1.1ML where the surface begins to roughen and enter into a transition phase (figure 5b). Near the segregation triggered S-K transition [7, 8] 2D growth slows, due to increasing In segregation toward the surface and, as a result of the increasing strain, limited sites remain for In incorporation.

![Figure 5](image_url)

**Figure 5.** a) 310x225nm² image at 400°C <1ML InAs: InAs (1×3) alloy has begun planarising the 2ML high c(4×4) starting surface. b) 310x225nm² image at 400°C ~1.1ML InAs: surface has roughened due to lack on In bonding sites in upper layer. c) c(4×4); dark circles: Ga, light circles: As. d) alloyed (1×3); dark circles: Ga; light circles: As; blue circles: In.

The images frequently exhibit scan lines as a consequence of In and As atom contamination of the tip interfering with tip-sample interaction. The scan lines are transient, meaning any material adsorbing onto the tip quickly desorbs. The tip, held in close proximity to the surface, reaches an equilibrium temperature of an order with the substrate. Hence impinging flux does not build up on the apex, provided low fluxes are applied.
Shortly before QDs form, a number of small pre-QD structures appear with a diameter of ~10-15nm and a height of 1.5nm (~5ML) (figure 6). These islands are quasi-stable, appearing and disappearing through a series of 10 images, similar to previous observations [17]. The tip interaction at nucleation sites is witnessed in several pre-QDs where the formation is “clipped” giving the dot a flat edge. This clipping does not seem to effect nucleation, as clipped pre-QD are present and whole in the following image.

The pre-QDs appear randomly across the surface, though are limited to the upper ¼ of the image, where tip shadowing is significantly reduced. This shows the sensitivity of the S-K transition to sub-ML growth profiles. The nucleation sites are not limited to step edges, nor do the nucleation sites appear distinct from other areas of the upper ¼ of the image where pre-QDs do not form. There the surface is covered in 2D structures, some displaying bright spots where local reconstruction has added an additional atomic layer. Some ripen into pre-QDs, though the ripening process appears random. This re-entrant behaviour continues until WL formation is complete at 1.4ML and full 3D structures with 60nm diameter and 7nm height form.

Figure 6. Series of sequential STM images showing pre-QD structures in the same sample area. Height 1.5nm, diameter 10-15nm.

5. Conclusion
The operation of e-beam sources to achieve MBSTM has been discussed for the III-V system, concentrating specifically on InAs/GaAs(001) epitaxial growth. Atomic resolution at high temperature and in the presence of an As flux has been used to observe reconstruction change from (2×4) to c(4×4). Low resolution imaging in the presence of In and As fluxes has further been shown to allow WL growth to be observed and provide dynamic results on pre-QD structures. Tip-flux-sample interactions in the form of shadowing, contamination and QD growth alteration have been shown to require consideration when analyzing observations.

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