Temperature dependence of Ga-assisted oxide desorption on GaAs(001)

F Bastiman¹, R Hogg¹, M Skolnick², AG Cullis¹ and M Hopkinson¹

¹The University of Sheffield, Department of Electronic and Electrical Engineering, Mappin Street, S1 3JD, UK
²The University of Sheffield, The Department of Physics and Astronomy, Hicks Building, Hounsfield Road, Sheffield, S3 7RH, UK

E-mail: f.bastiman@shef.ac.uk

Abstract. Removal of native oxide by conventional thermal desorption causes large scale degradation of the initial surface layer. Ga assisted oxide removal at 440-500°C has been shown to reduce damage and so-called µpit formation. We examine surfaces prepared by this technique over the 400-580°C range with dynamic reflection high-energy electron diffraction (RHEED) and in situ scanning tunnelling microscopy (STM) analysis. Surfaces with oxide clusters, pure GaAs and Ga droplets are found to exist sequentially for sub-monolayer increases in Ga deposition. The STM imaging shows that two distinct, temperature dependent cleaned surfaces exist within the prescribed range. Ga mobility is believed to underpin the mechanisms that produce each surface whilst step-edge density defines the resulting pit density.

1. Introduction
The surface of a GaAs wafer is covered in a native oxide layer. The removal of this oxide layer is an important cleaning step in ensuring the quality of the subsequent buffer layer and abruptness of epitaxial interfaces. Typically, conventional oxide desorption is performed under an As flux to stabilise the surface. Figure 1a shows the extent of the damage with dense arrays of coalescing µpits up to 75nm in diameter and 5-10 nm deep. Figure 1b shows the same surface after 10nm of growth. Whilst the areas around the pits display good (2×4) dimer rows, there are regions with either high step density or deep pits. The high step density is attributed to shallow pits, where material has been removed up to 4 monolayers (ML) deep at step edges, which have subsequently grown out. The µpits are areas where more material was removed and hence are difficult to over grow. It is these µpits that perpetuate throughout buffer layer growth and eventually are thought to lead to large-scale mound formation [1, 2].

Pits formed due to mass transport out of the bulk GaAs [3]. In order to sublime, non-volatile Ga₂O₃ requires Ga in order to generate volatile Ga₂O. The reaction with bulk GaAs is:

\[
\text{Ga}_2\text{O}_3 + 4\text{GaAs}_{\text{bulk}} \rightarrow 3\text{Ga}_2\text{O} \uparrow + 2\text{As} \uparrow
\] (1)

The mass transport of bulk Ga out of the crystal to accommodate oxide desorption is substantial and creates surface-wide damage up to 40 ML (~11nm) deep. However it has been shown recently that
externally supplying Ga from a standard effusion cell can reduce the requirement for this mass transport [3-5]. The reaction is characterised as:

$$Ga_2O_3 + 4Ga_{\text{flux}} \rightarrow 3Ga_2O \uparrow$$ (2)

Whilst the authors reported a reduction of oxide in all cases, ex situ AFM was employed to characterise the surface, inevitably exposing the wafer to substantial oxide regeneration. Furthermore, all work was carried out between 440 and 500°C, which represents a narrow temperature band in the viable range from 400-580°C. In this work in situ STM was performed after Ga-assisted oxide desorption over a range of temperatures. RHEED analysis during clean up indicates there is a strong temperature dependence of the clean-up process.

Figure 1: STM images of GaAs(001) surface, a) at clean up with dense pitting formation across the sample. Inset shows high magnification image of a pit, b) after 10nm of growth and a 2 hours anneal at 580°C. Inset shows high magnification of central feature: a 50×60 nm$^2$ pit with dimer rows across its floor.

2. Experimental
This work was performed on a commercially available Omicron molecular beam scanning tunnelling microscope (MBSTM) system. The system comprises an interconnected conventional molecular beam epitaxy (MBE) chamber and a variable temperature scanning tunnelling microscope (VT-STM). The former chamber is fitted with standard Ga and As$_4$ effusion sources and RHEED for dynamic surface analysis. The latter chamber maintains an ultra high vacuum (UHV) pressure of 2.0×10$^{-11}$ mBar to ensure low contamination during post growth imaging. More details of the equipment are published elsewhere [6].

An undoped 2° off-cut GaAs(001) epi-ready wafer was cleaved into 10 × 3.9 mm$^2$ chips in order to accommodate sample mounting. Heating was achieved through a heating plate, whereby current was passed through a piece of pyrolytic boron nitride (PBN) in close proximity to the sample. The plate has been shown to provide uniform heating when observed by a thermography camera.

With no further ex situ processing, the sample was out-gassed at 300°C for 30 minutes and 400°C for a further 30 minutes. At the end of the outgas stage the chamber background pressure returned to a system typical 1.0×10$^{-10}$ mBar. Sample temperatures between 390 and 520°C were then
maintained whilst the sample was irradiated with a 0.05ML/s Ga flux for 0-180s. The surface was monitored by RHEED throughout.

On cessation of the Ga flux, samples were annealed for 10 minutes at the preparation temperature before termination of the heating current and a rapid transfer to the STM chamber. Working in the absence of As$_4$ allows a background pressure of $1.0 \times 10^{-10}$ mBar throughout and negates the necessity for complicated quenching procedures [7].

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

Scanning into small amounts of residual oxide induces noise distortion into the standard filled state (negative bias) STM images. More stable imaging into the oxide was achieved with empty state imaging. A selection of scan areas from $1500 \times 1500$ nm$^2$ to $250 \times 250$ nm$^2$ was utilised to obtain a broad spectrum of detailed images.

3. Results and Discussion

Four temperature dependent regimes for Ga-assisted oxide desorption were identified in this work. The first (<400°C) and the last (>580°C) regimes proved detrimental to the process. Below 400°C irradiation by Ga flux produces Ga droplets on the sample surface, and hence this range is unsuitable for oxide removal [3]. STM imaging of the sample is hindered by the interaction of the droplets with the tip, resulting in interference in the form of a saw-toothed waveform. Above 580°C oxide thermally desorbs by the conventional mechanism, and hence attempts to utilise Ga assisted oxide desorption are circumvented. The remaining two ranges both prove suitable for the technique, however changes in Ga mobility seem to underpin the surface dynamics in each case.

![Figure 2](image.png)

**Figure 2.** a) STM image of GaAs(001) surface after 8ML of Ga at 460°C. Small pits have formed across the surface up to 2nm deep and 30nm diameter; most have a Ga droplet ring, giving them a volcano shape. The inset shows a high magnification of a volcano-pit, b) height profile across the [110] direction of a pit showing the asymmetry in the volcano lip and a height of 1.5nm.
For the temperature range 400-500°C, the RHEED pattern evolves from a broken 1× to a 2× along [110] after 7.75ML of Ga deposition. STM imaging after quenching at this point reveals a small amount of surface oxide through empty state imaging along with small, circular shaped pits (not shown). An additional 0.25ML of Ga leads to a partial removal of the oxide and the formation of small rings around the circular pits (Figure 2a). The surface is covered in small pits up to 2nm deep and 30nm diameter, however most have a Ga droplet ring around their perimeter, giving them a volcano like structure. The inset of the figure shows a high magnification image of the volcano-pit, showing it is asymmetrical. A cross-section of a pit in the [110] direction is given in Figure 2b; the lip increases the apparent depth, as it stands some 1.5nm above the surface normal. The volcano-pits can be planarized by high temperature annealing under As, however this leads to an increase in their area and depth profile.

Figure 3. RHEED pattern evolution along [110] azimuth for Ga deposition at 520°C, a) 7.5ML 2×, b) 7.75ML 3×, c) 8.0ML 4×

For the temperature range 500-580°C, the RHEED pattern is much more sensitive at the clean up point. After 7.5ML of Ga deposition the [110] azimuth reveals a strong 2× pattern (Figure 3a) which corresponds to an As-rich (2×4) reconstruction on the sample surface. The presence of As means that all the deposited Ga has contributed to the oxide removal, and hence none remains for Ga-rich reconstruction formation. After 7.75ML of deposition the RHEED pattern reveals a 3× reconstruction on the [110] azimuth, corresponding to a Ga-rich (3×n) reconstruction, where n is either 1, 4 or 6 but is unclear from the azimuth. STM imaging of the sample at this stage revealed there is still residual oxide, meaning that whilst Ga is involved in desorbing oxide, the distance between the patches is greater than the average diffusion length and hence not all Ga deposited reaches the oxide. After 8.0ML of deposition the [110] azimuth exhibits a strong 4× pattern, corresponding to Ga-rich (4×2), as expected from depositing 0.25ML of Ga on (3×1) [8]. Very low deposition rates are therefore necessary to prevent over supply of Ga. Occasionally the (4×2) reverts to (3×1) after a short anneal, meaning that excess Ga stored in the reconstruction can still contribute to oxide desorption, and hence deplete the Ga-rich surface. Presence of (4×2) or reversion to (3×1) corresponds to optimal oxide removal with this technique. Further increase in Ga deposition leads to droplet formation on the surface.

Figure 4a shows a surface after 8.0ML of Ga deposition at 520°C. The surface displays anisotropic pits aligned along the [110] direction. The alignment is liable to result from preferred Ga binding along step edges [9]. The pits are 50-60nm long and 20-30nm across with 1-1.5nm depth profiles.
None of the pits imaged showed the volcano structure corresponding to Ga droplet formation. The depth profile in Figure 4b along the [110] direction shows the pit floor has sub-ML height differences possibly due to localised reconstruction formation.

Figure 4. a) STM image of GaAs(001) surface after 8ML of Ga at 520°C. Small anisotropic pits have formed across the surface from 1.0-1.5nm deep and with area 50-60 × 20-30nm², b) height profile in the [110] direction showing reconstruction on the pit floor.

All the pits formed after Ga deposition are of a similar density and appear to be linked to the step-edge distribution, which has ~8.5nm spacing for a 2° off-cut sample. Principally, the small pits could form under the exact same mechanism as the larger µpits. Above 400°C Ga₂O thermally desorbs from the surface, and hence there is a small fraction of the bulk GaAs that is consumed to contribute to this thermally desorbed oxide. However since most of the Ga₂O₃ breaks down from externally supplied Ga the pits are smaller and less frequent. It is also possible that these small pits are a consequence of ex situ sample ageing, resulting in a small amount of Ga₂O₃ growth on the surface over time [10].

The difference in the pit shape at the two temperatures can be described in terms of Ga mobility and surface reconstruction formation. The pits represent areas where the oxide has been removed rapidly due to thermal desorption, hence they are areas where surface GaAs is exposed amidst residual oxide. At low temperatures <500°C the mobility of Ga is sufficiently small that deposition on these pitted areas leads to droplet formation, as the excess Ga neither contributes of reconstruction change (simply not enough GaAs is exposed to accommodate the deposited Ga) nor oxide removal (the oxide is further away than the mean diffusion length). Under this mechanism not all the oxide can be removed before droplet formation. However above 500°C, the Ga deposited on these regions can migrate to nearby oxide, reducing the percentage coverage. Excess Ga is temporarily stored in Ga-rich (4x2) before migrating to nearby oxide. Under this mechanism all the oxide is removed before droplet formation.

4. Conclusion
The temperature dependence of Ga assisted oxide removal on GaAs(001) epi-ready wafers has been investigated by RHEED and in situ STM. Two key temperatures have been identified, leading to two distinct shallow pit shapes. Variation of Ga mobility has been invoked to explain the differences between samples prepared in the two temperatures ranges. It has been shown that performing Ga assisted oxide removal above 500°C eliminates nano-sized Ga droplet formation and significantly reduces surface damage induced by conventional oxide removal under an As flux.
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