

Surface morphologies associated with thermal desorption: Scanning tunneling microscopy studies of Br–GaAs(110)

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Scanning tunneling microscopy was used to characterize the developing surface morphology found during typical temperature programmed desorption experiments for halogen–GaAs. Surfaces exposed to Br₂ at 300 K were heated to temperatures between 450 and 675 K, followed by scanning at room temperature. This made it possible to relate the temperature-dependent gas phase etch product distribution to the surface structure and thereby examine atomic-level surface processes associated with the evolution of volatile products. We associate the desorption of GaBr₃ around 500 K with the initiation of single-layer-deep terrace pits. Desorption of GaBr and As₂ above 600 K accounts for the lateral enlargement of the pits. © 1997 American Vacuum Society. [S0734-211X(97)00203-5]

I. INTRODUCTION

The interaction of halogens with semiconductor surfaces is of technological importance because chlorine- and bromine-containing reactants are used in dry-etching processes. Accordingly, much effort has been devoted to define and understand the relevant surface processes. Pivotal understanding of the underlying chemistry was gained by temperature programmed desorption (TPD) experiments that identified the volatile reaction products. Detailed work by Tyrrell *et al.*,¹ Su *et al.*,² Ludviksson *et al.*,³ and French *et al.*⁴ demonstrated that the distribution of these products will depend on the initial halogen exposure (initial surface concentration) and on the surface temperature. In work with the Cl–GaAs(100) system, they showed the desorption of GaCl, GaCl₃, and As₂(As₄), with rates that varied with processing conditions.

Etching reactions are more complex than elemental desorption processes because they require the formation of volatile products involving substrate atoms. Since these formation and desorption processes have activation energies that depend on the particular surface site, the relative importance of the various reaction pathways should vary with the local morphology. In turn, the local morphology changes as material is removed. Unfortunately, there have been few studies that provide “snapshots” of the surface structure so as to complement gas-phase product analysis.

Scanning tunneling microscopy (STM) makes it possible to observe surface structures with atomic resolution. Previously, it was used to characterize GaAs(110) surface etching at elevated temperature during continuous exposure to molecular halogen beams.⁵ In those experiments, the steady state surface concentration of halogens reflected the balance between halogen adsorption and the desorption of the various volatile reaction products. It follows that the concentration depends on temperature because of the different desorption energies for the products.

In the present work, we used STM to investigate Br-exposed GaAs(110) after heating to successively higher temperatures between 450 and 675 K. The initial submonolayer surface concentration was selected by exposure at a temperature below the desorption threshold. The images, obtained at room temperature after each heating cycle, reflect conditions representative of surfaces realized in thermal desorption investigations where the concentration diminishes and reflects the activation of different processes. We found evidence for two distinct stages of surface modification associated with two stages of etching identified previously in desorption studies.^{1–4} The first is associated with the creation of single-layer-deep etch pits on terraces. This sets in at about 500 K where TPD of Cl–GaAs has shown GaCl₃ desorption. The second stage, activated above 600 K, involves lateral enlargement of the etch pits. This stage can be related to etching via GaCl loss and the desorption of As₂(As₄). The TPD-like etching studied here produces quite different surface morphologies than those reached with steady state etching⁵ because of the dependence of the reaction channels on surface halogen concentration.

II. EXPERIMENTAL PROCEDURE

Our experiments were conducted in an ultrahigh vacuum system housing a Park Scientific Instruments STM. Clean GaAs(110) surfaces were obtained by cleaving *p*-type posts (Zn doped at $2 \times 10^{18} \text{ cm}^{-3}$). Electrochemically etched tungsten wire was used for the tips of the STM. These tips were cleaned by electron bombardment prior to use. STM topographs were acquired in the constant current mode, with the sample bias between -1.5 and -3.5 V. A solid state AgBr–CdBr₂ electrochemical cell was used as a source for Br₂. The Br exposure is expressed in mA s, corresponding to operation of the cell with a current of $5 \mu\text{A}$ for a defined duration. For reference, an exposure of 1 mA s at 300 K results in about 0.5 monolayer (ML) surface coverage, determined by counting the adsorbate features. After exposure to Br₂ at 300 K, the sample was heated by tungsten filaments

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mounted on the holder.⁶ Upon reaching the designated temperature, $450 \leq T \leq 675$ K as measured with a pyrometer, the sample was cooled to ambient and was characterized by STM. The process was then repeated for the next higher temperature.

Thermally activated reactions can be described by the Arrhenius form $k = \nu \exp(-E_A/kT)$ where E_A is the activation energy and ν is the probing frequency of the reaction. With a given heating time, only surface reactions that are fast on the experimental time scale will lead to measureable changes of the surface morphology. Thus, after each heating cycle the surface reflects a configuration where reactions that are fast have saturated at the maximum temperature. Extended annealing at the maximum temperature would lead to gradual changes of the surface structure, but would not initiate etching pathways with significantly higher activation energies. We verified this by annealing samples for 20 min at maximum temperature after first reaching this temperature during desorption cycles. The fact that the maximum temperature and not the time at that temperature determined the morphology justifies our approach of simulating TPD-related surface structures with a series of heating cycles.

III. RESULTS

A. Previous TPD results

In TPD, a surface is initially exposed to a specified amount of gas phase reactant at a fixed temperature. It is then heated in a controlled fashion while the desorbing species are analyzed with a mass spectrometer.⁷ The energetics and order of surface reactions can be deduced from the desorption temperatures, the intensities of particular masses, and the dependencies on initial coverage and ramping rate. The published TPD results for Cl/GaAs(100) agree that the primary desorbing species is GaCl₃ below 600 K, but that desorption of GaCl, As₂, and As₄ dominates above 600 K.¹⁻⁴ The intensity of the trihalide contribution is enhanced by higher initial coverages up to saturation at 300 K. While AsCl₃ is not observed following exposure at 300 K, this species can be formed when multilayers of Cl₂ are condensed on GaAs at low temperature. In agreement with this, photoemission experiments have shown AsBr₃ on the surface at low temperature and its desorption at about 150 K.⁸

B. STM results

Figure 1(a) is a STM image of a GaAs(110) surface that was exposed to 1.5 mA s of Br₂ at 300 K. This surface is nearly saturated with Br adatoms. Figures 1(b)–1(e) are images of the same surface after heating to 450, 500, 600, and 675 K and with no further Br exposure. As shown by Patrin and Weaver,⁵ Br atoms bond to Ga and As sites, forming adsorption islands in which every Ga atom and every second As atom is Br terminated. The maximum Br coverage that can be attained with this structure is 0.75 ML where 1 ML is the atom density of GaAs(110). The bright objects in Figs. 1(a)–1(c) correspond to Br atoms chemisorbed on As sites, producing mixed (2×1) and c(2×2) symmetry (see Fig. 3

of Ref. 5 for models of the structures). The Br atoms on Ga sites are lower in height and are less visible, appearing as the darker background.⁵ Island formation reflects an attractive interaction among Br adsorption sites. This picture is supported by photoemission studies by Stepniak *et al.*⁹ and by first-principles calculations by Khoo and Ong¹⁰ and by Corkill and Chelikowsky.¹¹ In the low coverage regime, the Br atoms form narrow chains elongated along [001]. The underlying adsorbate interaction stretches the adsorption islands along [001], as is rationalized by the calculations by Corkill and Chelikowsky.¹² These chains coalesce at higher coverage.

The image of the surface heated to 450 K in Fig. 1(b) shows no significant etching, and the surface is almost saturated with Br structures. There is, however, an increased occurrence of (2×1) structures compared to Fig. 1(a). This indicates that the (2×1) island structure is energetically favored relative to the c(2×2) islands. Although they have the same adsorbate density, the (2×1) structure has As rows free of Br along [001]. It is possible that (2×1) enables a rowwise buckling with 2× periodicity along [110] that allows better relaxation than c(2×2), where the vacant As sites are staggered.

Heating to 500 K significantly reduces the density of bright features attributed to Br on As sites, Fig. 1(c). The remnant Br appears in narrow chains. By analogy to the low coverage results of Patrin and Weaver,⁵ we associate these chains to elongated Br–As chains with double rows of Br–Ga features at lower height. The zigzag row structure of exposed GaAs(110) is visible in some regions. We associate the dark patches with the onset of etching (labeled II). Most of the surface remains covered with poorly ordered adsorption features, and it is impossible to quantify the amount of Br that has desorbed by etching.

Heating to 600 K results in the surface structure shown in Fig. 1(d). Here, the zigzag row structure of GaAs(110) is clearly visible, with lighter areas marking the original top layer (labeled I) and darker ones revealing the second layer (labeled II). The second layer remains intact with almost no pits in it. In contrast to Figs. 1(a)–1(c), the regular Br features have vanished in Fig. 1(d). While the top layer is decorated with irregular structures, their density is much reduced. We attribute them to Br bonded to Ga and to As released during etching.

As₂ was observed to desorb at ~600 K in the TPD spectra from Cl/GaAs(100).¹⁻⁴ The fact that GaCl₃ desorbs at lower temperature implies that the surface will be As rich between the onset of etching and the onset of As₂ desorption. Such As enrichment was observed by Simpson *et al.*¹³ in photoemission of Cl/GaAs(110). Thermodynamically, As₂ formation is favored by 382 kJ/mol compared to atomic As.¹⁴ The accumulation of As₂ on the GaAs(110) surface would help to explain the absence of ordered Br islands in Figs. 1(c) and 1(d) because surface As₂ would hinder the diffusion of Br. The nearly exposed lower terraces remain free of As₂ features, perhaps because As atoms ejected onto the lower terrace are accommodated at steps.

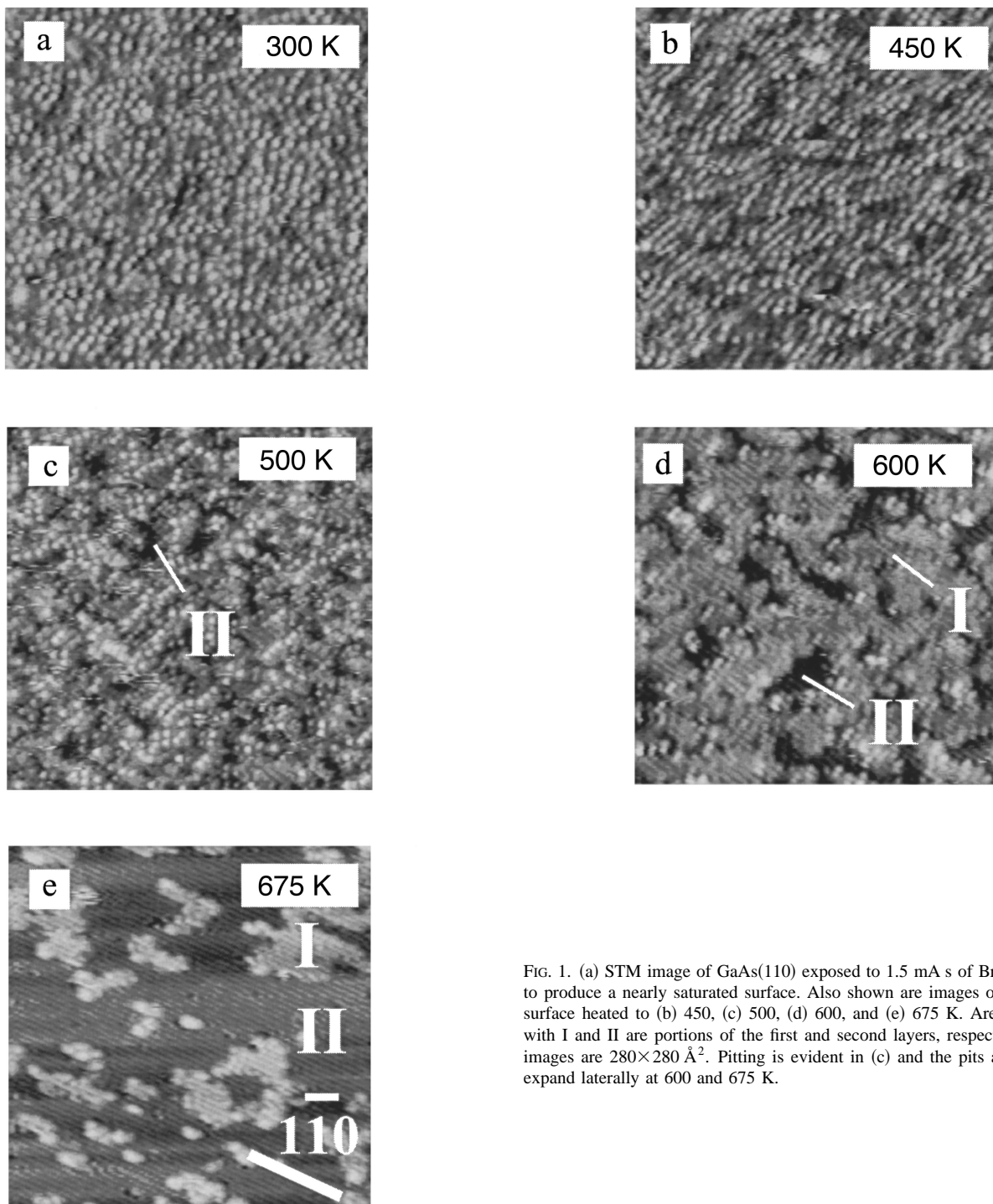


FIG. 1. (a) STM image of GaAs(110) exposed to 1.5 mA s of Br_2 at 300 K to produce a nearly saturated surface. Also shown are images of the same surface heated to (b) 450, (c) 500, (d) 600, and (e) 675 K. Areas marked with I and II are portions of the first and second layers, respectively. The images are $280 \times 280 \text{ \AA}^2$. Pitting is evident in (c) and the pits are seen to expand laterally at 600 and 675 K.

When the sample that was represented by Fig. 1(d) was heated to 675 K, there was significant removal of surface material. The fact that the top layer was reduced to small islands with only a few isolated adsorption features demonstrates that there was appreciable residual Br at 600 K. Pitting was minimal.

These STM results show that the morphology exhibits two distinct etching stages. The first is characterized by development of small single-layer-deep terrace pits at ~ 500 K. The rest of the terrace is covered with features

derived from Br and As_2 . The second stage at $T \geq 600$ K is characterized by the lateral enlargement of the pits and desorption of the features that decorate the terraces. Most of the substrate material is removed in stage two.

IV. DISCUSSION

Examination of TPD results¹⁻⁴ in light of the STM data suggests that the evolution of GaBr_3 at lower temperature corresponds to terrace pit initiation, whereas GaBr and

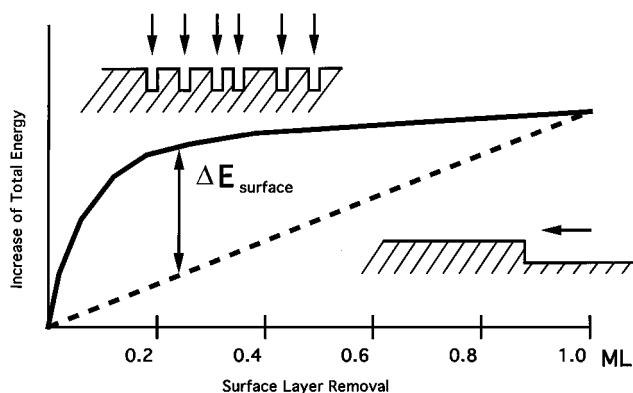


FIG. 2. Diagram that illustrates the increase in the GaAs system energy with physical atomic-layer removal as Ga and As atoms are placed at infinity. Such atom removal by retreat of a single step leads to a linear, minimal energy increase that corresponds to the cohesive energy times the number of atoms of the surface (dashed line). In this case, there is no change in surface energy. Terrace pitting increases the surface energy due to the step and kink energy components (solid line). The surface contribution decreases as the pits coalesce. This diagram neglects thermochemical gains associated with (exothermic) etching of GaAs by Br.

$\text{As}_2(\text{As}_4)$ desorption at higher temperature reflects etch pit enlargement. On an atomic scale, the evolving surface reflects the details of bonding, with terrace atoms being more tightly bound than those at steps or kinks. Thermodynamically, the removal pathway that keeps the surface energy at a minimum is the one where atoms desorb from step kinks so that steps retreat. Such step retreat is depicted in Fig. 2 where the dashed line in the plot represents the linear increase in the total energy, scaling with atom removal as atoms are taken to infinity and the remaining crystal stays in its thermodynamic ground state. In contrast, atom removal from a terrace site (pitting) increases the surface energy because it creates steps and kinks. This contributes to an increase in the total energy, as shown in Fig. 2, although greatly exaggerated, since the step energy may be a few tenths of an eV per atom compared to a cohesive energy of 6.5 eV per Ga-As pair. As the pits coalesce, they reduce the surface energy because the total step length and kink density diminish. In addition to these considerations of the physical removal of atoms to infinity, etching involves chemical bonding with an extrinsic species. Thermochemically, the monobromide reaction $3 \text{GaAs(s)} + 3/2 \text{Br}_2(\text{g}) \rightarrow 3 \text{GaBr(g)} + 3/2 \text{As}_2(\text{g})$ is exothermic by ~ 270 kJ/mol, whereas the tribromide evolution $\text{GaAs(s)} + 3/2 \text{Br}_2(\text{g}) \rightarrow \text{GaBr}_3(\text{g}) + 1/2 \text{As}_2(\text{g})$ is exothermic by ~ 426 kJ/mol (Ref. 15). Clearly the desorption branch that produces GaBr_3 is thermochemically favored over the GaBr branch. When added to Fig. 2, this would result in a reduction in overall energy.

The likelihood of probing the GaBr_3 etching pathway is determined by the local Br concentration. While islands of the $2 \times 1/c(2 \times 2)$ structure are stable at 300 K, they are likely to be lost at etching temperatures as Br moves onto the terrace. It follows then that, at low initial concentration, Br would be dispersed and this would make attainment of the precursor state unlikely (kinetically limited). For high initial

concentrations, the local concentration is maintained and the lateral motion of Br atoms is inhibited.

GaBr_3 formation is limited by a barrier related to Br insertion into the backbonds and the associated disordering of the structure. Once GaBr_3 is formed on the surface, it is readily desorbed. This was indicated by molecular beam scattering experiments by DeLouise on GaAs(110) that showed that GaBr_3 desorption involves almost no activation barrier.¹⁶ A possible surface precursor state is one in which both As sites are occupied next to a Br-terminated Ga site. That configuration with 1×1 symmetry would also tend to weaken the Ga backbonds. While not a stable structure at 300 K, it could be populated at high temperature within $2 \times 1/c(2 \times 2)$ islands via next-neighbor jumps of Br atoms on As sites. Overall, the barrier associated with such GaBr_3 formation must be less than the desorption barrier of GaBr because GaBr_3 is the lower temperature desorption product.

The halogen concentration will decrease as a consequence of etching during the temperature rampup for a nearly saturated starting configuration. At the start of that process, the concentration is high and the temperature is low. Hence, etching is biased toward GaBr_3 evolution and creation of small etch pits [Fig. 1(c)]. This relates to the GaBr_3 peaks observed around 500 K in TPD. As the Br concentration decreases and the temperature increases, etching via step retreat is favored, and the pits formed at lower temperature provide ample sites for such etching. That process relates to GaBr evolution. The absence of appreciable pitting of the second layer supports the notion that the Br concentration on this layer never reaches the density needed for trihalide formation. Instead, Br is consumed by step etching reactions.

The net contributions of the GaBr_3 and GaBr desorption pathways depend on the initial coverage, with the former gaining weight at higher coverage, in agreement with TPD results. The coverage dependent ratio of these pathways manifests itself in the etch yield, i.e., the number of atoms removed per Br atom. With GaBr_3 etching, three Br atoms participate in the removal of one Ga atom, whereas GaBr etching requires only one. An increased contribution of GaBr_3 evolution would reduce the yield. This has been observed in studies where we varied the initial coverage and evaluated the total number of surface atoms removed after annealing to 700 K. As discussed in Ref. 17, the yield was close to 2 at very low initial Br concentration (each Br atom removes one Ga atom and As_2 desorbed spontaneously). The yield fell to ~ 1.6 for an initial coverage near saturation. The relative contribution of the two etching pathways was estimated by fitting the measured coverage dependence of the yield to a reaction kinetic model. For starting coverages below about 0.1 ML, the GaBr_3 contribution was lower than 1%. For an initial coverage of 0.5 ML, it rose to 12%. As a result, it was possible to quantitatively describe the competition between a first-order and a third-order bromide desorption pathway.

V. CONCLUSIONS

This work has characterized the evolution of Br-exposed GaAs(110) as the temperature was ramped from 300 K. With

STM, we gained morphological information about processes often found in TPD.¹⁻⁴ By considering atom-level reaction mechanisms, we correlated gas phase reaction products and surface processes. Heating a saturated surface to 500 K results in the formation of scattered single-layer etch pits that we associate with GaBr₃ evolution. Such desorption is the low barrier/high concentration channel. The initiation of etch pits creates high energy step sites at which GaBr desorption can occur when the temperature is increased. This is the high barrier/low concentration channel. The change of surface structure reflects the removal of atoms from the perimeters of first-layer islands with little pitting in the exposed second layer.

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