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Dynamics of spontaneous roughening on the GaAs(0 0 1)-(2×4) surface

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Abstract

The dynamics of a random distribution of spontaneously formed 2D GaAs islands are studied using scanning tunneling microscopy. The equilibrium concentration of islands is easily tuned from 0% to 50% coverage by only changing the As_4 overpressure. Images taken during the early stages of island formation reveal the roughening transition primarily occurs through an intermediate pit formation phase. Interestingly, pit formation in the middle of an otherwise pristine terrace is overwhelmingly preferred to atom detachment from the edges of the terraces.

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1. Introduction

The phenomenal growth in wireless communications and optoelectronics technology is making zinc-blende III–V semiconductor substrates an increasingly important component of the semiconductor industry (see for example, [1]). Naturally, there is an extensive effort to develop both higher performance devices as well as novel multifunctional devices, all of which require stricter control over the growth process. To achieve this, a deeper understanding of the fundamental processes involved in making device structures, such as attachment–detachment rates, diffusion and nucleation is required.

Macroscopic measurements of gallium adatom diffusion using kinetic studies has dominated the research community. For example, monitoring growth under a shadow mask, has been used to estimate the Ga diffusion length [2]. In addition, the decay of intensity oscillations in reflection high-energy electron diffraction (RHEED) with increasing temperature has been used extensively to study diffusion of Ga on GaAs [3–5]. Surface diffusion studies for the III–V compound semiconductors are necessarily complicated since these are binary compounds.

Recently, many studies on the GaAs(0 0 1) surface have documented the phenomenon of spontaneous formation of GaAs islands [6–10]. These studies show that by simply altering the As_4

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overpressure or changing the substrate temperature, an equilibrium concentration of GaAs islands can be obtained, and that the island coverage can be reversibly tuned without changing the local atomic structure. This discovery allows an entirely new approach to studying the dynamics of growth, mainly without depositing any Ga and using entropy-driven statistical mechanics instead of kinetic rate equations.

In this article, we take advantage of the well-documented crystal structure and surface morphology of the GaAs(0 0 1)-(2×4) reconstructed surface to learn about surface dynamics. Specifically, we prepare a pristine, island-free GaAs surface then, by quickly changing the As_4 overpressure, watch as the surface relaxes to its new equilibrium configuration consisting of one that is half covered with islands. From this we learn about atom detachment processes and pathways to equilibrium.

2. Experimental

Experiments were carried out in an ultra-high vacuum (UHV) multi–chamber facility ($5–8\times10^{-11}$ Torr throughout) which contains a solid-source molecular beam epitaxy (MBE) chamber (Riber 32P). The MBE chamber is equipped with a substrate temperature determination system accurate to $\pm2^\circ$ [11], and an arsenic cell with an automated valve and controller. The MBE chamber also has an all UHV connection to a surface analysis chamber, which contains a custom integrated STM (Omicron) [12]. Without any chemical cleaning, commercially available "epi-ready," $n+$ (Si doped $10^{18}/\mathrm{cm}^3$) GaAs(0 0 1) $\pm0.05^\circ$ substrates were loaded into the MBE system. The surface oxide layer was removed and a 1.5 μm thick GaAs buffer layer was grown at 580° using an As_4 to Ga beam equivalent pressure (BEP) ratio of 15 and a growth rate of 1.0 μm/h. as determined by RHEED oscillations.

To study the time evolution of the spontaneously formed islands, a procedure was developed using the known equilibrium properties of the system [8]. First, the substrate was annealed at 560° while exposed to an As_4 BEP of 10 μTorr to produce a flat surface without islands. Next, the As_4 BEP was abruptly lowered (in less than a minute) to a level which would produce a surface half covered with islands if allowed to reach equilibrium (reaching equilibrium requires 2–16 h of annealing) [8]. The sample was then annealed under these conditions for various fractions of the total time to reach equilibrium. At these various times, the substrate was then quenched to room temperature using a procedure that freezes in the surface morphology present at the higher temperatures and has been described elsewhere [13]. The samples were transferred to the STM without breaking UHV and imaged at room temperature. Each sample that was prepared with different anneal times, used the above procedure starting with a regrowth of the buffer layer. All totaled a series of samples with the same initial conditions but increasing anneal times were prepared. The high degree of reproducibility of the images indicates that this is a reliable procedure.

For every sample grown, 5–10 1 μm × 1 μm filled-state STM images were acquired using tips made from single crystal ⟨1 1 1⟩-oriented tungsten wire, a sample bias of −3.0 V, and a tunneling current of 0.05–0.1 nA. To compute the fraction of the surface covered by islands and pits, 10–20 200 nm × 200 nm regions are cropped far from terrace edges from 5–10 larger images, and then thresholded to compute an average coverage for each. The remaining fraction of the surface is the terrace, and the averages have a uniform standard deviation of ~5%.

3. Results

An STM image of the surface prepared by annealing at 560° while under a 10.0 μTorr As_4 flux shows a flat (2×4)-reconstructed surface with a low density of defects and is displayed in Fig. 1(a). This 1 μm × 1 μm STM image is shown in gray scale with each terrace separated by a monolayer high step and given a different color shade. The terraces are present due to the intentional slight miscut of the substrate. A snap shot of the surface morphology taken just 5 min after changing the As_4 flux from 10.0 to 0.03 μTorr

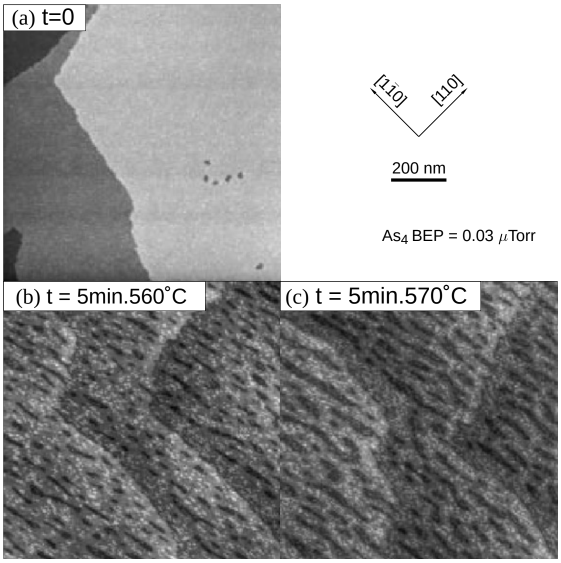

Fig. 1. Three 1 μm × 1 μm STM images shown in gray scale and acquired using a sample bias of −3 V and tunneling current of 0.5 nA. (a) Surface morphology prior to changing the As_4 BEP to 0.03 μTorr, which triggers the spontaneous island formation phenomenon. (b) and (c) Surface morphology after changing the As_4 BEP and annealing for 5 min at 560° and 570°, respectively.

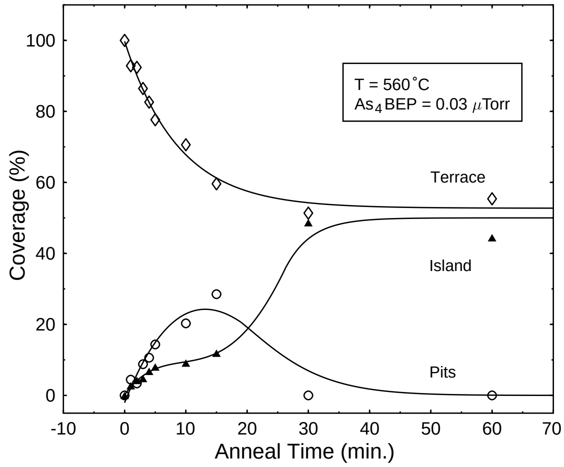

Fig. 2. Percent coverage of the total surface in terms of pits, islands, and remaining terrace for the STM data set taken at 560°. Initially, the surface is 100% terrace. Quickly, the coverage of pits and islands increases for the first 15 min. Thereafter, the coverage of pits rapidly decreases while the coverage of islands rapidly increases.

is visually displayed in Fig. 1(b). The original terraces of the GaAs(0 0 1) surface are still present and primarily run diagonally across the image. However, now each terrace is littered with one monolayer high islands and one monolayer deep pits. Notice that the pits occupy larger surface area than the islands do, but that the number of pits is less than the number of islands. To determine the coverage of pits and islands (namely, the fraction of surface area occupied by pits and islands), several 200 nm × 200 nm regions were sectioned out of the 1 μm × 1 μm images far from terrace edges and other defects in order to minimize their influence on the data analysis. Then, a histogram was produced to reveal the fraction of the image that was low, middle and high, which represents the fraction that was pits, terrace and islands, respectively. Nevertheless, the coverage of pits is larger than that of islands at this stage. The islands and pits are elongated in the [1 $\bar{1}$ 0] direction and double-height steps are never formed. This same experiment done at 570° is visually displayed in Fig. 1(c). This result is nearly identical to the 560° result. Notice, however that the pits are less numerous, much larger in size, and some even extend through the edge of the terrace forming an "inlet-" or "bay-type" structure one might find along the coastline of a land mass. Once this happens, we no longer consider this feature a pit. Also, notice that the number of islands has significantly increased while the average size of the islands is still about the same. In both cases, double-height steps are never observed. We also noticed that the surface morphology after 5 min at 570° is nearly identical to the surface morphology after 10 min at 560°.

The fraction of the surface covered with pits, islands, and the remaining terrace surface area vs. anneal time for a much larger data set are plotted in Fig. 2. An overall assessment of the coverages shows that there are three distinct categories in time. Initially, from 0 to 15 min the coverage of pits and islands increase rapidly from 0% to 20% and 10%, respectively. From 15 to 30 min the island coverage accelerates to its final equilibrium target value of 50%, while the pit coverage decreases to zero. Finally, from 30 min to over 4 h the concentration of the islands stays at 50% while the geometry of the islands continuously evolves toward its final equilibrium configuration [8].

4. Discussion

Observations of islands spontaneously forming on the GaAs(0 0 1)-(2×4) reconstructed surface have been previously reported and shown to arise from entropic factors controlling the free energy minimization process [8]. Those details are described elsewhere and will not be discussed here [8]. The dynamics of this phenomenon have not been studied until now. The first 5 min of the spontaneous island formation process tells a surprising story about the pathway to equilibrium. Mainly, that the Ga atoms which form the GaAs islands come from the middle of the terraces via pit formation. This is a surprising result. Throughout the surface science literature it is assumed that the most likely source of atoms on a terrace would be from the edge of the terrace. This is an extremely reasonable guess, because atoms at the edge of the terrace should be under-coordinated, and therefore require significantly less energy to break free when compared to an atom embedded in the middle of the terrace. However, this general policy assumes there is a coordination difference between these two atomic sites. The atomic structure model for the GaAs(0 0 1)-(2×4) reconstructed surface is locally multi-leveled or corrugated such that every unit cell on the pristine terrace is nearly identical to the local structure at a terrace edge site [13]. Given that there is a much larger number of middle terrace sites compared to edge terrace sites, it is clear why pit formation is preferred. Based on the same reason, the middle terrace sites contribute much more to the pit and island formation than the terrace edge sites do.

Once a small pit is formed, atoms continue to break away from the edge of the pit and climb out of the pit to form more islands on the terrace. This indicates that there is no difference between the energy barrier for an atom to diffuse over a step and an atom to diffuse across a flat terrace (i.e., no significant Schwoebel barrier) [14]. The lack of a Schwoebel barrier on the GaAs(0 0 1)-(2×4) reconstructed surface is simply due to the same atomic structure existing at the edge of the terrace and the middle of the terrace, i.e., diffusion across a pristine terrace is identical to diffusion across a terrace edge or step.

It is significant that the coverage of pits and islands in the beginning stages of island formation are equal. This indicates that the islands were formed by making adjacent pits. In time, however, the pits preferentially spread out in the $[1\bar{1}0]$ direction and merge into each other forming large pits. This is the direction of the top-layer arsenic dimer bond, and has been previously shown to be the fast diffusion and preferential growth direction [15]. Here, we see it is also the preferential etching or dissociation direction. Once the pits grow to the size of the terrace, they punch through the edge of the terrace forming an "inlet-" or "bay-type" structure. The geometry of the inlet structure slowly evolves from something long and narrow to no inlet at all. The islands on the other hand nucleate with a small number of atoms in the beginning. The small islands tend to be very stable or meta-stable and kinetics drives the formation of more islands rather than making the existing islands bigger (even though this is what the pits prefer to do). In addition, double height steps never form, so the islands tend to stay small to avoid step edges. This is interesting because without a Schwoebel barrier, we know individual atoms can easily flow over step edges. Since, small islands must avoid the step edge, there is a many-body requirement playing a significant role in the dynamics. This higher-order effect would normally be ignored when modeling the surface kinetics using atomistic models.

5. Conclusion

In summary, we have utilized the phenomenon of spontaneous island formation to learn about the dynamics of the technologically important GaAs(0 0 1)-(2×4) reconstructed surface. Atoms are found to easily break away from embedded positions within the middle of an otherwise pristine terrace. This is consistent with the surface reconstruction being corrugated and a lack of a Schwoebel barrier. In addition, small clusters of Ga and As atoms in the form of an island is extremely stable, and will avoid forming double-height steps. Adatoms can easily cross a step edge, however, once they attach to an island the adatom avoids being near steps, indicating that many-body effects are important. It is interesting to note that the atomic structural model for GaAs(0 0 1)-(2×4) provides significant aid in understanding the dynamics of GaAs.

Acknowledgements

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