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Activation energy for Ga diffusion on the GaAs(0 0 1)-(2 × 4) surface: an MBE-STM study

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Abstract

The pure migration of individual Ga atoms on the technologically important GaAs(0 0 1)-(2 × 4) reconstructed surface has been studied as a function of substrate temperature using a combined molecular beam epitaxy and scanning tunneling microscopy (STM) ultra-high vacuum, multi-chamber facility. We have successfully deposited $\frac{1}{10}$ of a plane of Ga atoms onto a pristine GaAs surface under a constant As₄ beam equivalent pressure of 10^{-6} Torr, at various substrate temperatures. After deposition the substrate was quenched to room temperature and transferred to the surface analysis chamber for STM imaging. A plot of the number density of islands formed as a function of deposition temperature follows an Arrhenius relationship. Assuming either a pure one-dimensional diffusion model or a pure isotropic two-dimensional diffusion model, the activation energy for diffusion is 2.3 or 1.7 eV, respectively. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Activation energy; Ga diffusion; GaAs (0 0 1)-(2 × 4) surface

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 [1]. Naturally, there is an extensive effort to develop both higher performance devices as well as novel multi-functional 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 diffusion, nucleation and growth is required.

Macroscopic measurements of gallium diffusion, such as, monitoring film growth under a shadow mask [2], have been used to estimate the Ga diffusion length. 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]. Using these results to predict the pure migration of Ga atoms can be ambiguous since the

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influence of surface defects, steps, and interactions between the adatoms themselves cannot be accounted for. The pure migration of Si adatoms on the Si(001) surface was successfully measured without these complications by depositing submonolayer coverages onto an otherwise pristine surface held at various temperatures, and then quenching to room temperature. The activation energy was calculated by comparing the number density of islands measured by scanning tunneling microscopy (STM) with random walk simulations [6]. This approach was also used successfully for diffusion studies of Fe on Fe(001) [7]. Surface diffusion studies for the III–V compound semiconductors are complicated since these are binary compounds, yet they are more critical than Si surface diffusion, because epitaxial techniques are used to make III–V devices, while Si-based devices are primarily fabricated by ion beam implantation, where surface diffusion of atoms is not an issue [8]. To address this need, we have combined into a single multi-chamber, ultra-high vacuum (UHV) facility, a state-of-the-art molecular beam epitaxy (MBE) growth chamber with precision substrate temperature monitoring [9] and an STM for surface analysis [10].

For the first time we present STM measurements of the island number density produced by depositing $\frac{1}{10}$ of a plane of Ga atoms onto a pristine GaAs(001)-(2×4) reconstructed surface held at various substrate temperatures. The atomic-scale resolution images obtained with the STM enables us to account for the effect of steps, defect sites, and the orientation of the dimer rows on the surface diffusion.

2. Experimental procedure

The experiments are carried out in an UHV system ($4\text{--}8 \times 10^{-11}$ Torr) which contains a III–V semiconductor MBE growth chamber (Riber 32P), incorporating a new, highly accurate ($\pm 2^\circ\text{C}$), optical transmission thermometry system for substrate temperature determination [9,11]. In addition, this chamber is connected to an Omicron surface analysis chamber which contains an STM for surface morphology measurements [10].

Commercially made, well oriented, *epi-ready*, GaAs(001) $\pm 0.1^\circ$, n + (Si doped $10^{18}/\text{cm}^2$) substrates are used without any chemical cleaning. The surface oxide layer is removed and a 1- μm -thick GaAs buffer layer is grown at 590°C with a Ga deposition rate of 1 ML/s as determined by RHEED oscillations. The following procedure is used repeatedly to produce a surface with $\frac{1}{10}$ of a monolayer of GaAs islands. GaAs is deposited for 15 min at 590°C using a Ga deposition rate of 0.2 ML/s and an As_4 beam equivalent pressure (BEP) of 5×10^{-6} Torr. The substrate is subsequently annealed at 600°C for 15 min under an As_4 BEP of 10^{-6} Torr, followed by an anneal at 570°C for another 15 min using an As_4 BEP of 8×10^{-7} Torr, which produces a near perfect, defect-free surface with 0.5- μm -wide terraces. Next, the power delivered to the substrate heater is set to zero which, after a short delay, causes the substrate temperature to fall at $\sim 1.5^\circ\text{C/s}$, as determined by our optical temperature measurement system (see Fig. 1). As the substrate cools, the As valve is stepped in 10^{-7} Torr increments for every 10°C drop in sample temperature to hold the GaAs surface together, yet not drive the surface to the c(4×4) surface reconstruction. After a specified time delay, the computer automatically opens the As valve to achieve a BEP of 10^{-6} Torr and then opens the Ga

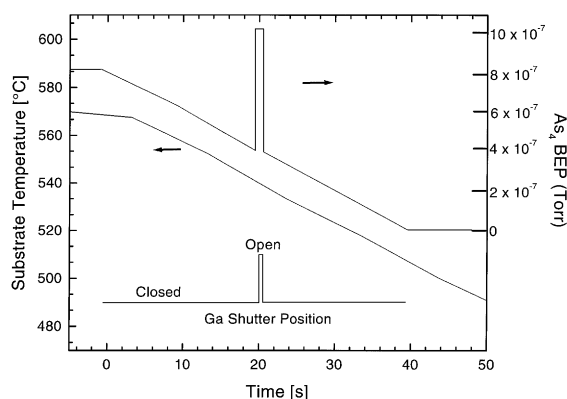


Fig. 1. Timing chart showing the substrate temperature determined using a fundamental optical transmission thermometry technique, the Ga shutter motion, and the As_4 beam equivalent pressure as a function of time for the deposition that took place after waiting 20 s.

shutter for 0.5 s which produces a total GaAs growth of 0.1 ML (see Fig. 1). Control runs that repeat every step of this algorithm except for the Ga shutter motion have been performed and reveal a near-perfect (2×4) reconstructed surface free of islands. The time delays between cutting the heater power and depositing the Ga were 5, 20, 30, 50 and 70 s, which yielded substrate temperatures of 564, 541, 522, 491, and 464°C, respectively. After the deposition was completed, the sample temperature was allowed to fall below 450°C, at which time the heater was turned back on in order to hold the substrate at 450°C for 15 min. This anneal does not affect the island number density or geometry but allows the ion pump to remove As₄ from the chamber, avoiding As₄ condensation on the sample surface [12]. The heater power was once again set to zero and the sample cooled to 200°C in about 5 min after which it was transferred to the surface analysis chamber for STM measurements of the surface morphology. Once the sample and the STM reached thermal equilibrium, multiple images (6–12) were acquired from several, random, step-free regions that were either 200 nm × 200 nm or

100 nm × 100 nm in size. The number of islands was counted for each image and an average island number density was computed for each sample.

3. Results

Characteristic STM images of the GaAs surface after the deposition of $\frac{1}{10}$ of a monolayer are shown in Fig. 2. A 1 μm × 1 μm region acquired after deposition at 464°C reveals the enormous substrate terraces (0.5–1.0 μm) achieved in our growths (see Fig. 2a). Note, in Fig. 2, each gray level represents a monolayer high step (0.28 nm). The inset images within Fig. 2a show a high-resolution image of the GaAs (2×4) surface reconstruction where individual As-dimers are resolved, revealing a highly ordered, nearly perfect crystalline surface. A 100 nm × 100 nm image showing about 70 islands covering about $\frac{1}{10}$ of the surface is shown in Fig. 2b. From a set of 6–10 high-resolution images, an average island number density was computed, then repeated for each substrate temperature. The island number density is plotted versus inverse

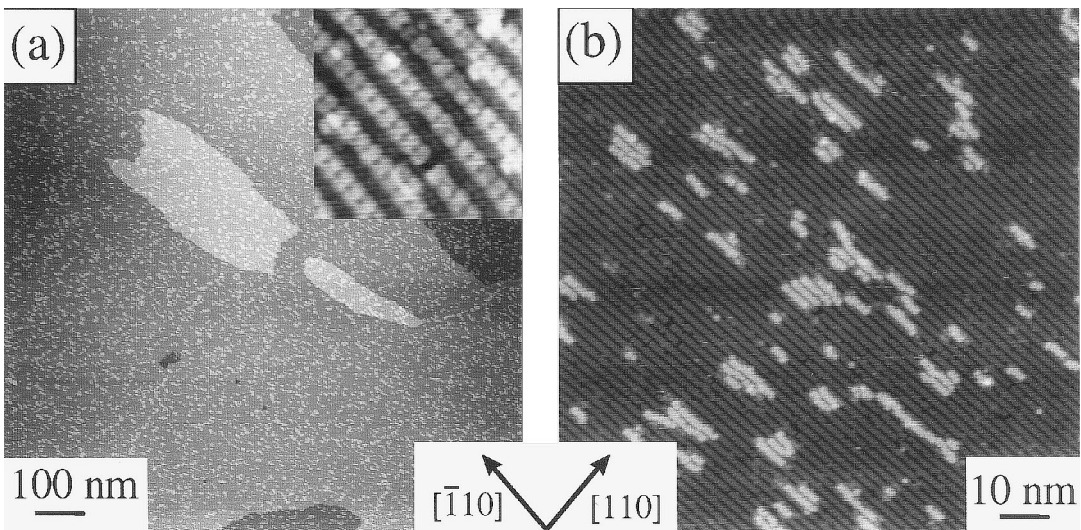


Fig. 2. Filled state STM images (~ 3.0 V, ~ 0.2 nA) of the GaAs(001)-(2×4) reconstructed surface after deposition of $\frac{1}{10}$ of a monolayer of GaAs onto a pristine surface; (a) 1 μm × 1 μm image showing the substrate terrace width is near 1 μm; the inset figure shows a high-resolution image where the individual As-dimers are resolved, showing that the surface is extremely well ordered and nearly perfect (diagonal rows along the $[\bar{1}10]$ direction are separated by 1.6 nm); (b) 100 nm × 100 nm image showing about 70 islands (0.28 nm high). Note, the islands tend to be longer along the $[\bar{1}10]$ direction than the $[110]$ direction.

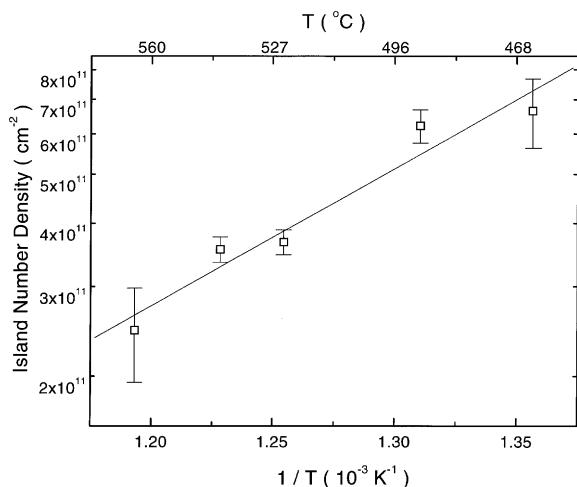


Fig. 3. Measured island number density as a function of the inverse deposition temperature. The error bars represent ± 1 standard deviation as calculated from a set of images.

temperature in Fig. 3. The error bars represent ± 1 standard deviation from the average number of islands counted.

4. Discussion

The island number density follows an Arrhenius relationship with the deposition temperature. The diffusion coefficient also follows an Arrhenius relationship with the deposition temperature, given by $D = D_0 \exp[-E_a/(k_B T)]$, where E_a is the activation energy for hopping from one atomic site to another, D_0 is the prefactor, and k_B is Boltzmann's constant. Note, for simplicity our discussion and analysis of the island number density assumes that the mobile species are individual Ga atoms and not Ga–As molecules. For both pure one-dimensional diffusion and isotropic two-dimensional diffusion, a relatively simple analytical relationship exists between the number density of islands, N , and the diffusion coefficient, D . This can be understood by realizing that the Ga atoms arrive at random locations on the surface with an arrival rate determined by the deposition rate. Furthermore, depositions at higher temperatures cause the atoms to diffuse more quickly and form a smaller number of large islands, while at lower temperatures the atoms dif-

fuse more slowly and form a larger number of small islands. The analytical relationship between the number density of islands and the diffusion coefficient [13], shows that for pure one-dimensional diffusion, $D \propto N^{-4}$, while for pure isotropic two-dimensional diffusion, $D \propto N^{-3}$. The activation energies are computed using the slope of the line in Fig. 3, the Arrhenius relationship for the diffusion coefficient, and the analytical relationship between the number density of islands and the diffusion coefficient. For the pure one-dimensional diffusion the activation energy is $E_a = 2.3$ eV, and for the pure, isotropic two-dimensional diffusion the activation energy is $E_a = 1.7$ eV. Most likely, the actual surface diffusion is anisotropic two-dimensional rather than purely one or two-dimensional. This is consistent with recent first principles calculations by Kley et al., which determined that diffusion is anisotropic since the activation energy barrier for hopping is 1.5 eV along the $[1\ 1\ 0]$, while only 1.2 eV along the $[\bar{1}\ 1\ 0]$ direction [14]. These activation energies are similar to our experimental activation energies, however, random walk computer simulations are necessary to extract a true experimental activation energy [6], and are planned for this study [15].

The observation of the elongated islands in the $[\bar{1}\ 1\ 0]$ direction suggests that the sticking probabilities to the island edges are different. This is in agreement with a recent article by Itoh et al., which showed that islands formed on the GaAs(001)-(2×4) surface favor formation along the $[\bar{1}\ 1\ 0]$ direction due to a repulsive interaction which inhibits the growth across the dimer rows [16]. These observations indicate that not only is the diffusion anisotropic, but also the relative sticking probabilities are different.

5. Conclusions

We have devised a growth algorithm for the deposition of $\frac{1}{10}$ of a plane of Ga onto a pristine GaAs(001)-(2×4) reconstructed surface with a constant As_4 BEP, as a function of substrate temperature. Furthermore, we have used in situ STM to image the GaAs islands that are formed and computed an average island number density.

The average island number density is shown to have an Arrhenius relationship with the deposition temperature. Using random walk analytical equations we find an activation energy of 2.3 eV if the diffusion is purely one-dimensional, while pure, isotropic two-dimensional diffusion gives an activation energy of 1.7 eV. Both of these correspond to the pure migration of single Ga atoms unaffected by defects. Based on the measured island number density and geometry, we believe that both the diffusion and sticking are anisotropic, favoring the $[1\ 1\ 0]$ direction.

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