Role of As_4 in Ga diffusion on the GaAs(001)-(2×4) surface: A molecular beam epitaxy-scanning tunneling microscopy study

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The role of As_4 molecules in Ga diffusion on the GaAs(001)-(2×4) reconstructed surface has been studied using a combined molecular beam epitaxy and scanning tunneling microscopy multichamber facility. We deposited 10% of a plane of Ga atoms onto an otherwise pristine surface, while exposed to two separate As_4 beam equivalent pressures of 10^{-5} and 10^{-6} Torr. The higher As_4 flux resulted in the production of fewer and larger islands, indicating that increasing the As_4 flux increases the total interrogation area available to the Ga atoms before forming islands. © *1999 American Vacuum Society.* [S0734-211X(99)05904-1]

I. INTRODUCTION

The fabrication of III–V semiconductor structures is a major component of the rapidly growing wireless communications and optoelectronics industry.[1] Unlike silicon based devices, which are mainly fabricated by ion implantation,[2] III–V semiconductor structures must be fabricated by depositing one plane of atoms on top of another until the entire structure is formed. Consequently, III–V structure fabrication occurs solely at a surface. Naturally, a deeper understanding of the fundamental processes involved in growth, such as surface diffusion and island nucleation, may result in higher performance structures.[3] The most utilized surface for devices, and hence the most important surface for developing this understanding, is the GaAs(001)-(2×4) reconstructed surface.

To date, Ga surface diffusion on the GaAs(001) surface has been extensively investigated using reflection high-energy electron diffraction (RHEED).[4,5] These studies have played an important role in making predictions for the diffusion coefficient and the activation energy for the migration of Ga atoms. However, associating these values with the pure migration of Ga atoms can be ambiguous since the influence of surface defects, steps, and interactions between other adatoms cannot be taken into account. The pure migration of individual adatoms on elemental semiconductor surfaces has been successfully measured without these complications by depositing submonolayer coverages onto otherwise pristine surfaces and using scanning tunneling microscopy (STM) to quantify the outcome.[6] For binary compound semiconductors there is added complexity due to the unknown influence of the group V species, however we previously reported how to overcome these complications and successfully measured the Ga diffusion under normal growth conditions using STM.[7,8] In molecular beam epitaxy (MBE) growth of GaAs, the flux of the Ga determines the growth rate, while the flux of the arsenic is self-limiting. However, it is not known exactly how the As_4 flux effects the surface diffusion of the Ga atoms. In this article, we investigate the role of the arsenic molecules on the migration of the Ga adatoms.

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II. EXPERIMENTAL PROCEDURE

Experiments were carried out in an ultrahigh vacuum (UHV) multichamber facility ($5-8\times10^{-11}$ Torr throughout) which contains a customized, commercial MBE (Riber 32P) chamber and a surface analysis chamber with a commercial STM (Omicron).[9] The MBE chamber was modified to include a highly accurate and fast optical substrate temperature measurement system (±2 °C from 0 to 700 °C and updated at 1 Hz) which utilizes the temperature dependence of the fundamental band gap.[10] Commercially available, ‘‘epiready,’’ $n+$ (Si doped $10^{18}/cm^3$) GaAs(001)±0.1° substrates were loaded into the MBE system without any chemical cleaning. Once the surface oxide layer was removed, a 1.5 μm thick GaAs buffer layer was grown at ~1 μm/h as determined by RHEED.

The surface of the buffer layer was found to have several monolayers of roughness and a multitude of other atomic-scale defects. An algorithm was developed to remove this roughness and produce enormous terraces (~1 μm wide) essentially free of defects while cooling the sample quickly to room temperature. The algorithm consisted of first holding the substrate temperature at 600 °C under an As_4 beam equivalent pressure (BEP) of 10^{-6} Torr for 15 min to eliminate step bunching and produce large terraces. The substrate is then annealed at 570 °C under an As_4 flux of 8×10^{-7} Torr for another 15 min to eliminate adatom and vacancy islands on the terraces. Next, the sample temperature was set to drop (heater current set to zero) to 450 °C (~1.5 °C/s) while decrementing the As_4 flux in 10^{-7} Torr steps for every 10 °C drop in sample temperature (i.e., the As valve is closed once the sample temperature falls below 500 °C). Once the substrate temperature reaches 450 °C the power to the substrate heater was restored to maintain a constant temperature for 15 min. During this period the As_4 flux still inside the growth chamber was pumped out to minimize condensation onto the sample's surface.[11] Note, during the cool down from 570 to 500 °C, the As_4 flux plays a pivotal role in producing a high-quality surface. This is because above 500 °C arsenic sublimates from the GaAs surface and an impinging As_4 flux is required to replenish the lost arsenic. However, too much arsenic flux will drive the surface into supersaturation and

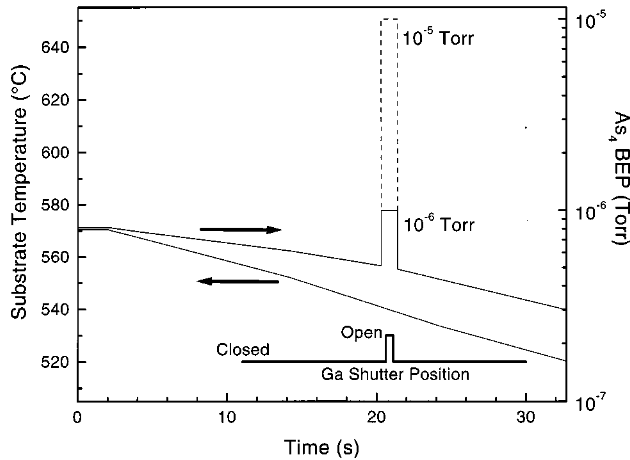

FIG. 1. Timing chart showing substrate temperature, Ga shutter position, and the As_4 BEP for a deposition scenario near 540 °C. Once the power to the substrate heater is turned off, the substrate temperature decreases at a rate of ~1.5 °C/s. Once the substrate reaches the desired temperature, the As_4 flux is increased to either 10^{-6} (solid line) or 10^{-5} (dashed line) Torr and the Ga shutter is opened for 0.5 s, resulting in a growth of 0.1 ML of GaAs.

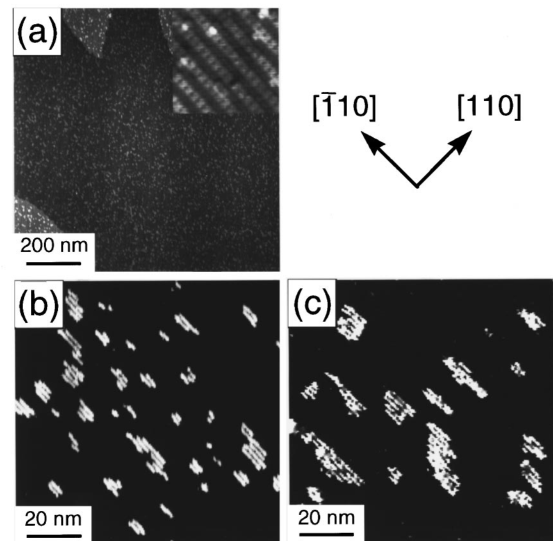

FIG. 2. Filled state STM images (~3.0 V, ~0.2 nA) of the GaAs(001)-(2×4) surface after deposition of 10% of a monolayer of GaAs onto a pristine surface. The deposition temperature is 540 °C for all the images: (a) 1 μm by 1 μm image, inset image shows an atomically well-ordered substrate; (b) 100 nm by 100 nm image of surface prepared with an As_4 BEP of 10^{-6} Torr, yielding 41 islands; (c) same conditions as in (b) but with an As_4 BEP of 10^{-5} Torr yielding 19 islands.

the (2×4) surface reconstruction will be driven into the more arsenic rich $c(4\times4)$ surface reconstruction.

The above algorithm allows for an island-free surface with larger terraces to be produced. This algorithm was slightly modified to allow us to deposit 10% of a plane of Ga atoms, while simultaneously exposing the surface to two different As_4 BEPs. To illustrate how the growth of the submonolayer coverages was completed, a timing chart showing the substrate temperature, the Ga shutter position, and the As_4 BEP is shown in Fig. 1. Just prior to deposition, as stated above, the substrate is annealed at 570 °C while exposed to an As_4 BEP of 8×10^{-7} Torr. Next, the heater power to the sample is set to zero and the sample begins to cool at ~1.5 °C/s. Once the sample temperature has reached the desired value the As_4 BEP is increased to either 10^{-6} or 10^{-5} Torr, and the Ga shutter is opened for 0.5 s to deposit 10% of a plane of GaAs (i.e., the growth rate is set to 20% of a plane per second). Since all the Ga metal is deposited in 0.5 s, and the sample temperature is dropping at ~1.5 °C/s we can accurately determine the temperature. The As_4 BEP of 10^{-6} Torr and the Ga deposition rate of 20% of a plane per second yields an As_4/Ga flux ratio of ~15, thereby recreating typical GaAs growth conditions which use a ratio between 10 and 20. When the As_4 BEP is 10^{-5} Torr, the As_4/Ga flux ratio is ~150, which allows us to study the Ga diffusion under extremely high arsenic concentration conditions. Note, we could not study the Ga diffusion at lower arsenic fluxes, because, as explained earlier, the surface begins to degrade if the arsenic pressure is too low.

The Ga deposition on the (2×4) surface reconstruction was studied over as large a substrate temperature range as possible (570–460 °C) with two different arsenic fluxes. After deposition, the sample was transferred to the STM chamber through an all UHV transfer module. Once the sample and the STM reached thermal equilibrium with the STM imaging stage (~15 min), multiple images (6–12) were acquired from several, random, step-free regions that were either 200 nm by 200 nm or 100 nm by 100 nm in size to get an average island number density for each run.

III. RESULTS AND DISCUSSION

Typical filled state STM images of the GaAs surface after the deposition of 10% of a monolayer are shown in Fig. 2. The routine observation of 1-μm-wide terraces allowed for

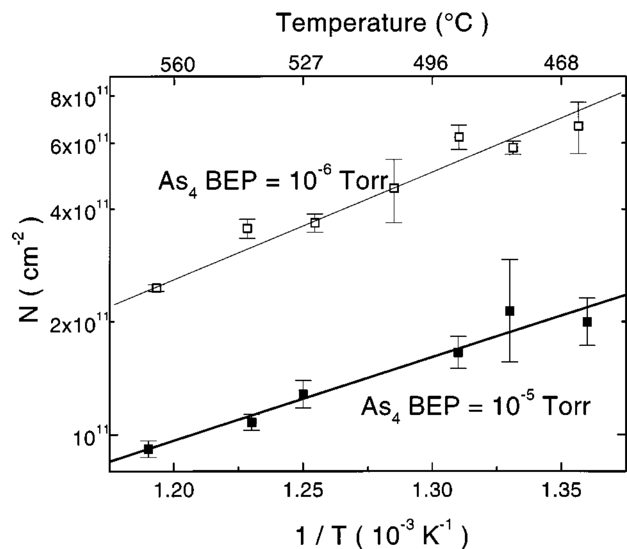

FIG. 3. Complete data set of island number density vs substrate temperature for two different As_4 BEP values. The error bars represent ±1 standard deviation as calculated from a set of images from each deposition temperature.

these and several other STM images to be acquired far from surface steps and shown in Fig. 2(a). The surfaces were well ordered and essentially free of defects down to the atomic scale as shown in the inset image within Fig. 2(a). Typical STM images for 10% of a plane of Ga atoms deposited on a surface at 540 °C using an As_4 BEP of 10^{-6} and 10^{-5} Torr are shown in Figs. 2(b) and 2(c), respectively. One striking feature is that there are less islands and the islands are larger in size when the As_4 BEP is higher. The increase in the island size is because the same amount of material is deposited for both As_4 BEPs, however a fewer number of islands were created.

The tendency of producing larger and hence fewer islands when the Ga atoms are deposited in a higher As_4 BEP environment persisted across the entire temperature range studied. For both As_4 BEPs, the average island number density is plotted on a logarithmic scale versus inverse temperature and shown in Fig. 3. These data points represent the average island number densities counted from all STM images acquired. One surprising feature is that the slopes for both 10^{-6} and 10^{-5} Torr As_4 BEPs are almost identical. This indicates that the activation energy barrier height for Ga diffusion is the same. However, the intercepts for these data sets are significantly different. The intercept change reflects the change in island number density between the two As_4 BEPs. Fewer islands under higher As_4 pressures indicates that the Ga atoms are able to interrogate a larger area of the surface than when exposed to lower As_4 pressures.

First-principles total-energy calculations of the activation energy for the pure migration of Ga atoms in an arsenic-free environment show that the diffusion is highly anisotropic.[12] The barrier height was found to be 1.5 eV along the $[110]$ direction, while only 1.2 eV along the $[1\bar{1}0]$ direction. This difference results in Ga atoms being 100 times more likely to diffuse along the $[1\bar{1}0]$ direction than along the $[110]$ direction at normal growth temperatures. Consequently, the Ga atoms in an arsenic-free environment are diffusing only in one dimension or along a line on the crystal's surface. Therefore, the Ga atoms will interrogate much fewer surface sites in a given unit time, than if they were able to diffuse freely in all directions.

We believe the low arsenic pressure data represent essentially the pure migration of Ga atoms on the surface with minimal influence due to arsenic. Under these conditions the Ga diffuses only in one dimension and hence can only interrogate the crystal surface along a line. When the arsenic pressure is high, the Ga atom diffusion is modified in such a way that the Ga atom can interrogate a larger area of the crystal surface but still experience the same energy barrier height (see Fig. 3). Thus, we believe the effect of the increase in the As_4 flux is to lower the activation energy barrier for hopping in the $[110]$ direction closer to the barrier height in the $[1\bar{1}0]$ direction (1.2 eV). This results in the Ga atoms diffusing more isotropic in two dimensions, which allows them to interrogate a much greater area of the surface, while still yielding the same activation energy for hopping.

IV. CONCLUSION

The effect of As_4 flux on the diffusion of Ga atoms on the GaAs(001)-(2×4) reconstructed surface has been studied. It has been determined that the higher arsenic pressure leads to the production of larger and fewer islands when compared to those obtained at the lower As_4 BEP. These two observations suggest that the additional arsenic flux increases the mobility of the Ga atoms by possibly opening previously prohibited diffusion channels.

ACKNOWLEDGMENTS

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