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Hydrogen as the Cause of Step Bunching Formed on Vicinal GaAs(001)

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In order to elucidate the cause of step bunching formed on vicinal GaAs(001) annealed in AsH_3/H_2 ambient, we investigated the surface of vicinal GaAs(001) annealed in H_2, AsH_3/N_2, AsH_3/H_2, and N_2 by scanning tunneling microscope. Since step bunches always formed on surfaces annealed with hydrogen but not on surfaces annealed in ambients without hydrogen, we conclude that hydrogen is crucial in the formation of step bunching.

KEYWORDS: scanning tunneling microscopy; diffusion and migration; growth; surface diffusion; surface structure, gallium arsenide, stepped single-crystal surface

1. Introduction

Step bunches on vicinal GaAs(001), the sizes of which are on the scale of μm, were observed on layers grown by liquid phase epitaxy.[1,2] Recently, Fukui and Saito reported the formation of another type of step bunches on layers grown by metal-organic chemical vapor deposition (MOCVD).[3] These step bunches are small, with size on the scale of nm. Therefore, they have the potential to serve as templates for the fabrication of nanostructures.[4] In order to utilize this step bunching, the characteristics, dynamics, and formation mechanism of step bunching must be elucidated. Only with this understanding, will it become possible to artificially control the size, shape, and morphology of the step bunches at their full potential. However, no general consensus concerning the characteristics of step bunching has been reached. Even the formation mechanism remains an open question.[5–7] This is because epitaxial growth is a very complicated process in which many factors influence the dynamics.

Step bunches similar to those observed on layers grown by MOCVD form upon annealing vicinal GaAs(001) in AsH_3/H_2 ambient.[8–10] The characteristics of these two types of step bunches are very similar, and they are likely to form due to the same cause. The dynamics of annealing is much simple than that of epitaxial growth, thus step bunching caused by annealing in AsH_3/H_2 ambient will serve as a foundation to understand the nature of the step bunches which form in MOCVD ambients. Since step bunching always occurred when vicinal GaAs(001) surfaces were annealed in AsH_3/H_2 ambient for a very wide range of annealing conditions, while it usually did not occur on vicinal GaAs(001) surfaces annealed in ultra high vacuum (UHV),[11,12] it was proposed that AsH_3/H_2 is the direct cause of this step bunching.[10]

In this letter, we investigate the cause of step bunching by observing the surface of vicinal GaAs(001) annealed in H_2, AsH_3/N_2, AsH_3/H_2 and N_2 using a scanning tunneling microscope (STM). Under the annealing conditions employed in this research, step bunches always formed on vicinal GaAs(001) annealed in an ambient which includes hydrogen but never on substrates annealed in ambients which do not include hydrogen, which strongly suggests that hydrogen is crucial to the formation of step bunching.

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2. Experimental

The annealing process is very similar to that of MOCVD growth; the only difference is that no III-species is exposed, thus there is no crystal growth. Before annealing, the sample was cleaned by H_2SO_4, followed by chemical etching in an $H_2SO_4 : H_2O_2 : H_2O = 4 : 1 : 1$ solution. Next, the substrate was placed on a GaAs-coated carbon susceptor (MOCVD chamber) and annealed by radiation field heating. The rates of increase and decrease of temperature were 50°C and 100°C per min, respectively. Substrates were Si-doped with a carrier concentration of 4×10^{17} cm^{-3}. Dopants are shown to have no influence on the formation of step bunches.[13] The tunneling current and voltage were in the range of 0.9 nA to 3 nA and -1.8 V to -3.0 V, respectively. STM images obtained with tunneling voltage and current in this range were very similar.

First, we annealed vicinal GaAs(100) in H_2 ambient. Determining the annealing temperature involves a delicate tradeoff. If the annealing temperature is too high, As will desorb from the surface resulting in surface roughening and Ga droplet formation. On the other hand, if the annealing temperature is too low, kinetic processes such as surface diffusion will freeze out, and the time required for step bunching to occur will become too long to measure by ordinal experiments. Another important factor which must be considered is the presence of the oxidized layer. Ellipsometry measurement suggests that the surface is covered with oxidized layers of a thickness around -20 Å. In order to achieve a clean surface, we have to anneal the substrate and remove this oxidized compound. This requires an annealing temperature above 580°C in UHV ambient. However, when hydrogen is exposed to the surface, it etches the oxidized layer, and it is reported that a clean surface is obtainable at far lower annealing temperatures compared to that of UHV.[14,15] Kisker *et al*. have shown that an annealing temperature of 500°C in hydrogen ambient is sufficient to remove the oxidized layer and to achieve a clean surface.[14] Taking into account these effects, the annealing temperature was determined to be in the ranged of 500°C to 650°C with an annealing time of 10 to 20 min. The flow rates of H_2/N_2 and AsH_3 were 4000 sccm and 40 sccm, respectively. The total pressure was 1.3×10^4 Pa, therefore the partial pressures of H_2/N_2 and AsH_3 were 1.3×10^4 Pa, and 1.3×10^2 Pa, respectively. N_2 was produced by evaporating liquid nitrogen and passing the evaporated gas through a nitrogen purifier, which produces the purest nitrogen gas

available. The concentrations of impurities are estimated to be lower than 1.0 ppm for H_2O, 0.05 ppm for O_2, and 0.1 ppm for CO_2.

3. Results and Discussion

Figures 1 and 2 show sets of typical STM images of the surfaces of vicinal GaAs(001)-[100]2° annealed in H_2 and N_2, respectively, at 550°C for 20 min ((a),(b)) and 650°C for 10 min ((c),(d)). Surfaces exposed to N_2 were taken for comparsion. Many stripes running against the miscut direction are observed in Fig. 1. The average distance between these stripes is greater than ∼20 nm, which is greater than 8 nm; the step-step distance calculated from the net misorientation angle; thus the observed stripes represent step bunches. The facet edges of these step bunches are wavy and the surface is not completely smooth. On the other hand, no step bunches form on surfaces annealed in N_2, the surfaces remain rough and messy, similar to the surface just after chemical etching, as shown in Fig. 3(d).

STM images of the surface annealed in H_2 ambient at 650°C were similar to those annealed at 550°C. There was no evidence of surface roughening due to As desorption. In contrast, the roughness of the surface increased on the surface annealed in N_2 at 650°C compared to that annealed at 550°C. Small grains and pits observed on surfaces annealed at 550°C evolved in size and the number of exposed layers has increased.

Subsequently, with the intention of elucidating the role of AsH_3 in the formation process of step bunching, STM observations were carried out on vicinal GaAs(001)-[100]2° surfaces annealed in AsH_3 and N_2 ambient. As shown above, N_2 is unrelated to the occurrence of step bunching. It is supplied as a carrier gas to dilute the AsH_3 gas. Figure 3 shows STM images of vicinal GaAs(001)-[100]2° surfaces annealed at 650°C (a), and 700°C (b) for 10 minutes in N_2 and AsH_3. Step bunches have formed which are exactly the same in size and shape to those observed on surfaces annealed in AsH_3 and H_2 under the same annealing conditions, as displayed in Fig. 3(c).

Experimental results show that step bunches form on vicinal GaAs(001) annealed in H_2, AsH_3/H_2, and AsH_3/N_2 but not on surfaces annealed in N_2. Step bunching always occurred when hydrogen was present on the surface. Based on these results, we propose that the presence of hydrogen is the direct cause of step bunches. In order to describe the formation mechanism of step bunching where hydrogen is treated as the cause, we follow the model proposed in ref. 10. We assume that hydrogen produced by the dissociation of either AsH_3 or H_2 attaches to Ga atoms that terminate the step edges and influence the kinetics of step edge Ga atoms in the manner described in detail in ref. 10 (replace *AsHx* with hydrogen). Step bunches form when hydrogen at-

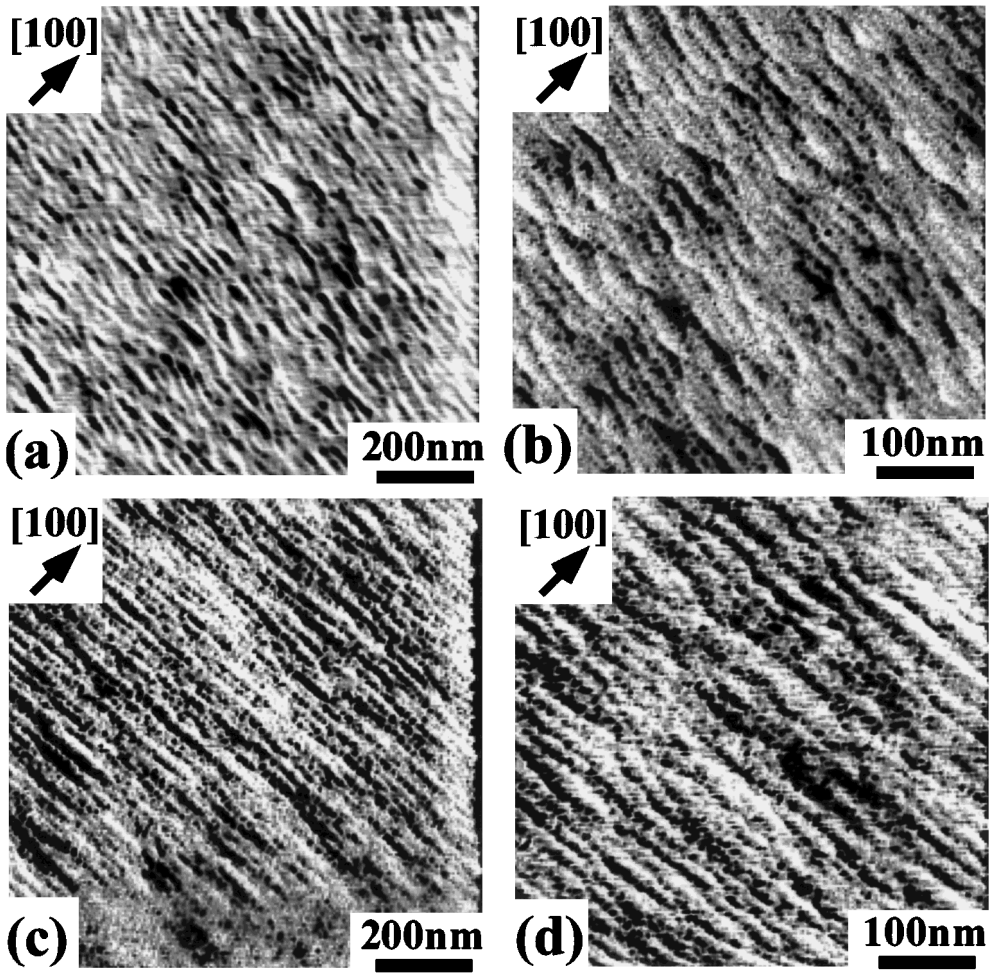

Fig. 1. STM images of the surface of vicinal GaAs(001)-[100]2° annealed in H_2 ambient for 550°C for 20 min, (a) and (b), and 650°C for 10 min, (c) and (d). The scale is 1000 × 1000 nm for (a) and (c), 500 × 500 nm for (b) and (d).

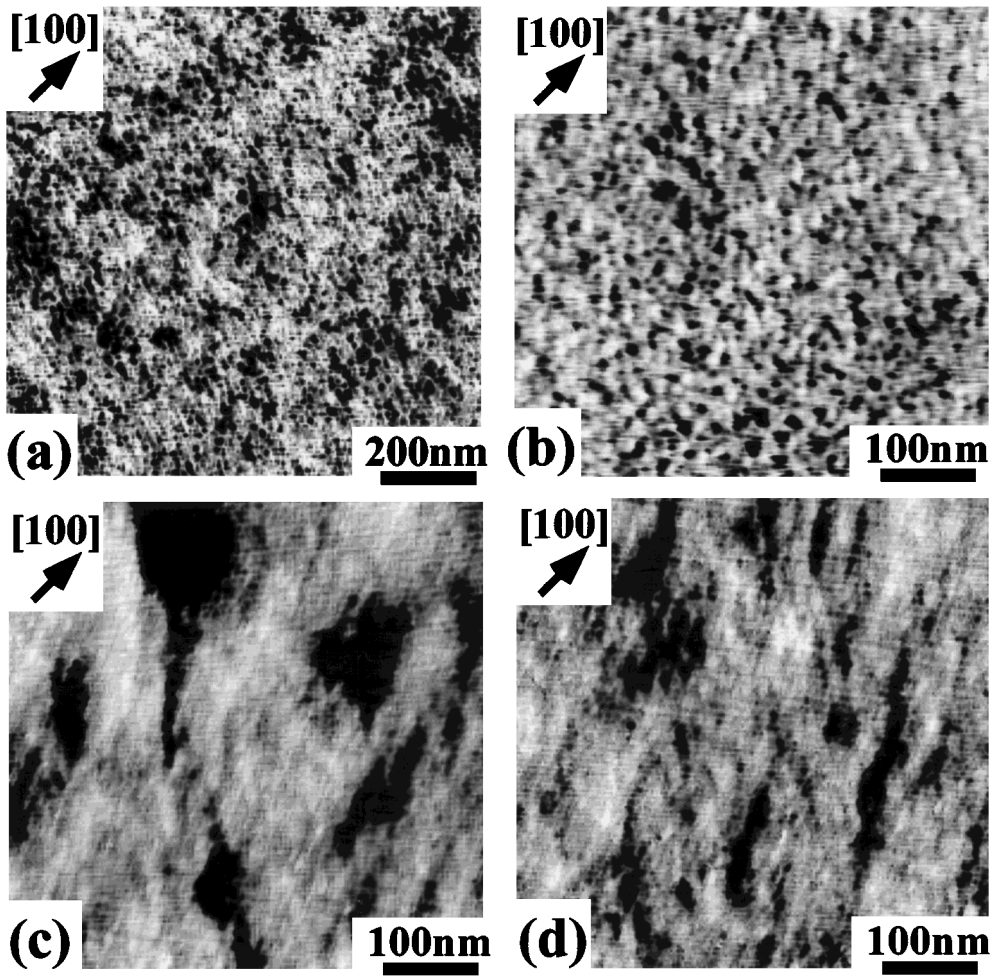

Fig. 2. STM images of the surface of vicinal GaAs(001)-[100]2° annealed in N_2 ambient for 550°C for 10 min, (a) and (b), and 550°C for 20 min, (c) and (d). The scale is 1000 × 1000 nm for (a) and (c), 500 × 500 nm for (b) and (d).

tached to step edges reduces the effective Schwoebel's barrier of attachment (detachment) of the Ga atoms to (from) step edges. Clear evidence that hydrogen does attach to step edges and influences step edge kinetics was found by Asahi *et al*, who demonstrated hydrogen-assisted step-flow growth during migration-enhanced epitaxy and molecular-beam epitaxy.[16] When hydrogen attached to step edges reduces the effective Schwoebel's barrier and creates a condition in which step bunching occurs, it is conjectured that Ga atoms diffusing on the terrace are more easily incorporated into the step edges,[10] providing a situation in which step-flow growth is more likely to take place. This result is in consistent with the observation of enhanced step-flow growth induced by hydrogen.

There are several possible explanations for the small and rough step bunches observed on vicinal GaAs(001) annealed in H_2 compared to the large step bunches observed on surfaces annealed with AsH_3 under the same annealing conditions. The first possibility is that H_2 does not react or dissociate efficiently on the surface to produce enough hydrogen atoms to cover the step edges and to cause step bunching. Whether a step bunch or a regular monostep array forms depends on the degree of the coverage of hydrogen on step edges; small coverage of hydrogen will result in small step bunches.[10] In addition, the surface reconstruction must be considered. Usually, a GaAs(001) surface annealed in AsH_3 and H_2 ambient reconstructs to the extra-As rich c(4 × 4) phase. On the other hand, surfaces annealed in H_2 ambient are reported to reconstruct to a Ga-rich c(8 × 4) or a 4 × 1 phase.[14,15] Different surface reconstructions have different atomic configurations around step edges and thus different step edge kinetics which means different step bunches.

It is well known that surfaces of vicinal GaAs(001) substrates show regular monostep arrays when grown by molecular-beam epitaxy or annealed in UHV[11,12] (no hydrogen in both cases). This suggests that there exists a repulsive interaction among steps. Practically, this is natural, as there usually exists elastic-[17] and entropic-repulsive interactions[18] among steps. Our results show that it is possible to overcome this repulsive interaction and induce a net attractive interaction among steps by exposing hydrogen, a method which may lead to a new way to artificially control step motion.

4. Conclusion

We showed that step bunching forms on vicinal GaAs(001) not only annealed in AsH_3/H_2 ambient but also annealed in H_2 and AsH_3/N_2 ambient but not on surfaces annealed in N_2 ambient. These experimental results strongly suggest that hydrogen is the direct cause of step bunching.

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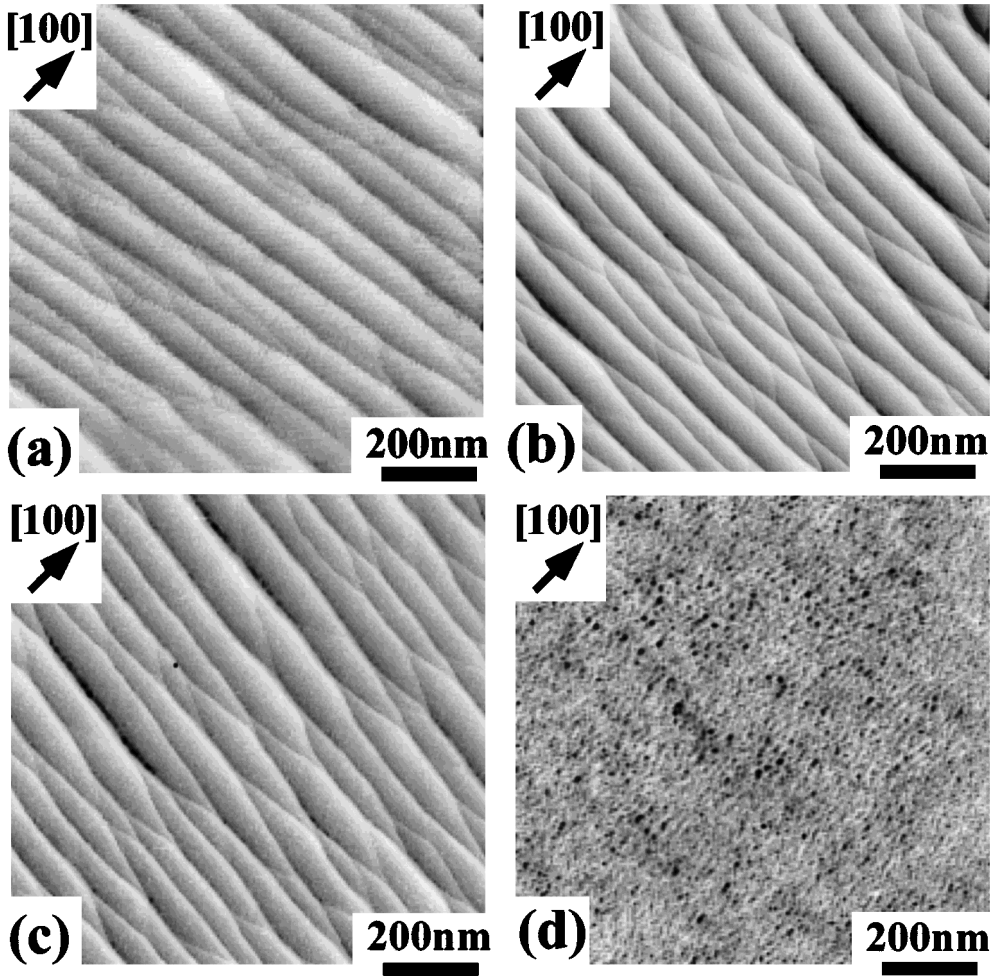

Fig. 3. STM images of the surface of vicinal GaAs(001)-[100]2° annealed in AsH_3 and N_2 ambient for 650°C (a) and 700°C (b) for 10 min and surface annealed in AsH_3 and H_2 at 700°C for 10 min (c) and just after chemical etching (no annealing) (d). Scale of all images is 1000×1000 nm.

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