How annealing conditions influence the fluctuation of step edges of step bunching on vicinal GaAs(100) formed by annealing in AsH_3 and H_2 ambient

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We report how annealing conditions influence the degree of fluctuation of step edges of step bunching formed by annealing a vicinal GaAs(001) surface in AsH_3 and H_2 and ambient. At 700 °C, when the partial pressure is high, B steps are straighter than A steps as reported before, however, as the AsH_3 partial pressure is decreased, A steps becomes straighter, finally, than the B steps at a partial pressure of 1×10^{-2} Torr. This reversal of the type of straight step edges can be explained by considering the (2×4)–$c(4\times4)$ phase transition. We will also apply the electron counting model established by Pashley in order to explain the experimental results, and by discussing its usefulness and limitations, finally conclude that we cannot determine the stability of steps only by this model. © *1997 American Vacuum Society.* [S0734-2101(97)60203-1]

I. INTRODUCTION

No step is free from fluctuations. A step's fluctuations play a critical role during crystal growth, its characteristics ultimately determine the equilibrium shape of crystals, and its regulation is indispensable in using steps as a template to fabricate quantum wires. In this sense, it is very important to clarify how step edges fluctuate with experimental conditions and understand what factor determine the degree. The characteristics of steps of GaAs are not clearly clarified. This is partly because the degree of fluctuation, characteristics, and morphology of steps are influenced by the reconstruction of the surface, which depends on the surface As stoichiometry. This means that the characteristics of steps of GaAs vary with the preparation procedure of surfaces in a complicated fashion.

One eminent phenomenon concerning steps is step bunching. Step bunching is a phenomenon in which the surface breaks up into regions with high step densities and regions with little or no steps. On vicinal GaAs(001), step bunching was first observed on layers grown by metal–organic chemical-vapor deposition (MOCVD).[1–4] In a previous article,[5] we have shown that MOCVD epitaxial growth is not indispensable in inducing step bunching; a similar step bunching to those observed on epitaxial grown layers can be formed by annealing vicinal GaAs(001) in AsH_3/H_2 ambient. Previous studies[3,5] show that this annealing-induced step bunching does not grow indefinitely with annealing time but, after it evolves into a particular size, its development stops, and the surface morphology remains unchanged. The surface has reached a *stationary state* with its ambient.[5,6]

In this article, we report that AsH_3 partial pressure ($P\mathrm{AsH_3}$) and the miscut directions of substrates influence the degree of fluctuation of the step edges of the step bunching in its stationary state. The reason we stick to the stationary state is that we believe it serves as the most simple sample to elucidate the characteristics of this step bunching. We will show that under high AsH_3 partial pressure, B steps are straighter than A steps as reported before, while as the AsH_3 partial pressure is decreased, A steps become straighter, and, finally, straighter than the B steps. This is a report to show that it is possible to produce a surface with straight A steps in the ambient of MOCVD. Our result shows that one can produce a surface with straight steps both on A and B vicinal surfaces by choosing annealing conditions. However, when one considers the density of branches (additional step bunchings that do not run in the miscut direction) on the surface, the situation is totally different for high and low AsH_3 partial pressure regions. In the low AsH_3 partial pressure region, many branches are observed on both A and B substrates. On the other hand, in the high AsH_3 partial pressure region, many branches are observed on the A substrate, though there were almost no branches observed on the B substrates. Indeed, annealing at high temperature and high AsH_3 partial pressure seems to provide a surface with the lowest density of branches and the straightest step edge.

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II. EXPERIMENT

We used vicinal substrates miscut toward [110]A, and [110]B by 2.0°. To impart the necessary conductivity to carry out scanning tunneling microscope (STM) observations, Si-doped substrates with a carrier concentration of 4×10^{17} cm^{-3} were used. The annealing process is quite similar to that of MOCVD growth, in fact, it is carried out in the same reactor used for MOCVD growth. The only difference between the annealing process and MOCVD growth is that the surface is not exposed to III species in the former, therefore, no crystal growth takes place. Before annealing, first the sample was cleaned by H_2SO_4 dipping, followed by chemical etching in a H_2SO_4, H_2O_2, H_2O; 4:1:1, solution. Approximately 2 μm of the surface layers were removed by this etching process to obtain a surface free from contamination. After chemical etching, the substrate was introduced into the MOCVD reactor system, and was placed on a GaAs-coated carbon susceptor and annealed by rf heating. The temperature was increased at a rate of approximately 50 °C/min to the annealing temperature and kept constant. In this study, we fixed the annealing temperature at 700 °C. After the sample was annealed, the temperature was decreased at the rate of 100 °C/min to room temperature. During cooling down of the sample, it was exposed to AsH_3 and hydrogen to avoid surface roughening due to As desorption. After the sample was quenched to room temperature, it was placed in a nitrogen-purged transfer box and the STM measurement was done as quickly as possible.

Previous studies showed that increasing and decreasing the substrate to 700 °C is sufficient for the step bunching to develop into the stationary stage, and the duration of annealing up to 40 min does not influence the stationary stage.[5] To confirm that we are certainly observing the stationary surface and not an intermediate stage, we prepared two substrates, annealed for 5 s and 20 min at 700 °C, compared the morphologies of these surfaces for every experimental condition, and verified that the surface has reached the stationary stage by checking that there was no major difference between them.

III. RESULTS

Figure 1 shows a set of STM images showing the stationary surface morphology of GaAs(001)2°-[110]A and -[110]B annealed at 700 °C with P_{AsH_3} ranging from 1×10^{-2} to 1 Torr. These STM images clearly show that P_{AsH_3} and the substrate miscut direction do influence the stationary surface morphology, and various step bunchings differing in size and shape can be observed. Strips observed on these images running against the miscut direction represent facets composed from several monosteps up to 15.[5] No, or little steps, exist between these strips, and they are (001) terraces.[5] It should be noted that a regular monostep array was not observed, and always step bunching formed for our experimental conditions.[7] The main features of these STM images were interpreted and analyzed from three points; degree of step-edge fluctuation, existence of branches, and size of step bunching. Here, in this article, we will focus our attention on the degree of the step-edge fluctuation, other aspects will be discussed elsewhere.[7,8]

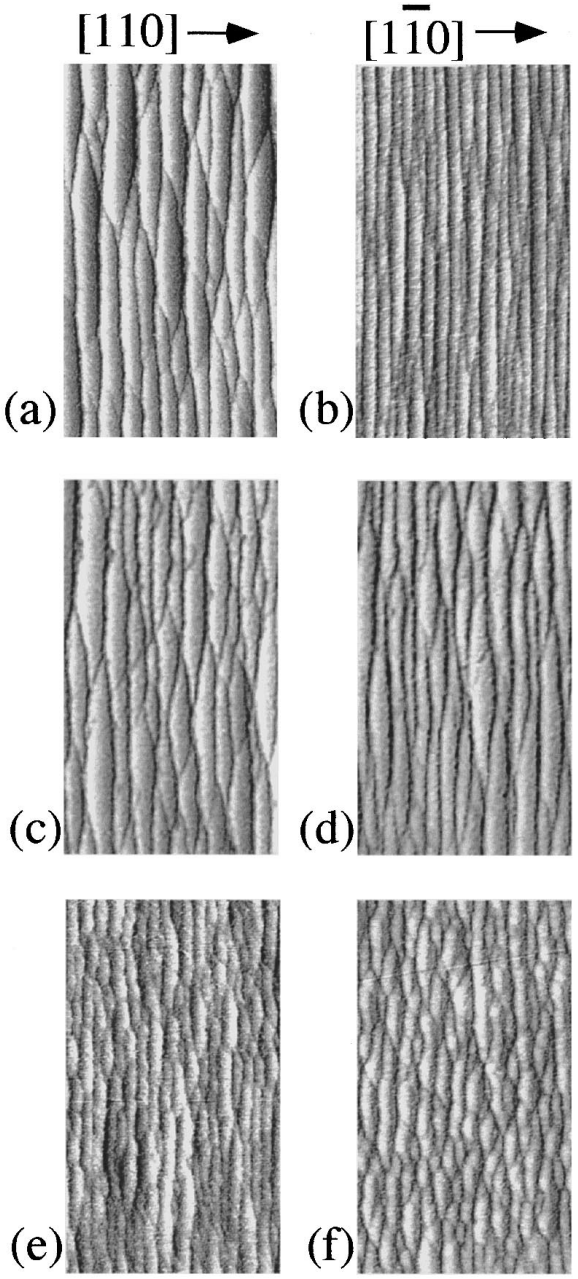

FIG. 1. STM images showing the surface morphology of stationary step bunching on GaAs(001)2°-[110]A and -[110]B substrates annealed at 700 °C with different P_{AsH_3}: (a), (c), and (e) are STM images of an A substrate, and (b), (d), and (f) of a B substrate. The P_{AsH_3} is 1 Torr for (a) and (b), 1×10^{-1} Torr for (c) and (d), and 1×10^{-2} Torr for (e) and (f). Scale is 500×875 nm.

As Fig. 1 clearly shows, additional strips (branches) connecting two facets can be observed. These strips are not monosteps but also represent facets composed by several monosteps. Branches do not run in arbitrary directions but, as the STM images show, they have a peculiar azimuth of ⟨210⟩, ⟨2$\bar{1}$0⟩, ⟨310⟩, and ⟨3$\bar{1}$0⟩. Branches having the same azimuth were also observed on the step bunched vicinal sur-

face with a miscut direction of [100]. The strong tendency of the branches with these peculiar azimuths to appear suggests that these facets have a relatively low free energy.[8] If these branches represent bunched forced kinks, which are due to misorientation against the net misoriented direction, then the population of the branches with azimuth reflecting the misorientation direction ($\langle 210\rangle$ and $\langle 310\rangle$, or $\langle 210\rangle$ and $\langle 310\rangle$) should dominate the opposite. Such domination of population was not observed, which means that these branches are not generated by external conditions but are an intrinsic factor of this step bunching.

As can be seen easily from Fig. 1, step edges of facets are not exactly straight but they are fluctuating. Also, its degree depends strongly on experimental conditions. The most straight step edge can be obtained on the B-vicinal surface annealed with high $P\mathrm{AsH_3}$. These are practically the experimental conditions used to fabricate fractional layer superlattices.[9] At 700 °C, in the high $P\mathrm{AsH_3}$ region (HP) ($P\mathrm{AsH_3}\approx 1$ Torr, HP), B step edges are straighter than those of the A steps, while in the medium region (MP) ($P\mathrm{AsH_3}\approx 0.1$ Torr, MP) there is no conspicuous difference, and in the low $P\mathrm{AsH_3}$ region ($P\mathrm{AsH_3}\approx 1\times 10^{-2}$ Torr, LP) A step edges become straighter. This is a report of a surface with straight A steps in the ambient of MOCVD. In contrast, at 600 °C (not shown), there is no such major difference compared with 700 °C, though, also, B step edges are generally straighter than A step edges.

IV. DISCUSSION

The degree of fluctuation of the step edges of the facets of step bunching depends on the miscut direction of the substrates and the partial pressure of $P\mathrm{AsH_3}$. Here, I will interpret the observed reversal of the substrate having the straighter step edge with $P\mathrm{AsH_3}$ by considering the (2×4)–$c(4\times 4)$ phase transition.

A phase diagram of the reconstruction of the GaAs surface as a function of substrate temperature and $P\mathrm{AsH_3}$ has been investigated by reflectance difference spectroscopy.[10] It shows that at 700 °C, the surface reconstruction is a mixed structure of $c(4\times 4)/d(4\times 4)$ and (2×4) in the high $P\mathrm{AsH_3}$ region, while as the $P\mathrm{AsH_3}$ goes lower, the $c(4\times 4)$ reconstruction cannot maintain its extra As-rich condition and the top As dimers desorb, resulting in the (2×4) reconstruction. STM observations carried out on these two reconstructions have shown that they have different types of straight step edges; the (2×4) reconstruction has a straight A step edge and a rough B step edge,[11] while the opposite holds true for the $c(4\times 4)$ reconstruction.[2] The step-edge fluctuation observed above is consistent with these well-accepted experimental results; in the high $P\mathrm{AsH_3}$ region, the surface takes the $c(4\times 4)$ reconstruction, which has a straight B step edge, and in the low $P\mathrm{AsH_3}$ region the reconstruction switches to (2×4), which has a straight A step edge.

This means that the A step structure is more stable than the B step structure in the (2×4) phases, while the opposite hold true in the $c(4\times 4)$ phases. The most simple guide to consider whether a structure is stable or not is the electron counting model proposed by Pashley.[12] He applied the electron counting model to the supposed step structures of (2×4) phase and explained why the (2×4) reconstruction has a stable A step edge and an unstable B step edge by showing that the structure of the A step edge satisfies the electron counting model while that of the B step edge does not.[12]

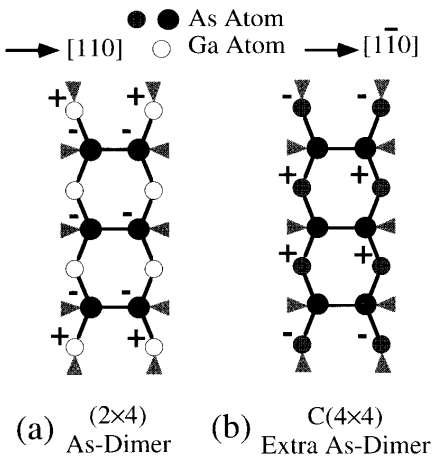

FIG. 2. Three top As dimers of the missing dimer model. Shaded and open circles represent As and Ga atoms. The larger circles are atoms in the top layer, the smaller circles in the second layer. The second layer atoms form a bond with the lower bulk (not shown). Atoms with excess electrons are indexed with $a+$ mark, while those that lack electrons are indexed with $a-$ mark.

In this section, we will consult whether or not the electron counting model can be applied to the $c(4\times 4)$ reconstruction and successfully explain the reason why the fluctuation of steps on the $c(4\times 4)$ reconstruction has a completely different characteristic from that of (2×4). Our conclusion is that we cannot determine whether or not the steps are stable from the electron counting model only. If we follow the method proposed by Pashley,[12] we can see that the B steps are more stable than the A steps in the $c(4\times 4)$ phases. However, we will show that by slightly modifying the original step-edge structure proposed by Pashley, it is possible to provide a B step-edge structure in the (2×4) phase and an A step-edge structure in the $c(4\times 4)$ phase, which satisfies the electron counting model.

The electron counting model asserts that a stable surface must satisfy a condition where the available electrons in the surface layer exactly fill all the states of As dangling bonds, and leave those of Ga empty. The excess/deficient number of electrons for each atom is counted according the following rules: As supplies 5/4 electrons to each As–Ga bond, and one for an As–As bond. The dangling bonds of As are filled, therefore, requiring 2 electrons. Ga supplies 3/4 electrons to each As–Ga bond. The dangling bonds are empty, requiring no electrons. Each As and Ga has 5 and 3 electrons available. The excess/deficient number of electrons for each atom is calculated by subtracting the available number of electron from the number of required electrons. The result is indexed in Fig. 2 as $+$; for excess electrons, and $-$; for deficient

electrons. If the total balance of the excess and deficient cancels out in a unit island cell, that structure is said to satisfy the electron counting model.

Figure 2 shows schematics of the missing dimer model and the extra As dimer model, which are generally accepted as the typical surface structure of the (2×4) and $c(4\times4)$ phases, respectively. In Fig. 2, only the three top As dimer rows and atoms in the second layer are shown. Atoms in the second layer form a covalent bond with the lower bulk (not displayed). Shaded and open circles represent As and Ga atoms, respectively, and large circles, atoms near to the surface. Atoms with excess and deficient electrons are indicated by the + and − mark. For the case of the missing dimer model, the four side atoms have 0.75 excess electrons each, while the six middle atoms lack 0.5 electrons. Thus, the total excess number of electrons for this structure is $0.75\times4-0.5\times6=0$; this structure satisfies the electron counting model. Similarly, in the case of the extra As dimer model, the four side As atoms at the second layer lack 0.5 electron each, and the four middle As atoms at the second layer have 0.5 excess electrons, thus, the extra As dimer model also satisfies the electron counting model.

Next, we will follow the method embodied by Pashley[12] to estimate the stability of steps. A perfect reconstructed surface is used as a template. Steps are modeled as an island structure extending infinitely along one direction and only one unit cell wide in the perpendicular direction. Under the island, we replace all of the extra As dimers for the $c(4\times4)$ phase and fill the missing dimer rows for both the $c(4\times4)$ and (2×4) phases with Ga atoms so that atoms buried by the island are in bulklike configurations. As shown in Figs. 3 and 4, the model island is made up from complete (2×4) or $c(4\times4)$ unit cells. Since the island overlaps two unit cells of the template surface, a unit cell of the island [enclosed by the dash–dotted line in Fig. 4(c)] is one unit wide in the infinitely extended direction and two units wide in the perpendicular direction.

Figures 3(a) and 3(b) show the A and B step-edge structures of the (2×4) phase originally proposed by Pashley. In Figs. 3 and 4, we have not indexed atoms that have the same excess/deficient electrons as the missing and extra As dimer models shown in Fig. 2, because as mentioned above, these structures satisfy the electron counting model. Considering this aspect, it is easy to see that the A step of the (2×4) reconstruction [Fig. 3(a)] satisfies the electron counting model. Indeed, this structure has no difference from the

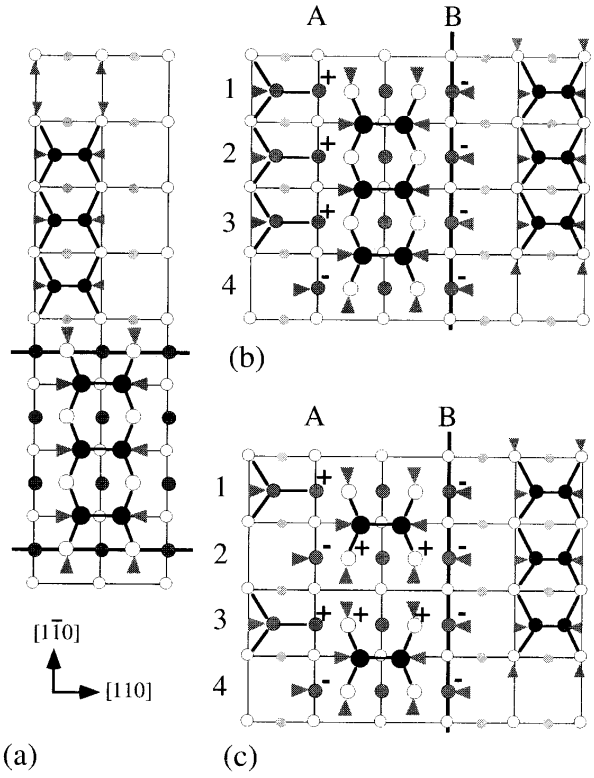

FIG. 3. (a), (b) Structure model for the A and B steps of the (2×4) reconstruction proposed by Pashley. Shaded and open circles represent As and Ga atoms, respectively, and large circles, atoms near to the surface. The A step satisfies the electron counting model while the B step does not. (c) The modified B step model structure that satisfies the electron counting model.

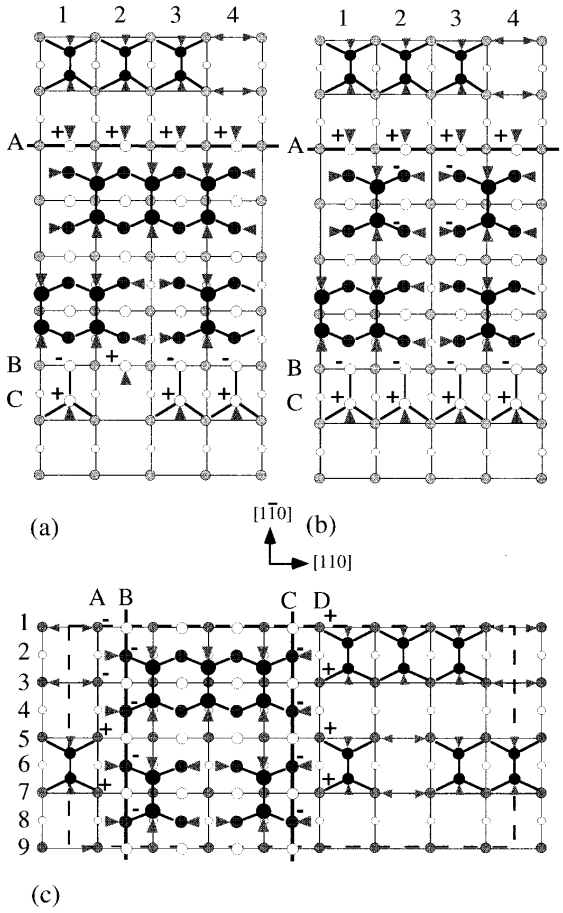

FIG. 4. (a), (b) Structure model for the A and B steps of the $c(4\times4)$ reconstruction constructed following the procedure proposed by Pashley. Shaded and open circles represent As and Ga atoms, respectively, and large circles represent atoms near to the surface. The A and B steps do not satisfy the electron counting model. (c) Modified B step model structure that satisfies the electron counting model.

TABLE I. The numbers of excess/deficient electrons in the step-edge structures formed by a procedure proposed by Pashley, and structures slightly modified from it. The rows correspond to the locations indexed in Figs. 3 and 4.

(2×4) A step	(2×4) B step	$C(4\times4)$ A step	$C(4\times4)$ B step	Modified (2×4) B step	Modified $C(4\times4)$ A step
None	Row A 0	Row A +3	Row A −1	Row A −1	Row A +3
	Row B −3	Row B 0	Row B −2	Row B −3	Row B −1
		Row C +2	Row C −2		Row C +2
			Row D +1	Remove	Remove
				As dimer +4	As dimer −4
Total 0	Total −3	Total +5	Total −4	Total 0	Total 0

missing dimer model in regard of the electron counting model. On the other hand, the situation completely differs for the B step structure shown in Fig. 3(b). While the excess and deficient electrons in row A counterbalance, there remains a deficit of three electrons in row B. The number of excess/deficient electrons of all of the structures shown in this article are arranged in Table I.

By the same process, we can construct the A and B step-edge structures of the $c(4\times4)$ reconstruction as shown in Figs. 4(a) and 4(c). As Table I shows, A and B steps have five excess and four deficit electrons, respectively. Therefore, both structures do not satisfy the electron counting model.

There is no conclusive reason for the step-edge structures to take the form proposed by Pashley. In this section, we will consider whether or not we can reasonably modify the step structures proposed by Pashley to satisfy the electron counting model. The most simple modification is to replace or remove the As dimers and the dimer vacancy on the islands. Table II lists the change of the excess/deficient electron numbers by these modifications. The modifications considered were filling the dimer vacancy by a (I) Ga or (II) As dimer, removing the top As dimer, and (III) leaving the dangling bonds unbonded (formation of a dimer vacancy), or (IV) rebonding the dangling bonds (formation of a rebonded vacancy), and (V) replacing the top As dimer with a Ga dimer. We found out operations (IV) and (V) do not change the total number of excess/deficient electrons for both (2×4) and $c(4\times4)$ reconstructions, and regardless of the location, the operation is carried out. However, for other operations, the situation is completely different for the (2×4) and $c(4\times4)$ reconstructions. Operations (I) and (II) increase, and operation (III) decreases the total excess electrons by 4 for the $c(4\times4)$ reconstruction, while for the (2×4) reconstruction, the situation is completely inverted. Therefore, any combination of these operations changes the total number of excess or deficient electrons only by a multiple of 4. Regarding this fact, we can see that among the three step-edge structures that did not satisfy the electron counting model *a priori*, the $c(4\times4)$ B step-edge structure can easily satisfy the electron counting model by filling one of the two dimer vacancy rows by a As dimer, while the (2×4)-B and $c(4\times4)$-A step-edge structures can never, by any combinations of the operations listed in Table II.

Therefore, considering the above discussion, one may conclude that the (2×4)-A and $c(4\times4)$-B steps are more stable than the (2×4)-B and $c(4\times4)$-A steps, because the former two satisfy the electron counting model while the latter ones do not. However, in this section, we will show that it is possible to construct (2×4)-B and $c(4\times4)$-A step structures, for which the number of excess/deficient electrons is a multiple of 4 by slightly modifying the structure of the step edge. Then, by modifying the As dimer or dimer vacancy on the island, we can construct a structure that satisfies the electron counting model. The modified structures are displayed in Figs. 3(c) and 4(b). As shown in Table I, by slightly modifying the step-edge structure, we have adjusted the number of excess/deficient electrons to +4 for the $c(4\times4)$-A step and −4 for the (2×4)-B step. Therefore, re-

TABLE II. Table showing how the numbers of excess/deficient electrons in the (2×4) and $c(4\times4)$ reconstructions change by modifying the top As dimer or the dimer vacancy. DP is an abbreviation of depends on places.

Reconstruction	Operation	Change in electron number	
$C(4\times4)$	Dimer vacancy→Ga dimer	$-2\rightarrow+2$	+4
	Dimer vacancy→As dimer	$-2\rightarrow+2$	+4
	As dimer→dimer vacancy	DP	−4
	As dimer→vacancy rebonded	DP	0
	As dimer→Ga dimer	DP	0
(2×4)	Dimer vacancy→Ga dimer	$+3\rightarrow-1$	−4
	Dimer vacancy→As dimer	$+3\rightarrow-1$	−4
	As dimer→dimer vacancy	DP	+4
	As dimer→vacancy rebonded	DP	0
	As Dimer→Ga dimer	DP	0

moving one of the top As dimers on the island will cause the whole structure to satisfy the electron counting model. Also, we will state that the proposed step-edge structure is as likely to exist as the (2×4)-B step structure proposed by Pashley [Fig. 3(b)], which focuses the grounds of his statement that the (2×4)-B step is unstable compared to the (2×4)-A step.

Summarizing, we have shown that we can construct for all of the steps considered in this article, a structure model that satisfies the electron counting model. This means that we cannot judge the stability of steps only from the electron counting model. In order to definitely state that a step is unstable, we have to show that all of the possible step-edge structures fail to satisfy the electron counting model, which would be a troublesome task because numerous possible structures exist. In order to make efficient use of the electron counting model, we need, at least, a STM image of the step with an atomic resolution to reduce the possible model structures to a manageable number. Finally, we would state that the electron counting model is not a perfect guideline to judge the stability of a structure, the real structure is determined by a competition of the energy gain obtained by charge transfer and the energy loss due to the strain. It is possible that the energy loss due to the strain is too large for the charge transfer to take place. In that case, the electron counting model would fail to judge the stability of the structure.

V. CONCLUSION

In conclusion, we have studied how the annealing conditions influence the degree of fluctuation of step edges of step bunching formed by annealing a vicinal GaAs(001) surface in AsH_3 and H_2 and ambient. We show that it is possible to produce a surface that has straighter A steps than B steps by annealing in low AsH_3 partial pressure at high temperatures. When the substrate was annealed with high AsH_3 partial pressure, the B steps were straighter than the A steps as reported before. This reversal of the type of straight steps can be understood by considering the $(2\times4)-c(4\times4)$ phase transition. We will also apply the electron counting model proposed by Pashley to consider whether or not it can explain why the A step edges are more stable than the B steps in the (2×4) phase, while the opposite holds true in the $c(4\times4)$ phase. Our results are that we cannot determine the stability of steps only by this model. Also, we have discussed the limitations and application of this model.

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