Kinetics in Surface Reconstructions on GaAs(001)

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We have successfully controlled the surface structures of GaAs(001) by changing incident As-molecular species. Under As_4 fluxes, the $c(4 \times 4)$ reconstruction with Ga-As dimers [$c(4 \times 4)\alpha$ structure] is obtained, but the formation of three As-As dimer structures [$c(4 \times 4)\beta$ structure] is kinetically limited. On the other hand, the structure change from the (2×4), through $c(4 \times 4)\alpha$, to $c(4 \times 4)\beta$ phases is observed under As_2 fluxes. We found that the $c(4 \times 4)\alpha$ structure is energetically metastable and provides a kinetic pathway for the structure change between the (2×4) and $c(4 \times 4)\beta$ phases under As_2 fluxes.

Surface reconstructions occur on the majority of semiconductor surfaces, leading to a periodicity different from that in a corresponding bulk structure. In particular, a variety of reconstructions has been found on the (001) surface of GaAs, ranging from the most As-rich $c(4 \times 4)$, through (2×4) and $(2 \times 6)/(3 \times 6)$, and to Ga-rich $c(8 \times 2)$ phases [1]. The simple picture of such reconstructions rests on the assumption of thermodynamic equilibrium: the surface is reconstructed in such a way that the surface energy is minimized. Thus, the sequence of structures on the GaAs(001) surface as a function of decreasing As coverage has been explained from the standpoint of equilibrium energetics [2–4]. As we show in this Letter, however, we found that kinetics also play an important role in the surface reconstructions on GaAs(001).

Surface structures of molecular-beam-epitaxy- (MBE-) grown GaAs(001) change with As pressure and substrate temperature. The $c(4 \times 4)$ structure is usually observed under most As-rich environments, and has been widely believed to have three As-As dimers per unit cell [Fig. 1(b)] [2–11]. On the other hand, a new structure model consisting of three Ga-As dimers instead of As-As dimers [Fig. 1(c)] has recently been proposed [12]. Here, we present the evidence that the atomic structures of $c(4 \times 4)$ kinetically depend on the species of incident As molecules: the Ga-As dimer [$c(4 \times 4)\alpha$] and As-As dimer [$c(4 \times 4)\beta$] structures are formed when the surfaces are prepared using As_4 and As_2 molecules, respectively. It is also found that the $c(4 \times 4)\alpha$ structure is energetically metastable, and provides an easy way for the structure change between the (2×4) and $c(4 \times 4)\beta$ phases under As_2 fluxes.

The experiments were performed in a system of interconnecting ultrahigh vacuum chambers for MBE growth and for online surface characterization by means of scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy [13,14]. The MBE chamber is equipped

with reflection high-energy electron diffraction (RHEED) and reflectance difference spectroscopy (RDS) apparatuses. Nondoped and nominally on-axis GaAs(001) substrates were used for the RHEED and RDS measurements, while the Si-doped [$N \approx (1–4) \times 10^{18}$ cm^{-3}] substrates were employed for the STM experiments. Cleaned GaAs(001)-(2×4) surfaces were first obtained by growing an undoped homoepitaxial layer (~ 0.5 μm) on a thermally cleaned GaAs(001) substrate. The more As-rich reconstructions of $c(4 \times 4)$ were obtained by cooling the (2×4) surfaces under As fluxes.
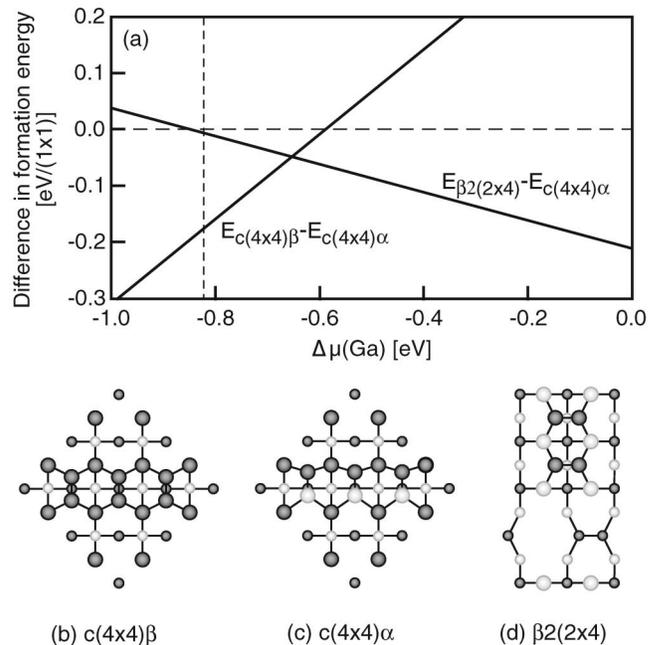
FIG. 1. (a) Difference in the formation energy of the (b) $c(4 \times 4)\beta$, (c) $c(4 \times 4)\alpha$, and (d) $\beta 2(2 \times 4)$ structures. The thermodynamically allowed range is between -0.823 eV (As rich) and 0.0 eV (Ga rich). Open (closed) circles denote Ga (As) atoms.

The As fluxes were generated using a valved cracker cell (EPI-500V-As). The RD spectra were obtained using a modified Jobin Yvon RD spectrometer. The spectra cover an energy range from 1.5 to 5.2 eV.

Relative stability of the surface structures was studied using first-principles calculations [15,16] based on density-functional theory [17] with the generalized gradient approximation [18]. The calculated lattice constant of GaAs is 5.699 Å which is close to the experimental value of 5.6538 Å. A slab geometry was used for the simple calculation, which has the supercell consisting of eight atomic layers of GaAs with surface dimers and of a vacuum region corresponding to six atomic layers in thickness. The back side of the slab is terminated with eight fictitious H atoms that eliminate artificial dangling bonds and prevent it from coupling with the front side. The wave functions were expanded in plane waves with a kinetic energy cutoff of 20 Ry. Four k points in the irreducible Brillouin zone of the $c(4 \times 4)$ and (2×4) surfaces were used for the integration in k space.

Figure 1(a) shows the difference in formation energies for the $c(4 \times 4)\beta$ [1(b)], $c(4 \times 4)\alpha$ [1(c)], and $\beta 2(2 \times 4)$ [1(d)] structures. The As coverages of these structure models are 1.75 [1(b)], 1.00 [1(c)], and 0.75 [1(d)]. It is clearly seen that, as expected, the (2×4) and $c(4 \times 4)\beta$ structures are more stable than the $c(4 \times 4)\alpha$ structure under Ga- and As-rich conditions, respectively. Surprisingly, the $c(4 \times 4)\alpha$ structure is unstable between two phases, although its existence has been confirmed by several experiments [12,14,19]: as we have already reported [12], the $c(4 \times 4)\alpha$ structure is observed in a wide range of substrate temperature under As$_4$ fluxes.

Figure 2(a) shows RD spectra obtained from GaAs(001) surfaces under the As$_4$ flux of 2.5×10^{-7} Torr. The shape of the spectrum measured at 540 °C is characteristic for the $\beta 2(2 \times 4)$ structure [Fig. 1(d)] [13]. As the temperature is decreased below 500 °C, the (2×4) phase begins to evolve into the more As-rich phase of $c(4 \times 4)\alpha$ [Fig. 1(c)], because the sticking probability of As$_4$ molecules increases with decreasing substrate temperature. The spectrum shape at 480 °C [Fig. 2(a)-B] is identical to that for the $c(4 \times 4)\alpha$ structure, indicating that the (2×4) to $c(4 \times 4)\alpha$ change is almost completed at this stage. When the temperature is further decreased to 200 °C, the spectrum shape stays essentially the same [Fig. 2(a)-C], indicating that the structure change to the most As-rich phase of $c(4 \times 4)\beta$ hardly occurs.

There are two discrepancies between the calculations and the experiments. (i) The experimentally observed phase of $c(4 \times 4)\alpha$ is energetically unstable. (ii) The stable phase of $c(4 \times 4)\beta$ was not observed in our experiment. However, as we show below, the latter discrepancy can be solved when the experiments are performed using As$_2$ molecules instead of As$_4$.
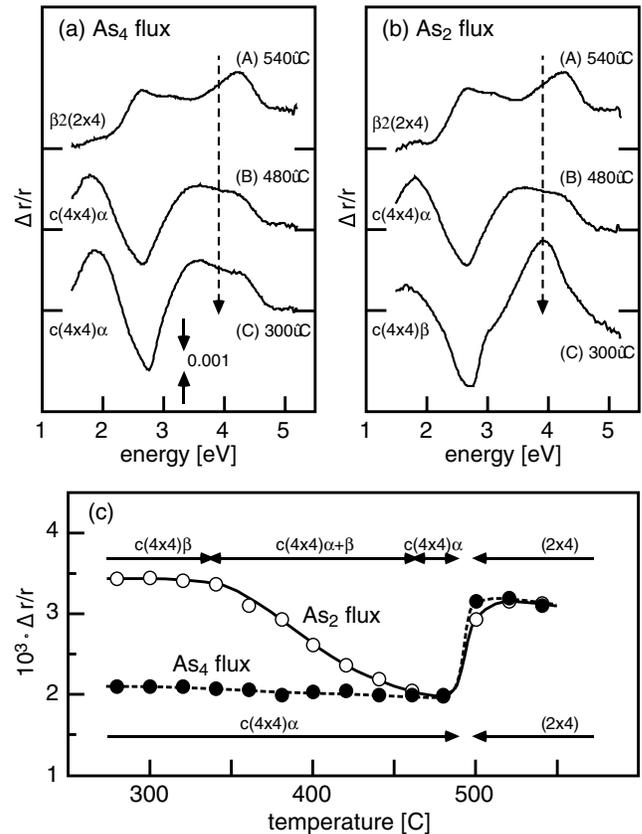
FIG. 2. RD spectra measured from GaAs(001) surfaces under (a) As$_4$ and (b) As$_2$ fluxes. (c) RD intensities at 3.9 eV plotted as a function of decreasing substrate temperature.

The As$_2$ molecules were produced by cracking As$_4$ molecules above 750 °C [20]. Shown in Fig. 2(b) are RDS results obtained under otherwise identical conditions as in Fig. 2(a). The (2×4) to $c(4 \times 4)\alpha$ change under the As$_2$ fluxes of 2.5×10^{-7} Torr occurs in a temperature range of 510–490 °C [Fig. 2(b)-B], similar to the case for As$_4$ fluxes. However, the $c(4 \times 4)\alpha$ phase is stable only in a limited range of temperature. As shown in Fig. 2(c), RD intensities measured under As$_2$ fluxes drastically change between 480–340 °C, while those for As$_4$ do not show any significant change below 480 °C. The change in the RD spectrum is almost completed at $\sim$340 °C, and the spectrum shape remains essentially unchanged between 340–280 °C. Figure 2(b)-C shows the RD spectrum measured at 300 °C, the shape of which is identical to that for the $c(4 \times 4)\beta$ structure [Fig. 1(b)] [14]. These results clearly show that the use of As$_2$ promotes the formation of As-As dimers.

Further experimental supports for the two types of structures were obtained by STM observations. Figures 3(a) and 3(b) show typical filled-state images taken from the $c(4 \times 4)$ surfaces prepared using As$_4$ and As$_2$ molecules, respectively. A brickwork pattern of symmetric features corresponding to As-As dimers are
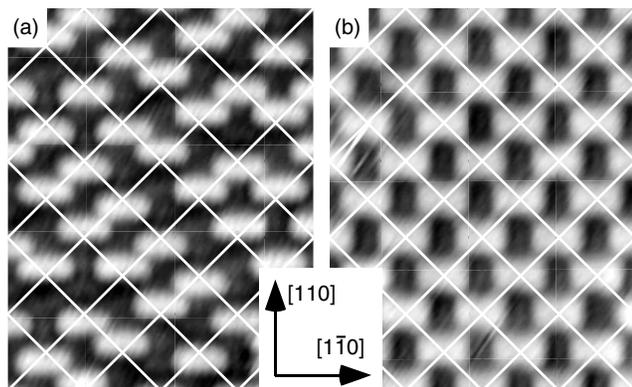
FIG. 3. Typical filled-state STM images obtained from the GaAs(001)-$c(4 \times 4)$ surface prepared under (a) As_4 and (b) As_2 fluxes. The images were taken with a sample bias of -2.5 V. (a) and (b) correspond to the Ga-As dimer [Fig. 1(c)] and As-As dimer [Fig. 1(b)] structures, respectively. The solid lines show the $c(4 \times 4)$ lattice mesh. Image dimensions are 64 Å $\times$ 80 Å.

observed in Fig. 3(b), while asymmetric features in Fig. 3(a) evidence the existence of Ga-As dimers [12].

At first sight, one may attribute the difference in the experimental results between As_4 and As_2 to higher sticking probability of As_2 molecules. Indeed, the As_2 molecules are adsorbed on the GaAs(001) surface forming amorphous As layers below 250 °C, while the adsorption of As_4 hardly occurs even at a lower temperature of 200 °C. Thus, we checked whether the $c(4 \times 4)\beta$ structure is formed under higher As_4 fluxes. However, the $c(4 \times 4)\beta$ phase does not emerge under the higher As_4 flux of 1.0×10^{-6} Torr, even though the (2×4) to $c(4 \times 4)\alpha$ change occurs at a higher temperature of ~ 530 °C. Although the β phase could be formed under an extreme As-rich environment (low temperatures and high As_4 fluxes), such a surface is usually disordered because of the lowering in diffusivity of surface atoms at low temperatures [14,21]. From these results, it appears likely that the formation of $c(4 \times 4)\beta$ from $c(4 \times 4)\alpha$ is kinetically limited under As_4 fluxes.

It is well established that the reaction of As_4 molecules with GaAs(001) is much more complex than As_2: As_4 molecules have to be dissociated into As_2 precursors before being incorporated into the lattice sites [22,23]. For this to happen, pairs of As_4 molecules are required to interact on adjacent Ga sites in advance [22,23]. In contrast to the case for the $\beta 2(2 \times 4)$ structure (which is discussed later), fewer Ga sites are available on the $c(4 \times 4)\alpha$ structure, which makes it difficult to react As_4 molecules with GaAs(001) to form the β structure.

In order to obtain details about formation processes of the $c(4 \times 4)\beta$ structure under As_2 fluxes, we studied intermediate states between α and β phases. After being annealed at $400-440$ °C under As_2 fluxes, the samples were cooled to room temperature without As fluxes.

Figure 4(a) shows the STM image of the sample prepared at 400 °C. This image was obtained at a negative sample bias of 3.4 V, in which the As atoms are imaged. It is clearly seen that bright features consisting of three to 6 As atoms are arranged to form the $c(4 \times 4)$ periodicity. This is consistent with our RHEED observations: the $c(4 \times 4)$ periodicity is preserved throughout the structure change from $c(4 \times 4)\alpha$ to $c(4 \times 4)\beta$ [24].

Bright features in Fig. 4(a) are classified into types A, B, C, and D, as indicated in the figure. The type-A and type-D features correspond to the α and β structures, respectively. Also seen in Fig. 4(a) is the defected α structure (type A'), in which one of the outer dimers is arranged in the opposite orientation with the other two dimers. Such a defected structure has an energy higher by 0.08 eV per $c(4 \times 4)$ unit cell, and the density of which is $\sim 18\%$ of the type-A structure. The type-B (type-C) feature is interpreted as the unit cell having two (one) Ga-As and one (two) As-As dimers. Figure 4(b) shows the distributions of types $A-D$ features in samples prepared at 400 and 440 °C. As expected, the densities of features A and B (C and D) decrease (increase) with decreasing temperature. At either temperature, the density of
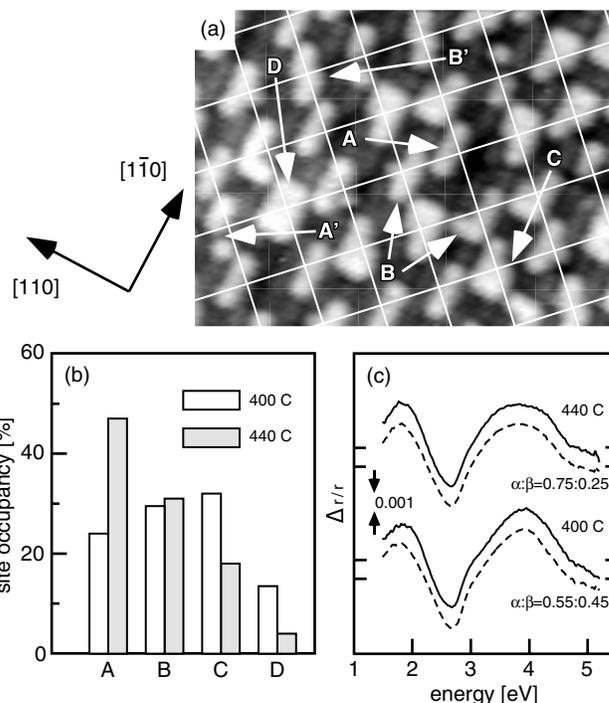
FIG. 4. (a) Filled state STM image of the sample prepared at 400 °C taken with a sample bias of -3.4 V. The solid lines show the $c(4 \times 4)$ lattice mesh. Image dimensions are 80 Å $\times$ 60 Å. Bright features are classified as types A, B, C, and D, as indicated. (b) Distributions of features $A-D$ in the samples prepared at 400 and 440 °C. (c) RD spectra measured from the $c(4 \times 4)$ surface at 400 and 440 °C under As_2 flux. The dashed curves are RD spectra synthesized from linear combinations of the $c(4 \times 4)\alpha$ and $c(4 \times 4)\beta$ spectra.

intermediate structures $(B + C)$ is larger than 60%. Thus, it is unlikely that three Ga-As dimers in the unit cell are simultaneously replaced by three As-As dimers.

The coverage of surface As atoms is estimated to be $55\% \pm 4\%$ ($45\% \pm 4\%$) in the sample prepared at 400 (440) °C, indicating that $\sim$45% ($\sim$25%) of Ga-As dimers are replaced by As-As dimers. This is confirmed by the RDS analysis: as shown in Fig. 4(c), the shape of the RD spectra measured at 400 and 440 °C (solid curve) is well reproduced by the linear combination of α and β spectra (dashed curve).

Finally, we discuss possible mechanisms for the formation of the metastable $c(4 \times 4)\alpha$ structure between the (2×4) and $c(4 \times 4)\beta$ phases. In general, if the direct formation of an equilibrium phase has a large kinetic barrier, a system finds it easier to reach this state through intermediate phases. It has been reported that the $c(4 \times 4)$ structure arises in the original (2×4) phase one atomic layer below the top layer of the $\beta2(2 \times 4)$ structure [8,25]. Such a structure change is likely to have a relatively high activation barrier, because Ga atoms at the second layer of the $\beta2(2 \times 4)$ structure have to be completely removed. On the other hand, previous studies have shown that As molecules are preferentially adsorbed at the trench site of the $\beta2(2 \times 4)$ structure [7,26]. Adsorption at this site enables the As atom to be three coordinated with its nearest neighbor atoms, forming a bond with one of the three-coordinated Ga atoms in the second layer of the $\beta2(2 \times 4)$ structure [26]. Such an atomic process provides an easy way for the formation of Ga-As dimers, because this process does not require the addition and/or the removal of other surface atoms. Thus, we conclude that the $c(4 \times 4)\alpha$ structure has a lower barrier for the formation and plays a key role in the structure change between (2×4) and $c(4 \times 4)\beta$ phases.

We confirmed that the structure change between $c(4 \times 4)\beta$ and (2×4) under As_2 fluxes is reversible: the RD intensities behave similarly to those in Fig. 2(c) as a function of the substrate temperature when the β surface is heated. On the other hand, the β structure prepared with As_2 fluxes was preserved up to $\sim$340 °C even under As_4 fluxes, beyond which the β surface begins to coexist with the α structure. Thus, it is likely that the use of As_4 does not significantly degrade thermal stability of the β structure, although the temperature range, in which the α structure is observed, is expanded (450–490 °C). This further evidences that the formation of the β structure under As_4 fluxes is limited by kinetics rather than energetics.

In conclusion, we present the evidence that the surface structure of GaAs(001)-$c(4 \times 4)$ can be controlled to either Ga-As dimer or As-As dimer structures by changing the incident As-molecular species. The formation of the Ga-As dimer structure is found to be energetically unfavorable, and can be regarded as a kinetic pathway in

the structure change between (2×4) and $c(4 \times 4)\beta$ phases. The present results clearly show that the surface reconstruction critically depends on the kinetics, and provides a new perspective for a more complete understanding of surface reconstructions.

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