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 As4 fluxes, the c(4 × 4) reconstruction with Ga-As dimers [c(4 × 4)α structure] is obtained, but the formation of three As-As dimer structures [c(4 × 4)β structure] is kinetically limited. On the other hand, the structure change from the (2 × 4), through c(4 × 4)α, to c(4 × 4)β phases is observed under As2 fluxes. We found that the c(4 × 4)α structure is energetically metastable and provides a kinetic pathway for the structure change between the (2 × 4) and c(4 × 4)β phases under As2 fluxes.

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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(4×4), through (2×4) and (2×6)/(3×6), and to Ga-rich c(8×2) 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 × 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 × 4) kinetically depend on the species of incident As molecules: the Ga-As dimer [c(4 × 4)α] and As-As dimer [c(4 × 4)β] structures are formed when the surfaces are prepared using As4 and As2 molecules, respectively. It is also found that the c(4 × 4)α structure is energetically metastable, and provides an easy way for the structure change between the (2 × 4) and c(4 × 4)β phases under As2 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 = (1–4) × 10^{18} \text{ 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 × 4) were obtained by cooling the (2 × 4) surfaces under As fluxes.

FIG. 1. (a) Difference in the formation energy of the (b) c(4×4)β, (c) c(4×4)α, and (d) β(2×4) 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 (4×4) and (2×4) surfaces were used for the integration in k space.

Figure 1(a) shows the difference in formation energies for the (4×4)β [1(b)], c(4×4)α [1(c)], and β2(2×4) [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(4×4)β structures are more stable than the c(4×4)α structure under Ga- and As-rich conditions, respectively. Surprisingly, the c(4×4)α 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(4×4)α structure is observed in a wide range of substrate temperature under As4 fluxes.

Figure 2(a) shows RD spectra obtained from GaAs(001) surfaces under the As4 flux of 2.5×10\(^{-7}\) Torr. The shape of the spectrum measured at 540 °C is characteristic for the β2(2×4) 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(4×4)α [Fig. 1(c)], because the sticking probability of As4 molecules increases with decreasing substrate temperature. The spectrum shape at 480 °C [Fig. 2(a)-B] is identical to that for the c(4×4)α structure, indicating that the (2×4) to c(4×4)α 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(4×4)β hardly occurs.

There are two discrepancies between the calculations and the experiments. (i) The experimentally observed phase of c(4×4)α is energetically unstable. (ii) The stable phase of c(4×4)β was not observed in our experiment. However, as we show below, the latter discrepancy can be solved when the experiments are performed using As2 molecules instead of As4.

![FIG. 2. RD spectra measured from GaAs(001) surfaces under (a) As4 and (b) As2 fluxes. (c) RD intensities at 3.9 eV plotted as a function of decreasing substrate temperature.](image-url)
As4/c structure is formed under higher annealed at 400–440 C. This observation of As2 fluxes. However, the As4 structure is formed under higher As4 fluxes. However, the c(4×4)B phase does not emerge under the higher As4 flux of 1.0 × 10^-6 Torr, even though the (2×4) to c(4×4)α 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 As4 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(4×4)β from c(4×4)α is kinetically limited under As4 fluxes.

At first sight, one may attribute the difference in the experimental results between As4 and As2 to higher sticking probability of As2 molecules. Indeed, the As2 molecules are adsorbed on the GaAs(001) surface forming amorphous As layers below 250 °C, while the adsorption of As4 hardly occurs even at a lower temperature of 200 °C. Thus, we checked whether the c(4×4)β structure is formed under higher As4 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(4×4) periodicity. This is consistent with our RHEED observations: the c(4×4) periodicity is preserved throughout the structure change from c(4×4)α to c(4×4)β [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(4×4) unit cell, and the density of which is ≈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. 3. Typical filled-state STM images obtained from the GaAs(001)-c(4×4) surface prepared under (a) As4 and (b) As2 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)], respectively. The solid lines show the c(4×4) lattice mesh. Image dimensions are 64 Å × 80 Å.

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(4×4) lattice mesh. Image dimensions are 80 Å × 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(4×4) surface at 400 and 440 °C under As4 flux. The dashed curves are RD spectra synthesized from linear combinations of the c(4×4)α and c(4×4)β spectra.

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

In order to obtain details about formation processes of the c(4×4)β structure under As2 fluxes, we studied intermediate states between α and β phases. After being annealed at 400–440 °C under As2 fluxes, the samples were cooled to room temperature without As fluxes.

It is well established that the reaction of As4 molecules with GaAs(001) is much more complex than As2: As4 molecules have to be dissociated into As2 precursors before being incorporated into the lattice sites [22,23]. For this to happen, pairs of As4 molecules are required to interact on adjacent Ga sites in advance [22,23]. In contrast to the case for the β2(2×4) structure (which is discussed later), fewer Ga sites are available on the c(4×4)α structure, which makes it difficult to react As4 molecules with GaAs(001) to form the β structure.

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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% ± 4% (45% ± 4%) in the sample prepared at 400 (440) °C, indicating that ~45% (~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 \(\alpha\) and \(\beta\) spectra (dashed curve).

Finally, we discuss possible mechanisms for the formation of the metastable \(c(4 \times 4)\alpha\) structure between the \((2 \times 4)\) 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 \((2 \times 4)\) phase one atomic layer below the top layer of the \(\beta 2(2 \times 4)\) 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 \(\beta 2(2 \times 4)\) 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 \(\beta 2(2 \times 4)\) 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 \(\beta 2(2 \times 4)\) 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 \((2 \times 4)\) and \(c(4 \times 4)\beta\) phases.

We confirmed that the structure change between \(c(4 \times 4)\beta\) and \((2 \times 4)\) under \(\text{As}_2\) fluxes is reversible: the RD intensities behave similarly to those in Fig. 2(c) as a function of the substrate temperature when the \(\beta\) surface is heated. On the other hand, the \(\beta\) structure prepared with \(\text{As}_2\) fluxes was preserved up to ~340 °C even under \(\text{As}_4\) fluxes, beyond which the \(\beta\) surface begins to coexist with the \(\alpha\) structure. Thus, it is likely that the use of \(\text{As}_4\) does not significantly degrade thermal stability of the \(\beta\) structure, although the temperature range, in which the \(\alpha\) structure is observed, is expanded (450–490 °C). This further evidences that the formation of the \(\beta\) structure under \(\text{As}_4\) 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 \((2 \times 4)\) 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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[24] While sharp \(c(4 \times 4)\) RHEED patterns are observed throughout the structure change, RHEED intensities changed with decreasing temperature.
