Surface dynamics during phase transitions of GaAs(100)

Z. M. Wang* and G. J. Salamo
Physics Department, University of Arkansas, Fayetteville, Arkansas 72701
(Received 17 December 2002; revised manuscript received 10 February 2003; published 31 March 2003)

Scanning tunneling microscopy is used to capture the initial stage of the transition from $c(4\times4)$ to (2×4) reconstruction on a GaAs(100) surface. A model for the transition is proposed in which surface atoms escape from the $c(4\times4)$ reconstructed area to form (2×4) reconstructed islands and pits. The proposed explanation is consistent with $c(4\times4)$ models having species intermixing in the first or second layer.

DOI: 10.1103/PhysRevB.67.125324 PACS number(s): 81.15.Hi, 81.07.−b, 68.37.Ef, 61.14.Hg

The GaAs(100) surface has a large number of stoichiometry-dependent surface reconstructions.[1] An understanding of these reconstructed surfaces can play a significant role in the fabrication of GaAs devices. For example, the (2×4) and $c(4\times4)$ As-stable reconstructions are particularly important for GaAs-based optoeletronics, since growth by molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition generally takes place under As-rich conditions. As a results of extensive experimental and theoretical investigations, it is generally accepted that the (2×4) reconstruction contains two As dimers on the top layer and another As dimer at the third layer,[2,3] as shown in Fig. 1(a). In comparison with the (2×4) reconstruction, results from structural investigations of the $c(4\times4)$ reconstructed surface are less certain.[2,4–8] In one $c(4\times4)$ model the top two As monolayers (ML's) are structured as shown in Fig. 1(b). In this model, an excess 0.75 ML of As atoms are chemisorbed on an already As-terminated surface to form [011]-oriented As dimers in the $c(4\times4)$ symmetry, with one missing dimer occurring at every four As dimers. While this model is accepted by many research groups, results from recent efforts to understand the transition between the (2×4) and the $c(4\times4)$ reconstruction argue the accuracy of this $c(4\times4)$ model. For example, the transition from (2×4) to $c(4\times4)$ reconstruction is observed at a low substrate temperature of 400–500 °C. Consequently, the Ga surface atoms are expected to be relatively immobile in this temperature range.[6,9] As a result, one must suspect that the simple addition of As atoms to the (2×4) surface leads to a $c(4\times4)$ surface with Ga and As intermixing in the third layer, as shown in Fig. 1(c). Accordingly, a $c(4\times4)$ reconstructed region should stand above the (2×4) reconstructed region when the two phases coexist.[6] However, all current investigations have demonstrated that the $c(4\times4)$ region is actually located below the (2×4) region.[2,7,10] As a result of the observation of the coexistence of both reconstructed surfaces, a $c(4\times4)$ model with Ga and As intermixing in the second layer has been proposed[7] [Fig. 1(d)]. This model is consistent with results from both medium-energy ion scattering studies[11] and scanning tunneling microscopy (STM) studies.[4,7] More recently, yet another model for the $c(4\times4)$ structure with three mixed Ga-As dimers on top,[8] as shown in Fig. 1(e), is also claimed to be compatible with experimental and theoretical studies. Apparently, there is still some doubt as to which model is correct. While each of these models are plausible several require that surface transport of a huge amount of Ga atoms has to be involved in the phase transition between the (2×4) and the $c(4\times4)$ reconstruction. For example, it is already noted that the (2×4) phase has to melt first in order to accommodate the $c(4\times4)$ configuration using the model with a top 1.75 ML of As.[10] Extremely long surface diffusion of Ga atoms is proposed as the Ga source of the phase transition.[10] Given the uncertainty of a model for the $c(4\times4)$ reconstruction, a study focused on the surface transition between the (2×4) and $c(4\times4)$ reconstructions can lead to better understanding of the $c(4\times4)$ structure.

In this paper, we report on STM experiments that have observed the initial stages of the transition from the $c(4\times4)$ to (2×4) reconstructed surfaces. Based on observations in these experiments, the primary source of surface Ga atoms needed to support the transition from the $c(4\times4)$ to (2×4) surface reconstructions is Ga atoms jumping over a short range. In particular, the transition is observed to be characterized by an intermediate structure composed of (2×4) reconstructed islands and pits.

The experiment was carried out in a combined MBE-STM system under ultrahigh vacuum (UHV). The system is equipped with an *in situ* optical system that monitors the substrate band edge to give accurate growth temperatures. Epitaxial ready *N*-type GaAs(100) wafers were used for this experiment. After the growth of a 500-nm GaAs buffer layer, the sample was annealed for 10 min at 580 °C under a constant As_4 flux of 1.0×10^{-5} Torr in order to achieve a smooth growth front. A highly ordered (2×4) reconstruction was maintained under this condition. The evolution of surface reconstructions was monitored by reflection high-energy electron diffraction (RHEED). By reducing the substrate temperature to 480 °C at ramping rate of 30 °C per min, a well ordered $c(4\times4)$ RHEED pattern was developed. The substrate temperature was then increased to 500 °C at ramping rate of 20 °C per minute to trigger the transition from $c(4\times4)$ to (2×4) reconstruction. Although the RHEED pattern was $c(4\times4)$-like still at 500 °C, it became less ordered. Directly after the temperature reached 500 °C, the resulting surface morphology was quickly quenched by turning off the substrate heater power and closing the As shutter. During this time the RHEED pattern remained constant. The sample was subsequently transferred through a UHV transfer chamber into the STM chamber. Constant current STM im-

 ©2003 The American Physical Society

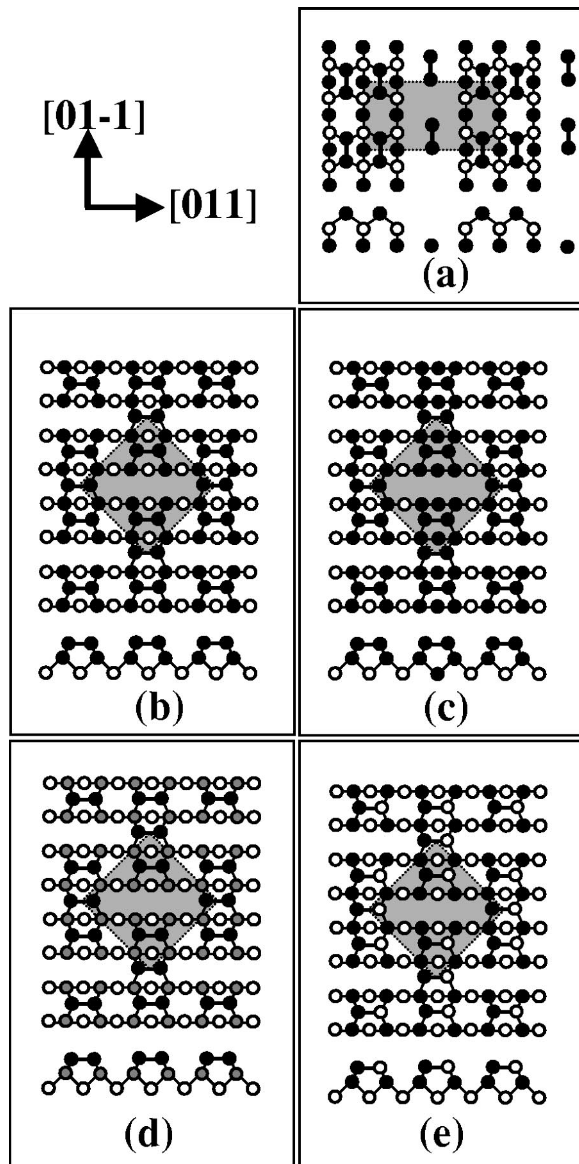

FIG. 1. Top and lateral views of structure models. (a) for the (2×4) phase, (b) for the $c(4\times4)$ phase with top 1.75 monolayer As, (c) and (d) for the $c(4\times4)$ phases with species intermixing in the third and second layer, respectively, (e) for the $c(4\times4)$ phase with Ga-As mixed dimers in the first layer. Dark filled (open) circles denote As (Ga) atoms. Gray filled circles in (d) indicate species intermixing, denoting As or Ga atoms. The unit cells are defined by shadows.

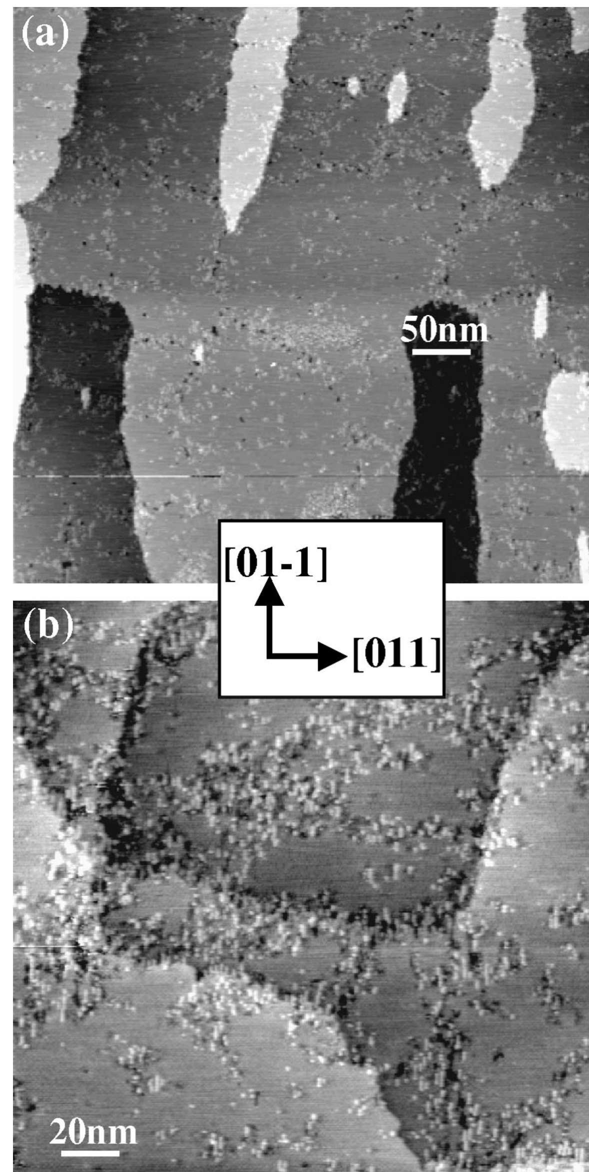

FIG. 2. STM images during the phase transition between $c(4\times4)$ and (2×4) in different magnifications. (a) 500×500 nm^2, (b) 200×200 nm^2.

ages were obtained using a tunneling current of around 0.1 nA and a sample bias of -3.0 V.

A large-scale STM image of the resulting surface is shown in Fig. 2(a). High anisotropic terraces are observed with well-defined bilayer steps (the step height is 0.28 nm). The long steps along [01-1] are type *A* and the short steps along [011] are type *B*. The most apparent feature here is that the wide terraces are covered by nanometer size islands and pits. Apparently, the islands and pits are not randomly distributed on the large terraces. The clean area with a low density of islands and pits are surrounded by boundaries with a high density of islands and pits. The steps, regardless of the step type *A* or *B*, frequently happen to be the boundaries as shown in Fig. 2(b). The islands are highly disordered but elongated along [01-1]. They are actually (2×4)-like reconstructed, as shown in Fig. 3(a). The line profile of Fig. 3(b) is taken across the islands and pits in Fig. 3(a)and shows that the islands are one-atomic-layer (0.15 nm) higher (the pits one-atomic-layer lower) than the terrace. Obviously, the islands have a bigger population than pits, with about one pit for every five islands. On the other hand, the pits are similar to the islands with (2×4)-like reconstructed and elongated along [01-1]. The view in Fig. 3(c) reveals that the wide terraces are $c(4\times4)$ reconstructed with the typical brickwork pattern of bright rectangular blocks. The observation of the clean $c(4\times4)$ domains surrounded by crowded regions with islands and pits suggests that the $c(4\times4)$ domain boundaries are possible nucleation centers for the (2×4).

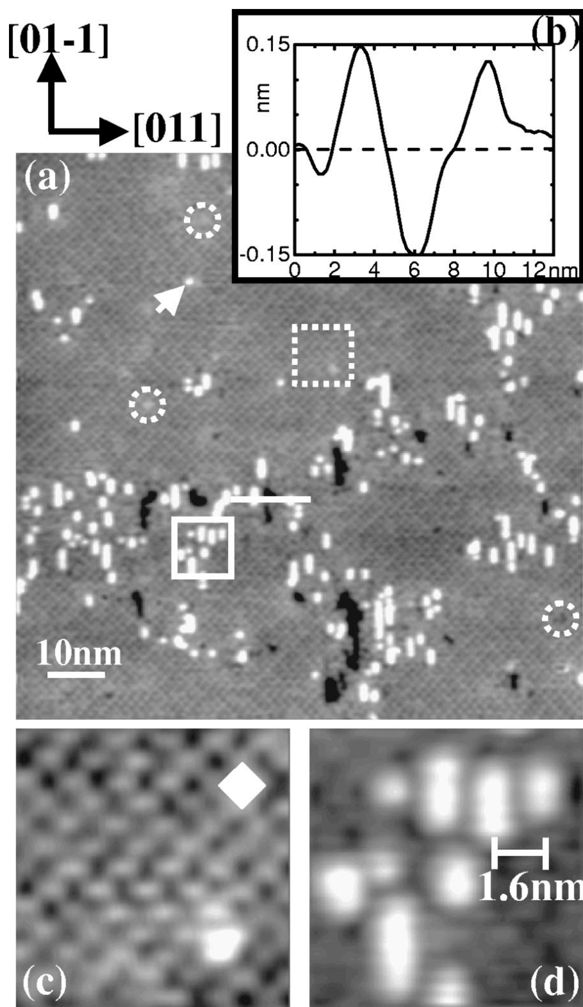

FIG. 3. (a) 100×100 nm^2 STM image during the phase transition between $c(4\times4)$ and (2×4). (b) Height profile of the white line in (a) crossing islands and pits on the terrace. (c) and (d) magnified 10×10 nm^2 STM images of squares defined by dash and solid white line, respectively. The solid white square in (c) is the $c(4\times4)$ unit cell. The minimum nucleus is pointed out by a white arrow in (a). Two bright bumps and one dark dip with measured height modulation of less than one atomic layer are outlined by dash white circles.

The steps are natural boundaries of the $c(4\times4)$ domains. In many ways, our observation is similar to former reports on the observation that the two phases can coexist.[7,10] In our case, the remarkable surprise is the observation of the (2×4)-like reconstructed pits within the $c(4\times4)$ reconstructed terraces. It is also notable that our islands are smaller than indicated in earlier observations.[7,10] About half of the islands observed here are at the minimum size[10] [shown by an arrow in Fig. 3(a)] for a (2×4) structure on a $c(4\times4)$ surface consistent with an early stage of the phase transition from $c(4\times4)$ to (2×4). Although the developing islands are still highly disordered, they are clearly (2×4) reconstructed, as shown in Fig. 3(d).

While we cannot rule out the possibility that Ga atoms originating from surface steps (via long-range diffusion) act as a source for the phase transition between $c(4\times4)$ and (2×4),[10] based on our observation, a more likely alternative explanation is that surface atoms leave the $c(4\times4)$ reconstructed terrace, leaving (2×4) reconstructed pits, while forming (2×4) reconstructed islands located near the pits. In this scenario, initially, the pit coverage and the island coverage are expected to be the same, however, subsequently, the pit coverage decreases quickly, as the surface evolves towards its final equilibrium configuration. At equilibrium, the surface is characterized by only (2×4) islands surrounded by $c(4\times4)$ regions.[10,7] Previous work has noted that (2×4) reconstructed pits in the $c(4\times4)$ terraces will form during the phase transition.[12] This prediction is based on the fact that calculations show that the configuration of $c(4\times4)$ above (2×4) costs more energy than that of (2×4) above $c(4\times4)$.[12] However, to our knowledge, this configuration has never been observed experimentally.

For GaAs, the jump of Ga atoms out from the surface is the prerequisite for the simultaneously formation of islands and pits. While the Ga atoms for the phase transition are only locally available (limited by Ga surface diffusion), As atoms can globally be lost or taken from the As background. Although this type of atomic jump during a phase transition has not been discussed before, either experimentally or theoretically, the assumption of an the atomic jump helps to clarify the $c(4\times4)$ reconstruction. For the typical $c(4\times4)$ model shown in Fig. 1(b), with a top 1.75 ML of As, and for a more As rich model with species intermixing in the third layer, shown in Fig. 1(c), there are no Ga atoms in the top two atomic layers. The Ga atoms are available only in the third layer and it is therefore unlikely to expect Ga atoms to jump to form single atomic steps. Our observation therefore favors a more recent model, shown in Fig. 1(e), where Ga-As mixed dimers make Ga atoms available on the top layer.[8] The Ga atoms in the first atomic layer of the $c(4\times4)$ structure then leave the surface with the necessary loss of As atoms, leaving single-layer deep pits. Meanwhile, the freed Ga atoms replace As atoms in the first layer and are covered by As dimers again to form single-layer high islands. While, our observation cannot rule out the possibility of the structure with Ga and As species intermixing in the second layer as shown in Fig. 1(d),[7] a more complex scenario would be necessary to form the observed single atomic layer of pits and islands. The Ga atoms in the second layer could escape and leave bilayer pits, but the exposed third Ga atomic layer is unstable under a flux of plentiful free As. Consequently, the bilayer pits would be filled by As atoms to form single-layer pits. The escaped Ga atoms can replace the top As layer but covered by As dimers again to form single-layer high islands. Therefore, based on our observations, recent $c(4\times4)$ models with species intermixing in the first or second atomic layer are preferred.

In comparison with models that require the existing steps to serve as a source for the phase transition, via extremely long Ga surface diffusion, our model based on a Ga atomic jump does not suffer from a mass transfer limitation. However, it should be noted that a strong driving force is required to promote the atomic jump at short range. The possibility of a Ga atomic jump has been suggested by recent studies on spontaneous formation of GaAs islands on GaAs(100)

surfaces.[13–16] However, this phenomenon only occurs at relatively high substrate temperatures (about 600 °C) and relatively low As background, and without changing the (2×4) configuration. Islands and pits with bilayer steps are formed in this case. A higher temperature and a low As pressure are all helpful to enhance the activity of surface Ga atoms, but not so obvious for the phase transition between (2×4) and $c(4\times4)$. This transition happens at a low temperature (near 500 °C) and a high As background where the activity of Ga atoms is traditionally believed to be very limited.[9] However, it has been recognized that the activity of Ga atoms can be enhanced by phase transitions.[10] During the phase transition between (2×4) and $c(4\times4)$, both reconstructions are unstable.[17] Electrons can occupy the antibonding state of the Ga-As bond, and weaken the bond strength. Thus the Ga atoms would be kicked out to form pits and islands during the transition period. As shown in Fig. 3(a), marked by dashed circles, there are many bumps and dips with nonuniform height modulation of less than one atomic layer distributed on the $c(4\times4)$ terrace. Obviously, structural corrugation cannot result in this nonuniform height modulation of less than one atomic layer. In the region where the transition has apparently occurred, near (2×4) reconstructed islands or pits, the $c(4\times4)$ area is more disordered and has a fuzzy or cloudy nature. We believe all of these features arise from local charges resulting from the phase transition.

According to the above discussion, a Ga atomic jump induced by a phase transition is expected to be an observed surface phenomenon. Indeed, this behavior is suggested by recent studies on step formation on GaAs (311) surfaces,[18] phase transitions induced by Si deposition on GaAs(100) surfaces,[19–21] surface roughening caused by a transition of the surface reconstructions,[22,23] and surface reorganization during initial stages of strained-layer overgrowth on GaAs(311)A.[24]

In conclusion, an alternative scenario for the phase transition from $c(4\times4)$ to (2×4) is presented. The first observation of (2×4) reconstructed islands and pits within $c(4\times4)$ reconstructed terraces strongly suggests a mechanism of a phase-transition-induced Ga atomic jump.

*Electronic address: zmwang@uark.edu

[1] L. Daweritz and R. Hey, Surf. Sci. **236**, 15 (1990).
[2] T. Hashizume, Q.K. Xue, J. Zhou, A. Ichimiye, and T. Sakurai, Phys. Rev. Lett. **73**, 2208 (1994).
[3] V.P. LaBella, H. Yang, D.W. Bullock, P.M. Thibado, P. Kratzer, and M. Scheffler, Phys. Rev. Lett. **83**, 2989 (1999).
[4] D.K. Biegelsen, R.D. Bringans, J.E. Northrup, and L.E. Swartz, Phys. Rev. B **41**, 5701 (1990).
[5] J.E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1993).
[6] A.R. Avery, D.M. Holmes, J. Sudijono, T.S. Jones, and B.A. Joyce, Surf. Sci. **323**, 91 (1995).
[7] G.R. Bell, J.G. Belk, C.F. McConville, and T.S. Jones, Phys. Rev. B **59**, 2947 (1999).
[8] A. Ohtake, J. Nakamura, S. Tsukamoto, N. Koguchi, and A. Natori, Phys. Rev. Lett. **89**, 206102 (2002).
[9] J. Sudijono, M.D. Johnson, C.W. Snyder, M.B. Elowitz, and B.G. Orr, Phys. Rev. Lett. **69**, 2811 (1992).
[10] K. Kanisawa and H. Yamaguchi, Phys. Rev. B **56**, 12 080 (1997).
[11] J. Falta, R.M. Tromp, M. Copel, G.D. Petit, and P.D. Kirchner, Phys. Rev. B **48**, 5282 (1993).
[12] K. Shiraishi, T. Ito, Y. Suzuki, H. Kageshima, K. Kanisawa, and H. Yamaguchi, Surf. Sci. **433-435**, 382 (1999).
[13] K.T.L.M.D. Johnson, A. Birch, B.G. Orr, and J. Tersoff, Surf. Sci. **350**, 254 (1996).
[14] J. Tersoff, M.D. Johnson, and B.G. Orr, Phys. Rev. Lett. **78**, 282 (1997).
[15] V.P. Labella, D.W. Bullock, M. Anser, Z. Ding, C. Emery, L. Bellaiche, and P.M. Thibado, Phys. Rev. Lett. **84**, 4152 (2000).
[16] Z. Ding, D.W. Bullock, W.F. Oliver, P.M. Thibado, and V.P. Labella, J. Cryst. Growth (to be published).
[17] Q.K. Xue, T. Hashizume, and T. Sakurai, Appl. Surf. Sci. **141**, 244 (1999).
[18] Z.M. Wang, V.R. Yazdanpanah, C.L. Workman, W.Q. Ma, J.L. Shultz, and G.J. Salamo, Phys. Rev. B **66**, 193313 (2002).
[19] Z.M. Wang, L. Daweritz, P. Schutzendube, and K.H. Ploog, Phys. Rev. B **61**, R2440 (2000).
[20] Z.M. Wang, L. Daweritz, and K.H. Ploog, Surf. Sci. **459**, L482 (2000).
[21] Z.M. Wang, L. Daweritz, P. Schutzendube, and K.H. Ploog, J. Vac. Sci. Technol. B **18**, 2204 (2000).
[22] A.S. Bracker, B.Z. Nosho, W. Barvosa-Carter, L.J. Whitman, B.R. Bennett, B.V. Shanabrook, and J.C. Culbertson, Appl. Phys. Lett. **78**, 2440 (2001).
[23] B.Z. Nosho, W.H. Weinberg, W. Barvosa-Carter, B.R. Bennett, B.V. Shanabrook, and L.J. Whitman, Appl. Phys. Lett. **74**, 1704 (1999).
[24] M. Ilg, R. Notzel, and K.H. Ploog, Appl. Phys. Lett. **62**, 1472 (1993).